NRA Wales 162

NATIONAL RIVERS AUTHORITY

AWDURDOD AFONYDD CENEDLAETHOL

WELSH REGION

RHANBARTH CYMRU

AAC

NRA

Guardians of the Water Environment

Diogelwyr Amgylchedd Dŵr

EA WATER QUALITY

LLYN BRIANNE ACID WATERS PROJECT

Final Report, May 1992

Participant organizations:

National Rivers Authority

Institute of Terrestrial Ecology

Institute of Hydrology

University of Wales College of Cardiff

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EXECUTIVE SUMMARY

1. This report covers Phase II of the Llyn Brianne Acid Waters Project, October 1987 to March 1991. The project is a multidisciplinary investigation into the effects of atmospheric deposition and land management on surface water acidification.

2. At the moderately high altitude of the study area (c.300-500 m) occult deposition was important. Solute concentrations in cloudwater were up to 11x those in bulk precipitation. The cloudwater ions were dominated by sea-salts, though 45% of the sulphate was of non-marine origin, compared to 69% in bulk precipitation. Data on cloudwaters are important in revising estimates of deposition.

3. Soil hydrology is an important influence on stream acidity and aluminium concentrations. Field measurement and hydrochemical modelling showed that flow pathways were dependent on soil type and land use. Forestry may cause a more flashy storm flow response with a more variable contribution to stream flow of groundwaters which are usually well-buffered in comparison to soil waters in surface horizons. Storm runoff in a forested catchment was dominated by highly acidic flow along drainage ditches which may have mobilized aluminium from the ditch surfaces.

4. There were some significant trends in stream chemistry in unmanipulated catchments. Base cation concentrations, alkalinity and pH increased at most sites, apart from the catchment with a conifer plantation approaching canopy closure. Stream aluminium concentrations increased only in this juvenile forest catchment and in a mature plantation. This provided further evidence of the effect of conifer plantations in enhancing acidification.

5. Catchment manipulations demonstrated the effectiveness of source area liming in buffering stream acidity and reducing aluminium concentrations. The results indicated that a catchment could be treated by the application of around 15 - 20 t ha^{-1} of powdered limestone to c. 5% of its area. Treatments have been studied for up to three years and the duration of treatment effectiveness is not yet established. The impacts of liming on wetland ecosystems are the subject of current research.

6. In situ studies with different life stages of brown trout showed the improvement of fish survival in limed streams. Variations in resident trout populations were consistent with this benefit, including a significant increase in juvenile densities in the moorland stream which was source-area limed. Changes in macroinvertebrate and macrofloral communities have so far been limited, but have been consistent with model predictions for circumneutral chemistry.

7. Models were developed to predict macroinvertebrate faunas and trout densities from stream chemistry, and vice versa. Mean values of chemical parameters were shown to be adequate predictors, measures of episodicity giving only small improvements in performance. Indicator species, particularly macroinvertebrates, were reasonably accurate measures of stream acidity and the presence of other organisms. These indicators offer a potentially cost-effective approach to the biological monitoring of acid waters.

8. A hydrochemical model (MAGIC) was applied to streams across the Welsh region. The simulations suggested that 40% of streams and lakes have declined in pH by > 0.5 units since the early 19th century. For the future, a 30-50% reduction in 1984 rates of acidic deposition would prevent further acidification, while reductions of 60-90% would lead to a progressive recovery. Biological simulations suggested that sensitive species of stream invertebrates, salmonid fish and dippers have declined as surface waters acidified. Recovery of these organisms would also require 60-90% reductions in acid deposition.

9. In conclusion, reductions of greater than c.60% in acidic deposition would cause reductions in the acidification of surface waters in Wales. This response will be modified according to catchment land use. Conifer afforestation will tend to counteract the effects of decreasing acidic inputs, while liming catchments can ameliorate stream acidity.

KEY WORDS

Acidification, afforestation, biology, chemistry, hydrology, liming, modelling, soil, water.

1. Introduction

The second phase of the Llyn Brianne Project was completed on 31 March 1991. The book, 'Acid Waters in Wales' (edited by Edwards, Gee & Stoner, 1990), included summaries of the project findings up to the start of 1989. Since then, important progress has been made in several areas of the work and is summarized in this final report. Scientific publications have continued to be a major output from the project, and have made important contributions to the understanding of acidification, land management and environmental change. This information is helping to guide policy on the control of acidifying emissions, and on catchment management in sensitive areas.

Progress since 1989 has been based mainly on continued monitoring of experimental treatments (Table 1.1, Figure 1.1), data analysis and model development. The installation of a flume on stream LI1 has enhanced the reliability of flow data. In addition, the operation of a cloudwater collector has refined information on atmospheric deposition to the catchments.

The catchment liming treatments have been studied for up to 3.5 years to the end of the project second phase, and will continue to be assessed through the NRA R&D programme until 1994 at least. These studies are essential in determining the nature and longevity of the effects of liming. Plot liming experiments at the Upper Cothi site are providing more information on the effects of lime dosing rates and type of limestone used. Monitoring the effects of liming is also in the DoE AQ Research Programme for 1992-93.

The application of hydrochemical and biological models developed in the Brianne project, has allowed an assessment of the possible effects of future changes in sulphate deposition on surface waters in the Welsh region. This approach is important in providing guidance on the derivation of critical loads and emissions controls and in determining strategies for managing the impact of acidification. Refining these models has therefore been a central task in the second phase of the project.

Table 1.1. Summary of reference and treated catchments

Catchment	Land use/ treatment	Start date	Area (ha) Total	Area (ha) Treated	Limestone (t)
CI1	Moorland	—	15	—	—
CI2	Liming moorland	6/88	59	4	80
CI3	Moorland, agric. improvement	6/86	84	20	200
CI4	Moorland, forestry ploughing	10/86	49	8	—
CI5	Moorland, liming	9/87	34	33	300
CI6	Moorland	—	72	—	—
UC4	Moorland	—	237	—	—
LI1	Conifer forest, planted c.1959	—	253	—	—
LI2	Bankside clearance and liming, forest	9/86	105	6	60
LI3	Pelletized liming	11/88	64	9	105
LI4	Liming, forest	11/87 12/87	33 33	4 0.8	100 20
LI5	Moorland	—	66	—	—
LI6	Moorland	—	68	—	—
LI7	Moorland	—	73	—	—
LI8	Conifer forest, planted 1971-77	—	66	—	—
GI1	Oak woodland	—	18	—	—

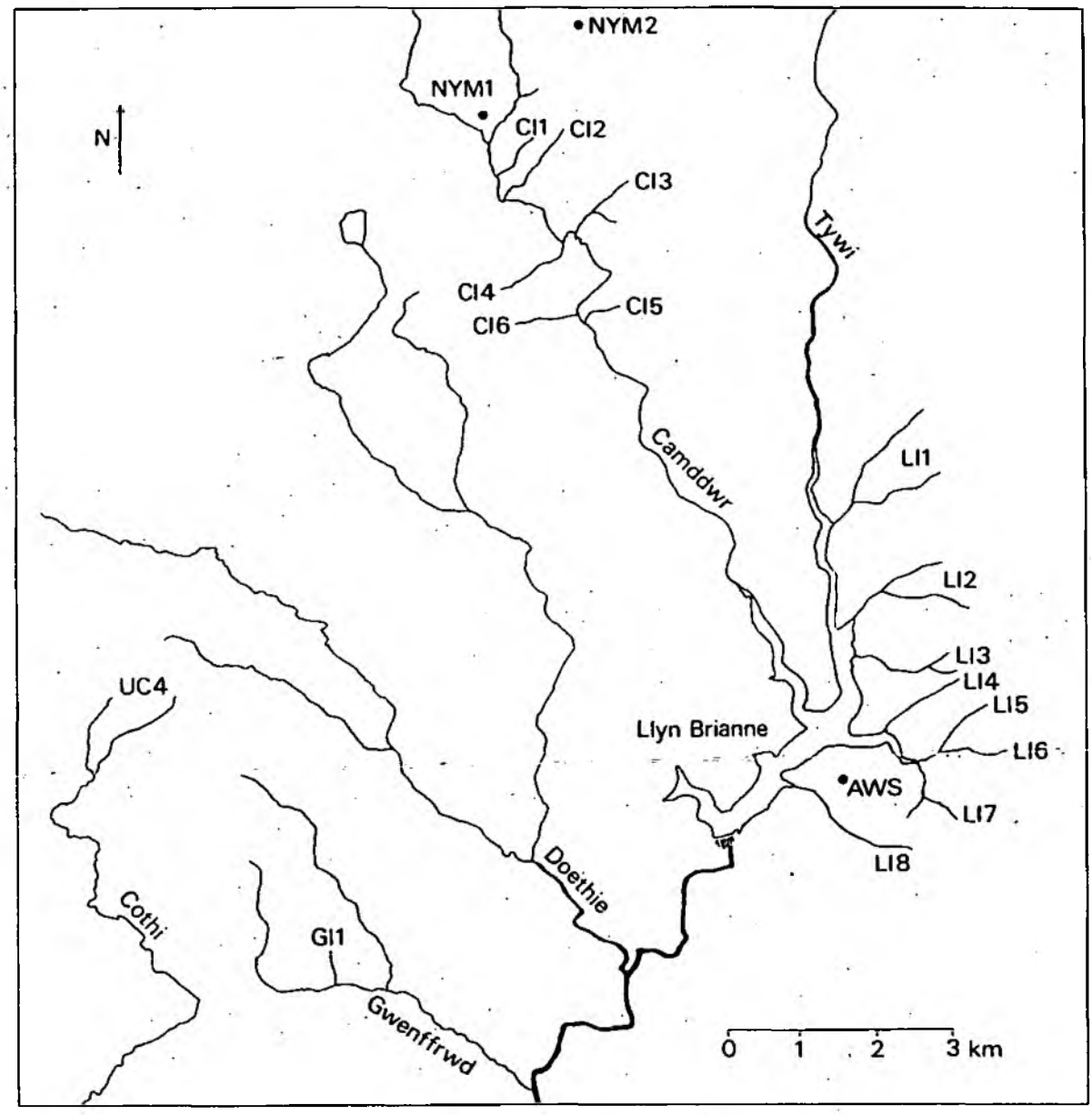

Figure 1.1 Location of study catchments (Llyn Brianne is at 3°45′W 52°8′N, NGR SN8050). AWS is the automatic weather station at Trawsnant. NYM1 and NYM2 are, respectively, the daily rainfall and cloud water collectors at Nant y Maen.

2. DEPOSITION

2.1 Bulk deposition

Bulk deposition has been collected at the Automatic Weather Station at Trawsnant (AWS, Figure 1.1) on a weekly basis during the project, and at Nant y Maen (NYM1) on a daily basis since August 1987. For comparability with data from other sites in the UK monitoring network, the weekly data summarized here are those from the Warren Spring collector, available from 1986 onwards.

Mean deposition of hydrogen ions at the AWS from 1986 to 1990 was 0.027 g m^{-2} yr^{-1} (Figure 2.1). Deposition of sulphate-sulphur was 0.91 g m^{-2} yr^{-1}, of which 0.63 g m^{-2} yr^{-1} was of non-marine origin. The rates for nitrate-nitrogen and ammonium nitrogen were 0.28 and 0.30 g m^{-2} yr^{-1} respectively. These values were all typical of many parts of Wales which receive low rates of acid deposition by comparison to industrialized areas of the UK, though higher than regions with lower rainfall or which are more remote. As there are only five years' data from Llyn Brianne it is not surprizing that no trends in deposition are apparent.

The daily data from Nant y Maen allow rainfall events to be described with good resolution and also to be related to wind direction. Whilst over 70% of rainfall came from the south and south-west, 71% of the hydrogen ion load, 55% of excess sulphate and 70% of total oxidized nitrogen could be ascribed to easterly wind sectors (Figure 2.2). This pattern is consistent with modelling studies of air pollution, which indicate that major contributions to sulphur and nitrogen deposition in mid-Wales come from the industrialized English midlands and northern parts of continental Europe.

2.2 Cloudwater

The chemical composition of cloud water was monitored at a hilltop site (520m above sea level) above Nant y Maen Farm at the northern end of the Llyn Brianne catchments (NYM2, Figure 1.1). Cloud water was sampled using a continuously exposed passive collector fitted with a plastic covered lid designed to exclude rain drops larger than 0.5 mm in diameter at windspeeds less than 5 m s^{-1} (Milne et al 1988). Cloud water and bulk precipitation samples were collected weekly for chemical analysis. The extent to which cloud water samples were contaminated by rain was assessed using data from two tipping bucket rainguages, one of which was connected to a second lidded cloud water collector, in combination with windspeed data from an automatic weather station (Milne et al 1988, Reynolds 1991).

Ions derived from sea spray dominate the chemistry of the cloud water accounting for approximately 77% of the mean total ion sum (Tables 2.1 and 2.2). The sodium to chloride ratio (0.821) is lower than the theoretical ratio for seawater (0.853), which may be due to chloride in the form of hydrochloric acid from pollution sources.

Excess sulphate, calculated using the theoretical seawater ratio for sodium to sulphate, comprises approximately 45% of the total sulphate in the cloud water (Table 2.2). Although a marine component to the excess sulphur fraction, for example from biogenic dimethyl sulphide emissions (Turner and Liss 1985), cannot be ignored, the results suggest that the pollutant content of cloud water may be quite large. This was qualitatively observed in cloudwater samples which were frequently black or grey in colour due to a suspension of fine particulates.

The range in cloud water solute concentrations is large but not exceptional when compared with other published data (e.g. Aneja et al 1990). A part of this variation relates to the origin of the solutes in cloud water which is determined by wind direction and air mass trajectory prior

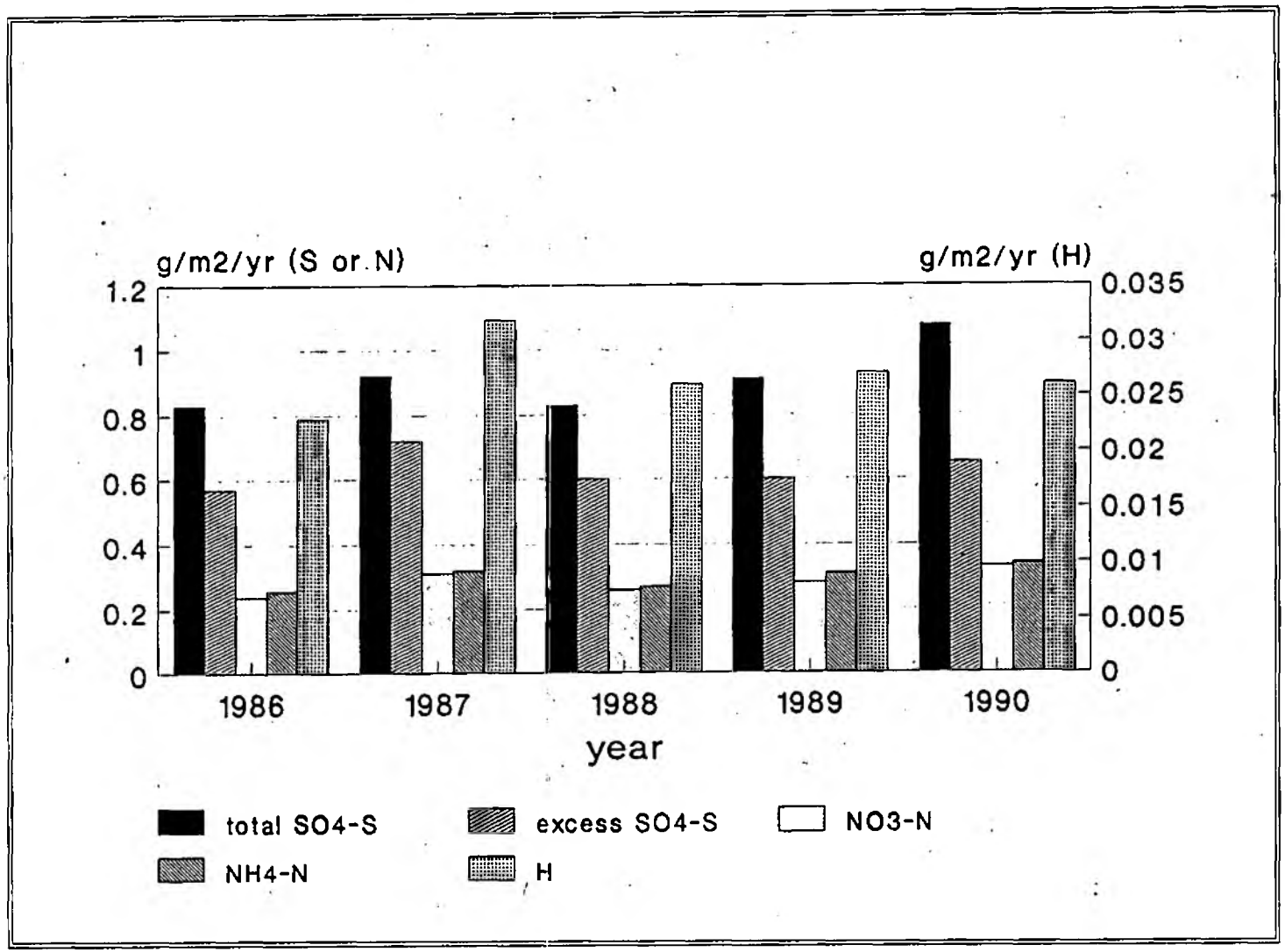

Figure 2.1 Annual bulk deposition of selected ions at the Llyn Brianne automatic weather station site, 1986-1990. Derived from data supplied by the Warren Spring Laboratory.

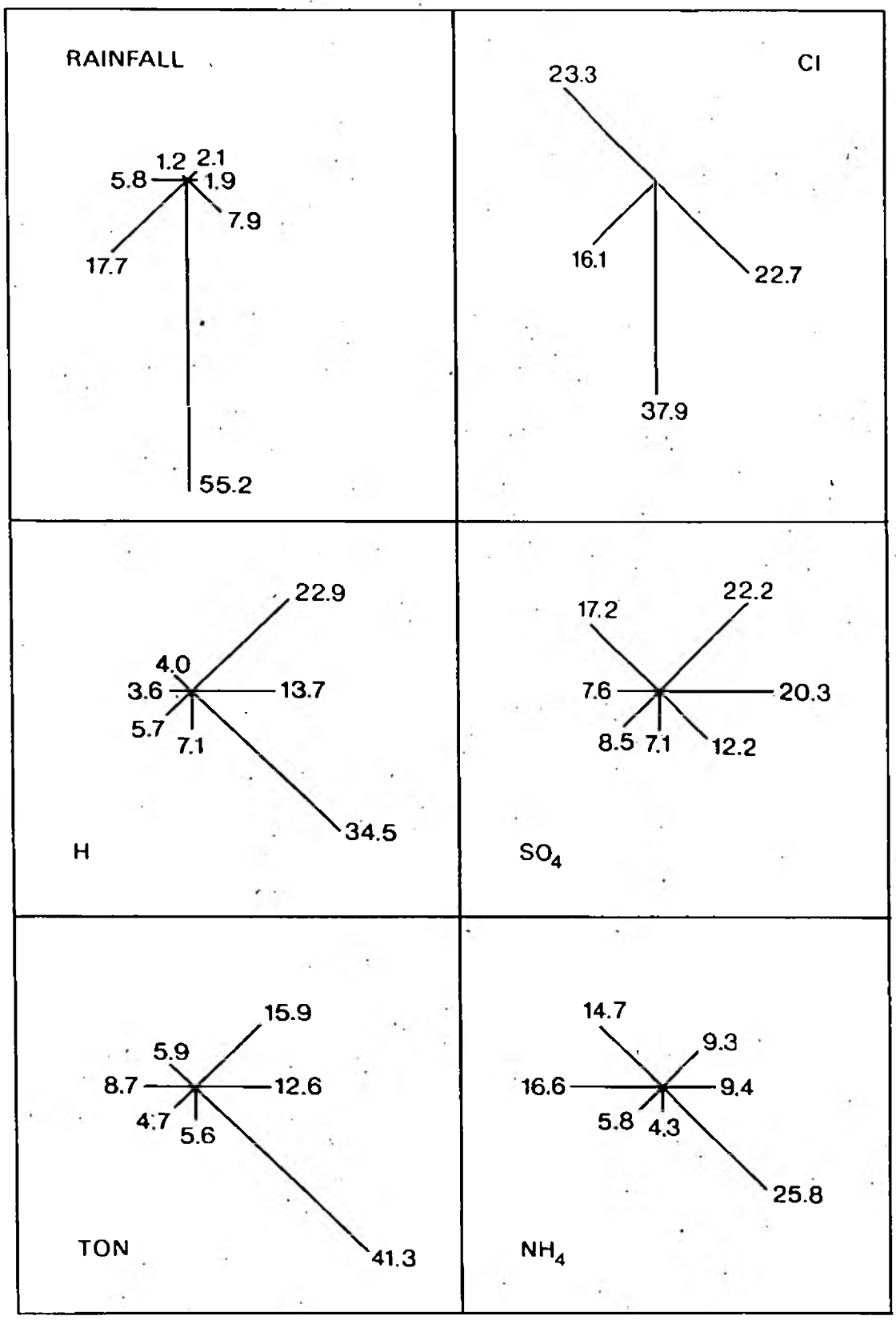

Figure 2.2 Percentages of rainfall and ion loadings associated with each wind sector at Nant y Maen, based on daily data 1.8.87 - 31.7.90.

to reaching Nant y Maen (Section 2.1). Ionic concentrations in cloud water are also related to cloud liquid water content which is strongly dependent on altitude. The largest concentrations occur at cloud base and decrease with height as liquid water content increases causing dilution of solutes (Fowler et al 1988).

Although solute concentrations in cloud water are large relative to those in bulk precipitation (Tables 2.1 and 2.2), they are not exceptional when compared to literature values. However, the degree of enrichment in cloud water with respect to precipitation varies with solute and is generally much higher than at other sites. This may be attributed to a number of factors. High windspeeds at Nant y Maen will lead to aerodynamic sorting of the raindrop size spectrum causing many of the smaller drops to be carried over or around the bulk precipitation collector. As the chemical composition of rain varies with dropsize (smaller drops having a higher concentration), there will be a systematic underestimate of major ion concentrations in bulk precipitation. With continuously exposed collectors, dry and particulate deposition will occur between as well as during cloud and rain events. The cloud and precipitation gauges have very different aerodynamic and surface characteristics. Different amounts of gaseous and particulate material will be deposited on the gauges to be subsequently washed into the rain or cloud water sample. The extent of this 'contamination' is unknown, and will vary with the type of material deposited and the characteristics of the surface. In particular, the cloud water collector probably captures more salt particles than the bulk precipitation collector, contributing to the large enrichment of seasalt-derived ions in cloud water samples. A further consideration with passive gauges is the enhancement of solute concentrations by evaporation from the collector strings. This has not been evaluated for this study, but work in Scotland with similar collectors suggests that enhancement ratios ranging between 1.1 and 1.5 can be expected (Milne et al 1988).

Despite having lids on the cloud water collectors, they are subject to "contamination" by wind-driven rain. Using the combination of measurements described earlier, it was possible to identify five weeks during which this contamination was relatively small (< 30%) and to estimate cloud liquid water content and sulphate and nitrate aerosol concentrations (Reynolds 1991). The mean cloud liquid water content for the five weeks was 0.18 g m^{-3} which is within the expected range of 0.1 - 0.4 g m^{-3} for orographic cloud in upland Britain (Fowler D., personal communication 1991) and close to measurements reported by Gallagher et al (1988) for Great Dun Fell. Estimates of aerosol sulphate concentration ranged between 0.6 and 2.6 μg S m^{-3} and are consistent with measurements made elsewhere in the UK (UKRGAR 1990). Aerosol nitrate concentrations ranged between 0.7 and 1.2 μg N m^{-3}. Rather fewer data are available for comparison, but values between 0.5 and 1.0 μg N m^{-3} are not untypical in the UK (UKRGAR 1987, Fowler, D. personal communication 1991).

The original solute data used in the estimates of aerosol nitrate and sulphate concentrations are typical of the full range of cloud water data. Taken together with the estimates of cloud liquid water content, these calculations give credence to the data gathered using the lidded passive collectors. However, it is apparent that the cloud water samples frequently contained rainwater. Additionally, it is probable that sea salt particles were deposited on the cloud gauge leading to highly enriched samples. Thus caution must be exercised in any extensive use or further interpretation of these data.

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Table 2.1 Cation concentrations ($\mu eq\ l^{-1}$) and pH of bulk precipitation and cloudwater showing enrichment (to nearest 0.5) of cloudwater solutes relative to bulk precipitation at Nant y Maen. Values for bulk precipitation are rainfall weighted means. For cloudwater the mean concentrations from log transformed data are presented. Ranges in concentration and enrichment are shown in brackets.

	Bulk Precipitation	Cloudwater	Enrichment	No. of samples
pH	4.96 (4.21 — 6.80)	4.47 (3.71 — 6.50)	—	30
H^+	11 (<1 — 62)	34 (<1 — 195)	3.5 (<1 — 126)	30
Na^+	94 (18 — 289)	1032 (104 — 3484)	11 (1 — 35)	18
K^+	3 (<1 — 20)	20 (<1 — 84)	6.5 (<3 — 14)	18
Ca^{2+}	15 (3 — 39)	72 (32 — 763)	5 (2 — 25)	18
Mg^{2+}	23 (5 — 70)	250 (36 — 1037)	11 (1 — 47)	19
NH_4^+	15 (2 — 88)	128 (<1 — 435)	8.5 (2 — 20)	19
Xs Ca^{2+}	11 (2 — 34)	37 (10 — 128)	3.5 (<1 — 10)	17

Table 2.2 Anion ($\mu eq\ l^{-1}$) and DOC ($mg\ l^{-1}$) concentrations in bulk precipitation and cloudwater showing enrichment (to nearest 0.5) of cloudwater solutes relative to bulk precipitation at Nant y Maen. Values for bulk precipitation are rainfall weighted means. For cloudwater the mean concentrations from log transformed data are presented. Ranges in concentration and enrichment are shown in brackets.

	Bulk Precipitation	Cloudwater	Enrichment	No. of samples
NO_3^-	13 (5 — 118)	95 (21 — 436)	7.5 (4 — 16)	8
SO_4^{2-}	38 (22 — 100)	281 (196 — 856)	7.5 (3.5 — 15)	17
Cl^-	123 (28 — 368)	1334 (28 — 4415)	11 (3 — 42)	19
XS SO_4^{2-}	26 (10 — 62)	163 (20 — 578)	6.5 (3 — 12)	15
DOC	0.6 (<0.1 — 4.1)	1.5 (0.5 — 7.4)	2.5 (<1 — 10.5)	29

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3. CLIMATE AND HYDROLOGY

3.1 Introduction

The principal objectives of the latter part of the project were:

- to continue to provide climatic data for the project

- to compile comprehensive rainfall series (monthly, daily, hourly) at two key raingauge sites at AWS Trawsnant and Maesglas/Camddwr

- to develop a method for estimating rainfall inputs for each sub-catchment from rainfall data at the two key stations

- to establish the relationship between altitude and rainfall in the Llyn Brianne area

- to maintain, update and where possible improve stage discharge ratings for the sub-catchment streams

The principal findings are reported here, but detailed results are given in Walsh and Boakes (1991a, 1991b, 1991c).

3.2 Climate and Rainfall at AWS Trawsnant and Maesglas/Camddwr

Climatic records at the Automatic Weather Station at Trawsnant (altitude 372m) have now been collected on a continuous basis since March 1985. The completeness of the records has improved since the switch from cassette recorders to a data logger system during 1988 and from heavy duty batteries to a solar power panel in May 1989, since which time there have been no gaps in the record. Hourly and daily data on rainfall, air and soil temperature, relative humidity, wind direction, wind speed, solar and net radiation, and Penman evaporation are recorded at the station. A comprehensive daily and monthly summary for the entire project period has been produced (Walsh and Boakes 1991a).

Daily and monthly rainfall series have been produced at the two key project stations at AWS Trawsnant (1985 to date) and Maesglas (mid-1986 to date). Any gaps in their record were filled by using the records at an adjacent sub-catchment tipping bucket raingauge (with adjustment to the groundlevel gauge at the key station). Monthly and annual rainfall at the two stations during the project are given in Table 3.1 (see Figure 3.1). With the exception of the wet year of 1986, annual rainfalls have varied little from year to year both at AWS Trawsnant and Maesglas. Annual rainfall was on average 212 mm higher at AWS Trawsnant (2032 mm) than at Maesglas (1820 mm) during the project period. Both stations exhibited the marked autumn/winter maximum rainfall characteristic of western Britain. The wettest individual months were November 1986 and January 1990 (both 404 mm at Trawsnant). February 1986 (10 mm), September 1986 (31 mm) and June 1988 (38 mm) were the driest months.

As streamwater acidity problems are greatest during storm runoff events, of particular note is the high frequency of rainstorms (Table 3.2). On average, rainfall occurred on 236 days per annum at AWS Trawsnant. Falls of at least 10 mm in a day, which might be expected to produce at least minor streamflow responses, occurred on 78 occasions per year on average, with most occurring in the period October - March. Major storms exceeding 25 mm in a day occurred on average 16 times per year, compared with 6 days per year at Swansea and 1 per year in South East England. December (3.5 per year) is the peak month for such events.

Table 3.1 Rainfall (mm) at AWS Trawsnant (1985-90) and Maesglas (1986-90).

AWS Trawsnant

Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec	Year
1985	105	60	133	182	108	211	162	301	75	156	137	338	1967
1986	306	10	223	134	213	75	114	225	31	216	404	370	2320
1987	62	147	222	137	84	186	98	69	167	339	159	239	1908
1988	340	140	256	83	137	38	266	188	183	160	119	110	2019
1989	176	180	278	136	51	100	48	141	115	252	170	306	1953
1990	405	366	72	78	46	139	102	89	111	227	170	223	2026
Mean	232	151	197	125	107	125	132	169	114	225	193	264	2032

Maesglas

Year	Jan	Feb	Mar	Apr	May	June	July	Aug	Sep	Oct	Nov	Dec	Year
1986								201	31	187	314	345	—
1987	77	121	201	132	83	174	97	68	152	325	157	144	1731
1988	281	112	250	56	135	33	222	167	203	149	91	102	1801
1989	138	187	225	122	43	93	53	110	92	254	155	252	1725
1990	343	288	57	77	35	123	81	96	119	206	167	217	1806
Mean	210	177	183	97	74	105	113	128	119	224	177	212	1820

Table 3.2 Mean annual frequencies of raindays, 10 mm and 25 mm daily rainfalls at AWS Trawsnant 1985-90.

Parameter	Jan	Feb	Mar	Apr	May	Jun	July	Aug	Sep	Oct	Nov	Dec	Year
Raindays	22	21	24	17	16	16	19	22	16	22	19	22	236
Days >10mm	11.8	7.8	7.0	4.7	3.8	3.7	4.7	5.8	3.8	8.5	7.7	9.0	78.3
Days >25mm	2.5	1.8	1.3	0.7	0.2	0.8	0.7	1.2	0.8	1.5	1.3	3.5	16.3

3.3 Rainfall-altitude relationships and generation of sub-catchment rainfall data

A major objective of the latter part of the project was to provide accurate rainfall data for the study sub-catchments. The approach adopted was to derive simple correction factors to transform rainfall data at the two key stations (AWS Trawsnant for the LI catchments and Maesglas for the Camddwr catchments) to sub-catchment rainfall estimates. The correction factors were based upon:

1. The difference in altitude between the mean altitude of the sub-catchment and the altitude of the key station.

2. The rate of increase in rainfall with altitude in the Llyn Brianne area.

In order to establish a relationship between rainfall and altitude in the project areas, high altitude ground-level rainfall gauges were established in 1988 and 1989 in the CI5, LI8 and LI1 catchments. The gauges were monitored over the period 1988-91 and the results were compared with rainfall at the key stations at AWS Trawsnant and Maesglas. Rates of increase with altitude were calculated

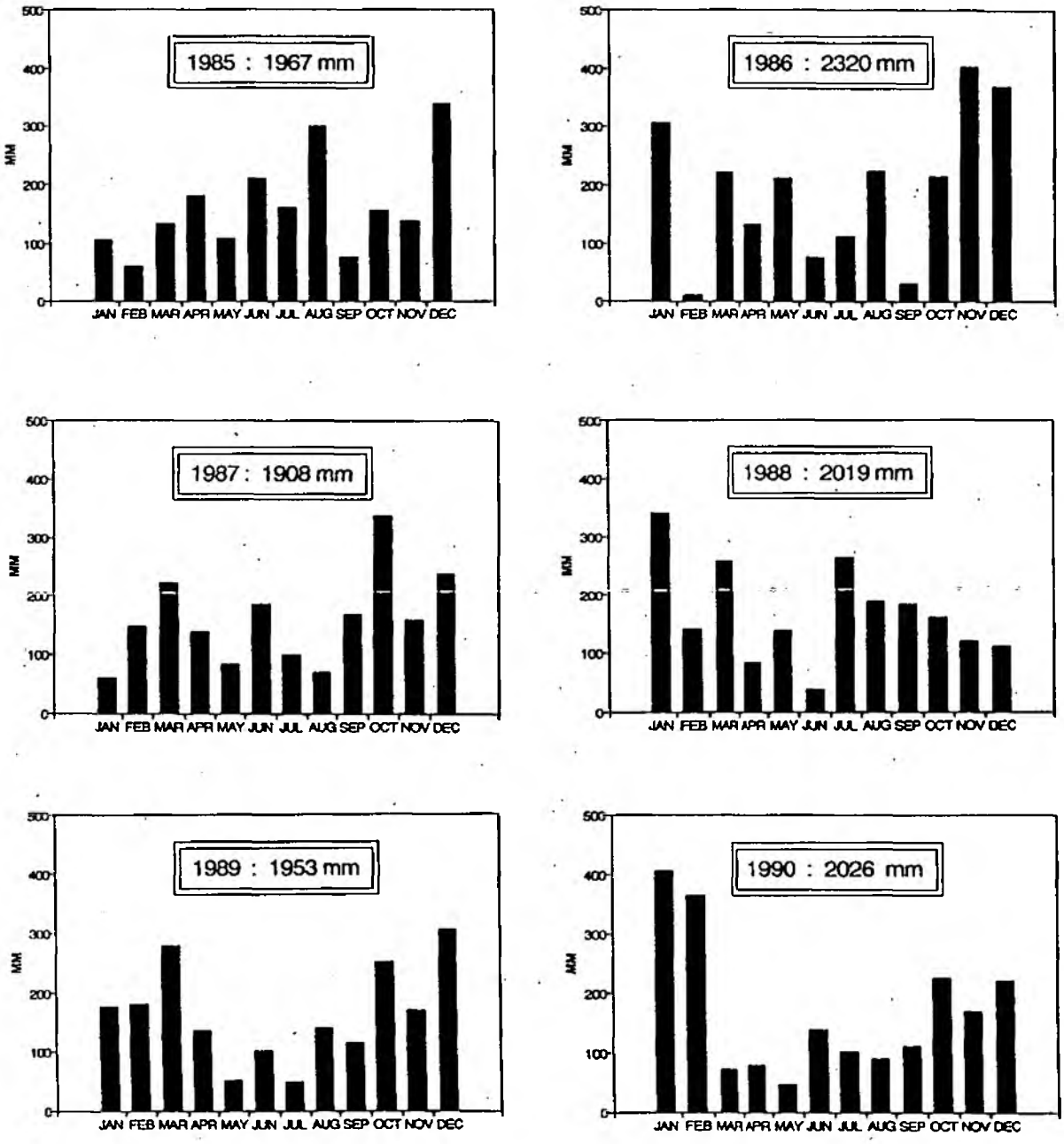

Figure 3.1 Rainfall at AWS Trawsnant 1985-90.

independently for each high altitude station in relation to the nearest key station (Table 3.3). The results, which suggested an overall mean rate of increase with altitude of around 0.0011 mm mm^{-1} rain m^{-1} altitude difference, were consistent not only with each other, but also with rates calculated by comparing rainfall at the lower altitude stations of Rhandirmwyn and Ystradffin with that at AWS Trawsnant.

There is some evidence that the rate of increase varies with origin of rainfall, wind speed and season. Rates of increase were somewhat higher (0.0014 mm mm^{-1} m^{-1}) in the initial calibration periods, which were more characterized by strong westerly weather. Orographic intensification processes are particularly effective when strong moist westerly or south westerly airstreams (often associated with deep depressions of autumn and winter) rise over the Welsh mountains; rates of increase in rainfall with altitude exceeded 0.003 mm mm^{-1} m^{-1} during two such periods (Table 3.3). In contrast, in less windy conditions, particularly in the summer months when much of the rainfall is partly convectional, rates of increase with altitude can be very low.

Table 3.3 Rates of rainfall increase with altitude in the Llyn Brianne area 1988-91.

Station	Altitude m	Period of Record	Rainfall mm	Rate of Increase mm/mm/m*
(a) Overall relationships				
LI1 Top	483	6/12/89-3/5/91	3360	0.00119
AWS	372		2968	
LI8 Top	472	6/2/90-13/11/90	1974	0.00113
AWS	372	23/1/91-3/5/91	1774	
CI5 Top	479	12/8/88-12/12/90	4587	0.00102
Maesglas	351		4055	
(b) Initial calibration periods more dominated by westerly weather				
LI1 Top	483	6/12/89-6/2/90	859	0.00145
AWS	372		740	
CI5 Top	479	12/8/88-20/7/89	1811	0.00147
Maesglas	351		1526	
(c) Orographic enhancement in shorter very wet periods				
CI5 Top	479	2/2/89-11/5/89	754	0.00318
Maesglas	351		535	
CI5 Top	483	13/11/90-12/12/90	252	0.00375
Maesglas	351		170	

*Rate of increase is expressed as millimetres increase in rainfall per unit millimetre at the lower station per metre increase in altitude above the lower station.

The equations for converting rainfall at the key stations to sub-catchment rainfalls are given in Table 3.4. The equations can be used in estimating monthly, daily or hourly rainfall in the sub-catchments and the Initial Calibration Period sets have been used in rainfall-runoff and catchment budget modelling studies by the Institute of Hydrology.

3.4 Stage-discharge ratings

Table 3.5 summarizes stage-discharge relationships for the Llyn Brianne study catchments during the project. It gives details of the various rating equations, their periods of applicability, confidence limits, and the monitored stage and flow ranges that they were based upon. During the latter part of the project additional dilution gauging particularly at higher flows and more detailed stage-discharge analysis have permitted some significant improvements to the quality of the stage-discharge relationships. The dilution gauging technique developed by Ian Littlewood has proven both rapid and highly accurate.

Table 3.4 Correction factors for sub-catchment rainfall estimation.

Catchment & Area (km^2)		Mean Altitude (m)	Conversion Equation (Initial period)	Conversion Equation (Overall period)
LI1	2.549	441.8	R = 1.1016 AWS	R = 1.0811 AWS
LI2	1.089	432.5	R = 1.0881 AWS	R = 1.0703 AWS
LI3	0.655	414.9	R = 1.0625 AWS	R = 1.0499 AWS
LI4	0.311	418.2	R = 1.0673 AWS	R = 1.0537 AWS
LI6	0.735	437.4	R = 1.0952 AWS	R = 1.0761 AWS
LI7	0.734	462.0	R = 1.1310 AWS	R = 1.1045 AWS
LI8	0.657	453.8	R = 1.1191 AWS	R = 1.0950 AWS
CI2	0.535	476.3	R = 1.1825 M	R = 1.1314 M
CI3	0.861	450.3	R = 1.1456 M	R = 1.1046 M
CI4	0.501	442.9	R = 1.1352 M	R = 1.0973 M
CI5	0.334	430.7	R = 1.1179 M	R = 1.0849 M
CI6	0.607	410.3	R = 1.0890 M	R = 1.0641 M
UC4	1.980	368.4	Use Upper Cothi rainfall data	
GI1	0.180	326.9	Use Gwenffrwd rainfall data	

Altitudinal rates of increase (mm/mm rain/metre altitude difference) used were:
Initial Calibration Period: 0.00145 (LI catchments) & 0.00147 (Camddwr catchments); Overall Period: 0.00116 (LI catchments) & 0.00102 (Camddwr catchments).

The durability and reliability of the equations vary from catchment to catchment. Not surprizingly, ratings were particularly reliable at those catchments with rectangular sharp-crested weirs (LI4, CI4, CI5 and CI6). Some of the catchments with natural rated sections (LI2, LI3 and CI2) also had reasonably consistent and reliable relationships. This reflected the stability of their channel cross-sections, especially after the initial effect of the in-stream cages housing the water quality sensors in causing bank erosion had worn off or been stabilized.

There were big problems with channel erosion and bed material movement at LI1, UC4, LI6 and LI8. At LI6, work by Ian Littlewood to some extent managed to keep pace with channel change during the relatively short period (1985-87) that the catchment was being monitored. At LI1, the reliability of the ratings varied with time period, with a good relationship from August 1985 until massive bank erosion in December 1986; a very poor relationship until bank stabilization measures had been completed in April 1987; and then reasonable relationships for flows contained within the channel. Drainage ditching has increased the frequency of overbank flooding in the afforested catchments and the installation of a flume by the Institute of Hydrology proved the only way of accurately monitoring the full range of flows at LI1. UC4 also had a stable rating until a large storm destroyed the gauging station. Subsequent ratings have been rather poor as a result of continued bedload movement.

Table 3.5 Stage-discharge relationships for Llyn Brianne catchments 1985-91.

Catchment & Rating		Period Applicable	Stage-Discharge Equation C	A0	B	r	n	95% Confidence Limits Min	At Hmin	At Hmax	Monitored Flow Range Stage (m)	Flows (l/s)	Remarks
LI1	A	01/08/85-14/12/86	2923.3	−0.086	1.6532	n/a	24	3.0 −2.9	7.0 −6.5	5.6 −5.3	0.12-0.64	10.3-1270	Up to stage 0.65m
	B	15/12/86-31/03/87	44431	0.000	3.699	0.995	6	15.1 −13.1	37.7 −27.4	20.8 −17.2	0.14-0.33	36-662	Rough guide only
	C	01/04/87-31/08/88	1799.1	−0.112	1.2397	0.999	9	4.8 −4.6	9.3 −8.5	12.7 −11.3	0.13-0.50	11-580	Up to stage 0.65m
	D	01/09/88-30/04/91	2431.4	−0.077	1.788	0.989	19	8.2 −9.2	17.4 −16.9	15.9 −14.6	0.14-0.51	19-548	Up to stage 0.65m
LI2	A	Up to 26/08/86	2696.2	−0.063	1.8210	n/a	25	8.4 −7.8	24.0 −20.0	20.0 −16.0	0.08-0.295	2.6-187	Up to stage 0.30
	B	01/09/86-05/10/88	1611.9	−0.069	1.630	0.974	31	7.5 −7.0	18.3 −15.4	27.2 −21.4	0.09-0.42	4.6-275	Up to stage 0.42
LI3	A	Up to 09/11/86	3868.3	−0.071	1.711	n/a	15	5.4 −5.1	8.4 −7.7	13.0 −12.0	0.10-0.21	8.5-126	Up to stage 0.21
	B	10/11/86-11/04/89	9518.0	−0.025	2.341	0.991	43	4.3 −4.2	10.3 −9.3	7.3 −6.8	0.062-0.186	7.6-132	Up to stage 0.24+
LI4	A	1985-91	1309.0	0.000	1.484	0.996	20	4.8 −4.6	7.9 −7.3	10.1 −9.1	0.0-0.12	0.0-67	Up to 0.25 stage (top of weir)
LI6	A	Up to 08/10/85	3253.1	−0.048	2.369	—	27	4.5 −4.4	10.0 −9.2	10.0 −9.0	0.14-0.36	12.2-189	Up to stage 0.36
	B	14/10/85-30/06/86	4307.3	−0.011	1.728	—	20	7.6 −7.0	18.0 −15.0	14.0 −12.0	0.033-0.147	10.0-150	Up to stage 0.15
	C	06/07/86-25/08/86	92727	0.100	5.277	—	23	6.1 −5.8	12.0 −11.0	12.0 −11.0	0.045-0.150	—	Up to stage 0.15

Table 3.5 continued.

Catchment & Rating		Period Applicable	Stage-Discharge Equation C	A0	B	r
LI8	A	Up to Aug 1986	10519	−0.051	1.933	—
	B	01/09/86-24/02/87	1718.0	−0.05	1.732	0.930
	C	Series of poor relationships as channel has eroded				
	D	07/04/89-29/08/90	13078.8	−0.040	2.249	0.985
CI2	A	28/02/87-13/01/89	753.0	−0.032	1.979	0.994
	B	14/01/89-27/03/91	1633.6	−0.050	2.186	0.993
CI3	A	1985-86	296.7	−0.211	1.285	0.992
			158291.2	0.00	8.331	0.990
	B	1987-89	7150.3	−0.128	2.981	1.000
			6711.3	−0.294	1.000	1.000
CI4	Old	1985-87	1268.9	−0.012	1.279	0.994
	New	1988-90	1875.9	0.001	1.481	0.999

n	95% Confidence Limits Min	At Hmin	At Hmax	Monitored Flow Range Stage (m)	Flows (l/s)	Remarks
26	12.0 −11.0	30.0 −23.0	28.0 −22.0	0.059-0.205	0.9-216	Up to stage 0.21
14	Very wide limits			0.071-0.240	3.1-187	Not very reliable Very unreliable
16	11.7 −10.5	23.8 −19.2	30.6 −23.4	0.064-0.200	3.3-186	Much improved
8	9.1 −8.3	24.0 −19.3	13.1 −11.5	0.038-0.223	3.8-52.9	Stage range only
14	6.9 −6.4	11.9 −10.6	22.0 −18.0	0.005-0.305	4.4-169.4	Quite good
11	4.6 −4.4	14.1 −12.3	7.5 −7.0	0.245-0.353	3.8-26.3	Low flows H<0.35m
4	30.6 −23.4	46.5 −31.8	44.4 −30.0	0.353-0.415	26.3-110.9	High flows H>0.35m
5	2.4 −2.3	5.8 −4.8	3.1 −3.0	0.212-0.300	4.0-36.8	Low flows H<0.30m
3	n/a	n/a	n/a	0.30-0.315	36.8-138.2	High flows H>0.30m
13	10.1 −9.2	27.0 −21.0	20.0 −17.0	0.03-0.17	8.4-154.0	Good to top of weir (0.40m stage)
7	5.2 −4.9	8.0 −7.4	11.4 −10.2	0.015-0.160	3.9-127.1	Excellent and close to theoretical

Table 3.5 continued.

Catchment & Rating		Period Applicable	Stage-Discharge Equation C	A0	B	r	n	95% Confidence Limits Min	At Hmin	At Hmax	Monitored Flow Range Stage (m)	Flows (l/s)	Remarks
CI5	A	1985-90	2383.0	0.000	1.520	0.999	4	17.8 -15.1	26.9 -21.2	25.4 -20.3	0.011-0.108	2.4-81.6	Much improved on former rating
CI6	A	1985-90	1375.7	-0.010	1.5207	0.997	23	3.8 -3.7	9.2 -8.4	8.9 -8.1	0.022-0.255	2.0-183	Excellent. Applies to 0.4m top of weir
UC4	A	Up to Dec. 1986	1322.8	-0.051	2.245	n/a	15	8.2 -7.6	20.6 -17.1	14.7 -12.8	0.175-0.550	45-291	Good within stage range.
	B	Station destroyed by flood; no reliable rating until channel reach stabilized by works at weir											
	C	06/11/87-31/12/89	1972.9	-0.162	1.556	0.995	7	22.5 -18.4	33.9 -25.3	44.2 -30.7	0.181-0.485	5.0-237	Reasonable only.
	D	1990-91	1772.0	-0.080	1.937	0.992	8	18.9 -15.9	36.8 -26.9	32.8 -24.7	0.131-0.485	5.0-237	Somewhat improved.

*Key: Rating Equation Formula is $Q = C (H + AO)^B$ where
Q = Streamflow (l/s); H = Stage (m); B, C, AO are coefficients;
r = correlation coefficient; n = number of flow gaugings.
Confidence limits are percentages of predicted Q values.

The greatest problems occurred in LI8 and CI3. The recent afforestation in LI8 meant that the channel was actively enlarging during the monitoring period, in response to the greatly increased flood flows associated with the expansion of the channel network by forestry drainage ditches. Eventually, further channel erosion (and some excavation work at the station) created a stable semi-circular cross-section in bedrock. This allowed the development of a stable rating for the latter part of the project since 1989. Though improved, the precision of the rating is reduced because the width of the channel cross-section means that a small increase in stage results in a large increase in discharge. Stage-discharge ratings for sub-catchment CI3 are very unreliable, despite the apparently narrow confidence limits (Table 3.4). It proved necessary to fit two curves (one for low flows, one for high flows) to each rating data set. The high flow ratings are merely rough guides, as flow increases very rapidly with increases in stage in the very wide upper sections of the channel. The channels were also greatly affected by bank erosion and seasonal vegetational growth in the stream.

Despite the improvements to the stage-discharge ratings, however, it was clear that the only realistic way of generating flow data over the full range of flows for catchment budget purposes would be by modelling via cross-correlation from the more accurate flow data at catchments CI6 and LI1 (since the flume was established), and/or via rainfall-runoff modelling.

3.5 Hydrological pathways and surface water hydrochemistry

A three year investigation into the importance of hillslope hydrological pathways in influencing surface water hydrochemistry was carried out in LI1. Water flow paths and associated hydrochemical changes were examined in stagnohumic gleys, stagnopodzols and peats. These cover 19, 8 and 24% of the catchment respectively. The main aim of the investigation was to identify the principal hydrological pathways governing the transfer of acid, aluminium-rich water from soils into streams. A summary of the results from the stagnopodzol and peat investigations are also given; fuller details can be found in Soulsby (1991).

Soil moisture variations during a hydrological year in a stagnohumic gley along a 20m hillslope transect (on a 9° slope) are shown in Figure 3.2. The measurements were made with tensiometers in the O (organic), E and B/C horizons, corresponding to depths of 15cm, 25cm and 65cm respectively. The soils were very wet during the winter period of October 1988 - March 1989 (days 1-180). Significant spatial variations in soil moisture were detected. The lower slope site, which was 1m upslope of a major forest drain, consistently showed the wettest conditions, with the soil being drier at the upslope sites. These patterns were especially clear during the summer of 1989.

During storm periods, saturated conditions (pressure potentials >0 kPa) were observed throughout the soil profile in the lower slope area. Upslope, the deeper soil horizons remained unsaturated but saturation was frequently detected in the O horizon. This was found to be due to profile variations in hydraulic conductivity. The saturated hydraulic conductivity in the well-structured, organic O horizon was 2 orders of magnitude greater than that measured in the more compact, mineral subsoil. Consequently, during storm events, impeded vertical drainage caused the soil O horizon to saturate and water rapidly moved laterally towards the forest drainage ditch. This is clearly illustrated by considering the hydraulic head distribution across the stagnohumic gley hillslope at the peak of a 55 mm storm on 14 March 1989 (Figure 3.3). Water movement on diagrams showing hydraulic head profiles is assumed to be perpendicular to the equipotential lines. The hillslope can therefore be viewed as drying prior to the event. However, by the event peak a 2-phase flow system develops. In the upper 20cm O horizon of the profile, water movement is clearly lateral towards the drainage ditch. In the lower profile of the hillslope, water movement is directed vertically to the deeper groundwater zone in the underlying drift.

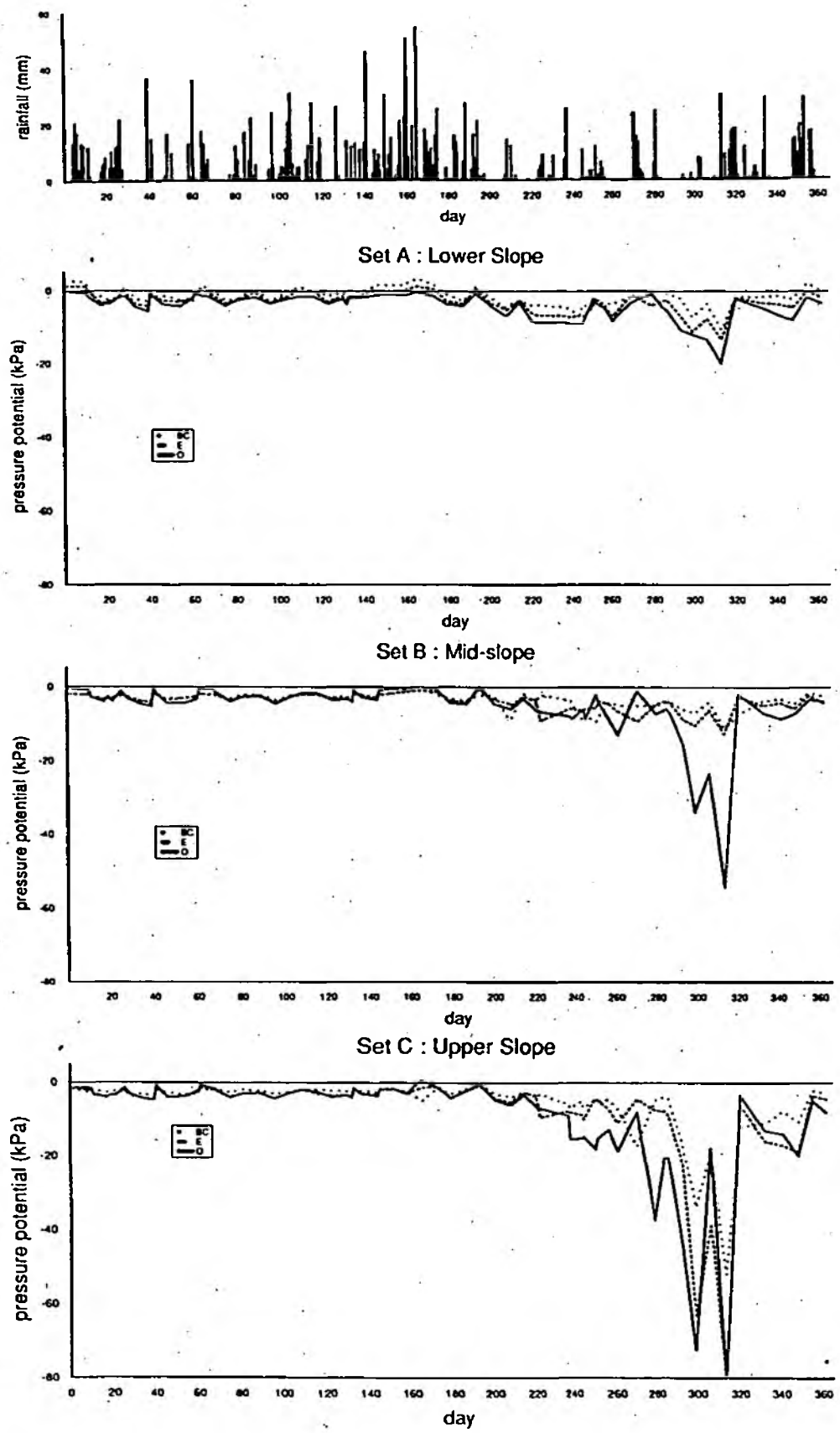

Figure 3.2 Stagnohumic gley soil water regime, October 1988 — September 1989.

As water moved through the soils, aluminium was mobilized. The chemical composition of soil solutions was also monitored during the study period. Data analysis confirmed the earlier indication of ITE studies at Llyn Brianne that cation exchange, driven by enhanced deposition of atmospheric anions, was the dominant short-term control on aluminium mobilization. This is illustrated in Figure 3.4 where theoretical cation exchange equations were used to predict increases in aluminium, as well as divalent and monovalent cations. In each major horizon the theoretical equations gave a good description of actual cation concentrations.

Monitoring of ditchwater hydrochemistry showed that the aluminium mobilized in the soil was transported by the dominant flow paths into surface waters. A typical storm response on 8th November 1988 is shown in Figure 3.5. Prior to the onset of rainfall, groundwater seepage from unaltered drift below the soil profile sustained ditch flows. As flows increased, the rapid switch in the dominant hydrological pathway resulted in a fall of pH and increased aluminium concentrations. The chemistry of ditchwaters was found to be very similar to the composition of O horizon soil solutions. The increased DOC concentrations and the dilution of Ca and Mg further indicate the switch in flow paths from groundwater to the upper soil zone.

Given their spatial extent, the hydrology of stagnohumic gley soils has an important influence on the storm event hydrochemistry of LI1. Streamwater draining from these soils has a very similar chemical composition to that of LI1 and hence probably makes a significant contribution to the LI1 catchment storm response.

In contrast to the stagnohumic gleys, the water flow paths in the stagnopodzol were found to be vertical due to a highly structured and freely draining soil profile. Lateral water movement was only detected in large storm episodes when a saturated wedge developed at the soil/bedrock interface at a depth of 1m. Although this flow path is probably too slow to contribute to the initial catchment storm response, it is likely to help sustain high aluminium concentrations in surface waters during the recession limb of the hydrograph.

The hydrology of forest peat soils was dominated by saturation overland flow along plough furrows. This was found to be highly acidic (pH 3.5), but had very low aluminium concentrations. Nevertheless, there was some indication that this acid water was able to mobilize some aluminium from the bed and sides of drainage ditches.

Although this work on hydrological pathways yielded some informative results on the hydrology and hydrochemistry of some of the major forest soil types, results of similar investigations into the behaviour of other soils (e.g. brown podzolics and riparian peats and gleys) at Llyn Brianne and elsewhere in Wales would help to improve models that simulate short-term changes in surface water hydrochemistry. The hydrochemistry of particular soil types is clearly important to catchment management for the amelioration of acidification in upland areas.

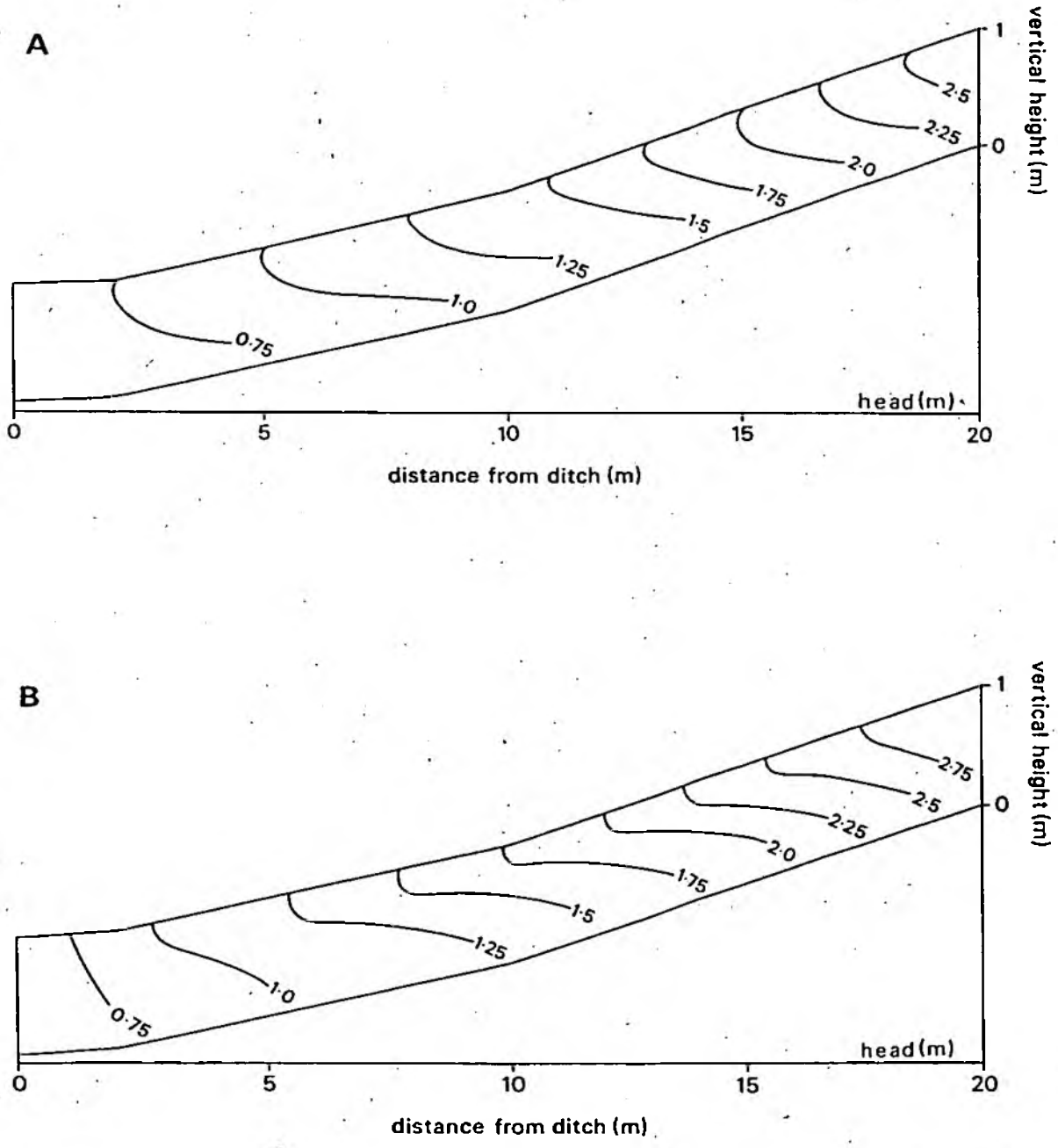

Figure 3.3 Stagnohumic gley hillslope, hydraulic head profile (a) before and (b) during event, 14. March 1989.

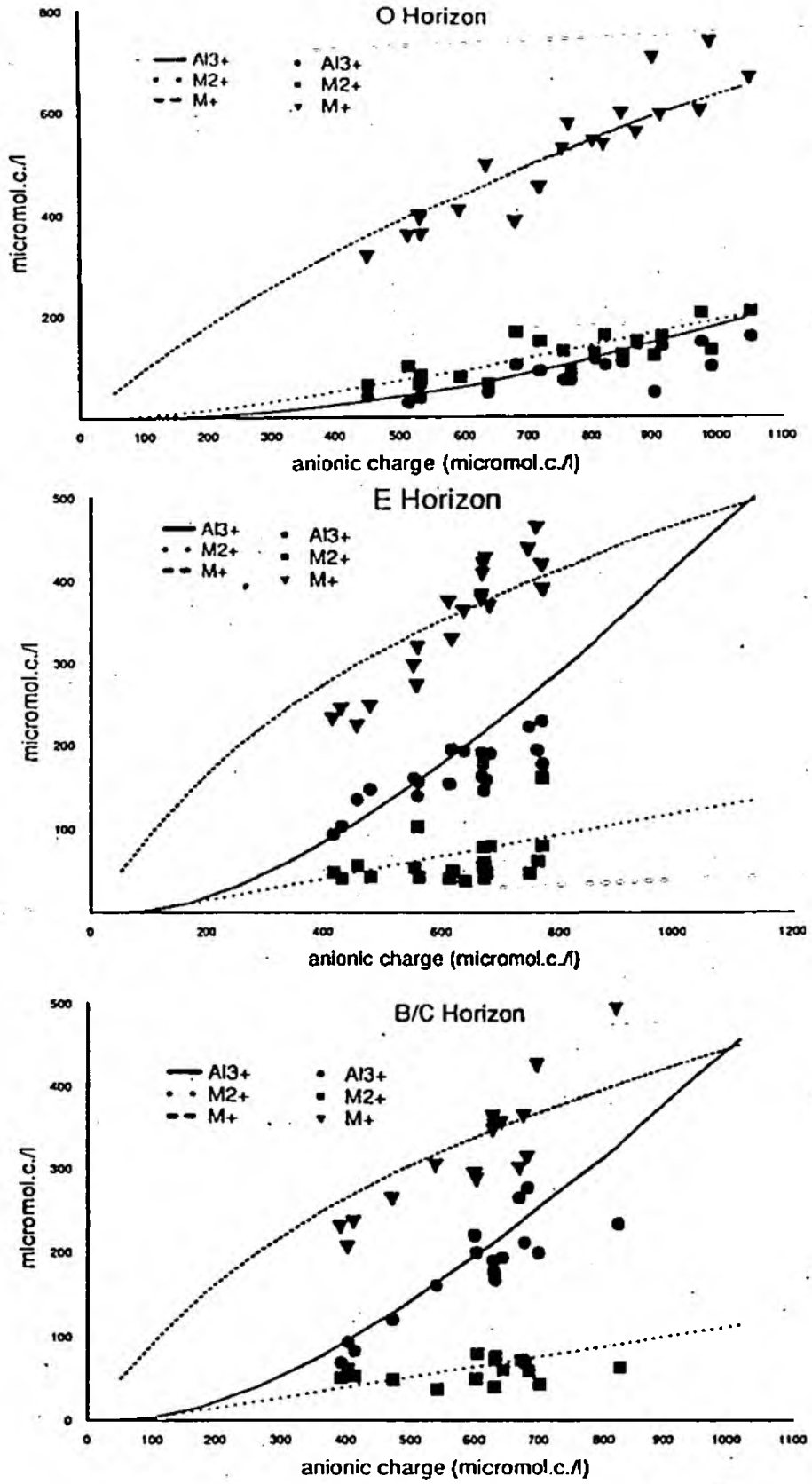

Figure 3.4 Predicted and measured variations in concentrations of M^{+}, M^{2+} and Al^{3+} with total anion concentrations, in stagnohumic gley soil solutions.

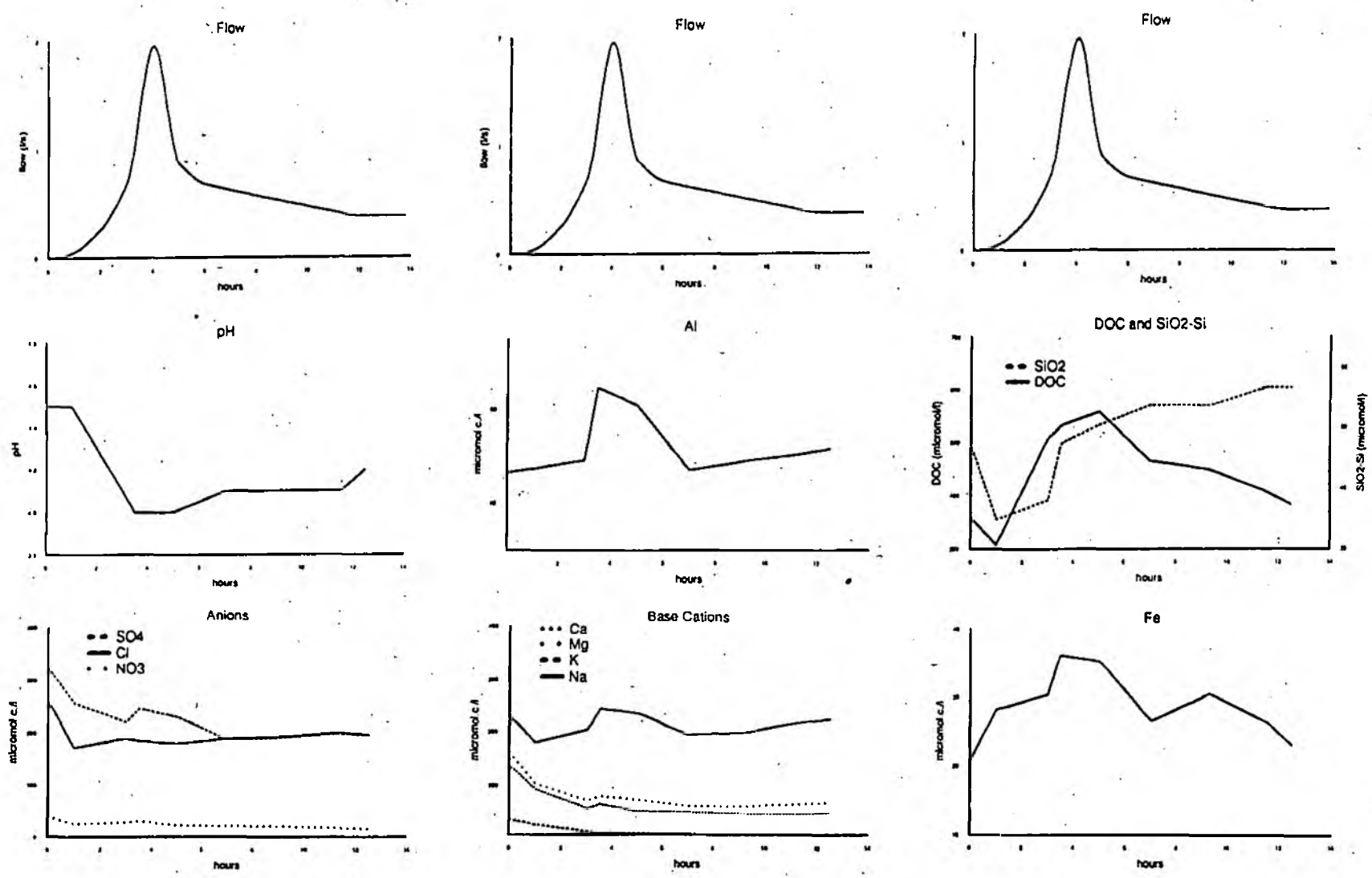

Figure 3.5 Hydrochemical response of stagnohumic gley ditch, 8 November 1988.

4. SOIL STUDIES

4.1 Limed Catchments

4.1.1 Introduction

Amongst the experimental manipulations undertaken at Llyn Brianne, those in catchments CI5, CI3 and LI4 have provided the most satisfactory data for an evaluation and comparison of the effects of different treatments to ameliorate soil water acidity. At CI3, an area of soils (site C32) comprising ferric stagnopodzol-brown podzolic intergrades was agriculturally improved by ploughing, application of powdered magnesian limestone, addition of compound fertilizer and re-seeding. At CI5 powdered calcium carbonate was applied, at a rate of approximately 9 t ha^{-1}, to an area of stagnopodzol soils supporting acid moorland vegetation (site C51). Data from these sites allow the effects of two different treatments of podzolic soils to be compared. The response of source area and valley bottom peats can be evaluated using data from LI4 and CI5. In the former forested catchment, 4 ha of deep peat within the unplanted headwaters was treated with fine powdered limestone at a rate of 25 t ha^{-1} (site L42). The same material was applied at a rate of approximately 9 t ha^{-1} to an area of valley bottom peat within the CI5 catchments (site C53). Soil waters were sampled every two weeks from 4 depths in the podzol soils and at two depths in the peats using a combination of tensionless and suction lysimeters described in detail in Reynolds and Emmett (1990).

4.1.2 Podzolic soils

At both sites, the treatments significantly increased mean soil water calcium and alkalinity concentrations in the surface organic-rich soil (0) horizons for two to three years after treatment (Table 4.1, Figure 4.1). Soil water acidity decreased although total filterable aluminium remained unchanged compared with control and pre-treatment concentrations until two or three years after treatment (Table 4.2; Figures 4.1, 4.2). In the year following treatment, at both sites, mean nitrate concentrations were significantly greater than control or pre-treatment values (Table 4.2, Figure 4.2). At C32 (catchment CI3) ploughing of the surface mineral (A) horizon allowed lime to penetrate into the soil so that calcium concentrations and alkalinity increased whilst aluminium and acidity decreased (Tables 4.1, 4.2). At C51 (catchment CI5), which was not ploughed, the mean acidity and aluminium content of the soil waters in the surface mineral (E) horizon increased along with calcium and nitrate in the first year following liming (Figures 4.1, 4.2). By the second year, mean acidity and aluminium concentrations were significantly below pre-treatment values.

In the first year following treatment at C51, despite a large increase in calcium concentrations, the acidity, aluminium and nitrate contents of lower (B and C) horizon soil waters were greater than pre-treatment and control values (Table 4.2, Figure 4.2). By the second year, acidity and aluminium concentrations had declined, although nitrate concentrations remained high. Liming and cultivation can increase the net mineralization of soil organic nitrogen (Nyborg and Hoyt 1978, Nyborg et al 1988), resulting in elevated concentrations of inorganic nitrogen. An increase in the amount of available ammonium and a decrease in acidity probably stimulated nitrification in the surface organic-rich horizons. At C32, the fertilizer provided additional ammonium and nutrients which probably further stimulated nitrification (Haynes and Swift 1988). Whilst nitrogen mineralization and nitrification was probably most active in the surface organic-rich soil layers, nitrification may also have occurred lower in the profile. Presumably at both sites nitrate production in the first year after treatment was in excess of plant requirements so that excess nitrate was leached to the lower soil horizons. At C51, liming was completed towards the end of the growing season when plant uptake was declining. However, providing soil temperature and moisture conditions remained favourable, mineralization and nitrification may have continued throughout much of the winter, so that large quantities of nitrate were available for leaching.

At C32, mineralization and nitrification was probably active in advance of a demand from the newly sown grass, resulting in nitrate leaching to the lower soils. During subsequent years nitrate concentrations decreased in the soils, probably reflecting a decline in nitrogen mineralization and nitrification rates. Nyborg and Hoyt (1978) have indicated that the effects of liming as a stimulus to nitrogen mineralization are relatively short-lived, and at C32 the developing sward will have provided an increasing sink for nitrogen.

Table 4.1 Annual mean acidity (μeq $H^+ l^{-1}$), alkalinity (mg $CaCO_3$ l^{-1}) and calcium (mg l^{-1}) concentrations in soil waters from improved podzolic soils at sites C31 (control) and C32 (treated) in catchment CI3, in three years (1-3) post-treatment. a = significantly different from control ($p < 0.05$).

H^+		O	A	B	C
1	C31	23.3	8.3	13.9	13.3
	C32	4.8[a]	0.3[a]	23.0	35.0[a]
2	C31	23.7	12.1	20.8	29.7
	C32	2.9[a]	0.3[a]	7.0[a]	12.5[a]
3	C31	23.4	14.0	11.8	27.6
	C32	0.9[a]	1.1[a]	4.0[a]	6.8[a]
Ca		**O**	**A**	**B**	**C**
1	C31	0.8	0.4	0.6	0.7
	C32	7.8[a]	11.5[a]	5.8[a]	6.1[a]
2	C31	0.7	0.5	1.0	1.0
	C32	4.9[a]	7.0[a]	3.5[a]	3.8[a]
3	C31	1.0	0.6	0.6	1.0
	C32	8.5[a]	11.8[a]	4.3[a]	4.1[a]
Alkalinity		**O**	**A**	**B**	**C**
1	C31	1.3	1.6	1.2	1.3
	C32	8.0[a]	26.3[a]	5.6[a]	3.0[a]
2	C31	1.4	1.3	1.2	0.6
	C32	10.6[a]	18.3[a]	3.1[a]	2.5[a]
3	C31	1.0	1.8	1.5	1.5
	C32	16.7[a]	14.4[a]	4.1[a]	3.9[a]

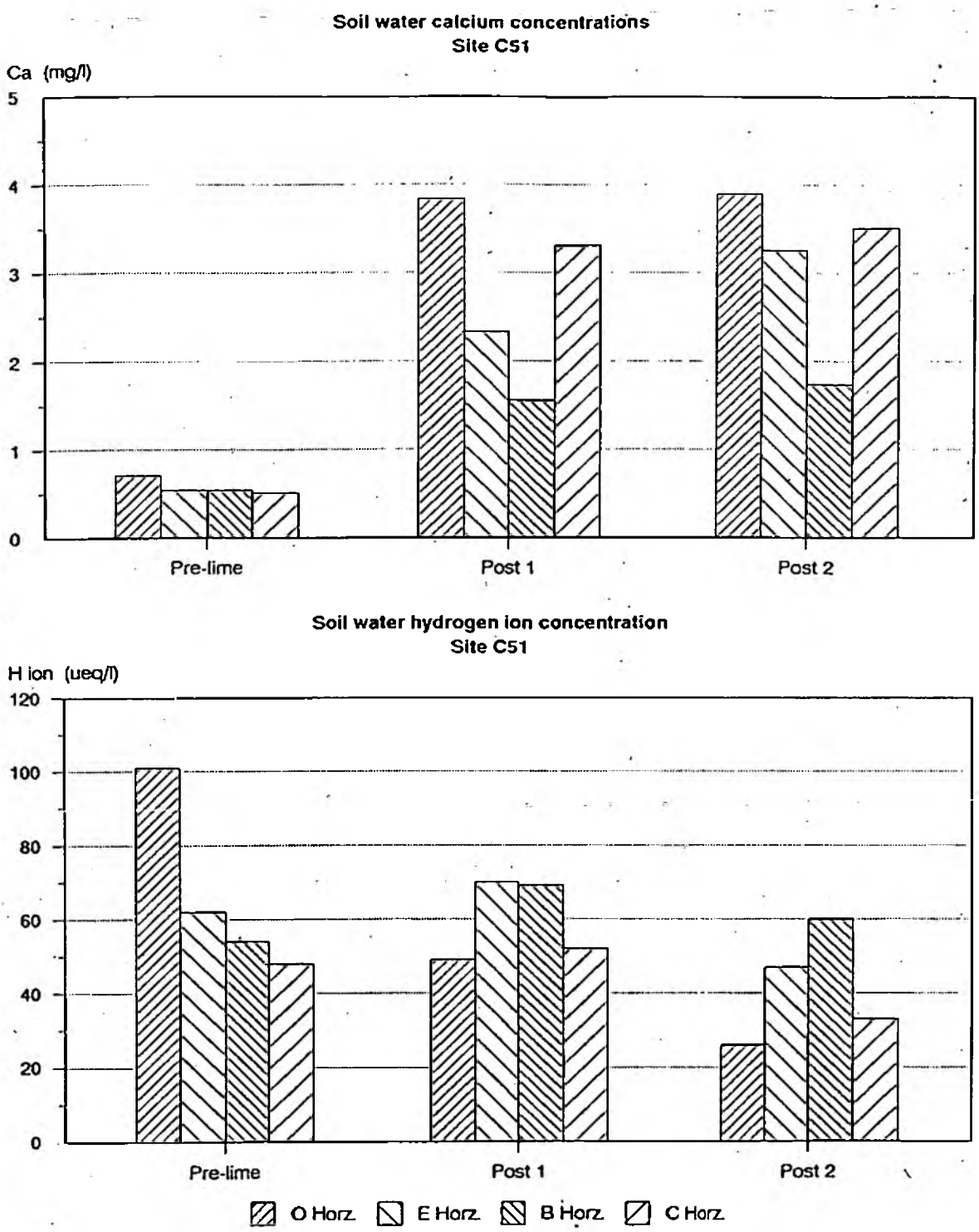

Figure 4.1 Annual mean calcium and hydrogen ion concentrations in a surface limed stagnopodzol soil at site C51 (catchment CI5).

Table 4.2 Annual mean total filterable aluminium and nitrate concentrations (mg l^{-1}) in soil waters from improved podzolic soils at sites C31 (control) and C32 (treated) in catchment CI3, in three years (1-3) post-treatment. a = significantly different from control ($p < 0.05$).

Al(tot)		O	A	B	C
1	C31	0.26	0.26	0.45	0.61
	C32	0.28	0.13[a]	2.40[a]	3.00[a]
2	C31	0.23	0.35	0.75	2.41
	C32	0.22	0.17[a]	0.38[a]	0.86[a]
3	C31	0.25	0.47	0.53	2.52
	C32	0.15[a]	0.14[a]	0.27[a]	0.61[a]
NO_3 – N		**O**	**A**	**B**	**C**
1	C31	0.1	0.3	0.8	1.0
	C32	6.2[a]	6.3[a]	11.7[a]	11.6[a]
2	C31	0.3	<0.1	1.5	4.9
	C32	3.6[a]	2.2[a]	1.6	3.2
3	C31	0.2	2.3	0.7	5.0
	C32	2.2[a]	4.2	2.0[a]	3.5[a]

Nitrification is an acidifying process in which two hydrogen ions are released per mole of ammonium converted to nitrate (Helyar 1976), although the overall effect of nitrification on soil water acidity ultimately depends on the fate of the nitrate (Reuss and Johnson 1986). In the surface soil it is probable that dissolution of calcium carbonate prevented soil water acidification caused by increased rates of nitrification. Ploughing at C32 also helped to improve the effectiveness of the lime in the surface mineral layer. Lower in the profile, in the absence of free calcium carbonate, soil waters were acidified and aluminium was released via ion exchange in response to the increased concentration of 'mobile anions'. Calcium concentrations also increased with nitrate and aluminium. Since the base saturation of the B and C horizons of the untreated soils lies between 7 and 14%, most of the calcium was probably leached from the added lime. By the second year after treatment, at both sites, acidity, aluminium and nitrate concentrations had declined towards or below pre-treatment and control values.

4.1.3 Peats

At both peat sites (L42 and C53, in catchments LI4 and CI5 respectively), liming led to significant increases in annual mean calcium concentrations and alkalinity in the surface organic (0) layer (Tables 4.3, 4.4). More calcium was present and the alkalinity was greater at site L42, presumably reflecting the higher lime application rate. The acidity and aluminium content of the peat water decreased at both sites following liming. Annual mean nitrate concentrations were significantly greater in the surface peat in the year following liming at both sites (Tables 4.3, 4.4). A much larger increase was observed at site L42 in the source area peat compared with the valley bottom site (C53). This may indicate that mineralization and nitrification rates were lower in the valley bottom, with losses of nitrogen occurring through denitrification if the site was wetter. Differences

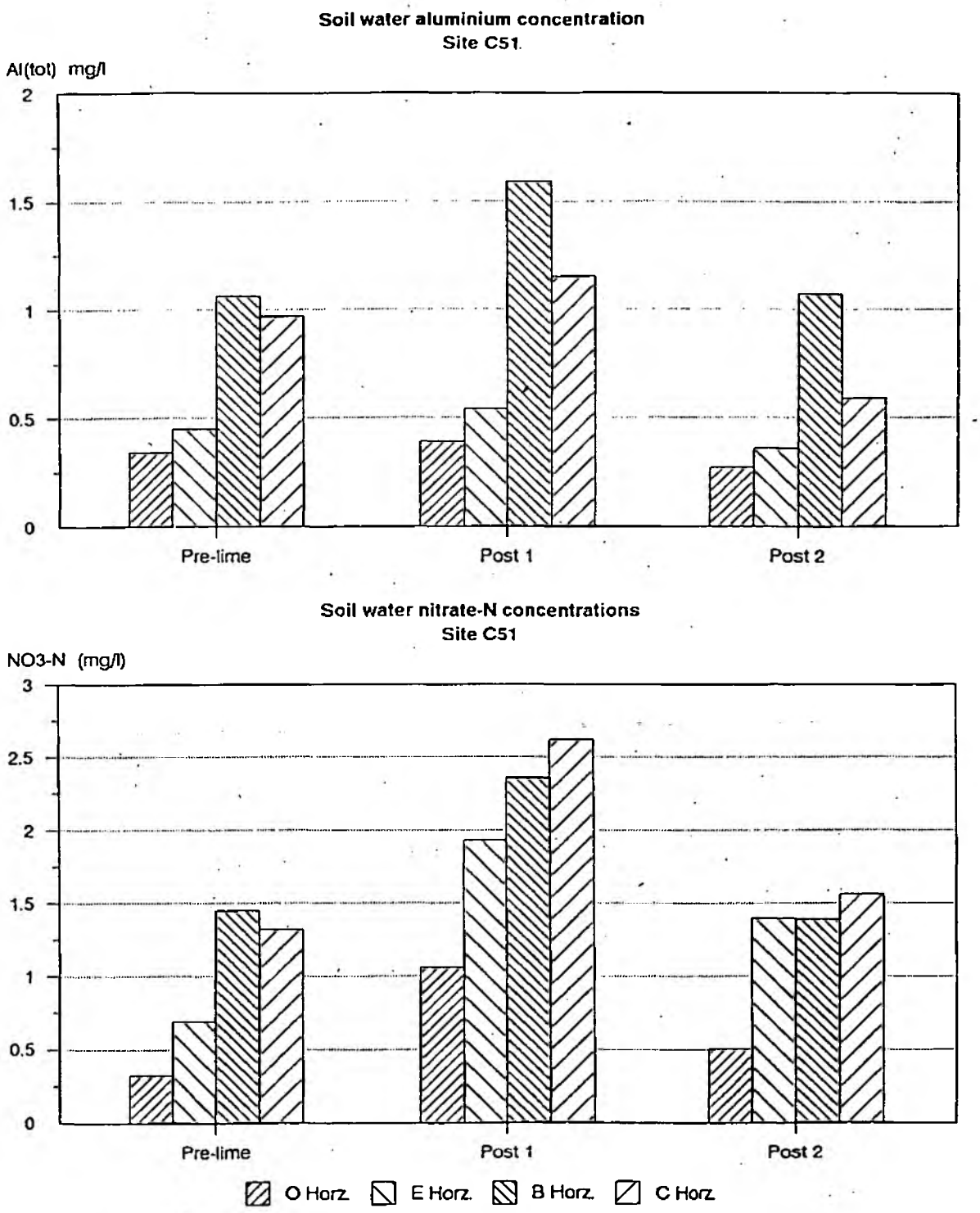

Figure 4.2 Annual mean aluminium and nitrate-N concentrations in a surface limed stagnopodzol soil at site C51 (catchment CI5).

in plant uptake at the two sites may also have contributed to the difference in nitrate concentrations. At neither site was the increase in nitrate accompanied by acidification of the peat water due to the presence of free calcium carbonate. By the second year after liming at C53, the annual mean nitrate concentration had declined to below the pre-liming value. Unfortunately there were insufficient data extending into the second year post liming to comment on trends at L42.

Table 4.3 Annual mean solute concentrations in surface peat (O) and deep peat (P) waters from surface limed source area at site L42 in catchment LI4. Units mg l^{-1} except H^+ μeq l^{-1} and alkalinity mg $CaCO_3 l^{-1}$. Post 1 = first year after lime application, a = significantly different from pre-liming values ($p < 0.05$).

	Pre-lime	Post 1
H^+		
O	78	4[a]
P	15	19[a]
Ca		
O	0.5	36.2[a]
P	0.5	1.1
Al (tot)		
O	0.12	0.09[a]
P	0.38	0.40
NO_3—N		
O	0.15	1.39[a]
P	<0.01	<0.01
Alkalinity		
O	0	72[a]
P	2.0	1.7

Table 4.4 Annual mean solute concentrations in surface peat (O) and deep peat (P) waters from surface limed valley bottom at site C53, catchment CI5. Units mg l^{-1} except H^+ μeq l^{-1} and alkalinity mg $CaCO_3 l^{-1}$. Post 1 and Post 2 = first and second years respectively after lime application, a = significantly different from pre-lime values, b = significantly different from Post 1 values ($p < 0.05$).

	Pre-lime	Post 1	Post 2
H^+			
O	12.1	3.2[a]	3.1[a]
P	8.4	8.5	7.9
Ca			
O	1.0	4.1[a]	3.5[a]
P	0.8	1.1	1.3[a]
Al (tot)			
O	0.10	0.07[a]	0.06[a]
P	0.09	0.09	0.11
NO_3—N			
O	0.08	0.27[a]	0.01[a b]
P	< 0.01	<0.01	0.01
Alkalinity			
O	2.2	8.4[a]	5.2[a b]
P	3.3	3.2	3.4

At both sites there is little evidence of an effect of liming on the chemistry of deep peat water (P) at a depth of 50cm. At C53 however, the mean calcium concentration for the second year following liming was significantly higher than for the year before treatment. In general, the results indicate that there is little migration of lime or lime-rich water from the top few centimetres of the peat. Similar behaviour was observed at Loch Fleet (Wilson et al 1988) and is consistent with current concepts of peat hydrology which suggest that the transfer of water between the surface and the body of deep peat is very slow (Makert and Thornton 1990).

4.2 Plot Liming

4.2.1 Introduction

Two types of limestone have been applied at two application rates (10 and 20 t ha^{-1}) to small replicate plots established in an upland wetland located in the Upper Cothi catchment, UC4 (Emmett and Reynolds 1991). The limestones used were finely powdered magnesium limestone and finely powdered calcium carbonate (Minfil 50). Changes in soil solution chemistry at three depths are being monitored following application of the treatments. Peat samples at 0-5cm and 5-10cm depths have been collected 3 and 18 months following application of the lime and will again be collected 30 months post-lime application. Exchangeable cations, CEC and 'free lime' determinations are carried out to determine lime dissolution rates. Changes in vegetation composition in the different treatment plots are assessed annually (Wallace 1989, 1991).

4.2.2 Site description

The experiment required an area of undisturbed, unimproved deep peat with a relatively homogenous vegetation cover. The area chosen in the Upper Cothi catchment in the Llyn Brianne area is gently sloping, dominated by *Molinia*, 30m from the Afon Cothi. The site vegetation has been classified as a species-poor wet heath community associated with thinner, better drained ombrogenous peats. The overwhelming dominance by *Molinia* and the absence of well-developed *Sphagnum* carpets characteristic of wetter communities, is unfortunate as the effect of liming on the flora of more species-rich wet ombrogenous mires would be of greater interest. However, the experiment will provide results applicable to large areas throughout the U.K. which are dominated by this widespread, though impoverished, vegetation.

4.2.3 Experimental design and methodology

The four liming treatments were applied to 10m x 5m plots, which together with the control treatment are arranged in a randomized block design. There are three replicate plots per treatment with each treatment represented in each of the three blocks. Lime was applied in August 1989. Control plots were covered with plastic sheeting to prevent lime contamination during application. Lime was washed from the vegetation in the lime plots using a backpack sprayer to prevent cross-contamination.

Soil waters are collected every fortnight from three depths and analyzed for all major cations and anions. A porous ceramic suction sampler is installed at a depth of 50cm in the centre of each plot and zero-tension lysimeters at 10cm depth. Surface run-off is collected at the downslope edge of each plot.

To determine exchangeable cations and 'free lime', fifteen peat samples (10cm x 10cm x 10cm) are collected from each plot. The vegetation is carefully removed for 'free lime' determinations and the peat divided into 0-5cm and 5-10cm depths.

Fifteen permanent quadrats (0.5m x 0.5m) in each plot are assessed annually for percentage cover of all vascular and bryophyte species. The percentage cover of litter and the area of base peat are also recorded together with mean herb height and maximum depth of *Sphagnum* tussocks.

4.2.4 Results and Conclusions

Water chemistry has changed significantly following lime application in the upper peat horizons with no change recorded at 20cm or 50cm depths. Changes in the upper peat water chemistry include an increase in pH, calcium, magnesium and oxidised nitrogen concentrations. Minfil 50 was found to be more effective in raising pH, alkalinity and calcium concentrations, with the pH and alkalinity increase greatest in the 20 t ha^{-1} treatments plots.

Few conclusions can be made concerning the effect of lime type on the rate of lime dissolution as only initial results are available. No significant difference in the amount of lime recovered was observed between the Minfil and magnesium limestone treatment plots 3 months post-liming. Total recovery was 8.9 (s.e. Ñ 1.4) t ha^{-1} and 12.0 (s.e. Ñ 3.5) t ha^{-1} in the Minfil 10 and 20 t ha^{-1} plots respectively, and 5.6 (s.e. Ñ 2.3) t ha^{-1} and 14.9 (s.e. Ñ 2.9) t ha^{-1} in the magnesium limestone 10 and 20 t ha^{-1} plots respectively. The effect of application rate on lime remaining after 3 months is significant, with more lime remaining on the 20 t ha^{-1} plots than the 10 t ha^{-1} plots for both lime types.

The distribution of the lime however, appeared to be different for the two types of lime. Between 93% and 95% of the Minfil was recovered in the vegetation compared to only 84-89% in the magnesium limestone plots. This may be a consequence of the smaller particle size of the Minfil and/or its greater solubility resulting in faster penetration through the vegetation. In both liming treatments there has been little penetration of the lime to depth with < 0.1 t ha^{-1} calcium carbonate equivalents recorded at 5-10cm depth in all treatment plots. This is reflected in the smaller increases in pH in the lower peat horizon (0.5 - 1.0 pH units) relative to the upper 0-5cm peat (2.2 - 3.0 pH units). The Minfil was more effective at raising pH relative to the magnesium limestone in the 5-10cm depth peat, and there were larger increases in the pH of the 0-5cm peat in the higher application plots of both lime types. The pH of the peat in the control plots are 3.0 and 3.1 at the 0-5cm and 5-10cm depths respectively. There has been no treatment effect on cation exchange capacity of the peat relative to the control plots.

Information is available for the Minfil 50 treatment plots only, following the 18 month post-liming sampling. This limited data indicates that application rate (10 to 20 t ha^{-1}) has a significant effect on the timing of the dissolution rate of Minfil 50 but not on the total lime lost over 18 months which was approximately 8 t ha^{-1} for both application rates. Total lime recovered was 2.86 (s.e. Ñ 0.55) t ha^{-1} in the 10 t ha^{-1} plots and 11.58 (s.e. Ñ 1.00) t ha^{-1} in the 20 t ha^{-1} plots.

There has been a change in vegetation composition in all limed plots, one year post-liming. All lime treatments have resulted in a loss of *Sphagnum* spp., *Sphagnum tenellum* showing the greatest loss. *Molinia* cover increased significantly in the magnesium limestone plots with the response increasing with application rate. In contrast, Molinia cover has decreased in the control and Minfil 50 treatment plots. This may be a consequence of increased nutrient availability in the magnesium limestone plots as *Molinia* is known to be able to capitalize on increases in nutrients, particularly phosphate. There has been a decrease in the litter cover in the magnesium limestone plots and an increase in the control and Minfil plots. The removal of grazing in the experimental plots and two dry summers may have resulted in the increase in litter in the control plots. Some species such as the liverworts *Calypogeia muellerana* and *Cephaloziella* spp., characteristic of wetter mires, have declined in lime treated plots. Others such as *Deschampsia flexuosa* and *Hypnum jutlandicum* of drier habitats have increased. Changes in vegetation cover and species composition are likely to become more pronounced with time. *Sphagnum* cover may decline further resulting in space becoming available for the invasion of new species.

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5. CLIMATE AND HYDROLOGY

5.1 Trends in stream chemistry and catchment solute budgets

D.J. Waters, A. Jenkins, and D. Butterfield

5.1.1 Trend analysis

Streamwater quality trends for all major ionic species (pH, Ca, Mg, Na, K, Cl, SO_4, TON, Al, Alk and DOC) were identified for all unmanipulated Llyn Brianne catchments using a modified seasonal Kendal test. This non-parametric technique for trend detection is unaffected by the complicating characteristics associated with time series data, such as non-normal distribution, seasonality, missing values and autocorrelation. At least five years of data is recommended when using the modified seasonal Kendal test, which resulted in seven catchments, i.e. LI1, LI5, LI6, LI8, CI4, CI6 and UC4 with records suitable for analysis.

Table 5.1 shows the trend directions for all the major determinands. pH has increased in all catchments apart from LI8, which is the young afforested catchment approaching canopy closure. It is likely that the combination of increased scavenging of pollutants and maximum uptake of base cations is the reason for a pH decline in the stream water in this catchment. With the exception of Ca in LI8, concentrations of Ca, Mg and Na have increased in all the catchments with most of the trends being statistically significant. The concurrent rise in Cl concentrations implicates an increasing seasalt input to the area. Concentrations of K have remained stationary or have even decreased in the subcatchments. There is no general trend direction for sulphate, with increases and decreases throughout the catchments, however, there is a statistically significant

Table 5.1 Absolute change (mg l^{-1} or pH units) in stream concentrations of major determinands in seven catchments, assessed by a seasonal Kendal test. * indicates significance at $p < 0.05$.

Determinand Data (yrs)	CI4 6	CI6 6	LI1 9	LI5 5	LI6 9	LI8 8	UC4 4
pH	0.12	0.42*	0.15	0.08	0.39*	—0.09	0.75*
Ca	0.49*	0.45*	0.36*	0.45*	0.94	0*	0.81*
Mg	0.36*	0.30*	.27*	0.35*	0.45	0.14	0.61*
Na	1.46*	1.33*	3.59*	1.15*	1.33*	2.21*	1.61*
K	0	—0.06*	0	00	—0.09	—0.12*	—0.03*
SO_4	0.33	—0.21	—0.03*	0.98	0.55	—0.94	0.68
Cl	1.01	1.45*	4.50*	1.50*	0.61	2.00	1.30
Alk	0.45	0.57*	—0.03	0.25	2.11*	—0.08	2.85*
Al	0.02	0	0.12*	0	0	0.06*	0
TON	0	—0.06	0	0.01	0	—0.14*	0
Amm	0	0	0	0*	0	0	0
DOC	—0.38	0.26	0.38	0.05	0	0.40	0.80

decrease in LI1, the mature forested control catchment. The concentration trends for alkalinity are the reverse of pH. Aluminium concentrations are fairly stable with increases in three catchments, which are statistically significant in LI1 and LI8. The direction of the trend for aluminium in LI8 is associated with acidification of the streamwater, however this explanation cannot be used for LI1 which has a rising pH. TON decreases in three catchments and remains stationary in the remaining four. Ammonium concentrations are fairly stable with no trend in any subcatchment. DOC concentration trend directions are variable.

The seasonal Kendal slope estimator gives an indication of the magnitude of the trend which is shown in Table 5.1. The largest absolute concentration changes are for Na and Cl with large alkalinity increases for LI6 and UC4.

5.1.2 Budget calculations

Estimation of accurate catchment solute budgets requires information on quantitative and qualitative atmospheric inputs, and similar data for streamwater outputs. Deriving a water balance for a catchment is often difficult and is frequently hindered by missing data. Wet deposition from bulk deposition collectors can be quantified relatively accurately but estimation of dry deposited materials is poor and is often derived by mass balance calculations based on an assumed conservative component. Some of these problems of data preparation/collation are addressed in the next section.

Data preparation/collation

Rainfall records were supplied by UC Swansea. Ionic concentrations were measured at two locations, weekly quality data are provided at the Trawsnant (Automatic Weather Station) site and daily data at Nant y Maen. Monthly mean concentrations were calculated for both sites. Data generated for Trawsnant was used for LI1 and LI4, and data collated at Nant y Maen provided the qualitative inputs for CI5 and CI6.

Estimation of the output volumes was the most difficult task. Equipment failure and constraints on the stage discharge relationship led to gaps in the data record. Time series models to predict flow from rainfall were derived for each subcatchment, of the form:

$$Q = (-A_1 \times Q_{t-1}) + (B_0 \times R_t)$$

where A_1 and B_0 are estimated parameters, Q_{t-1} is runoff at time t-1 and R_t is rainfall at time t.

This simple modelling technique if considered in conjunction with basic catchment water balance properties provides an efficient method of flow infilling. The model requires daily data for rainfall and runoff and was calibrated on the longest continuous run of data for each catchment. The most appropriate model was chosen on the basis of the adjusted R^2 and other statistical parameters, i.e. residence time and gain. These parameters relate to the physical residence times of water in the catchment and the runoff coefficient, respectively, which were compared with real data. A parameter reflecting catchment wetness was investigated but did not improve the predictive performance of the basic model. After model validation the most suitable model for each subcatchment was used to infill the flow record. These models along with statistical information are given in Table 5.2. The coefficient of determination for each model for each subcatchment varies according to the amount of data available for calibration and validation, and the amount of missing data. Streamwater quality is sampled bi-weekly and is used to derive monthly mean concentrations. One problem is inconsistencies in data resolution/frequency and the possible effects on input and output load estimation. For example, ions which exhibit a strong positive relationship with flow yield the largest errors in mass load (Littlewood, 1990).

Table 5.2 Models selected to infill missing flows for four catchments. A_1 and B_0 are estimated parameters.

Parameter	CI6	CI5	LI1	LI4
A_1	—0.53124	—0.74176	—0.67023	—0.76135
B_0	2.6132	0.6833	5.662	0.2960
Residence Time	1.581 Days	3.30 Days	2.499 Days	3.668 Days
Gain	0.792	0.752	0.646	0.347
R^2	0.82	0.66	0.71	0.47

Input/output loads

Loads are calculated for two different periods, calendar and hydrological years. The latter assumes that water storages in the catchment such as groundwater recharge and accumulated snowfall are constant between time periods. Hence, these figures should give the best estimate for the water balance and, therefore, the most accurate solute budget calculations. The solute budgets shown in Tables 5.3 - 5.6, have not been corrected for sea salts, dry deposition or net nutrient uptake, but were derived from the raw data. Seasalt corrections are often hindered by the lack of a balance between inputs and outputs of chloride, even on an annual timescale. Dry deposition corrections can only be estimated from regional wet/dry ratios, and net nutrient uptake into the forest is not available from these sites. Hence corrections were not applied to the raw data.

The annual wet deposited sulphate input, according to the Trawsnant collector, is largest for the forested catchments, varying from approximately 42 to 92 kg SO_4 $ha^{-1}y^{-1}$. Wet deposited sulphate inputs for the moorland catchments (Nant y Maen collector) vary from 28 to 38 kg SO_4 $ha^{-1}y^{-1}$ and are much less variable. Chloride deposition is very similar to sulphate and variations in input appear to reflect annual differences in rainfall volume rather than variations in annual concentrations. Base metal inputs are very similar with greater wet deposited inputs to the forested catchments. It is quite probable that the overall differences in input between the moorland and forested catchments would be further exaggerated if dry deposited material was considered as it is generally accepted that the mature forest canopy scavenges more pollutants than a catchment primarily under grassland.

Stream water output of the acid anions, sulphate and chloride are much higher for the forested catchments. In general, sodium loads are higher for the forested catchments and as expected the highest output of calcium is for CI5 and LI4, both of which were limed during the latter part of 1987 (section 5.2). Calcium output data for the forested and moorland control catchments indicate no influence of land use type. Potassium and magnesium outputs are also fairly consistent between catchments.

Before discussing the individual solute budgets, the accuracy of the water balance for each catchment should be considered. The most consistent evapotranspiration figures were derived from LI1 and CI6 and this reflects the coefficient of determination of the flow infilling model as well as the limited amount of missing data at these sites. The mean runoff coefficients for the moorland catchments (i.e. CI6 - 70.7%., CI5 - 66%) were higher and an improvement on the forested catchments (LI1 - 65%, LI4 - 55%). Chloride is almost in balance for the moorland catchments reflecting the quality of the flow data and smaller proportion of dry deposition relative to the forested catchments. The output of chloride for LI1 is much greater than the input and suggests the need to correct the bulk deposition inputs with a seasalt and dry deposition component. The data for LI4 suggests a large chloride retention, however, it is probably the poor water balance which accounts for most of the apparent error. The output of sulphate, however, is very consistent between the catchments and suggests sulphate retention or absorption in LI1, considering the much larger inputs. The largest losses of calcium are from the terrestrially

Table 5.3 Annual solute budgets, input and output loads for catchment CI6 for hydrological years (October to September) and for calendar years.

Stream solute outputs (kg/ha/y)

Year	Annual runoff, mm	Ca	Mg	Na	K	SO_4	Cl
87/88	1773	19.24	13.45	59.80	3.08	71.67	102.56
88/89	968	14.04	8.58	38.09	2.52	44.07	54.26
89/90	1417	17.79	11.58	64.63	2.58	58.02	127.78
88	1518	17.74	12.46	56.23	2.84	64.17	97.60
89	915	14.46	8.53	37.18	2.64	42.80	50.95
90	1656	22.12	14.34	76.33	6.21	68.74	154.34

Rainfall inputs (kg/ha/y)

Year	Rainfall mm/year	Ca	Mg	Na	K	SO_4	Cl
87/88	2269	6.02	5.70	50.48	3.56	37.42	99.21
88/89	1533	6.30	4.39	32.78	3.46	28.87	50.56
89/90	1998	5.71	5.74	50.31	4.82	28.90	78.85
88	1961	5.65	4.96	43.85	3.50	35.35	86.27
89	1880	6.73	4.74	36.74	3.41	29.07	58.56
90	1920	5.62	6.11	52.04	4.70	29.62	81.29

Solute Budget

Year	Runoff Coeff	Catchment Loss Kg/ha/y					
		Ca	Mg	Na	K	SO_4	Cl
87/88	78.14	13.21	7.75	9.32	—0.48	34.25	3.35
88/89	63.16	7.75	4.19	5.31	—0.94	15.20	3.70
89/90	70.92	12.07	5.84	14.32	—2.23	29.11	48.94
88	77.42	12.08	7.50	12.38	—0.66	28.82	11.33
89	48.65	7.73	3.80	0.44	—0.77	13.74	—7.61
90	86.22	16.50	8.23	24.29	1.52	39.12	73.06

Table 5.4 Annual solute budgets, input and output loads for catchment CI5.

Stream solute outputs (kg/ha/y)

Year	Annual runoff, mm	Ca	Mg	Na	K	SO_4	Cl
87/88	1920	63.09	12.97	66.51	4.18	90.63	108.67
88/89	1074	29.84	8.53	40.78	2.53	54.22	65.05
89/90	1011	27.83	8.50	48.97	1.95	45.03	100.47
88	1637	49.41	11.84	58.21	3.20	78.12	99.87
89	1031	29.00	8.60	40.29	2.67	52.59	64.21
90	1157	30.94	9.53	56.29	2.18	53.54	114.05

Rainfall inputs (kg/ha/y)

Year	Rainfall mm/year	Ca	Mg	Na	K	SO_4	Cl
87/88	2329	6.19	5.85	51.83	3.65	38.42	101.85
88/89	1572	6.46	4.50	33.61	3.55	29.61	51.86
89/90	2051	5.86	5.89	51.65	4.94	29.67	80.94
88	2013	5.80	5.10	45.02	3.59	36.29	88.57
89	1928	6.90	4.86	37.67	3.49	29.81	60.07
90	1971	5.77	6.27	53.42	4.82	30.41	83.44

Solute Budget

Year	Runoff Coeff	Catchment Loss kg/ha/y					
		Ca	Mg	Na	K	SO_4	Cl
87/88	82.42	56.90	7.12	14.68	0.52	52.22	6.82
88/89	68.32	23.38	4.03	7.17	—1.02	24.61	13.19
89/90	49.29	21.97	2.60	—2.68	—2.99	15.36	19.53
88	81.33	43.61	6.75	13.19	—0.39	41.82	11.30
89	53.47	22.10	3.75	2.61	—0.82	22.78	4.14
90	58.68	25.17	3.26	2.87	—2.64	23.04	30.60

Table 5.5 Annual solute budgets, input and output loads for catchment LI1.

Stream solute outputs (kg/ha/y)

Year	Annual runoff, mm	Ca	Mg	Na	K	SO_4	Cl
86/87	1899	23.07	13.95	84.19	3.35	132.59	151.96
87/88	1507	18.68	11.58	71.92	3.07	103.36	129.39
88/89	1123	15.84	9.72	60.88	2.76	79.42	101.92
89/90	1400	32.53	13.97	90.74	2.58	107.82	162.24
87	1720	21.67	12.60	74.58	2.53	126.14	124.31
88	1364	17.46	10.95	67.62	3.15	93.72	127.30
89	1319	20.58	12.76	76.39	2.99	105.05	124.46
90	1275	29.89	12.16	88.22	2.27	85.92	164.97

Rainfall inputs (kg/ha/y)

Year	Rainfall mm/year	Ca	Mg	Na	K	SO_4	Cl
86/87	2380	20.95	9.42	61.68	8.21	92.82	112.42
87/88	2607	9.98	8.65	68.30	4.41	57.69	121.98
88/89	1778	12.09	5.46	38.99	4.24	44.12	62.03
89/90	2350	11.35	9.14	76.50	5.41	61.79	121.43
87	2101	21.90	7.90	49.56	7.46	86.50	83.30
88	2223	10.14	7.69	60.19	3.85	49.75	107.05
89	2152	11.08	7.33	54.38	4.67	51.17	92.06
90	2224	10.37	7.70	64.96	5.63	58.06	96.26

Solute Budget

Year	Runoff Coeff	Catchment Loss kg/ha/y					
		Ca	Mg	Na	K	SO_4	Cl
86/87	79.81	2.11	4.53	22.52	—4.86	39.77	39.54
87/88	57.78	8.70	2.93	3.62	—1.34	45.67	7.41
88/89	63.20	3.75	4.26	21.89	—1.48	35.30	39.89
89/90	59.56	21.18	4.65	14.24	—2.83	46.03	40.80
87	81.86	— 0.23	4.71	25.02	—4.93	39.64	41.00
88	61.37	7.32	3.27	7.43	—0.71	43.97	20.25
89	61.30	9.51	5.43	22.01	—1.68	53.88	32.40
90	57.32	19.52	4.46	23.25	—3.37	27.86	68.72

Table 5.6 Annual solute budgets, input and output loads for catchment LI4.

Stream solute outputs (kg/ha/y)

Year	Annual runoff, mm	Ca	Mg	Na	K	SO_4	Cl
86/87	983	19.16	7.46	37.51	2.40	71.23	65.18
87/88	774	40.73	6.59	32.63	1.43	60.72	56.27
88/89	1134	68.43	11.42	54.68	3.33	97.86	89.46
89/90	1781	81.12	18.15	94.97	3.41	133.28	186.09
87	875	19.58	6.70	33.23	1.68	67.00	54.23
88	660	43.11	5.80	29.09	1.12	52.33	49.90
89	1522	81.64	14.24	70.61	4.04	122.13	118.89
90	1353	62.78	15.00	76.32	2.71	105.08	153.10

Rainfall inputs (kg/ha/y)

Year	Rainfall mm/year	Ca	Mg	Na	K	SO_4	Cl
86/87	2306	20.30	9.12	59.76	7.96	89.93	108.92
87/88	2526	9.67	8.38	66.17	4.27	55.89	118.18
88/89	1722	11.71	5.29	37.78	4.10	42.75	60.10
89/90	2283	11.01	8.88	74.29	5.25	59.96	117.89
87	2036	21.21	7.65	48.02	7.23	83.81	80.71
88	2154	9.82	7.45	58.32	3.73	48.20	103.71
89	2085	10.73	7.10	52.68	4.53	49.58	89.19
90	2160	10.06	7.48	63.12	5.47	56.35	93.50

Solute Budget

Year	Runoff Coeff	Catchment Loss kg/ha/y					
		Ca	Mg	Na	K	SO_4	Cl
86/87	42.61	—1.14	—1.66	—22.25	—5.56	—18.70	—43.74
87/88	30.65	31.06	—1.80	—33.55	—2.84	4.83	—61.91
88/89	65.87	56.72	6.13	16.90	—0.78	55.12	29.36
89/90	78.01	70.12	9.27	20.68	—1.84	73.32	68.20
87	42.98	—1.63	—0.95	—14.79	—5.55	—16.81	—26.48
88	30.66	33.29	—1.64	—29.23	—2.61	4.13	—53.81
89	73.01	70.91	7.13	17.92	—0.48	72.55	29.70
90	62.63	52.72	7.52	13.20	—2.75	48.73	59.59

limed catchments as expected. Output of calcium from the moorland control catchment is greater than for the forest control, which is probably explained by enhanced net nutrient retention in the forested catchment. Potassium appears to be retained in all years regardless of the land use type. Sodium losses are greatest from the mature forest catchment which again probably reflects the larger seasalt input. The magnesium budget on the other hand is similar for each catchment.

5.1.3 Conclusions and future research

Some basic differences in the solute inputs, outputs and budgets have been identified from the raw data. Unfortunately the amount of missing data for LI4 and the ability of the flow infilling model to reproduce an accurate annual water balance, impaired its budget calculation. Future research should attempt to quantify the additional pollutant inputs such as dry and seasalt deposition and catchment storages, particularly net nutrient uptake into the vegetation. Once these inputs can be quantified the solute budgets can be adjusted accordingly.

Reference

Littlewood, I. (1990) Estimating loads transported by rivers. Department of the Environment report, contract no. PECD 7/7/317, 89pp.

5.2 Effects of Liming

5.2.1 Introduction

Details of the CI3 and LI2 experiments were discussed in Edwards et al (1990), while most of the remaining information was presented by Jenkins, Waters and Donald (1990), Waters et al (1991) and Forestry Commission (1991). As shown in section 5.1, some trends in stream chemistry independent of catchment manipulations were detected during the project. However, changes in reference catchments (Figures 5.1 and 5.4) were greatly exceeded in magnitude by the responses to catchment liming in CI2, CI5 and LI4 (Figures 5.2, 5.3 and 5.5).

5.2.2 Source area and total liming of moorland catchments (CI2, CI5)

The whole 34 ha catchment of CI5 was limed at nearly 9 t ha^{-1} in September 1987. Treatment raised mean pH from 5.2 to about 6.4, calcium from 0.9 to 2.8 mg l^{-1}, and reduced aluminium concentrations from a mean of 0.16 mg l^{-1} to 0.06 mg l^{-1} (Figure 5.2). Acid episodes were eliminated, high pH being maintained at all flows (Jenkins, Waters and Donald 1991, Figure 5.6). The initial peak in calcium concentrations may have been due to calcium saturation of the surface soil layers so that excess calcium was flushed rapidly into the stream. Lime deposited into or adjacent to the stream channel may also have been responsible.

Source areas in catchment CI2 were limed in June 1988. The areas were identified by topographic data, using a hydrological model (TOPMODEL; Waters et al, 1991). For any point, the ratio of the area drained per unit contour length to the slope gives an index of saturation. Thus points with low gradient which drain large areas have high index values and will be saturated frequently. These are 'hydrological source areas', though the value of the index used to classify them depends on individual catchment morphometry and is determined subjectively. The use of vegetation characteristics to indicate source areas is an alternative method which is being developed.

Target liming in CI2 raised stream pH from a mean of 5.1 to pH 6.7 (Figure 5.3). The treatment was again effective in eliminating acid episodes, as high pH occurred at all flows (Figure 5.1). Calcium concentrations increased from 0.7 mg l^{-1} before to 4.5 mg l^{-1} after liming. Mean aluminium concentrations before liming were 0.15 mg l^{-1}, falling to 0.11 mg l^{-1} but still exhibiting peaks of around 0.2 mg l^{-1} after liming. Stream pH after 30 months declined to around pH 6, but further data are required to establish the time course of reacidification.

Calcium losses from the catchments have been estimated from mean concentration in stream water and flow (section 5.1, Waters et al, 1991). In CI2 (source area liming), the pre-treatment export of calcium was 14 kg ha^{-1} $year^{-1}$, or 0.75 t $year^{-1}$ for the entire catchment. Liming increased these values to 85 kg ha^{-1} $year^{-1}$ and 4.6 t $year^{-1}$, the enhanced output in the first year representing c.12 % of the calcium added as limestone.

In CI5 (whole catchment liming), the change in calcium export was slightly less than in CI2, increasing from 14.8 to 59.9 kg ha^{-1} $year^{-1}$. This loss was equivalent to only 0.5 % of the calcium added to the catchment. Clearly, much of the limestone was placed in areas which contribute little to the stream flow, and therefore it will be leached only slowly in comparison to that in wetter source areas.

5.2.3 Pelletized liming of forest source area (LI3)

Bankside felling in catchment LI3 in 1983, before the current project, had no apparent effect on stream chemistry. The pelletized chalk application was carried out in November 1988. Fifteen percent of the catchment was treated in three separate blocks, two of which were on peaty gley soils and one a bog with *Molinia* and *Juncus*.

Within 4-5 months, soil lysimeters at 5cm depth showed an increase in soil water pH from pH 3.7 to pH > 6. At 15cm depth where the pre-treatment pH was below 4, from 7 months onwards the pH fluctuated from about pH 4 to greater than pH 6. At 30-50 cm there was no change in the pH of soil waters. Calcium concentrations parallelled the variations in pH, increasing from less than 1 mg l^{-1} to over 10 mg l^{-1} at a depth of 5cm. Aluminium concentrations showed little clear response to liming.

Of five small streams in the upper catchment, changes in chemistry occurred only in the stream draining the bog area. This showed intermittent increases in pH, mainly during dry periods. There was no evidence of significant effects in the main LI3 stream. This treatment failed probably for two main reasons. First, the chalk pellets, designed to penetrate the tree canopy, showed poor disintegration so that dissolution was inadequate. Secondly, the proportion of the hydrological source areas treated may have been too low, and the areas targetted not dominant sources for the stream. It should be noted that the aim of avoiding damage to the canopy was achieved, with no detectable influence on needle growth.

5.2.4 Source area liming of a forest catchment (LI4)

100 tonnes of limestone was spread over 4 ha of the upper catchment, and a further 20 tonnes to a small primary source area in November/December 1987. This treatment has now been monitored for over three years. Mean pH increased from 5.2 to 6.5, calcium from 2.6 to 6.5 mg l^{-1}, and filterable aluminium decreased to less than 0.1 mg l^{-1} (Figure 5.5). However, as reported previously, during low flows stream chemistry became more acidic with spikes in aluminium concentrations, apparently due to the increased influence of untreated sources in the lower catchment (Figure 5.6).

Three years after treatment, pH values are still well above pH 6, calcium concentrations have declined but are still c.4 mg l^{-1}, whilst aluminium continues to exhibit marked peaks in concentration.

In the year 1 October 1986 to 30 September 1987, the calcium budget for the catchment was -1.1 kg ha^{-1} yr^{-1} (section 5.1) . After liming, in 1988, 1989 and 1990, the net solute export was respectively 33, 71 and 53 kg Ca ha^{-1} yr^{-1}. The relative contributions to calcium export of the lime spread over the 4 hectares or the 20 tonnes dosed to the small, wetter source area are not clear. If only the latter 20 tonnes are being leached to the stream, the quoted net values are equivalent to about 5, 11 and 8% of the calcium added as limestone.

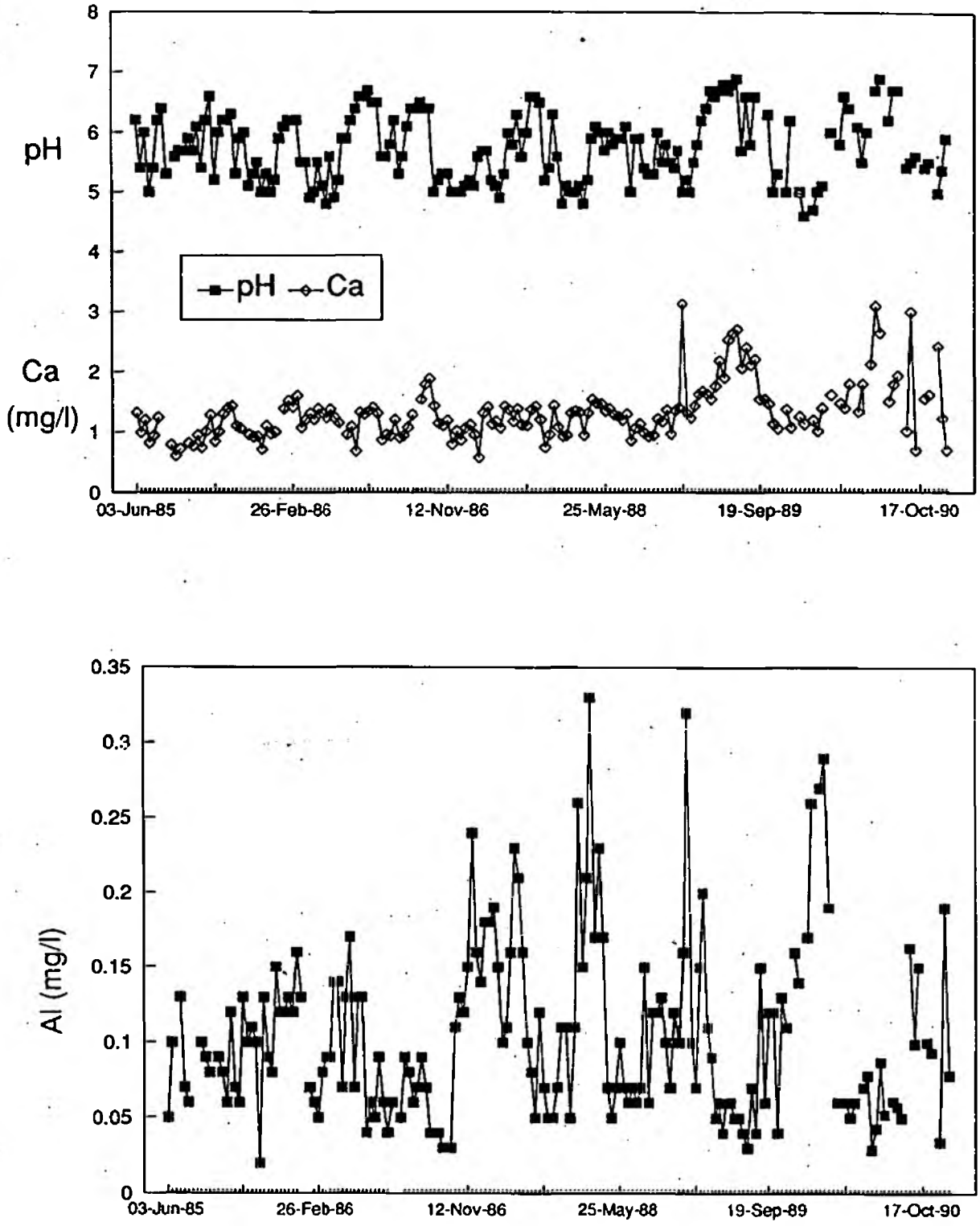
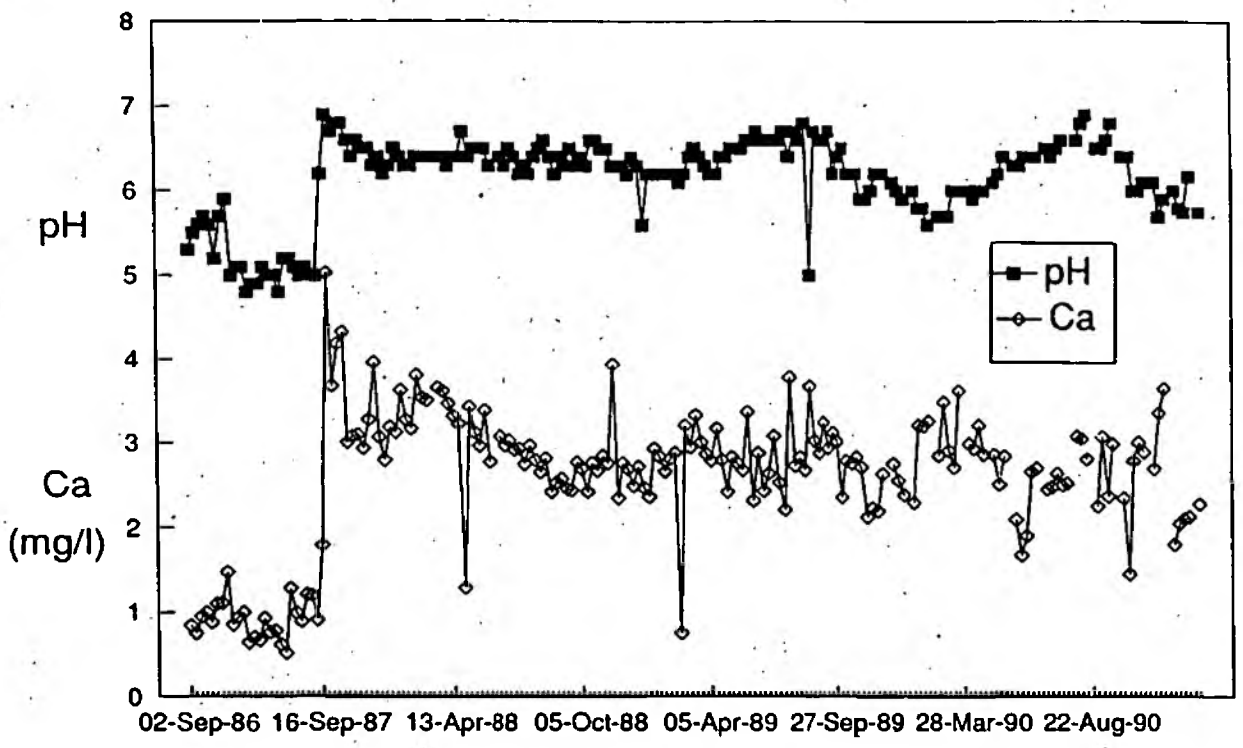


Figure 5.1 Spot sampled pH, calcium and aluminium concentrations in reference stream CI6, with an unmanipulated moorland catchment, 1985-1990.



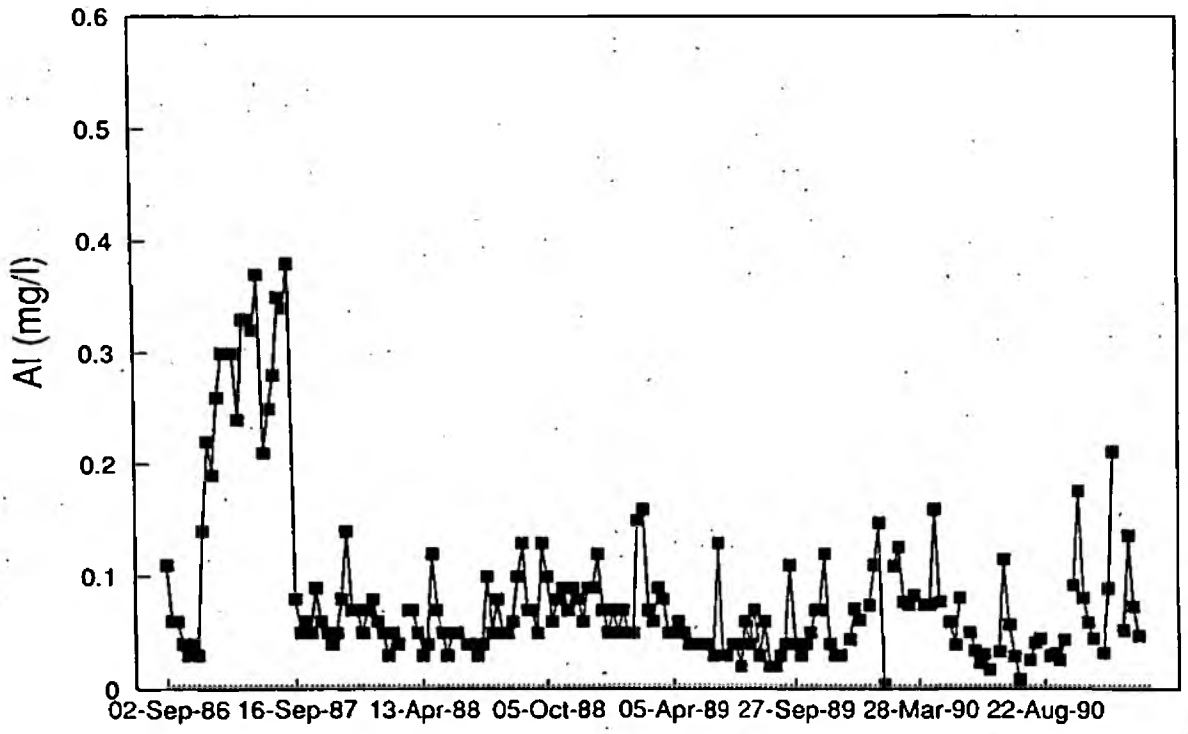
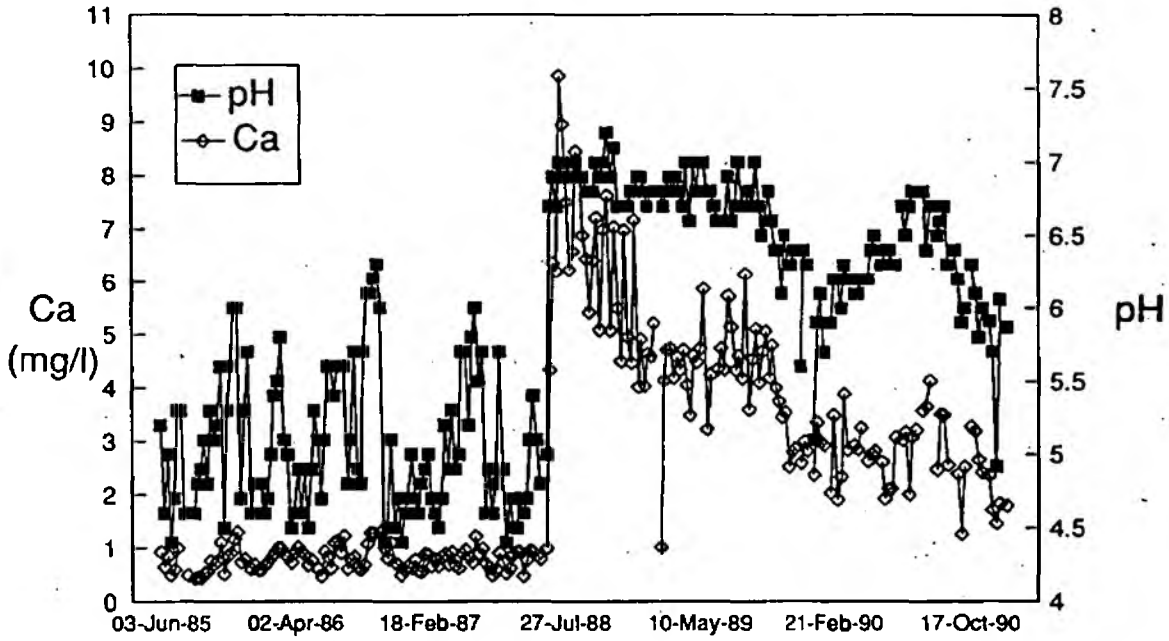


Figure 5.2 Spot sampled pH, calcium and aluminium concentrations in moorland stream CI5, 1986 - 1990. The whole catchment was limed in September 1987.



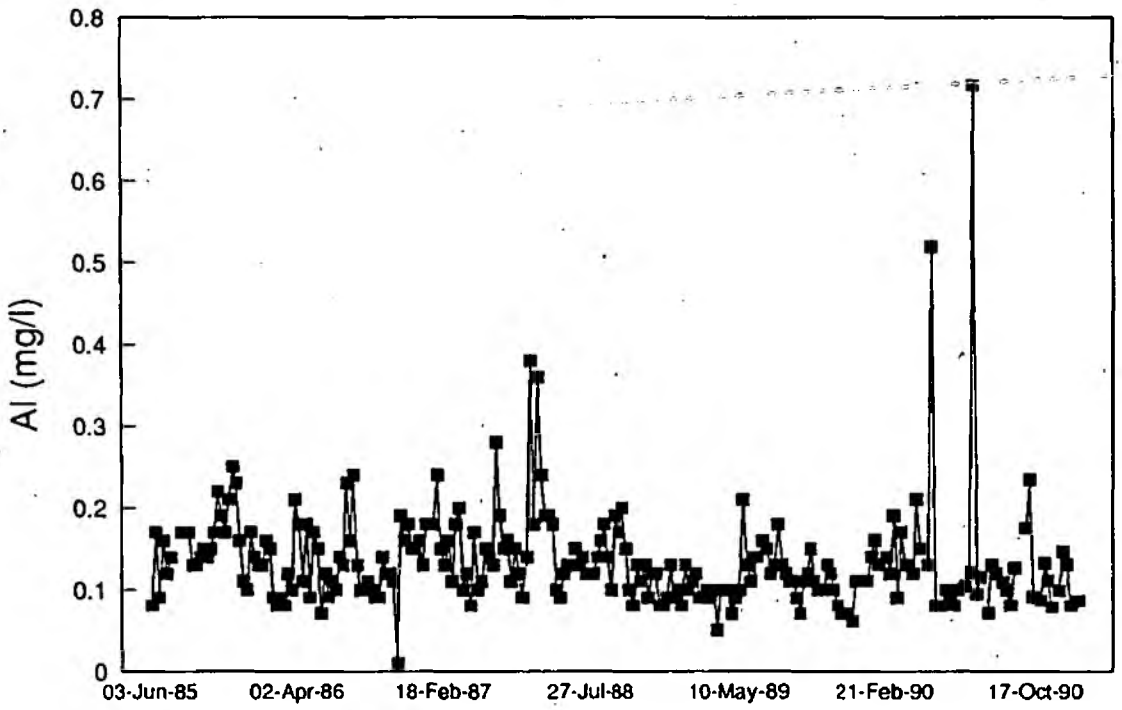
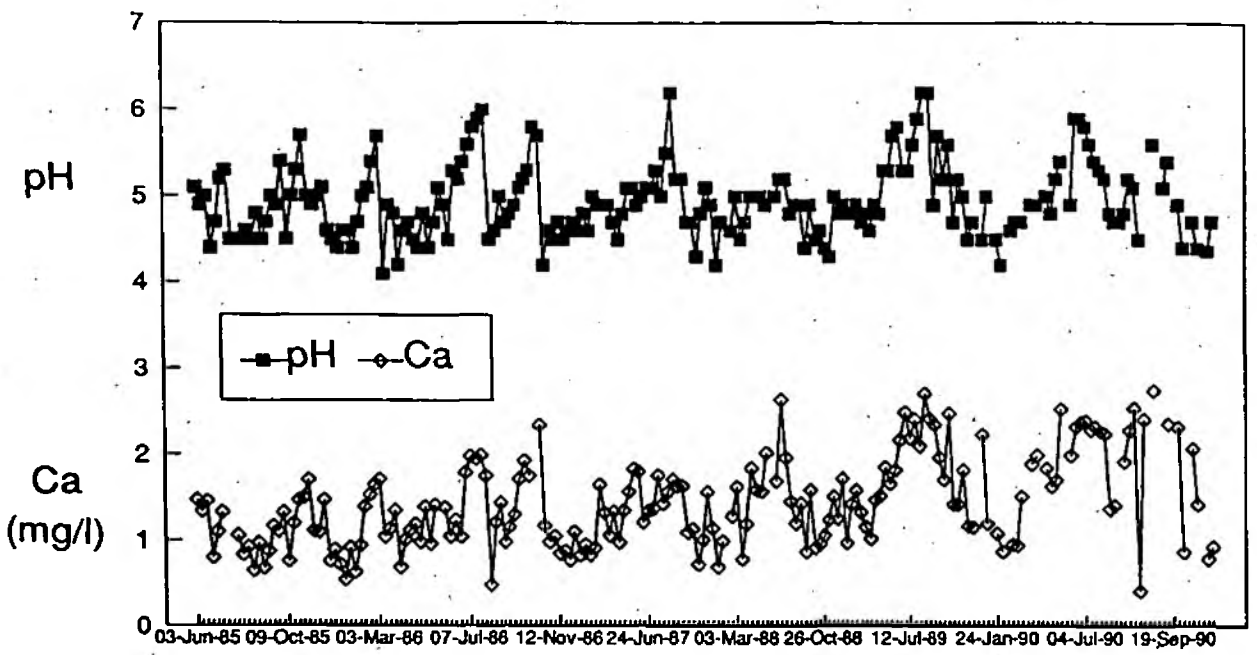


Figure 5.3 Spot sampled pH, calcium and aluminium concentrations in moorland stream CI2, 1985 - 1990. The hydrological source areas were limed in June 1988.



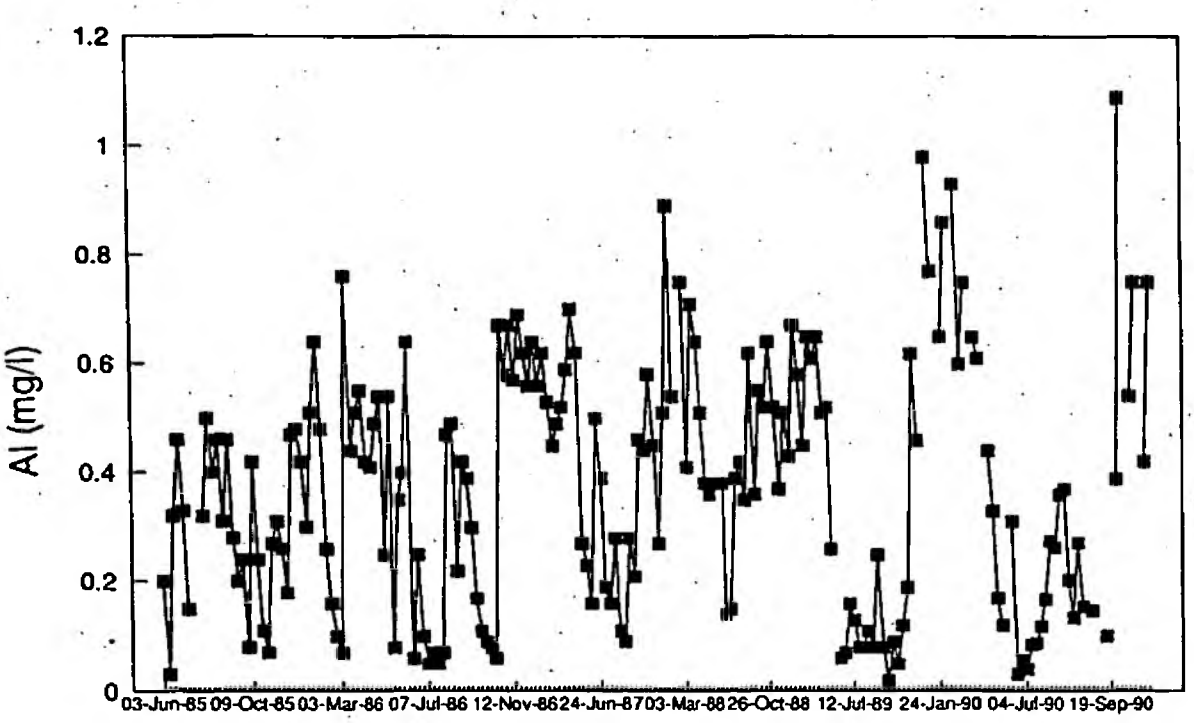
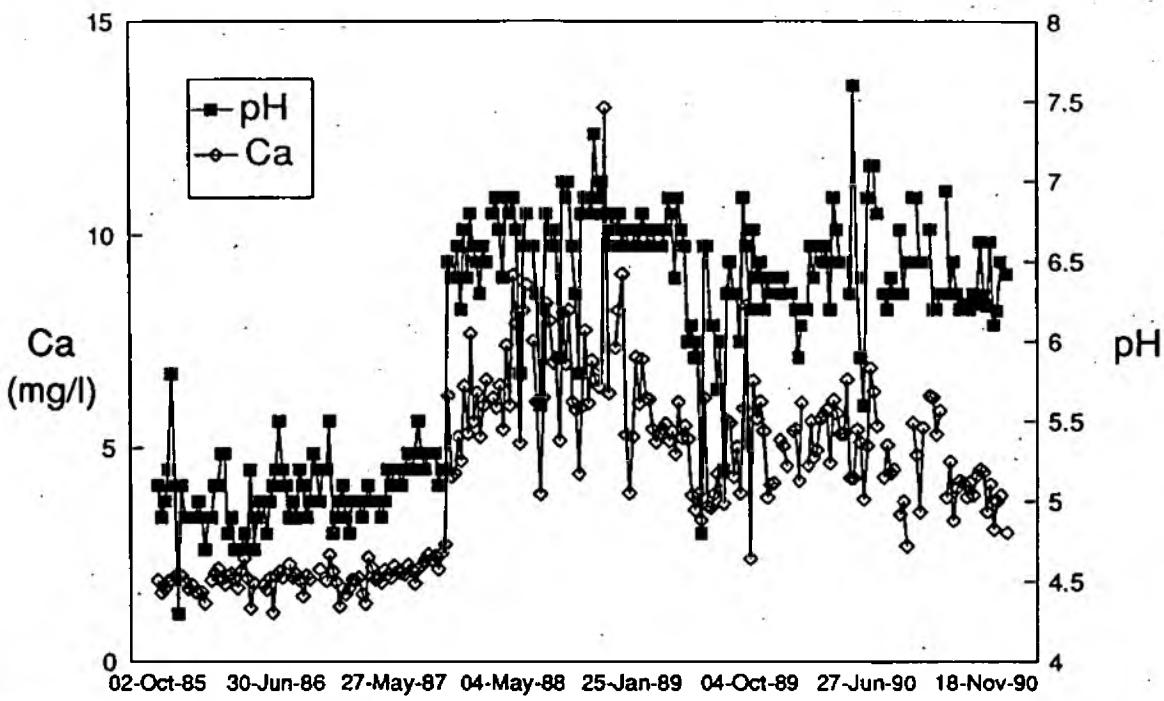


Figure 5.4 Spot sampled pH, calcium and aluminium concentrations in reference stream LI1, with an unmanipulated afforested catchment, 1985 - 1990.



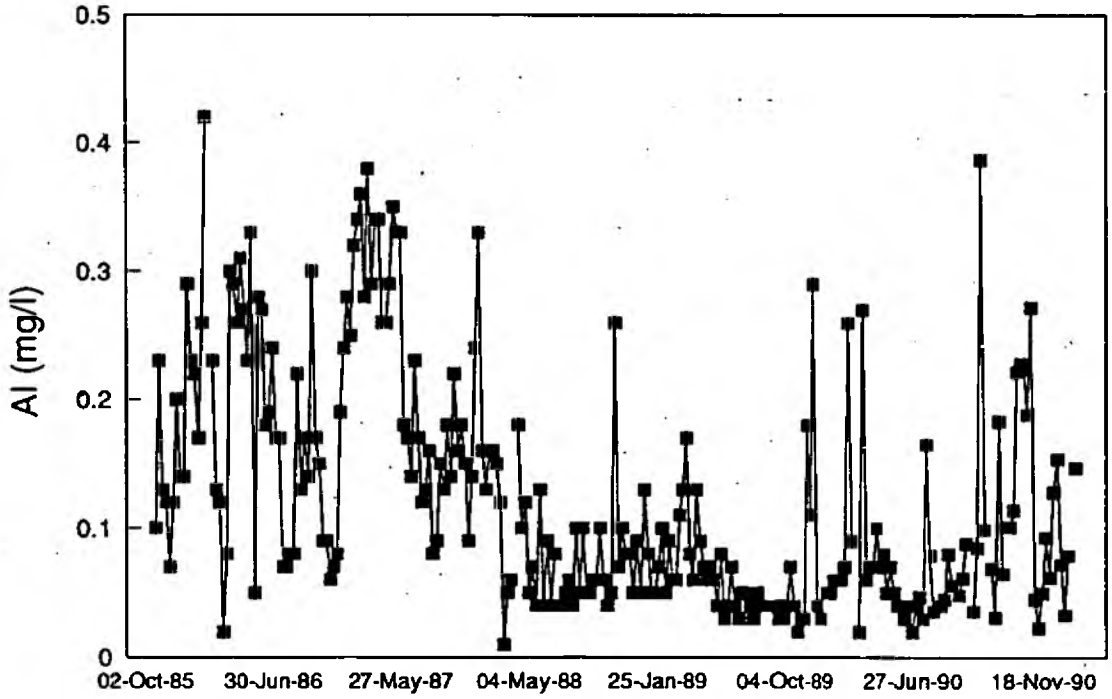


Figure 5.5 Spot sampled pH, calcium and aluminium concentrations in forest stream LI4, 1985 - 1990. The hydrological source areas were limed in December 1987.

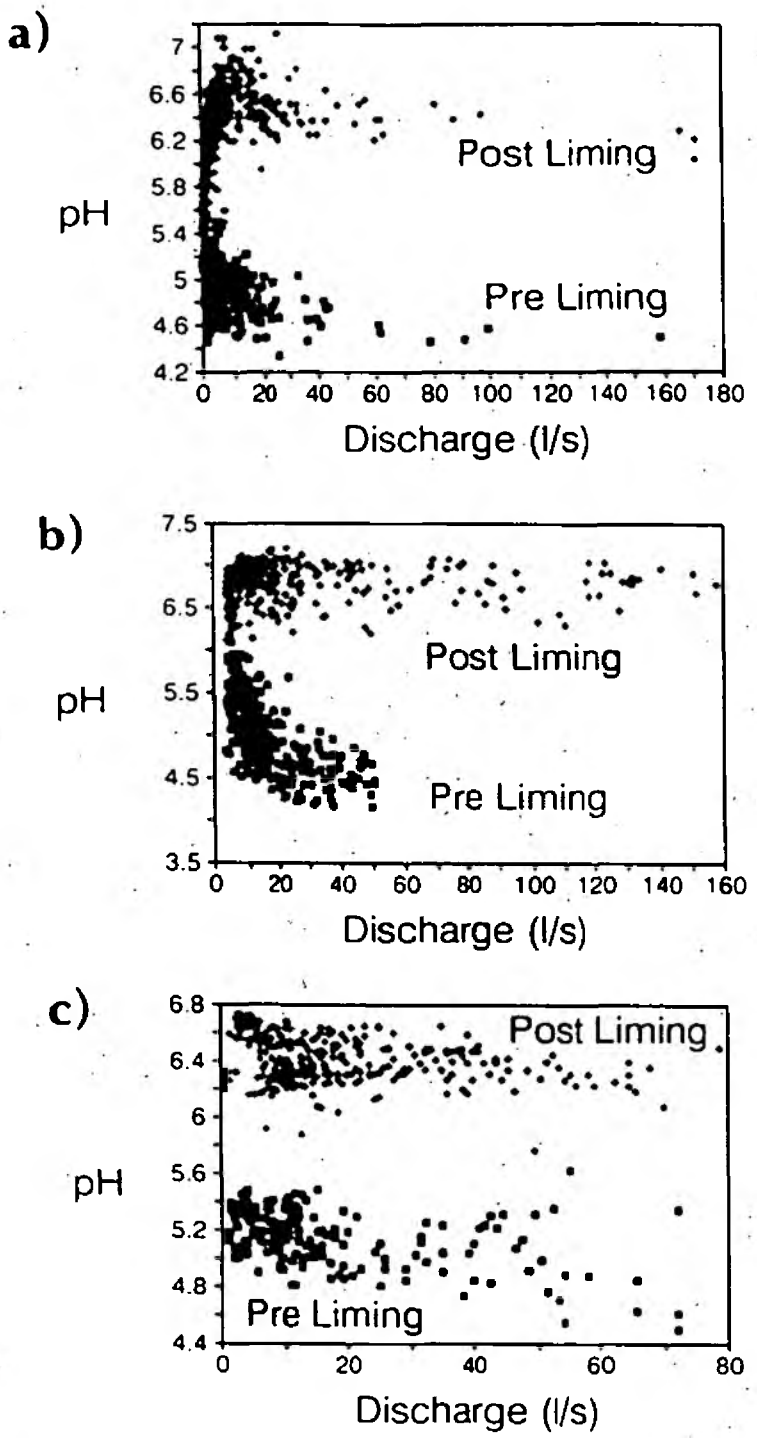


Figure 5.6 Maximum daily flow against minimum daily pH for one year before and one year after treatment at a) afforested catchment L14, source area limed, b) moorland catchment CI2, source area limed, c) moorland catchment CI5, whole catchment limed.

5.2.5 Synopsis of catchment liming experiments

Results from the experimental catchment manipulations at Llyn Brianne, in conjunction with other studies, have provided much information on the effects of land management on surface waters. The method of applying limestone determines its fate and consequently its effect on surface water chemistry. Unless lime is placed on hydrological source areas, it will not be leached at a rate sufficient to influence stream chemistry. Thus the project found no evidence that standard agricultural liming will have marked effects on surface water acidity. Similarly, the felling and liming of banksides in a forest catchment (LI2), had negligible impact on water acidity as the treated banks were not significant source areas.

The potential to reduce costs by liming source areas instead of whole catchments in order to neutralize surface waters, is demonstrated by the comparison between CI2 and CI5. For a similar result, source treatment involved less than 10% of the catchment and 17% of the limestone (per hectare of catchment) used in the whole catchment treatment. Full economic evaluation will require the necessary frequency of treatment to be known. Continued monitoring of the experimental catchments is therefore necessary. Prediction of the duration of effects may also be made by modelling techniques which may be applied to Llyn Brianne sites in the future. The Soil Liming Model (SLIM, Warfvinge and Sverdrup, 1988) describes limestone dissolution and run-off in acid soils, and simulations at Loch Fleet suggest that target liming could last up to a decade.

The role of source area liming in any strategy to ameliorate acidification also depends on the implications for the flora and fauna of acidic wetlands. Impacts of liming on the conservation value of these sites must be taken into account.

5.2.6 Reference

Warfvinge, P. and Sverdrup, H. (1988) Soil liming as a measure to mitigate acid runoff. Water Resources Research, 24, 701-712.

5.3 The influence of forestry

Previous studies relating forest presence to stream acidity and aluminium concentration were based on small numbers of catchments, often precluding the elimination of confounding influences on stream chemistry such as geology or soil type. Spatial patterns in aluminium and pH data from 113-136 Welsh catchments of contrasting land use were therefore analysed in three different ranges of acid sensitivity (< 10, 10-15, 15-25 mg $CaCO_3 l^{-1}$ total hardness; Ormerod, Donald and Brown 1989). In each range, pH declined and aluminium increased significantly with increasing percentage forest cover. There was no evidence that the relationships reflected a spurious effect of forest location, nor soil type. Where aluminium concentrations were elevated under forest in a sub-set of 13 streams, aluminium was present predominantly in the labile form which is the most toxic to fish.

The trend analysis (section 5.1) of stream chemistry in catchment LI8, with a forest approaching canopy closure, is consistent with these spatial analyses. In comparison with other catchments at Llyn Brianne, the LI8 time series indicates a progressive acidification and aluminium mobilization due to conifer afforestation in the catchment.

5.4 Sampling methodology

Four different methods of streamwater sampling have been operating simultaneously for several years in 4 catchments around Llyn Brianne. Other catchments have been monitored by 3 methods.

This study sought to determine whether or not any of the following methods were unecessarily duplicative:

1. SPOT sampling
2. INTEGRATED samplers
3. AUTO-samplers
4. CONTINUOUS monitoring

It was first established that:

- each stream needed to be monitored individually, since its chemistry could not accurately be estimated from the behaviour of another

- relationships between the chemical determinands were not strong enough to allow a predictor (derived from other determinands) to substitute for actual measurement of any determinand.

The continuous values for pH and conductivity compared reasonably to the spot samples. Differences in annual mean values did not exceed 0.28 pH units or 11 $\mu S\ cm^{-1}$ conductivity, and standard deviations were similar. Correlation between the 2 methods ranged from .548 to.953 for pH, and .476 to .897 for conductivity.

Integrated samplers should have shown results similar to the averages of flow-weighted values from the continuous monitor. At 2 sites pH means and standard deviations were very close between the two methods, but at the other 2 sites the discrepancy was about 0.4 units. Correlations between pH values from the two methods fell between 0.968 (at LI3) and 0.355; for conductivity, correlations ranged from 0.825 to insignificant (LI3). The maximum annual mean difference between integrated and (flow-weighted) continuous conductivity was 9.7 $\mu S\ cm^{-1}$.

Autosampler results should match the corresponding continuous monitor values. The pH of sampled water at LI3 was well corroborated by continuous values, but the same comparison at C2 showed no significant correlations in any of 3 events. The relationship between spot and integrated samples was also important, especially for Ca and Al, since they were not monitored continuously. Spot data provided slightly better estimates of integrated pH and conductivity than could be derived from complex manipulations of continuous data. Annual mean differences between spot and integrated calcium concentrations did not exceed 0.3 mg l^{-1} at 3 sites. Correlations between spot and integrated aluminium were similar to those for calcium, but systematic differences between the methods were marked. At CI2 the annual means were 126 and 75 $\mu g\ l^{-1}$ Al respectively, and at LI3 they were 299 and 175 $\mu g\ l^{-1}$ respectively.

In summary, consistency between sampling methods was variable between sites. Thus it is difficult to specify whether any elements of the sampling procedures used in this study could be discontinued. Decisions could only be made on a site-specific basis. Some of the discrepancies revealed are probably due to technical problems not recognized at the time, but others could be explained by appreciation of the local conditions in each catchment.

6. HYDROCHEMICAL MODELLING

A. Jenkins, D. Waters, A. Robson and I.G. Littlewood

6.1 Introduction

An important link between acidic oxide emissions and ecological impact is the transmission of acidity from land and vegetation surfaces to streams and lake waters. Soil, therefore, represents an important controlling factor since the chemical status of the soil matrix and the pore water greatly influence surface water quality. Soil also accumulates changes induced by the addition of pollutant through time and largely determines the travel time of water and ions moving through the system. The system behaviour through time reflects an extremely complex interaction of reactions and feedbacks centred on the soil. To estimate the rate and magnitude of acidification and the likely recovery under different deposition reduction and land management scenarios, it is necessary to incorporate representations of the major processes within this system in mathematical models.

The formulation and validation of short-term event based, essentially hydrologically driven models and long-term, essentially chemically driven, hydrochemical models at several sites in Wales, including most of the Llyn Brianne sub-catchments, was undertaken early in this study and is fully described by Whitehead et al (1990). Since then, modelling work has continued in an effort to address both the long term prognosis for surface water acidification status and to increase our understanding of, and ability to predict, stream chemistry response to short term precipitation input. The work has followed three main lines of study:

1. Assessment of future response of surface water chemistry across a large area of Wales.

2. Assessment of the effects of afforestation on long term stream water chemistry.

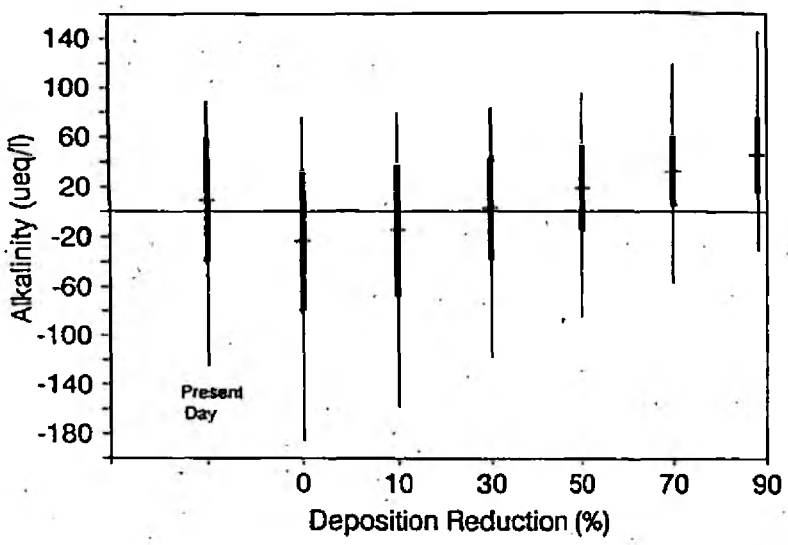
3. Development of new modelling techniques to predict episodic behaviour over long time periods i.e. a link between long and short time scale models.

6.2 The Regional Acidification Model

The MAGIC (Model of Acidification of Groundwater in Catchments) model has been adapted for modelling on a regional basis through the introduction of Monte Carlo techniques which assimilate regional variability. For example, weathering rates for base cations, soil depths and porosities, rainfall, cation exchange capacities, exchangeable base fractions on cation exchange sites and chemical inputs from precipitation vary across the region. In the model these factors are each represented by a model parameter and the Monte Carlo technique allows the parameter to vary across a wide range. Then for each of a large number of model runs, random values of the parameters are drawn from the previously defined observed distribution of these parameters. A large number of runs are then undertaken and those which produce a present day chemistry which falls within the defined distribution windows are kept as successful runs. When a sufficiently large number of successful runs have been accumulated the calibrated set of model runs has a distribution of chemistry that matches the distribution of the observed equivalents. The model calibration and validation is based upon a regional survey of surface water chemistry at 130 sampling sites across Wales undertaken during 1983/84. A full explanation of the technique and a detailed discussion of the results is presented in Jenkins et al (1990).

The regional model application gives a good match between predicted and observed water chemistry across the region. The historical change in water quality, simulated by the model, shows that since 1844 (pre-industrial times when acidic deposition is assumed to have been very low) mean pH dropped from 6.4 to 5.6 and alkalinity from 63 to 3 $\mu eq l^{-1}$.

More recent work has involved using the accepted model parameters from the successful calibrations, in an attempt to assess the ability of the region to recover from acidification. In this respect, the regional model lends a unique opportunity to assess the critical load concept as a tool for determining deposition reduction strategies which will enable recovery of the acidified surface waters and thereby protect the aquatic ecosystem from further damage. The effect of a range of deposition reduction scenarios on the regional distribution of pH and alkalinity is shown in figure 6.1. All of the deposition reduction scenarios relate to a uniformly sloped decrease to year 2000 and thereafter held constant at that level to 2034. Clearly a 30 - 50% reduction in acidic deposition would be required to maintain the 1984 distribution of water chemistry, but this is not acceptable under the critical load concept since many waters that have been historically impacted are still below the conventionally used target chemistry for brown trout i.e. positive alkalinity. At 70% deposition reduction the model simulations indicate that mean alkalinity in



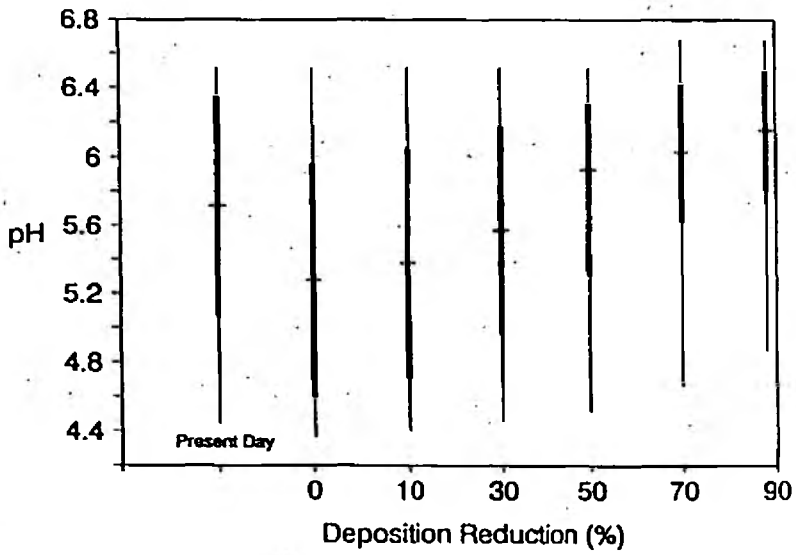


Figure 6.1 Forecast stream alkalinity and pH (mean, standard deviation and extremes of the distribution) in streams of the regional Welsh survey under a range of acidic deposition reduction strategies.

the region will be 29 $\mu eq\ l^{-1}$ with standard deviation 19 $\mu eq\ l^{-1}$ indicating that all but about 16% of surface waters would be protected. For a 90% reduction the model predicts that nearly all waters in the region will reach positive alkalinity although some extreme outliers of the distribution remain below zero. The implication is that the critical load at which the most sensitive surface water site will be protected cannot be met. Therefore the level of deposition reduction to the target load, which will be greater than the critical load, will have to be based on some percentage of surface water protected.

6.3 Modelling The Effects of Afforestation

Quantification of the impact of afforestation on surface water acidification has been attempted using paired catchment studies and long term monitoring. Paired catchment studies are beset by problems in determining the true comparability of soils, bedrock, hydrological response and planting history whilst long term records are difficult to interpret in the light of forest growth occurring over a time period when deposition of acidic oxides has been falling (i.e. 1980 - 1988). In an attempt to integrate all of the possible forest responses and determine the prognosis for surface water acidity at afforested sites, a modelling study was undertaken at LI8 (Waters and Jenkins 1991). This catchment was planted over 94% of its area between 1971 and 1977.

The application of the MAGIC model utilized 10 years deposition data, estimates of base cation uptake sequences and estimates of dry deposition to the forest canopy. Until afforestation in 1971 the site was under moorland vegetation and a water yield of 90% was assumed. This figure is consistent with other model applications to moorland sites in Scotland and with observed data from the moorland catchments at Plynlimon. Following planting in 1971 a 20 year growth period was assumed before canopy closure, during which time evapotranspiration increases linearly with age of the forest. At the point of canopy closure, evapotranspiration was assumed to be at its maximum and a water yield of 75% was chosen. Historical loading to the catchment for use in the reconstruction was derived in two stages. First, historical loading of wet deposition was assumed to follow the sequence of emissions described by the Warren Spring Laboratory, and second, observed wet deposition data was appended to that sequence from 1980 to the present day. Dry deposition scavenging by the forest canopy was calculated from the long term mass balance for chloride in the catchment and dry deposition in the absence of a forest canopy (i.e. to the moorland prior to 1971) was estimated from calculated dry deposition loads to moorland sites in the area. The estimation of net nutrient uptake by the growing forest is problematic given the difficulties of assessing processes such as crown leaching and below ground turnover. A general pattern was incorporated, however, based on observations that the greatest demand for soil nutrients occurs early in the life of a crop, during crown development and the rapid build up of foliar biomass (Cosby et al 1990).

The MAGIC pH simulation for the past 9 years compares well with observed data from LI8 (figure 6.2). The forecast for the site suggests that stream pH will continue to decline to 5.2 in ten years time, despite deposition being held constant at the 1989 level over that period. The age of forest effects on stream acidity are not, however, identical to those observed at LI1 where at twenty years age the drainage water had a pH of c.4.8. At LI8, simulated pH is 5.3 when the forest reaches 20 years age (1991). This is a direct consequence of the forest growing under a completely different pollution climate, namely much lower levels of acidic deposition during the 10 to 20 year age period.

6.4 Storm event models

The extensive database describing chemistry and rainfall runoff has enabled significant developments to be made in the formulation and validation of short term hydrochemical models. One approach utilizes a chemical mixing model to identify the chemical and hydrological behaviour of catchments (Robson and Neal 1990). The study attempted to identify two chemically

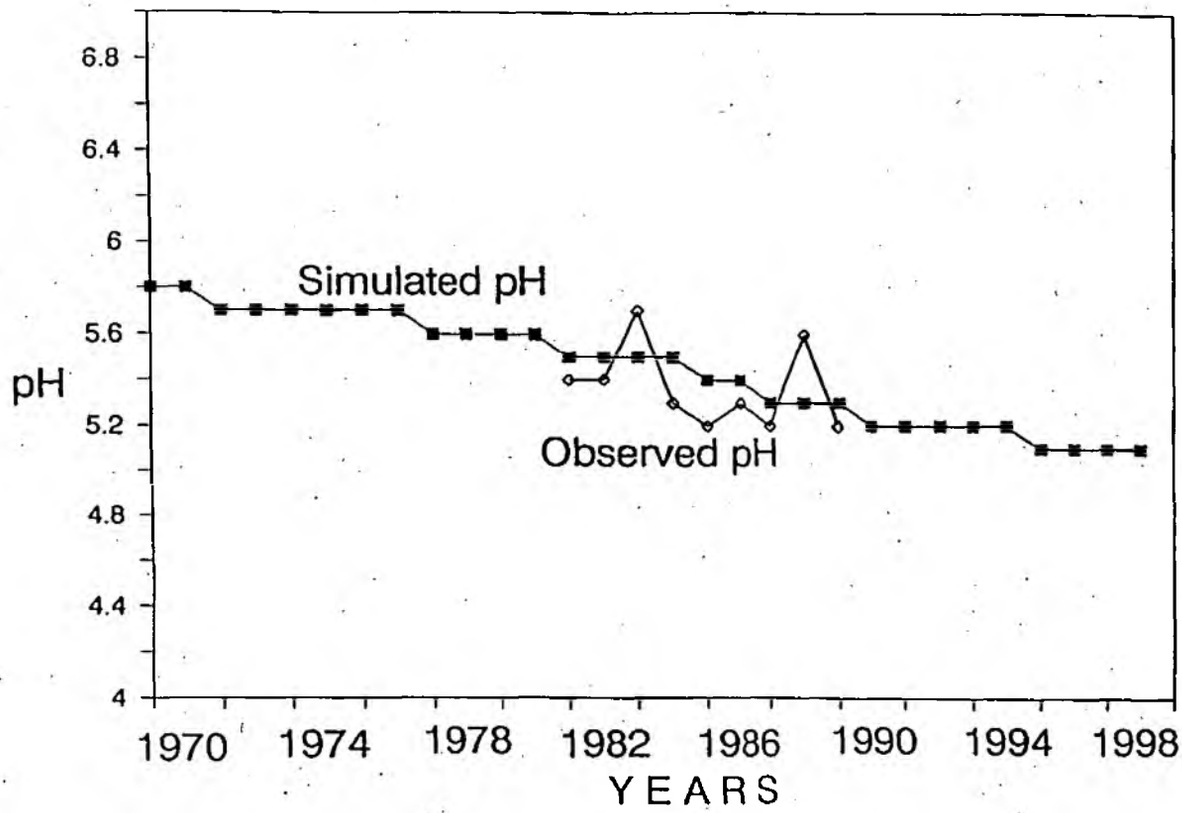


Figure 6.2 Observed and MAGIC model simulated stream pH for LI8 (young forest catchment).

distinct components of flow and used acid neutralizing capacity (ANC) as the chemical tracer. The basic concept being that during mixing ANC acts conservatively since it is not affected by CO_2 degassing or aluminium precipitation. The ANC of the resultant mixture of the two components can, therefore, be calculated as the volume weighted average of the input ANC's. It is assumed that each end-member composition remains fixed throughout the duration of the storm events, and ANC is estimated from the continuously monitored pH measurements at each site, after establishing relationships between aluminium and pH from the weekly spot and storm event samples.

The two component partitioning of runoff water is suggested by the marked difference in chemistry between storm waters and baseflow waters. The storm flow component is assumed to be described by soil water chemistry (sampled) and the baseflow component is assumed to represent deep groundwater, described by stream chemistry during low flow conditions. As a measure of uncertainty in the assumption and sampled soil waters, a range of soil waters were taken based on the ANC measured in different soil horizons. The results show that all four sites studied (CI4, CI6, LI2 and LI8) show a common behaviour. As flow increases the ANC declines, indicating an increased contribution from the soil water, and as flow decreases, the ANC increases indicating increased contribution from the groundwater. The results imply that deep water, as defined here, is a major contributor to stream water and frequently contributes more to the stream than the soil zones (Figure 6.3). More detailed comparison of the behaviour of the four sites indicates that LI2, the mature forested catchment, differs markedly from the others exhibiting a very 'flashy' response and the largest variation in the proportions of deep water (37-83%). In other words, at low flows LI2 has the highest contribution from deep water whilst at high flows it has the lowest deep water component. CI4 and CI6 exhibit similar responses, and given a fixed soil water composition the proportion of deep water does not vary greatly even during stormflow

at CI6. LI8, under juvenile forest, shows similar behaviour to CI6 and CI4. The results further suggest that hydrological pathways are affected by afforestation. The moorland sites show little variation in soil and ground water contributions during storm events compared to LI2. This difference could be explained in terms of rapid runoff along forest ditches.

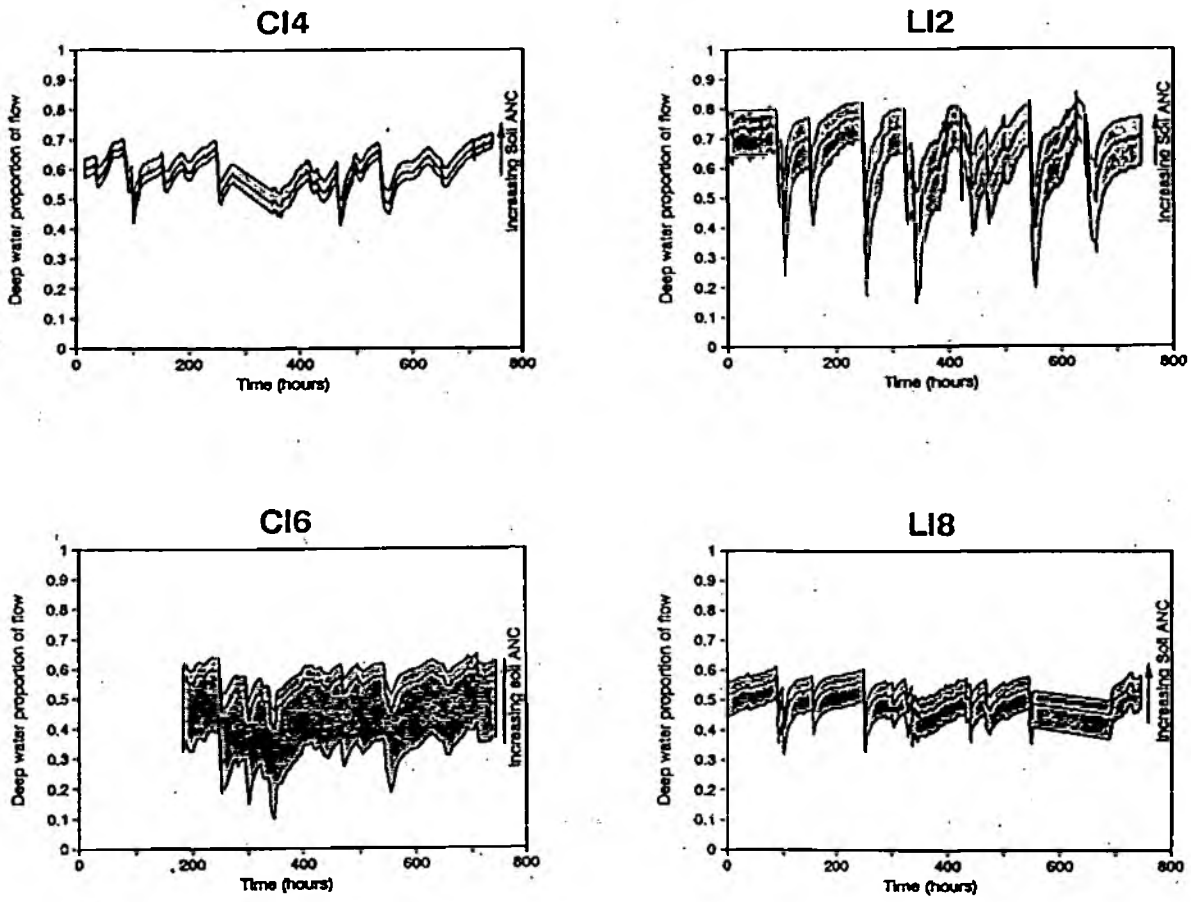


Figure 6.3 The change in deep-water proportion of total flow during August 1985. The shaded area shows the effects of uncertainty in the soil water chemistry.

Overall, this application of mixing analysis demonstrates that these techniques are capable of providing important information describing the predominant hyrochemical processes occurring in the streams and highlights differences in behaviour between the sites. Deep waters, neutralized by reactions with the bedrock, apparently provide a major input to stream flow but the location of large storages of water within the catchments is not known. Equally likely is that the deep water 'signature' is the result of interactions involving rapid water movement and chemical transfers with relatively small storage and so identifying the location and nature of the reaction zones is crucial to understanding the processes.

The importance of understanding the dynamics of long-term acidification of soils and surface waters has been well documented earlier in this chapter and more detailed, event based studies of this sort could improve this understanding. By using a mixing approach in conjunction with a two-box version of MAGIC, representing deep groundwater and soilwater, it is possible to assess the fluxes of water through each box and provide estimates of the mixing proportions as a function of flow. MAGIC can then be run forward in time, under some assumed deposition

scenario, to estimate the changes in the composition of each end-member and thereby allow long term predictions of stream episodic response. Such an analysis has recently been carried out for a stream draining the Plynlimon catchment in mid-Wales (Robson et al 1991, Neal et al in press).

Flow data from the Llyn Brianne sub-catchments have also been modelled using the recently developed rainall run-off model IHACRES (Jakeman et al 1990). In a detailed study of the moorland catchment C16 (Littlewood and Jakeman 1991), this approach confirmed that quickflow is the dominant contribution to stormflow and provides a comparison with the hydrograph separation by the chemical method of Robson and Neal (1990). This result, assessed in conjunction with the chemical mixing model results, implies that some component of the quickflow contribution exhibits well buffered or 'groundwater' chemistry.

6.5 Summary and recommendations for future work

The extensive hydrochemical modelling research carried out within the framework of the Llyn Brianne study has enabled the development, calibration and validation of a broad range of modelling approaches. The major research findings with implications for the region are:

1. Acidification of soils and surface waters will continue at many sites across Wales unless the current levels of acidic deposition are reduced.
2. The critical load for the region as a whole is zero, or very close to zero.
3. Afforestation enhances surface water and soil acidification in sensitive catchments.

From a research point of view the development and validation of the regional MAGIC model represents the most detailed study of its kind within the UK. The validation of the MAGIC model incorporating forestry sequences (for ion uptake, dry deposition and runoff), against ten years of hydrochemical data is the only such validation available to date. In both respects the model apparently captures the dominant processes occurring over long time periods within catchments and represents a useful tool for forecasting future chemical response. The analysis of short term event models has enabled important developments in the identification of hydrochemical flowpaths and mechanisms of streamflow generation. This remains, however, an area in which much work is needed, particularly the monitoring of soil and groundwaters during episodes. A further surface water survey in the future, re-sampling those sites sampled in 1984, would prove invaluable for determining the current acidification status of the region, assessing critical loads and further validating the regional MAGIC model. On a site specific basis, it is imperative that nitrogen dynamics be incorporated into both long term and short term hydrochemical models and this will require continued sampling with high quality chemical analysis together with a major review of existing data.

6.6 References

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7. BIOLOGICAL STUDIES

7.1 Stream macroflora

7.1.1 Relationships with acidity and other variables

Surveys of upland stream macroflora (bryophytes, filamentous algae and angiosperms) have been carried out over a three year period at sites around Llyn Brianne (Richardson, Weatherley and Ormerod, in prep.). Sites were classified using TWINSPAN and communities were related to physical and chemical factors. Acidic streams draining moorland and conifer afforested sites supported a characteristic community dominated by the liverwort *Nardia compressa*. Similarities between the flora of the forestry and moorland sites existed despite significant differences in chemistry, especially aluminium concentrations which are much higher in the forest streams. Streams draining base rich soils or deciduous woodland supported a very different macrofloral community which reflected the higher pH and steep slopes observed at these sites.

7.1.2 Responses to liming

The addition of lime to neutralize acidic sites resulted in the elimination of *Nardia*. Replacement by a more circumneutral flora has not been observed in the short term.

7.2 Stream invertebrates

7.2.1 Relationships to acidity and other variables

In previous work, the effects of acidity on stream macroinvertebrates have been modelled on the basis of empirical relationships between species assemblages and water chemistry. These models allow the type of assemblage or the occurrence of a species to be predicted for sites in the future or in different locations, according to their water chemistry. The necessary chemical information is derived either by sampling or by prediction from hydrochemical models. Recent work in this study has attempted to validate certain aspects of the invertebrate models. This is essential to establish the reliability of the models for determining critical loads of atmospheric pollutants, and of invertebrate taxa as indicators of water chemistry.

The background variation between years in assemblages in unperturbed conditions is central to the application of models derived from only one year's data and to the detection of significant ecosystem change. The constancy of invertebrate assemblages was examined in Llyn Brianne streams in riffle and margin habitats over five years (Weatherley and Ormerod 1990a). Classification and ordination of invertebrate data from unmanipulated streams were highly consistent between years, as were chemical variables related to acidity. Consequently, indicator species and models relating assemblage type to environmental variables in one year, were generally successful in classifying streams or predicting faunal types when applied to other years. The models based on single years were therefore reasonably robust to observed annual variability, though data from more than one year would be useful. Moreover, it was notable that within the five year study period there was some evidence of drift in faunal composition, which could become problematical for model application in the long term.

This study also revealed that persistence, in terms of relative abundance, of invertebrate faunas was lower in marginal samples than in riffles, and that lower persistence in riffles was associated with higher amounts of marginal vegetation. Whilst lower persistence in margins could have been a sampling artefact, it suggested that acidification may be detected more readily in riffles, but emphasized the potential importance of marginal habitats.

A further concern over the reliability of the biological models is their dependence on annual means of chemical variables. This constrains the models to ignore short term variations in chemistry, which are often severe in acidic streams and known to influence the biota. We therefore used data from the 1984 Welsh regional survey to explore relationships between invertebrate assemblages or trout densities (section 7.3) and measures of variation in pH and aluminium concentrations (Weatherley and Ormerod 1991a). The key result was that variability in pH and Al were closely related to mean pH and Al respectively (Figure 7.1), so that the biological influences of episodes could not be separated easily from those of the long term conditions. Variables describing episodicity, such as minimum pH, gave only moderate increases in precision when included in multivariate models of invertebrate assemblages, whilst mean Al was more effective than mean pH. For modelling purposes, it is therefore reasonable to use means of chemical variables in the case of macroinvertebrates, provided that enough sampling effort is applied to give adequate model calibration. Simulated chemical sampling suggested that 2-weekly samples over a year would establish a mean within 0.1 pH units of the true mean in most streams.

Further experimental studies were also carried out to examine the effects of episodes (Merrett et al 1991). Experimentally induced episodes of low pH and high Al over short durations (24 - 60 h) and in isolation were not sufficient to cause the death, or total depletion, of all organisms in some exposed populations. Repeated exposures were additive in their effects under field conditions. For some organisms, experimental episodes caused very limited mortality despite their scarcity in acid streams. These results confirmed that, while the importance of episodes cannot be discounted, perhaps only recurrent pH reductions are sufficient to cause biological change. This conclusion is consistent with the modelling results.

Experimentally induced episodes were also used to assess how interstitial waters provided refuge conditions during low pH (Edwards, Ormerod and Turner 1991).

The invertebrate models have been used to develop biological indicator keys, whereby stream chemistry can be inferred from the occurrence of a small number of indicator taxa. This may be a cost effective way of surveying extensive or remote areas. Rutt, Weatherley and Ormerod (1990) showed that invertebrate models similar to those for Welsh streams could be derived to cover England, Scotland and Wales. This study also provided an indicator key, based on invertebrate families, which could be used to estimate stream acidity (Figure 7.2). Similar keys from Llyn Brianne have been applied to data from the whole Welsh region and found to describe chemical conditions adequately (Ormerod and Edwards, in press).

Indicators can be used as surrogates for abiotic variables such as pH, the suitability of conditions for other biota, or the presence of other biota. Weatherley and Ormerod (in press) distinguished between directly affected indicators, such as those to which low pH was directly toxic, and indirectly affected indicators, for example those affected through changes in their food supply. Direct indicators, of which the mayfly *Baetis rhodani* is a possible example, may be more reliably related to acidity. An indirect indicator like the dipper, *Cinclus cinclus*, which is influenced by changes in its aquatic prey and therefore less simply related to acidity, may be a more useful indicator of stream ecosystem status as a whole. Analysis of the Welsh regional data, showed that invertebrate assemblage type was a good indicator of stream pH and of the density of brown trout (Figure 7.3). Invertebrates were also related to macrofloral assemblages, though less clearly, as the flora were less consistently related to pH (Figure 7.3). For dippers, only presence/absence data were available, from which a clear relationship with pH was shown, whilst correspondence with macroflora and invertebrate faunas was apparent though not proven statistically. Overall, invertebrates appeared to be useful indicators of acidity itself and of other biota. Dippers may also be valuable indicators for the aquatic biota, particularly as they are not directly affected by water chemistry.

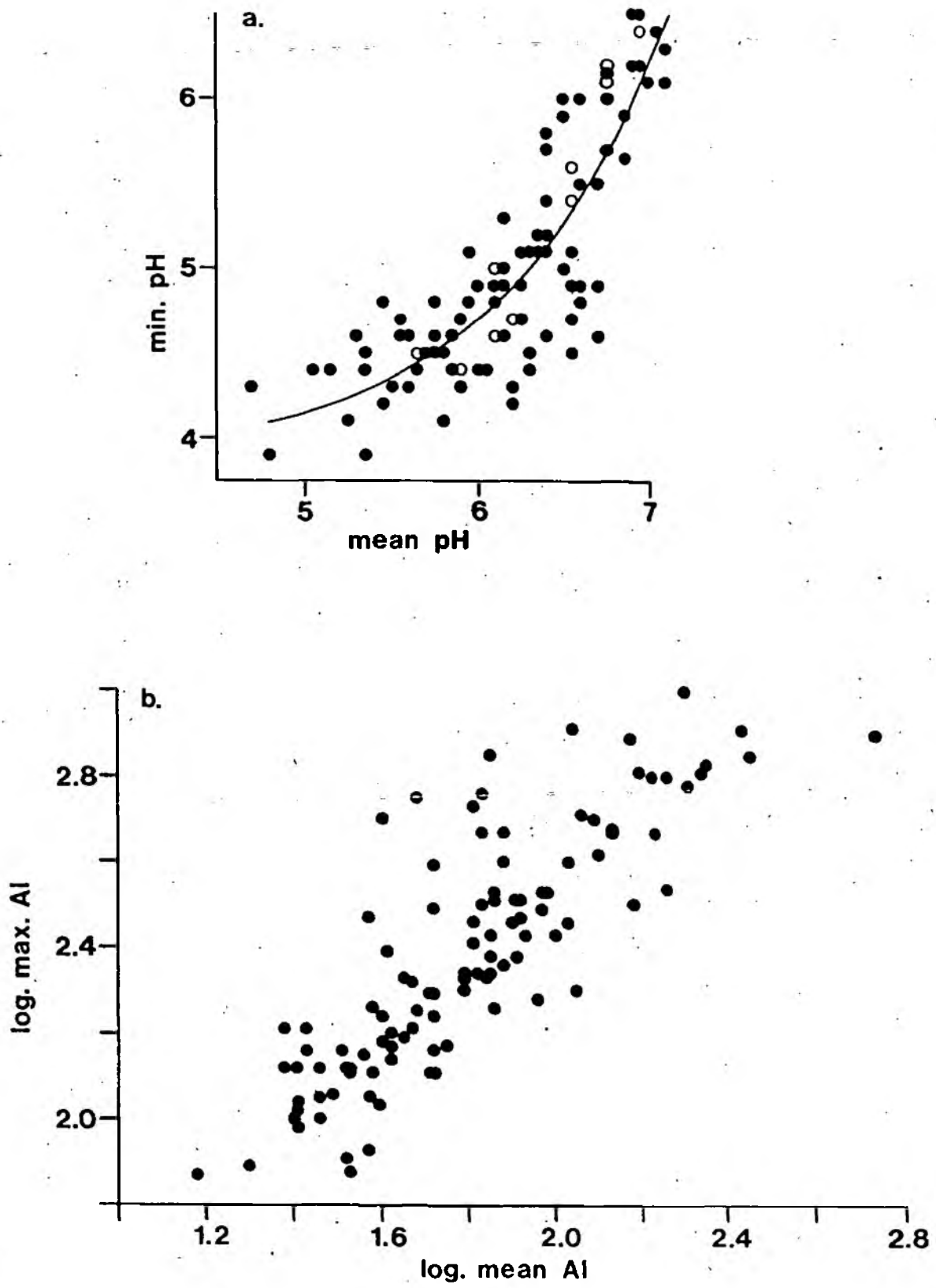

Figure 7.1 Plots of a) minimum against mean pH, b) log. maximum against log. mean aluminium concentrations ($\mu g\ l^{-1}$), derived from weekly samples between October 1983 and March 1984 in the Welsh regional survey. Open circles are two streams.

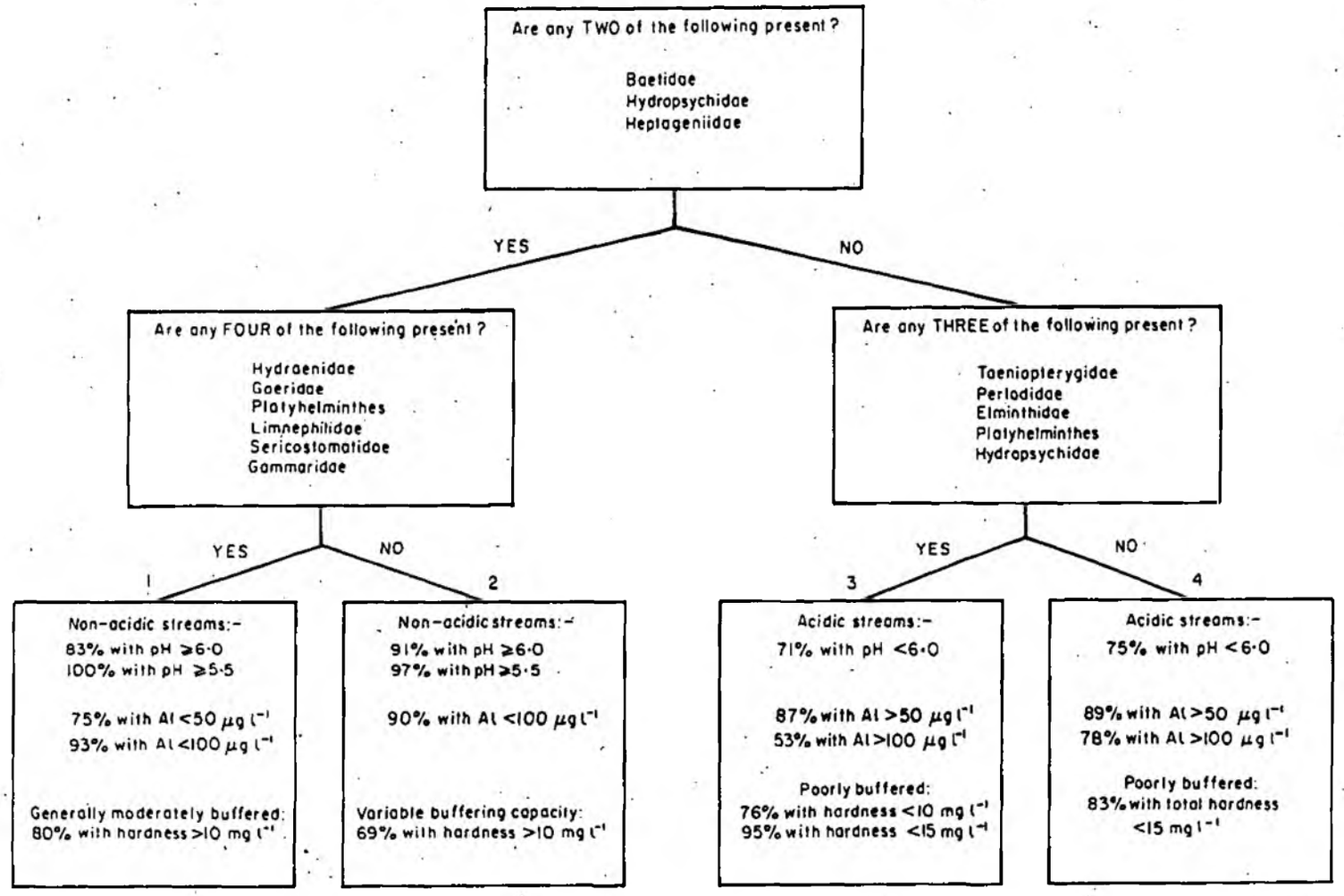

Figure 7.2 Macroinvertebrate indicator system for stream acidity in England, Scotland and Wales.

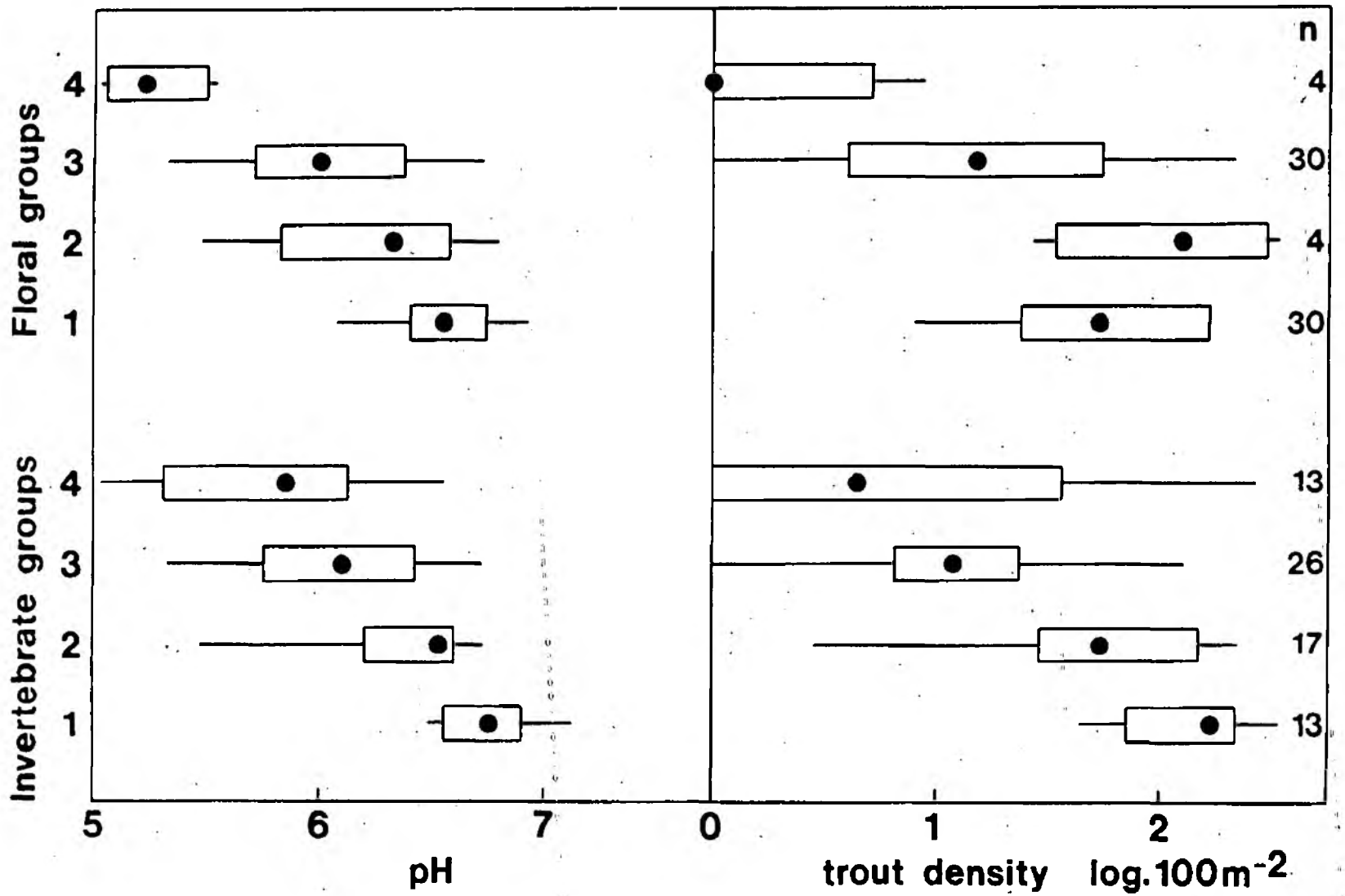

Figure 7.3 Distribution of pH and brown trout densities in Welsh streams classified by macroflora and macroinvertebrates. Circles indicate medians, boxes 25th-75th percentiles, whiskers 5th-95th percentiles.

Stream invertebrates are influenced by many factors other than chemistry, and awareness of these is necessary for the appropriate use of the acidification models. Streams in conifer plantations not only tend to be more acidic than moorland streams, but also have less marginal vegetation, probably due to greater erosiveness and shading (Rutt, Weatherley and Ormerod 1989, Ormerod et al in press, in preparation). Although acidity appeared to be the dominant determinant of macroinvertebrate distribution, certain species were associated with marginal vegetation and were therefore subject to an adverse physical influence by conifer plantations. The dragonfly larva, *Cordulegaster boltoni* was the subject of particular studies in this respect. Ormerod, Weatherley and Merrett (1990) showed that their distribution may be affected by land use, with larvae scarce in plantation forest streams. This scarcity is thought to be mediated by impacts by forestry on stream habitat structure, particularly through the erosion of marginal habitats often favoured by *C. boltoni*. Lloyd and Ormerod (in preparation) further investigated habitat selection by the larvae, looking at microdistribution amongst marginal habitats and riffles in some of the moorland streams in the Llyn Brianne catchment. Significantly more larvae occurred within stands of rushes and grass compared to bare soil and bankside mosses, whilst intermediate numbers occurred amongst the riffles. Larvae were not exclusively burrowers, as previously thought. Total body lengths and head capsule widths also varied significantly between the five habitats surveyed, the largest larvae occurring amongst rushes. Possible differences between habitats in the diet and foraging conditions in *C. boltoni* larvae were investigated by analysis of gut contents. In qualitative terms the percentage of larvae with empty guts increased in the order rushes< riffles< grass< moss<soil. However, no significant relationships were found between gut taxonomic composition and fullness, and habitat occurrence. It was concluded that *C. boltoni* larvae preferentially select certain types of marginal habitat, probably for reasons other than diet, possibilities including avoidance of predation, competition or strong currents.

In addition to being physiographically different, plantation streams tend to be warmer in winter and cooler in summer than comparable moorland streams (Weatherley and Ormerod 1990b). Simple simulations using real temperature data from Llyn Brianne, suggested that this temperature difference could retard egg and nymphal development of some insects in plantation streams. Mayflies (generally acid-sensitive) were more strongly affected than stoneflies (generally acid-tolerant) by the cooler summer temperatures, suggesting an alternative hypothesis to acidification to explain the absence of mayflies from many plantation streams.

In an attempt to quantify the impact of stream acidification on macroinvertebrate assemblages, faunal densities were sampled in six streams over a three year period (Weatherley, Rutt and Ormerod, 1989). Densities were highest in the one circumneutral stream, mainly due to the presence of mayflies. Amongst the other streams there were no clear relationships between mean invertebrate densities and either acidity or land use (moorland or conifer plantation). However, there were differences in seasonal patterns of abundance in streams of different acidity which may have implications for higher trophic levels.

7.2.2 Response to liming

Changes in invertebrate species composition due to liming were assessed in relation to species occurrence and persistence in both pre-treatment and unmanipulated streams (Weatherley and Ormerod 1990a). Observed changes were also compared with those predicted from stream chemistry according to the biological models (Weatherley and Ormerod, 1992). The models provided a way of assessing the efficacy of liming in restoring invertebrate assemblages, whilst the liming provided one of the few means of testing the models.

Of the small number of species colonizing limed streams (Table 7.1), all were predicted by the model to have a greatly increased chance of occurrence (Figure 7.4). For example, the acid-sensitive mayfly, *Baetis rhodani*, appeared in all three limed streams. The dipteran, *Elaeophila* sp., was the only taxon to disappear after liming (from CI2), corresponding with model predictions. However, only a small proportion of predicted species colonizations occurred within three years

of treatment. In each of the three streams twelve taxa whose probability of occurrence increased from below to above 0.5 have not yet been detected. It is not known whether this is due to inadequate sampling, limited dispersal abilities, or unsuitability of the post-liming conditions. It is possible that the models omit some important factor in which limed streams differ from naturally circumneutral waters. For example, in comparison with water chemistry simulated under low deposition scenarios, limed streams have substantially elevated calcium concentrations and hardness, though pH and aluminium may be similar (Ormerod et al 1990).

Table 7.1 Macroinvertebrate taxa colonizing or eliminated from three streams in 1989 and 1990 following catchment liming. —1988 indicates pre-treatment years.

	CI2			CI5			LI4		
	– 1988	1989	1990	– 1988	1989	1990	– 1988	1989	1990
Baetis rhodani (Ephemeroptera)	–	+	–	–	+	–	–	–	–
Heptagenia lateralis (Ephemeroptera)	–	+	+	–	–	–	–	–	–
Isoperla grammatica (Plecoptera)	+	+	+	+	+	+	–	+	+
Chloroperla tripunctata (Plecoptera)	–	+	–	–	–	–	–	–	–
Wormaldia sp. (Trichoptera)	–	–	–	–	–	–	–	+	–
Hydropsyche siltalai (Trichoptera)	–	–	+	–	–	–	–	–	–
Diplectrona felix (Trichoptera)	–	–	–	–	–	–	–	+	–
Elaeophila sp. (Diptera)	+	–	–	–	–	–	–	–	–

7.2.3 Other invertebrate groups: Micro-crustacean communities

Macroinvertebrate communities are only one component of the invertebrate fauna in streams. Less is known about the ecology of meiobenthic invertebrates. However, recent work has shown that diverse micro-crustacean communities do exist in streams, and that patterns in their distribution and abundance can be explained by physicochemical factors (Rundle and Hildrew 1990). They represent a gap in our basic understanding of the trophic dynamics in running water systems.

The micro-crustacean communities of thirteen streams in the Llyn Brianne area were surveyed in autumn 1990, and patterns in the distribution and abundance of animals related to physicochemical variables (Rundle and Ormerod, in prep). Benthic samples were taken from three microhabitats (riffles, runs and margins) using a fine mesh (100 μm) Surber sampler. All animals were then sorted and identified in the laboratory. Individuals from all four micro-crustacean groups were found (cyclopoid copepods, harpacticoid copepods, cladocerans and ostracods) and all, except ostracods, were determined to species.

Total absolute abundances were negatively correlated with aluminium concentration, and both total absolute abundances and total species richness showed a positive correlation with the proportion of macrophytes at a site. Harpacticoid species richness and absolute abundance and ostracod absolute abundance were also negatively correlated with aluminium concentration. In contrast cyclopoid copepod species richness and absolute abundances were negatively correlated with pH. Cladoceran species richness and absolute abundance were positively correlated with macrophyte cover. TWINSPAN clearly separated communities on the basis of land use, dividing moorland sites from conifer.

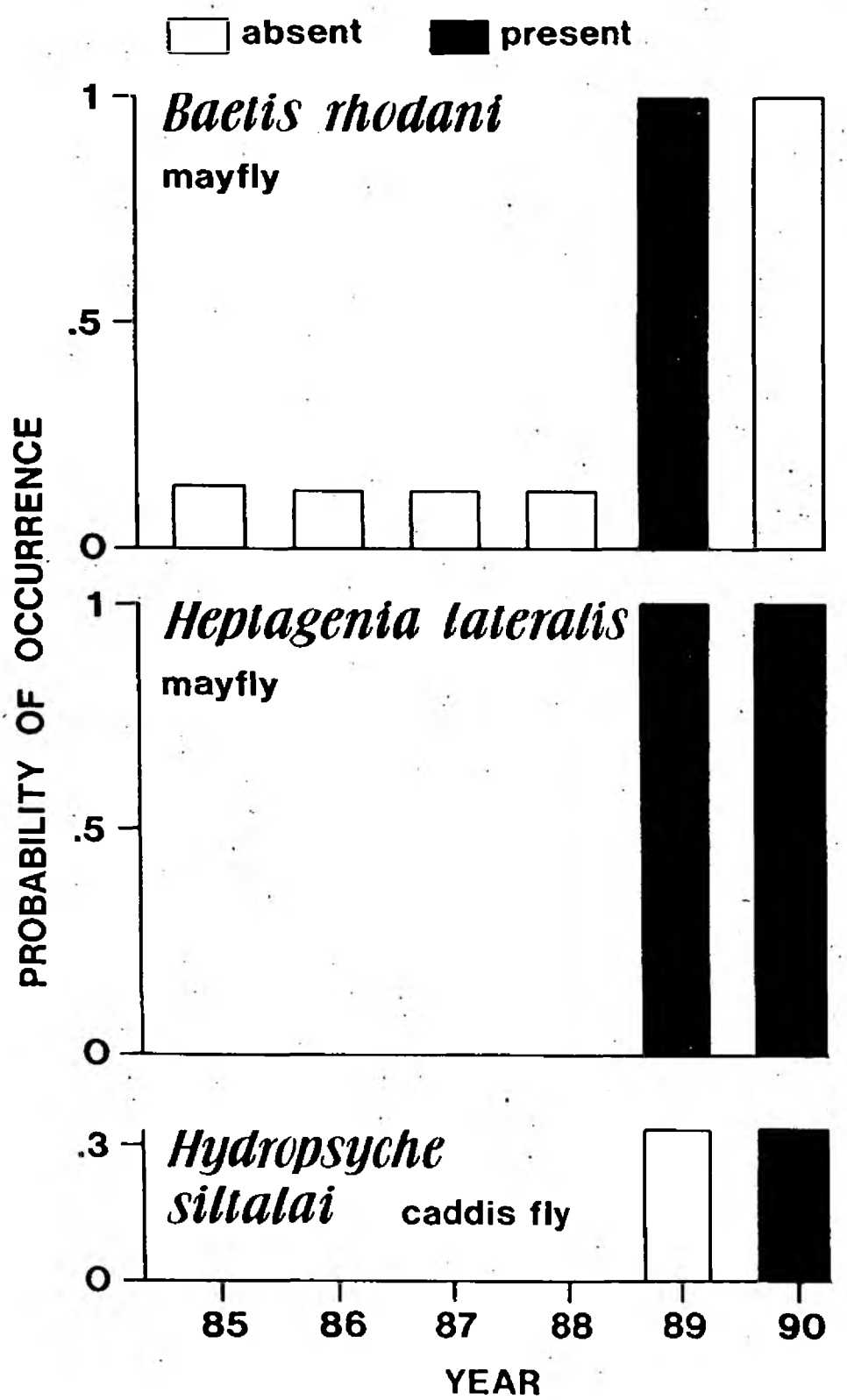

Figure 7.4 Probability of occurrence from 1985 to 1990, predicted from stream chemistry, of the invertebrate species colonizing stream CI2 after liming. Bars are shaded in years when the species was actually detected.

This preliminary study shows that this little known group of stream organisms provides yet a further example of a probable effect by stream pH and land use on stream biology.

7.3 Fish

7.3.1 Relationships with acidity and other factors

The survival of early life stages of brown trout was assessed in a range of Llyn Brianne streams in relation to acidity, with particular attention to aluminium speciation (Weatherley et al 1990). Survival of eggs, from just after fertilization to hatching, was usually high and independent of intragravel water chemistry. The survival of alevins exposed for 28 days (before 'swim-up') or 42 days (including 'swim-up') was most strongly related to mean total monomeric aluminium and to pH (Figure 7.5a). Swim-up alevins were most sensitive, with an approximate LC50 of 15 $\mu g\ l^{-1}$ total monomeric aluminium or 72 $\mu g\ l^{-1}$ 0.45 μm filterable aluminium (Figure 7.5b). Three month old parr had a 21-day LC50 between 84 and 105 $\mu g\ l^{-1}$ mean filterable aluminium. All these values were rough estimates since pH and the concentration of different aluminium fractions fluctuated widely during the experiments and were inter-related. These features are equally problematical for interpretation of field data or prediction from laboratory results.

The effect of including measures of episodicity in multivariate models of trout abundance was investigated using data from the Welsh regional survey (Weatherley and Ormerod 1991a). A model employing mean filterable aluminium concentration accounted for more variance in density than one based on mean pH, and neither could be improved by the inclusion of parameters describing variation in aluminium or pH respectively.

Simple empirical models of trout density in relation to acidity are confused by the high annual variability in density in soft-water streams (Weatherley and Ormerod, 1992). This suggests the need for repeated surveys to reduce errors in models developed in this way. Improved understanding or modelling of such annual variation in populations requires information on the underlying processes, which could be related to climate or episodic acidity.

In order to detect any effect of acidity on trout growth in Llyn Brianne streams, it was necessary to take differences in stream temperature into account (Weatherley and Ormerod 1990b, Weatherley, Campbell-Lendrum and Ormerod, 1991). In all streams, observed growth between October of the first and second year of life was approximately 60% of that expected from stream temperatures assuming maximum rations (all streams 1988, LI6 1985-1988). This fell to 30-40% in drought years (1989, 1990). Although no fish occurred in our forest streams, simulations indicated that cooler summer temperatures here would retard trout growth substantially. Where trout were found, neither growth nor condition factor ('fatness') were related to acidity.

Using this information, in conjunction with published models of development and growth, allowed preliminary exploration of climatic change scenarios (Campbell-Lendrum 1990, Weatherley, Campbell-Lendrum and Ormerod, 1991). Simulations indicated that moderate increases in temperatures would accelerate early development and growth, but the adverse impact of drought noted above could reduce or reverse these effects, as drought is also known to be associated with increased trout mortality.

Fish densities are known to be limited by habitat physiography. In order to understand whether such limitations occur at Llyn Brianne (and hence whether post-liming conditions might lead to restricted densities through such pathways), Campbell-Lendrum (1990) investigated habitat use by brown trout in Brianne streams in July and August 1990. The fish populations in ten contiguous 10 meter reaches were assessed by electrofishing in each of six moorland streams (CI1, CI2, CI3, UC4, LI5 and LI6). They contained only brown trout (*Salmo trutta* L.), the observed densities of which varied greatly from reach to reach for reasons which could not be identified.

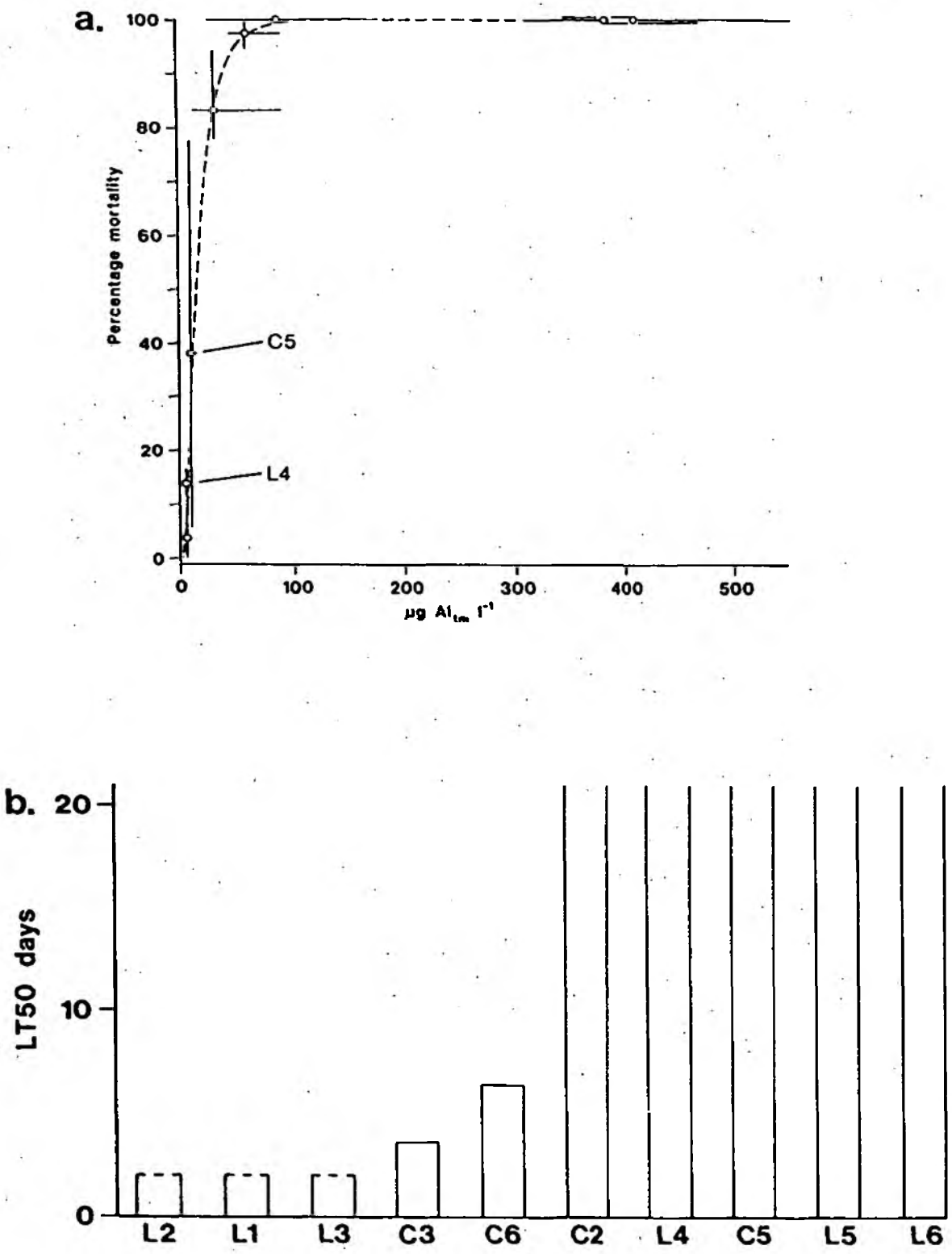

Figure 7.5 a) Percentage mortality of brown trout alevins exposed in streams for 42 days (including 'swim-up'), in relation to mean concentration of total monomeric aluminium. Bars indicate ranges, C5 and L4 were limed catchments.
b) Median survival time of 3 month old parr of brown trout exposed in Llyn Brianne streams for 21 days. C2, C5 and L4 had been limed. Open ended bars indicate LT50 exceeds limit of plot, dashed ends indicate LT50 is within the range of the bar.

Observed population densities were related to habitat quality using HABSCORE. This showed that the streams represent excellent brown trout habitat, although the population densities were well below carrying capacity. Thus, trout populations in the streams around Llyn Brianne are probably limited by acidity and not habitat.

7.3.2 Response to liming

The populations of brown trout in the study streams were assessed each year, usually in October/November. In CI2, O-group (fish in their first year) densities were significantly higher in post- than pre-liming years (1984-87 v. 1988-90, $p < 0.05$; Figure 7.6), whereas unmanipulated streams showed no such differences. Similarly, differences between pre- and post-liming I-group (fish in their second year) densities approached significance only in CI2 ($p = 0.053$, Figure 7.6). In CI5, only one year's pre-treatment data are available, precluding formal analysis, though the density of O-group trout in that year fell below the confidence limits for 1988-90 values. Trout remained absent from the long-term monitoring reach in LI4, but small numbers of O- and I-group fish were found in 1990 in the lower reaches, previously unfished. Although it cannot be proved that the presence of fish was due to liming, this is consistent with the low acidity induced in this stream by treatment. The beneficial effects of liming for trout populations were also indicated by high survival in the field experiments with early life stages (section 7.3.1).

There is concern that liming may create potentially toxic changes in aluminium speciation in zones where limed and acidic aluminium-rich waters mix (Weatherley et al 1991). To address this possibility a field experiment was performed, dosing stream LI2 with powdered limestone. An acidic tributary entered LI2 200 m below the dosing point, and chemical and fish monitoring points extended up to 100 m below the confluence. After 24 hours, brown trout mortality was 100% above the liming point, falling to zero within 100 m downstream. There was also a 70 % mortality 15m below the confluence, despite little change in pH or total aluminium. Mortalities were significantly correlated with concentrations of aluminium and iron in gill tissues, and with 0.22 μm filterable aluminium and iron in the water, but not with particulate metals. Aluminate ($Al(OH)^-_4$), precipitating aluminium or polymeric hydrolysis products were all possible causes of the toxicity. Iron may have been a contributary factor but concentrations were relatively low. The results suggested that aluminium toxicity could occur where waters of differing acidity mix, but the affected areas are likely to be limited in spatial extent.

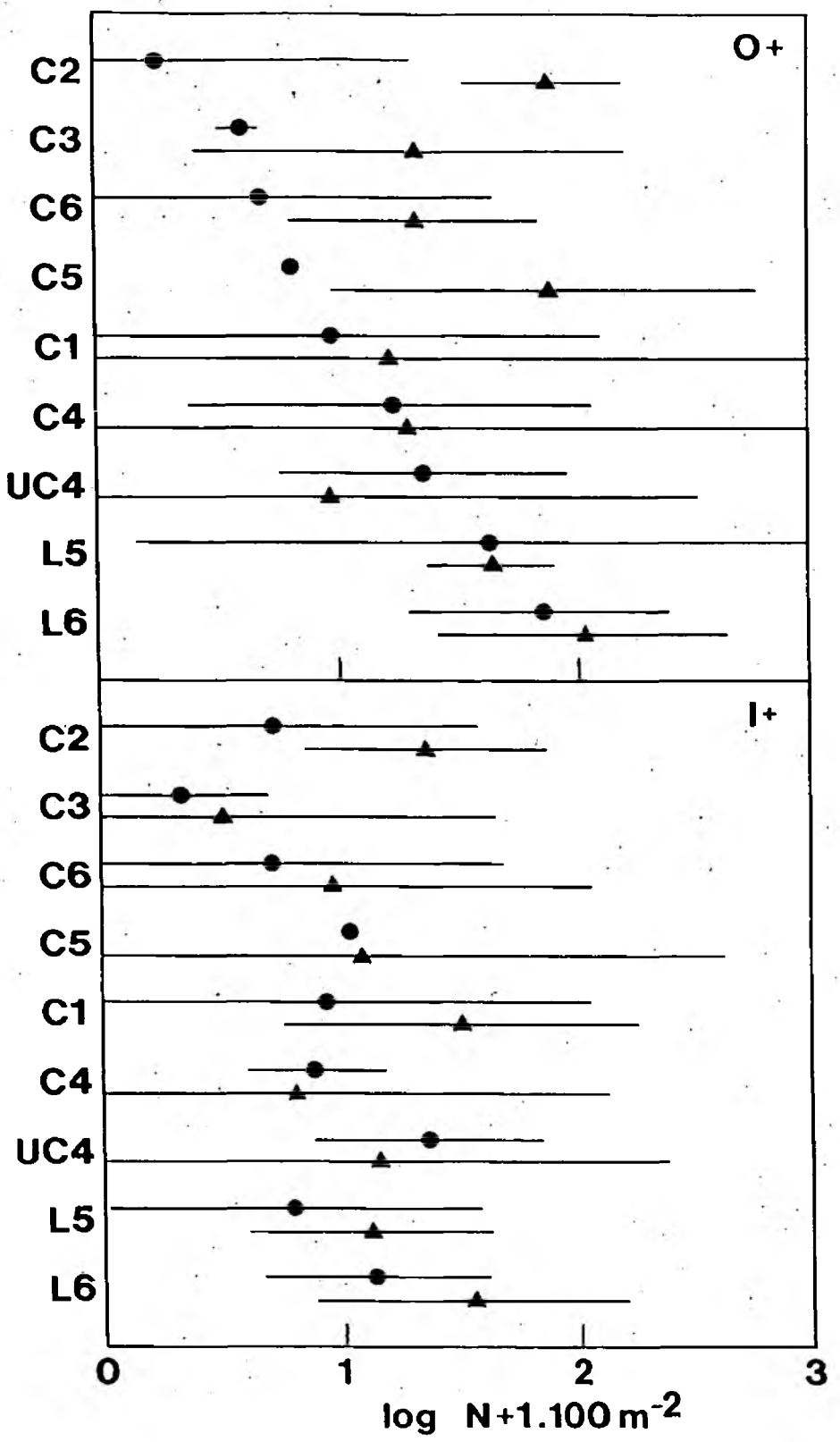

Figure 7.6 Mean density ± 95% confidence limits of 0-group and I-group brown trout in Llyn Brianne streams. Circles are 1984-1987 values, the pre-liming period, triangles are 1988-1990 values, after C2, C5 and L4 were limed.

8. CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

The Llyn Brianne Project has underpinned earlier studies which demonstrated strong links between atmospheric deposition, land management, stream acidity and stream ecology. Its focus on analytical and experimental investigations, has contributed to the development of models for these relationships. Although there are many imperfections in the models, their output shows a general conformity to data not used in their derivation. This justifies some confidence in using the predictions as guidelines for the effects of changes in land management and deposition on a regional and national basis.

The key conclusions of the project are as follows:

1. As a result of increased atmospheric deposition of sulphur, many soft waters throughout the Welsh uplands have increased in acidity since the mid-nineteenth century. There has been a concomitant increase in concentrations of metals, particularly aluminium.

2. Surface water acidification has been accompanied by a decline in biological diversity, affecting resources of conservation and economic value. This is due to the toxic action of acidity and high aluminium concentrations on some organisms, and indirect effects on others through ecological interactions. This accounts for losses of invertebrate and plant species, reductions in salmonid populations which include important fisheries, and impacts on terrestrial organisms such as the dipper, a riverine bird.

3. Land management affects the sensitivity of catchments to acidification. Afforestation with conifers enhances rates of occult and dry deposition of pollutants, so that streams in conifer plantations tend to have elevated aluminium concentrations. Other factors influencing surface water chemistry include forestry drainage which may accelerate run-off and reduce buffering in the catchment. The regulation of afforestation is therefore important in controlling the impacts of acidic deposition on sensitive catchments.

4. The project results show that target liming of hydrological source areas can reduce surface water acidity and sustain good populations of brown trout. Agricultural liming in such catchments does not influence surface water acidity substantially as it does not treat the main hydrological sources. Single target limings may be effective for a number of years though the duration is not yet established. The long-term effects on aquatic biota other than fish are also not yet clear, and adverse impacts on some acidic wetland ecosystems have been observed.

5. The MAGIC model suggests that reductions in sulphur deposition of about 30 - 50 % of 1984 rates (or 36 - 60% of 1980 values) would halt further acidification of surface waters in Wales. Reductions of 60 - 90 % would be needed to reduce the acidity of surface waters and, according to models, enable biological recovery towards a pre-impact state. Afforestation of a catchment would increase the extent of reductions necessary in the absence of other action.

6. The model simulations, in the context of current agreements on reductions of acidifying emissions, indicate that many surface waters in Wales will remain acidified for the forseeable future. Land management techniques, such as control of afforestation and liming, would allow some protection or partial restoration of freshwater ecosystems until future reductions in acidic deposition render such action unnecessary. Whatever emissions controls take place, certain areas may require sensitive land management indefinitely.

7. There are many uncertainties in model predictions of the effects of changes in acid deposition and land management, and the effects of liming are not fully understood. Careful evaluation of available knowledge and of the costs and benefits of alternative management strategies is therefore an ongoing requirement.

8.2 Future work

8.2.1 Llyn Brianne Phase III

The NRA, through its R&D programme will continue to study stream chemistry at Llyn Brianne for at least a further three years, until March 1994. In conjunction with this work, UWCC (funded by Welsh Office) will continue its biological studies on the streams. This extension to phases 1 and 2 is essential to establish the nature and duration of the long-term effects of catchment liming. The core work will be chemical monitoring of treated and reference streams, with annual surveys of stream biology, including trout populations.

8.2.2 Related work

The NRA R&D programme is funding the UWCC Catchment Research Group to investigate the potential impacts of source area liming on wetland ecology. The aim is to establish the likely significance of liming for wetland conservation, and provide means of identifying important areas at risk.

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