POST-DROUGHT FLUSH EFFECTS UPON RIVER WATER QUALITY AND SEDIMENT TRANSPORT IN UPLAND AND LOWLAND CATCHMENTS

IH, IFE and ITE
CENTRE FOR ECOLOGY AND HYDROLOGY (NERC)

R&D Technical Report P77

Acknowledgements

A review of this type would not have been possible without the active co-operation of a range of organisations involved in the acquisition and processing of hydrometric and river water quality data in the United Kingdom and other parts of western Europe. Particular thanks are due to the measuring authorities, principally the regional divisions of the Environment Agencies and the Meteorological Office, which collaborate in the joint Institute of Hydrology/British Geological Survey National Hydrological Monitoring programme.

The assistance of Samantha Green and Felicity Sanderson in undertaking analyses and preparing material for this paper is also gratefully acknowledged.

The IFE authors are grateful to Mr R Moore (Environment Agency, North-West Region) for supplying hydrological data. Thanks are also due to C Woof, E Rigg, B M Simon, A J Lawlor and J B James for carrying out the long-term chemical monitoring programme, and to M Scott (IFE / University of Manchester) for help with sampling at Great Dun Fell.

ITE acknowledge the financial support of the Welsh Office for the peatland manipulation experiment and the WAWS95. The latter is also supported by the Countryside Council for Wales, Forestry Authority, Environment Agency and NERC. ITE and IH authors would also like to express appreciation to staff at IH Plynlimon, IH Wallingford and ITE Merlewood for their valuable contributions to the field sampling and chemical analyses. Thanks are also due to Sarah Alexander from Imperial College for permission to use storm event data from the Hafren and Tanllwyth catchments.

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EXECUTIVE SUMMARY

This report describes two large scale Environment Agency / Natural Environmental Research Council (NERC) collaborative projects covering post-drought flushing during late 1995 and early 1996 in upland and lowland British catchments. The catchments were chosen to give good coverage of the impacts of the wetting-up, which followed the 1995 drought, upon river water quality. This was a unique opportunity to gather data covering important water quality events which are under-represented in both NRA routine data and research archives. The report describes work carried out on upland catchments in Wales (Plynlimon and Beddgelert) and England (Lake District). The lowland study was carried out on the Humber catchments included in the Land-Ocean Interaction Study (LOIS). The LOIS study sites selected for this project comprised an intensive reach of the River Aire and 11 representative catchments.

The "drought-break" was a very ill-defined event, unlike the end of most other droughts over the last twenty years. The end of the national drought occurred in September, with significant rainfalls in North west and Southern Britain. There remained small pockets which could be described as drought-bound well in to 1996 (eg. parts of the Pennines). The regional variations in response to drought break were also a function of variations in rainfall [time series] and operational river management, in addition to the catchment and river properties.

Some common features have emerged in relation to the hydrochemical response of upland streams to drought and drought-break conditions. A general characteristic of prolonged low flow conditions in all the upland streams studied was an increase in pH, alkalinity and in the concentrations of divalent base cations, predominantly calcium. This reflects the increasing contribution of groundwater to the streams and a decline in the input of more acidic soil drainage water. At drought-break, chemical conditions in the streams changed rapidly, with a sharp decline in pH, alkalinity and calcium and an increase in the concentrations of metals such as manganese and aluminium. This change in chemistry can be attributed to changes in the hydrological flowpaths operating within the catchment with increased contributions of water from surface soil horizons as the catchments 'wet up'. More detailed responses concerning

sulphate and nitrate, trace metals and other water quality variables are also described.

The study of the LOIS area included statistical analysis of water quality data from routine monitoring by the Environment Agency and additional sampling and analysis by LOIS teams. Samples collected at the representative catchments and on the River Aire in Yorkshire during periods of high flow during the post-drought period showed increased concentrations of sediment and associated metals. Comparison with historic data suggests these concentrations were not exceptional in most cases, but that they were outside the historical measured range for many determinands during the high flow event of 22 December 1995.

KEYWORDS: DROUGHT FLUSH, WATER CHEMISTRY, LOIS, METALS, NITRATE, SULPHATE, SEDIMENT TRANSPORT, LOWLAND RIVERS, UPLAND STREAMS, PENNINES, LAKE DISTRICT, WALES.

1.INTRODUCTION AND BACKGROUND

The purpose of this report is to describe two large scale Environment Agency / Natural Environmental Research Council collaborative projects covering the post-drought flushing during late 1995 and early 1996 in upland and lowland British catchments. The catchments were chosen to give good coverage of the impacts of the wetting-up, which followed the 1995 drought, upon river water quality. The post-drought period presented a unique opportunity to gather data covering important water quality events which are under-represented in both Environment Agency routine data and research archives. The report describes work carried out on upland catchments in Wales (Plynlimon and Beddgelert) and England (Lake District). The lowland study was carried out on the large-scale Humber catchments, included in the Land-Ocean interaction study (LOIS).

Antecedent conditions are an important control on the concentrations and transport of many substances through rivers. Past attempts to capture water quality and sediment data in runoff events immediately following extended drought have experienced great difficulties due to logistical and technical sampling problems. There is often difficulty in ensuring that autosamplers deployed for short periods of time collect representative samples, both in terms of catching the full range of flow conditions and the representation of concentration within the full cross-section. Routine manual sampling is often carried out with insufficient frequency to catch the full range of concentrations associated with post drought flushes. The most relevant approach is to combine manual and automatic bulk sampling using survey strategies which are responsive to rain and runoff events.

Generally, routine discontinuous water quality sampling following droughts over the past 20 years have failed to detect peak concentrations or the timing and release of pollutants during episodic autumn flushing. Observations of water quality following the 1976 drought demonstrated the importance of flushing of catchment stored pollutants. However, the overall historic river water quality archive data available to the Environment Agency is too sparse to adequately describe the pollutant peaks or the chemograph. Furthermore, not all catchments exhibit the same response to drought-break. With limited data, variations in water quality could not be attributed to properties such as catchment characteristics, since the apparent variability may have been an artefact of the infrequency of measurements or lack of uniformity in undirected sampling strategies.

The 1995 drought provided a major opportunity to gain an insight into the impacts of long periods of low rainfall/high temperatures upon river water quality. The understanding obtained from analysis of empirical data from a range of catchments will place this event in context, by comparison with existing archive data from key long term monitoring sites. It was expected that spikes would be observed in the stream concentrations and discharges of many determinands. Current models of fluxes of many substances do not adequately represent the wetting up period following drought. Therefore, additional model development is needed, eg. in the case of currently available nitrate, aluminium, colour and acidity models, to add the influence of wetting up of catchment systems. In the longer term it is hoped that these two studies will facilitate the development of further droughtbreak water quality models, provide comparative data for future droughtbreak events and will contribute to our understanding of some aspects of climate change. This is particularly significant, given that possible future environmental scenarios may include increases in drought frequencies.

1.1 Objectives

1) To assess the in-river impacts of post drought flushes in upland and lowland catchments following a period of extended drought condition upon:

    a) Nutrient loads.
    b) Other selected contaminants.
    c) Sediment loads.

2) To support development and improvement of river models.

3) To further develop concepts relating to the effects of flushing on river water quality following a prolonged dry period.

4)To produce a final report which summarises the findings from the upland and LOIS rivers study area projects.

1.2 Methods and Approach

The approach taken for this research was to design observational studies to identify typical flushing behaviour over a range of upland and lowland catchment types, to make comparisons with existing Environment Agency and Natural Environmental Research Council river water quality data and to improve quantification of pollutant transport during discrete weather events. There was considerable uncertainty over the timing of wetting events and the dry conditions and generation of significant runoff events extended through the autumn and early winter. The episodic nature of water quality responses during significant runoff events were measured using continuous monitors, manual bulk sampling and automatic bulk samplers. The chemical determinations used methods which are compatible with ongoing measurements in each area, thereby ensuring comparability with the long term record.

The range of determinands covered was flexible, including pH, conductivity, temperature, suspended sediment, major ions, nitrate, phosphate, ammonium, DOC, TOC, selected metals (eg. lead and chromium), as well as inorganic and total dissolved aluminium.

The immediate deliverables were:

1) Flow-related data on stream water quality during high flows following extreme drought.

2) Report assessing the impacts of post drought flushes on stream water quality in the selected upland and lowland catchments.

The upland and lowland studies were both carried out by large, but seperate project teams. The background studies and available archives were also drawn from many sources. As a result the study reporting, as outlined in chapters three and four, are very different in structure and content.

2. HYDROCLIMATOLOGICAL BACKGROUND TO THE 1995 DROUGHT AND THE POTENTIAL IMPACT OF DROUGHT-BREAKS ON RIVER MASS LOADS

2.1 Introduction

This chapter places the 1995/96 drought, and its partial termination in the autumn of 1995, in the context of the volatile hydroclimatological conditions experienced during recent years in the UK and other parts of western Europe (see the Appendix for locations of places referred to in the text). Brief comments are made on the impact of drought-breaks on the associated flushing of contaminant mass loads by rivers.

2.2 Hydroclimatology of recent droughts in the United Kingdom

2.2.1 Overview

Recent rainfall, evaporation and runoff patterns for the UK and other regions of maritime western Europe are examined within the historical perspective provided by representative long hydrometric records. The objective is to establish a hydrological framework in which to consider the results presented elsewhere in this report. The drought's development, decay and reintensification are examined with particular reference to the spatial variations in intensity and the significance, in runoff terms, of the exceptionally wet early autumn of 1995 which interrupted the drought. Comparisons are also made with the terminal phases of earlier UK drought events. By their nature, severe droughts are rare and post-drought flush events are similarly uncommon. However, their impact on the aquatic environment can be substantial and any change in the expected frequency of hitherto very unusual flush episodes could have important implications for river water quality and ecology. The magnitude and constitution of river mass flows to the shelf seas may also be affected. Therefore, consideration is also given to the degree to which recent conditions fall outside the range of historical variability, perhaps signalling a period of continuing climatic instability.

The 1995/96 drought is only the latest in a series of exceptional hydrological events to affect the UK in the recent past (Marsh, 1996). A clustering of extreme events has raised important questions regarding the resilience of existing water management practices and the vulnerability of the aquatic environment to periods of unusual weather patterns. Recent flood and drought episodes have also served to focus attention on many of the issues at the heart of hydrological science and its practical application in the UK. Water management in the United Kingdom, as elsewhere, is underpinned by the lack of trend in long-term hydrometric series, some of which extend back more than 150 years. In a climate as variable as that of the UK any short-term deviation from the average needs to be treated with considerable caution particularly as the clustering of wet or dry years is a feature of the climate of western Europe (Arnell and Reynard, 1993). Nonetheless, the hydrological characteristics of the last 20 years, and their broad consistency with a number of favoured climate change scenarios (Rowntree et al., 1993, Arnell and Reynard, 1996), imply that any assumptions of a continuing stationarity in runoff and aquifer recharge series need to be kept under continual review. In particular, any change in the amount of runoff, its temporal distribution and, especially, the frequency of extreme events, will impact on the physical and chemical characteristics of river-borne mass flows.

2.2.2 The recent past - a western European perspective

The exceptional climatic conditions experienced throughout much of maritime western Europe over the recent past have attracted considerable scientific attention not least because a number of monitoring programmes provide evidence of rainfall and runoff patterns which appear to have no close modern parallels (Green et al., 1996). Extensive drought conditions in the early 1990s (Marsh et al., 1994) were superseded by severe winter flooding and abundant outflows to the North Sea over the next three years. This period of extremely high runoff culminated in a number of very damaging flood events over the winter of 1994/95 (Black, 1995; Vokso, 1995). Intense drought conditions then returned to produce exceptionally steep declines in river flows through the spring and summer of 1995 (Anon, 1995a).

Recent climatic conditions have been characterised by large and sustained departures from the normal seasonal variation in rainfall and, more particularly, in runoff. In some regions the accentuated seasonal contrasts in precipitation patterns have been accompanied by an overall increase in rainfall totals. Figure 2.1 shows 5-year running mean annual rainfall for a number of sites in maritime western Europe. The most striking feature is the upward trend in annual totals from about 1970 to 1995 for Bergen and Fort William; similar upturns are also exhibited by other long rainfall records e.g. Loch Venachar (Scottish Highlands). Taking the 1976-95 period as a whole, rainfall in many catchments close to the western seaboards of Scotland and Norway has been more than 15% greater than the preceding average. To the south and east, protracted rainfall deficiencies have been common over the last decade but these have generally been punctuated by notably wet periods. Although some long rainfall series (e.g. Edinburgh, East Midlands and Kew) show a shallow decline since the turn of the century, generally amounting to less than 5% of the mean, in the context of the full historical records there appears to be, as yet, no significant departure from the long-term average.

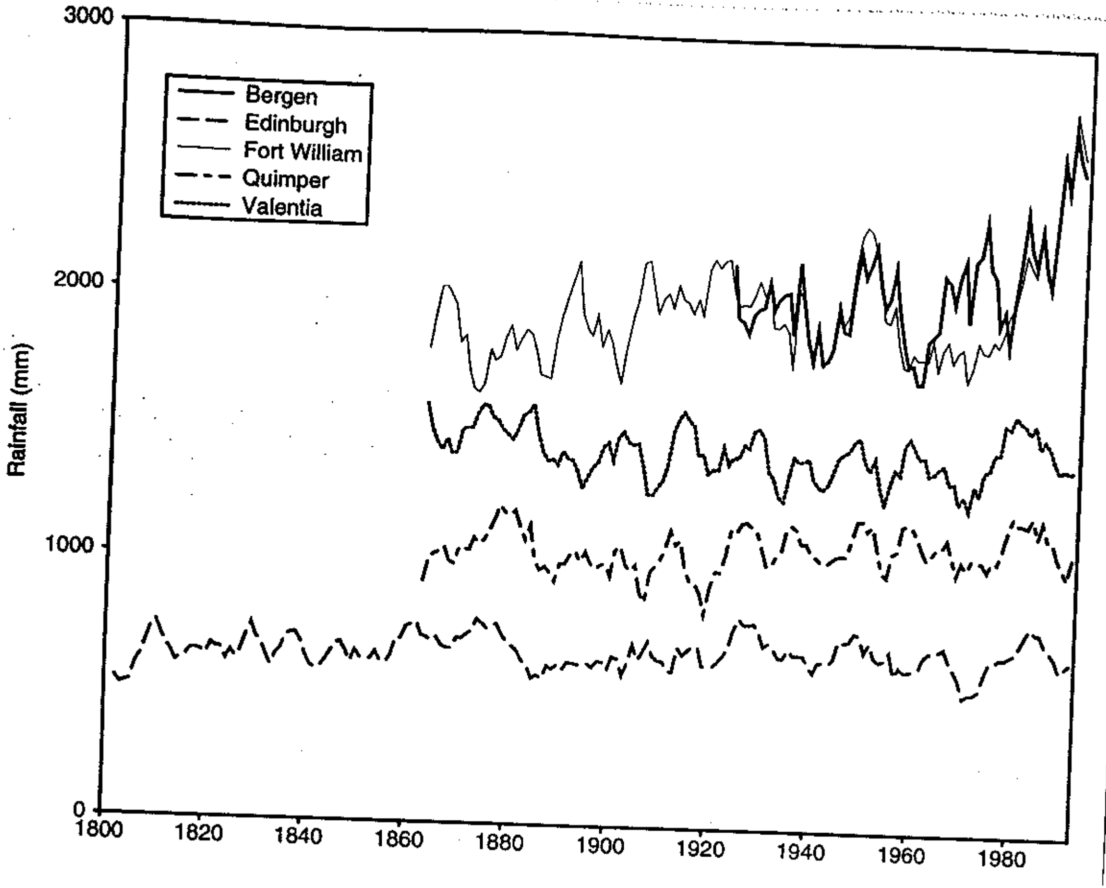


Figure 2.1 5-year running mean rainfall for selected long records in maritime western Europe

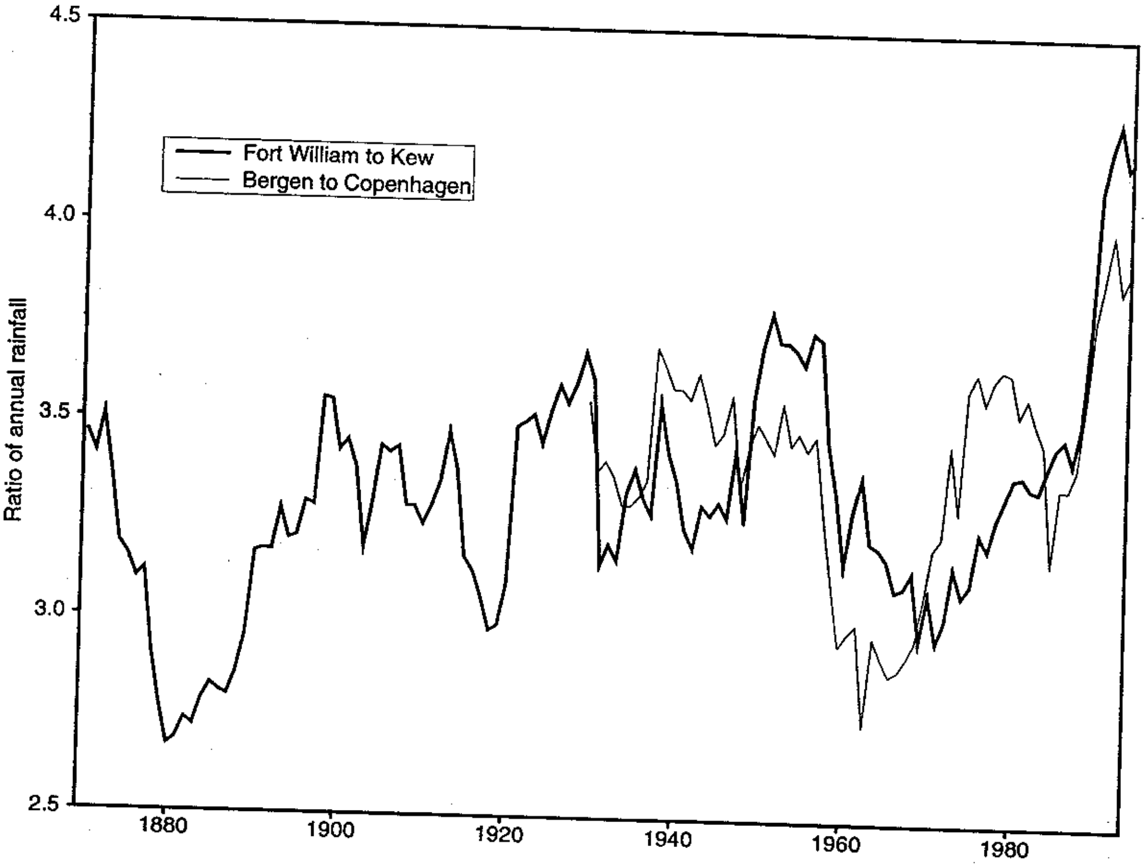


Figure 2.2 Ratio of Fort William to Kew rainfall (and Bergen : Copenhagen)

Considered together, recent rainfall patterns support the supposition that the preferred tracks of Atlantic frontal systems have followed a more northerly path over the last 20 years (Hisdal et al., 1995). Hurrell, (1995) has linked the exceptional wetness of parts of north-western Europe with the North Atlantic Oscillation, and Mayes (1995) has associated it with a modest decline in rainfall in the English lowlands and notes the similarities with some favoured climate change scenarios. A marked recent exaggeration in the NW/SE rainfall gradient across Great Britain is illustrated in Figure 2. 2 which illustrates annual precipitation totals for Fort William expressed as a ratio of the corresponding annual totals for Kew. The abrupt increase in the ratio since the mid-1960s, principally due to enhanced winter precipitation at Fort William, has produced unprecedented values for the ratio over the post-1987 period. Similar analyses based on regional rainfall series for western Scotland and south-east England up to the end of the 1994/95 winter confirm this strong reinforcement of the rainfall gradient across Great Britain. The Fort William/Kew ratio is echoed by the relationship between rainfall totals for Bergen and Copenhagen; the similarity between the two traces suggests a common synoptic causation. At the regional level, the effect has been to generate periods of severe hydrological stress: lowland drought conditions contrasting with clusters of notable floods in regions close to the Atlantic seaboard; in Scotland these have significantly reduced the expected frequency of outstanding runoff rates especially in rivers draining from the Highlands (Anon., 1995b).

The recent accentuation in regional rainfall contrasts has been accompanied, in many regions, by exceptional within-year variability. Figure 2.3 confirms a tendency towards a more distinct partitioning of rainfall between the winter and summer half-years at three representative sites in maritime western Europe. This has strengthened the normally muted seasonal contrasts in precipitation totals across the UK. The running mean plots of the ratio between winter (October-March) rainfall and that for the following half-year for Fort William, Bergen and Quimper suggest an increased continentality over the post-1970 period particularly. Over the full historic record, the winter/summer ratios display large temporal changes but their increase relative to the trough in the 1940s is substantial and the average for the 1990-94 period is generally the highest on record; the ratio for Great Britain as a whole displays similar characteristics.

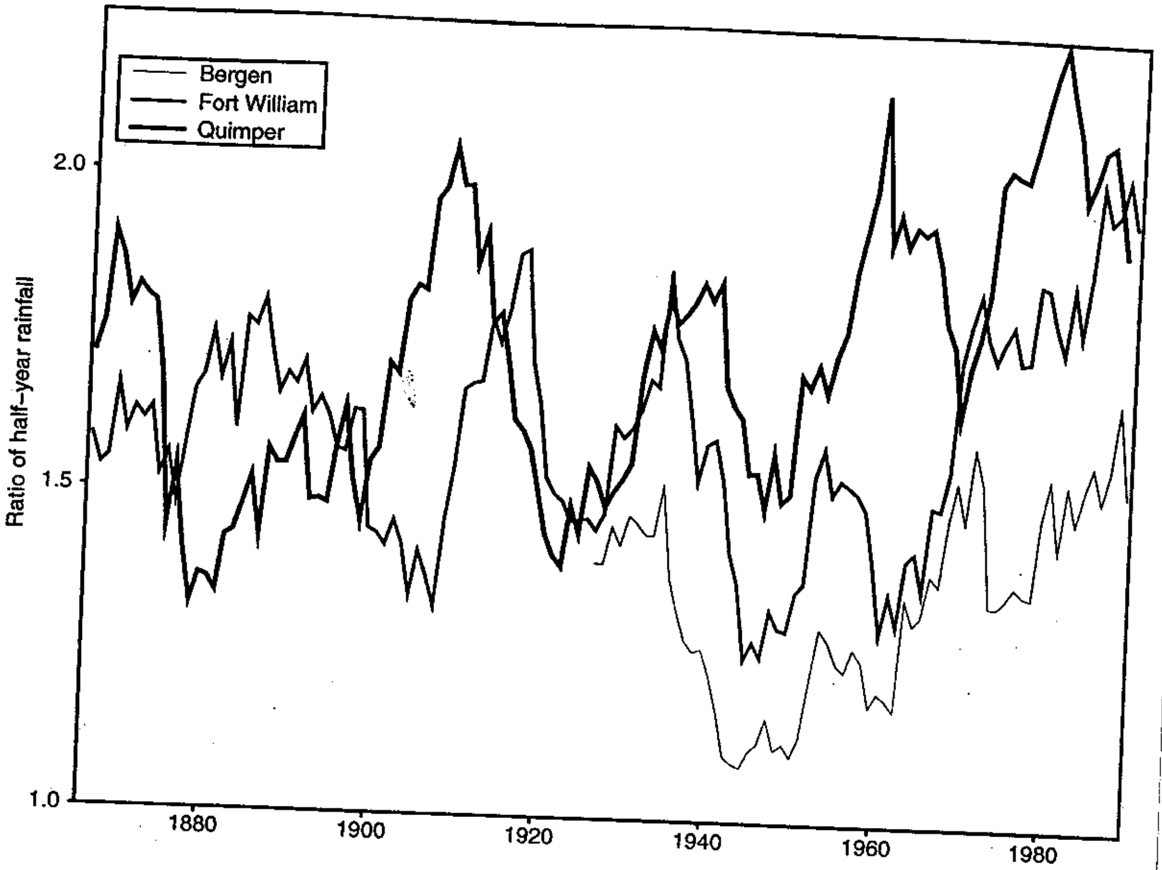


Figure 2.3 Ratio of Winter to Summer rainfall for selected European sites

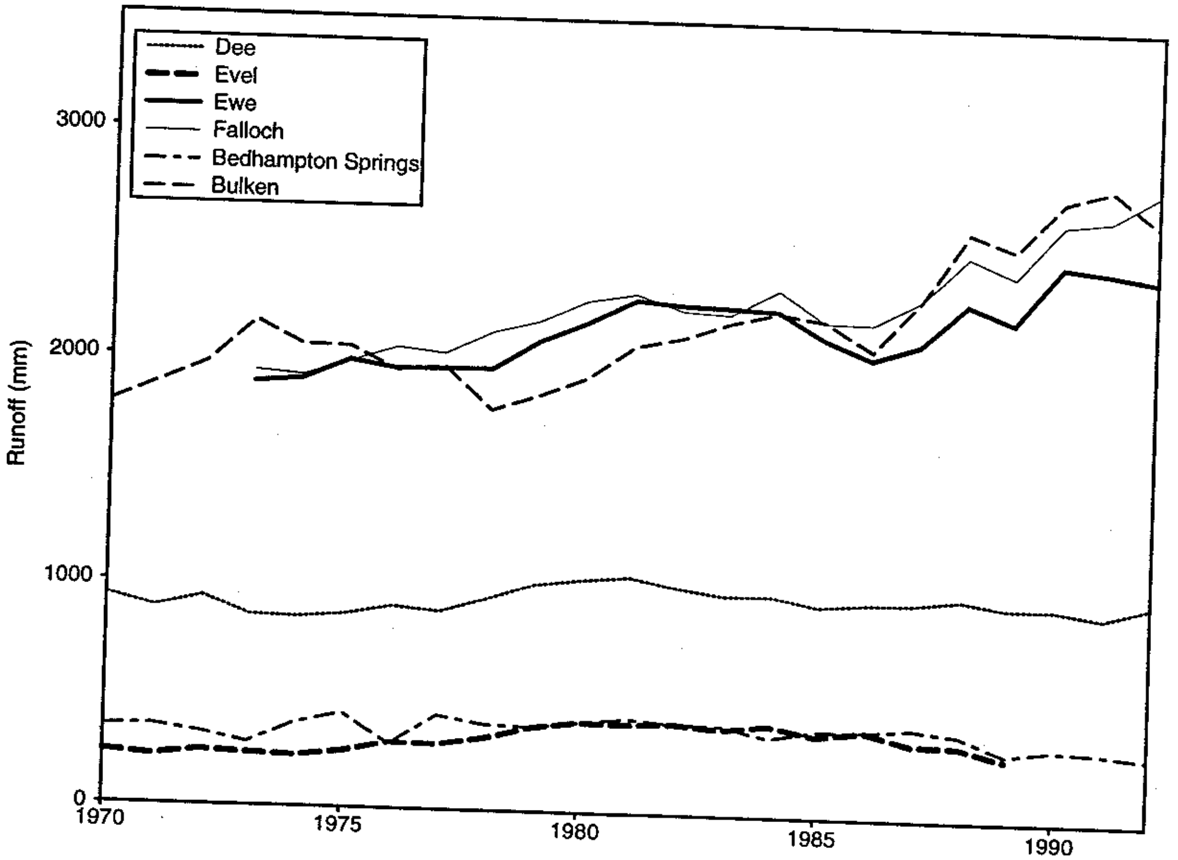


Figure 2.4 Runoff for selected rivers in maritime western Europe

Figure 2.4 confirms that the recent trends in rainfall are fully reflected in runoff patterns for a selection of western European catchments. Runoff for the River Bulken (Norway) since the mid-1970s (a period of sustained low flows) has increased substantially and totals for the 1988-95 period fall outside the historical range. This tendency is matched by a number of rivers in north-western Scotland (e.g. the Ewe and Falloch) but, as with rainfall, little or no upturn in average runoff may be identified to the east and south although depressed flows have characterised wide areas of the western European lowlands during the summers of the 1990s. The margin between average annual rainfall and average annual potential evaporation is already narrow in these sensitive areas. Any significant increase in evaporative demands could have a substantial impact on flow regimes in line with the increased seasonality implied by most climate change scenarios (Arnell and Reynard, 1996).

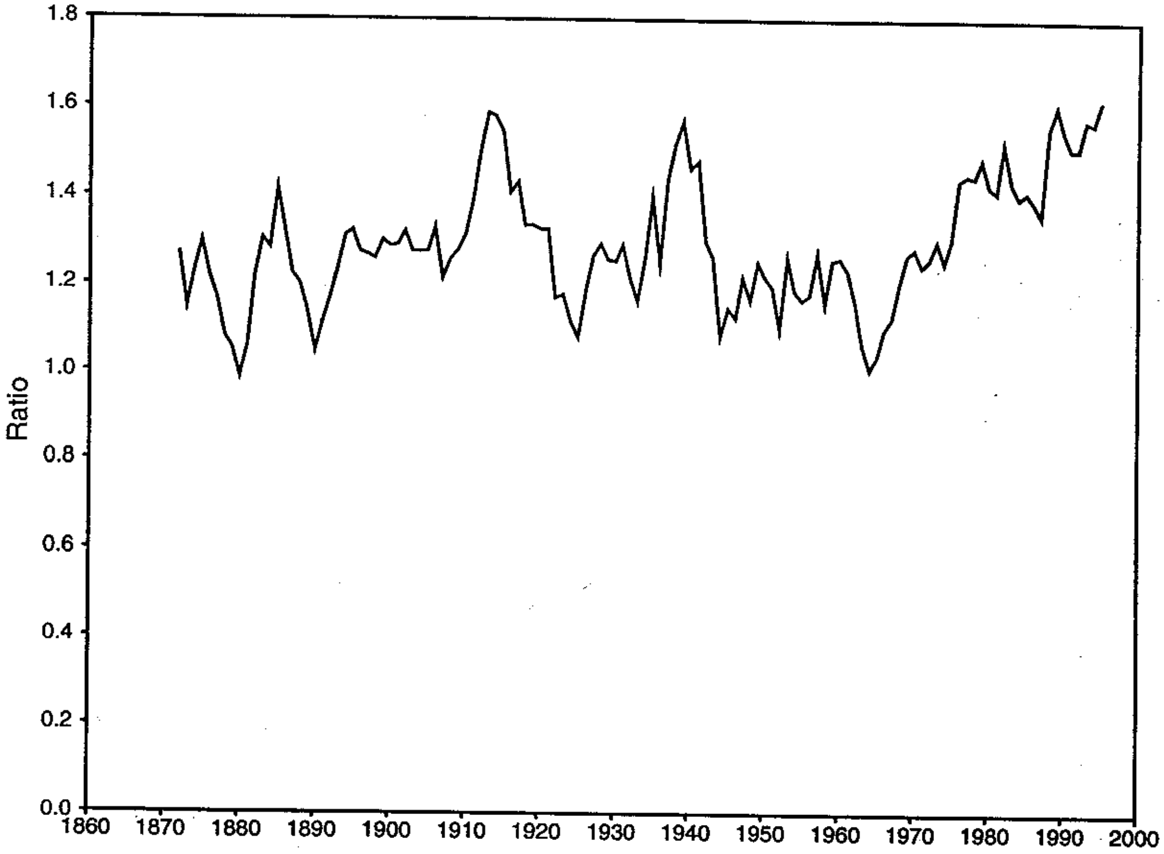


Figure 2.5 **Ratio of Winter to Summer rainfall for Great Britain (5-year running means)**

2.2.3 The 1976-95 period in the UK

2.2.3.1 Rainfall

Rainfall for the UK as a whole over both the 10 and 20 year periods to 1995 is close to the long-term average. However, within-year and between-year variability has been exceptional and protracted spells of very wet or very dry conditions have been relatively common. The direction, frequency and vigour of Atlantic frontal systems, together with the concentration of high relief in western Britain, which provides plenty of opportunity for rain shadow effects to become influential, is an important determinant of UK rainfall patterns. This has been well illustrated in the recent past. Anticyclonic conditions which excluded many Atlantic frontal systems from most of Britain during much of 1975/76, produced extreme drought intensities. The notably wet autumn of 1976 which terminated the drought, heralded a decade dominated by westerly influences with mild and wet conditions predominating. Taken together, the 10 years beginning in 1977 were marginally the wettest in a series from 1869. This mild and wet phase was interrupted by one severe, but short, drought during the spring and summer of 1984 which mainly affected northern and western Britain. However, the very dry winter of 1988/89 signalled a period of protracted rainfall deficiency in the English lowlands, punctuated by several very wet interludes. Large rainfall deficiencies in eastern and southern Britain coincided with outstandingly high accumulated rainfall totals in western Scotland.

Rainfall in Britain is normally distributed fairly evenly throughout the year and the ratio of October-March rainfall totals to those of the following April-September displays no overall trend over the first 100 years of the series (Figure 2.5). Since the early 1970s, however, the ratio has increased significantly. Protracted increases in this ratio are not without precedent (the period up to 1918 features a similar perturbation) but there are no close analogues to the 15 years ending in 1995 when winter rainfall has, on average, been around 20% greater than that for the ensuing summer.

2.2.3.2 Temperature and evaporation

The Central England Temperature (CET) series, a homogenised monthly dataset extending back to 1659 (Manley, 1974), provides a unique means of indexing the mildness of the 20 years to 1995. Mean CET temperatures for 1976-95 are around 0.4 degrees above the preceding average and the post-1987 period is the warmest eight-year sequence in the 337-year record by an appreciable margin (see Figure 2.6 - the enhanced variability in the eighteenth century reflects the registering of monthly mean temperatures in whole degrees). Correspondingly, potential evaporation (PE) losses have been persistently above average throughout the year and notably high in several recent summers. Figure 2.7 illustrates annual PE totals for three areas in Britain based on PE assessments derived by the Meterological Office's Rainfall and Evaporation Calculation System (MORECS; Thompson et al., 1981). The figures presented assume a grass cover and a soil of medium water retention capability. Year-on-year variability is considerable but average losses in Cornwall, central Scotland and East Anglia during the 1990s have been significantly greater than in the 1960s.

An important hydrological consequence of the more distinct partitioning of rainfall between winter and summer, and the notably high evaporative demands, has been the persistence of substantial soil moisture deficits well into the autumn. Over the 1989-91 period average end-of-November soil moisture deficits exceeded 60-80 mm over much of eastern England (Marsh et al., 1994). In a normal year such deficits would require around three months average rainfall to be satisfied in the eastern lowlands. If the ensuing winter is dry, runoff rates recover only sluggishly, spate conditions tend to be infrequent and the window of opportunity for aquifer recharge can be narrowed down to a matter of weeks. Such circumstances prevailed in eastern England during successive winters in the extended drought of 1988-92. Exceptionally dry soils mitigate the risk of flooding over the summer half-year but delay the seasonal recovery in runoff rates such that, importantly, a wet autumn and early winter may produce only a poorly defined flush of contaminants (both in spatial and temporal terms) following a sustained period of low rainfall.

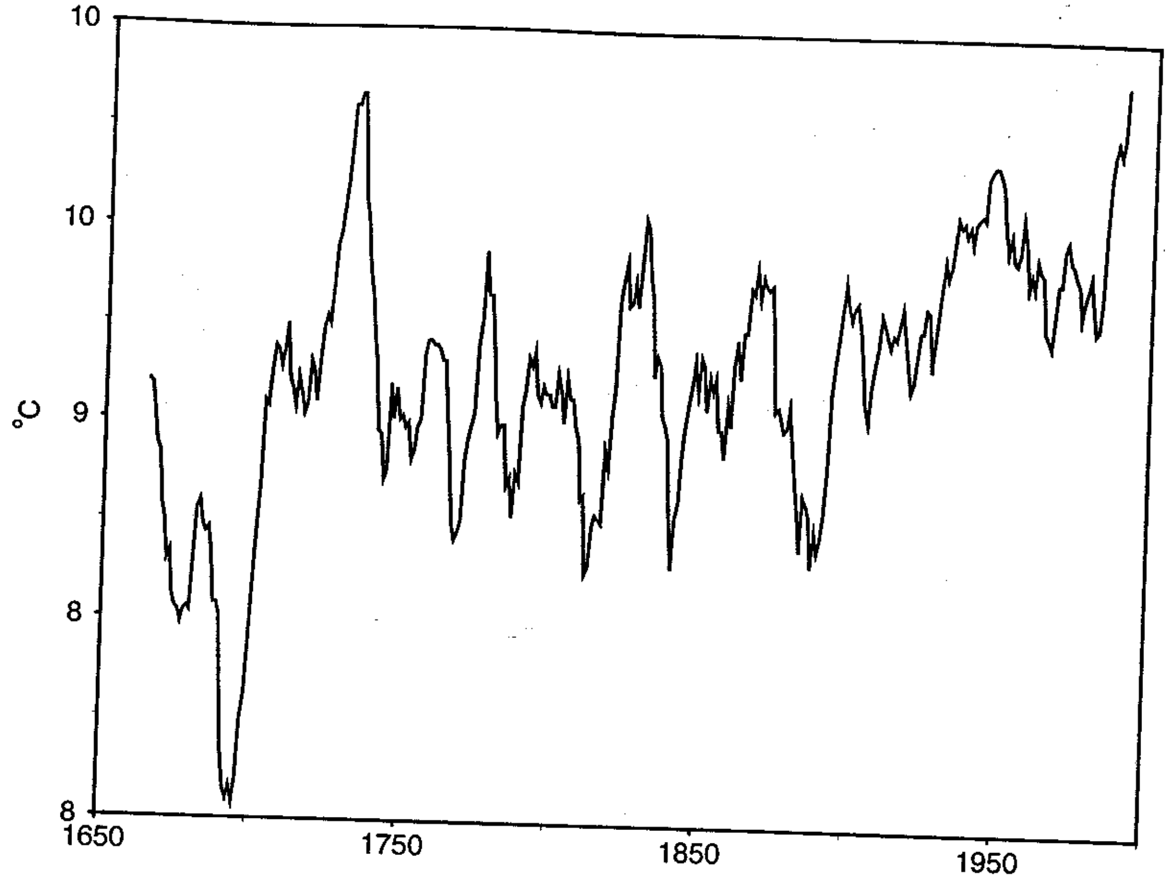


Figure 2.6 Annual Central England Temperature (10-year running mean)

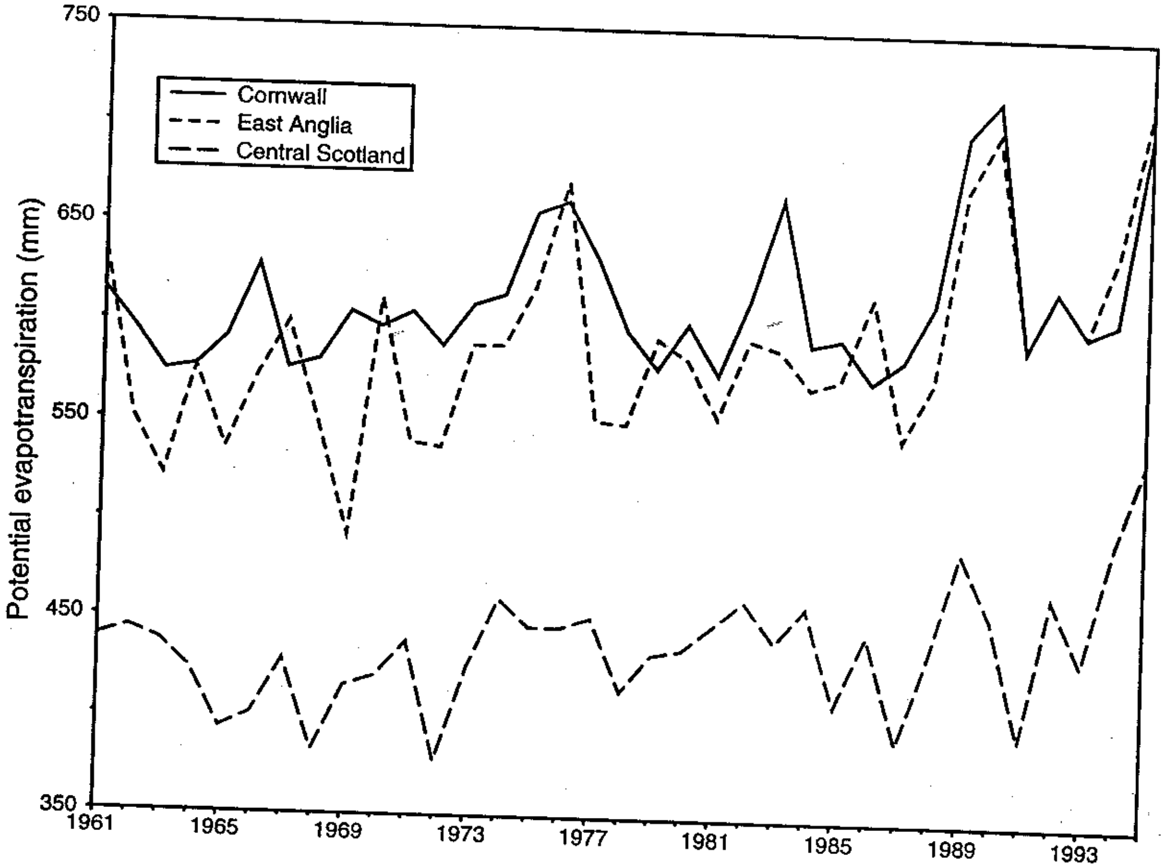


Figure 2.7 Annual potential evapotranspiration for three regions (source: MORECS)

2.2.3.3 1976-95 in summary

The very unusual nature of the 1976-95 period is well illustrated in Figure 8 which plots winter (December-February) and summer (June-August) rainfall and temperature anomalies for England and Wales since 1845; the national rainfall and CET series both extend back considerably further but the precision of the early data is limited. Recent winters exhibit wide departures from the average and a modest tendency to cluster in the warm/wet quadrant (not, though, the winter of 1995/96, when northerly airflows were a persistent feature and the December-February period was the coldest for 15 years). A pronounced tendency towards mild, wet winters has been identified for western Scotland (Green et al., 1996) with a number of recent winters plotting beyond the historical range. For England and Wales clustering is similarly marked over the June-August period; the summers of 1976 and 1995 are outstanding but most summers over the last 20 years group in the warm/dry quadrant. Since 1975, summer rainfall has been over 15% below, and temperatures 0.5 °C above, the preceding average.

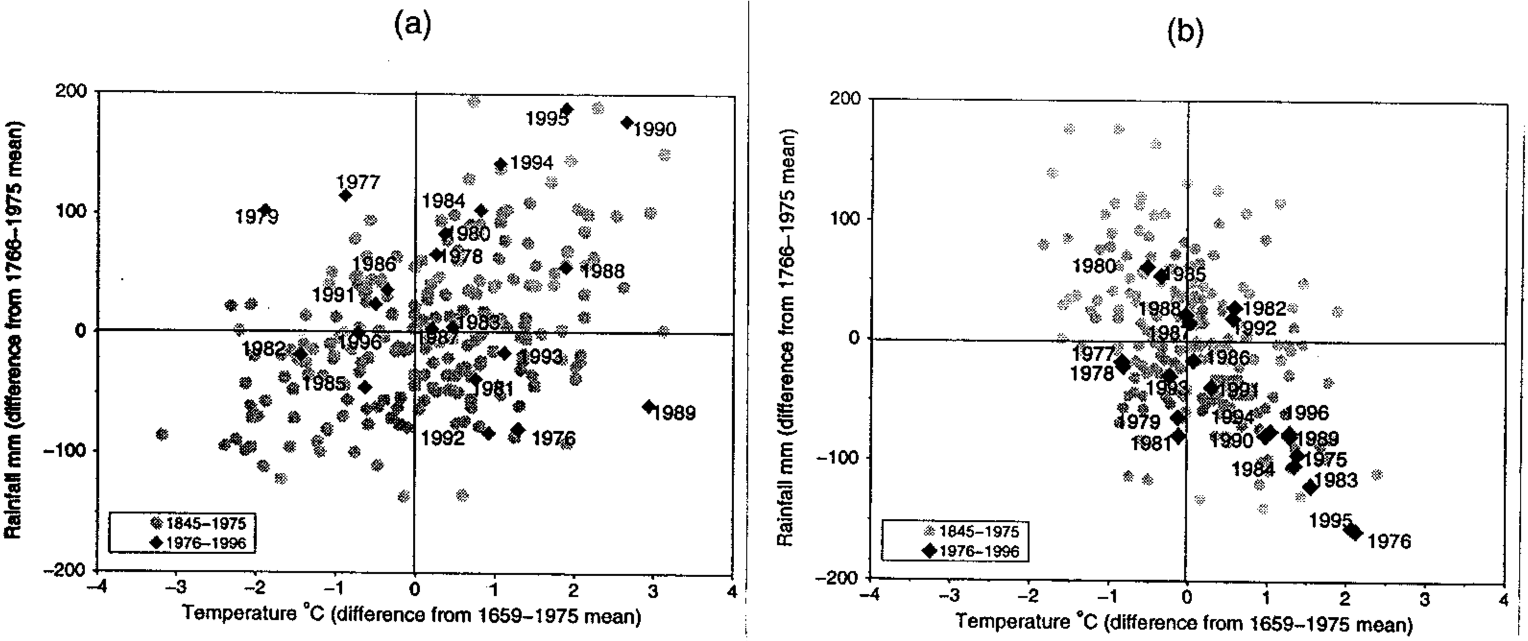


Figure 2.8 **England and Wales rainfall and temperature anomalies (a) Winter (December to February and (b) Summer (June to August)**

2.2.3.4 Recent runoff patterns

The interplay of rainfall, evaporation and soil moisture variations across the UK can result in complex changes to runoff patterns but, generally, the 10 years to 1995 have seen an accentuation in the seasonality of river flows, less so in some baseflow dominated rivers draining catchments with a long 'memory' where heavy winter rainfall has enhanced summer flow rates. Lengthy periods with flow rates well above or well below average have characterised flows in most rivers. Floods in Scotland have been exceptional and throughout southern Britain sustained spate conditions, rather than outstanding individual flood events, have been common in recent winters. Flow rates have been depressed in a number of recent summers e.g. 1989, 1990, 1992 (in the lowlands) and 1995. Although the 1976 minima have not been eclipsed in most catchments, summer (June-Aug) runoff totals over the last 10 years typically provide three or four of the lowest six on record.

2.2.3.5 Climate Change

Examination of the full England and Wales rainfall series reveals that a few precedents to the recent volatility in rainfall patterns may be found, for example in the 1850s. However, once account is taken of temperatures and evaporative demands, there are no close modern parallels to the recent past.

Regional climate change scenarios remain tentative in relation to temperatue increases and very uncertain in relation to changes in rainfall patterns. Nonetheless, the climatological and hydrological conditions experienced over the recent past exhibit some (but not complete) consistency with favoured climate change scenarios, e.g. those examined by the Climate Change Impact Review Group (CCIRG, 1996). The possibility that hitherto rare flood and drought interludes may recur with greater frequency in the future emphasises the need for caution when ascribing return periods to the recent notable runoff extremes. It also underlines the need for regional studies of river flow and water quality interactions, while paying attention to variations in river mass loads, to establish benchmarks against which to compare future patterns and to provide a greater understanding of the hydrological processes involved. This understanding will enable the potential impacts of climate change on hydrological systems to be quantified with greater confidence.

2.2.4 The 1995/96 drought

Runoff and aquifer recharge rates recovered dramatically following the minima established during the very protracted drought of 1988-92 (Marsh et al., 1994). This hydrological transformation has few, if any, modern parallels. For England and Wales, the driest 28-month sequence since the 1850s (ending in the summer of 1992) was followed directly by the wettest 32-month sequence this century. The latter culminated in the winter (December-February) of 1994/95, the wettest on record for the UK. As a consequence rivers were in spate, reservoirs were at capacity and groundwater levels close to seasonal maxima entering the spring of 1995.

However the frequency of Atlantic depressions declined rapidly during March, and for much of the spring and most of the summer, a northward extension of the Azores high pressure cell continued to deflect most rain-bearing frontal systems and bring subtropical air-masses across the British Isles. Rainfall deficiencies built-up quickly and a heatwave throughout much of July and August produced a marked intensification in drought conditions. August rainfall totals were less than 15% of average over wide areas and the mean temperature established the month as the second warmest, after July 1983, in the Central England Temperature series.

Rainfall figures for the 1995 summer indicate that the June-August period marginally eclipsed 1976 as the driest in the 229-year homogenised England and Wales rainfall series. With Scotland registering its second driest summer on record, the June-August rainfall total for Britain also established a new summer minimum in a series from 1869. In the five-month timeframe the aridity of England and Wales was even more exceptional.The April-August rainfall total is the lowest for *any* five-month sequence in over 200 years (Table 2.1). Only during the 1921 drought have five-month rainfall totals approaching the 1976 and 1995 minima been registered. Much of the late-spring and summer rainfall in 1995 resulted from patchy showers or localised thunderstorms. Some areas, including parts of West Yorkshire, failed to benefit from the spatially highly variable rainfall and experienced intense drought conditions. Substantially below average rainfall was recorded for each of the five months to August 1995 in most regions of Britain and accumulated rainfall totals were well below half of the 1961-90 average over wide areas (Table 2.2). Analyses using standard rainfall frequency tables based on rainfall variability over the 1911-70 period (Tabony, 1977), indicate return periods of 150 or more years for the April-August rainfall deficiency for most regions of England (these estimates assume a sensibly stable climate).

Table 2.1 **Lowest five-month rainfall totals for England and Wales 1845-1995**

Rank	Rainfall total (mm)	End month	Year
1	149	08	1995
2	155	08	1976
3	159	06	1921
4	184	06	1938
5	185	06	1929
6	186	06	1887
7	187	04	1854
8	188	07	1870
9	191	09	1959
10	191	03	1858
11	193	07	1990
12	194	06	1956

The exceptionally low rainfall, coupled with hot sunny conditions which resulted in evaporation demands exceeding the average, typically by 20%, meant that some stress on water supply and river systems was inevitable. The development and severity of the drought in runoff terms throughout much of the UK may be gauged from Figure 9 which shows hydrographs for major rivers in Scotland and England. By the late summer of 1995 monthly flow minima were established in a number of catchments in northern England, e.g. the Rivers Wharfe and Eden. Elsewhere flows remained above the 1976 minima but a large contraction in the headwater stream network could be recognised, in impermeable catchments especially.

Spring and summer rainfall deficiencies were notably high in the English lowlands. However, as a consequence of the abundant rainfall throughout the winter of 1994/95, groundwater levels in the Chalk, England's most important aquifer, remained mostly within the normal range. The relatively healthy groundwater stocks provided an important buffer against the effects of the exceptionally dry summer and sustained reasonable discharge rates in groundwater-fed streams; inflows into the southern North Sea were maintained well above drought minima. The groundwater level variation at The Holt borehole in Hertfordshire (Figure 2.10) provides confirmation of the generally healthy state of groundwater resources through the spring and summer of 1995, and also illustrates the remarkable range experienced between 1987 and mid-1996 characterised by wide and sustained departures from the normal seasonal variation.

Table 2.2 Rainfall (and return periods) before, during and after the 1995 drought

Country/Region		Apr93-Feb95	Est. Return Period, yrs	Apr95-Aug95	Est. Return Period, yrs	Apr95-Jun96	Est. Return Period, yrs	Sep95
England & Wales	mm	2127		149		814		113
	%LTA	124	80-120	46	>> 200	75	50-80	147
North West	mm	2679		215		917		97
	%LTA	116	10-20	51	120-170	64	>> 200	84
Northumbrian	mm	1926		162		831		111
	%LTA	118	20-30	50	>200	81	15-25	152
Severn Trent	mm	1808		126		685		94
	%LTA	125	60-90	43	>200	74	40-60	147
Yorkshire	mm	1890		132		675		96
	%LTA	120	30-45	42	>> 200	68	>200	141
Anglian	mm	1443		104		490		101
	%LTA	126	70-100	42	>> 200	66	>200	206
Thames	mm	1618		106		653		117
	%LTA	122	30-45	40	>200	77	20-30	198
Southern	mm	1994		97		695		140
	%LTA	133	>200	36	>> 200	74	30-50	203
Wessex	mm	2126		138		954		144
	%LTA	132	>200	48	80-120	95	2-5	200
South West	mm	3032		187		1247		136
	%LTA	135	>> 200	52	70-100	90	2-5	146
Welsh	mm	3100		224		1242		125
	%LTA	123	50-80	53	70-100	80	15-25	109
Scotland	mm	3040		314		1462		198
	%LTA	111	5-15	68	35-50	87	10-15	139
Highland	mm	3541		379		1623		251
	%LTA	105	2-5	74	10-20	80	35-50	147
North East	mm	1961		273		1248		297
	%LTA	105	2-5	77	5-15	107	2-5	341
Tay	mm	2717		254		1382		178
	%LTA	116	10-20	65	20-35	96	2-5	156
Forth	mm	2476		228		1116		136
	%LTA	117	25-40	61	40-60	85	5-15	124
Tweed	mm	2163		202		993		123
	%LTA	116	15-25	57	60-90	85	5-15	138
Solway	mm	3064		270		1446		102
	%LTA	112	5-15	59	50-80	87	5-10	71
Clyde	mm	3636		358		1667		138
	%LTA	112	5-15	70	15-25	85	10-15	77

LTA refers to the period 1961-90.
Return period assessments are based on tables provided by the Meteorological Office. The tables reflect rainfall totals over the period 1911-70 only and the estimate assumes a sensibly stable climate. They assume a start in a specified month; return periods for a start in any month may be expected to be an order of magnitude less - for the longest durations the return period estimates converge.
"Wet" return periods underlined.

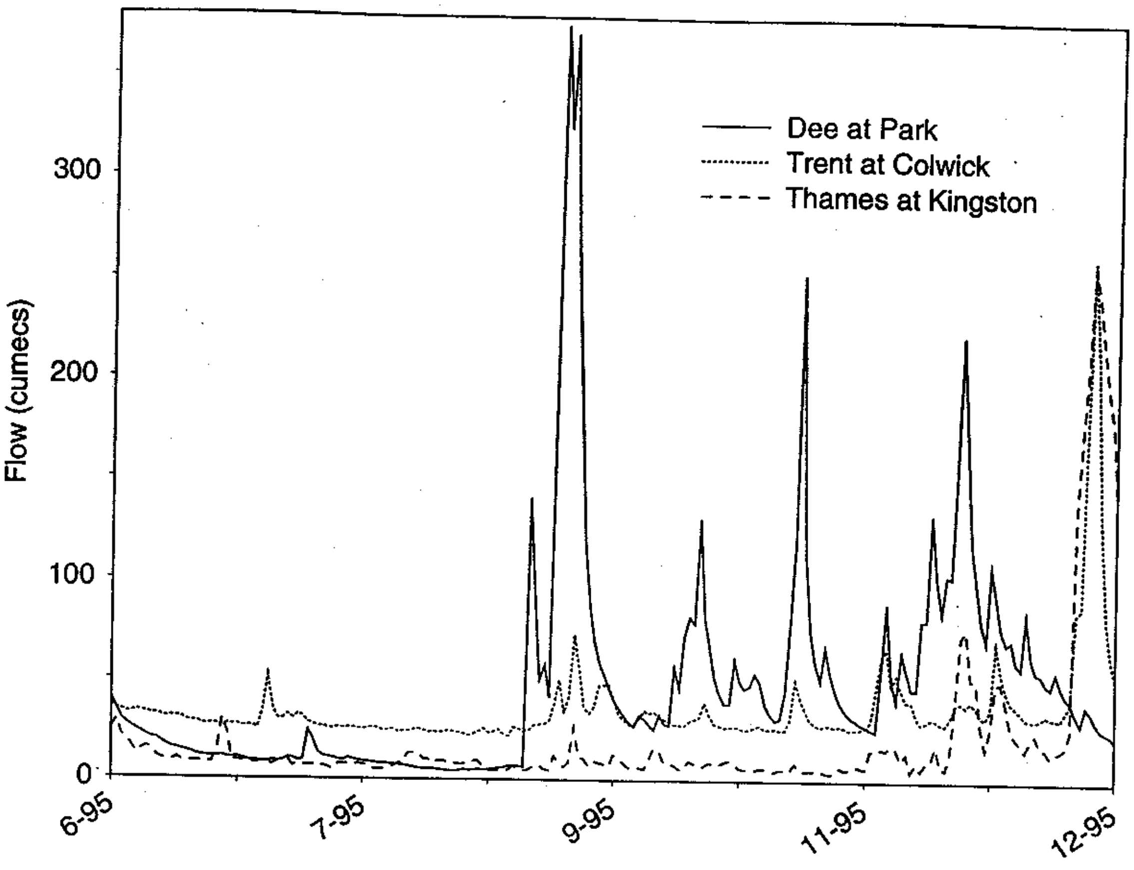


Figure 2.9 Daily mean flow hydrographs for the Dee (Scotland), the Trent and the Thames

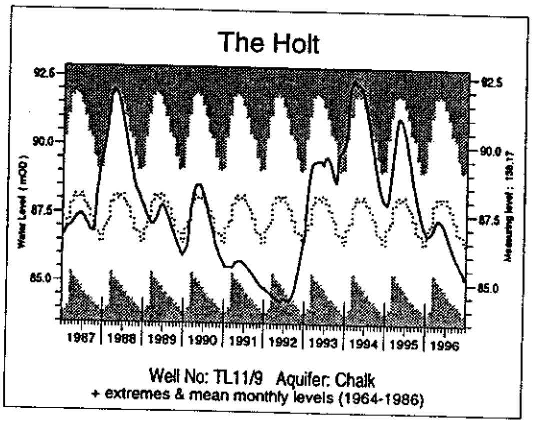


Figure 2.10 Groundwater level variation: The Holt, Hertfordshire

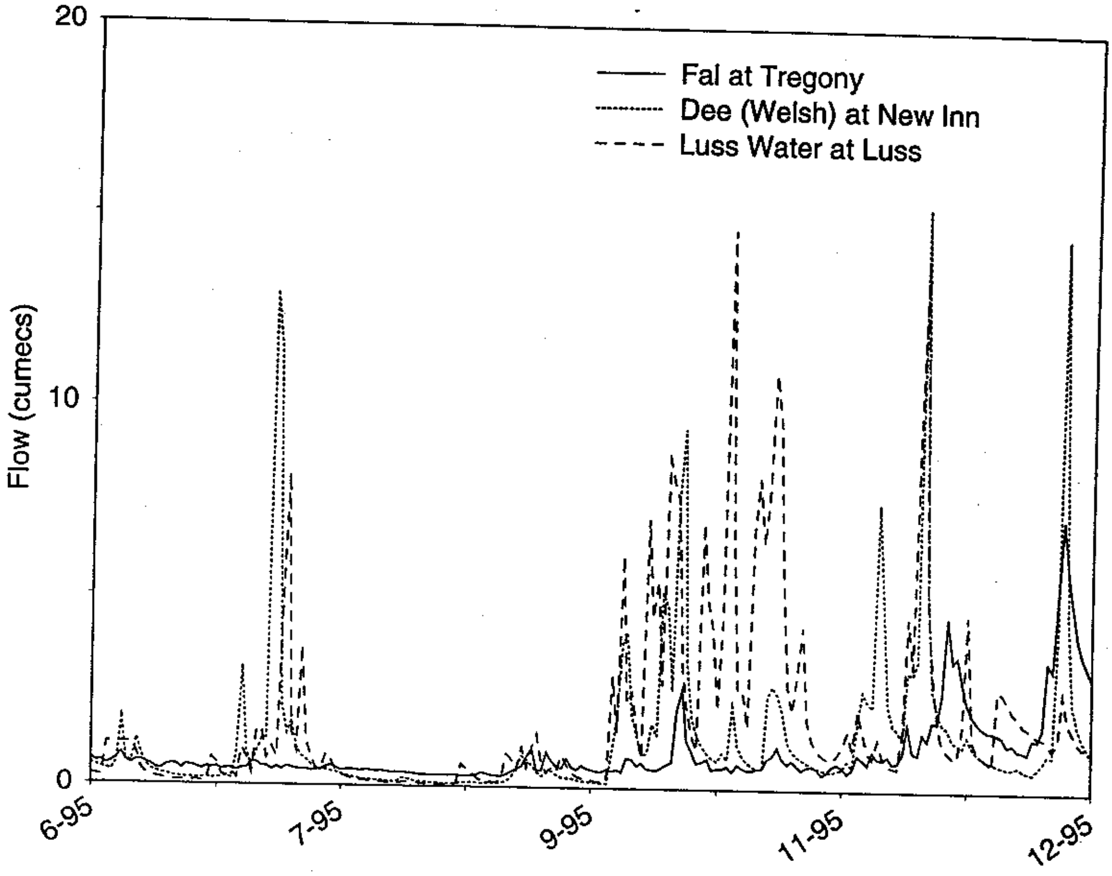


Figure 2.11 **Daily mean flow hydrographs for the Fal, the Dee (Wales) and the Luss**

2.2.4.1 Partial Termination of the 1995 Drought

Over wide areas, heavy and sustained rainfall in September 1995 produced a termination, albeit temporary, of the meteorological drought. In a few areas, e.g. north-east Scotland, the termination was dramatic but generally the rainfall failed to satisfy the exceptional soil moisture deficits and, hydrologically, the termination was weak and indistinct. A dry end to 1995 resulted in the drought entering a second phase (see below) which intensified through the winter and continued into the summer of 1996.

In rainfall terms the interruption of the drought was clear-cut in most regions. Light rainfall over the 1995 August Bank Holiday heralded a remarkably unsettled fortnight. Early September witnessed a further dramatic change in weather patterns with a sequence of active frontal systems sweeping across most regions. Several areas recorded more rainfall over the first 10 days of September than in the preceding 10 weeks. Rivers were in spate throughout much of north-eastern Scotland where the Dee (at Park) registered its highest September flow on record (Figure 2.9) and floodplain inundations were protracted and widespread in response to monthly rainfall totals of around three times the 1961-90 average. However, although much of Britain registered abundant rainfall in September, relatively few frontal systems penetrated to parts of northern England and many catchments reported below average rainfall. In southern Britain monthly rainfall totals mostly exceeded 150% of the 1961-90 average - substantially so in parts of East Anglia. But soil moisture deficits at the end of the second warmest summer on record exceeded 120-150 mm in most eastern catchments; these soil moisture deficits robbed the rainfall of its hydrological effectiveness and no significant spates could be identified in most rivers. The daily hydrograph trace for the Thames and Trent (Figure 2.9) confirm the lack of recovery in flows through the autumn, the only significant spate being recorded in late December. Even then, however, the peak flow was below the mean annual flood level. In eastern lowland rivers reliant principally on groundwater the September termination was barely recognisable and flow rates remained below average throughout most of the ensuing winter. Although runoff rates picked up more briskly in western catchments during the autumn of 1995, the seasonal recovery was again sluggish and few notable spates were registered through the 1995/96 winter. In western Scotland, Wales and the South-West, daily flow hydrographs for a selection of catchments (Figure 2.11) confirm the spatially variable response to the September rainfall.

2.2.4.2 Reintensification of the Drought

Throughout most of England and Wales, October 1995 was relatively dry and remarkably mild, concluding the warmest 12-month sequence in the entire CET series. Notwithstanding the wet September, rainfall deficiencies were also very notable at the national scale; the April-October period was the second driest, after 1921, in the England and Wales series which begins in 1767. Return periods associated with the regional deficiencies over the seven months confirmed the drought's focus on northern England. Particularly severe drought conditions continued in the southern Pennines where for some reservoired catchments the accumulated deficiencies since March, in a timeframe critical for water resource management, were the highest on record. With water-table recessions commonly extending over ten months, early November groundwater levels testified to an exceptional decline since the late winter of 1994/95. In some areas, e.g. the South Downs where groundwater levels at the Chilgrove House borehole had fallen over 40 metres since February, drought minima were being approached.

Declining baseflows contributed to notably low early winter flows in many permeable catchments by late 1995. Modest flow increases were registered in most catchments in February 1996 but runoff totals for the 1995/96 winter half-year were well below average throughout most of Britain. October-March runoff totals were typically 50-75% of average with rivers establishing new winter half-year minimum runoff totals showing a wide spatial distribution, e.g. the Carron, Eden, Wharfe, Welsh Dee (at New Inn) and the Kent Stour. In most regions, the 1996 river flow recessions were well established by May and drought conditions continued into the summer. For England and Wales the April 1995 - June 1996 rainfall total was the third lowest, in this timeframe, in the 230-year national rainfall series and large rainfall deficiencies extended across much of Britain. The return periods featured in Table 2.2 provide a guide to the regional variations in drought intensity. By early summer a few lowland rivers had registered 12 successive months with flows below the monthly average and many western and northern catchments reported only one or two months with above average flows in this timeframe. Thus for most rivers, a decisive recovery in flows following the depressed runoff rates in the summer of 1995 was still awaited.

2.2.5 Other drought terminations

Droughts are rarely ended by a single wet month although a number of droughts have been characterised by dramatic final phases (see below). Often, the drought termination may, like the drought itself, have a clear regional dimension and it is not unusual for a drought to break in rainfall terms long before runoff and recharge rates increase sufficiently to signal the end of the hydrological drought.

Post-drought flush effects are most readily identified when sustained, heavy and widespread, rainfall provides a sharp demarcation with the preceding drought. Such conditions obtained, for instance, in the spring of 1922, the winter of 1959/60 and more recently in the autumns of 1976 and 1984. However the termination of the latter events both began at the end of the summer when soils were extremely dry, especially in 1976. Exceptional soil moisture deficits had built up by late August 1976 as a result of the driest 16-month sequence in the 227-year England and Wales rainfall series. This was followed immediately by the second wettest September/October on record. This dramatic transformation caused soil moisture deficits to decline very rapidly in the early autumn but they still moderated the recovery in river flows, in the eastern lowlands especially. Figure 2.12 confirms a steep early autumn increase in flows on the Teifi and the Trent but spate conditions on the Thames were delayed until November and December, resulting in exceptional river mass flows for some determinands (e.g. nitrate) over the winter period.

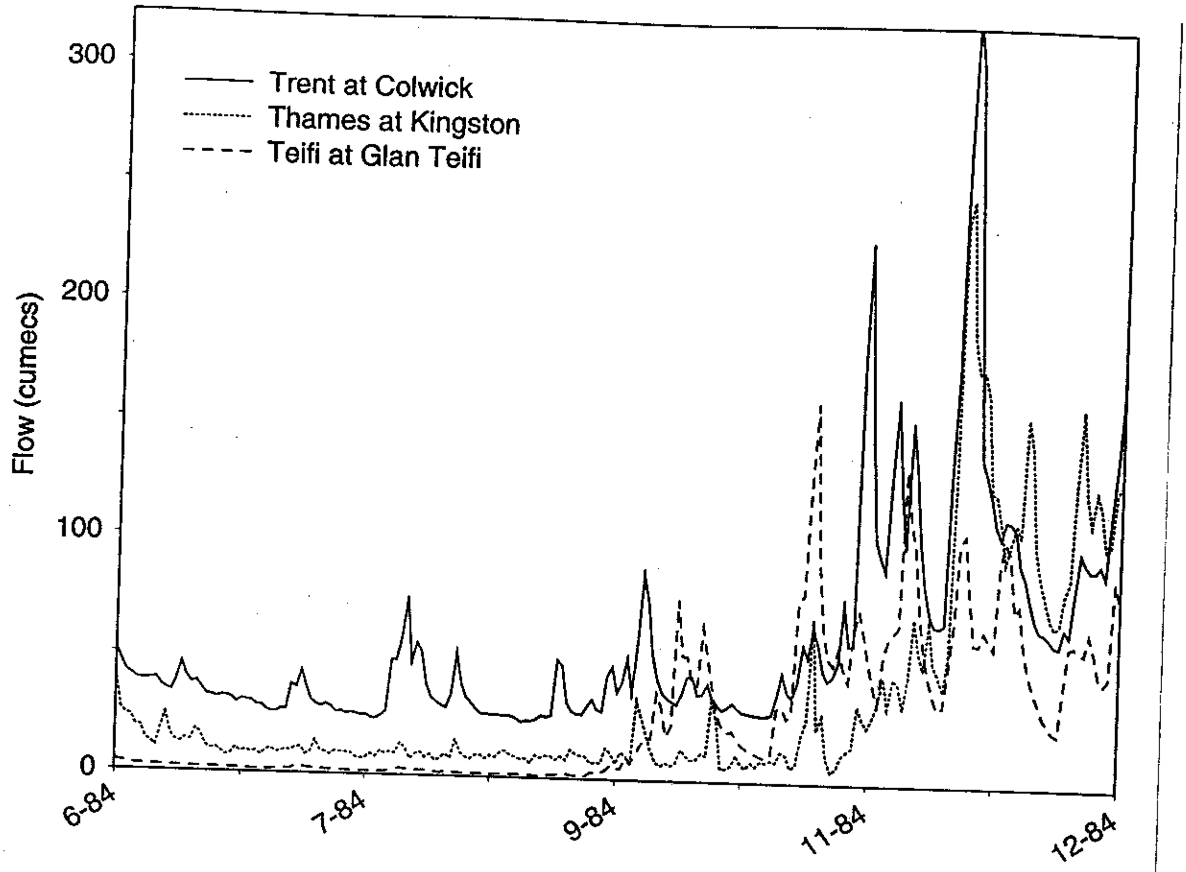


Figure 2.12 Daily mean flow hydrographs for the Trent, the Thames and the Teifi, 1976

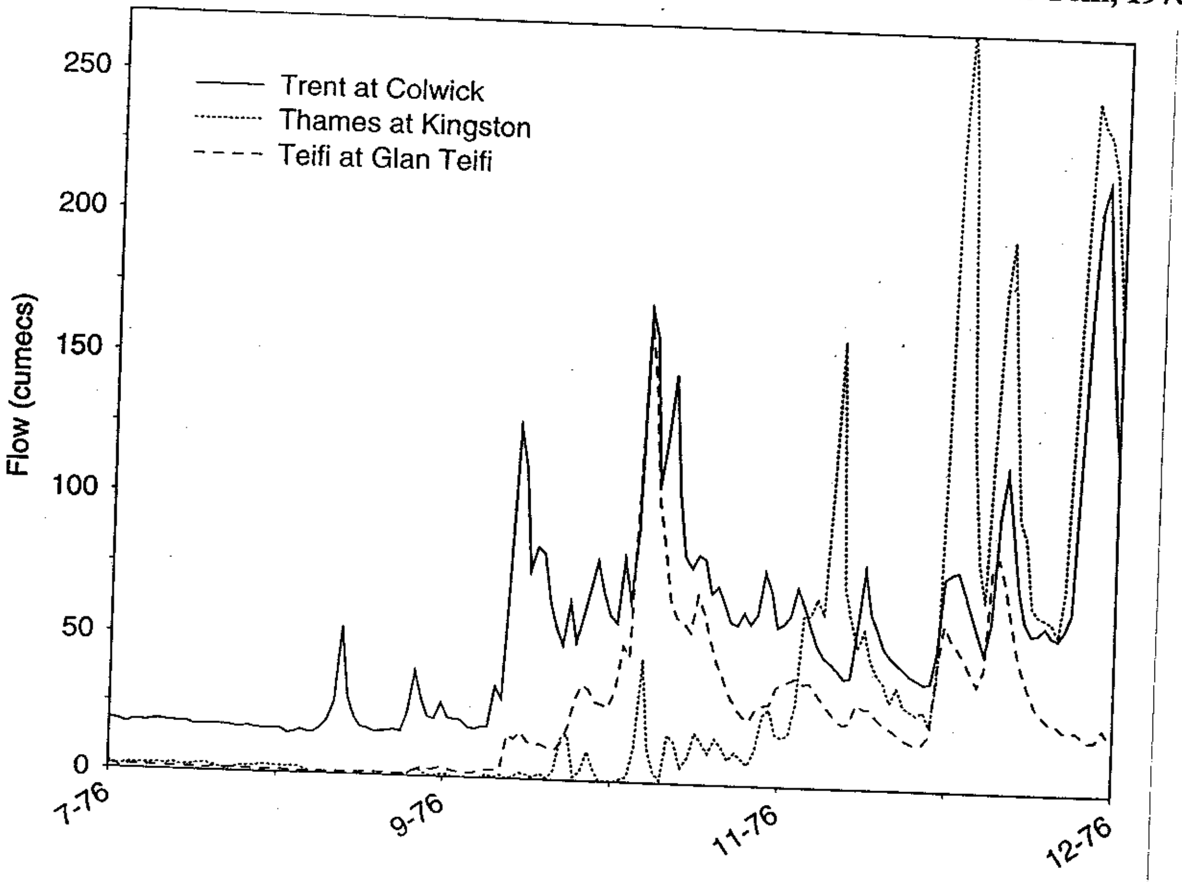


Figure 2.13 Daily mean flow hydrographs for the Trent, the Thames and the Teifi

A less prounced lag between the recovery of individual rivers was evident following the 1984 drought (see Figure 2.13) reflecting the greater spatial consistency of soil moisture deficits at the end of a drought which was significantly more severe in western and northern catchments. Catchment geology was also influential in determining the timing and magnitude of the post-drought spate conditions. In chalk rivers of the south-east, for instance, late summer soils were so parched that substantial infiltration did not occur until the late winter and notably high flows in the Lambourn did not occur until the early winter.

A much more complex runoff recovery, with a very disparate flush pattern, can arise when a drought is broken by heavy spring rainfall. This was well demonstrated towards the end of the protracted drought of 1988-92 (which achieved its greatest severity in the English lowlands). The drought's maximum intensity was achieved in February 1992 and above average rainfall in March and April triggered significant spates in the wet western and northern catchments. By contrast in the east the rainfall was insufficient to counterbalance the accelerating evaporation losses through the spring and the recovery in river flows generally could not be recognised until after an exceptionally wet September.

2.3 River water quality and mass loads

2.3.1 Introduction

As a prelude to detailed descriptions of changes in river water quality during and after the 1995 drought given later in this report, this section describes the mean seasonal variation of river flow and several water quality determinands for the River Ouse in Yorkshire, based on existing data from national datasets from 1974 to 1994. As an example, some of the issues involved in measuring and monitoring river mass loads generally and during drought-break are discussed briefly.

2.3.2 Average seasonal hydrological and hydrochemical responses in the Yorkshire Ouse

The nature of seasonal variations in river flow and water quality in the UK can be readily illustrated using existing national datasets. As an example, Figure 2.14 shows average monthly flow and concentrations of selected river water quality determinands for the Yorkshire Ouse close to its tidal limit over the period 1974 to 1994. The flow data were obtained from the National River Flow Archive (NRFA) managed by the Instititute of Hydrology, and the quality data were retrieved from the Harmonized Monitoring Scheme database managed by the Department of the Environment, Transport and the Regions. (Note that in Figure 2.14 a factor, *F*, has been applied to concentrations to facilitate presentation, on the same plot, of basic seasonal behaviour and any relationships to river flow.)

The mean monthly freshwater flow of the Ouse above its tidal limit varies from about $10m^3s^{-1}$ in summer (with a July minimum) to about $45m^3s^{-1}$ in winter. The corresponding variation in mean monthly suspended sediment concentration is from about 15 $mg.l^{-1}$ (also July) to about 40 $mg.l^{-1}$. Mean monthly nitrate-nitrogen concentration is also lower in summer than in winter; Figure 2.14 indicates a late summer/autumn (September) minimum concentration for nitrate-nitrogen. Conversely, mean monthly concentrations for orthophosphate, ammoniacal-nitrogen, and nitrite-nitrogen tend to be higher in summer than in winter (peaking in July, the time of minimum mean flow).

The mechanisms which control variations in river water quality through time are many and, for some determinands, very complex physically and chemically (as described in later parts of this report). However, Figure 2.14 indicates that the simple processes of dilution (e.g. orthophosphate, ammoniacal-nitrogen and nitrite-nitrogen) and purging/flushing (e.g. suspended solids and nitrate-nitrogen) are important seasonally. Nitrate-nitrogen is particularly interesting; the gradual decline through the summer months in Figure 2.14 is probably associated with denitrification in the river at higher summer water temperatures, whereas the subsequent flushing effect in late summer/autumn is caused by the products of nitrification and surplus agricultural fertilizers being transported to the river system from the catchment as it becomes wetter and generates more runoff via surface and near-surface processes. (In highly urbanised catchments, however, river concentrations of nitrate-nitrogen can be highest at times of low flows because of a lack of sewage effluent dilution.)

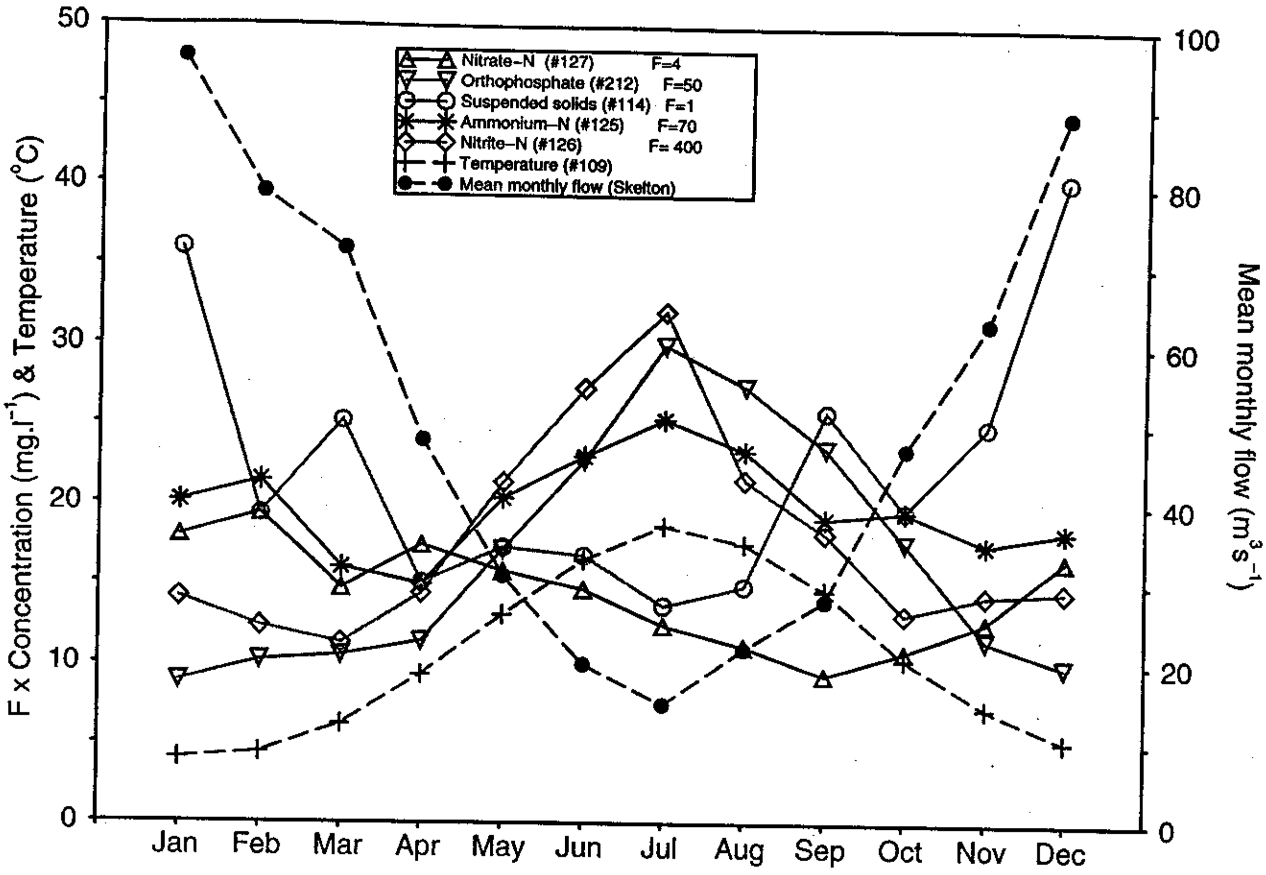


Figure 2.14 **Seasonal variation of river flow and water quality: Ouse at Naburn Weir, 1974 to 1994**

Although the seasonal pattern of river quality can be illustrated using existing national datasets, the detail of autumnal flushing from specific catchments is not so easy to establish from the same sources of data. Figure 15 shows NRFA daily mean flows for the Ouse at Skelton and HMS nitrate-nitrogen and suspended solids concentrations at Naburn from October 1975 to December 1977. Naburn is about 12 km downstream of Skelton. It can be observed that more samples were taken at low flows than at high flows during that period and, consequently, most suspended sediment concentrations are low values. On occasions when a sample was taken at a high flow, e.g. 2 December 1975 and 14 June 1977, Figure 15 shows that a high suspended solids concentration was also observed (note also the high nitrate-nitrogen concentration data during the autumn period after the break of the severe 1976 drought. In later chapters of this report, several examples of changes in river water quality during 1995, using more frequent sampling data, are presented.

2.3.3 Uncertainties in estimates of river mass loads

Although very large masses of nitrate-nitrogen and suspended solids were undoubtedly flushed out of the non-tidal Ouse catchment during September and October 1976, it is not possible to quantify the amounts reliably from the HMS data. Indeed, the reliable estimation of UK river mass loads over short periods (e.g. autumnal flushing events) can be problematical generally because of the paucity of concentration data, relative to that for flow data, (Littlewood, 1995). Many of the problems associated with estimating mass loads discharged by UK rivers have been considered in the context of calculating 'best' time series of annual mass loads, 1975 to 1994, for 15 key determinands, from HMS and NRFA data (Littlewood et al., 1997). There is considerable scope for periods of intensive sampling, as described in other chapters of this report, to gain better quantification and understanding of river mass loads, particularly during periods immediately following droughts.

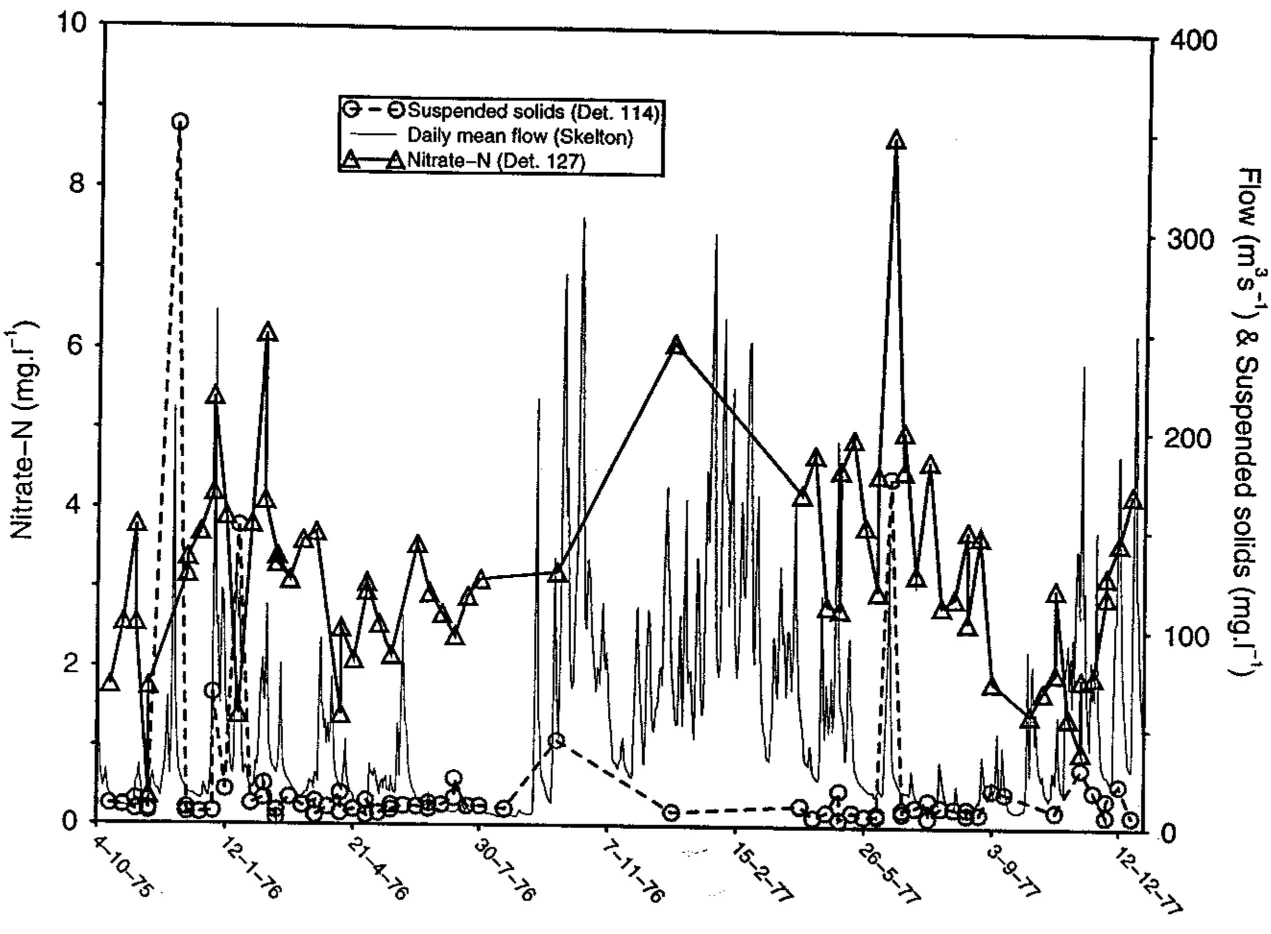


Figure 2.15 River flow and water quality 1975 to 1977: Ouse at Naburn Weir

Appendix

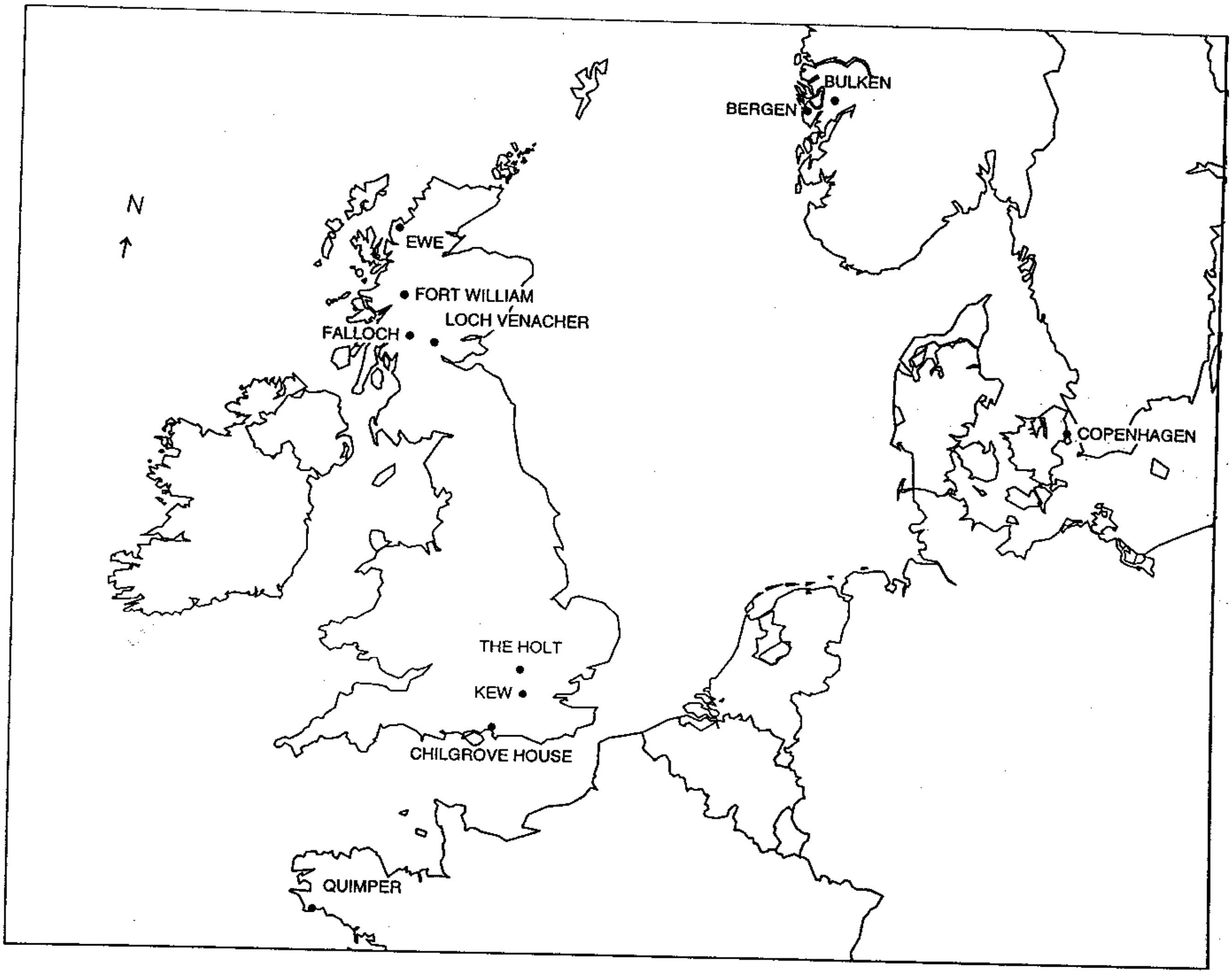


Figure A2.1 Location of selected places mentioned in chapter 2

3. HYDROCHEMICAL RESPONSE OF SELECTED UPLAND STREAMS TO DROUGHT BREAK

3.1 Introduction

The 1995 drought has provided a major opportunity to assess the impacts of prolonged periods of low rainfall on stream water quality and to investigate the release of nutrients and pollutants to surface waters during drought break. The work described was undertaken at a variety of upland sites in England and Wales, many of which have been subject to long-term intensive study for more than a decade. This provides the opportunity both to set the 1995 drought in context as well as to supplement routine monitoring with event based data in order to better characterise extremes of chemistry. This document is the result of a collaborative effort across three Institutes of the NERC Centre for Ecology and Hydrology. Individual authors and their affiliations are indicated in the reference section at the end of the chapter.

3.2 Evidence for hydrochemical responses to previous droughts

Long-term (c. 10 years) records of stream water chemistry now exist for a number of NERC research sites including Plynlimon and Llanbrynmair in mid-Wales and Beddgelert forest in north Wales. (Site details are given later in this chapter) These provide the opportunity of assessing the effects of the 1995 summer drought in the context of previous dry summers such as 1984 and 1990. The catchments provide a variety of upland landuse types including semi-natural acid grassland, agriculturally improved (limed) grassland and plantation conifer forest in various stages of maturity.

With regard to the analysis of long-term data, the changes caused by drought effects must be set in the context of other meteorological changes and varying pollutant input patterns. Presently, only data for the Afon Hafren at Plynlimon has been examined in detail for long term trends

(Robson and Neal, 1996). There were no convincing long term trends in rainfall chemistry although a wide range of contaminants exhibited higher peak concentrations from 1991 onwards; these include lead and chromium. The stream chemistry data indicate clear trends in DOC, iodine, bromide and iron, which increase over time, presumably due to increased breakdown of organic materials within the catchment.

For most other determinands, any changes in stream water quality were masked by the year to year variations in the quantity and quality of rainfall. For example, zinc and chromium exhibited stream variations which parallelled the rainfall concentration patterns. In the case of chromium, consistent rainfall/stream-water patterns occurred only during the mid to late 1980s when chromium in rainfall was enhanced. This was reflected in the stream water draining all of the Plynlimon catchments where trace element chemistry was available (Neal *et al.*, 1996), and was notably absent from the time-series for lead. During the 1990s, high rainfall chromium concentrations were not matched by high stream water concentrations; the high rainfall concentrations during this later period correspond to low rainfall volumes thus the lack of correlation might be expected.

The effects of rainfall patterns were very marked for marine derived elements such as chloride. For both total and non-marine sulphate, the stream water variations are the inverse of that for chloride (Neal *et al.*, 1996, Robson and Neal, 1996). This suggests that dry deposition of sulphur may vary with weather conditions; high when the air masses come from the land and low during periods when weather systems are predominantly frontal and laden with sea salts. These long term data demonstrate considerable variation in rainfall and streamwater solute concentrations. In the short term such variations might, incorrectly, be interpreted as a rising or falling trend. In the case of sulphur, for example, such apparent trends might appear for four to five years, however, the longer period of data demonstrates that this is merely part of a cycle driven by meteorological patterns bringing periods of predominantly marine deposition, followed by periods of terrestrially derived pollutant deposition. To determine true trends a data record much longer than ten years will be required (Robson and Neal, 1996).

In examiming long term records it is also impotant to take account of changes which are not directly related to rainfall variations. For example, an important change in baseflow chemistry took place in the Nant Tanllwyth, a tributory of the Hafren, following the introduction of a deep borehole near the river, just upstream of the sampling point. The borehole installation has clearly opened up a groundwater fissure system which connects to the main stream allowing the entry of base rich waters through the river bed. This was marked, at times of low flow, by the deposition of iron oxides in the stream. Stream water quality at low flow is now characterised by pH values of approximately 0.5 units higher and alkalinity values five times greater than in previous years. During 1997, the changes that occurred have persisted. The observations made at the site, to date, suggest that the borehole has tapped into a major groundwater supply and extensive underground fissure system capable of significantly improving the acidity of the stream. Indeed, during the winter period, the borehole became artesian and the outflow was so great that the borehole had to be capped.

At baseflow, pH and calcium concentrations are much lower at a "bridge site" above the borehole input (by a factor of 0.5 pH units and a factor of a half to a quarter for base cations; Ca, Mg, Sr and Ba). Indeed the characteristic changes are mainly associated with baseflow chemistry and solely for those components associated with weathering (base cations and alkalinity). For stormflow, the main differences are for a) calcium which is about 30% lower at the bridge site, b) alkalinity which is more negative at the bridge site and c) pH which is 0.4 units lower at the bridge site. The chemistry upstream at the bridge site reflects a composition very similar to that observed prior to the introduction of the borehole. Correlation of pH data for the Tanllwyth and Tanllwyth Bridge sites show a maximum discrepancy at intermediate pH values with differences of 1 to 1.5 pH units at pH 5 for the bridge site. Thus, the major influence of the borehole introduction has not only been confirmed, but the large changes in stream water chemistry, particularly at intermediate pHs, may well be sufficient to have significant ecological impacts. The scale of the change in chemistry is so large that it demonstrates a potential for the reversal of stream acidification by groundwater manipulation using boreholes.

There are a number of hydrochemical signals indicative of extended periods of low stream flow. The most consistently observed of these are elevated concentrations of calcium, along with raised pH and alkalinity (Figures 3.1 and 3.2) reflecting an increased dominance of base-rich groundwater in the stream as supplies of more acidic surface and near-surface soil water diminish. At Plynlimon, for example, the summers of 1984, 1989, 1990 and 1995 were marked by extended periods of low flow (Figure 3.2), and these are clearly distinguished by the calcium time-series (Figure 3.1). These responses are generally characteristic of upland streams and are accentuated in streams having particularly alkaline baseflow, for example the Cyff catchment at Plynlimon. At very acid sites, such as stream D3 at Beddgelert Forest in north Wales, the pH response is damped although calcium concentrations increase in low flow periods (Figures 3.3).

The drought break response for these solutes is a rapid decline in pH, alkalinity and calcium concentrations which is consistent with increasing soil water inputs from acidic surface and near-surface soil horizons. This response is evident even in catchments containing large areas of limed agricultural land. Thus although 39% of the Cyff is covered by limed grassland, there are sufficient areas of acidic peats, podzols and gley soils to generate acid runoff under most flow conditions. However, extreme acid responses are buffered in the Cyff by the combination of base-rich groundwater and runoff from limed soils (Reynolds *et al.*, 1986) as shown by the

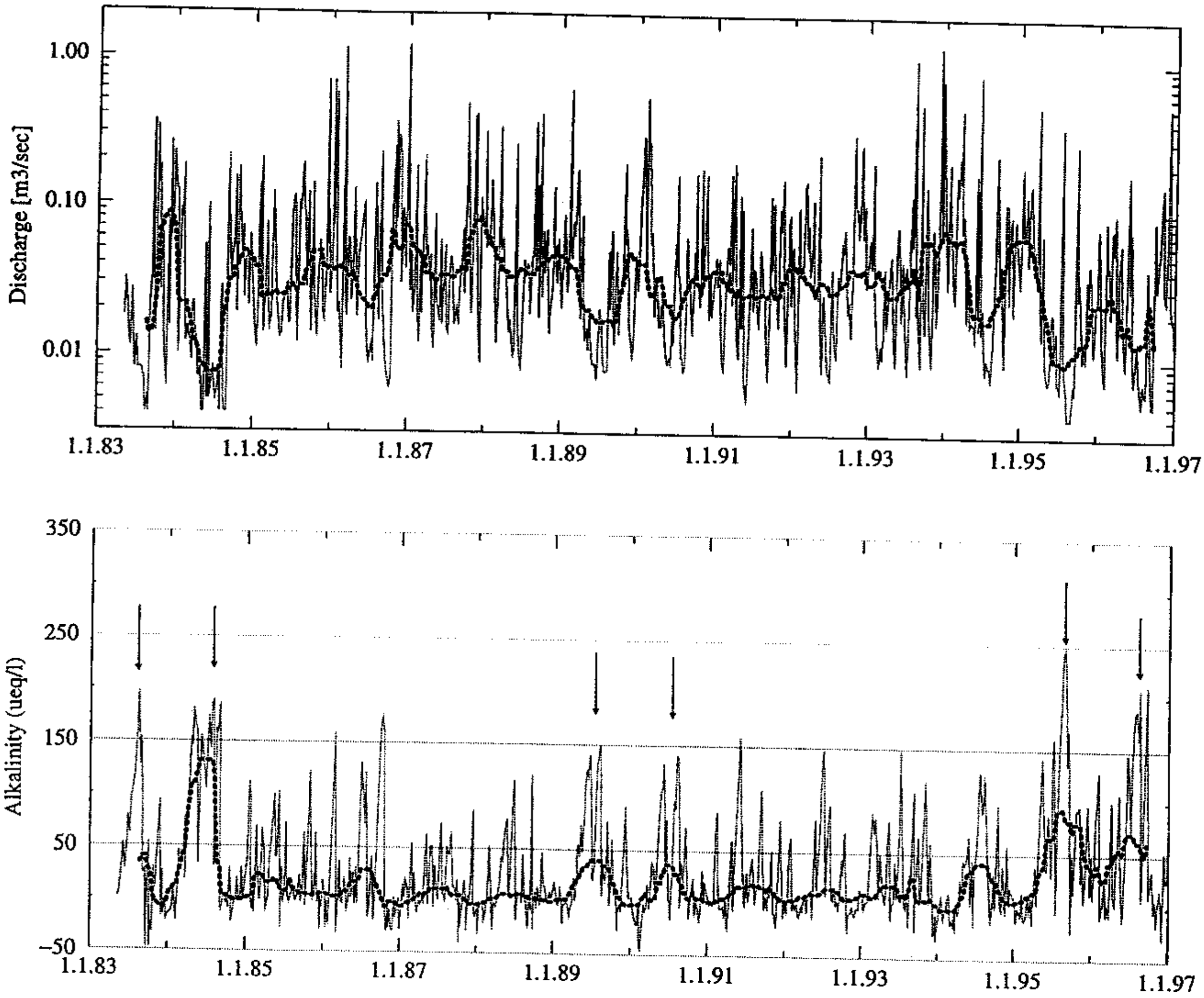


Figure 3.1 Long-term evidence for drought effects on upland stream water chemistry: Flow and alkalinity in the Afon Hore at Plynlimon, arrows show periods of prolonged dry weather resulting in the predominance of alkaline baseflow waters. Discharge is plotted on a log scale to normalise the data. The dotted lines are thirty day moving medians.

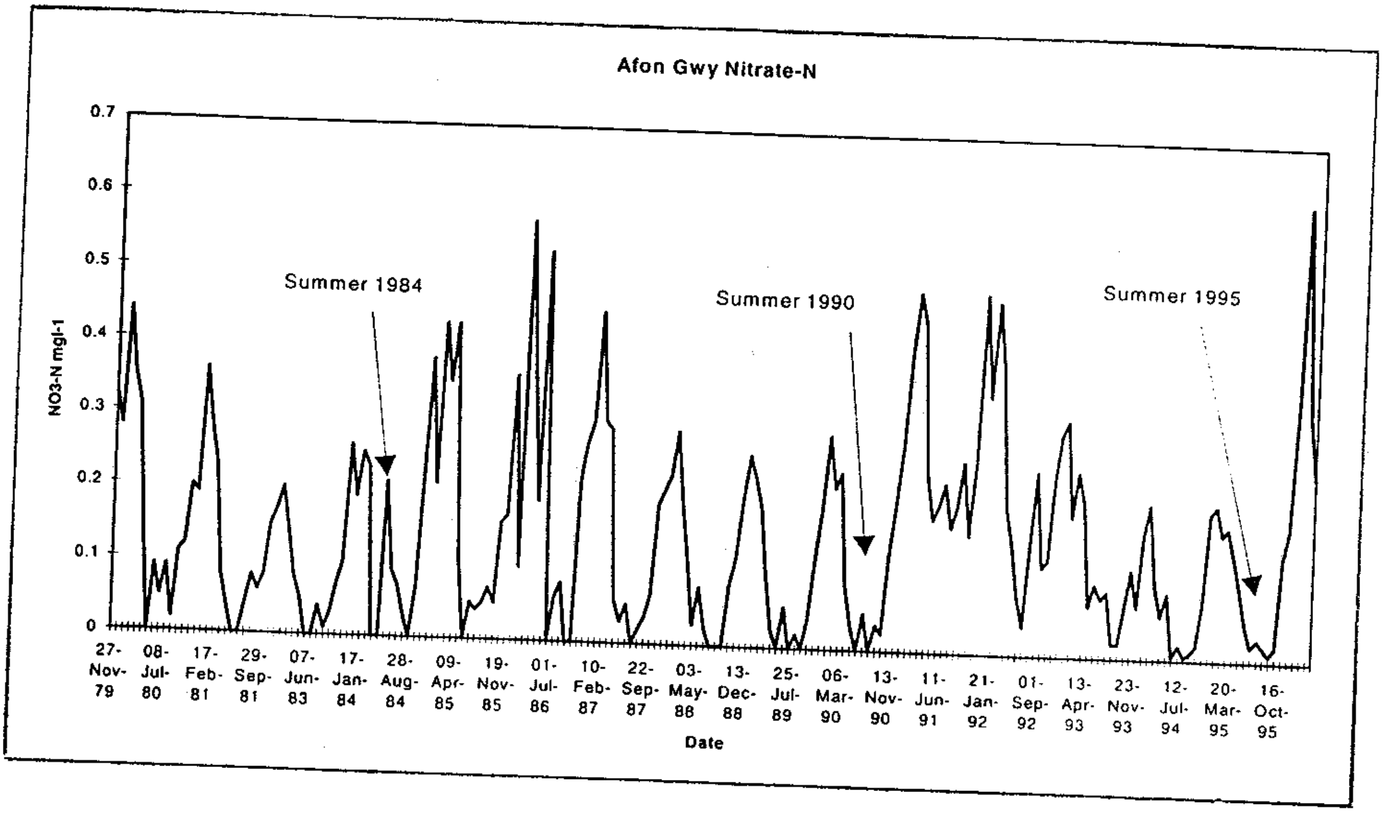


Figure 3.2 Time-series of nitrate-nitrogen concentration in the Afon Gwy at Plynlimon, mid Wales, showing evidence for the disruption of the nitrogen cycle during extended dry periods. Nitrogen output falls during the build-up of the drought rising steeply following drought-break and the acceleration of nitrification processes.

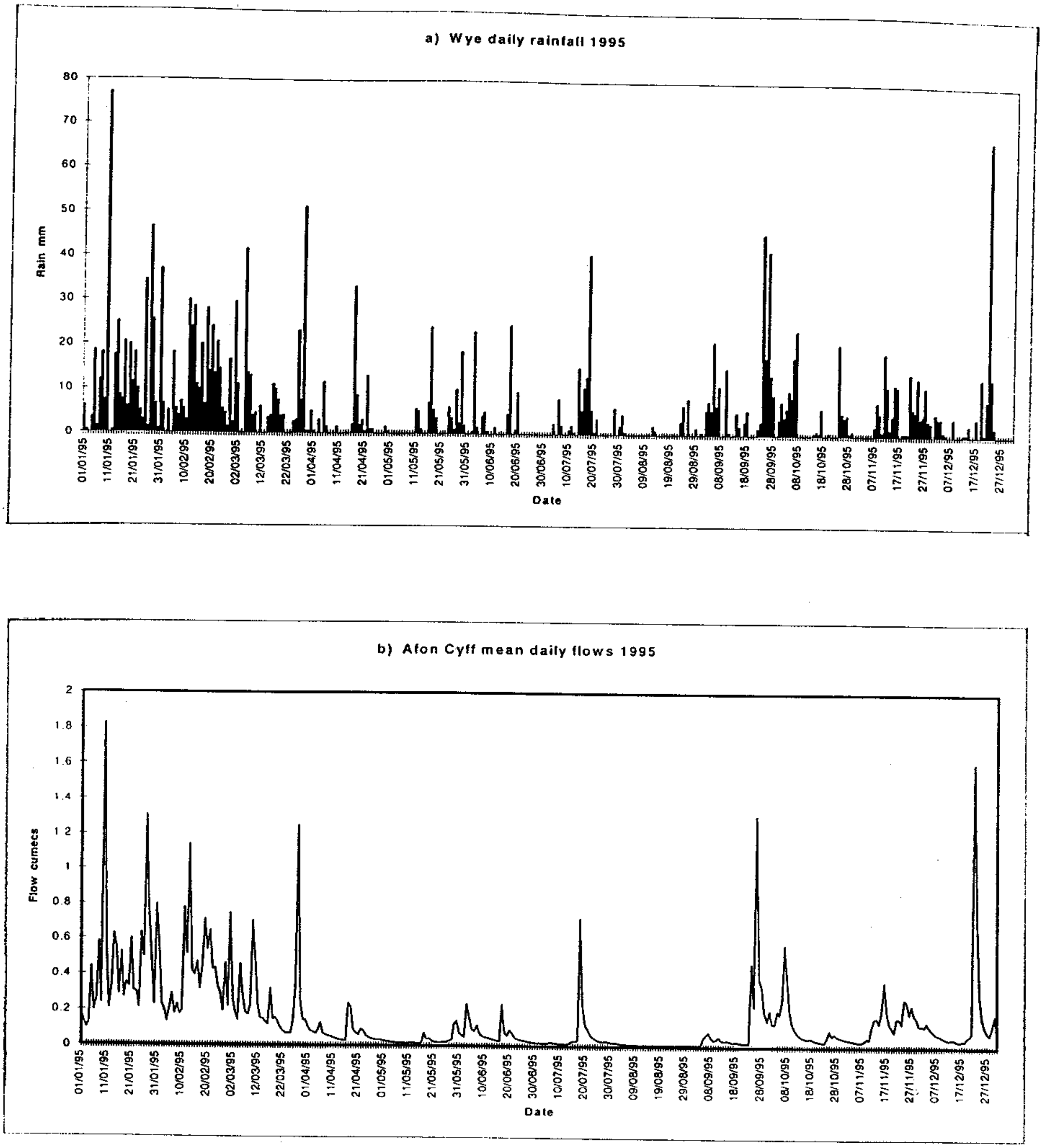


Figure 3.3 Rainfall at the Wye (Cyff and Gwy) catchments and stream mean daily flow in the Cyff from early 1995, through the development of the drought and eventual drought break in September 1995.

Table 3.1Range of pH and hydrogen ion concentrations in the Afon Gwy and Afon Cyff at Plynlimon.

	Afon Gwy	Afon Cyff
pH	4.21 - 6.90	4.93 - 7.26
H^+ meql^{-1}	0.1 - 61.6	0.05 - 11.7

Stream water nitrate concentrations show a more complex response to extended dry periods (Reynolds and Edwards 1995) with the effects being seen in subsequent years rather than during the immediate drought-break period. Under "normal" climatic conditions, a regular seasonal cycle of summer minima and winter maxima in nitrate concentrations is observed in upland streams draining semi-natural moorland catchments and those supporting low intensity agriculture. This pattern is generally explained in terms of the seasonal availability of nitrate within the soil for leaching (Edwards and Thornes 1973). Under most summer conditions, soil nitrate availability will be low if plant and microbial demand exceeds the rate of nitrogen supply from both the atmosphere and the soil. Under these conditions, lowest recorded stream water nitrate concentrations often fall below detection limits (<0.01 mgNl^{-1}). In the winter, atmospheric inputs increase and plant requirements decrease, so that more nitrate is available for leaching. As long as soil temperature and moisture conditions remain favourable, soil microbial activity may continue to produce nitrate through the winter. At sites where the nitrogen available in the soil during the summer is not fully utilised by plant and microbial uptake, summer leaching may occur and the seasonal cycle may disappear or in extreme cases be reversed. Such effects have been attributed to forest die-back (Hauhs *et al.*, 1989), reduced nitrogen utilisation by old forests (Stevens *et al.*, 1993) and excessive nitrogen deposition to acid hill peats (Black *et al.*, 1993). The cycle may be further disrupted by forest management activities such as harvesting which can result in a flush of nitrate lasting up to five years following felling (Reynolds *et al.*, 1995)

At Plynlimon and Beddgelert, the seasonal cycles of stream water nitrate concentrations were disrupted in the grassland catchments following the dry summers of 1984 and 1990 (Figure 3.4). Large increases in winter maxima and elevated summer concentrations were observed in subsequent years particularly following the 1990 dry summer. Soil water studies at Plynlimon indicated that soil solution nitrate concentrations increased during the summer of 1984 due to a combination of enhanced evaporation and reduced plant uptake resulting from drought stress (Reynolds *et al.,* 1992). As the soils re-wetted during the autumn, this nitrate was leached and was probably supplemented by flushes of mineralisation and nitrification. The amount of nitrogen produced by the latter processes is positively related to the length of the dry period, the dryness of the soil and the temperature (Birch 1960) and thus will be determined by the preceding drought conditions. The persistence of relatively large nitrate concentrations into subsequent years could reflect a delay in plant response due to root damage sustained during the drought. In addition, the production of inorganic nitrogen by soil microbes may be stimulated by the presence of a readily available substrate in the form of fine roots and lysed microbial biomass accumulated through the previous summer.

Although the effects of the 1984 and 1990 summer droughts on stream water nitrate concentrations at Plynlimon and Beddgelert were large relative to normally observed values, maximum concentrations were very low compared to those typically encountered in lowland streams and rivers. Furthermore, whilst the summer of 1989 produced a period of sustained low flows at both sites, giving a stream response for calcium, there was no effect on nitrate concentrations. Presumably conditions were not severe enough to disrupt the terrestrial nitrogen cycle.

The patterns of response for the forest catchments are less consistent. In the Cwm catchment at Llanbrynmair which is about 90% afforested with young Sitka spruce still at a pre-canopy closure stage, the pattern of response is similar to that observed in grassland catchments (Figure 3.5). For the Hafren catchment at Plynlimon, which is about 50% afforested with mixed age, first and second rotation Sitka spruce, a regular cycle of nitrate concentrations is observed, although summer minima are typically between 0.5 and 1.0 mgN l^{-1}. The summer of 1984 had a marked effect on nitrate concentrations in this catchment although there was only a small effect following the 1990 summer. In contrast to other sites, in stream D3 at Beddgelert, which is 100% afforested with 60 year old Sitka spruce, the pattern of variation is much less regular. The lowest nitrate concentrations are about 0.5 mgN l^{-1} compared with summer values below 0.01 mgN l^{-1} in the adjacent D6 acid grassland catchment. There were, however, periods of sustained, elevated nitrate concentrations in D3 following the summers of 1984 and 1990.

Whilst other major, minor and trace solutes measured at the NERC sites exhibit annual and seasonal fluctuations, these can not be readily related to the occurrence of summer droughts.

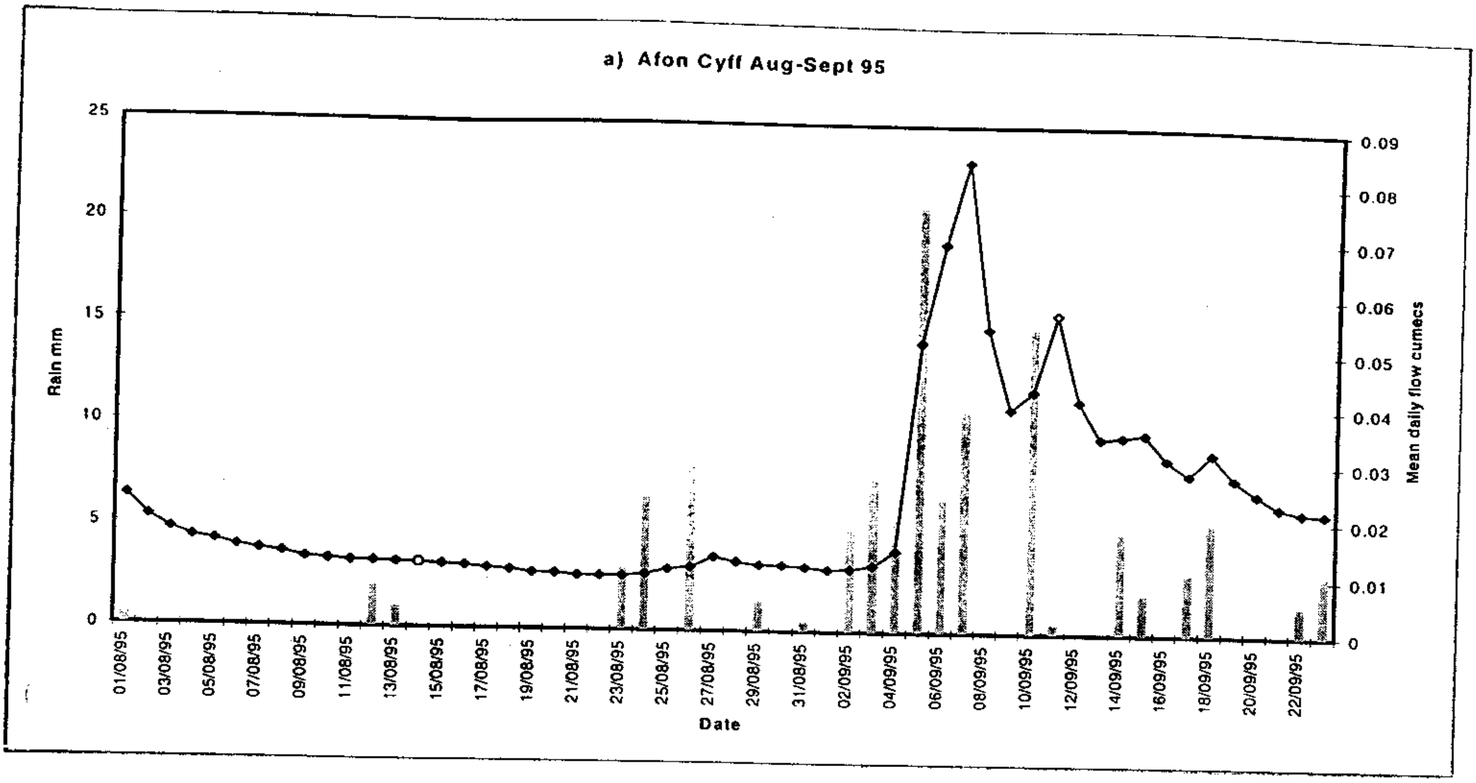


Figure 3.4 Rainfall at the Wye (Cyff and Gwy) catchments and stream mean daily flow in the Cyff. The first stream response to rainfall at the end of the summer period.

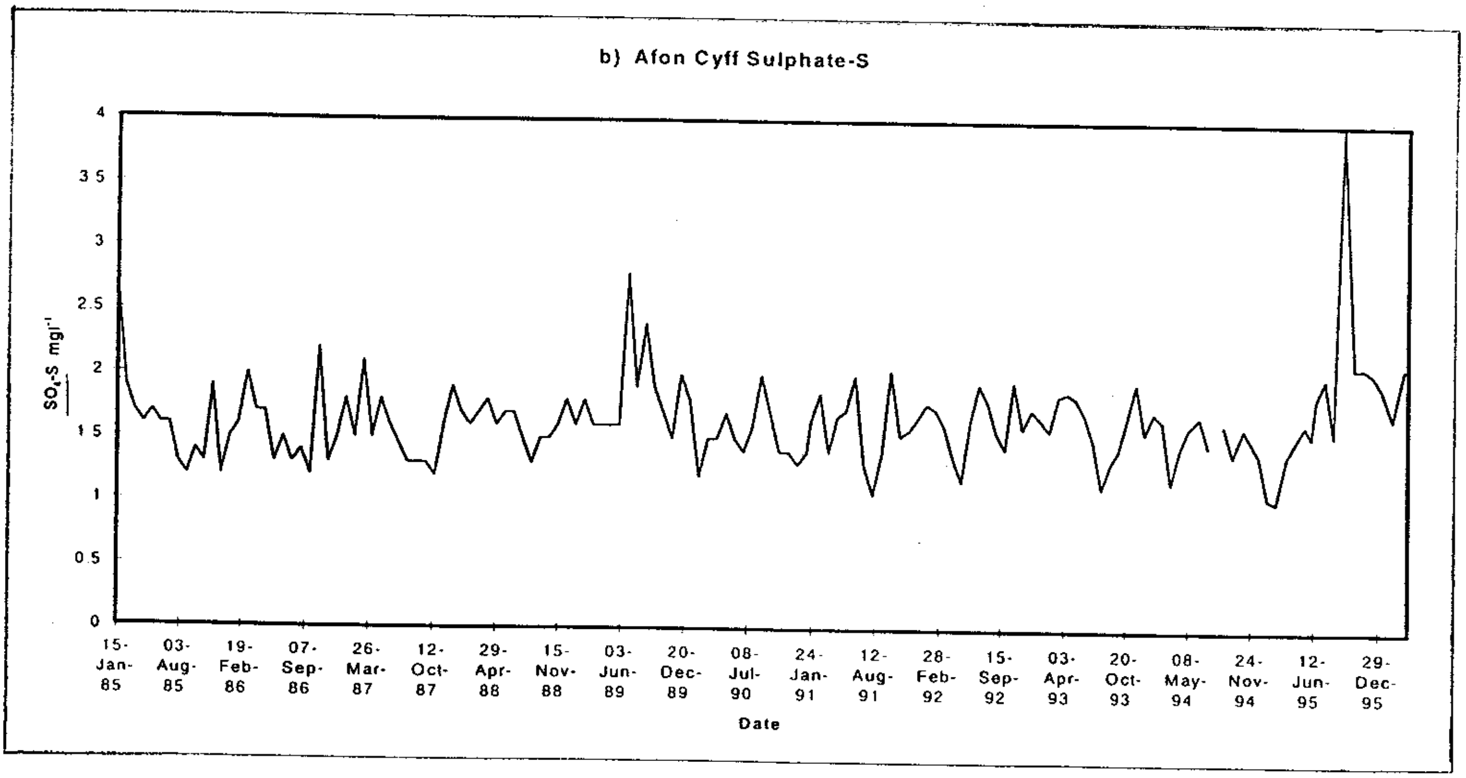


Figure 3.5 Time series of sulphate-sulphur concentration in the Afon Cyff at Plynlimon, mid Wales, showing the huge peak in concentration at drought-break in September 1995.

3.3 Wales

3.3.1 The Plynlimon catchments

Site descriptions

The catchments of the Afon Gwy (376 ha) and the Afon Cyff (307 ha) lie within the headwaters of the River Wye whilst the Afon Hafren (357 ha) and Nant Tanllwyth (97 ha) form part of the headwaters of the River Severn. The area lies to the east of Plynlimon approximately 24 km from the west coast of Wales and the catchments range in altitude between 340 m and 740 m above sea level. The mean annual rainfall is 2500 mm.

The Plynlimon catchments are underlain by base-poor Lower Palaeozoic shales, mudstones and grits. Drift deposits within the catchments are locally derived, consisting of stoney boulder clay at the base of slopes with shale or grit colluvium on the slopes themselves. A mosaic of acid upland soils occurs throughout the catchments, consisting of peats, stagnopodzols, acid brown earths and stagnogleys.

The dominant vegetation of the Cyff and Gwy catchments is an acid *Nardus-Festuca* grassland which is present on the long, well-drained slopes with podzolic soils. The hill-top peats support *Eriophorum, Calluna* and *Vaccinium* communities, in contrast to the valley bottom peats and stagnogleys which are dominated by *Molinia* and *Juncus*. These catchments are part of a large hill-farm and are grazed by sheep at a density of about 2.5 ewes ha^{-1}. About 40% of the Cyff and 7% of the Gwy catchment have been agriculturally improved over the last 60 years. A variety of treatments has been used including additions of basic slag, ploughing followed by ground limestone addition and, more recently, surface rotivation with compound fertilizer and lime additions together with re-seeding with more productive grasses (Hornung *et al.*, 1986).

Forty eight percent of the Hafren catchment and 100% of the Tanllwyth were afforested in three phases between 1942 and 1964. The main tree species are Sitka spruce (*Picea sitchensis*) and Norway spruce (*Picea abies*), although Japanese larch (*Larix kaempferi*) and Lodgepole pine

(*Pinus contorta*) were also planted in some areas of the catchment. Prior to planting, areas of poorly drained soils were ploughed and drained. In the autumn of 1974, the forest received aerial applications of potash (200 kg ha^{-1}) and phosphate (375 kg ha^{-1}).

As mentioned in section 3.2, with regards to the Nant Tanllwyth catchment, a major change in baseflow chemistry was observed early in 1995 following the introduction of a deep borehole near the river just upstream of the sampling point. The borehole installation had clearly opened a groundwater fracture route thus allowing base rich waters to enter the stream through the bottom gravels in the river. This was marked in the stream by the deposition of iron oxides at times of low flow. Due to this borehole installation, stream water low flow is now characterised by pH values about 0.5 units higher and calcium concentrations five times higher than for previous years. Over the year, the changes occurring have remained without any decline. Indeed, during the winter period, the borehole became artesian with very high outflows and consequently, it had to be sealed with a capping.

Methods

Rainfall to the experimental catchments is monitored by a network of ground-level gauges supplemented by automatic weather stations which provide data as to the timing of individual rain events. Streamflow from the Plynlimon catchments is monitored by the Institute of Hydrology using steep stream flumes (Smart 1977). The water level within the flume is recorded on an electronic data logger at fifteen minute intervals. Water level is converted to stream discharge using theoretical rating equations which have been extensively validated using dilution gauging, current metering and volumetric gauging (Kirby *et al.*, 1991).

Since November 1979, samples of streamwater have been collected every four weeks from a point just upstream of the flow gauging structures in the Cyff and Gwy catchments. On return to the laboratory, pH and alkalinity are measured on an unfiltered subsample whilst Na^+,K^+, Mg^{2+}, Ca^{2+}, Al, Fe, SO_4^{2-}, Cl^-, NO_3^-, NH_4^+ and DOC are determined using standard techniques after filtration through 0.45 mm membrane filters (see Reynolds *et al.*, 1986). Samples of rain water from the Carreg Wen site (NGR SN827885, 600 m) and stream water from just upstream of the Hafren flow gauging site (NGR SN 843877, 335 m) have been collected at weekly intervals since 1983, and on the Tanllwyth (NGR SN844873, 340 m) since 1991. Alkalinity (Gran titration) and pH are determined on unfiltered subsamples. Major, minor and trace metals are determined respectively by inductively coupled optical emission spectroscopy and plasma emission mass spectrometry. Anions are analysed by automated colorimetric techniques following filtration through 0.2 mm glass fibre filters (Neal *et al.*, 1992).

From 19th June until 30th September 1995, stream water samples were collected daily from the Hafren and Tanllwyth sites. These samples were analysed following the protocols used for the grassland catchments, although subsequent analyses were undertaken for selected trace metals according to Neal *et al.* (1992).

3.3.1.1Results for the grassland catchments

The close proximity of the Cyff and Gwy catchments means that rainfall patterns and hydrograph responses are broadly similar. Consequently, hydrograph data for the Cyff are presented along with rainfall recorded at the automatic weather station at Cefn Brwyn near the catchment outlet.

The summer period from the beginning of May through to the end of September was characterised by a series of rain events of 2-4 days duration interspersed with dry periods lasting up to a maximum of a month (Figure 3.6). Following a significant storm in the middle of July, relatively little rain fell for a period of approximately six weeks. Isolated showers were recorded during this period (Figure 3.6), but these were insufficient to generate a stream flow response. The first rain to produce a streamflow response occurred at the beginning of September. An eightfold increase in mean daily flow to 0.08 cumecs occurred between 1st and 7th of September (Figure 3.7) with a maximum flow of 0.14 cumecs occurring on 7th September. This small event was followed at the end of September by further significant amounts of rainfall with daily totals up to 45 mm which produced a major hydrograph response with a peak mean daily flow of 1.3 cumecs and a maximum recorded flow of 3.1 cumecs.

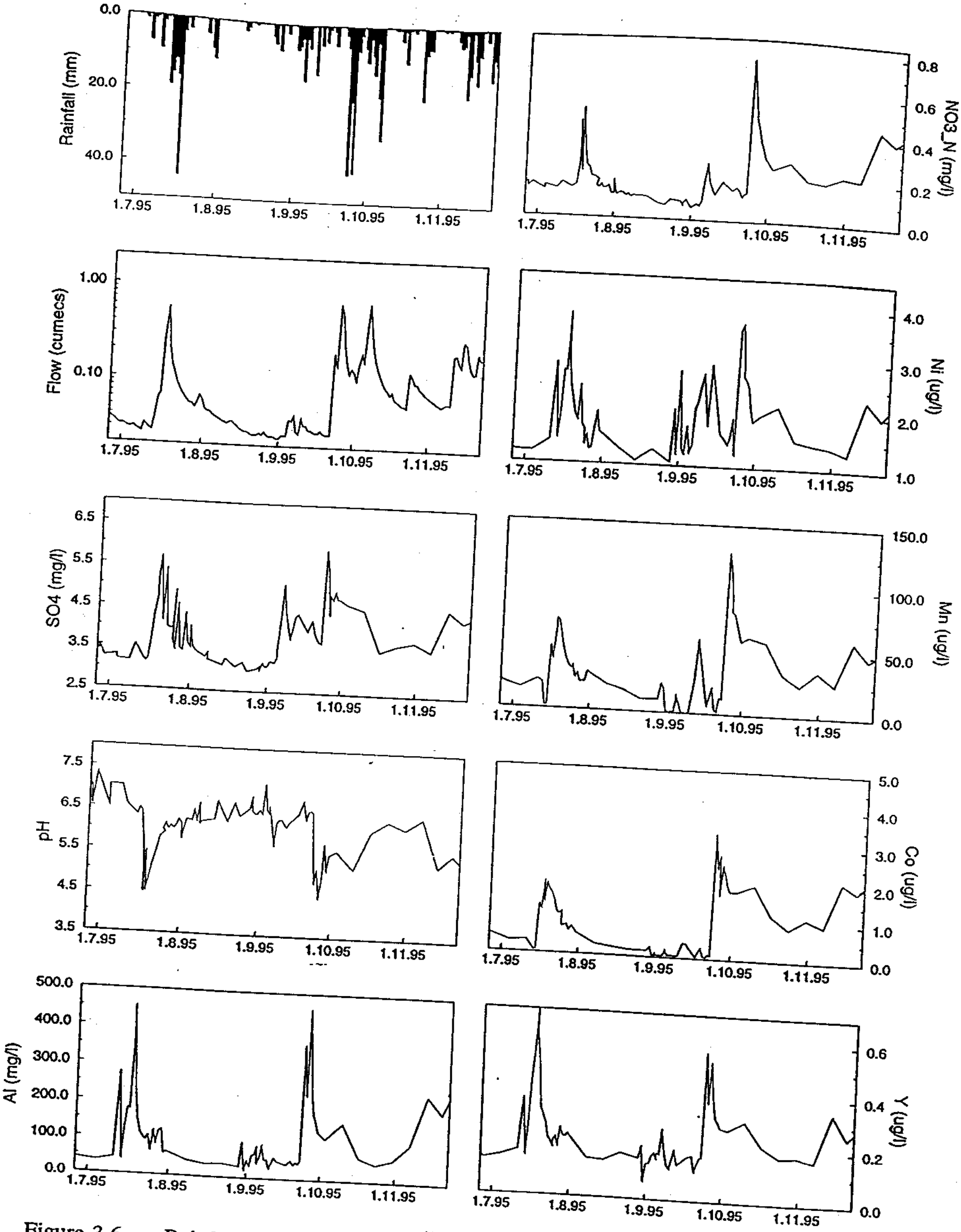


Figure 3.6 Rainfall at Plynlimon, mean daily stream flow in the Afon Hafren and changes in selected major and trace constituents in Afon Hafren streamwater, showing the response to drought-break towards the end of September 1995.

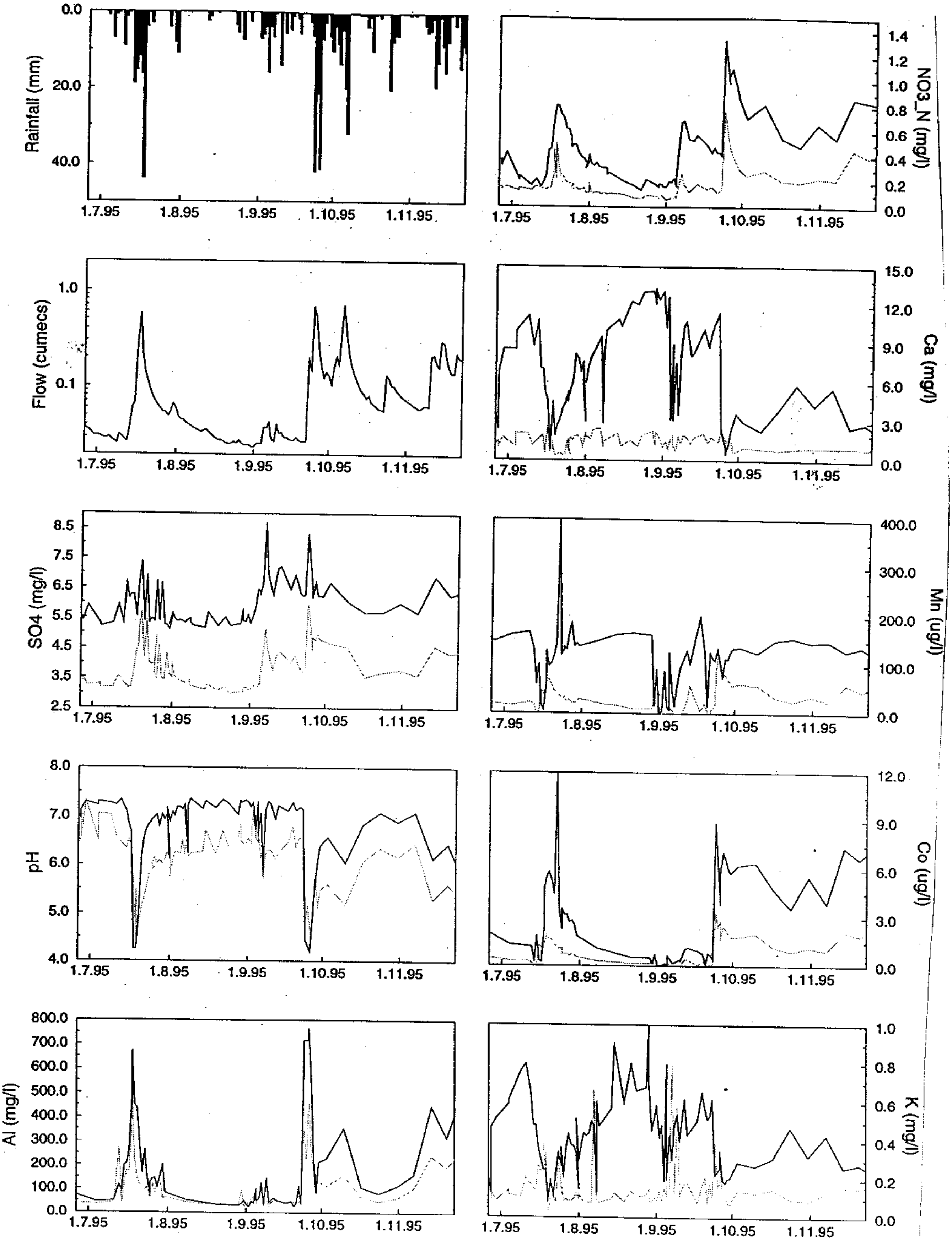


Figure 3.7 Rainfall at Plynlimon, mean daily stream flow in the Afon Hafren and changes in selected major and trace constituents in Tanllwyth and Afon Hafren (feint line) streamwater, showing the response to drought-break towards the end of September 1995.

As noted in Section 3.2, divalent base cation concentrations, pH and alkalinity increased during the prolonged low flow conditions (Figures 3.1 and 3.2). A rapid change from alkaline conditions occurred at drought break reflecting a change in the dominant hydrological pathways from groundwater to a mix of groundwater and more acidic runoff from surface soils in response to incoming rainfall.

Samples were collected from the grassland catchments as part of the NERC routine sampling programme on the 14th August and 11th September. The August sample was taken at about the middle of the six week low flow period whereas the September sample coincided with the small rain event. The September sulphate concentrations of c. 4 mgS l^{-1} in the Cyff and 2 mgS l^{-1} in the Gwy were amongst the largest observed since high quality sulphate analyses (Dionex IC) were introduced in 1985 and represented a 2.5 times increase on the low flow values measured in August (Table 3.2). The increase in sulphate was accompanied by an increase in divalent base cation concentrations and decreases in alkalinity and pH (Table 3.2). The concentrations of other solutes were generally unaffected. Sulphate concentrations in both streams have remained elevated through the subsequent autumn and winter periods.

Table 3.2 Concentrations of selected solutes in samples collected from the Cyff and Gwy on August 14th and September 11th 1995

Cyff	Ca mgl^{-1}	Mg mgl^{-1}	SO_4-S mgl^{-1}	pH	H^+ meql^{-1}	Alkalinity meql^{-1}
Aug 14th	2.88	1.34	1.55	7.03	0.09	210
Sept 11th	3.06	1.76	3.99	6.64	0.23	74
Gwy						
Aug 14th	1.16	0.78	0.84	6.45	0.35	48
Sept 11th	1.44	1.12	1.93	6.12	0.76	28

The flush of sulphate with the first significant hydrological event probably reflects the removal of oxidised organic sulphur from the soil stores. Furthermore, it is probable that the soil moisture and temperature conditions prior to drought break were an important control on the magnitude of the sulphate release. Mineralisation of organic matter is inhibited if soils become too dry, but the low intensity rainfall at the end of August / beginning of September was probably sufficient to stimulate and sustain microbial mineralisation of soil organic matter in the catchments. As this rainfall only produced very small hydrological responses in the streams, it is likely that mineralisation and oxidation products accumulated in the soil during this period. It was not until the 4th and 5th of September that there was sufficient rainfall to induce a significant hydrological response and this would have leached sulphate into the stream. It is unfortunate that only the latter part of this event was sampled as it is possible that sulphate concentrations might have been even larger at the onset. It is also probable, by analogy with data from other sites (see Section 3.3.1.2) that nitrate and possibly ammonium would have been leached in to the stream during the initial stages of the event. Subsequent monitoring through the 95-96 winter has revealed large concentrations of nitrate with maximum values amongst the highest recorded since 1979. This increase in nitrate is consistent with the patterns observed following previous dry summers discussed in Section 3.2.

3.3.1.2 Results for forested catchments

Afon Hafren: General observations

Both long-term weekly and intensive daily data for the Afon Hafren have been examined. The patterns in chemistry through the drought and drought-break periods broadly coincide with those observed at the other sites in the UK examined in this study.

The main changes in chemistry coincided with the changing hydrological source of the water feeding the stream through the study period. In the pre-drought period the stream was fed by a combination of surface, near-surface and groundwaters. As the drought proceeded and the upper soil layers dried out the groundwater source began to dominate the stream chemistry. This situation persisted until the drought breaking storm of 23 September 1995.

Major and trace element chemistry

Throughout the early part of 1995 up to the drought break, alkalinity and calcium concentrations and pH values increased steadily reflecting the increasing proportion of base cation-rich groundwater entering the stream as the upper soil layers dried out. At the drought break on 23 September 1995, alkalinity, pH and calcium plunged to just above pre-drought levels. With the major storm events came dramatic peaks in aluminium, DOC, sulphate, nitrate-N, iron and boron concentrations; sulphate approximately doubled in concentration, the increase in nitrate-N was almost threefold (Figures 3.8-3.10; Table 3.3). The peaks in acid anion concentrations were reflected in the sharp decline in pH; from about 6.6 to 4.4 units. The peak in aluminium would have been due to leaching in the upper soil horizons caused by the high acid anion concentrations. These effects were only transitory, the concentrations undergoing rapid exponential decline to pre-storm values. The effect of the drought break on alkalinity and calcium were longer term with their values remaining below drought levels well into 1996, indicating wetting-up and sustained drainage of the upper soil horizons. Sodium, magnesium and potassium showed no marked response to the drought, although this was not the case in the Tanllwyth, as discussed later.

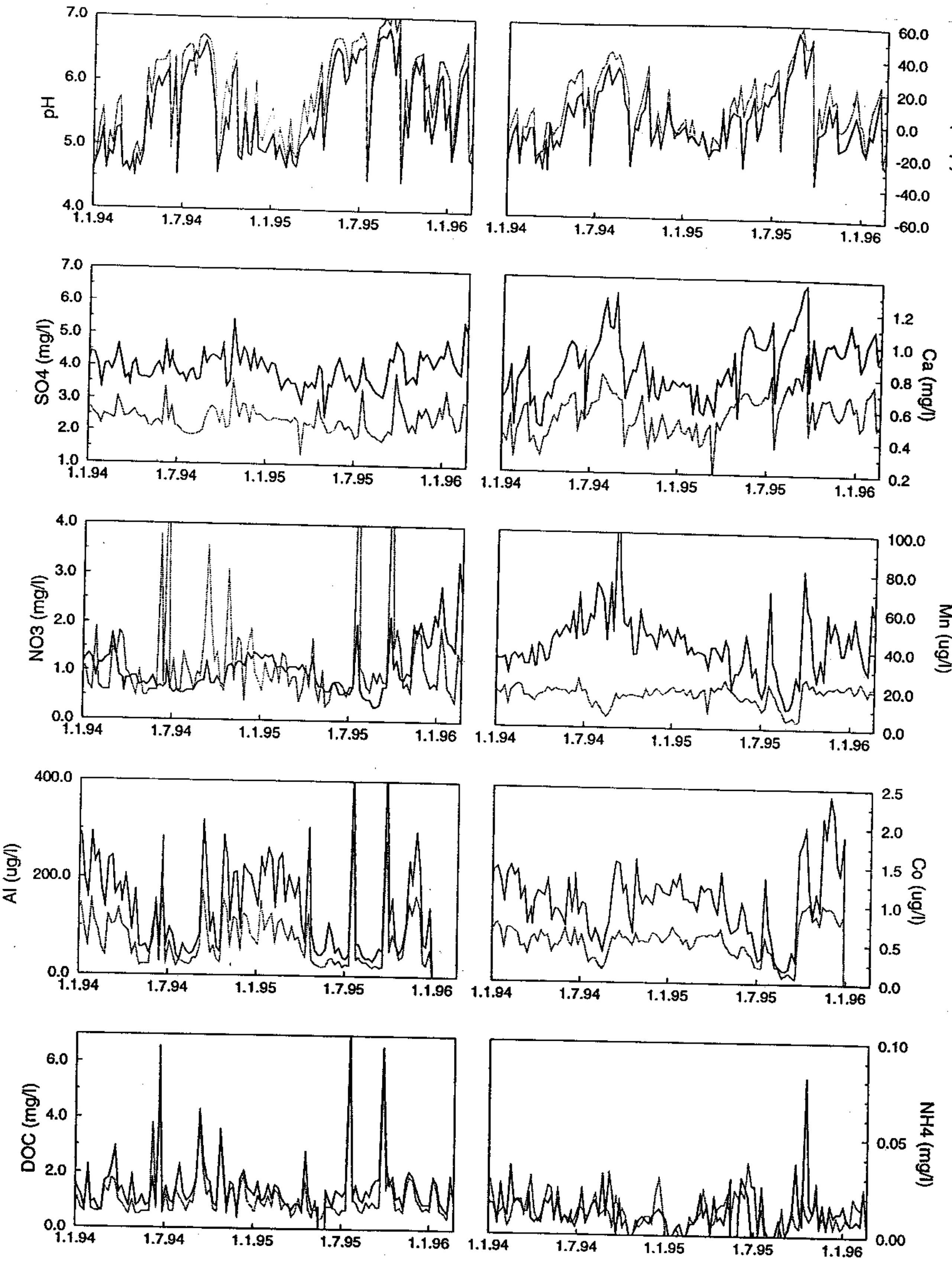


Figure 3.8 Weekly stream chemistry data for the forested Afon Hafren (dark line), and the moorland upper Afon Hafren (feint line), for the period January 1994 to January 1996. The drought-break coincides with the second low pH episode in September 1995.

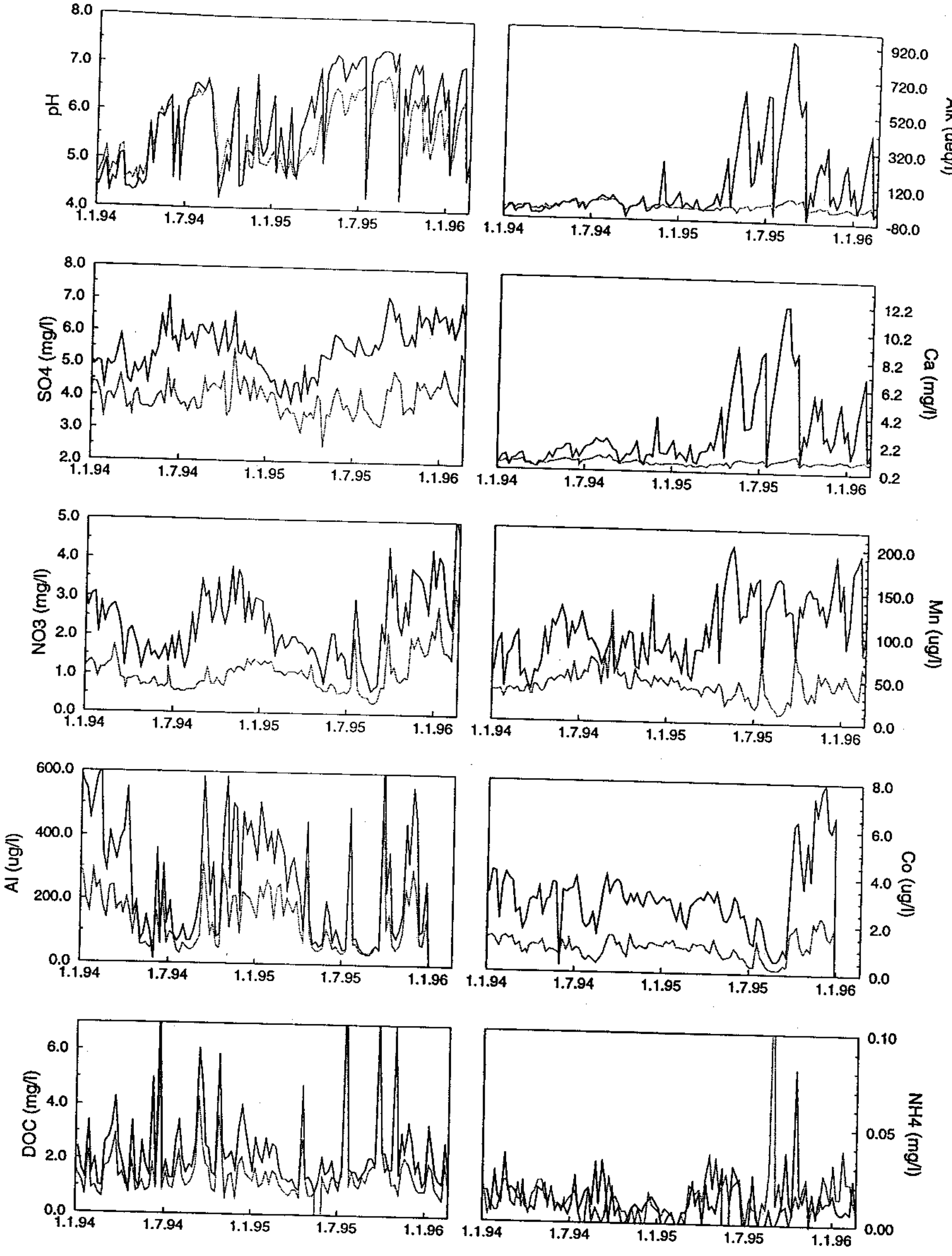


Figure 3.9 Weekly stream chemistry data for the forested Nant Tanllwyth (solid line), and the Hafren (feint line), for the period January 1994 to January 1996. The drought break coincides with the second low pH episode in September 1995.

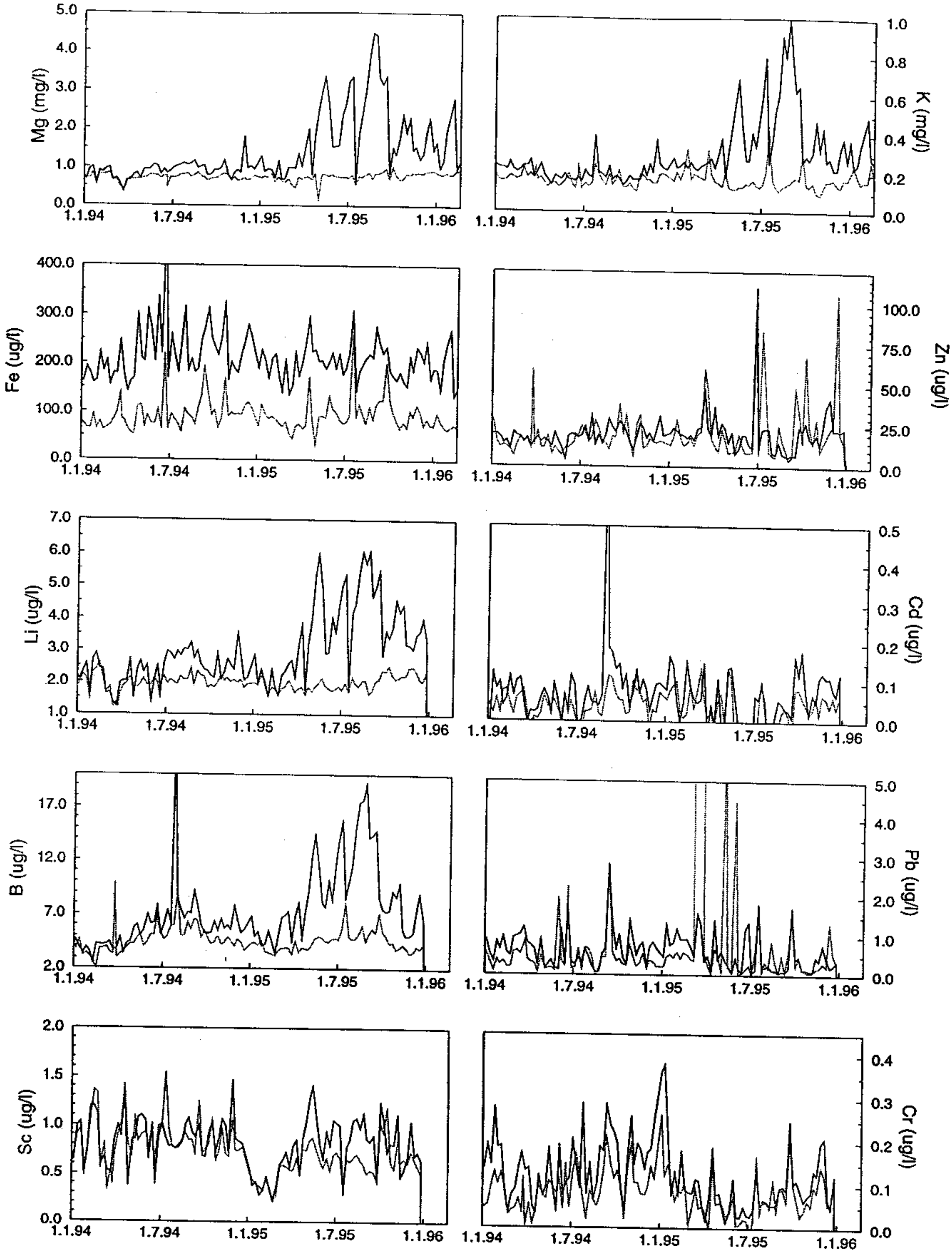


Figure 3.10 Weekly stream chemistry data for the forested Nant Tanllwyth (solid line), and the Hafren (feint line), for the period January 1994 to January 1996. The drought break coincides with the second low pH episode in September 1995.

Table 3.3Summary data for the drought of summer 1995 for Afon Hafren at Plynlimon. Mean concentrations of various water quality determinands for the month preceding the drought break, in the month following the drought, and the actual values for samples collected during the drought breaking storm are given.

Afon Hafren		Drought mean concentration	Drought-break concentration	Post-drought mean concentration
pH		6.59	4.5	5.79
Alkalinity	meql^{-1}	43.3	-38.0	-0.8
Na	mgl^{-1}	4.40	4.59	4.19
K	mgl^{-1}	0.17	0.39	0.13
Ca	mgl^{-1}	1.69	2.32	0.93
Mg	mgl^{-1}	0.90	0.71	0.81
Fe	mgl^{-1}	111.5	202.0	92.1
Mn	mgl^{-1}	18.3	254.0	44.2
Co	mgl^{-1}	0.27	3.35	1.47
Ni	mgl^{-1}	1.39	2.70	1.77
Cr	mgl^{-1}	0.07	0.20	0.06
Pb	mgl^{-1}	0.31	1.43	0.24
Al	mgl^{-1}	45.4	459	95.8
SO$_4$	mgl^{-1}	3.79	5.94	4.1
NO$_3$-N	mgl^{-1}	0.12	0.76	0.23
NH$_4$-N	mgl^{-1}	0.076	0.213	0.029
DOC	mgl^{-1}	1.60	6.60	1.75

Longer term responses to the drought break were also evident in the time series for manganese and cobalt, and to a lesser extent chromium, nickel and ammonium. This was clearly demonstrated for the trace elements in the daily data (Figure 3.10) which also showed that the Al spike coinciding with the storms was a step increase followed by an exponential decline to pre-storm values. Manganese, cobalt, nickel and yttrium also exhibited this step increase and then declined exponentially, but not to pre-storm values; their concentrations remained elevated as shown in the long-term data (Figure 3.8).

Examination of the long-term data shows that the concentrations of manganese, cobalt, chromium and nickel declined as the drought proceeded and as alkalinity and calcium concentrations increased. At drought-break the concentrations rose dramatically, manganese underwent a tenfold increase in concentration along with the acid anions. Unlike aluminium, manganese concentrations remained elevated after the main storm flows had receded although the reason for this is uncertain.

The peak concentrations observed at drought break probably result from a combination of the washout of contaminants accumulated as dry deposition on the forest canopy, the leaching of mineralisation and oxidation products derived from soil organic matter and the remobilisation of metals from oxide phases with soil re-wetting. As noted previously, the moisture status of the soil during the drought will have been crucial to the outcome of these different processes. With the progress of the drought, it would be anticipated that manganese concentrations would decline as the soils dried and became more aerated resulting in the oxidation of the mobile divalent manganese ion to the insoluble Mn^{4+} and precipitation of manganese oxides (MnO_2), probably in association with humic materials. These manganese oxides strongly sorb trace metals, in particular Co and Cd (McKenzie, 1970). Examination of the rainfall record shows that there were frequent small rainfall events during the drought period. Although these were too small to produce a stream flow response and probably did not influence the redox environment of the soil, they may have been sufficient to transfer accumulated dry deposited metals from the tree canopy to the soil where they would be rapidly scavenged by the manganese oxides. It is likely that the input of rain from the 23rd September onwards was sufficient to lead to the development of anaerobic conditions within the soil, at least at the micro-site scale, promoting re-mobilisation of manganese from the oxide phase and release of the associated trace metals. Soil re-wetting and the development of anaerobic conditions will have been a gradual process following the drought and may be the reason why manganese, cobalt, nickel, chromium and yttrium concentrations were sustained in the stream despite the decline in discharge.

The role of soil moisture conditions in the mobilisation of sulphur from soil organic matter has already been discussed in relation to the grassland catchments in Section 3.3.1.1 and is explored more fully in Section 3.5. During the drought, dry deposition of sulphur dioxide will have occurred in both the grassland and forest catchments. However, significantly more sulphur dioxide will have been deposited on the taller, rougher forest canopy compared to the short grassland vegetation (Reynolds *et al.* in press), providing a greater enhancement through wash-off in addition to any sulphur released from soil sources.

In the case of nitrogen, dry deposition of ammonia and NOx will have occurred during the drought, with larger fluxes to the forest canopy compared to the grassland (Reynolds *et al.* in press). However the role of these nitrogen compounds in relation to the stream drought break response is less clear. The primary sites for NOx uptake by vegetation are the stomata with negligible uptake occurring on the vegetation surface (Hargreaves *et al.*, 1992). Thus it is unlikely that this nitrogen would be available for leaching from the canopy with the onset of rain. Very large ammonia deposition rates have been observed to both moorland and forest systems (Sutton *et al.*, 1992a; 1993) and even in the presence of small ambient air concentrations, the input of nitrogen as ammonia to these unfertilised systems can be as large as or larger than wet deposition. Ammonia is very soluble in water especially if the solution is acidic, for example due to the dissolution of sulphur dioxide. Thus the intermittent rain showers during the drought may have enhanced capture of ammonia by the wet vegetation canopies. However upward ammonia fluxes have been observed over senescent heather and moorland vegetation during warm, dry conditions (Sutton *et al.*, 1992b). As with oxidised forms of nitrogen, the fate of the dry deposited ammonia on the canopy is uncertain as assimilation of ammonium by epiphytes in the canopy has been reported (Parker 1983).

On balance it seems likely that microbial release of nitrogen from the soil organic store will be the dominant process determining the stream nitrogen response to drought break. Whilst nitrogen mineralisation can be inhibited by drought stress, it is probable that the intermittent rain during the drought will have stimulated periodic flushes of mineralisation and nitrification throughout the period. In the absence of any soil water flow and the continuing removal of soil water by the trees, this will have resulted in a build up of inorganic nitrogen in the soil solution similar to that observed in the grassland C2 catchment at Plynlimon during the 1984 drought (Reynolds *et al.*, 1992). The accumulated inorganic nitrogen will have been flushed from the soil during the first major rainfall at the end of September. An interesting feature of the nitrogen data is the increase in stream water ammonium concentrations at drought break. Nitrification is limited in these soils by the supply of ammonium substrate and thus is stimulated by an increase in mineralisation rates. Leakage of ammonium into the stream suggests that nitrification may have been limited by some other factor or that nitrifier populations were unable to respond quickly enough to the increased ammonium availability resulting from the flush of mineralisation at the end of the drought.

Nant Tanllwyth

The Tanllwyth stream exhibited similar behaviour to the Afon Hafren although certain differences were observed as a result of the very high groundwater contribution to the stream flow. As with the Hafren alkalinity, pH and calcium underwent steady increases as the drought progressed from early 1995 to the drought break in September 1995. Acid flushes occurred during the major storm events when pH fell from about 7.2 to 4.2 pH units, coincident with this were increases in aluminium, sulphate and nitrate-N, dissolved organic carbon, lead and to a lesser extent cadmium (Table 3.4; Figure 3.11).

The groundwater feeding the Tanllwyth contains large concentrations of all base cations, unlike the Hafren where calcium is the dominant base cation. Hence sodium, potassium, calcium and magnesium, as well as trace elements iron, manganese, lithium, boron, barium, strontium, scandium, cesium and rubidium were all autocorrelated and followed alkalinity, increasing during the drought and falling to just above pre-drought values after the drought break. Comparison of the long-term manganese data for the Afon Hafren and Nant Tanllwyth (Figure 3.11) shows that manganese concentrations in the Tanllwyth did the opposite of the Hafren data. Manganese concentrations increased with alkalinity and underwent sharp dilution with each storm event. At the drought break (23 September 1995), however, the concentration decreased with the peak flow, but then returned to approximately the same value that had prevailed towards the end of the drought. In the Hafren the manganese peaked with the storm and fell slightly to remain at an elevated concentration.

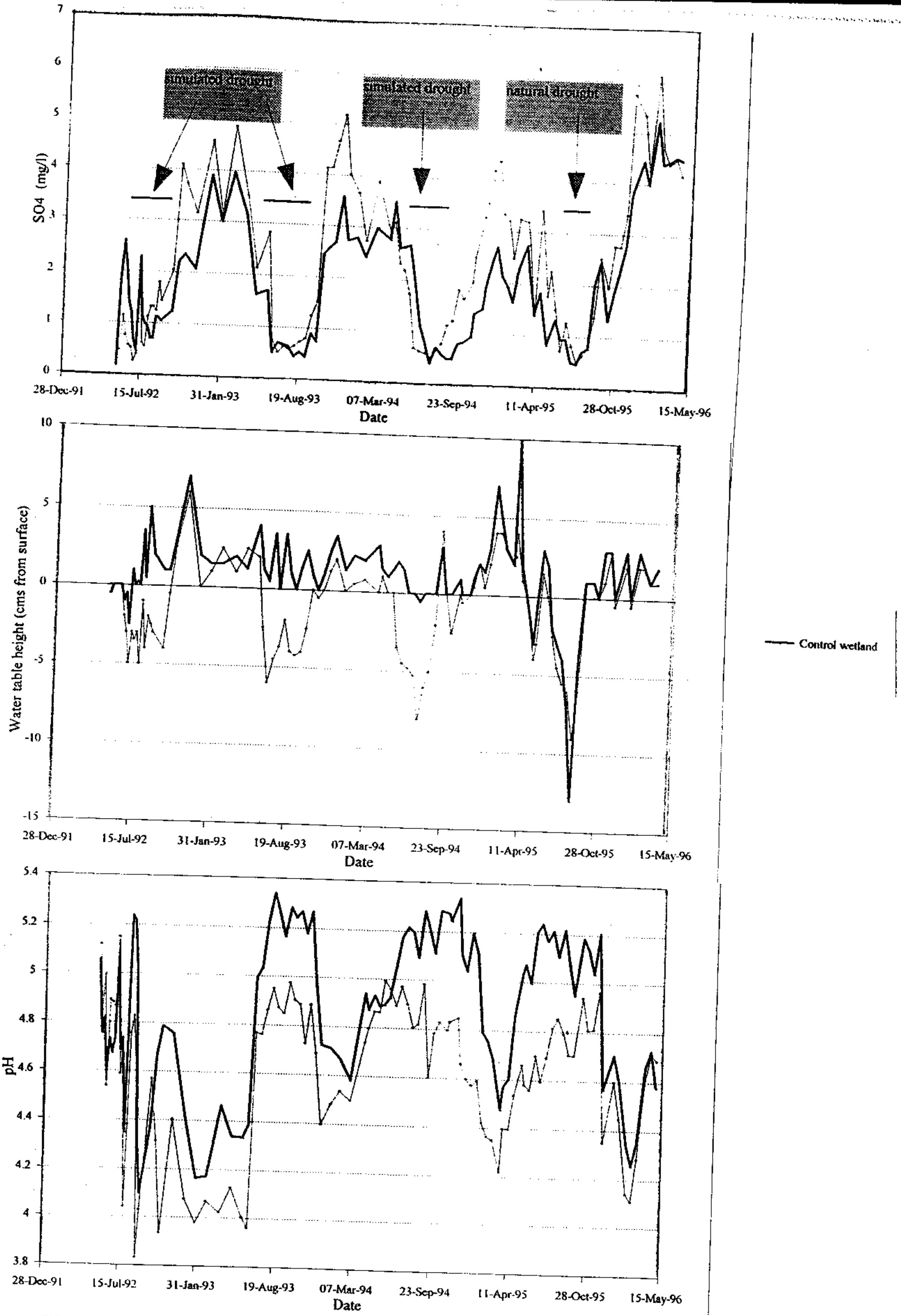


Figure 3.11 Time series plot of water levels, sulphate concentrations and pH, in the dip wells in the control and experimentally droughted peatlands at Cerrig-yr-Wyn, Plynlimon.

Table 3.4Summary water quality data for the drought of summer 1995 for Nant Tanllwyth at Plynlimon.

Nant Tanllwyth		Drought mean concentration	Drought-break concentration	Post-drought mean concentration
pH		7.21	4.18	6.63
Alkalinity	μeql^{-1CaCo}	670	-65.0	146.7
Na	mgl^{-1}	5.61	4.54	5.34
K	mgl^{-1}	0.77	0.22	0.33
Ca	mgl^{-1}	9.48	0.59	3.73
Mg	mgl^{-1}	3.56	0.94	1.75
Fe	mgl^{-1}	150.9	368.0	177.2
Mn	mgl^{-1}	136.4	78.6	141.5
Co	mgl^{-1}	0.38	9.20	5.26
Pb	mgl^{-1}	0.12	1.73	0.30
Cd	mgl^{-1}	0.03	0.16	0.10
Al	mgl^{-1}	48.2	715	193.3
SO_4	mgl^{-1}	6.43	8.32	6.02
NO_3-N	mgl^{-1}	0.41	1.33	0.63
NH_4-N	mgl^{-1}	0.045	0.01	0.008
DOC	mgl^{-1}	1.93	7.40	2.0

Mean concentrations of various water quality determinands for the month preceding the drought break, in the month following the drought, and the actual values for samples collected during the drought breaking storm are given.

The contrasting response for manganese in the two adjacent streams suggests a significant groundwater source of manganese in the Tanllwyth, perhaps resulting from leaching of manganese from the more anaerobic peaty gley soils that dominate much of the catchment. At the drought break, concentrations of base cations and manganese decline sharply, suggesting dilution of groundwater inputs. However, whereas base cation concentrations subsequently remain low, manganese concentrations increase again towards drought flow values. The high post-drought manganese concentrations are presumably maintained by the onset of anaerobic conditions in the soil and leaching by soil water moving in to the stream. Indeed, the behaviour of cobalt appears to support this hypothesis, in that cobalt concentrations declined throughout the drought subsequently undergoing a tenfold increase at drought-break. This may have been due to release from manganese oxides as conditions became more anaerobic in the soils following re-wetting.

The changes in nitrate-N were more pronounced than in the Hafren. Nitrate-N fell steadily following the autumn high flows of 1994, with occasional peaks coinciding with major storm flows. The minimum nitrate-N value at the height of the drought was 0.4 mgl^{-1}. The drought breaking storm caused a peak of 1.3 mgl^{-1} falling to remain at more than twice the lowest drought concentration.

3.3.2Llanbrynmair

Site description

The Cwm catchment at Llanbrynmair in mid-Wales (outflow NGR SH916080) is about 300 ha in area and ranges in altitude between 250 and 500 m asl. The catchment is underlain by Silurian shales and grits on which are developed a mosaic of acid upland soils ranging from deep peats on the interfluves in the north and east of the catchment, through peaty podzols on moderate slopes to brown podzolic soils on the steeper valley sides with peaty gleys in the valley bottom. Approximately 88% of the catchment was afforested with Sitka spruce between 1984 and 1986 with 76% of the catchment being ploughed prior to planting.

Hydrochemical response

Stream flow at the catchment outlet is monitored using a Crump weir and data logger. Rainfall events are recorded using a tipping bucket rainguage and data logger near the catchment outlet. Stream water samples are collected every two weeks at the catchment outflow. These are filtered through 0.45 mm filters and analysed for major cations and anions, iron and aluminium whilst pH and Gran alkalinity are determined on unfiltered subsamples. As the alkalinity data are currently incomplete, charge balance alkalinity (CBALK) has been estimated here as the difference between the sum of base cations (Na^++K^++Ca^{++}+Mg^{++}) and acid anions (Cl^-+NO+SO).

From January through to the beginning of April 1995, there was rain on most days and stream flows were sustained above 0.05 cumecs. From April onwards, rainfall was more irregular, although periods without any rain rarely extended beyond a week. Stream flow steadily declined during this period until the middle of July when a particularly intense period of rain resulted in a large storm event. From the end of July until the end of September, rainfall was again irregular with relatively little rain falling during August. This resulted in a month of sustained low stream flows. The first major rain event occurred on the 2 September and lasted about five days, however the stream flow response was small with peak flows below 0.02 cumecs. A more continuous spell of wet weather began on September 23 and lasted until October 7. This signalled the end of the dry summer period.

The stream chemistry time series for 1995 showed the predictable increases in pH, alkalinity and base cation concentrations reflecting the low flow conditions. Unexpectedly, in parallel with the divalent base cations and alkalinity, stream water sulphate concentrations also increased steadily, from a minimum of 65 meql^{-1} in February to about 200 meql^{-1} by August 29. A low flow spatial hydrochemical survey of the Cwm catchment undertaken in July revealed a set of chemically distinct waters clustered in a group of small tributaries towards the centre of the catchment. These samples had the highest observed pH and Gran alkalinity values of any of the samples collected in the catchment and were relatively enriched in divalent base cations. Sulphate concentrations were also unexpectedly large (c. 180 meql^{-1}). These highly alkaline waters had the lowest recorded temperatures which, coupled with the chemistry, may indicate a groundwater source.

The fortnightly sampling regime at Llanbrynmair coincided with the two periods of rainfall at the end of the 1995 summer. The highest sulphate concentration recorded since monitoring began in April 1990 (300 meql^{-1}) was observed following the short period of rain at the beginning of September. A similar concentration was recorded a fortnight later as stream levels began to rise in response to the onset of the next period of rain. Divalent base cation concentrations progressively declined during this period from their summer (and annual) maximum values (c. 600 meql^{-1}) presumably reflecting dilution of baseflow by base cation depleted runoff from surface soils and peats. Stream alkalinity was also depleted although the pH changed very little, dropping from 7.3 on August 29 to a minimum value of 6.1 on October 9. As none of the metals responded in parallel with the sulphate, it must be assumed that H^+ was the accompanying cation. However, severe stream acidification was prevented as there was sufficient alkalinity to buffer the acid inputs.

3.3.4 1995 Welsh Acid Waters Survey (WAWS 95)

One component of WAWS 95 involved monthly collection of stream water samples for one year from October 1994 to September 1995 at 104 stream sites throughout upland Wales. The August samples were all obtained during the summer drought when flow conditions for all streams were reported as 'low' or 'very low' by the sampling teams. Between the August and September collections, rain occurred throughout Wales, but quantities varied considerably. Consequently, only in approximately half of the streams were flow conditions in September reported as being any higher than in August, and there were no cases in September where flow conditions were reported as being any higher than 'moderate'.

Table 3.5 **Geometric mean solute concentrations for the 104 streams of the Acid Waters Survey.**

	Mean Oct-Aug. inc.	Aug.	Sept.
Ph	6.13	6.45	6.22
Conductivity mS cm^{-1}	44.2	44.8	56.4
Alkalinity mgl -1 CaCo3	8.0	13.3	15.4
Cl mgl^{-1}	8.2	8.2	8.3
SO_4 mgl^{-1}	4.8	5.3	9.7
NO_3-N mgl^{-1}	0.16	0.14	0.10
Na mgl^{-1}	4.8	5.1	5.4
K mgl^{-1}	0.21	0.17	0.27
Mg mgl^{-1}	1.06	1.31	1.60
Ca mgl^{-1}	1.92	2.60	2.95
Al mgl^{-1}	0.055	0.026	0.043
Zn mgl^{-1}	7.6	5.0	8.3
Mn mgl^{-1}	23.3	12.8	22.5
Fe mgl^{-1}	59.5	67.4	80.6

Despite the limited impact on flow conditions of the initial rainfall, some sizeable changes in chemistry were observed, especially for sulphate. The geometric mean sulphate concentration for all 104 streams for August was 5.3 mg l^{-1}, but 9.7 mg l^{-1} in September (Table 3.5). The latter was far higher than any of the other monthly geometric means which were all less than 5.5 mg l^{-1}.

This large increase shown by the means masks a wide range of responses by individual streams. In some cases, there was no increase in sulphate concentration from August to September (or even a slight decrease). At the other extreme, a five-fold increase was observed for the Alwen (on the Denbigh Moors) where sulphate concentrations rose from 2.8 to 15.6 mg l^{-1}. Table 3.5 indicates that the increase in sulphate was accompanied by increased concentrations of base cations and a reduction in pH.

Since the increase in sulphate concentrations from August to September was so variable from catchment to catchment, multiple regression analysis of this increase in relation to catchment characteristics was carried out. This procedure indicated that the increase was greater ($r^2 = 33.8\%$, $F = 11.6$, $p<0.001$) in high altitude, low gradient catchments dominated by peat or peaty-topped soils (eg peaty gleys, peaty podzols and peat rankers) in which flow conditions during the September sampling were higher than in August. The most likely explanation for these observations is mineralisation of sulphur in organic soils during the dry summer, followed by a flushing effect at the onset of the autumn rainfall.

A more detailed analysis of the WAWS95 data indicates that some of the drought break effects are influenced by catchment landuse. The 104 sites were divided into two groups on the criteria of the catchment being more than 30% covered by forestry and monthly median solute concentrations were calculated for each group. Table 3.6 summarises the maximum median concentration and the August and September median values for selected major and trace solutes. The summary confirms the large increase in sulphate associated with the September sampling. The largest concentrations (although not the largest change in concentration) were observed in the catchments with more than 30% conifer cover. The September values were the highest monthly median concentrations observed throughout the year. Increases in calcium, magnesium and acidity were relatively modest as was the decline in alkalinity. The most noticeable changes were for zinc and manganese. The latter increased by over a factor of two in the <30% afforested catchments and by a factor of 4 at the sites with more than 30% forest cover.

Table 3.6 Maximum monthly median and August and September median concentrations at WAWS95 sites with greater or less than 30% forest cover.

	< 30% forest cover			> 30% forest cover		
	Max	Aug	Sept	Max	Aug	Sept
Ca mgl^{-1}	3.61	3.20	3.61	2.92	2.37	2.92
Mg mgl^{-1}	1.72	1.40	1.72	1.67	1.24	1.67
H^+meql^{-1}	1.24	0.22	0.26	5.01	0.38	0.54
Alk mgl-1 caCo3	9.00	9.00	8.65	3.74	3.74	3.42
SO_4 mgl^{-1}	9.25	4.89	9.25	10.04	6.42	10.04
DOC mgl^{-1}	2.95	1.96	2.95	2.75	1.03	2.75
Zn mgl^{-1}	8.9	4.9	5.8	11.4	4.55	8.9
Mn mgl^{-1}	30.3	9.1	17.5	59.2	8.5	35.0
Al mgl^{-1}	66.0	20.0	30.0	153.5	34.5	67.5

For both zinc and manganese, the September median values were still less than the maximum median concentrations observed during the year. These occurred during the winter months when high flow, more acid conditions prevailed. The increased trace metal concentrations were accompanied by increases in DOC, which reached the largest monthly median values observed during the year.

3.4 Cumbria

3.4.1 Mosedale Beck, Tarn Head Beck and Castle How Beck

Site descriptions

The three streams are located in the south-western part of the Lake District, within 3 km of each other. The catchments of Mosedale Beck and Tarn Head Beck consist entirely of moorland, while Castle How Beck drains a catchment with an appreciable area of coniferous forest. The catchment areas are 2.7 km^2 (Mosedale), 3.8 km^2 (Tarn Head) and 1.4 km^2 (Castle How).

Mosedale Beck rises (NY238037, 350 m) at the head of Mosedale, a steep-sided glaciated valley with an altitude of over 700 m on its eastern flank. It flows south-southeast through upland grazing along a boggy valley floor to meet the River Duddon at Cockley Beck Bridge. The sampling point is approximately 100 m above the confluence (NY246017, 200 m). Tarn Head Beck rises at approximately 600 m on the western flank of the Old Man of Coniston. It flows south through upland grazing for approximately 1 km before turning west into Seathwaite Tarn. The stream was sampled above the tarn inflow at NY259992. The catchment consists mainly of steep west-facing mountainsides rising to over 750 m in places, with an area of flat boggy ground on the valley floor. Castle How Beck rises on the western side of the Duddon Valley (NY223002, 500 m). It flows east through upland grazing and a coniferous plantation to meet the River Duddon at NY239002 (195 m). The sampling point is immediately above the confluence.

At higher altitudes the soil of all three catchments is shallow and acid, with a mineral horizon topped by a peaty organic layer, classified as the part of the Bangor Association (Jarvis *et al.*, 1984). The entire catchment of Tarn Head Beck falls into this category. The soil in the valley floor of Mosedale is acid but more organic (Winter Hill Association), and gives way, at the south end of the valley, to the Wilcocks 1 association which is composed of slowly permeable seasonally waterlogged fine loamy and sometimes clayey soils with a peat surface horizon. In the Castle How Beck catchment, the Malvern Association, consisting of well drained stony loamy soil, is found at lower altitudes, while on the valley floor is found the Enborne association, a deep stoneless fine loamy and clayey soil over river alluvium. The catchments are underlain by rocks of the Borrowdale Volcanic Series, comprising a range of metamorphosed igneous rocks of varying acid character (Moseley *et al.*, 1978).

Climate is characterised by high rainfall with annual totals typically in the range 2000 - 3000 mm depending on altitude (Tipping *et al* 1989). Mean annual temperature is *ca.* 8°C (Pearsall and Pennington, 1989).

Rainfall

Daily rainfall volumes are measured by the Environment Agency at Seathwaite Tarn (SD 250985). Comparative data for the years 1993, 1994 and 1995 are given in Table 3.7. In 1995, the early part of the year was relatively wet, but rainfall in August was very low, and only at the end of September did appreciable amounts of rain fall, giving an abrupt end to the drought. Rainfall chemistry is measured on samples collected monthly at Cockley Beck Bridge (NY 247017). The chemical compositions of samples collected during 1995 are presented in Table 3.8. The volume-weighted annual mean composition is similar to previous years, but showing slightly lower pH and higher sodium and chloride.

Table 3.7 **Annual and late summer/autumn rainfall (mm) collected by the rain gauge at Seathwaite Tarn (SD 240985).**

Year	Ann	Jun	Jul	Aug	Sep	Oct
1993			196	134	153	
1994	2548	157	78	156	166	211
1995	2167	76*	137	42	116	365

* data available for 17 Jun - 30 Jun only.

Streamwater

Spot measurements of discharge in each of the study streams were made periodically during September and October 1995. Mean daily discharge data for the River Duddon at Ulpha, 10-15 km downstream of the sampling sites, were obtained from the Environment Agency for the period 1st January 1989 to 21st March 1996. Comparisons of discharges are presented in Table 3.9, and they show that the Ulpha values give a reasonable indication of the flow behaviours of the three headwater streams. The Ulpha record demonstrates the extreme hydrograph for 1995, with a wet winter followed by an exceptionally dry summer, especially during August and the first part of September.

Table 3.8 **Compositions of rain samples collected at Cockley Beck Bridge (NY 247017) in 1995. Concentrations are in mequivalents per litre.**

Collection period	pH	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	Cl^-	NO3-	$SO4^{2-}$
6 Jan - 6 Feb	5.95	290	66	7	37	15	347	11	58
6 Feb - 6 Mar	5.45	237	62	6	27	13	335	14	56
6 Mar - 3 Apr	6.18	165	39	3	37	47	198	24	67
3 Apr - 2 May	4.62	90	20	1	37	83	51	94	80
2 May - 1 Jun	4.43	41	10	1	15	41	56	38	54
1 Jun - 6 Jul	6.02	27	7	2	56	15	35	15	63
6 Jul - 3 Aug	4.75	26	6	1	20	54	23	28	58
3 Aug - 6 Sept	5.54	80	19	2	31	0	76	0	40
6 Sept - 5 Oct	4.73	100	22	2	9	0	116	3	34
5 Oct - 2 Nov	4.78	131	30	4	13	0	158	1	44
2 Nov - 5 Dec	4.75	58	14	2	13	23	65	26	45
Mean 1995	4.74	107	19	4	14	18	114	17	49
1994	5.25	76	20	2	32	18	87	18	41
1993	4.74	49	13	2	19	24	57	24	42

Table 3.9 **Ratios of discharges (spot measurements) of the three study streams with those for the River Duddon at Ulpha (continuous measurements), for the period immediately before and immediately after the drought break.**

Stream	n	Ratio	r^2
Mosedale Beck	15	1.20	0.79
Tarn Head Beck	15	0.75 (1.60)	0.25 (0.38)
Castle How Beck	15	1.35	0.93

The spot measurements were assumed to be representative of the daily discharge, and all discharges were expressed as mm day^{-1}. The values in brackets for Tarn Head Beck were obtained after the omission of an apparent outlier.

Streamwater samples are collected and analysed monthly as part of IFE's monitoring programme. Additional samples were taken before and after the drought break.

The general pattern of water chemistry for the streams is for the streamwater to be acid and rich in dissolved aluminium at high flow, with, at low flows, pH rising to values above 5.5 and the concentration of aluminium falling to about. 1 mM. Very simply, this can be interpreted in terms of inputs of water from the bottom of the soil profile, or from groundwater, at low flows, with an increasing contribution from shallower, more acid, horizons as flows increase. Concentrations of Al during summer high flows tend to be lower than those during winter high flows, for the same pH.

During the period of the 1995 drought, streamwater pH values rose to high levels, and concentrations of dissolved aluminium fell to low values, as would be expected. Only for Mosedale Beck, however, was the pH exceptionally high, exceeding pH 6 for the only time in the 3-year record. The drought break brought about a sharp decrease in pH, and a concomitant rise in dissolved aluminium concentration, but the values attained were within the longer-term ranges. The sharp rates of change in streamwater chemistry are probably not exceptional, although they appear to be so because the sampling resolution was greater during the period leading up to and following the drought break. Thus, the rapid change in streamwater pH associated with the drought break was no more abrupt than has been frequently observed by continuous monitoring of pH in Tarn Head Beck (George and Davison, 1992; Tipping, 1996b).

The increases in hydrogen ion and aluminium concentrations are compensated by increases in nitrate and to some extent sulphate concentrations, and by decreases in the concentrations of the alkaline earth cations.

It was not possible to make frequent measurements of concentrations of dissolved organic carbon during the period before and after the drought break, but values of optical absorbance at 340nm (A_{340}) were recorded; these give an indication of the concentrations of dissolved humic matter (Tipping, 1988). Although an increase in A_{340} was observed at the drought break, the values are within the longer-term ranges, and so there is no evidence of a major flush of organic acids that might have been stored within the catchment during the drought period.

The behaviour of nitrate is noteworthy, in that in both Mosedale Beck and Castle How Beck concentrations during the winter of 1995-6 were higher than previously observed. However, because stream discharges in the same period were relatively low, this may not represent an increased output flux from the catchment. Another point is that during March 1996, there were high concentrations of both nitrate and ammonia in the rainfall. Thus, the elevated post-drought nitrate concentrations may not be causatively linked to the drought itself.

The concentrations of sodium, magnesium, potassium, calcium, chloride and soluble reactive phosphate (SRP) during the drought break and afterwards do not suggest that any of these chemical components were affected significantly by the drought.

Hydrochemical modelling

The CHemistry of the Uplands Model (CHUM; Tipping, 1996a) simulates streamwater chemistry on a daily timestep, using rainfall amount and composition, temperature, and soil chemistry as its principal inputs. CHUM was applied to Tarn Head Beck in order to investigate whether the observed streamwater chemistry for 1995 differed from that expected, in the anticipation that any differences would provide insight into processes not represented by the model, for example the mineralisation of organic sulphur stores and consequent increased concentrations of sulphate in streamwater. The model had been configured for the Tarn Head Beck catchment on the basis of data obtained in 1991 and 1992 (Tipping, 1996a,b; Tipping and Rigg, 1995), and so the outputs for 1993-1995 can be considered predictions. Generally, it is found that the model simulates streamwater for 1995 neither better nor worse than for the two preceding years. The possible exception is nitrate, the autumn/winter increase in which is calculated to be later than observed. However, the simulation for 1994 was also somewhat mistimed, and so this discrepancy between prediction and observation can only be regarded as suggestive of an additional process at this stage.

3.4.2 Bannisdale Beck

Site description

This stream rises northeast of Kendal at NY503057, at an altitude of 520 m (Map 4.4). It descends to the floor of Bannisdale at Bannisdale Head (NY515043, 265 m) where sampling takes place. It joins Ashstead Beck at NY552005 to form the River Mint which joins the River Kent above Kendal. The catchment area is 2.9 km^2. The stream passes over a variety of rock types including limestone, calcareous siltstone, sandstone and mudstone. The Winter Hill soil association, composed of perennially wet, thick, very acid raw peat soil over blanket peat, exists above approximately 450 m. The Manod association, composed of well drained loamy or silty soils, occurs below this altitude.

Climate is characterised by high rainfall with annual totals typically in the range 1500 - 2500 mm depending on altitude. The mean annual temperature is *ca.* 8°C.

Rainfall

Daily rainfall volumes are collected by the Meteorological Office at Ambleside (NY 375405), approximately 13.5 km west of the sampling location. Comparative data for the years 1993, 1994 and 1995 are given in Table 3.10. The rainfall patterns are similar to those for the streams in the south-west Lake District (Section 3.4.1). In 1995, the early part of the year was relatively wet, but rainfall in August was very low, and only at the end of September did appreciable amounts of rain fall, giving an abrupt end to the drought. October 1995 was relatively wet.

Table 3.10 **Annual and late summer/autumn rainfall (mm) collected by the rain gauge at Ambleside (NY 375405).**

Year	Ann	Jun	Jul	Aug	Sep	Oct
1993	1719	56	149	76	110	51
1994	2261	116	88	155	148	162
1995	1780	45	70	20	120	307

Rainfall for chemical analysis is collected weekly by IFE at Bannisdale Head, on behalf of AEA Technology. The monthly volume-weighted chemical compositions of samples collected for 1995 are presented in Table 3.11. The results are broadly similar to those for the site at Cockley Beck Bridge, 27 km to the west, and not different to non-drought years.

Table 3.11 **Compositions of rain samples collected at Bannisdale Head (NY 515042) in 1995. Concentrations are in mequivalents per litre.**

Collection period	pH	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	Cl^-	NO3-	$SO4^{2-}$
18 Jan - 15 Feb	4.82	141	35	3	7	18	175	12	36
15 Feb - 15 Mar	5.24	268	76	6	24	31	325	13	55
15 Mar - 10 Apr	5.62	61	18	3	25	62	68	24	59
12 Apr - 10 May	4.52	21	8	3	25	65	27	47	79
10 May - 7 Jun	4.41	42	10	5	17	79	42	48	78
7 Jun - 5 Jul	4.92	25	8	1	7	33	29	16	35
5 Jul - 2 Aug	4.45	15	5	3	21	55	20	38	62
2 Aug - 5 Sept	4.60	17	3	1	14	42	24	34	48
5 Sept - 3 Oct	5.05	146	41	3	17	14	162	14	44
3 Oct - 7 Nov	4.93	98	30	2	28	74	109	21	76
7 Nov - 5 Dec	4.47	75	21	5	14	25	97	26	51
Mean 1995	4.80	129	35		17	36	151	21	53
1994	4.70	95	27	3	16	32	109	22	48
1993									

Streamwater

Spot measurements of streamflow were made periodically during September and October 1995. Mean daily discharge measurements for the River Mint at Mint Bridge, approximately 16.8 km downstream, were obtained from the Environment Agency for the period 1st January 1993 to 31st December 1995. The spot discharges for Bannisdale Beck showed a strong correlation ($r^2 = 0.91$) with corresponding values for River Mint, but the ratio of discharges, expressed in mm day^{-1}, was *ca.* 4. Presumably this reflects the much flashier nature of the Bannisdale catchment, which is small and of greater relief than that of the River Mint. It is also possible that during the drought break at Bannisdale, appreciable amounts of precipitation were transferred to the stream by passage through the upper soil horizons, or as overland flow, because of incomplete infiltration. Therefore, the discharge record for the River Mint is only useful as a qualitative guide to discharge in Bannisdale Beck.

Streamwater samples are collected and analysed monthly as part of IFE's monitoring programme. Additional samples were taken before and after the drought break. At low flows the stream is circumneutral, with calcium concentrations in the range 200 - 400 meq l^{-1}, magnesium 100 -200 meq l^{-1} and alkalinity 200 - 600 meq l^{-1}. At high flows the water is more acid, but never such to pose an ecological threat.

During the period of the 1995 drought, the streamwater pH rose to almost 8, calcium concentration to over 600 meq l^{-1}, magnesium concentration to over 200 meq l^{-1} and alkalinity to around 1000 meq l^{-1}. These are the most extreme chemical conditions observed during the monitoring period from 1993 onwards. The drought-break brought about a sharp change in the direction of acidification, with pH falling to the lowest value recorded during the period of monitoring from 1993 onwards. As with the Lake District sites (Section 3.4.1) however, the fast rates of change in stream chemistry probably arise because of the greater sampling frequency during the period immediately before and after the drought break.

Concentrations of dissolved aluminium rose to about 4 mM at the drought-break which are the highest values observed during the monitoring period. However, there is little likelihood that the metal would have posed a toxic threat, since calculations with WHAM (Tipping, 1994) show that more than 99% of the aluminium will be organically complexed. Indeed the export of aluminium is doubtless due to transport as organic complexes.

The behaviour of sulphate is of interest. Just before the end of the drought its concentration started to rise, and it rose even more during the drought break. The high concentrations coupled with the high discharge mean that a substantial extra flux of sulphate came out of the catchment. This probably reflects the oxidation of organic sulphur in the catchment soils during the drought period (cf. Hughes and Heathwaite, 1995). The high sulphate concentrations are probably responsible for the relatively acid water during the drought-break.

An interesting observation is the small pulse of nitrate associated with the first, fairly minor, increase in discharge following the drought. This suggests that there was some accumulation within the catchment of oxidised nitrogen, although the impact upon the streamwater must have been small.

As mentioned earlier it was not possible to make frequent measurements of concentrations of dissolved organic carbon during the period before and after the drought break were not made. However, optical absorbance at 340nm (A_{340}) were recorded; to indicate dissolved humic matter concenrations. It should be noted that the long-term values of A_{340} are typically at least five times greater than those observed for the south-west Lake District streams (Section 3.4.1), reflecting the more peaty character of the Bannisdale soils. A substantial increase in A_{340}, and therefore in dissolved organic matter, was observed at the drought break. Given the high discharges at the drought-break, which were considerably greater than suggested by the discharges for the River Mint, as discussed above, the observed increase in organic matter concentration appears to represent a substantial output flux of dissolved organic matter. It cannot be stated with certainty whether this reflects the build-up of potentially leachable organic matter during the drought; another possible explanation is uncommon hydrological conditions, with an exceptional contribution of organic-rich throughflow to the streamwater.

3.4.3 Pools at Great Dun Fell

Site description

Great Dun Fell is a hill of altitude 845 m in the northern Pennines (NY 702298). At an altitude of 480 m on the western flank, is a plateau of area *ca.* 0.05 km^2. The soil consists almost entirely of peat, within which are situated some 20 small pools. Two of these, designated X and Y, have been sampled monthly for water chemistry since 1991. Rainfall at the site is *ca.* 1500 mm, and mean annual temperature is *ca.* 6°C.

Rainfall

Rainfall is collected monthly for the determination of chemical composition at a site near to the pools (NY 690295), and volumes are also recorded. The 1995 drought was characterised by very low August and low September rainfall followed by high October rainfall. The results are broadly similar to those in the Lake District, and not different to non-drought years.

Table 3.12 Compositions of rain samples collected at Great Dun Fell (NY 702298) in 1995. Concentrations are in mequivalents per litre.

Collection period	pH	Na^+	Mg^{2+}	K^+	Ca^{2+}	NH_4^+	Cl^-	NO3-	SO4^{2-}
16 Jan - 13 Feb	4.86	115	25	3	10	20	128	14	49
13 Feb - 13 Mar	5.05	195	47	4	18	23	234	13	51
13 Mar - 10 Apr	5.22	148	35	1	46	50	151	20	67
10 Apr - 8 May	4.58	97	21	1	33	17	99	34	70
8 May - 5 Jun	4.52	45	10	1	16	30	51	31	54
5 Jun - 3 Jul	4.59	16	5	4	12	22	35	11	36
3 Jul - 1 Aug	4.96	28	14	12	56	33	44	39	73
1 Aug - 29 Aug	6.07	52	20	19	50	3	60	0	34
29 Aug - 25 Sep	4.66	21	5	2	9	9	45	16	41
25 Sep - 23 Oct	4.97	101	20	6	14	1	100	15	46
23 Oct - 21 Nov	4.76	54	11	4	17	18	50	21	31
21 Nov - 4 Dec	4.40	77	21	3	16	13	105	35	61
Mean 1995	4.80	100	23	4	20	22	113	20	50
1994	4.63	60	17	2	13	19	76	22	46
1993	4.52	59	15	2	15	27	68	27	53

Pool chemistry

The general pattern for pool X is for a strongly acidic water typically of pH less than 5, rich in aluminium and dissolved organic carbon, both of which show a tendency to higher concentrations during the summer months. Pool Y is also rich in dissolved organic matter, but the pH is some 2 units higher, concentrations of aluminium are lower, those of calcium are higher, and there is appreciable alkalinity.

During the drought of 1995, the pools dried up for a period of about 12 weeks. The first sample taken from pool X following refilling showed highly elevated concentrations of sodium, magnesium, aluminium, calcium, manganese (total and filtrable) and sulphate, while pH was depressed to below 4. A similar result was found for pool Y, except that the rise in aluminium was not observed, and the pH only fell to 5.8. After these abrupt changes in chemistry, concentrations returned to values within the long-term observed ranges the following month. A similar effect was noted following the drying of the pools in summer 1992. No effects of the drought on the concentrations of potassium, chloride, nitrate, iron (total and ferrous) or phosphorus (total and soluble reactive) were apparent.

The major changes in water chemistry in both pools following the drought are strong evidence that drying out of the surrounding peat resulted in oxidation and mineralisation of organic sulphur, to form sulphate. This anion then dissolved in percolating water during rewetting and mobilised a number of cations (H^+, Na^+, Mg^{2+}, Al^{3+}, Ca^{2+} and Mn^{2+}).

Dissolved organic carbon and absorbance at 340nm (A_{340}) were within their long-term observed ranges following the drought. Similar results were seen following the dry summer of 1992. However, it has been observed (i.e. Naden and McDonald, 1989) that the rewetting of peat following a drought is a long-term process and that the greatest flushing of stored organic acids may occur in the autumn of the year *following* the drought year. The highest observed levels of both DOC and A_{340} in pools X and Y were seen during the summer of 1993, approximately 12 months following the dry summer of 1992. However, caution is needed here, since not only concentrations but also fluxes need to be determined in order properly to assess the influence of drought conditions.

There is an indication that nitrate levels in both pools remained high following the drought, which is reminiscent of the results for the Lake District (Section 3.4.1).

3.4.4. Conclusions

The results for the Cumbrian sites suggest that the greater the amount of peat in a catchment, the greater are the effects of drought on streamwater chemistry. Three streams in the south-west of the Lake District (Section 3.4.1) did not show any definite response to the 1995 drought, except perhaps an elevation of nitrate concentrations during the period following the drought-break. Further east, sulphate concentrations in Bannisdale Beck were found to be exceptionally high during the drought-break, suggesting mineralisation of organic sulphur during the drought, and the wash-out of sulphate when the first rainstorms arrived. This catchment also responded with a pulse of nitrate, and there are indications that the drought-break caused a major export of dissolved organic matter.

The pools at Great Dun Fell responded most dramatically to the 1995 drought. In the first place, they dried out. Then, when refilling took place the water was exceptionally high in sulphate and balancing cations (hydrogen ions, sodium, magnesium, aluminium, calcium and manganese). As with Bannisdale Beck, it is assumed that the sulphate was produced by the oxidation and mineralisation of organic sulphur present in the peat surrounding the pools. The Great Dun Fell pools did not show any evidence of increased concentrations of dissolved organic matter at the end of the 1995 drought, but it may be that the response of the peat in this regard is slower, and elevated concentrations and fluxes may be observed in 1996 (cf. Naden & McDonald, 1989).

The implications of these findings are that headwaters of the Pennines may be particularly sensitive to the effects of drought, since their catchments tend to have the greatest quantities of peat. This is clearly the case for peaty pools, but further work is required to ascertain the impacts on running waters, where the relative contribution of peat areas to runoff is the crucial issue. Another significant question regards the response of toxic metals to the flush of sulphate that follows a period of drought; the mobilisation of aluminium and manganese has been demonstrated here, but other metals, not monitored in the present study, such as copper, zinc and lead, would be expected to respond similarly.

3.5 Peat water responses to experimentally induced drought

Brief site and experiment description

A field experiment was initiated in 1992 to investigate potential impacts of climatic change on flush wetlands in Wales (Freeman *et al.*, 1993; 1994). A small area of flush wetland was subjected to three successive years of simulated summer drought/rewetting (autumn-spring) cycles (1992/93-94/95). Simulated drought was achieved by diverting streamwater around the experimental wetland during the summer, the wetland only receiving precipitation inputs during that time. The effects on peat hydrochemistry in the rhizosphere at 10 cm depth were monitored at regular intervals until spring 1996, and comparisons made with a control which continued to receive its natural water supply.

Hydrochemical response

Simulated summer drought succeeded in lowering the water table by between 5-10 cms, relative to the control, in each of the three years. It can also be seen that the control generally remained waterlogged throughout these periods. Moreover, Figure 3.25 also shows that a more intense natural drought, of somewhat shorter duration, impacted on the wetlands during July-August 1995 (a year originally intended to be monitored as a ‘recovery’ year).

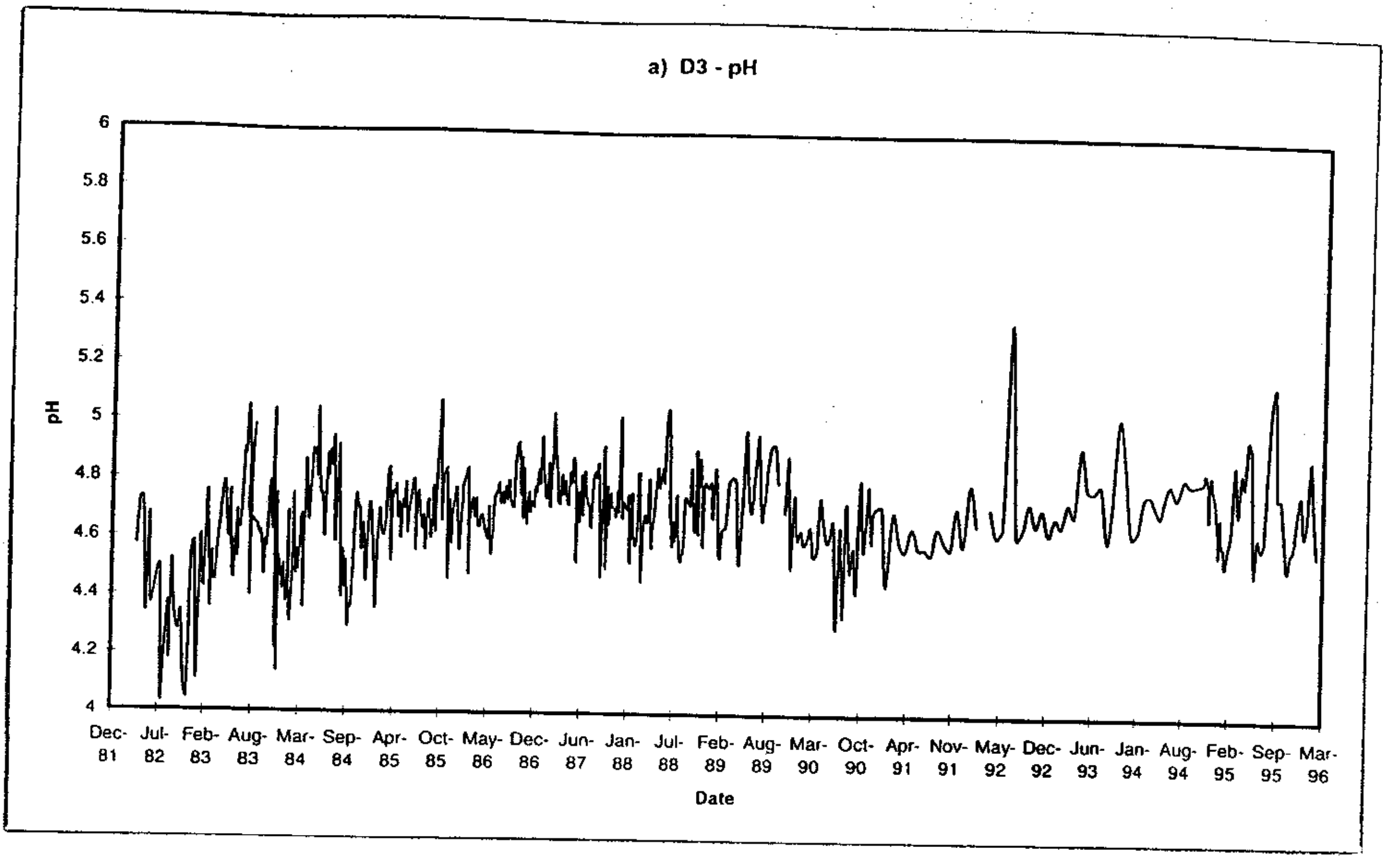
Sulphate concentrations in the peat-water showed strong natural seasonal cycles in the mire, with peaks occurring during autumn-winter and troughs during summer (Figure 3.26). Summer troughs probably resulted from a number of contributory factors, which may have included increased assimilatory uptake of sulphate by wetland vegetation and soil microbes and dissimilatory uptake by sulphate reducing bacteria during the growing season (Urban *et al.*, 1989). Sulphur cycling in wetlands, however, is known to be complex and sulphur mineralisation and oxidation rates in the wetlands are also likely to have increased during the summer, possibly leading to a dynamic cycle of oxidation and reduction in the mire (Urban *et al.*, 1989). On balance however, and in the absence of drought conditions in the control, demand for pore-water sulphate by assimilatory and/or dissimilatory uptake must have been sufficiently large to offset any additional release of sulphate to pore-water by mineralisation/oxidation during the summer.

In contrast, natural autumn-winter peaks in sulphate in the pore-water probably partly reflected increased release of sulphate from bio-senescence during the autumn, coupled with increased sulphur deposition, especially that of marine origin, during the winter months (DOE, 1990) (the influence of the latter may have been further enhanced by the expectation that rates of internal S-cycling were likely to be inhibited by low temperatures during the winter). Moreover, additional sulphate is likely to have been mobilised during autumn-winter emanating from reoxidation of reduced-S species during dynamic sulphur cycling during the summer, and subsequently 'washed off' from the peat surfaces during rewetting (Ponnamperuma, 1972). Although the scope of our present study does not provide for detailed information on the mechanisms of sulphate release, it seems likely that this mechanism may be of some importance following drought conditions, and indeed, has been proposed previously by a number of researchers to explain autumnal sulphate pulses in wetland drainage waters following dry periods (Gorham *et al.*, 1984; Bayley *et al.*, 1986; LaZerte, 1993). Whichever mechanisms are responsible, results reveal a significant enhancement of the natural autumn-winter peaks in pore-water sulphate concentrations in the experimental wetland, relative to the control, following successive simulated droughts. It is also interesting to note the fact that the autumn-winter peaks in sulphate concentrations in both control and experimental wetlands following the natural drought in 1995 were of similar magnitude to those induced by simulated drought in the experimental wetland in the previous 3 years. This is both supportive of the basis of the original experiment, *i.e.* in that the hydrological manipulation succeeded in simulating actual drought conditions in the mire, and that the observations following the natural (and simulated) drought(s) are true drought/rewet effects and not simply consequences of natural annual fluctuations reflecting differences in annual sulphur deposition.

Hydrogen ion accompanied sulphate was released to the peat-water in the winter, with a sharp decrease in pH observed during these periods and with very little additional release of base cations being detected. This was anticipated for a base-poor wetland in an area of moderately-high acid sulphur deposition (wet deposition: *c.* 0.9-1.2 g S m^{-2} yr^{-1}) (DOE, 1990), and may have wider consequences in terms of the water quality of surface waters draining upland catchments in Wales following very dry summers. The possibility exists that periodic acid pulses may occur during large rainfall events following rewetting, when runoff from surface peat would be expected to increase.

APPENDIX A3.

Supplementary diagrams showing drought break effects



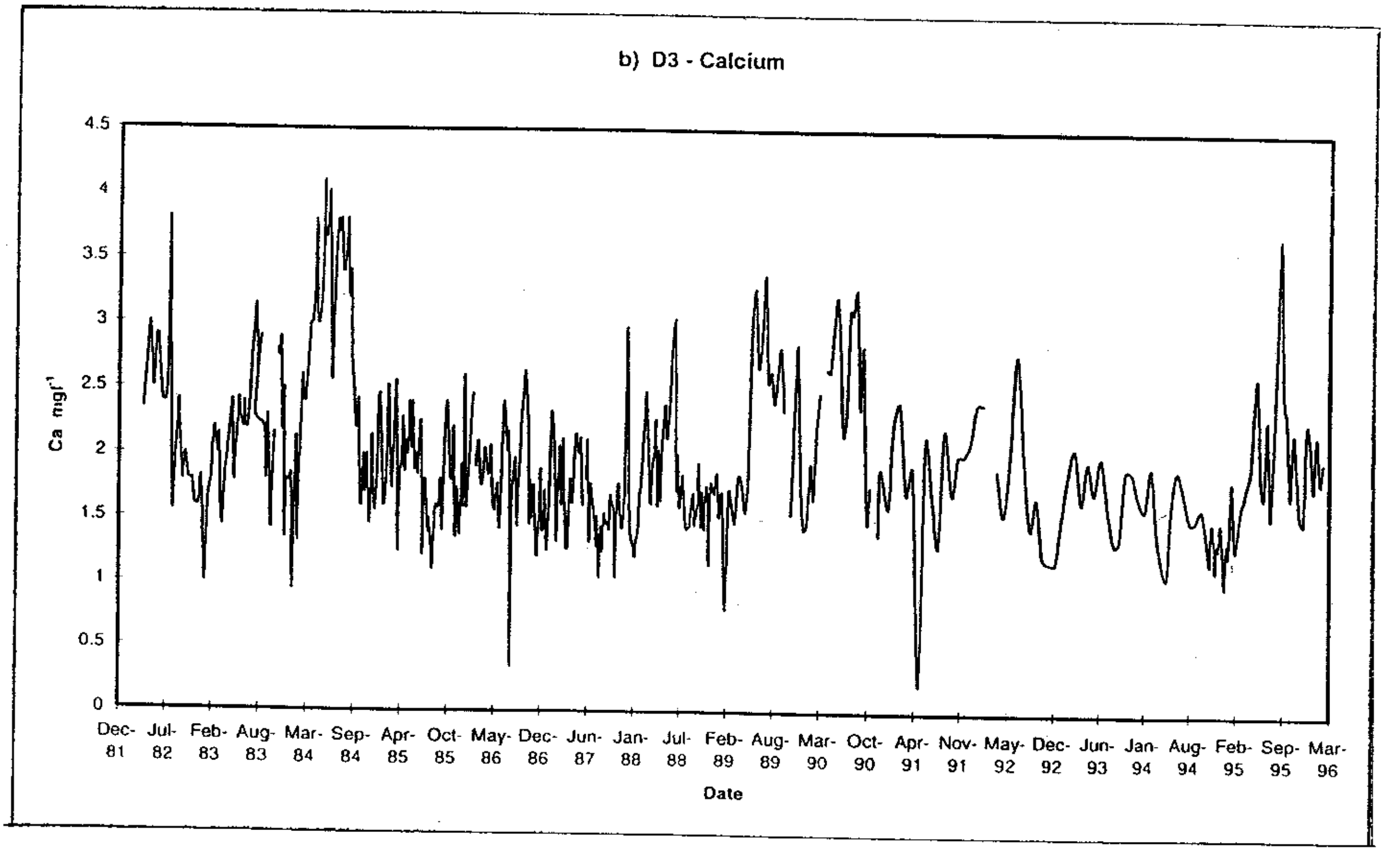
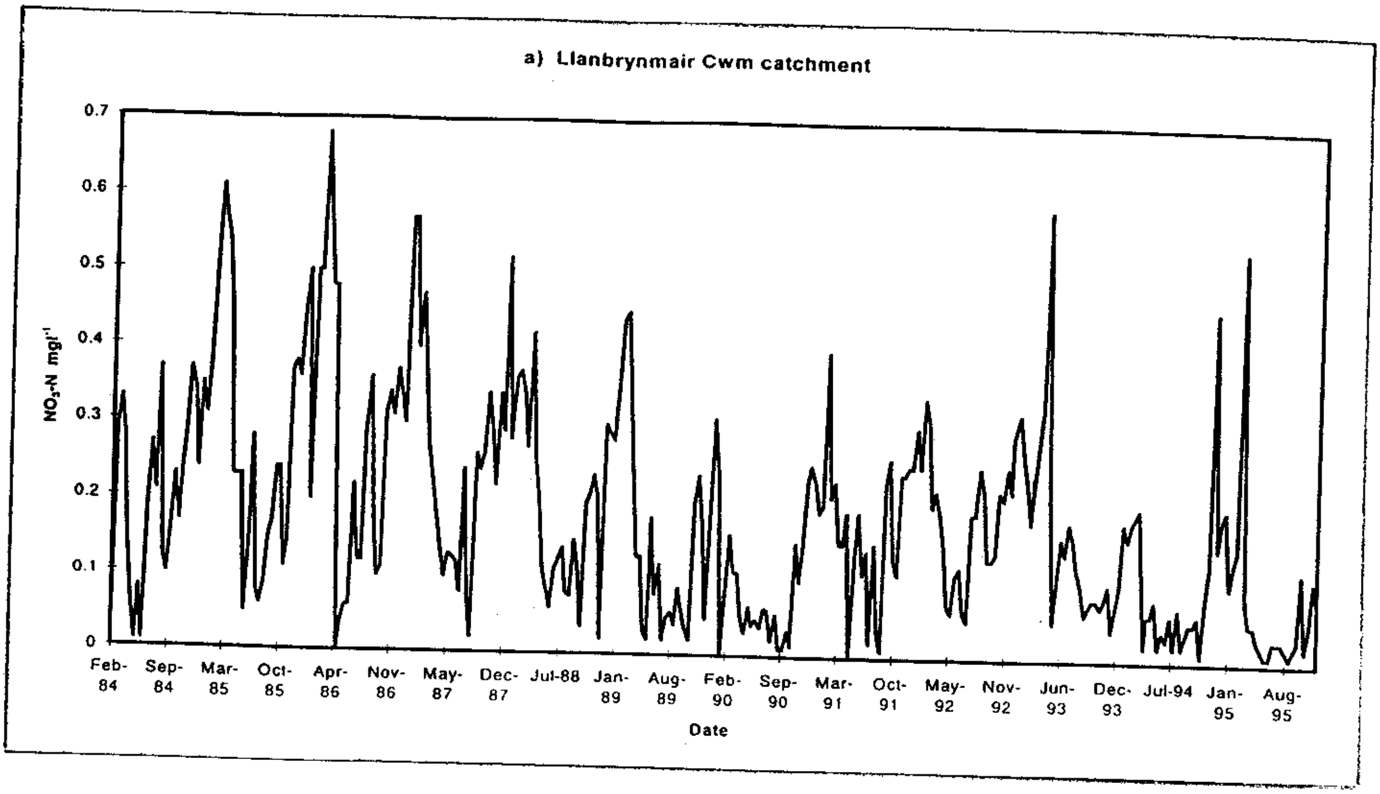


Figure A3.1 Time series of pH and calcium concentration in stream D3 in Beddgelert Forest, north Wales showing periods of dominant baseflow chemistry during the low flow the summer periods of 1984, 1989, 1990 and 1995.



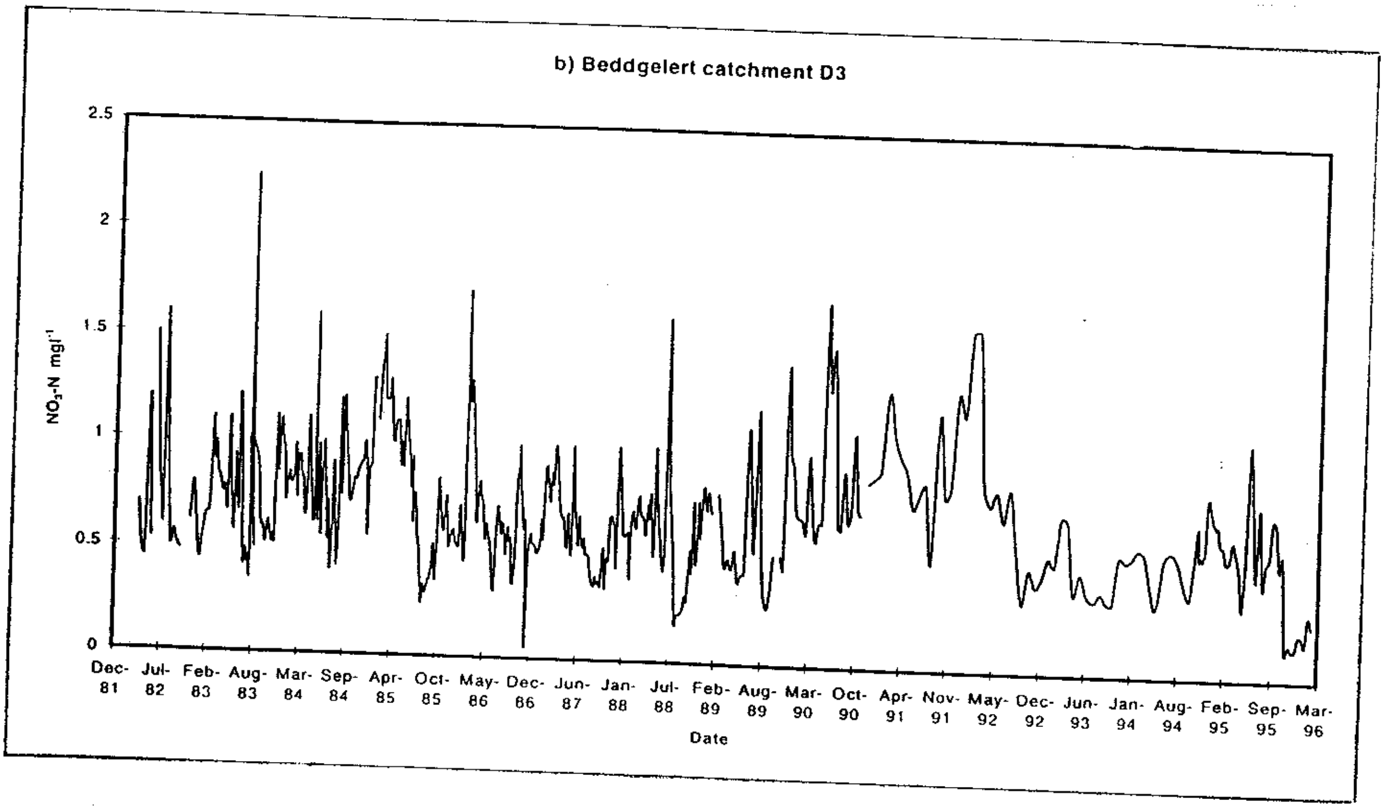


Figure A3.2 Time-series of nitrate-nitrogen concentration in runoff from the Cwm catchment at Llanbrynmair and stream D3 in Beddgelert Forest, north Wales, showing evidence for the disruption of the nitrogen cycle during extended dry periods. Nitrogen output falls during the build-up of the drought rising following drought-break and the acceleration of nitrofication processes.

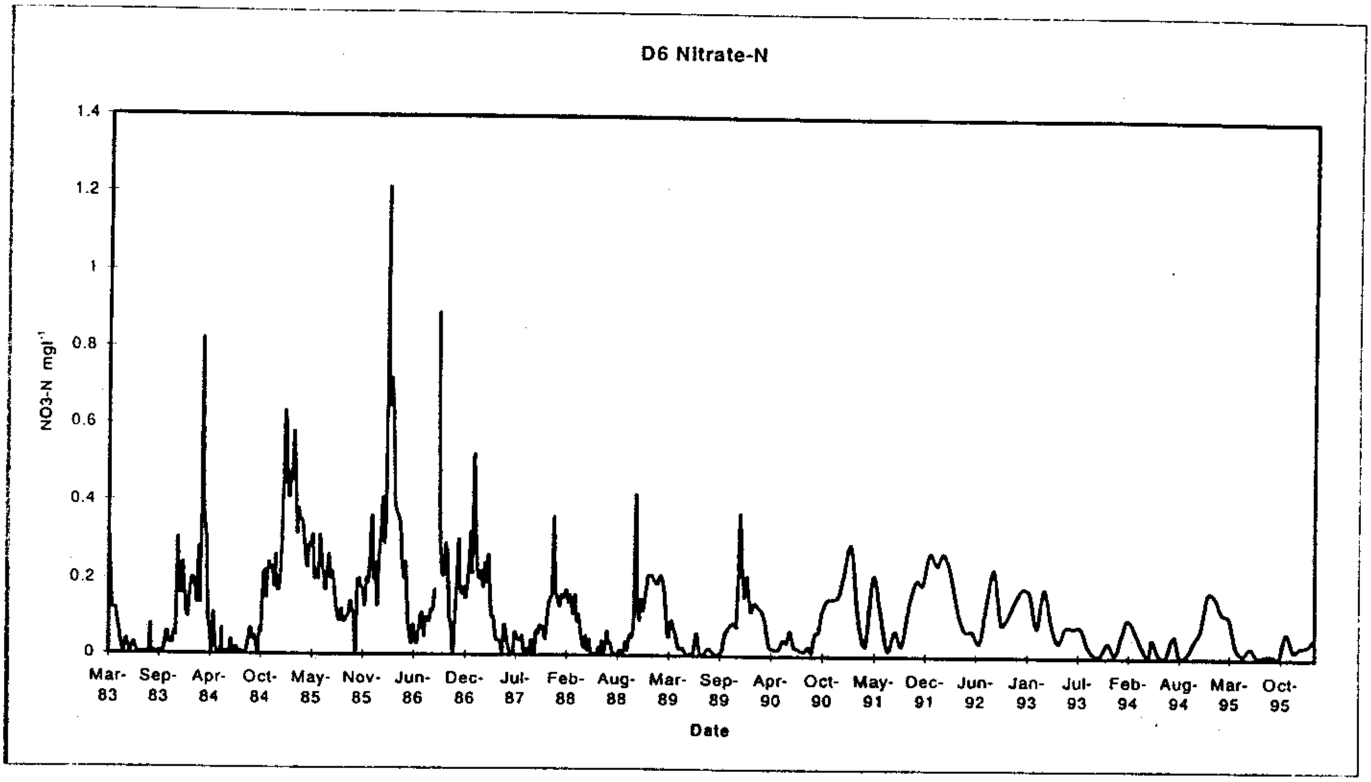
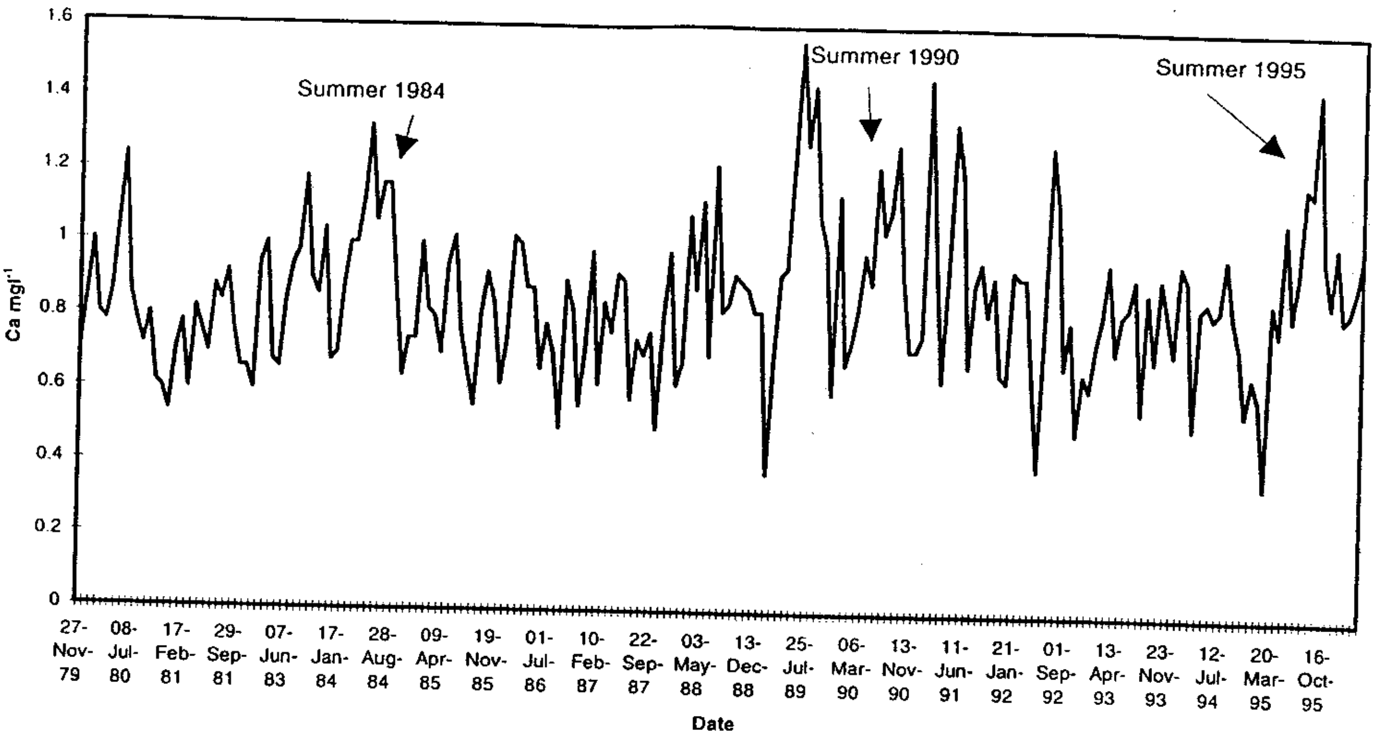


Figure A3.3 Time-series of nitrate-nitrogen concentration in stream D6 at Beddgelert, north Wales, showing evidence for the disruption of the nitrogen cycle during extended dry periods.

a) Afon Gwy - Calcium



b) Afon Gwy - pH

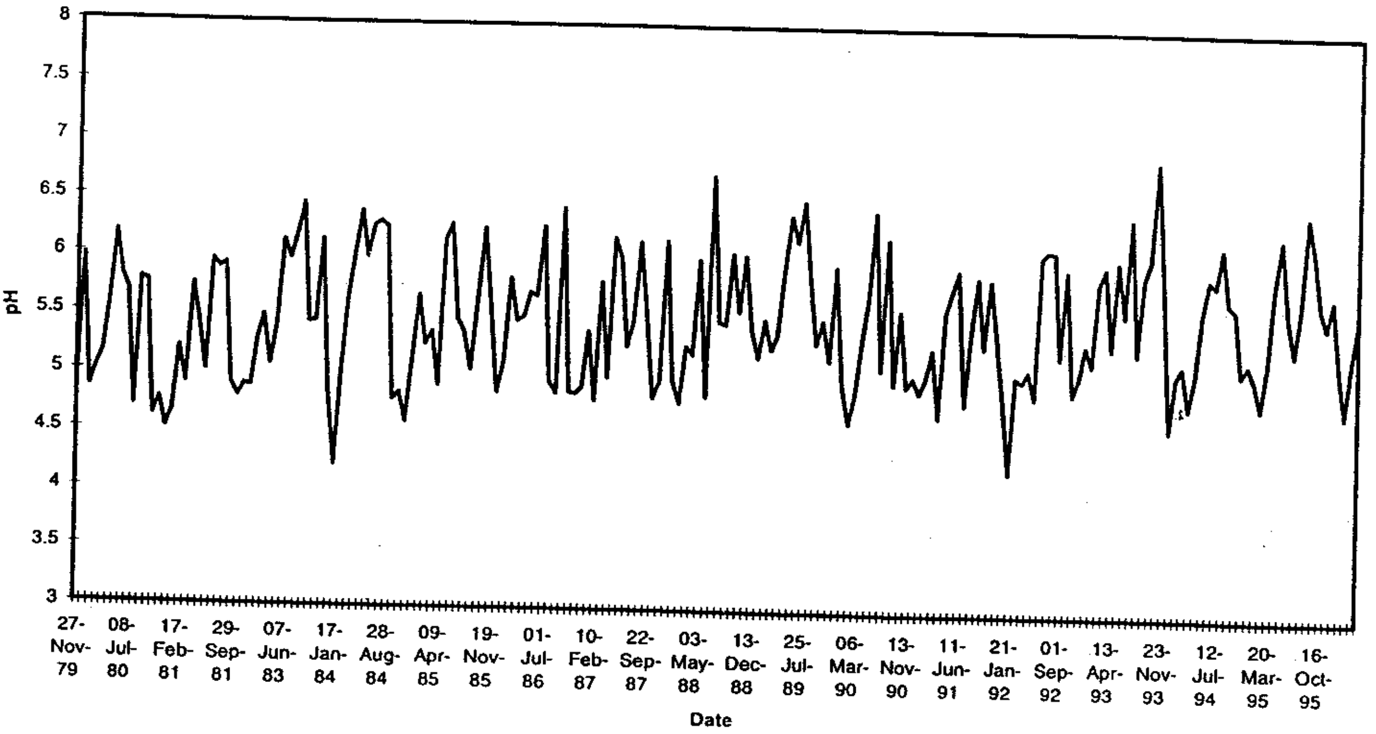


Figure A3.4 Time series of calcium concentration and pH in the Afon Gwy at Plynlimon, north Wales, showing periods of dominant baseflow chemistry during the low flow the summer periods of 1984, 1989, 1990 and 1995.

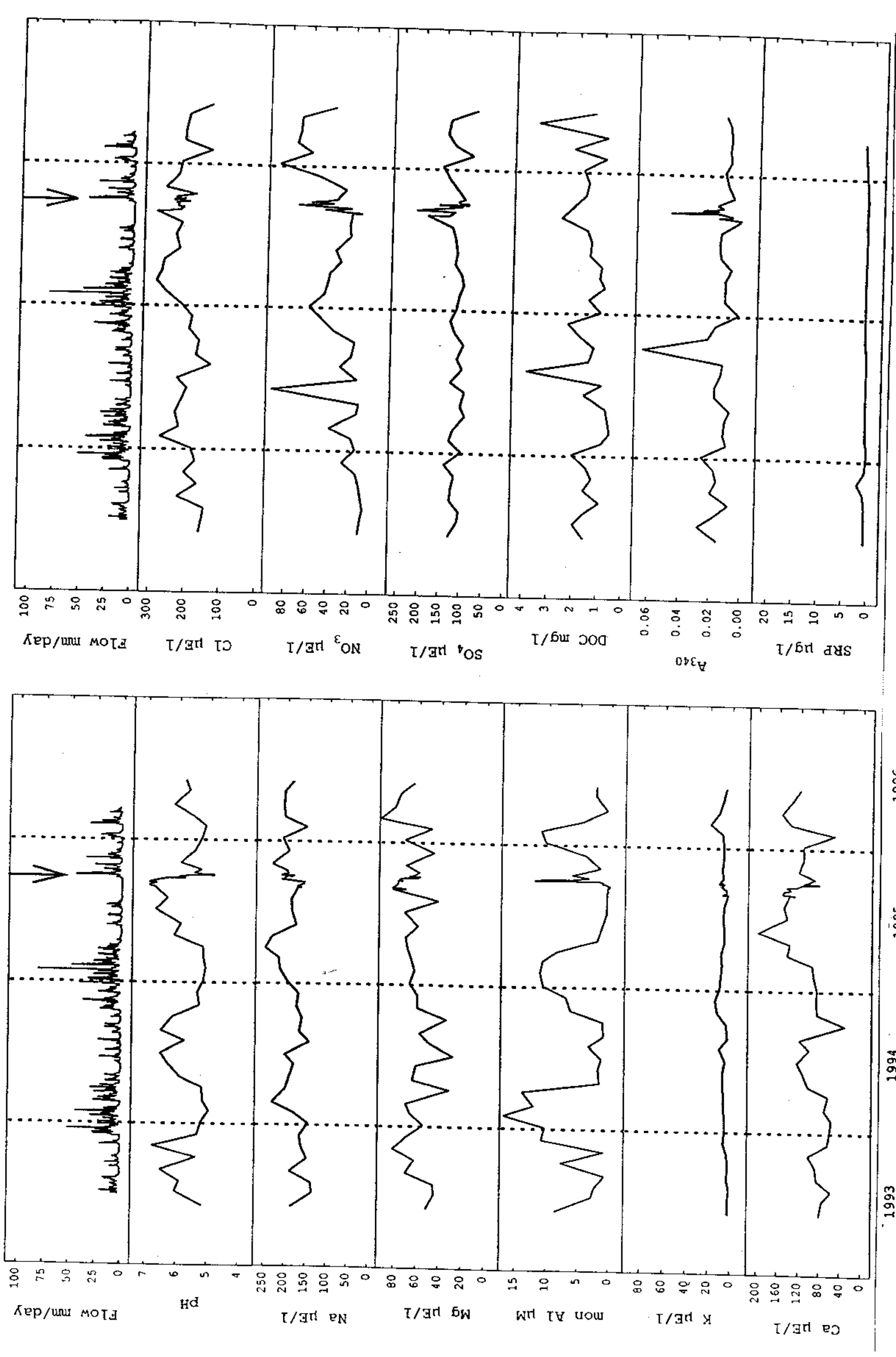


Figure A3.5 Water chemistry of Castle How Beck and flow in the River Duddon at Ulpha, 2 June 1993 to 6 May 1996. 1995 drought-break indicated by arrow.

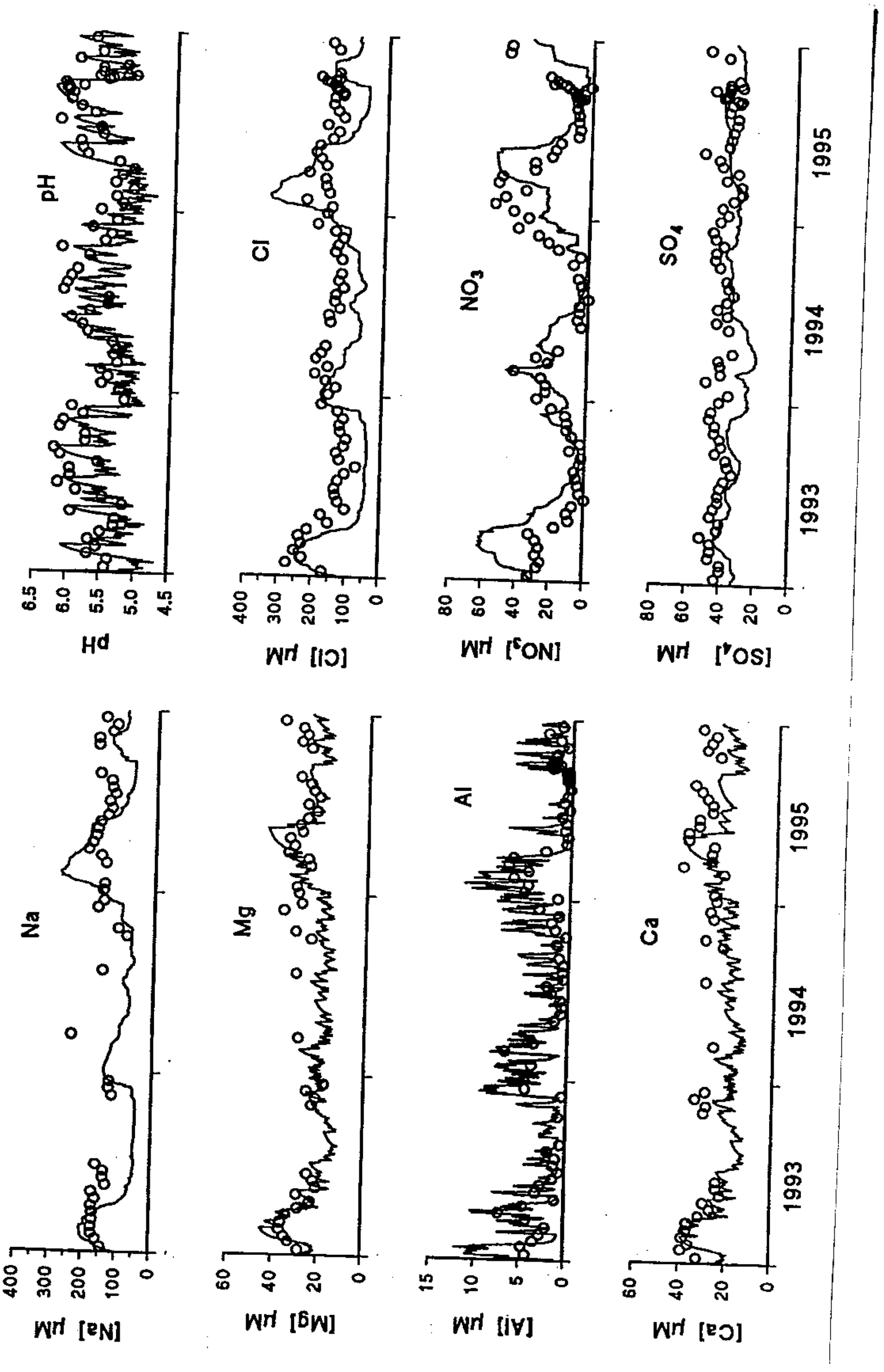


Figure A3.6a Hydrochemical modelling of Tarn Head Beck, Cumbria. Observations (spot samples) are denoted by open circles, and CHUM simulations (daily time-step) with the continuous lines.

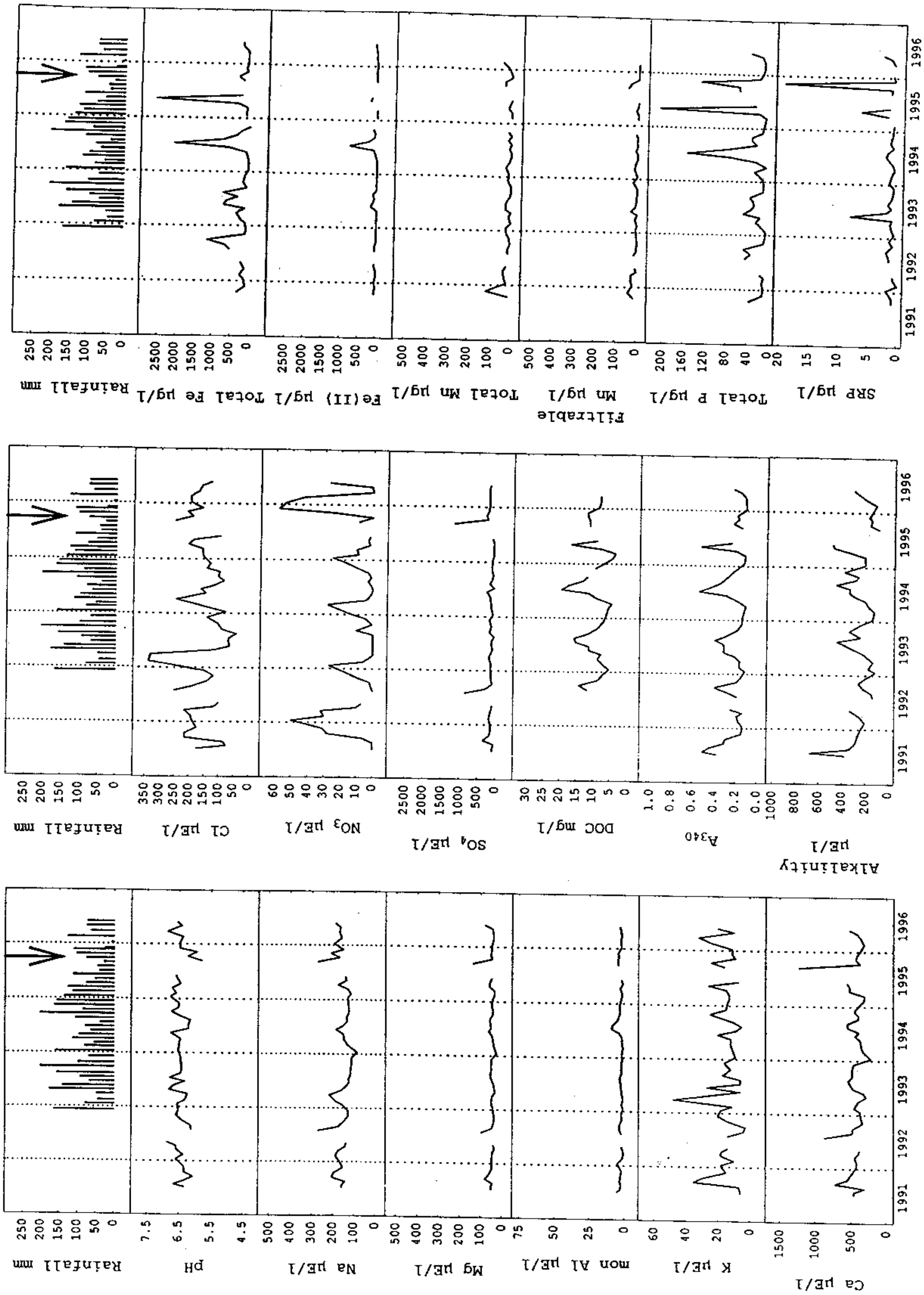
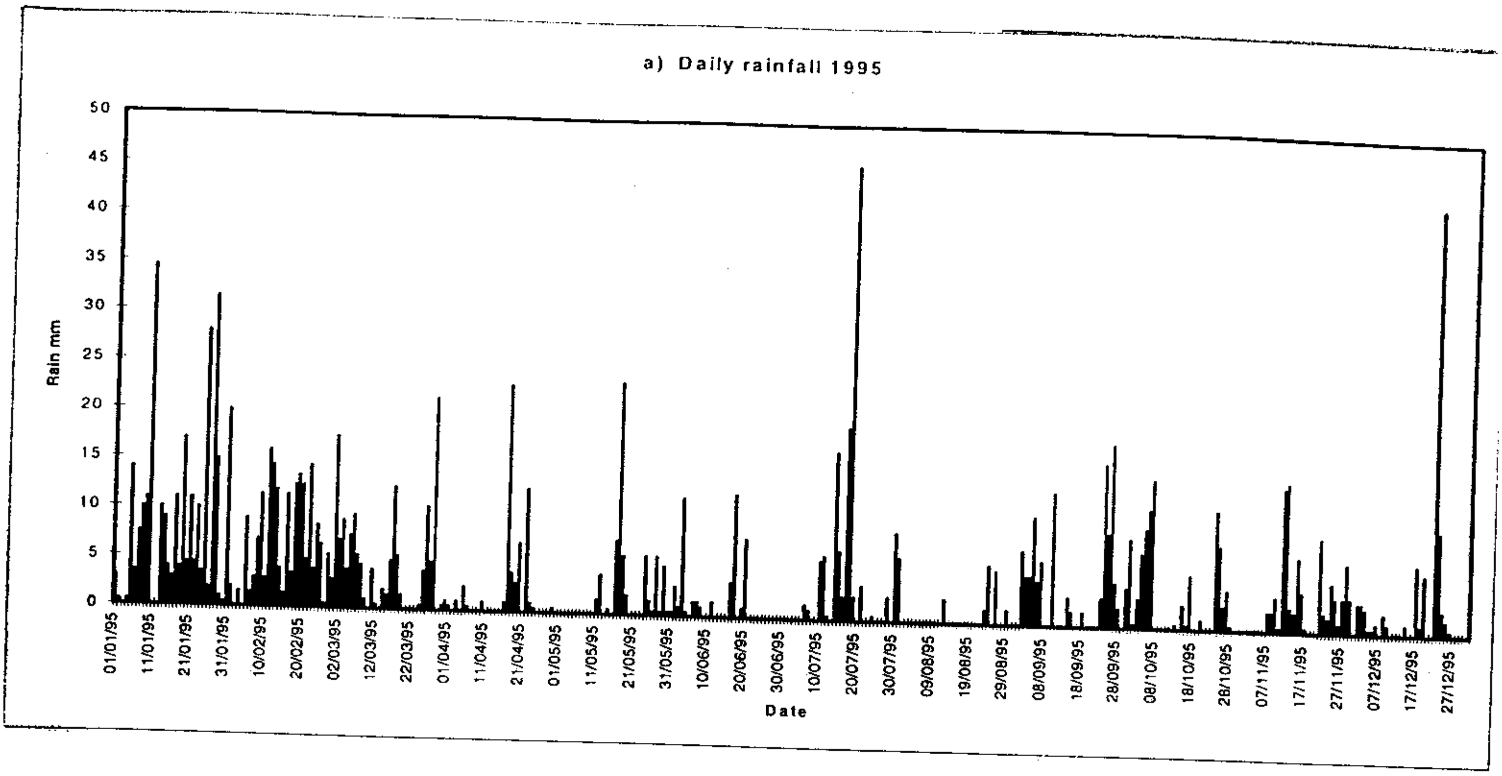
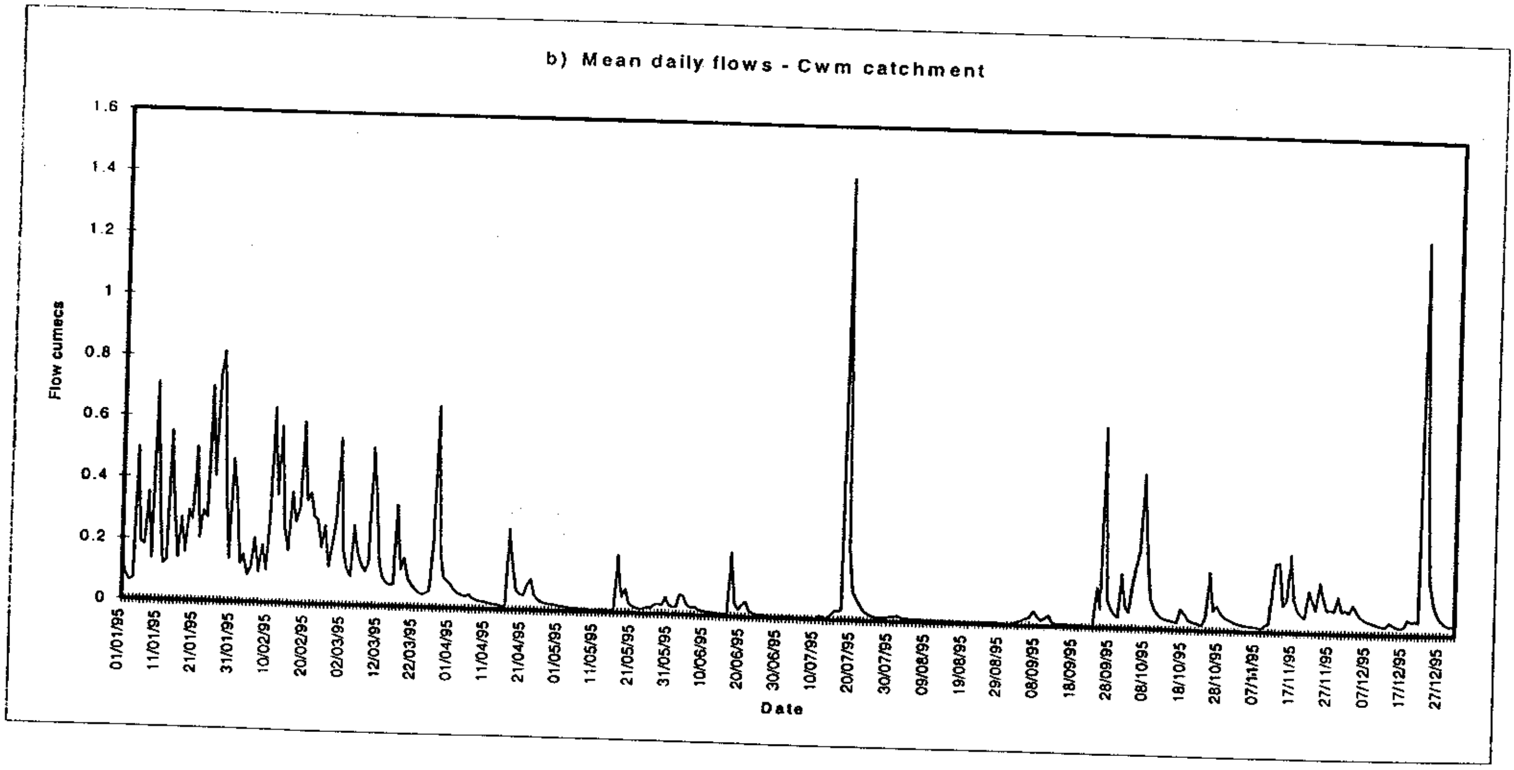


Figure A3.6b Water chemistry of Pool Y at Great Dun Fell and monthly rainfall volumes, 2 June 1993 to 6 May 1996. 1995 drought-break indicated by arrow.

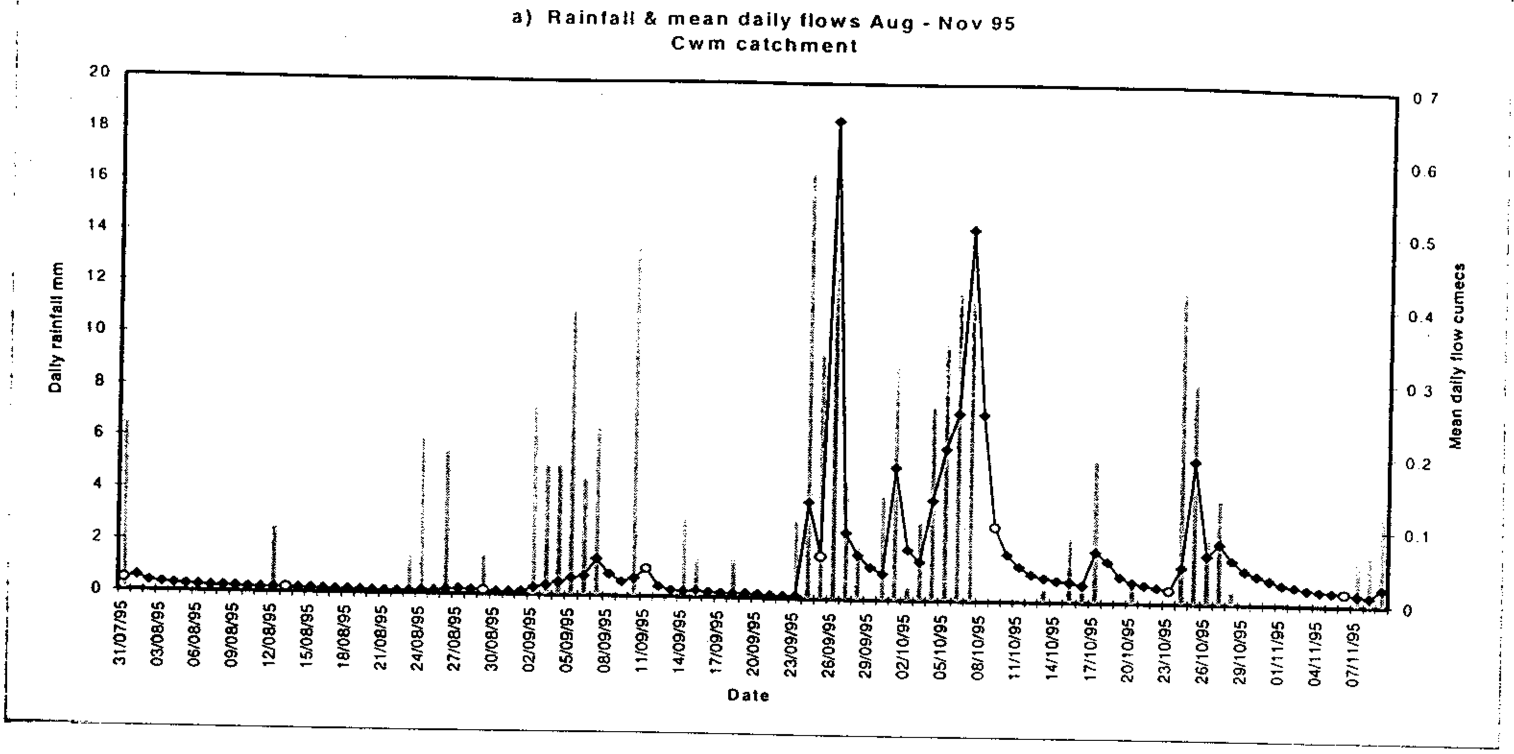


a) Daily rainfall 1995



b) Mean daily flows - Cwm catchment

Figure A3.7 Time series plots of a) daily rainfall and b) mean daily flows for 1995 for the Cwm catchment at Llanbrynmair.



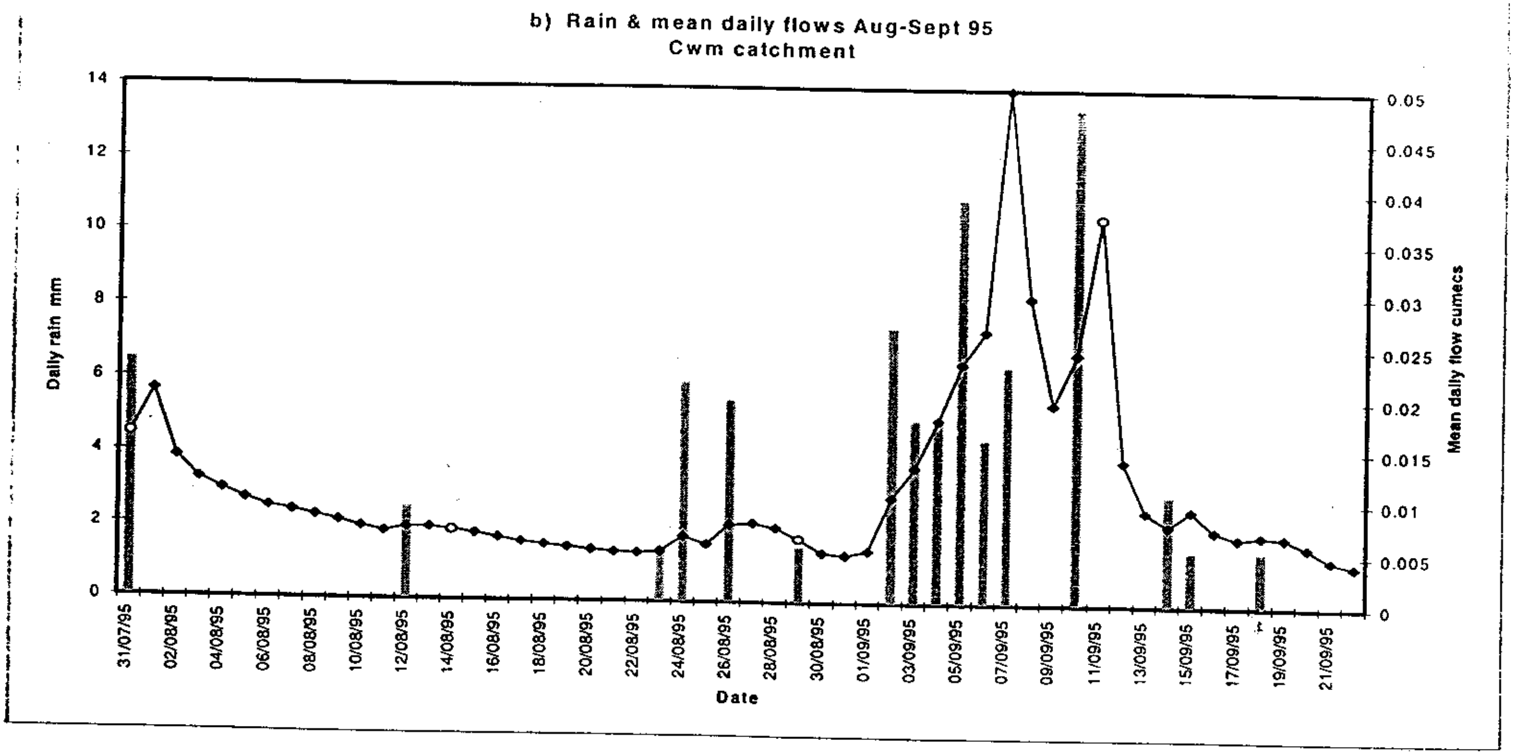
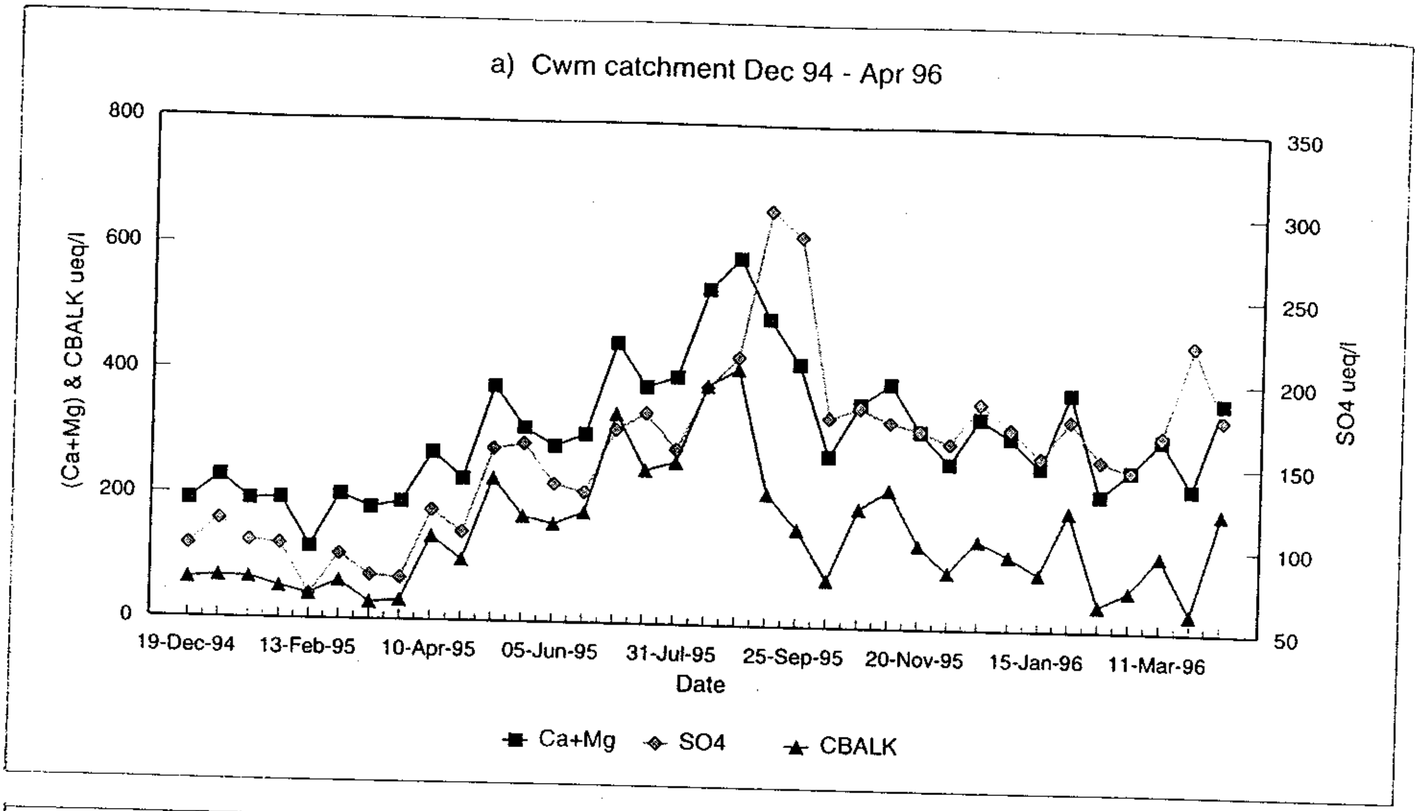


Figure A3.8 Time series of plots daily rainfall and mean daily flows in the Cwm catchment for the periods a) August to November 1995 and b) August to September 1995.



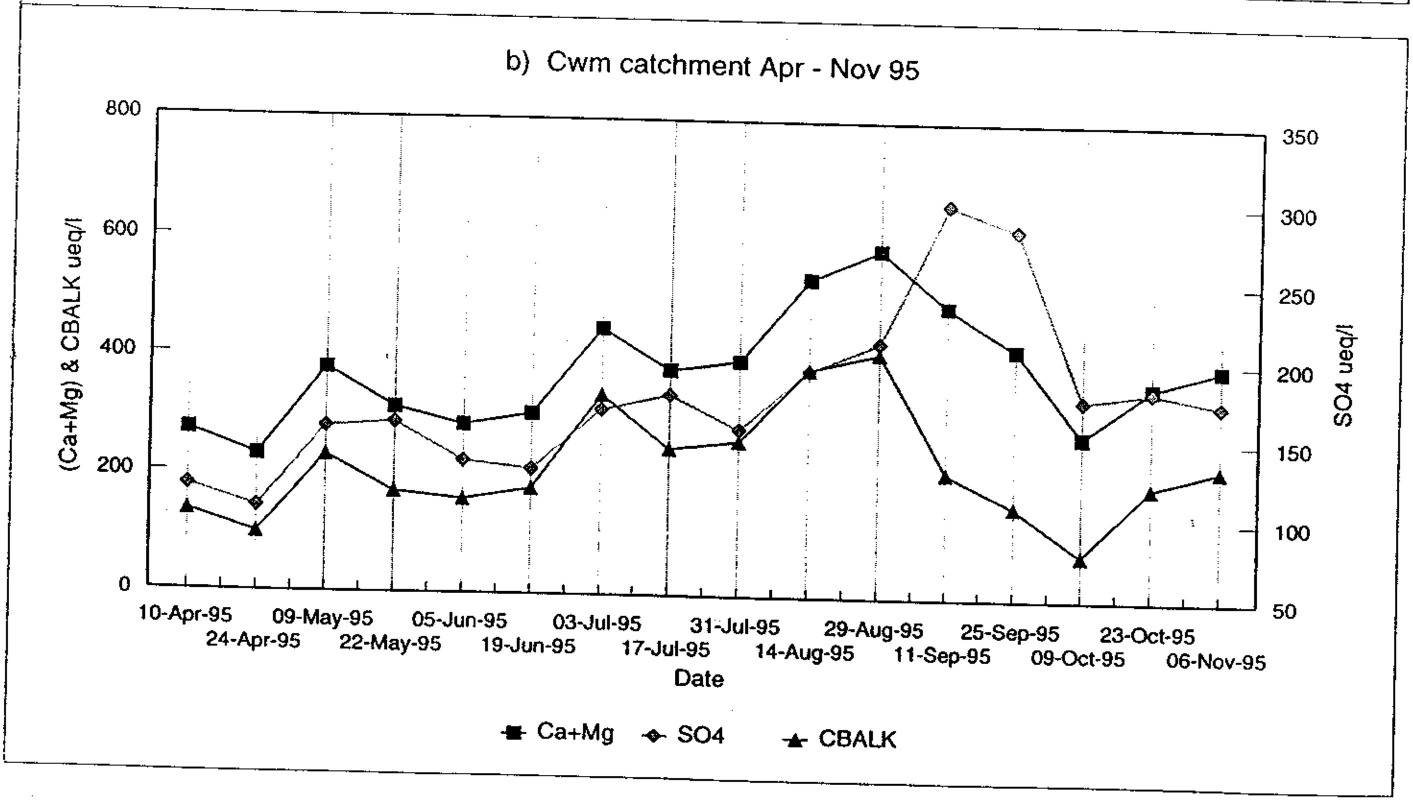


Figure A3.9 Time series plots of divalent base cations, charge balance alkalinity and sulphate in stream water in the Cwm catchment for a) 1995 and b) April to November 1995.

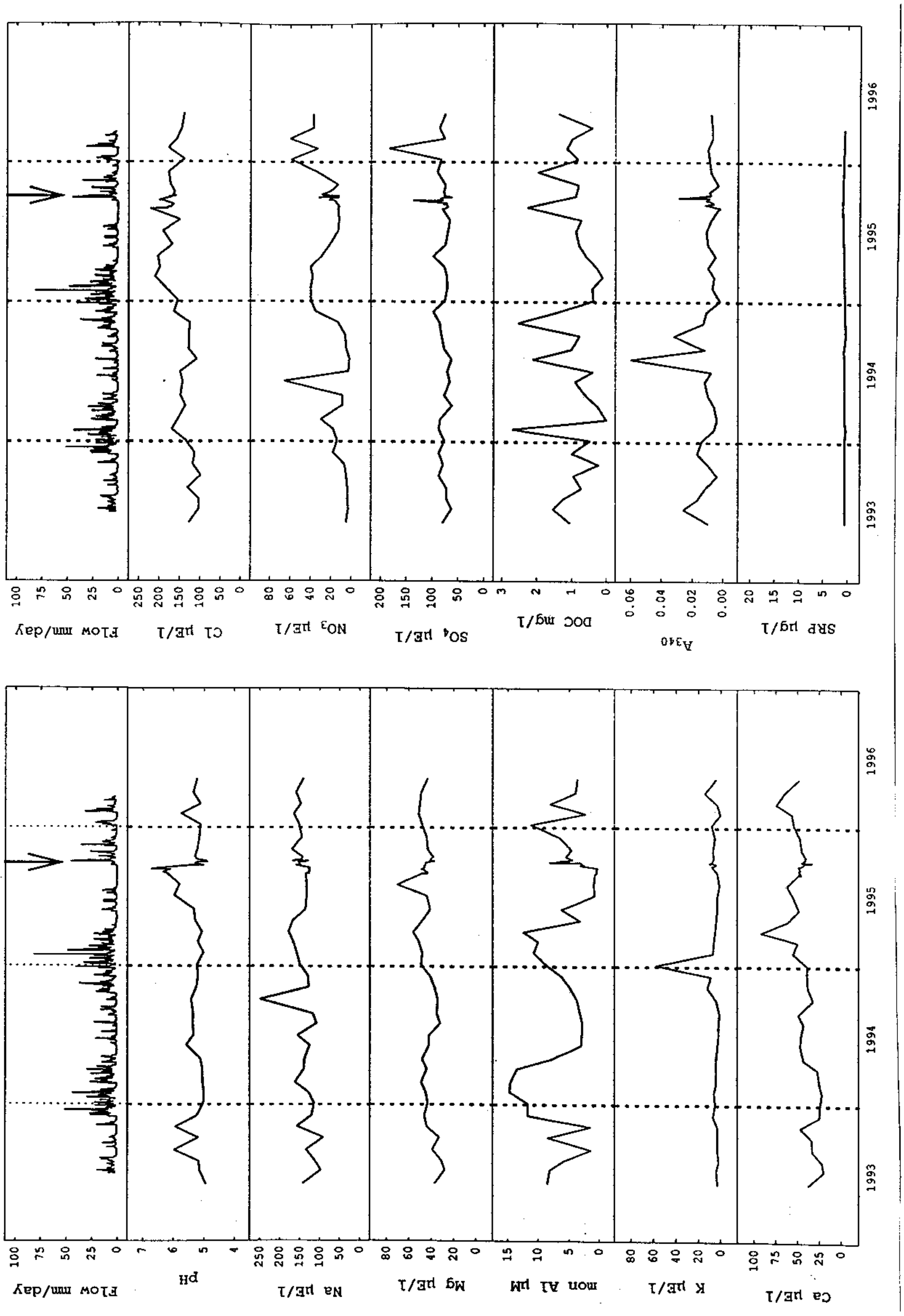


Figure A3.10 Water chemistry of Mosedale Beck and flow in the River Duddon at Ulpha, 2 June 1993 to 6 May 1996. 1995 drought-break indicated by arrow.

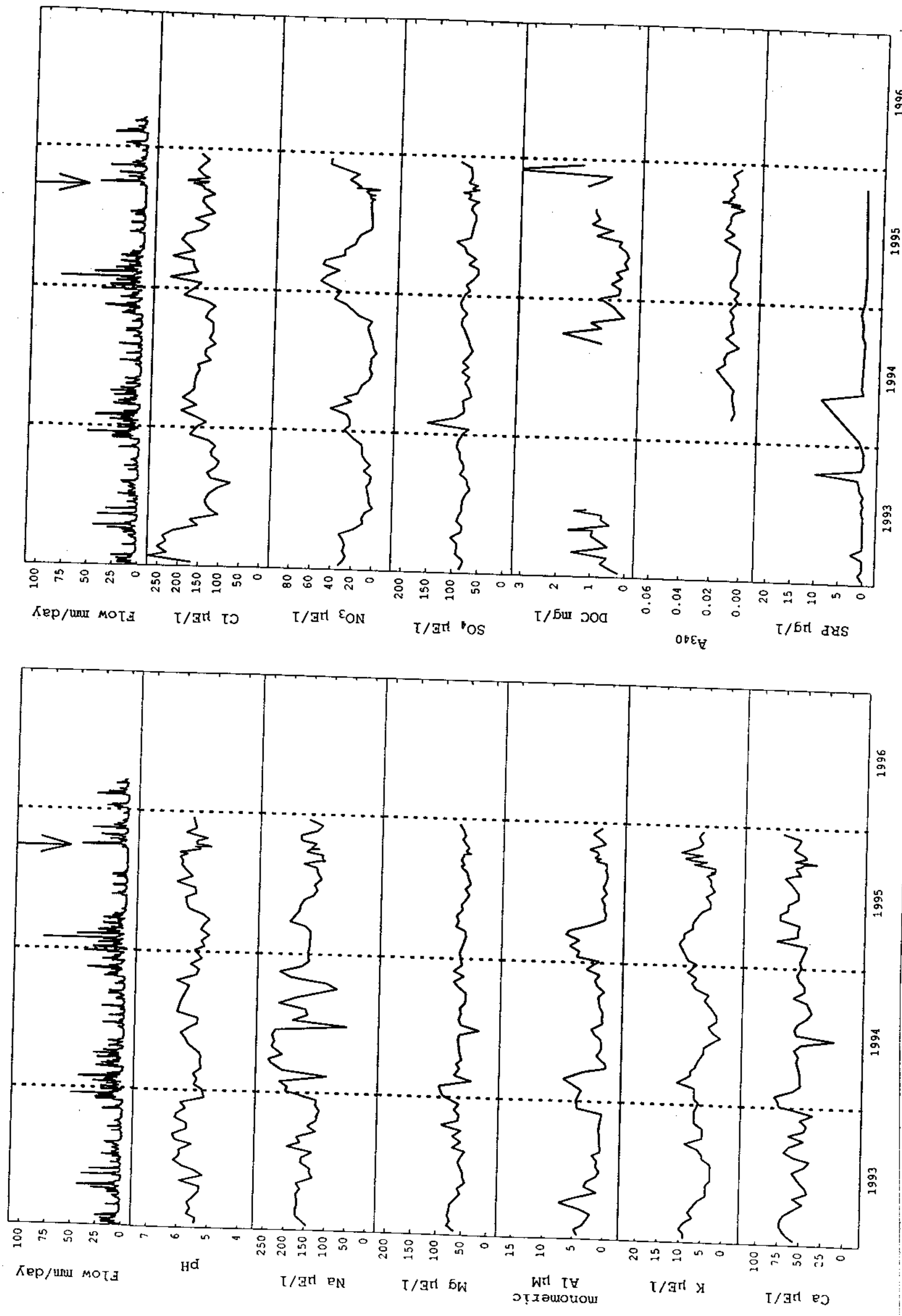


Figure A3.11 Water chemistry of Tarn Head Beck and flow in the River Duddon at Ulpha, 2 June 1993 to 6 May 1996. 1995 drought-break indicated by arrow.

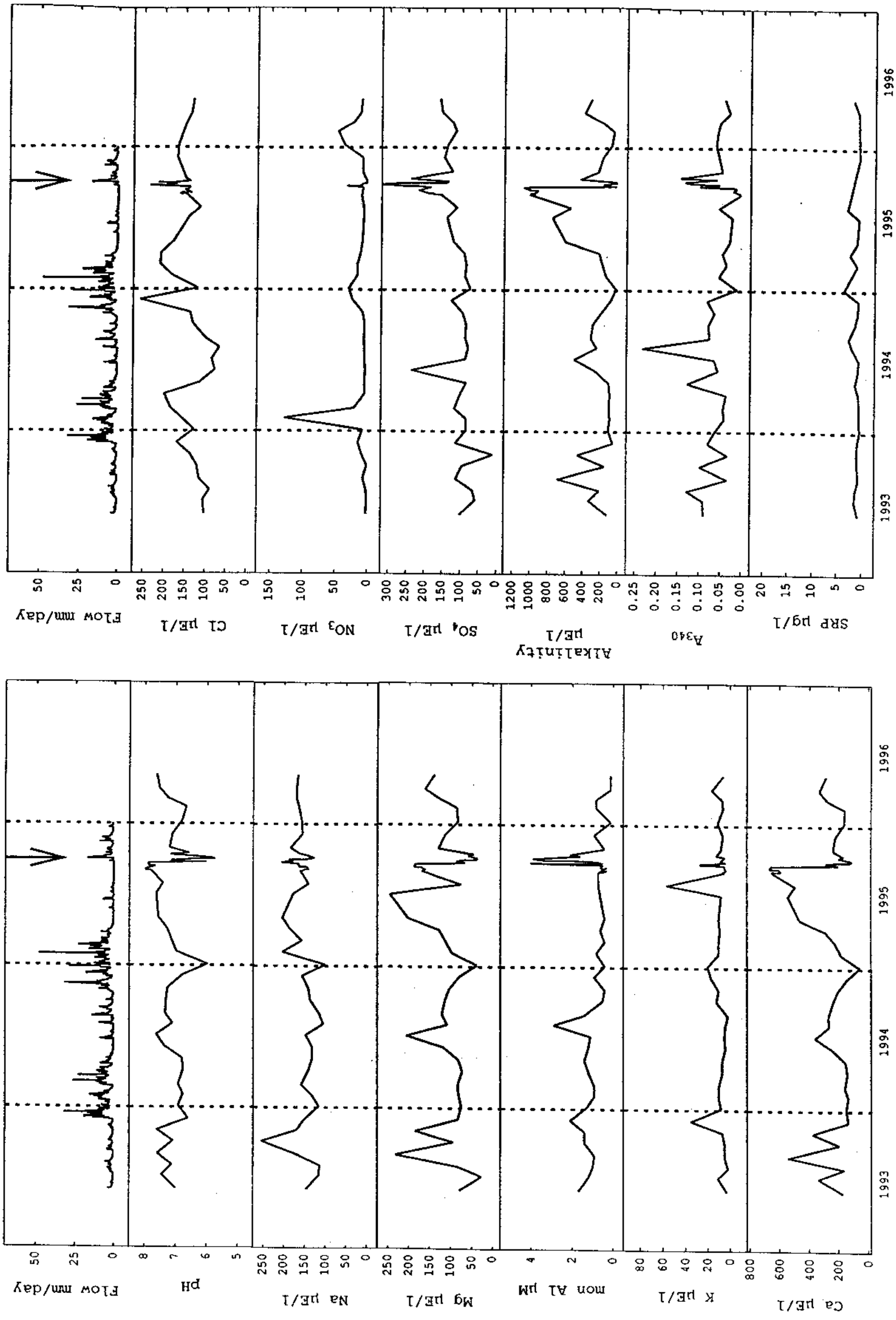


Figure A3.12 Water chemistry of Bannisdale Beck and flow in the River Mint, 2 June 1993 to 6 May 1996. 1995 drought-break indicated by arrow.

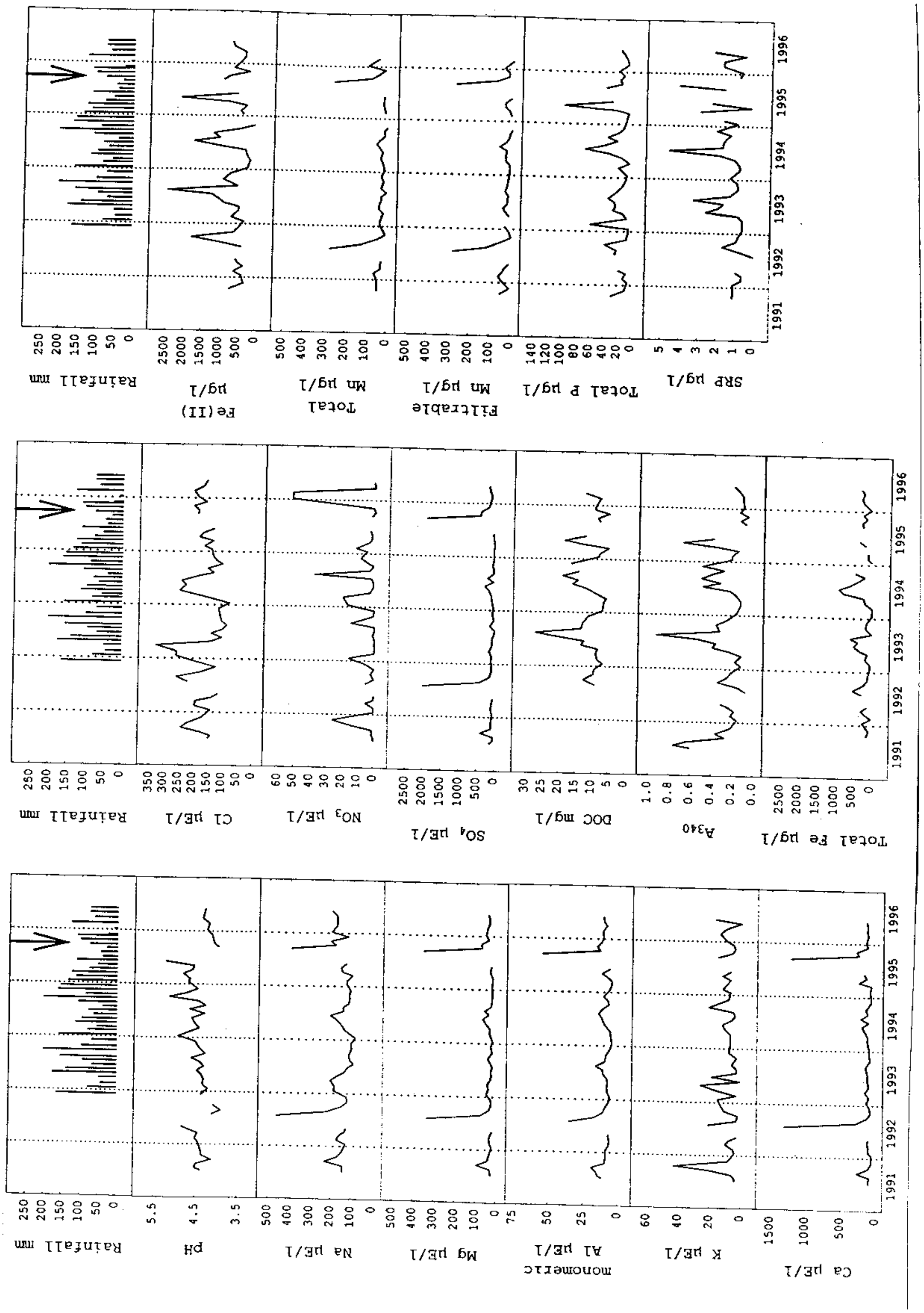


Figure A3.13 Water chemistry of Pool X at Great Dun Fell and monthly rainfall volumes, 2 June 1993 to 6 May 1996. 1995 drought-break indicated by arrow.

4. POST-DROUGHT WETTING (LOIS AREA)

4.1 Study Area

The quality of water in Yorkshire rivers has been studied under the NERC-funded LOIS (Land Ocean Interaction Study) programme. Water samples are being collected manually at weekly intervals at sites on several of the main rivers, and at some locations automatic sampling devices have been installed. Samples are analysed for a wide range of determinands at the LOIS laboratories in York, and at other NERC laboratories. Studies under the LOIS program also include statistical analysis of water quality data from routine monitoring by the NRA, now being continued by the EA.

The existence of a related program of work in Yorkshire, and the seriousness of the drought there, made it worthwhile to extend sampling and analysis to include an assessment of any post-drought flush during the autumn of 1995. This was done by additional sampling through periods of high discharge at eleven representative catchments in Yorkshire and Derbyshire and at four sites on the river Aire. These were intended to represent a range of land uses, geologies and soil types at the 100 - 200km^2 catchment scales.

The eleven representative catchments are shown in Figure 4.1 and their EA water quality sampling and flow gauging site names are given in Table 4.1. The Seven and the Dove are adjacent catchments draining the North Yorkshire Moors, predominantly moorland and afforested, with some better quality pasture but arable land restricted to a small proportion of the catchments. The solute load in these streams is generally low.

The Wiske, Blackfoss Beck and the Went drain more intensively farmed land with a high proportion of arable land. The diffuse agricultural component of drainage is high in these catchments. The Dearne, Skell and Bedale Beck catchments are mixed agricultural, with an upland component, while the Doe Lea is mixed but lowland. The Dearne and Doe Lea catchments include existing and derelict industrial or mining areas.

Bradford Beck drains an area which is almost exclusively urban, and the Holme catchment is a mixture of urban and upland areas, including some reservoirs.

The Aire is one of the major rivers of the LOIS study area, with a reach between Leeds and Castleford being used for model testing. This reach includes sampling sites at Armley, Thwaite Mill, Fleet Weir and Allerton Bywater. These are all EA water quality sampling sites, and Armley and Fleet Weir are telemetered flow gauging sites.

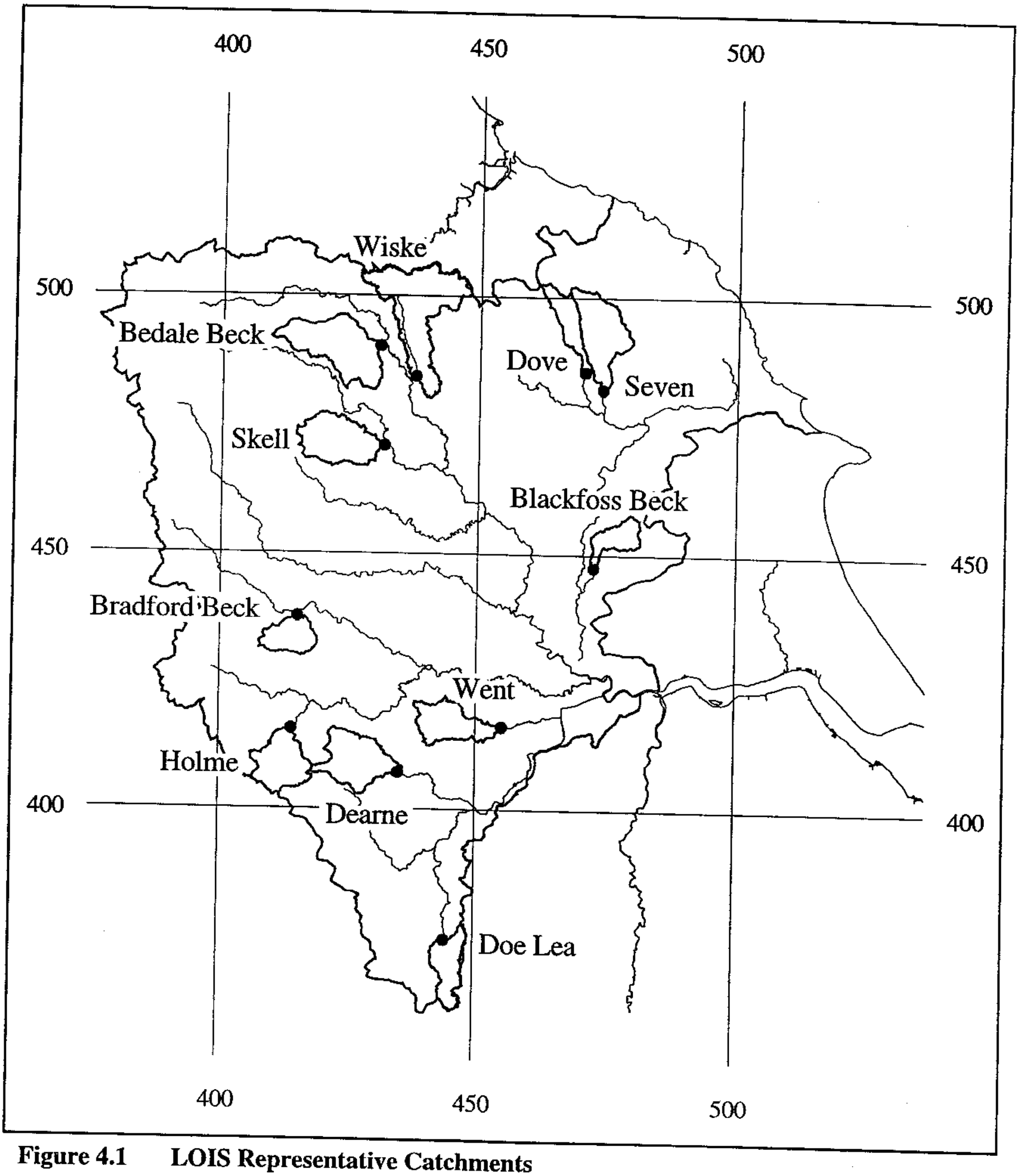


Figure 4.1 LOIS Representative Catchments

Table 4.1 Representative catchment sampling and measurement points

Type	Site Name	Grid Ref
WQ	RIVER DOE LEA AT RENISHAW	4443 3770
Flow	Doe Lea @ Staveley	4443 3746
WQ	DEARNE @ STAR PAPER MILL	4351 4072
Flow	Dearne @ Barnsley Weir	4350 4073
WQ	RIVER HOLME AT QUEENS MILL	4142 4157
Flow	Holme @ Queens Mill	4142 4157
WQ	BRADFORD BECK - SHIPLEY	4151 4376
Flow	Bradford Beck @ Shipley	4151 4375
WQ	RIVER WENT AT WALDEN STUBBS	4548 4162
Flow	Went @ Walden Stubbs	4551 4163
WQ	RIVER SKELL AT WOODBRIDGE, RIPON	4318 4709
Flow	Skell @ Alma Weir	4316 4709
WQ	BEDALE BECK AT LEEMING	4294 4897
Flow	Bedale Beck @ Leeming	4306 4902
WQ	RIVER WISKE AT KIRBY WISKE	4377 4848
Flow	Wiske @ Kirby Wiske	4375 4844
WQ	RIVER DOVE AT KIRKBY MILLS	4704 4860
Flow	Dove @ Kirkby Mills	4705 4855
WQ	RIVER SEVEN AT GREAT BARUGH	4744 4791
Flow	Seven @ Normanby	4736 4821
WQ	BLACKFOSS BECK AT SUTTON ON DERWENT	4725 4474
Flow	Blackfoss Beck @ Sandhills Bridge	4725 4475

4.2 Sampling

4.2.1 Representative catchments

The first significant rainfall of the autumn in Yorkshire fell on 7th September, giving a small increase in flow of most rivers. Further occasional moderate storms through the autumn produced some increase in flow, but there was no single major event defining the end of the drought.

The southern representative catchments of the Doe Lea, Dearne, Went, Holme and Bradford Beck were sampled manually at the EA sampling site shown in Table 1 on the evening of the 6th September before rain started, then four times on the 7th, after the first rain, but through a period of heavy showers. A further sample on the 8th covered the post-storm period. The northern catchments of the Skell, Bedale Beck, Wiske, Dove, Seven and Blackfoss Beck were sampled twice on 7th September.

Subsequently samples were collected from all catchments at the EA sampling site either once or twice during an event, when it was possible to mobilise staff. Events which occurred over a weekend were not sampled. On some occasions anticipated rainfall was less than forecast, and there was little significant rise in river levels, and on others the peak flows during an event were missed. Sampling times and 15 minute flows are shown for all catchments in Figure 4.2. The mixed success of manual sampling in capturing high flow periods is apparent, and further discussion is confined to Bradford Beck, the Dearne, Doe Lea, Holme and Went.

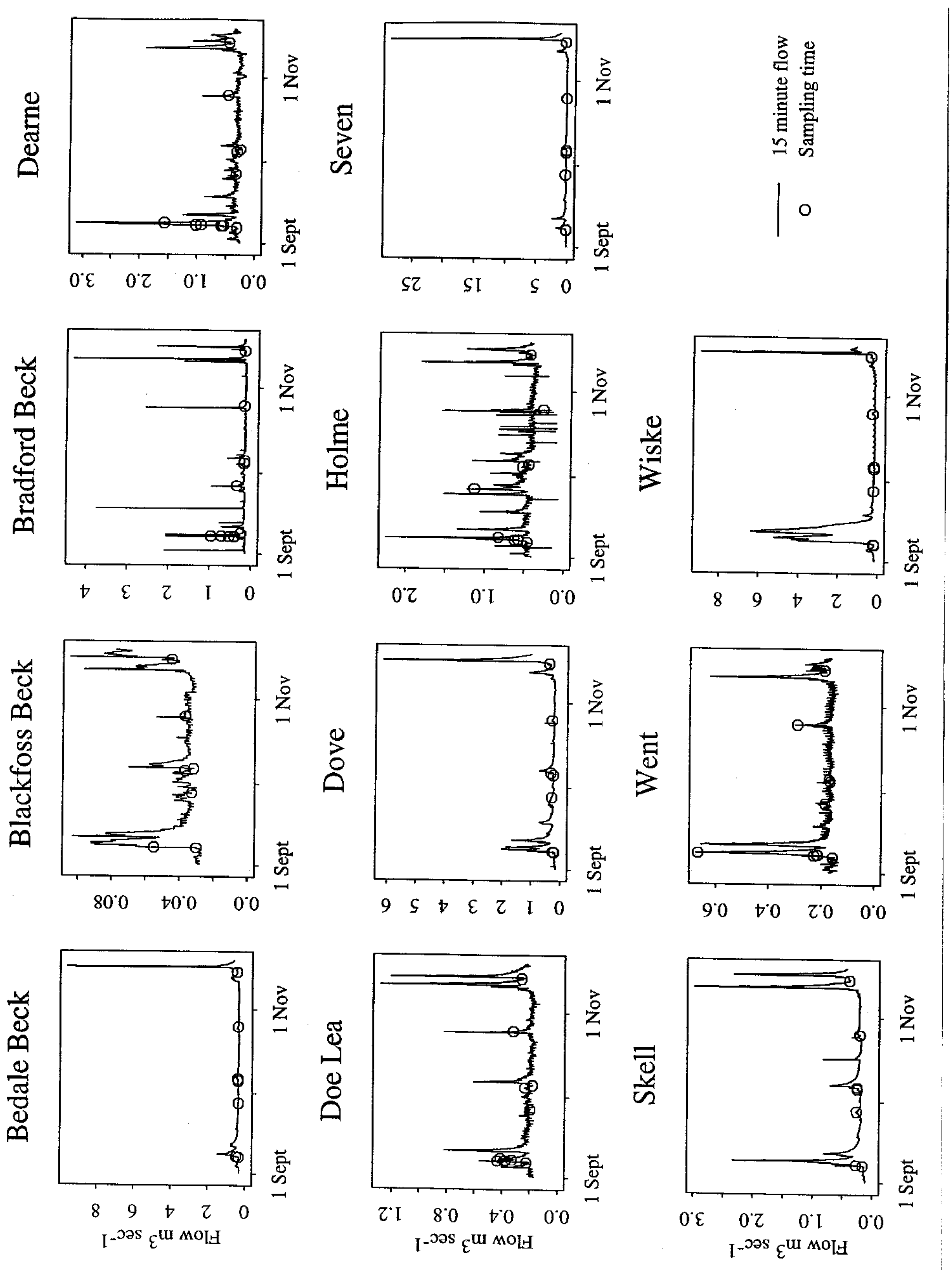


Figure 4.2 **Representative Catchments - Autumn 1995**

4.2.2 River Aire

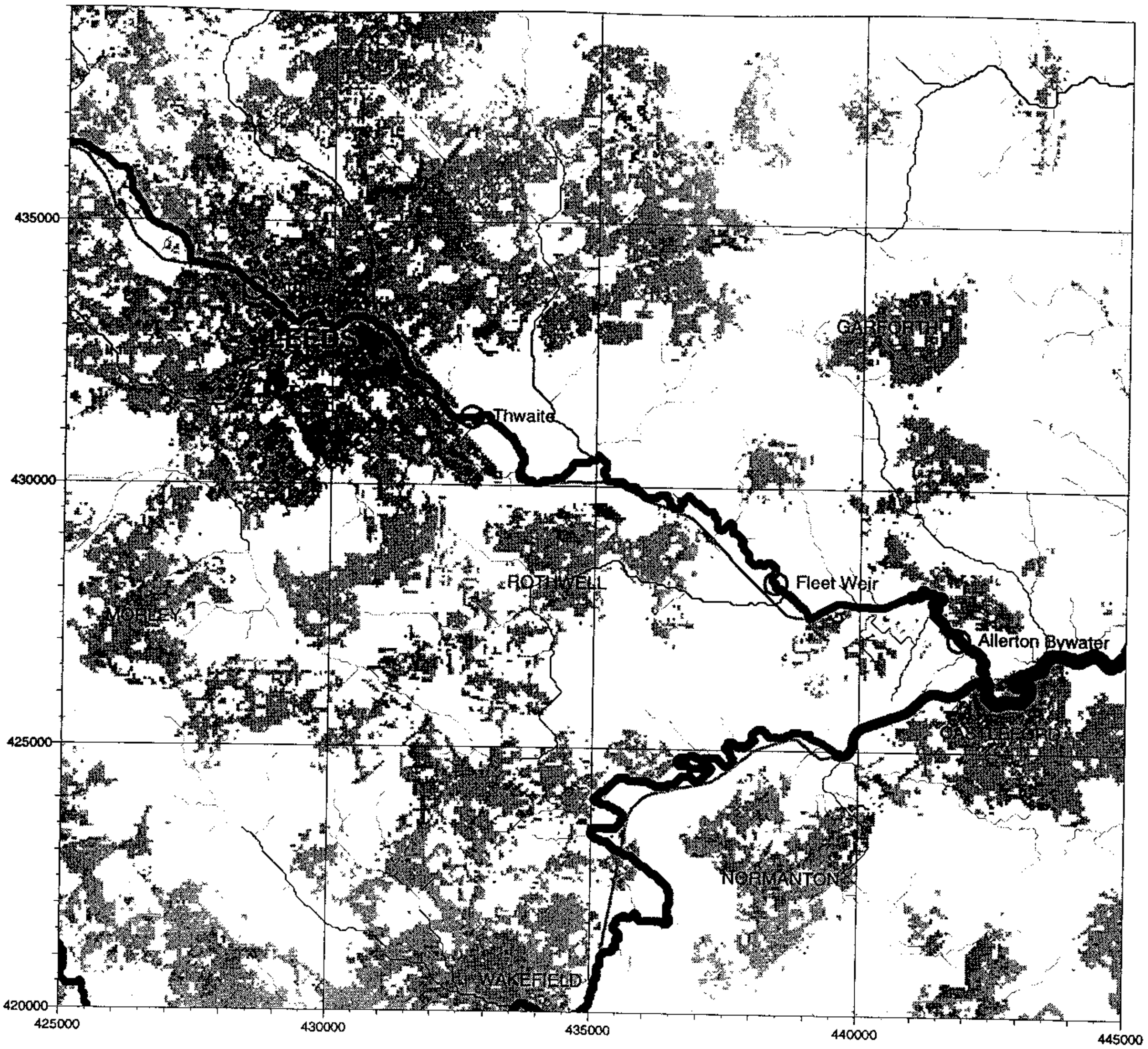
Paired EPIC automatic water quality samplers were installed at four sites on the Aire during 1995-96. (Figure 4.3) Sampling began at three of these, Armley, Thwaite Mill and Allerton Bywater, during early November 1995.

The EPIC samplers at each site were programmed to be stage-triggered, with a selected fixed sampling interval and a maximum of 24 samples available before collection and resetting. Armley is a telemetered flow gauging site with a well-established stage discharge relationship and historic flow record. These known features of the site were used to set an initial trigger stage level. The appropriate trigger stage at each the remaining sites was adjusted in the sequence of events.

Samples were collected during 5 periods of high river discharge from November 1995 to January 1996. These included the main events in the later wetting-up period following the 1995 drought, but sampling began too late to capture some of the smaller events earlier in the autumn. Figure 4.4 shows rainfall, flow and sampling times at Armley.

The success of the EPIC stage-triggered sampling strategy in capturing high flow events is evident. Figure 4.5 shows a comparison between daily flow measurements during 1992 and 15 minute flows over the post drought period at Armley.

Water quality sampling times show the improvement of EPIC stage triggered sampling over EA routine sampling in obtaining a large number of samples over periods of high flow. The routine sampling scheme does have the advantage of providing an unbiased estimate of long term loads when used with standard simple estimation procedures.



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KEY

Some of the material contained in this plot has been reproduced from an Ordnance Survey map with the permission of the Controller of Her Majesty's Stationery Office.

Land Use/Urban/suburban areas are provided by the Institute of Terrestrial Ecology from its Land Cover Map of Great Britain. For more information, contact Sue Wallis or Robin Fuller (Telephone: 014873 381)

The place names shown on this map are from data licensed from AA Developments Ltd.

▨ built-up urban

▨ built-up suburban

Canals

Rivers

Figure 4.3 Rivers Aire and Calder

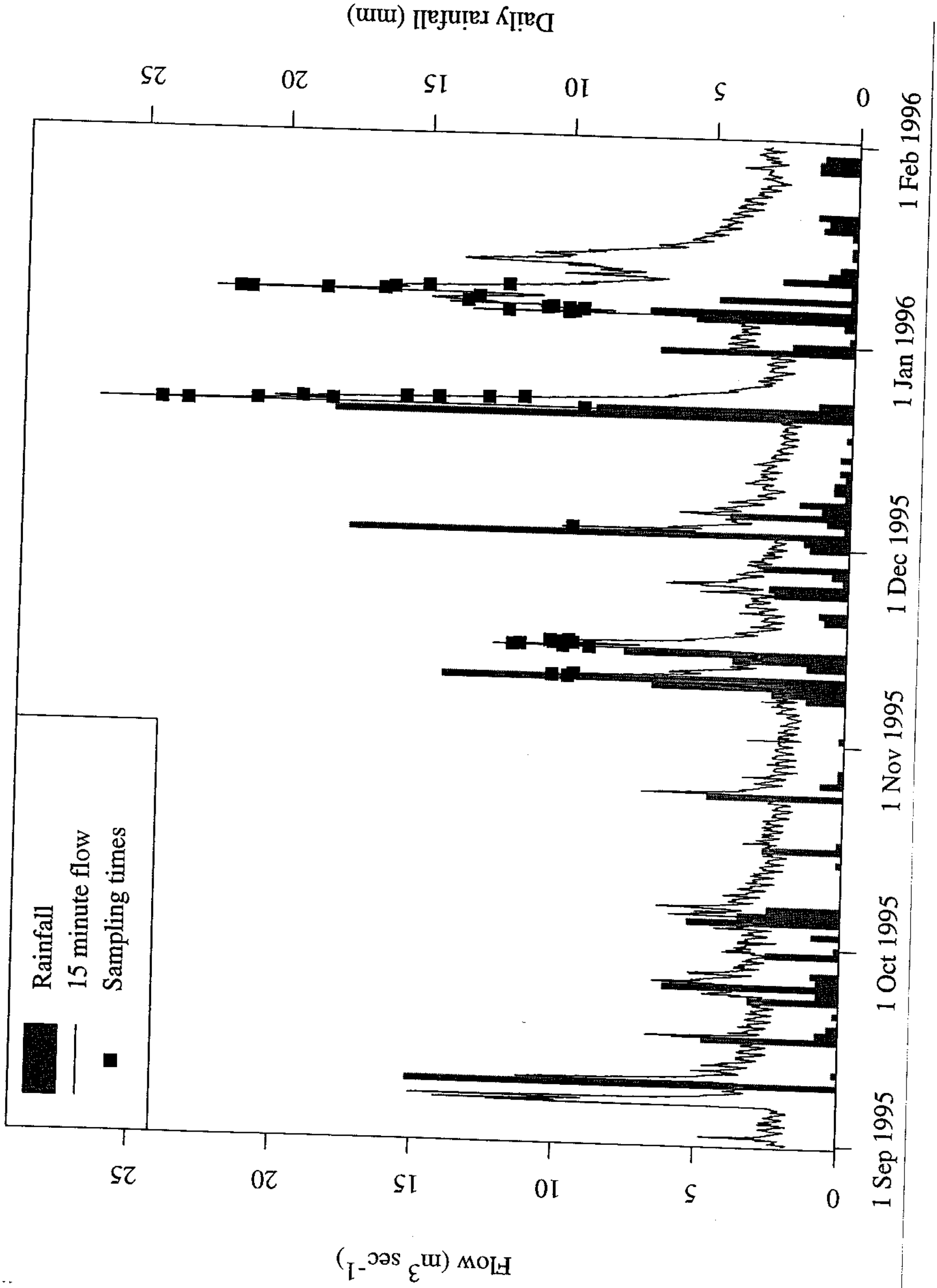

Figure 4.4 **Flow and Sampling Times, Aire at Armley and Rainfall, Bradford.**

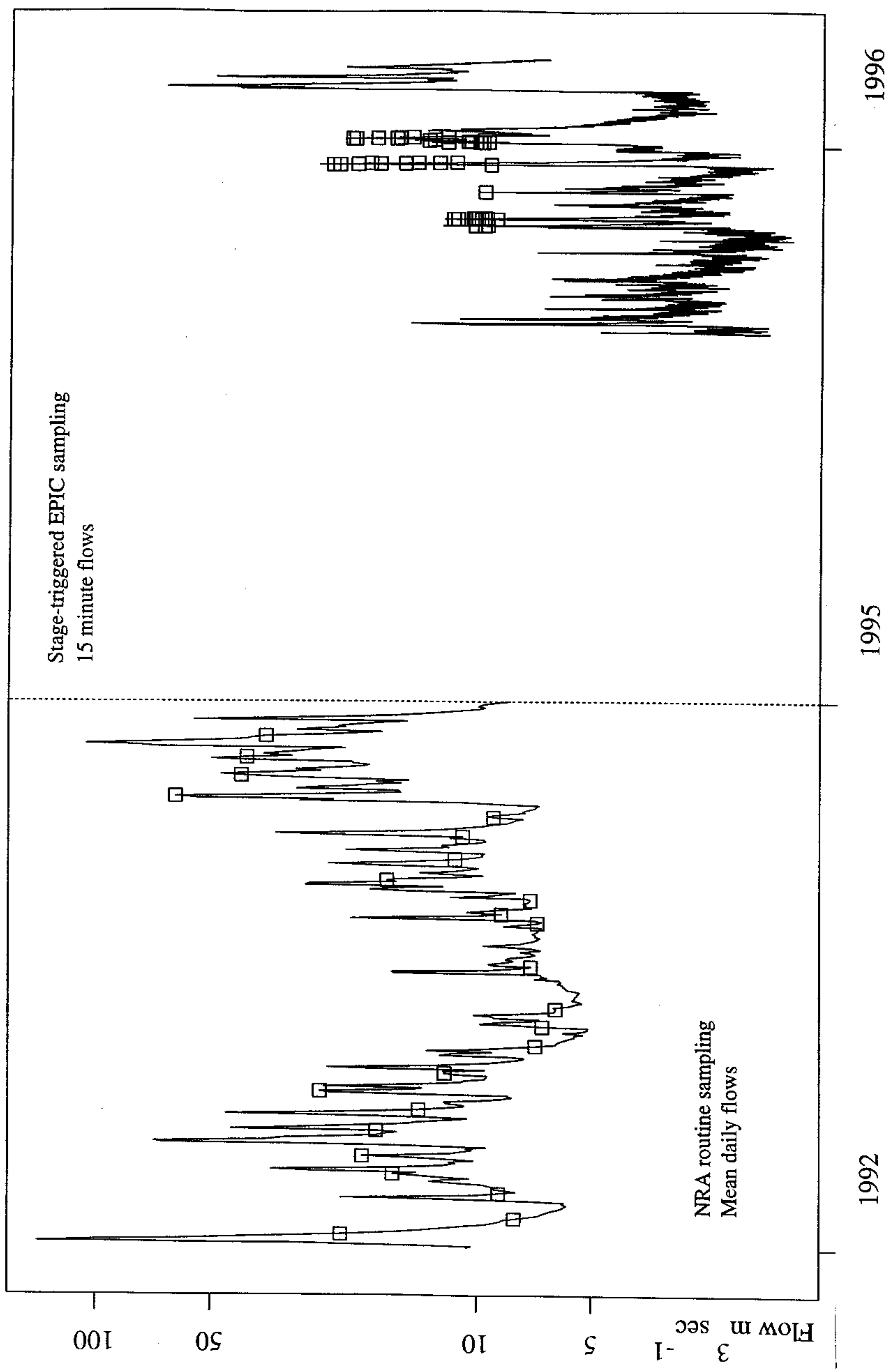

Figure 4.5 **Flow and Sampling Times at Armley**

4.3 Chemical analysis

Samples collected from the representative catchments and the River Aire were chemically analysed for the following trace metals using ICPMS analysis:

B, Sr, Ba, Mn, Fe, Li, Be, Al, Sc, Cr, Ni, Co, Cu, Zn, As, Rb, Y, Cd, Sn, Sb, La, Ce, Nd, Sm, Gd, Pb, U.

Samples were divided, with one subsample filtered immediately and acidified with 1% concentrated nitric acid before analysis. The remaining subsample was acidified and left for a few days before filtering and analysis. The first treatment gave an estimate of the dissolved metal concentration in river water and the second the concentrations dissolved or loosely bound metal potentially available in solution through natural biochemical release. This approximates the total metal concentration often quoted by the EA.

Samples were also analysed for suspended sediment and the following major ions and other determinands:

Cl, NO_2, Br, NO_3, PO_4, SO_4, Na, NH_4, K, Mg, Ca.

Samples from the representative catchments only were analysed for soluble reactive phosphorus (SRP) and colour. Whenever possible, measurements of conductivity, pH and temperature were made at each catchment at the time a water quality sample was taken.

Samples from the Aire only were analysed for Si and DOC.

Microorganics are a notable omission from the determinands analysed. These remain a possible subject for further investigation.

4.4 Data analysis

It is recognised that in assessing the importance of flushing, attention should focus on those determinands which are of biological significance, particularly those which are subject to Environmental Quality Standards. Some key weathering components may also be of interest as nutrients and in confirming provenance of some mixture components of streamwater. For this reason, although presented graphically where detected, the following determinands are not discussed individually: Li, Be, Sc, Rb, Y, Mb, Sb, Sn, Ln, Ce, Ne, Sm, Gd.

4.4.1 Representative catchments

Plots of determinand concentration against flow and sediment respectively have been examined for the samples collected at Bradford Beck, the Dearne, Doe Lea, Holme and Went. These include only unfiltered concentrations of ICPMS metals. Filtered concentrations were available only for samples taken after the 8th September, reducing the data available to a handful of samples, most of which were not associated with high flows.

Although data for a large number of determinands are available, many behave in a similar fashion, and some overall inferences can be made. There is a distinction first between sediment, whose concentrations are determined largely by availability and the mechanical action of the river, and other determinands which are either associated with sediment, or whose concentrations are biochemically determined.

Data from the representative catchments show a few samples with high sediment concentration, usually associated with high flow. At Bradford Beck there is a range of sediment concentrations, up to 600mg l^{-1}, the highest value measured in any representative catchment, and a clear relationship with flow. The key data points are those taken during the first high flow period, 6-8 September. One sample from the Dearne showed significantly higher sediment concentration than all other samples, and this was associated with the highest flow. The Doe Lea shows a poor relationship between flow and sediment concentration. The highest sediment concentration is associated with a relatively low flow during an event at the end of October. Higher flows during the event of 6-8 September generated a lower concentration of sediment. The Holme shows the converse, with higher sediment concentration and lower flow for samples taken from 6-8 September, compared to a later event, this time in late September. The lowest flow is probably anomalous, judging by the flow record of of Figure 4.2. Data from the Went (ignoring an anomalous point) are similar to the Dearne, with one sample collected at a time of particularly high flow and sediment concentration.

Concentrations of determinands other than sediment at all sites show two broad patterns. There is a distinction between those which tend to attach to sediment and those which do not. For those which remain in solution, soluble (filtered) and total (unfiltered) concentrations are similar, while metals associated with sediment may show at least an order of magnitude difference between the two concentrations. Total concentrations of these metals tend to be highly correlated with sediment concentration, while solute concentrations may be unrelated.

Concentrations of the most soluble determinands tend to decrease as flow increases. This is true of soluble concentrations of the major ions Cl, SO_4, Na, Mg, and Ca and also Sr. Of the ICPMS-determined metals of interest, those whose total concentration is associated with a high sediment-related component are: Ba, Mn, Fe, Al, Cr, Ni, Co, Cu, Pb. Of the remaining metals, total Zn and Cd show no evidence of a relationship with sediment concentration, and As varies between catchments, as does NO_3 and PO_4. Boron is the only ICPMS-determined element of interest which does not attach to sediment and tends to be diluted at high flows.

The strength of the relationship between sediment and total metal concentrations above varies between catchments and metals. It is weak for the Doe Lea.

The main processes influencing concentrations in these catchments are inferred to be dilution of the most soluble determinands as flow increases, and an increase in the total concentration of many metals as sediment concentrations increase. On the basis of these data, any adverse post-drought flush effect is likely to be associated with high total metal concentrations accompanying high sediment loads.

A comparison of flow and concentration data collected during the autumn of 1995 compare with past data collected by the NRA from 1985 to 1992 at the same sites shows that values from samples collected during the post-drought period were generally not out of the ordinary for determinands in common. Large differences for some determinands (Mg, Ca and Cl) on the Dearne and Doe Lea have been identified as due to riparian disturbance and not post drought flushing.

In terms of absolute water quality in the rivers concerned, apart from other considerations, the Cl and SO_4 concentrations would make them unsuitable for the provision of drinking water, judged by the EC guideline concentrations. Of the ICPMS-determined metals, Fe and Mn are generally above EC limits, as is Cr on the Holme. In terms of fisheries, for which dissolved Cu and total Zn are the only metal concentrations specified for "designated rivers", mandatory limits are not breached.

4.4.2 River Aire

Samples were collected using EPICs at three sites on the Aire, at Armley, Thwaite Mill and Allerton Bywater. Discussion is confined here to Armley, which in general shows highest concentrations of determinands, with downstream concentrations at the other sites reduced by dispersion.

Figures 4.6 and 4.7 show sediment and total zinc concentrations at Armley during the sampling period were particularly high during the event of 22 December compared with the event of 6-8 January, although the maximum flow in each was comparable. This may be a flush effect, but may also be caused by the different distribution of rainfall over the catchment for the two events, or even some local contamination source present during the earlier event. Whatever its source, the difference in concentration between these two events is also characteristic of many other sediment-associated determinands.

The relationships between determinand concentrations and time, flow and sediment concentration over the five events sampled have been examined. Unlike the samples from the representative catchments, these include dissolved as well as total concentrations of ICPMS-determined elements.

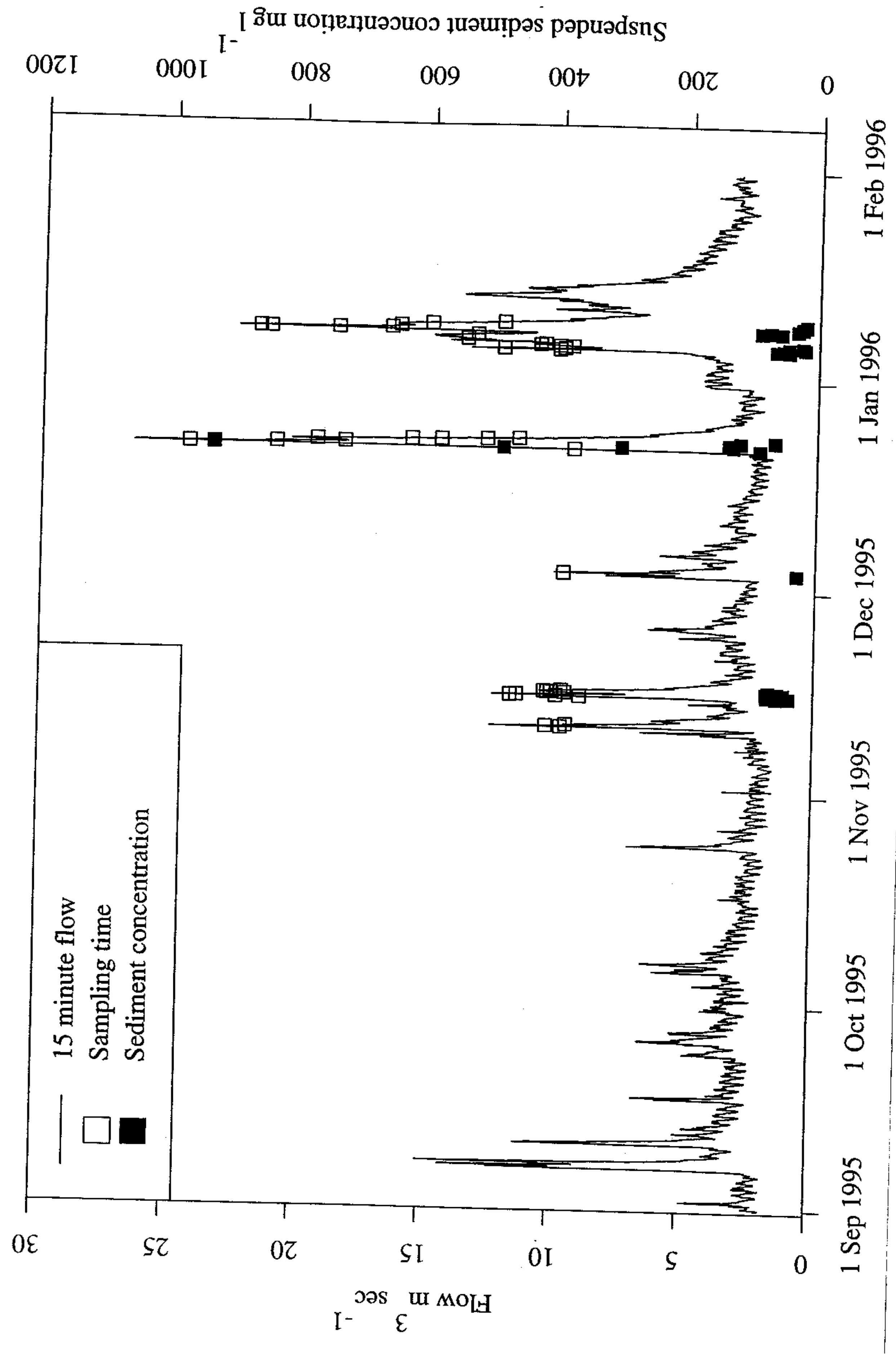

Figure 4.6 **Suspended sediment concentration and flow, Aire at Armley**

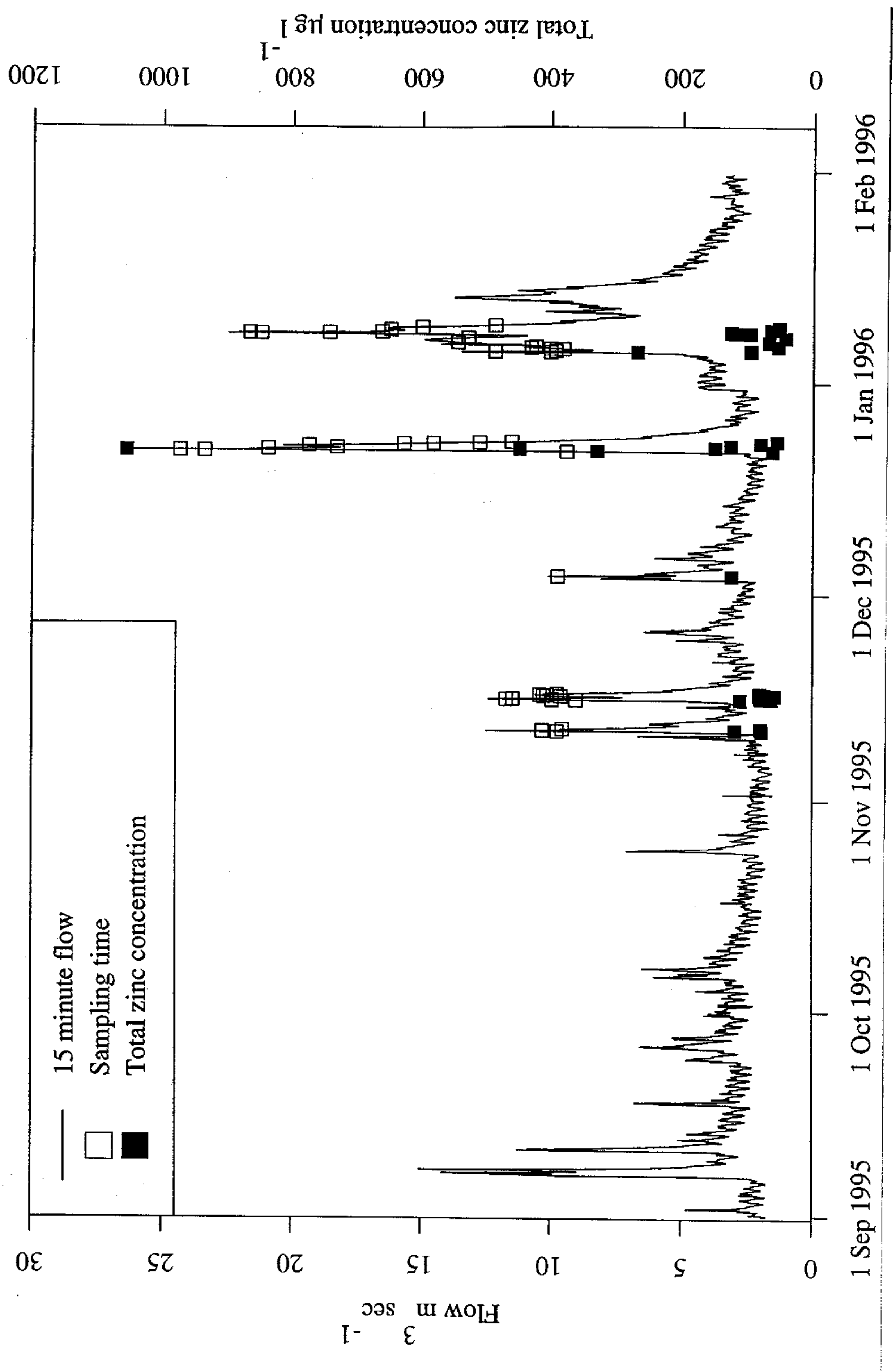

Figure 4.7 **Total zinc concentration and flow, Aire at Armley**

For the major ions Na, Mg, Ca, Cl and SO_4 there is no simple reduction of concentration with flow since concentrations during the peak of the event of December 22 were uniformly high. Similarly, the dissolved concentrations of ICPMS-determined elements were high during this event. Close inspection of the data shows that high dissolved concentrations are associated with the early part of the event of 22 December. These high concentrations remained through the peak of the event, but then declined during the recession period. Similarly, in the event of 8 January, the highest concentrations of many solutes (where data are available) were highest in the early part of the event.

The total concentrations of ICPMS-determinands show a very close relationship with suspended sediment concentration. In many cases dissolved concentrations of these elements are also apparently related to sediment concentration. It is believed that this may be an artifact of the sampling procedure, and that some of the material analysed is particulate material which has remained in samples following filtration, partly because some particles have a diameter less than 0.45mm. However, some metals showed raised concentrations during the event of November 11, when flow was low. Although sediment was not measured for this event, it is inferred that concentrations were low. If this was the case this would provide evidence of a flush of soluble metals during this event.

The relationship between total metal concentration and suspended sediment concentration is in many cases sufficiently good for an estimate of the metal concentration on sediment to be calculated. Estimates based on regression equations are given in Table 4.2

Table 4 2 Approximate concentration of metals on sediment in the Aire

Determinand	Mn	Fe	Al	Cr	Ni	Co	Cu	Zn	As	Cd	U
Concentration in sediment (mg g^{-1})	2.0	20.0	10.0	0.1	0.1	0.01	0.25	1.0	0.01	0.003	0.002

Figures 4.8a, 4.8b and 4.8c show a comparison between flow and concentration on the Aire over the period 1985-92 and the post-drought period November 1995 to January 1996. Note here that the flows for the historic period are mean daily values while the more recent flows are 15 minute. Also, the historic water quality measurements were made at Kirkstall Bridge, 2 km upstream of Armley under the NRA routine monitoring scheme. Local differences in the river configuration may mean that sediment concentration tends to be consistently different between the two sites under particular flow conditions. However, sediment concentrations up to 500 mg l^{-1} were recorded at Thwaite Mill on 22 December, a figure which is consistent with the higher values at Armley. Historic measured sediment concentrations at Fleet Weir, downstream of both Armley and Thwaite Mill are similar to those measured at Kirkstall Bridge. Despite difficulties in comparing sites, it is therefore likely that the values recorded on December 22 gave a good general indication of sediment concentrations in the Aire in the Leeds area during the event. These were well outside the measured historic range. Total concentrations of sediment-associated metals were also outside their previously recorded range. Concentrations of some other determinands were outside the historic range for a given flow condition for this event. It is also clear that the maximum flow on December 22 was nowhere near the extreme of previously measured daily averages. This was not a major flood.

One consequence of the high sediment concentration on December 22 is that the total Zn concentration exceeded the EC limit for designated Salmonid and Cyprinid waters for the water hardness of the Aire measured as mg l^{-1} $CaCO_3$ (around 150). All measured concentrations in the historic period were below both limits. This is an indication firstly that routine sampling may fail to detect short-term water quality extremes which may be biologically significant, and secondly that flush events at the end of droughts may produce such extremes.

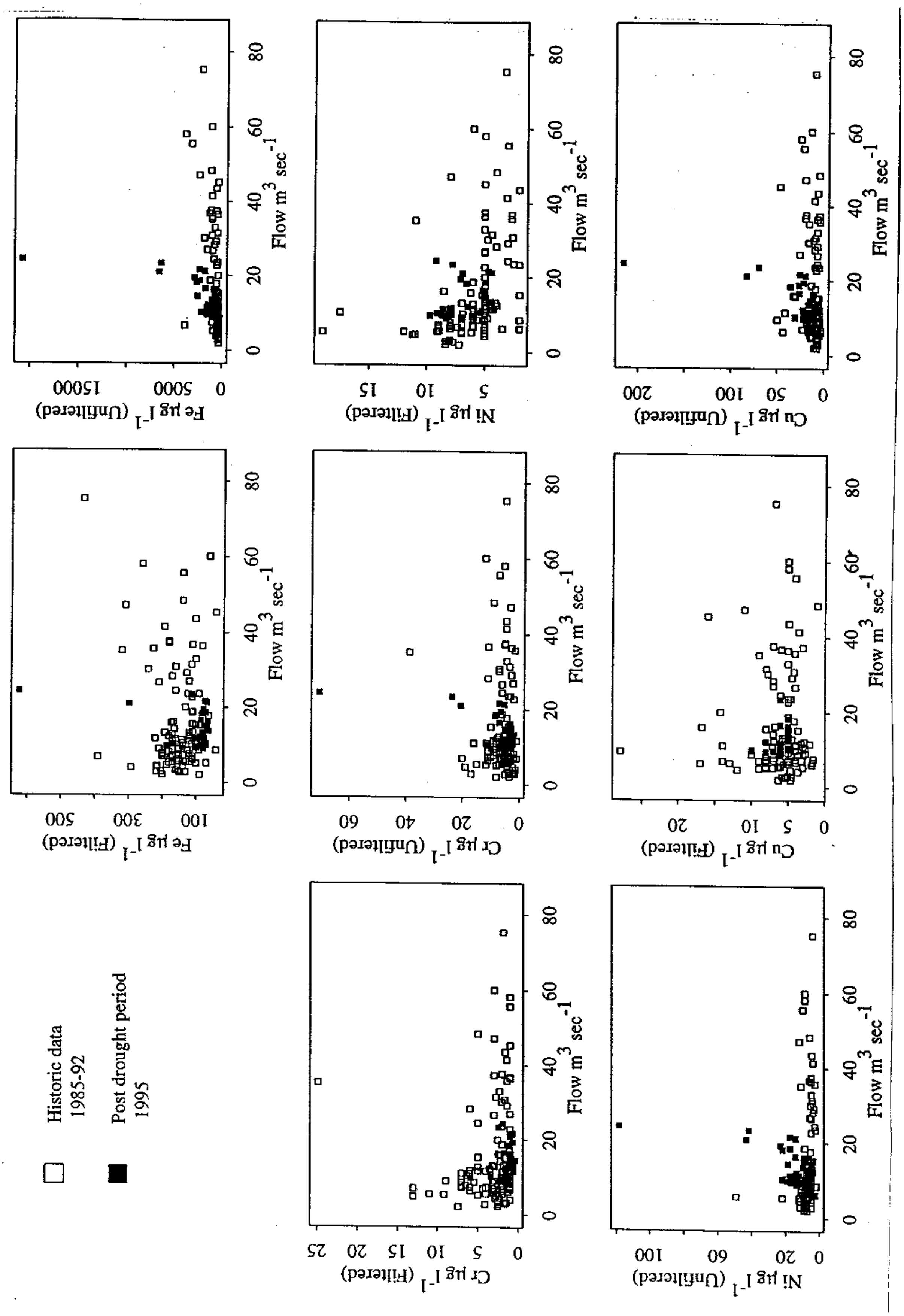

Figure 4.8a Aire - historic NRA and 1995 EPIC concentrations

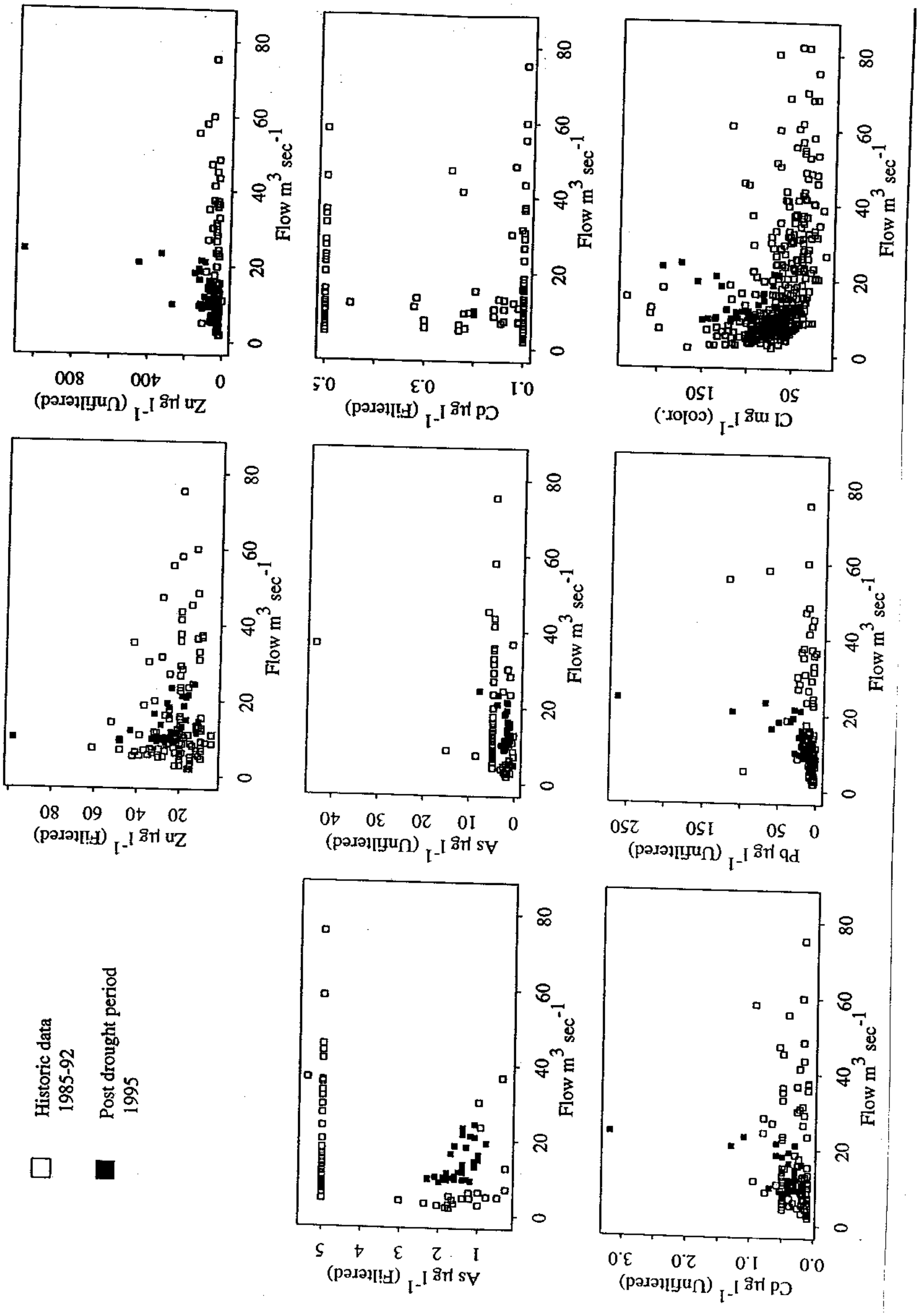

Figure 4.8b Aire - historic NRA and 1995 EPIC concentrations

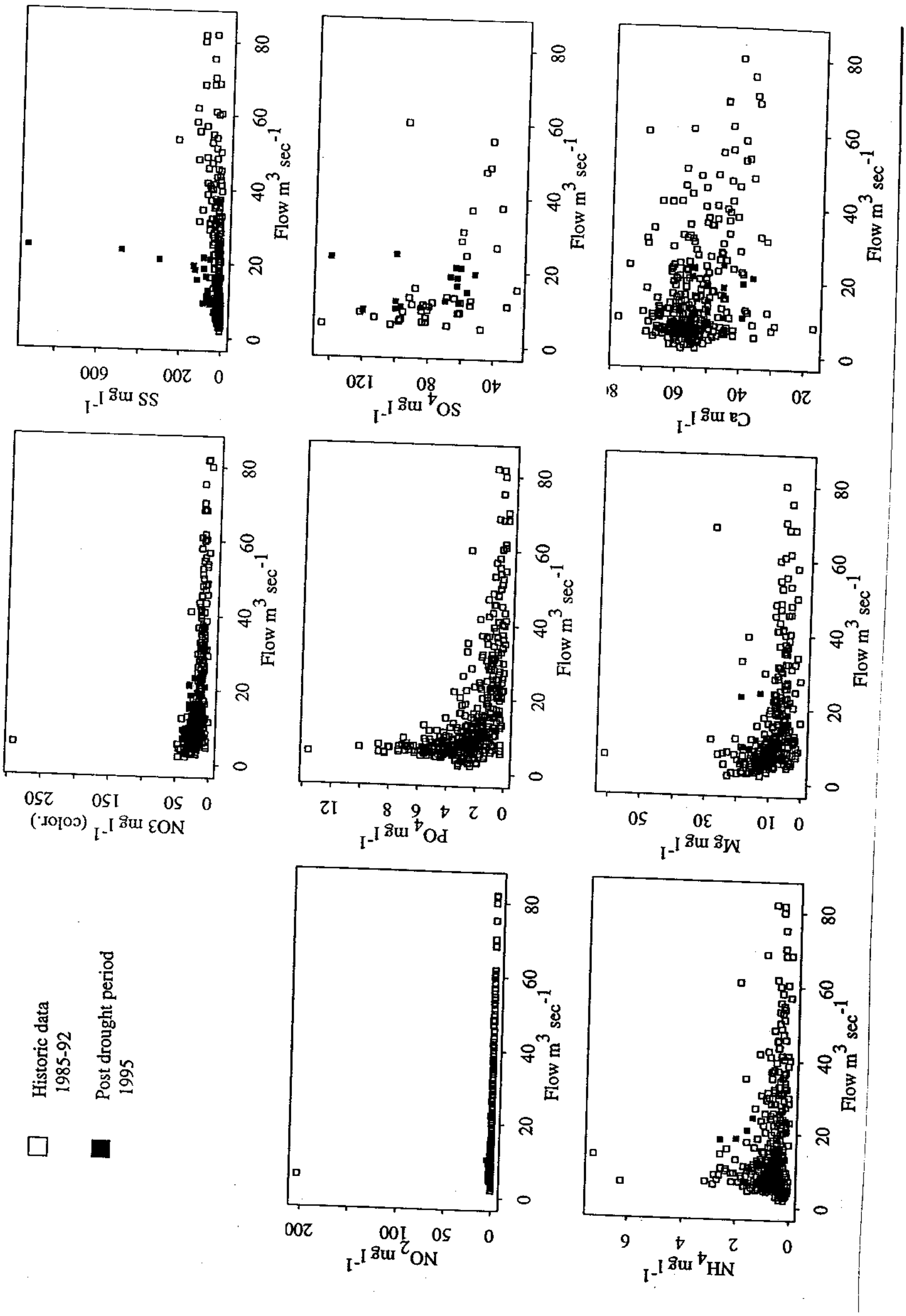

Figure 4.8c Aire - historic NRA and 1995 EPIC concentrations

5. CONCLUSIONS

The 1995 drought presented a major opportunity to monitor the release of nutrients and pollutants to surface waters during the following drought break. The observations indicate a range of complex responses in lowland and upland rivers in England and Wales. These responses have been compared with longer term scientific studies and EA archives. The data collected and statistical analyses both for the upland and lowland studies will form valuable baseline data for comparative study of the impacts of future drought-break events upon river water quality in England and Wales. In summary, the general conclusions from the upland and lowland studies are given below:

5.1 The 1995 drought in perspective

Chapter 2 described the hydroclimatological background to the 1995 drought in some detail. In summary, the ratio of winter (October to March) to summer rainfall (April to September) for Great Britain increased from about unity (i.e. similar rainfall amounts in summer and winter) in 1965 to about 1.6 in the 1990s (see Fig. 2.5). Similar increases in the seasonality of rainfall have been observed at widely-spaced maritime sites in north-western Europe, e.g. Quimper (north-western France) and Bergen (Norway). A broad feature of recent climate in the region to the end of 1995 is that winter rainfall increased in parts of Scotland, while summer rainfall decreased in many areas further south in the UK. For England and Wales as a whole, recent winters have tended to be warm and wet (relative to the long-term averages since about the mid-17th and mid-18th centuries respectively) but recent summers have exhibited extraordinary characteristics. Between 1975 and 1995 (inclusive) 15 out of the 21 summers were relatively warm in England and Wales, and 10 were relatively warm *and* dry (see Fig. 2.8). On the basis of the long-term averages, only about 5 (one quarter) of these summers would be expected to have been relatively warm and dry. The summers of 1976 and 1995 were extreme and plot very closely together in Fig. 2.8.

In some areas river networks contracted during recent summers as the headwaters of streams dried up, and lower than (long-term) average summer river flows have been widely observed. Hydrological droughts have, therefore, been common in recent years. In 1995 there were severe problems of water supply in some areas due to depleted surface reservoir stocks. We have, therefore, witnessed a period (1975 to 1995) during which riverine ecological systems in England and Wales were more likely than before to experience stress in the summer months.

Chapter 2 also outlined seasonal relationships between river flow and selected aspects of water quality for a lowland river site in England, the Yorkshire Ouse at Naburn Weir, (see Fig 2.14). The flushing of materials during the first period of high flows after a drought is a well-known phenomenon, and large amounts of nitrate-N and suspended solids were probably carried by the Ouse during the partial drought-break in 1995. However, the irregular sampling at relatively low frequencies common in routine monitoring schemes for lowland sites (e.g. the HMS) are not suitable for accurate determination of monthly river mass loads. The more detailed information on drought-break river responses in a range of catchments collated in this report provide an overview of the riverine hydrochemical effects of the 1995 drought and its partial break in the winter of 1995/96.

5.2 Drought and Droughtbreak response in upland catchments

A number of common features have emerged in relation to the hydrochemical response of upland streams to drought and drought break conditions. A general characteristic of prolonged low flow conditions in all the upland streams studied was an increase in pH, alkalinity and in the concentrations of divalent base cations, predominantly calcium. Presumably, this reflected the increasing contribution of groundwater to the streams and a decline in the input of more acidic soil drainage water. At drought break, chemical conditions in the streams changed rapidly, with a sharp decline in pH, alkalinity and calcium and an increase in the concentrations of metals such as manganese and aluminium. This change in chemistry can be attributed to a switch in the hydrological flowpaths operating within the catchment with increased contributions of water from surface soil horizons as the catchments ‘wet up’.

Within this generalised pattern, there were a number detailed responses for individual solutes which highlight potentially important processes which should be the subject of further study. The sulphate and possibly to a lesser extent nitrate flush at drought break appeared to be determined by the amount of peat in the catchment. However, the exact nature of the biogeochemical processes controlling sulphate release are uncertain, although results from the peatland manipulation experiment suggest that drought conditions exacerbate the natural cycle of sulphate concentrations in peat waters. The drought break responses reported here also suggest that soil moisture conditions during the drought and immediately prior to drought break are an important factor conditioning the behaviour of solutes for which microbial and redox processes are important. Soil moisture conditions are a key variable in the mineralisation of organic matter and the conversion of ammonium to nitrate via nitrification. They also largely determine the redox environment within the soil and hence the mobility of manganese and associated trace metals. At the catchment scale, the vegetation cover, physical characteristics and spatial distribution of soils will be important factors controlling soil moisture conditions. The results suggest that upland areas characterised by a predominance of organic-rich soils (peats and mineral soils with a thick organic surface layer) and soils with impeded drainage (gleys) will be the most vulnerable to drought break events. Such areas include the Pennines and large parts of north and mid Wales. There is a requirement therefore that future research should focus on the role of such soils in determining stream chemical responses to drought and drought break conditions.

The drought break data indicate that trace metal mobility was enhanced in the more extensively afforested catchments. This may be an artefact of the sampling strategies, or may reflect genuine differences between the systems. For example, there will have been greater dry deposition of trace metals to the taller, rougher forest canopy compared to the short grassland vegetation providing a potentially highly mobile pool of metals to be washed from the canopy with the onset of rainfall. However the relative importance of this process versus soil mediated effects is unknown.

In addition to the nitrate flush at drought break, long-term data from a number of sites have shown that the nitrate response to drought becomes evident over subsequent years. This gives rise to a series of medium term (3-5 year duration) fluctuations which may confound the identification of longer-term trends, for example relating to the onset of nitrogen saturation of the terrestrial ecosystem due to increased atmospheric nitrogen deposition. Increased nitrate leaching and the loss of the regular annual cycle in streamwater nitrate concentrations have both been proposed as symptoms of nitrogen saturation. Thus data from short to medium term sampling programmes could be misinterpreted as indicative of atmospheric pollution effects whereas the trends actually reflect climatically induced perturbations. As with sulphate release, a number of mechanisms and hypotheses can be suggested to account for the observations. There is however a need to quantify these processes so that they can be represented in catchment scale hydrochemical models.

An intriguing feature of the data from many sites was the recording of extremes in concentration during the 1995 drought and drought break periods. For example, at Bannisdale Beck the highest and lowest pH values were observed since sampling began in 1993 and the largest sulphate concentration in 15 years was observed in the Cyff catchment at Plynlimon. The recording of such extremes is partly coincidence and partly reflects the more intensive sampling which surrounded the drought break period at some of the sites. In both cases, these observations highlight the dilemma of maintaining long-term, relatively low sampling frequency data sets to identify trends whilst at the same time requiring high temporal resolution sampling in order to characterise extreme events. This drought break study has demonstrated the need for consistent funding to maintain well established long-term sites supplemented by a co-ordinated programme of selective event sampling.

With climate change, upland water resources could assume a greater importance for water supply in the UK. As a consequence, effective and accessible models would be required in order to inform and direct policy in relation to potential upland water quality problems associated with extremes of flow and to identify how these interface with catchment landuse and atmospheric pollution. Several processes have been alluded to in this study in order to account for the drought break response of a number of solutes. However, many of these are not sufficiently well understood to be incorporated into predictive hydrochemical models. Thus there is an urgent need for research to focus on these processes so that models can be adequately parameterised in the future.

5.3 Conclusions from Humber rivers droughtbreak events

Samples collected at the LOIS representative catchments and on the Aire during periods of high flow during the post-drought period showed increased concentrations of sediment and associated metals. Comparison with historic data suggests these concentrations were not exceptional in most cases, but that they were outside the historic measured range for many determinands during the event of 22 December. It is also apparent that none of the events captured during the post-drought period was a major flood. High measured concentrations of determinands cannot be identified with certainty as due to flushing, owing to possible confounding with spatially varying rainfall or a local transient point source. In addition, the historic sampling scheme was not designed to capture short-term event data and many events of the type observed on 22 December 1995 may previously have gone undetected.

The total zinc concentrations associated with the event of 22 December exceeded the mandatory upper limit for zinc for designated Salmonid and Cyprinid waters for a short time.

If rates of sediment accumulation during droughts could be estimated it might be possible to predict likely concentrations of determinands under a variety of drought-breaking rainfall scenarios for catchments with particular land use and other characteristics. While the data available from the representative catchments and the Aire confirm that the transport of metals is largely associated with the mobilisation of sediment, it is not possible to identify and quantify a separate flushing effect, or make generalisations about flushing at other locations or future years. A comprehensive study of flushing effects would require event monitoring through a period of several years.

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