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The Impact of Conifer Harvesting and Replanting on Upland Water Quality

R&D Progress Report for Period
January - July 1994

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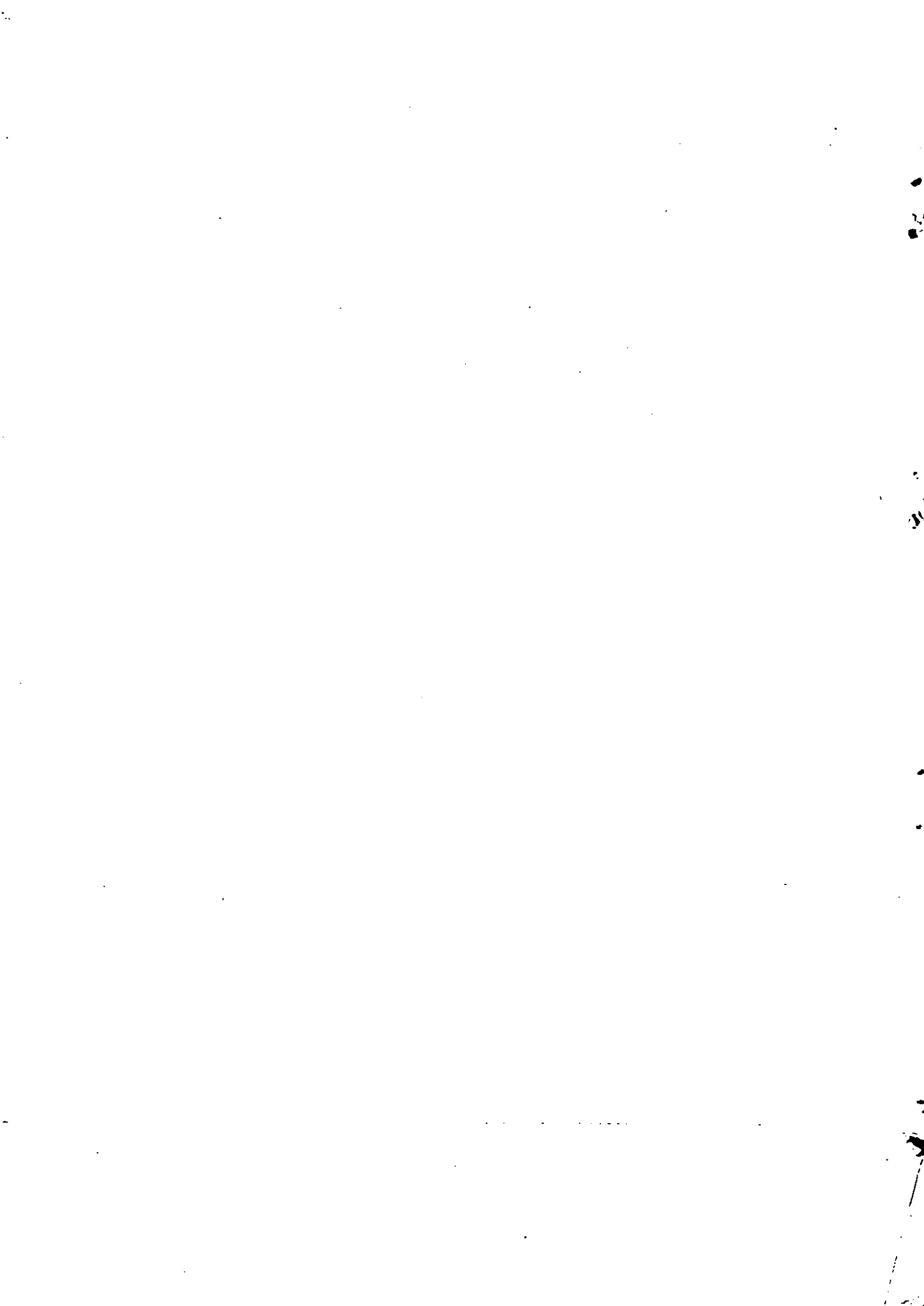
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R&D Progress Report 502/1/W



NRA

National Rivers Authority



**THE IMPACT OF CONIFER HARVESTING AND REPLANTING ON
UPLAND WATER QUALITY**

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R&D Project 502

The Impact of Conifer Harvesting and Replanting on Upland Water Quality

C. Neal, A.J. Robson and B. Reynolds

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January - June 1994

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CONTENTS

1. Overall project objective
2. Overall approach
3. Specific objectives
4. Specific Work
5. A review of the first six months
6. Priority areas for the next six months

Appendix 1: Background information for Beddgelert forest

Appendix 2: Forest sites at Llyn Efymwy (Lake Vymwy)

Appendix 3: Questionnaire

Appendix 4: Publications

1. OVERALL PROJECT OBJECTIVE

To assess the impacts of conifer harvesting and replanting on upland stream water quality with a view to identifying "best practice" management strategies and the development of a model and guidelines for environmental impact assessment.

2. OVERALL APPROACH

To undertake detailed water quality studies, structuring them in such a way that the results can be applied on a regional basis.

Changes in surface water quality following from felling are being examined for small catchments which characterize the main U.K. upland soil types. For logistical reasons, most of these catchments have been located at Plynlimon. Additional sites will also be used to ensure that all major soil types are represented. In addition, dominant processes and flow routing effects are being identified through study of the contributing hydrological components (soil and groundwaters).

In parallel, a regional perspective on forestry effects will be attempted through collation and analysis of existing data from the NRA and other sources. This will be used in conjunction with results from the detailed studies allowing an overview of forestry effects in the U.K.

At a later stage current and proposed forest practice policies will be examined and assessed to see how they might affect stream water response. This will involve integration of the knowledge accumulated in the earlier stages and development of a simple regional environmental impact model. From this, recommendations for minimising detrimental environmental effects of forestry will be provided.

3. SPECIFIC OBJECTIVES

- (a) To study and model variations in relevant major, minor and trace element concentrations and colour in streams, near-surface drainage (soil) water and groundwaters during conifer harvesting and replanting, for catchment areas with contrasting soil types and acidification potentials;
- (b) To identify flow routing pathways and contributing source areas to the stream using chemical fingerprinting techniques;
- (c) To develop an environmental assessment model and guidelines to allow operational NRA staff to assess the environmental impacts of forestry practice on stream water quality;
- (d) To identify and evaluate strategies for ameliorating adverse environmental impact in order to produce "best practice" guidelines for operational NRA staff and foresters

which are sufficiently flexible to encompass a wide range of circumstances throughout England and Wales;

- (c) To produce an R&D Note containing the key findings, "best practice" management strategies and a model and guidelines for environmental impact assessment.

4. SPECIFIC WORK

Detailed sampling programs

- (a) Continue to monitor, on a weekly basis, the streams draining the Hafren Forest, Plynlimon: the Afon Hore, Afon Hafren and Tanllwyth. Collect weekly rainfall and mist samples. Analyze samples for major, minor and trace elements and for alkalinity, acidity and colour;
- (b) Establish new sampling sites which represent the main soil types found in the UK uplands. Examine the chemical changes in the soil and groundwater zones following from felling by sampling shallow and deep groundwaters. For this, monitor near surface drainage waters and obtain groundwater samples by drilling and sampling boreholes. For each soil type, establish control sites, as well as the sites where felling will occur. Sample both sites weekly aiming to obtain data for at least one year prior to felling operations;
- (c) Identify suitable sites for monitoring at locations with soil types not represented at Plynlimon. Consider whether a site in the Pennines is feasible, in consultation with Northumbria and Yorkshire region and linking in with IH's involvement in the LOIS programme. Make full use of the ITE water quality work at Beddgelert site in North Wales by providing two boreholes to obtain groundwater chemistries. Continue to monitor waters draining the soil zone at south2hore, Plynlimon, thereby giving longer term information on shallow chemical changes associated with clearfelling and replanting;

Interpretation of detailed data

- (d) Use the data from the Plynlimon monitoring network to make a quantitative assessment of the effects of changes in stream water quality following deforestation and replanting. In particular, study long term effects of felling followed by replanting using information from the Hore catchment. Study the effects of felling on a highly acid sensitive, acidified, base depleted catchment using the Afon Hafren (parts to be felled, possibly in 1995 or 96). Examine the hydrogeochemistry of an acid moorland area using the upper Afon Hafren site;
- (e) Use rainfall and stream water data to provide an overall view of the flux and dynamics of chemical transfers through the hydrological cycle at Plynlimon. This will be aided by continuous measurements of conductivity for the rainfall and streamwaters and flow and turbidity for the stream waters;

- (f) Assess the influence of subsurface water supplies on stream water chemistry. Use the changing soil and groundwater chemistry following harvesting as a natural tracer to determine flow routing and contributing source areas to the stream. Establish the dominant reactions occurring in the soil and groundwater zones. Use chemical mixing equations to predict short and long term changes in surface water quality;
- (g) Use the information gained from the field programme, with summary information on hydrology and sediment yield for the catchments, to assess the mechanisms which determine stream water quality.

Collation of other relevant data

- (h) Identify sites where detailed studies of felling have been undertaken and where pre- and post-felling data exist. Examine this data in relation to soil type. Sites already identified include Beddgelert in Welsh Region, Kershope in North West England and Balquhiddy in Central Scotland;
- (i) Make full use of existing NRA data for regions where water chemistry may have been measured before and after felling. For example consider Kielder in Northumbria & Yorkshire Region, and the Afon Biga and Afon Llwyd in the Upper Severn area. Other sites in the various regions will be identified via a questionnaire directed to the NRA and associated bodies;

Towards formulating forest management practice, policy and guidelines

Based on the detailed field studies and associated regional surveys, the following will be undertaken:-

- (j) Development of a simple operational management model for use by NRA staff to assess the impacts of harvesting and replanting on stream water quality at any acid sensitive site in England and Wales;
- (k) Assessment of a potential range of practicable ameliorative management strategies; approaches will include i) varying the extent of felling in a catchment with regard to the distance from the watercourse; ii) whole tree harvesting; iii) liming; and iv) burning brush, the aim will be to produce "best practice" guidelines for NRA operational staff which are sufficiently flexible to cover the wide range of circumstances throughout England and Wales;

Reporting

Reporting will be as follows,

- (l) an interim report will be produced after two years covering the results and key findings and making any necessary case for an extension to the project;

- (m) a project record containing all of the results of the study will be produced;
- (n) an R&D Note containing the key findings, "best practice" guidelines for ameliorative management strategies will be produced together with a model and guidelines for environmental impact assessment;
- (o) continued publication of new findings in peer reviewed scientific journals;

5. A REVIEW OF THE FIRST SIX MONTHS

The work has focused on getting the detailed sampling programme fully operational. In addition, investigation of existing NRA data has begun.

Detailed sampling programs

Effort has centred on expanding the detailed monitoring work at Plynlimon. New sites have had to be introduced and sampling schemes formulated. The work is in addition to the ongoing collection and data analysis for the weekly sampling of rainfall, mist and stream waters at the five major sites.

It has been necessary to locate and set up the sampling sites which characterise the main UK soils of concern. For each of these sites we have aimed to establish a control site and an adjacent site where felling is planned in about 12 to 18 months time. At each site, surface runoff from small ephemeral streams and groundwater samples will be collected. The idea of collecting data from such small streams is to obtain an integrated measure of the soil water chemistry without the influence of groundwater inputs. Surface runoff is taken in preference to direct soil water measurements owing to the very high degree of spatial variability in soil water chemistry and the near impossibility of obtaining a representative sample using standard collection devices. The groundwater samples necessitate the drilling of boreholes.

The main soil types which need to be studied are podzol, gley, brown earth and deep peat. Not all of these types are present at Plynlimon and major effort has had to be placed in identifying sites, even at Plynlimon: detailed discussions with forestry commission over sites, felling, timing and practicalities, plus scrutiny of soil and land survey maps have been needed. Here we detail our progress to date.

Gleys: sites have been located within the Tanllwyth catchment at Plynlimon (Figure 1). This represents an ideal choice area as the Tanllwyth is one of the major tributaries entering the Hafren, it is nearly completely forested and there is a large amount of background data - we have undertaken sampling for the past four years as part of the ongoing monitoring programme and detailed flow records are available. The control and felling sites have been located and sampling of ephemeral streams has begun. The associated boreholes have been drilled but one of them (the control) cannot be used owing to contamination by a perched aquifer. A new control borehole will be drilled in early July. Sampling for chemical analysis will begin in August after the well has been developed: disturbance is inevitable during borehole construction so water samples will only be analyzed after the boreholes have been

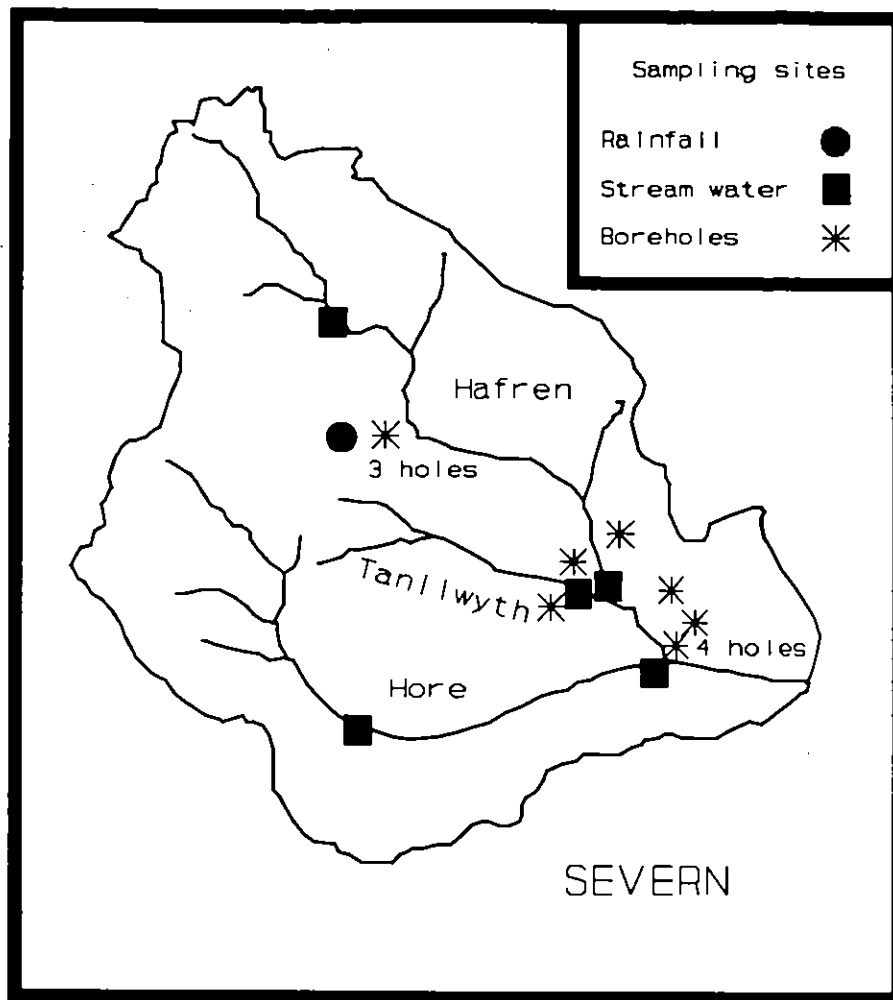


Figure 1 Plynlimon sampling sites

thoroughly flushed and cleaned- this will take about a month.

Podzol: sites have been located in the Hafren catchment. As with the gley sites, ephemeral streams are being sampled and boreholes have been drilled. The monitoring programme timing is as for the Tanllwyth except that one of the boreholes has already been established from the previous years field programme and interesting results are already accruing (see next section). As mentioned above, boreholes will also be established at Beddgelert to supplement the ongoing ITE study of deforestation and replanting of Sitka spruce at a very acidic site. Sites for these boreholes have been established and details together with site description are given in Appendix 1.

Brown earth: no site is available at Plynlimon but control and felling sites have now been found next to Lake Vyrnwy (Figure 2). This area can be sampled by the NRA for us and ephemeral stream monitoring will begin in July subject to NRA logistical support. Drilling of

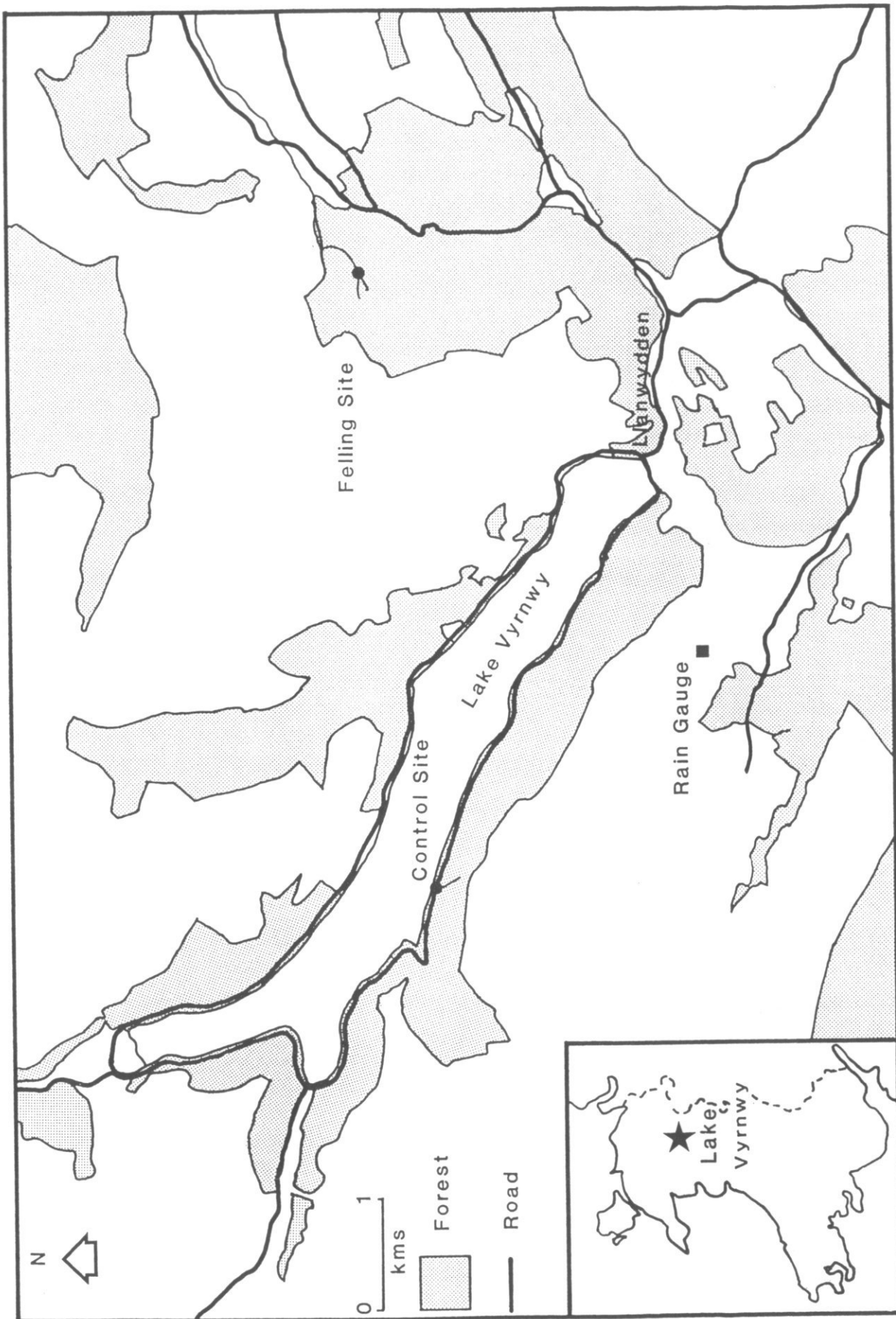


Figure 2 Vyrnwy sampling sites

boreholes will proceed in July or August. Details of the site are provided in Appendix 2.

Deep peat: potential sites in the north of England, in other parts of Wales and in Scotland have been considered. However, no suitable area has yet to be found. Practical limitations may mean that a site will have to be looked for at Plynlimon.

Interim results

Borehole results: Chemical data for one of the boreholes cutting through podzols has been monitored for the past 2 months. The borehole was drilled into mudstones to a depth of 11 metres. Water was initially struck during drilling at a depth of 5.3 m. The upper regions of the borehole have been sealed to prevent downwards movement of soilwater into the borehole. The bottom 3 metres of the hole have been screened so that ground waters at this depth can be sampled. The results for water levels, pH and alkalinity are provided in Figure 3. We appear to have found a water source which is hydrologically and chemically active, even though this is an area where rocks are considered by many to be impermeable and groundwaters are assumed not to exist. Water levels have varied between 2.5 and 5.5 metres during the last few months and the hole has been observed to refill quickly after emptying.

Previously, the presence of groundwater has been suggested by the baseflow chemistry of the streams. Whereas stormflow stream chemistry is highly acidic and can be explained by increased contributions from acidic soil waters, baseflow water is of moderate alkalinity and relatively high pH and unlike any water type previously sampled within the catchment. The chemistry of the borehole water samples is more alkaline than anything seen in the soils and may well prove to help explain the source of baseflow stream waters.

The increase in alkalinity seen during the period of sampling (Figure 3) corresponds to a time of flow recession. As flows have decreased the chemistry of the borehole has moved towards higher pH and alkalinity. High inorganic carbon levels (with visible degassing) have been found - excess pCO₂ values have been between 4 and 37 times atmospheric i.e. at times significantly higher than in the stream.

Rainfall-stream water relationships: throughout the project emphasis has been placed on interrogation of the data as it becomes available. Over the past six months two important sets of analysis have been produced. Data from the south2hore site has been analyzed and the effects of deforestation on near surface runoff from an ephemeral stream draining podzol have been described. Deforestation has led to an increase in nitrate, DOC and acidity: the perturbations have, however, only lasted for about 3 years as regrowth of vegetation has started to mitigate the changes. From a theoretical standpoint, the work casts doubt over the applicability of the cation exchange equations which are commonly used in environmental impact studies. This could well have important ramifications for the current environmental impact models of acidic systems: the full text is given in Appendix 4. In the other study, we have begun to examine the longer term aspects of stream water quality changes and have examined trends in the Hafren stream waters and related these to rainfall inputs. The results suggest that there is little evidence of further increases in acidity or of depletion of base cations. However, we have found rises of DOC, bromide and iodine in the stream waters suggesting that there may have been an increase in organic breakdown over the last decade:

Borehole Water Time Series

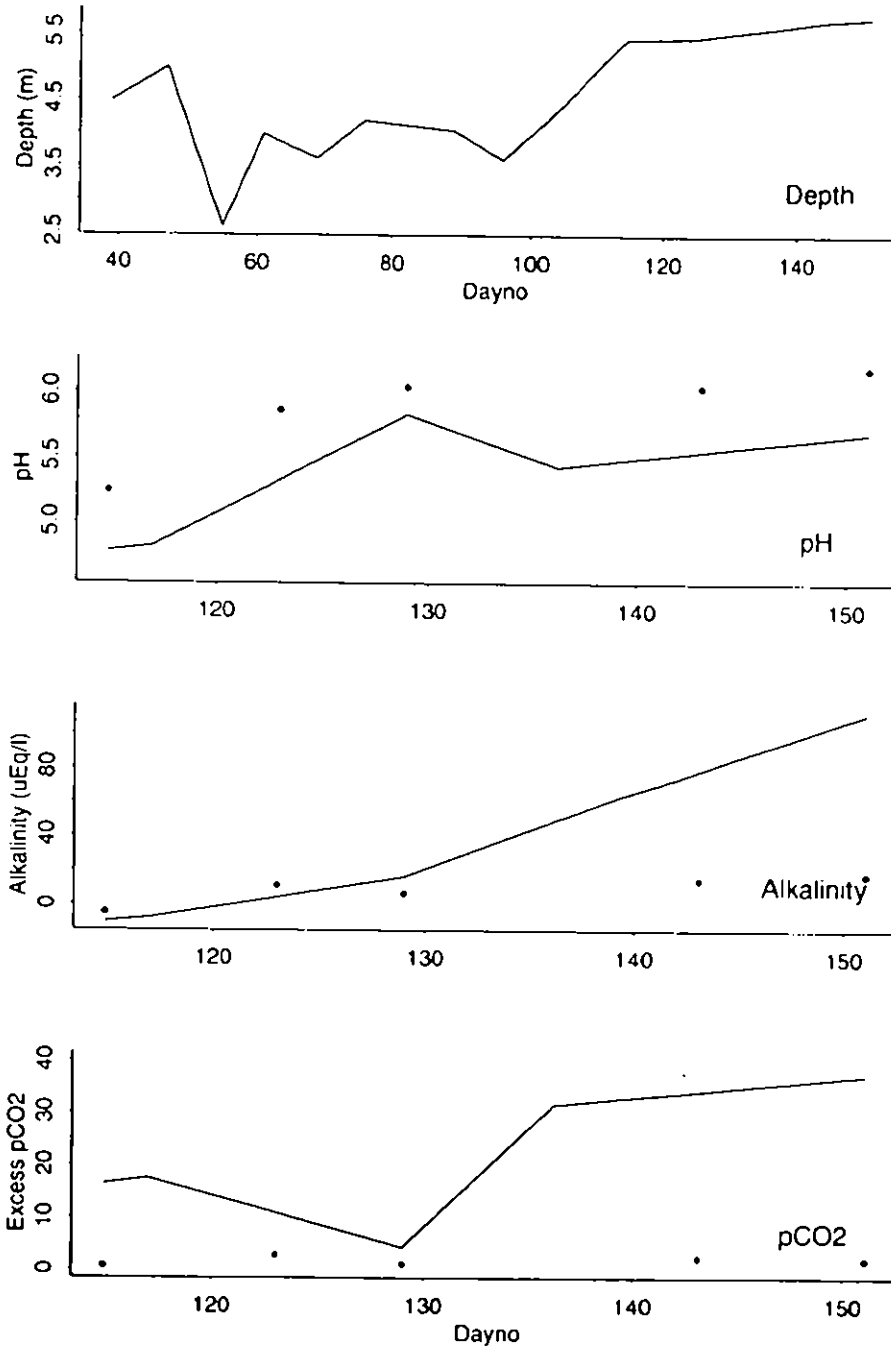


Figure 3 Plynlimon borehole data. Lines show borehole results. Points show corresponding measurements for the Hafren stream.

see Appendix 4 for further details.

Investigation of external NRA data: Two main areas have been covered during the past six months.

First, data for the NRA sites of the upper Severn (Afon Biga and Afon Llwyd) have been obtained and examined: the full data set is shown in Figure 4. The following was found.

- 1) In the last five years temperature, pH, conductivity, T.O.C., chloride, alkalinity, sulphate and hardness have been measured. Rather more determinands were measured for the period 1984 - 1989 but these have since been discontinued.
- 2) Only pH, conductivity and chloride have complete and regularly sampled data records for the full period (1985 to 1994)
- 3) Sampling has been more frequent over the last five years but is still sparse (approximately every month).
- 4) There is no recent data for many of the determinands of primary interest, eg. nitrate, potassium, base cations, aluminium.
- 5) The data for the Afon Biga and the Afon Llwyd are very similar.

We conclude that there is very little that can be done in terms of modelling of the data or even establishing effects of felling.

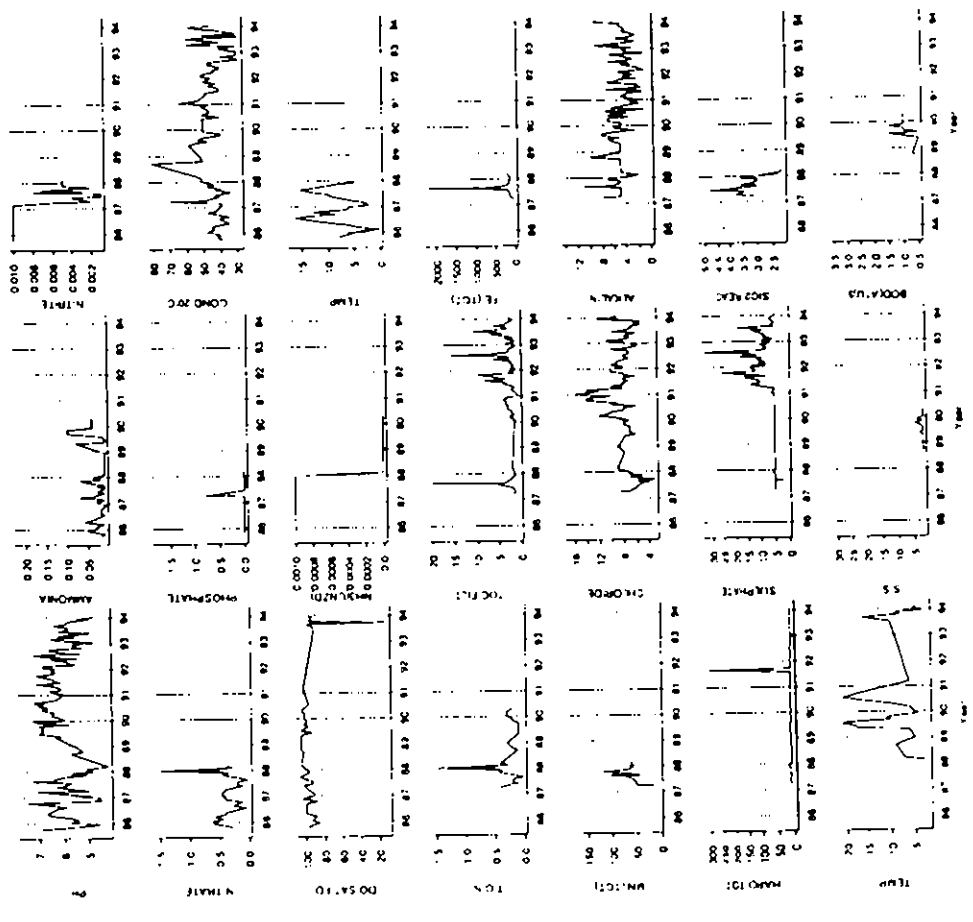
Second, an attempt is underway to identify other UK sites where water quality is available. A questionnaire has been designed which will be sent to the NRA regions (Appendix 3). Any useful data which is located will be of value in providing a regional perspective on our findings.

6. PRIORITY AREAS FOR THE NEXT SIX MONTHS

The main work for the next six months involves the following.

- 1) Continuing data collection for the present network of sites.
- 2) Completing the borehole network at Plynlimon (and Beddgelert).
- 3) Setting up sampling routines and drilling boreholes for the Vyrnwy brown earth sites.
- 4) Identifying, if possible, a deep peat site and commencing sampling.
- 5) Circulating questionnaires regarding existing data and beginning the collation of any data identified,
- 6) Comparing data for the different streams, surface waters and boreholes after six months data has been collected,
- 7) Examining the nature of groundwaters and investigating water movement by installing continuous borehole-level recorders.
- 8) Reviewing stream sampling frequency at Beddgelert, in the light of the borehole emplacement, and assessing the condition of hydrological structures at this site with

ROAD BRIDGE AFON LWYD TRIB 5



ROAD BRIDGE AFON BIGA TRIB 4

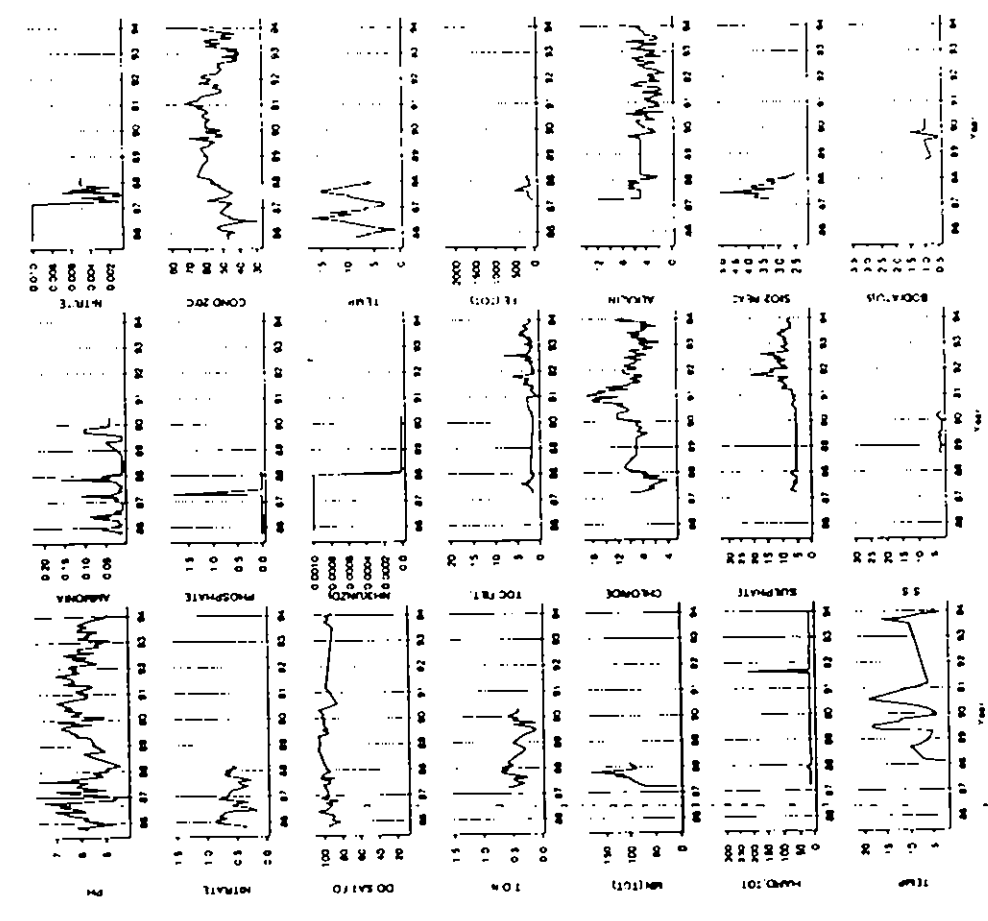


Figure 4 Llywd and Biga time series data

- a view to reintroducing more regular sampling and refurbishing the structures.
- 9) determining the background catchment characteristics for Vymwy sites - ie catchment area, altitude range, stream length, and information relating to site climate.

APPENDIX 1

Background information for Beddgelert forest

Since the spring of 1982, streamwater chemistry has been monitored at Beddgelert forest in three small catchments located in a north-east facing, former glacial cwm 12 km from the north Wales coast. Catchment D3 (4.7 ha) has remained as an unfelled control throughout this period, but felling of 62% and 28% respectively of the catchments of the other streams, D2 (1.4 ha) and D4 (6.1 ha), took place in September and June 1984 respectively. The unfelled control catchment has remained as closed-canopy spruce plantations throughout, with no ground flora apart from scattered ferns and bryophytes and no forest management has taken place. The catchments at Beddgelert have a similar geology and range of soils to those at Plynlimon and were planted with Sitka spruce in the 1930's. The catchments are at an altitude of approximately 400 m and receive an average annual rainfall of 2600 mm.

The streams at Beddgelert forest were sampled weekly from 1982 to 1992 and gauged with V-notch weirs from which flows at the time of sampling were calculated. Subsequent to 1992, samples have been collected monthly and the site has been kept running on a 'care and maintenance' basis. Trees in the harvested catchments have now reached canopy closure, with a dense cover of re-planted and naturally regenerated Sitka spruce. The site is therefore well advanced into the second rotation and should be incorporated within the remit of the study. It is intended that the boreholes should be drilled at the site. The surface water sampling frequency will also be reviewed with the possibility of weekly sampling being re-introduced.

APPENDIX 2

Forest sites at Llyn Efyrrwy (Lake Vyrnwy)

Following three visits to the Vyrnwy catchment, two sites have been selected for the study. Whilst the relative locations of the sites may not be ideal, exhaustive discussions with the local forester have shown that these are the only options available. A formal request for access has been submitted to Mr Mike Duggleby (Lake Vyrnwy Estate Manager for Severn-Trent Water Ltd). This should not present a problem. The local forester (Mr Neil Muir) is very co-operative and is willing, as far as possible, to accommodate the project objectives.

Control site

The control site is a small steep, perennial stream flowing into the southern margin of the lake. The stream is accessible from the roadside, and a small layby would provide a site for a borehole. The site details are shown below and the forester has confirmed that no felling will take place for the duration of the project.

Control site	
Location	Southern side of lake, NGR SH982213
Forest crop	Sitka spruce planted in 1943 & 1955. Small area of Japanese larch planted in 1955.
Thinning	To be confirmed - 1:3 line thinning?
Windblow	None of significance
Soils	Brown podzolic
Altitude	Mid point 350 m

Felling site

Felling site	
Location	Forest block to northeast of the lake, NGR SJ036219.
Forest crop	Sitka spruce planted in 1963. Yield class 22.
Thinning	One thinning in 1989/90
Windblow	Western edge of block at head of stream has blown down and been cleared.
Soils	Brown podzolic, with some localised gleying.
Altitude	Mid-point 340 m

The felling site is located on a moderately steep, perennial stream. The stream is accessible from a forest road and there is a suitable location for a borehole. At the head of the stream is an area of windblow that has been cleared and has now re-vegetated with grasses and rushes (*Juncus*). Close inspection of the site by walking the length of the stream, has shown that this area contributes relatively little water to the stream. The extensive vegetation cover should also limit any nitrate leaching from the windblown area. Although not ideal, this is the only option for a felling site on the Vyrnwy estate located on brown podzolic soils. It is our view that the site should be used and that the signal from clearfelling the remainder of the catchment will not be significantly affected (if at all) by the windblow damage. The area is due to be felled in 12 to 18 months time, although the forester has indicated that the exact timing can be altered to fit in with the aims of the project.

The soils of the felling site are brown podzolics but there are some areas where gleying occurs at the surface of the brown podzolic profile. This reflects poorer drainage on some of the shallower slopes. This should not materially affect the results of the study, and will still provide a major contrast between the podzol, gley and deep peat soils at the other sites.

Rainfall collection

A bulk precipitation collector is required to monitor rainfall chemistry for the sites. There is a conventional volumetric raingauge sited on high ground on the southern side of the lake, about mid-way between the two forest sites. The exact location has to be confirmed as there has been some confusion over the grid reference. The gauge is located in moorland above the forest within square SJ000190. The site is fenced and will be visited soon to check its suitability for a chemistry collector. Access is via a forest track and a short walk. Given the location of this site, it is probable that only one chemistry collector will be required.

APPENDIX 4

Publications

1. Chemical variations in near surface drainage water for an acidic spruce forested UK upland area subjected to timber harvesting: inferences on cation exchange processes in the soil.
2. Water quality trends at an upland welsh site
3. Stream chemistry impacts of conifer harvesting in welsh catchments

Chemical variations in near surface drainage water for an acidic spruce forested UK upland area subjected to timber harvesting: inferences on cation exchange processes in the soil

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Abstract

Hydrochemical variations in the major, minor and trace element concentrations of a first order stream draining a plantation of sitka spruce (*Picea sitchensis* (Bong.) Carr.), subjected to felling, are described. The stream water is acidic and aluminium bearing as the area drained comprises thin, acidic, organic-rich soils. The chemical composition of the stream varies with time and the data is scattered owing to the complex hydrological, chemical and biological interactions involved. None the less, the catchment has the ability to damp down the chemical signal of the rainfall. There is no statistically significant correlation between rainfall and stream water chemistry for any of the components measured. Deforestation leads to increased concentrations of NO_3 , K, H^+ , the major elements and Al together with a decrease in alkalinity. The changes last for ~ 2-3 years conditions then revert to pre-felling levels. These results fit well with previous findings in that deforestation leads to the disruption of the biochemical functioning of the catchment (releasing nitrate and potassium and acidifying the soil water). The major element changes are linked to increased leaching of the soil waters as a consequence of changing hydrology (evapotranspiration is probably reduced and the catchment soils wet up). However, the variations in Al, dissolved organic carbon, Br and I are less than would be anticipated based on previous results for a companion study of the main drainage area. Dissolved organic carbon, Fe, Cd, Y and La show increases, but these changes occur after the felling is complete and there has been no return to pre-felling values 3 years on. The applicability of classically used cation exchange theory for the soil, the basis for many of the conclusions derived in the soil acidification debate, is questioned and found to be highly suspect.

Keywords: AUTHOR PLEASE SUPPLY 3-6 KEYWORDS

1. Introduction

Much of the upland UK environment is acidic and acid sensitive and there is concern over stream water quality deterioration due to the effects of acidic deposition and conifer afforestation

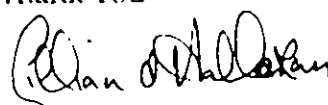
(UKAWRG, 1988; Whitehead et al., 1988). The commonest land use change in these areas, this century, has been the afforestation of acid grassland with conifers (Adamson and Hornung, 1990). This was in response to a national need for increased home-produced timber. While the earlier plantations have now been harvested and replanted, there is an increasing need for forest clearance: the major portion of the afforested

* Corresponding author.

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areas are now almost of harvestable age, they correspond with the peak rate of afforestation in the 1960s. There is growing concern that such deforestation will lead to a further decline in stream water quality, particularly with regard to nitrate, acidity, organic carbon and aluminium levels (UKAWRG, 1988; Hornung et al., 1989; Adamson and Hornung, 1990; Hughes et al., 1990; Neal et al., 1992a; 1992b). However, relatively little published data is available and patterns of change are not always uniform, while soil types and underlying geology are very varied. Thus, our understanding of the effects of deforestation has not yet reached the stage where regionalised predictions can be made.

To add to the base knowledge, new information is provided here on the water quality effects of deforestation for a first order stream in the Hafren forest, mid-Wales. The information presented relates to that area of the catchment, the hillslope soils, which (1) supplies the most acidic and lowest quality water to the main streams (Neal et al., 1990c) and (2) is most directly impacted by deforestation. This work complements a companion study which deals with the progressive deforestation of the main drainage area and the added hydrochemical complexity of groundwater supply (Neal et al., 1992a; 1992b). The work also provides an important example of the limitations of presently used equations which describe cation exchange reactions between the soil and its associated solution. This aspect is of fundamental importance for the production of lumped hydrochemical models which describe the impacts of acidic deposition and land use change at the catchment scale (Neal, 1992; Neal and Robson, 1993).

2. Location, sampling and chemical analysis

The work was conducted at the Institute of Hydrology's Plymlimon catchments in mid-Wales (Newson, 1976; Kirby et al., 1990). Here, since May 1983, there has been an extensive hydrochemical study of the upper parts of the River Severn, draining sitka spruce (*Picea sitchensis* (Bong.) Carr.) plantation and moorland areas. The approach taken has been to examine a wide

variety of chemical determinands in rainfall, throughfall, stemflow, mist and stream water. This was undertaken in order to (1) describe the consequence of timber harvesting on stream water quality and (2) see if chemical fingerprinting techniques can be used to provide information on how rain water is transported to the stream at the catchment scale (Neal et al., 1990a; 1990b; 1990c; 1992a; 1992b).

Weekly sampling of a first order stream draining a spruce forested hill-slope for a major, minor and trace element study, began in May 1988. This stream, south2-Hore, which is the major subject of this paper, drains an area of 13.7 ha with an average slope of 12°. The soils are acidic. They are comprised of stagnopodzol and stagnogley soils, typically < 1 m thick, overlying impermeable slates and shales. South2-Hore constitutes one of the streamlets supplying water to the Afon Hore from the northern slopes of its catchment. The lower 75% of the main drainage area of the upper Severn was afforested in the 1930s; prior to afforestation the area was acid moorland. The Hore catchment area was clearfelled over a 5-year period (1985-1989) and the south2-Hore part of it was clearfelled in the autumn months of 1989. With clearfelling, the stumps of the trees were left on site, together with a considerable amount of slash (needles and branches). This ensured that the development of new vegetation was and continues to be severely hampered.

The south2-Hore waters sampled were filtered in the field using 0.45 µm membranes. On immediate return to the laboratory, electrometric determinations were made for the pH, conductivity, acidity and alkalinity (the latter two, using Gran titrations). Waters were stored in the dark at 4°C in acid-washed polyethylene and glass bottles prior to analysis of the other determinands. For the metal determinations, after filtration through 0.45 µm membranes, polyethylene bottle storage was used and the samples were acidified with high purity concentrated nitric acid to 1% v/v: this minimised adsorption and precipitation reactions. Analysis involved mainly automated-colourimetry and inductively-coupled-plasma emission and mass spectrometry techniques. For all the chemical determinations, quality control standards are

included in the routine analyses. With each batch, for ICPOES and ICPMS analysis, the Institute of Hydrology's own quality control standards are included. These standards are checked weekly against international quality control references. The Institute's laboratory takes part in UK and international inter-laboratory comparison exercises and a rigorous quality assurance system is maintained.

3. Cation exchange modelling: rationale, model and testing

Much emphasis has been placed within catchment acidification research on describing soil acidification in relation to the depletion of base cations from the exchange fraction of the soil. Hydrochemical and environmental management models have used equations and concepts taken from the classical soil science literature to describe these changes (Christophersen et al., 1982; Cosby et al., 1985a; 1985b; Whitehead et al., 1988; Jenkins et al., 1990). However, the validity of the cation exchange formulations used must be questioned on the basis of field evidence and computer simulation (Neal et al., 1990b; Neal, 1992; Neal and Robson, 1993). In order to assess the validity of the presently used cation exchange equilibria at the catchment scale, field based experiments at a representative level are required (Neal and Robson, 1993). Such experiments must be enacted at field sites where the large spacial variations in soil water chemistry are smoothed out: multiple inputs to the stream (e.g. from soil and groundwater sources) confuse the issue. The data collected in this study provides a situation for the testing of the cation exchange theory given the drainage pattern and the absence of groundwater sources.

Here, the cation exchange theory tested is a simple mechanistic one taken from the classical soil science text books and used within most of the acidification models. The technique employed follows directly from the approach taken by Reuss (1980) and Christophersen et al. (1982) as ex-

tended by Neal (1992). It considers the soil as a single homogeneous unit and that the amounts of cations within the soil's cation exchange components are much higher than the amounts in the associated soil water solutions. For such a system, simple relationships between the concentrations of cations in the soil solution (strictly chemical activities) hold. Thus, for monovalent (M^+), divalent (M^{2+}) and trivalent ions (M^{3+}), their concentrations follow the relationship that the ratios $\{M^+\}^2/\{M^{2+}\}$, $\{M^+\}^3/\{M^{3+}\}$ and $\{M^{2+}\}^3/\{M^{3+}\}^2$ remain constant as anion content varies. In other words, for any two cations, M and N, of respective charge $m+$ and $n+$, their concentrations are related to each other by the power relationship —

$$\{M^{m+}\} = a\{M^{n+}\}^b \quad (1)$$

where a and b are constants and $b = m/n$. This corresponds to the theory known as the 'mobile anion concept' (Seip, 1980). As anion concentration increases, so also does the concentrations of all the cations; the rates of cation increase are in the order $[M^+] < [M^{2+}] < [M^{3+}]$ (Reynolds et al., 1988).

Here, these equations are examined against the south2-Hore stream water data by linking the cation concentrations with the soil water compositions. This linkage is required since it is the soil water rather than the stream water which is in equilibrium with the soil's cation exchanger. As the soil water enters the stream, CO_2 degasses and the hydrogen ion concentration decreases while aluminium speciation changes. For this study a back calculation has been performed to estimate the hydrogen ion concentration in the soil water before testing the cation exchange formulations. Aluminium speciation calculations were required to determine the concentration of Al^{3+} present. To do so, a thermodynamic speciation model, ALCHEMI (Schecher and Driscoll, 1988), was used. For each calculation, the total aluminium concentration in the soil was set to the stream water value and an allowance was made for aluminium complexes with hydroxide, sulphate, silicate and organic matter as well as for temperature.

4. Results and preliminary discussion

The south2-Hore streamlet has run-off characterised by acidic and aluminium-bearing waters with a variable major, minor and trace element chemistry (Table 1). As a starting point to describing the changes seen in the stream and relating them to the underlying processes, it is valuable to initially compare the average and ranges in the chemistries of the rainfall input and stream output and to describe the temporal changes in the stream water chemistry. It is then appropriate to examine the cation exchange controls on the major cations.

As a large number of chemicals have been determined and most of these are mentioned in the text, it is appropriate to present the data for all of them as a time series of plots (with the exception of those components always near the detection level). These plots are provided at the end of this paper (Appendix 1a-e).

4.1. Chemical variations in the south2-Hore stream and their relationships to rainfall chemistry

Westerly winds bring rain to the Plynlimon area from over the Irish sea and the North Atlantic. Such rain is enriched in sea salts (Na, Mg, Cl and SO_4) and components fractionated at the air-sea interface with sea spray generation (Br and I). In contrast, air masses with a more complex trajectory, particularly those passing over the UK's industrial and agricultural areas, pick up pollutant components (NH_4 , NO_3 and SO_4). Consequently, rain falling at Plynlimon has a variable chemical composition, the variability being determined by the relative contribution of both the maritime and pollutant components (Table 1).

On transport to the stream, the rainfall signal is modified and the variations in chemistry are reduced (even with the added constraint of perturbation associated with deforestation): the only exception to this is for aluminium, where its concentration in the stream is dominated by catchment supplies (Table 1). There is no statistically significant relationship between the rainfall and the stream water composition for any of the chemical components measured ($r < 0.1$ for $n = 205$). In general, concentrations are higher in

the stream water than in the rainfall. This reflects, in part, evaporation of water: chemically conservative components such as chloride average ~ 50% higher concentrations in the stream compared with the ~~soil~~ ^{rain}. For most of the major components (K, Ca, Mg, SO_4 , NO_3 , SiO_2 and DOC), many of the trace components (Al, Ba, Be, Co, F, Fe, Li, Mn, Ni, Sc, Y and Zn), DOC and acidity, there is a net supply to the stream from within the catchment. This results from acidity generation by organic acid production, chemical weathering within the soils and mobilization of the easily hydrolysable transition metals. There are, none the less, important exceptions. In the case of sodium, there is a net input-output balance. This reflects the limited degree of uptake/release of this component from the vegetation and soils. Also, there are some components which are taken into the soil from the rainfall input. The most noticeable of these are the nutrients NH_4 , PO_4 , Br and I: the two main nutrients, NO_3 and K, show an enrichment which is mainly associated with the effect of deforestation, as discussed later. There are also a few trace metals that show a net absorption (Cd, Cr, Cu and Pb).

Because of the catchment controls and various catchment supplies, there are similarities in the patterns of behaviour for groups of chemicals from hydrochemically similar environments. For the sea salt components (Na, Mg and Cl), which are essentially derived from the atmosphere, there are very high inter-correlations ($r > 0.95$, $n = 205$). Also, there are high correlations ($r > 0.7$, $n = 205$) for many of the divalent metals (Ca, Sr, Ba, Mn, Co and Ni) and these are correlated with the sea salts and silica. K and NO_3 are also correlated, with temperature, as are Y and La. All of these patterns are essentially the same for the periods prior to felling, post felling and for the full sampling period.

While flow has not been measured for the south2-Hore stream, hydrology is clearly an important factor in determining the composition for some chemical constituents in the stream (Fig. 1). This can be gauged using flow information for the upper Hore gauging point. Inverse relationships with flow are found for Ca, SO_4 , Si, Mn, Co and Ni (there are also lower concentrations at high

Table 1
Rainfall and south2-Hore stream water concentrations and ranges

	Rain avg (mg/l)	Stream avg (mg/l)	Catch avg (%)	Rain range (mg/l)	Stream range (mg/l)
Na	2.86	4.19	- 2	0-21	2.3-8.3
K	0.13	0.52	62	0-2	0.5-1.2
Ca	0.21	0.52	41	0-2	0.2-1.2
Mg	0.35	0.69	24	0-2.5	0.4-1.3
NH ₄	0.32	0.02	- 2220	0-2.7	0-0.3
Cl	5.37	8.05	0	0-41	4-19
SO ₄	1.74	3.77	31	0-10	2-7
NO ₃	0.79	2.45	52	0-10	0-9
PO ₄	0.03	0.01	- 345	0-1.2	0-0.5
Si	0.13	0.94	79	0-20	0.3-1.8
DOC	0.50	2.34	68	0-2.4	0.3-5.6
	(µg/l)	(µg/l)	(%)	(µg/l)	(µg/l)
Al	7.11	365.65	97	0-180	155-596
B	3.66	5.80	5	0-44	2-18
Ba	1.31	4.36	55	0-198	1.3-10.3
Be	0.00	0.04	100	0-0.2	0-0.13
Br	19.40	24.27	- 20	4-128	16-45
Cd	0.19	0.19	- 51	0-6	0-0.9
Co	0.05	1.08	93	0-4	0.2-2.9
Cr	1.70	1.35	- 89	0-15	0.1-7.7
Cu	1.13	1.21	- 40	0-28	0.3-13.1
F	20.14	34.96	14	0-120	0-100
Fe	5.48	74.80	89	1-108	22-153
I	1.35	1.23	- 65	0.6-4.6	0.7-2.6
La	0.19	0.28	0	0-8	0-2
Li	0.07	1.52	93	0-4	1-3
Mn	1.15	60.02	97	0-18	22-153
Mo	0.17	0.26	0	0-40	0-2
Ni	0.68	2.55	60	0-16	1-5
Pb	6.78	1.37	- 639	0-160	0-7
Se	0.02	0.04	31	0-0.8	0-1.6
Sr	2.30	3.73	8	0-14	2-7
V	0.13	0.02	- 906	0-3	0-1
Y	0.01	0.08	85	0-1.4	0-2.4
Zn	4.73	11.11	36	0-126	7-27
Zr	0.13	0.22	12	0-6	0-1.5
	(µEq/l)	(µEq/l)	(%)	(µEq/l)	(µEq/l)
Alk	- 14.15	- 27.72	24	- 463-31	- 52- - 10
H Ion	14.94	25.55	12	0-436	5-64

The term 'catch avg' gives an estimate of the percentage of a chemical in the stream associated with catchment supplies, as opposed to the atmospheric contribution. The calculation is based on the assumption that chloride is chemically conserved within the catchment and that the change in chloride concentration between rainfall and the stream is representative of evaporation. For the calculations, volume weighted averages are used. The concentrations are expressed in mg/l or µg/l as the element/species listed in column 1 (e.g. NO₃ and SO₄ are expressed as mg NO₃/l and mg SO₄/l, respectively), except for alkalinity and H⁺ which are both given in µEq/l units.

flow for many of the major ions, but the scatter is much higher than for the components shown in Fig. 1). Positive relationships with flow occur for Fe and DOC. These relationships occur because of varying flow routing over time. Under drier conditions, more water comes from the lower soils which are more inorganic in nature with a higher content of inorganic weathering components. In contrast, under higher flow conditions, more water is supplied from the upper soils which are more acidic and enriched in organic acids. However, flow is not the only determining factor and there are two inter-related aspects to consider.

(1) *Felling related changes.* The effects of deforestation are observed for NO_3^- , K, alkalinity and H^+ . NO_3^- , K and H^+ concentrations increase while alkalinity decreases with felling. These changes remain for 2–3 years post-felling, after which they decline back to pre-felling values. The changes are associated with the disruption of the biological cycle with harvesting and the subsequent regeneration of the vegetation (Neal et al., 1992a; 1992b). With harvesting, there is a reduction in the nitrogen uptake by the vegetation. This leads to increases in nitrate levels and enhanced acidification. As the biological controls re-establish themselves, nitrate levels decline and thus acidification is reduced. For the major cations and chloride, there are similar increases in concentration for the 1st year following felling: there is then a reduction to background levels. In this case, the changes are probably associated with a flushing of salts from the catchment as tree loss results in a reduction in evapotranspiration, wetter conditions in the soil and increased leaching of salts. There may be some limited increases in concentration for aluminium for 2–3 years after the onset of felling (10–30%) and a subsequent decline to values lower than those encountered prior to felling. In contrast to this, dissolved organic carbon, Fe, Cd, Y and La show increases: the changes occur mainly after the felling is complete and there has been no return to pre-felling values even 3 years on. Presumably these changes reflect an increased supply of humic materials, the metals associated with the dissolved organic

carbon being related to metal-humic binding. For many of the other chemicals, there may be a small effect associated either with deforestation or some longer term behaviour. This is evidenced by small declining concentrations post-felling (e.g. fluoride); chromium is exceptional in that concentrations clearly decrease sharply following harvesting.

(2) *Seasonal variations.* There are cyclical patterns of behaviour observed for the nutrients NO_3^- , K, B, Br and I, as well as for Cr and Li, although there is much data scatter. Throughout the study period, the concentrations for this group of chemicals peak during the summer and early autumn periods when biological activity is at its highest and low flows predominate. These variations probably come about due to the biological controls for the nutrients and from increased weathering of the bedrock for lithium.

4.2. Cation inter-relationships and the testing of cation exchange theory as applied to the hillslope scale

For the major cations (Na^+ , Ca^{2+} and Mg^{2+}), chloride and the sum of the anions, there are high inter-correlations (Fig. 2; $r > 0.7$, $n = 205$). These patterns are essentially the same for the periods prior to felling, post-felling and for the full sampling period. There is a poor correlation between the major cations and the sum of the anions with H^+ and trivalent-aluminium (Fig. 2). The results show that the concentrations of Na^+ , Ca^{2+} and Mg^{2+} as well as the sum of the anions are linearly correlated with near zero intercepts (Fig. 2). Linear regression analysis of logged concentrations give power terms (b), as depicted by Eq. 1, which are quite different from the theoretical values (Table 2). In the case of H^+ and Al^{3+} , no well defined relationship occurs between them or the major cations and the data is highly scattered: as with the major cations, the power relationships are far removed from those given by theory (Table 2).

The results described here indicate that while there is a broad relationship between the cation concentrations and the sum of the major anions, there is no compatibility with the mobile anion

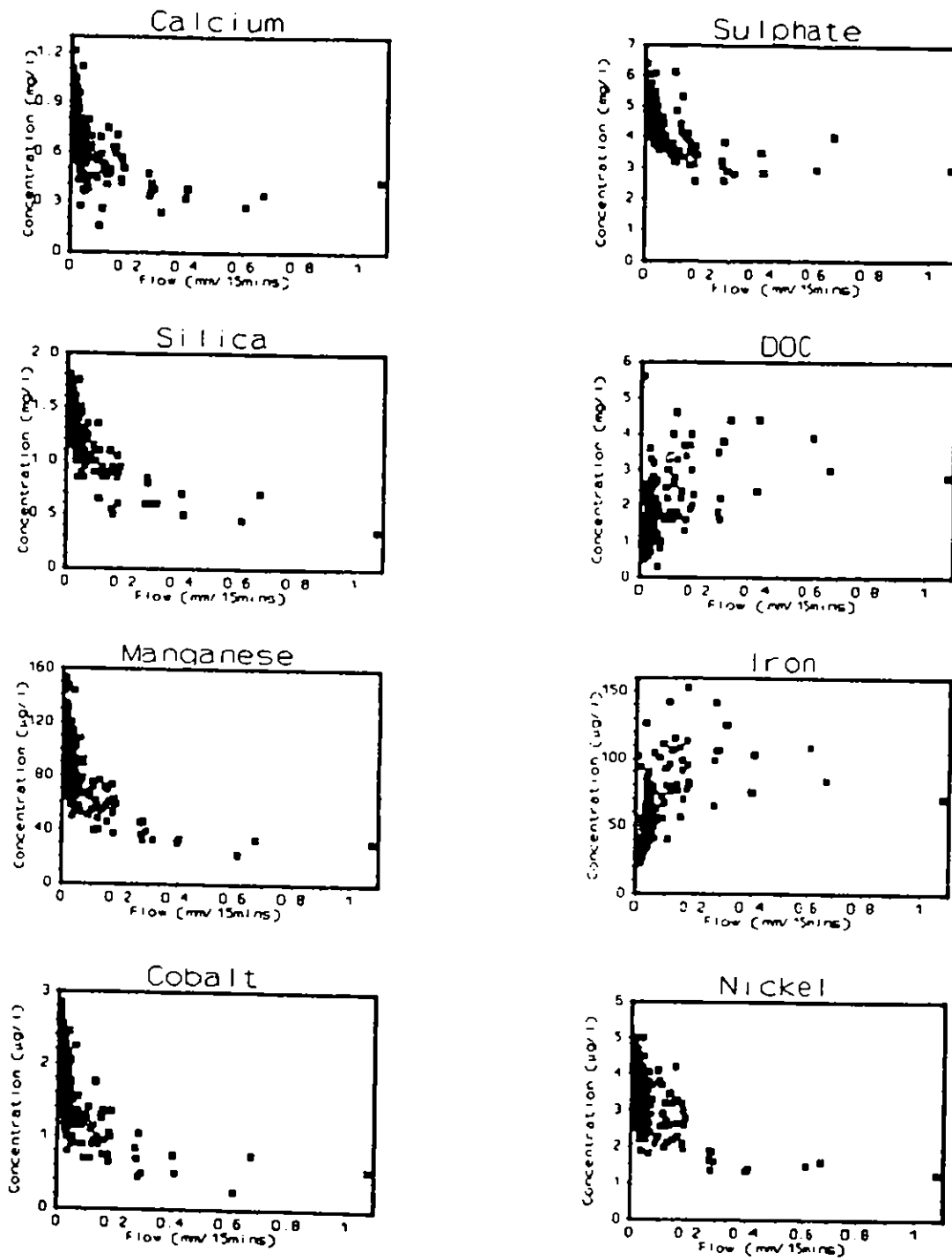


Fig. 1. A comparison of major and trace metal relations with flow for the south2-Hore stream: the flow values are those of the upper Hore as there is no gauging structure at the south2-hore site.

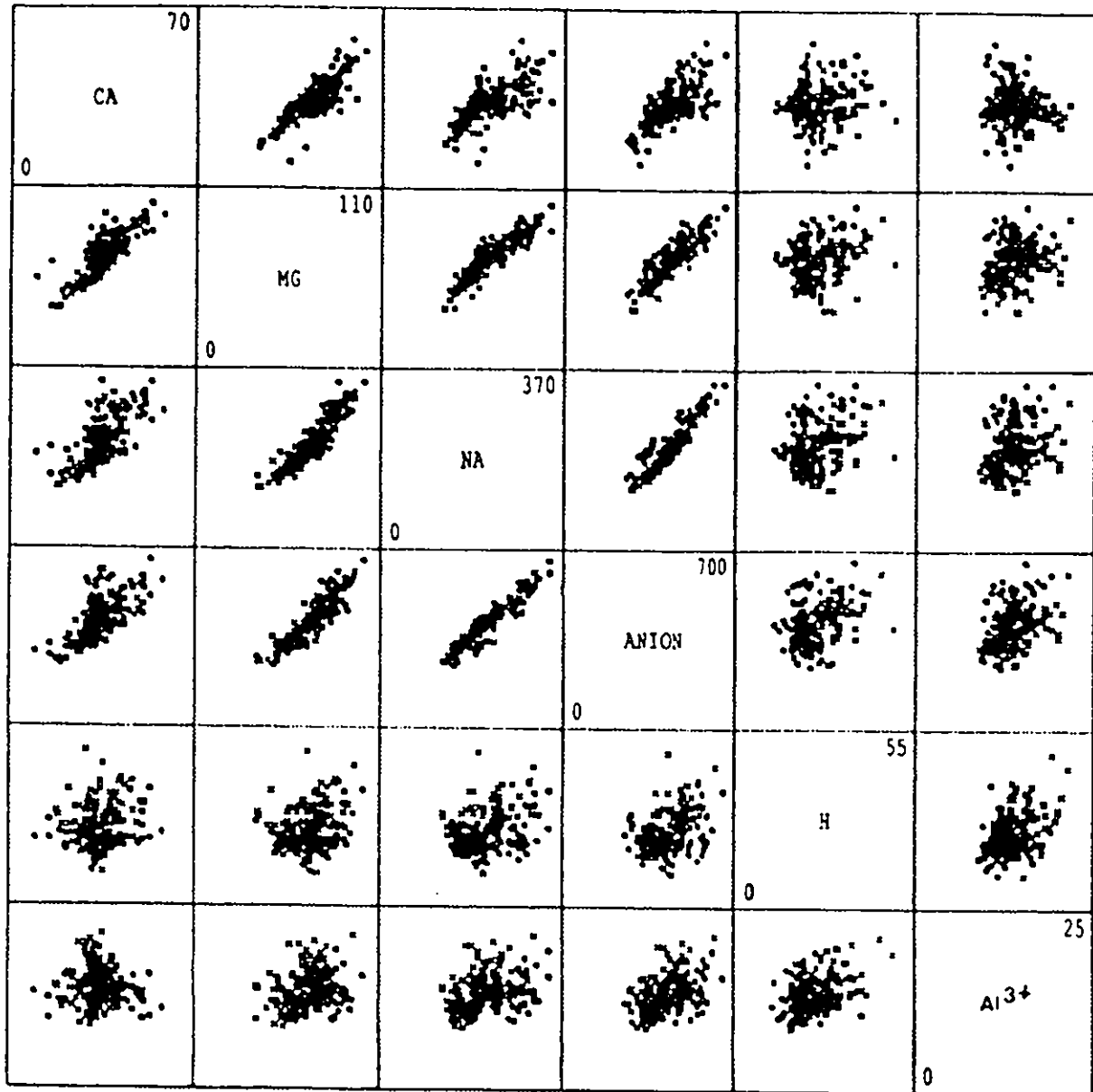


Fig. 2. Major cation, H^+ and Al^{3+} concentration inter-relationships for the south2-Hore stream.

concept. For the major cations, the power relationships describing their co-variations lie between the theoretical values and unity. This is compatible with a recent theory for spatially and temporally heterogeneous cation exchange where (a) simple cation exchange reactions occur within the micropores within the soils and (b) on passage

to the stream, the soil water chemistry is not modified by the soils cation exchanger (Neal, 1992). However, the decoupling of H^+ and Al^{3+} from the major cations implies that these components are not primarily determined by simple cation exchange reactions in the soil as depicted in the 'acid rain' literature. Indeed, previous work

Table 2
Linear regression data for logged concentration data for the south2-Hore stream

	r^2	Gradient (b) (regression)	Gradient (b) (theory)
Na ⁺ — Ca ²⁺	0.422	0.73 ± 0.12	0.50
Na ⁺ — Mg ²⁺	0.828	0.78 ± 0.05	0.5
Na ⁺ — Al ³⁺	0.123	0.54 ± 0.20	0.33
Na ⁺ — H ⁺	0.080	0.24 ± 0.11	1.00
Ca ²⁺ — Mg ²⁺	0.641	0.61 ± 0.06	1.00
Ca ²⁺ — Al ³⁺	0.007	0.12 ± 0.20	0.67
Ca ²⁺ — H ⁺	0.018	0.10 ± 0.11	2.00
H ⁺ — Al ³⁺	0.271	0.94 ± 0.21	0.33

The gradients correspond to the power relationships between cations (Eq. 1) and the bracketed terms are twice them standard error; $n = 205$. The term on the left hand side of column one is the independent variable.

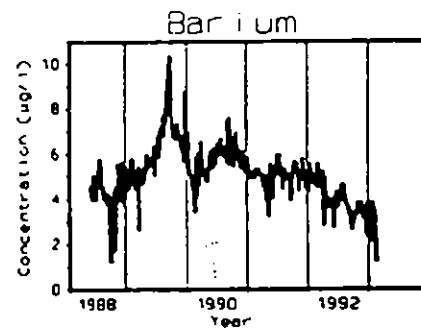
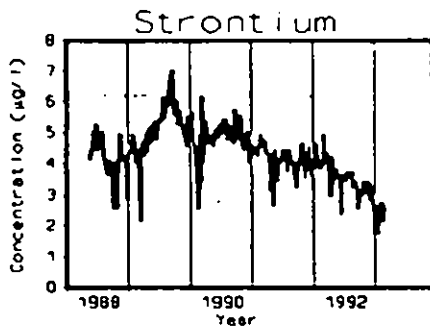
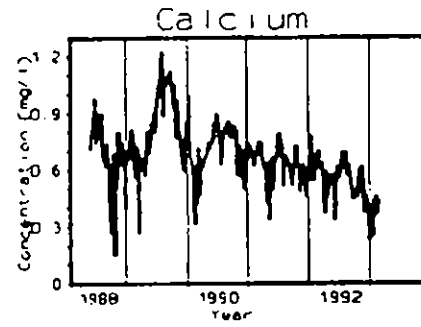
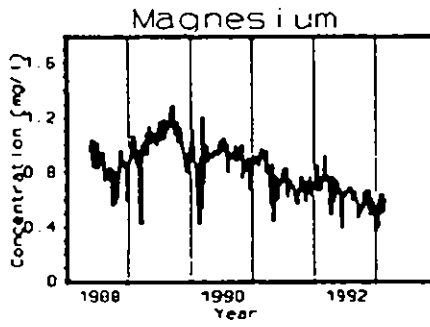
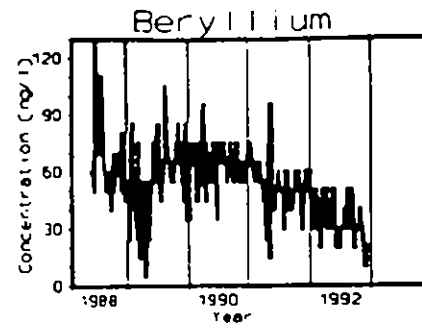
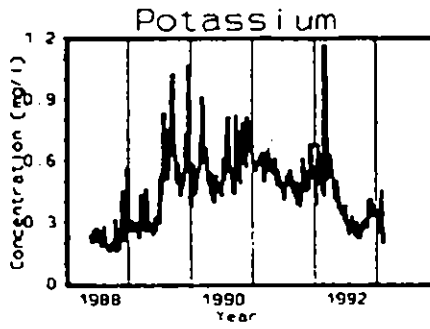
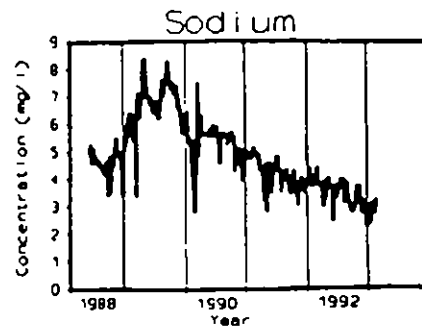
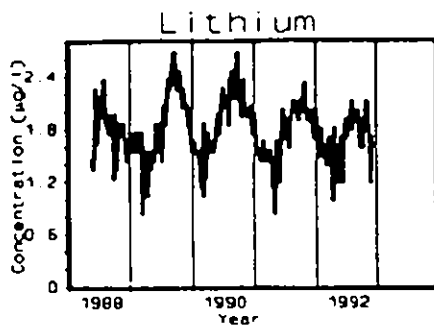
at Plynilimon indicates that aluminium release to drainage water can be associated with kinetic 'weathering' type reactions involving proton consumption (Reynolds and Hughes, 1989).

5. Discussion

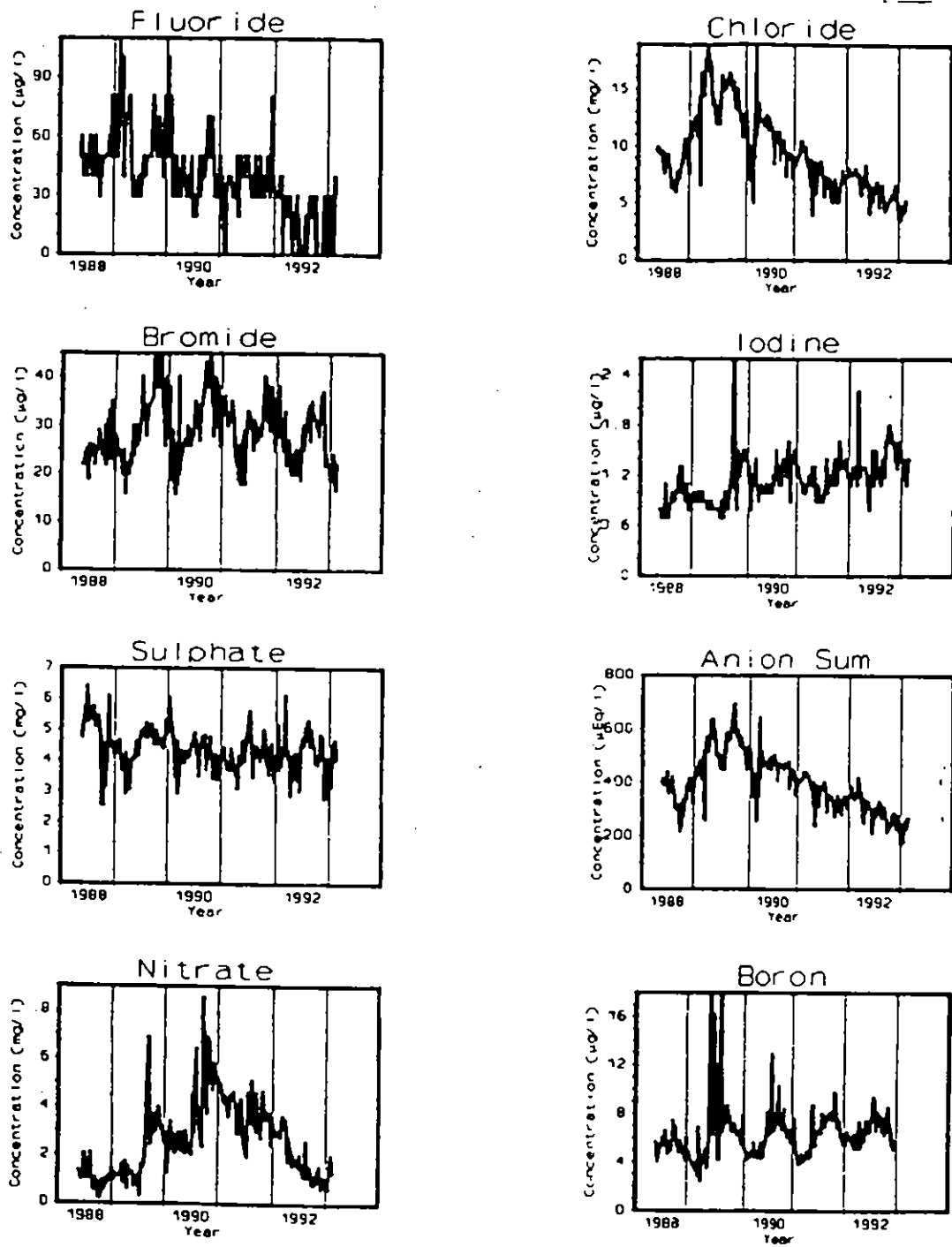
The results provide a clear indication of a deterioration in stream water quality following tree harvesting that fit in well with previous observations for NO₃, K, H⁺ and alkalinity (Likens et al, 1970; Lawrence et al, 1987; Lawrence, 1989; Stevens and Hornung, 1987; Stevens et al., 1989; Hornung et al, 1989; Adamson and Hornung, 1990; Reynolds et al., 1991; Neal et al., 1992a; 1992b). The disruption of the natural biological cycles results in increased NO₃ and K production in the soil water. This flux is transferred from the soil to the south2-Hore stream, quadrupling the concentrations for a period of 2–3 years. At the same time, the stream becomes more acidic and Al increases by ~10–30%, although the scatter is high. In part, the changes observed are very similar to those found for the main stream channels at Plynilimon for H⁺, NO₃ and K. However, the extent of the increase is larger for NO₃ and K and the changes in the baseflow chemistry are different owing to the very different groundwater inputs. It seems that after a 2-year period, the initial deforestation disturbance has essentially worked through the system, eventhough the vegetation remains sparse. There may, however, be a subsequent deteriora-

tion in water quality with forest regrowth. This hypothesised longer term effect is associated with base cation uptake into the developing biomass and the depletion of base cations from the soils chemical store (Jenkins et al., 1990). For the main river, the deforestation effects are of reduced size and extended length for NO₃ and K owing to progressive felling over a 5-year period, compared with the south2-Hore stream where the area was felled over a few months. However, for Al, Br and I, the changes observed in south2-Hore are smaller than would be anticipated based on changes observed in the main river. Also, for dissolved organic carbon at south2-Hore, the increases seem to be observed for a longer period after felling than for the main stream. This probably means that the soils in different parts of the Hore catchment respond in different ways to deforestation, for these components.

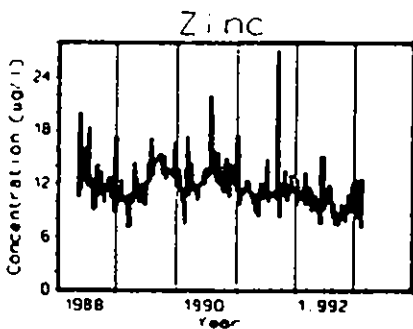
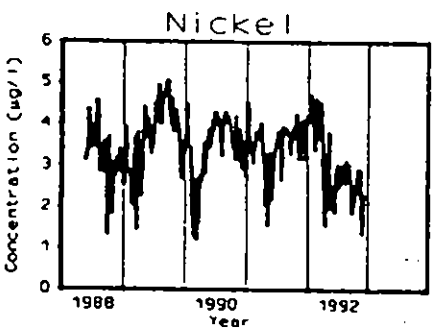
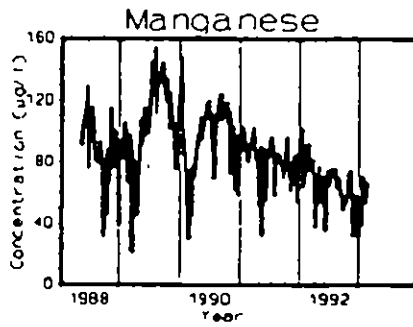
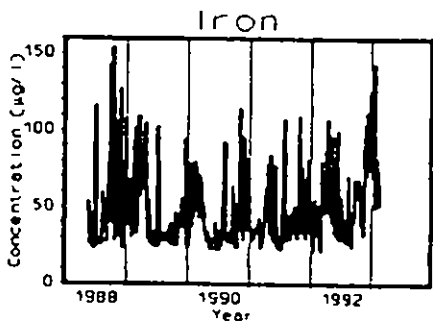
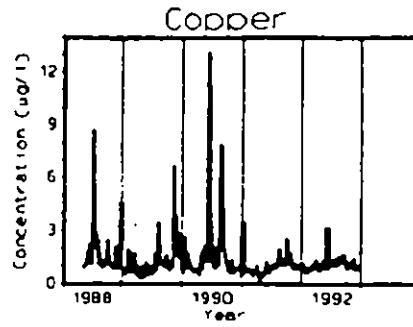
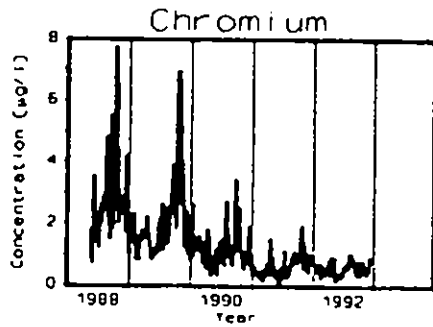
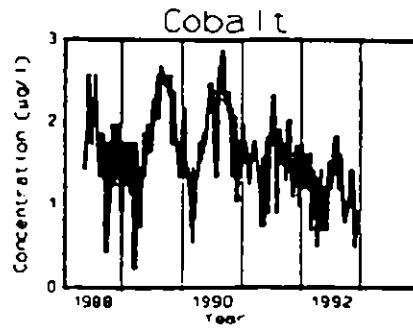
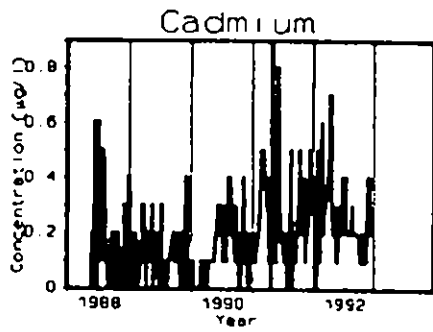
The present study re-emphasises that there are major difficulties over the appropriateness of simple cation exchange formulations when dealing with catchment scale modelling. Even under a near ideal case for observing the equilibrium process, it is clear that there is no evidence for any equilibrium. Most disturbingly, there is a general lack of a relationship between the base cations and H⁺ and Al. As the acidification models are driven by relationships between these components, it seems that a mathematically sound model is still required for determining the two ecologically harmful components of the water that need environmental modelling, H⁺ and Al.



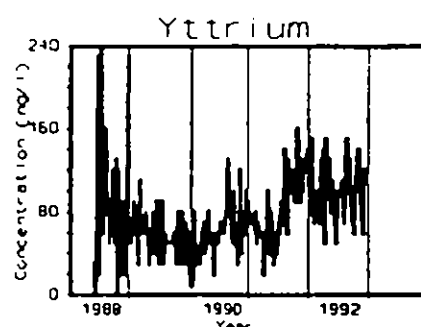
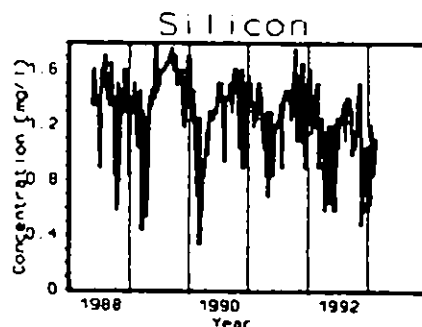
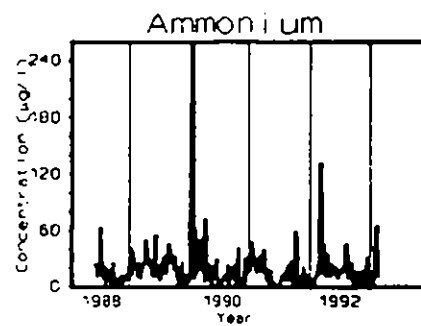
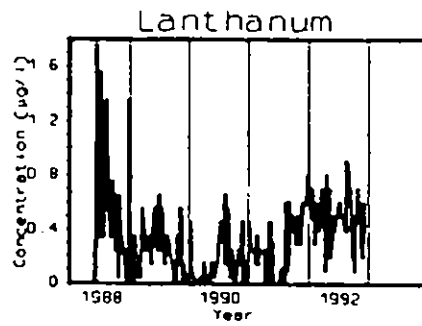
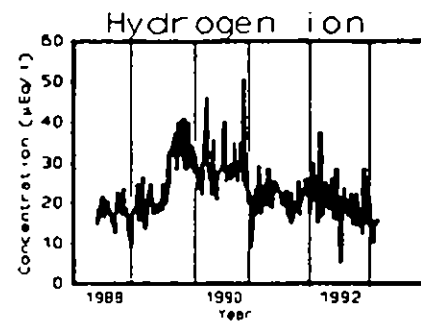
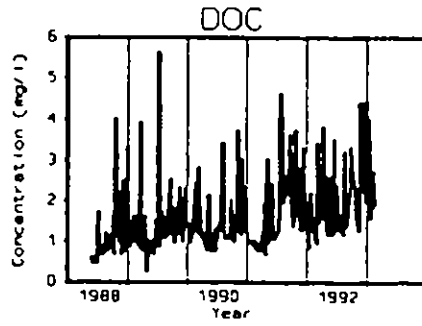
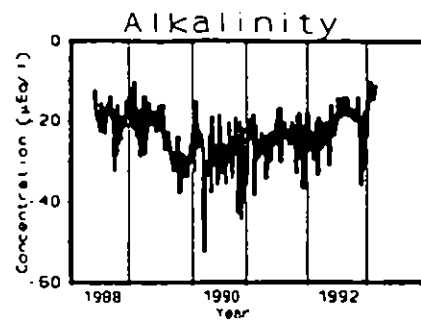
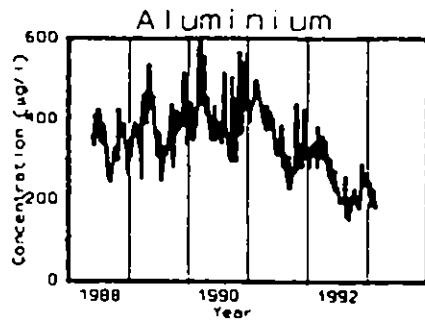
Appendix 1a: time series plots of base cation concentrations.



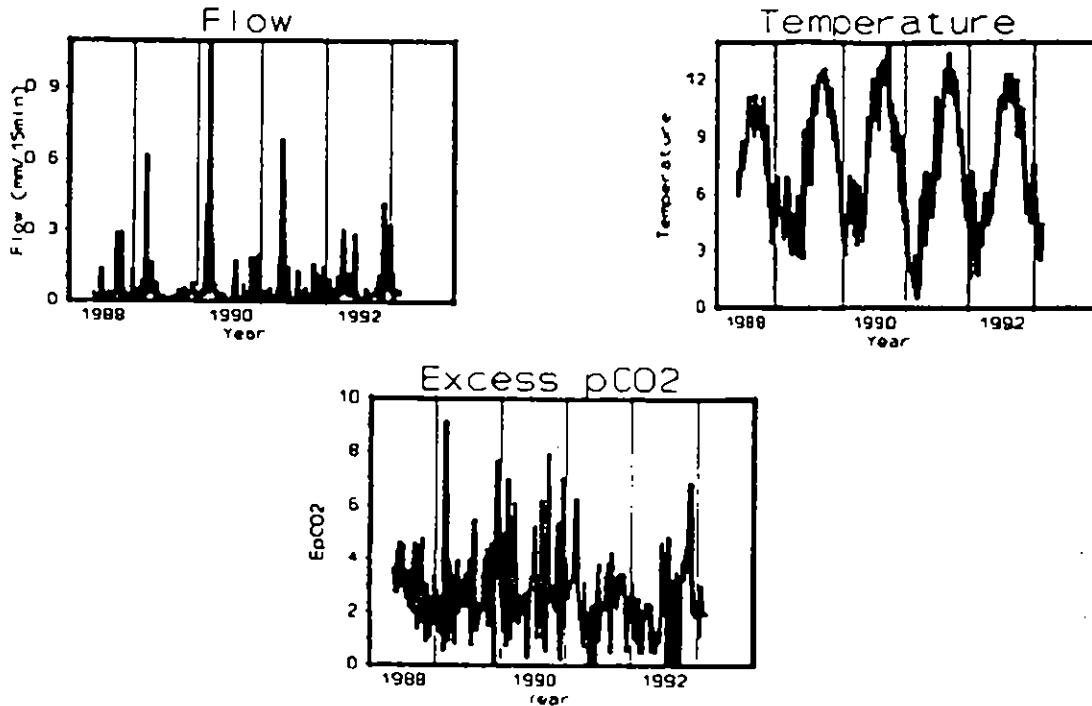
Appendix 1b: time series plots of anion concentrations.



Appendix 1c. time series plots of transition metal concentrations.



Appendix 10: time series plots of other concentrations.

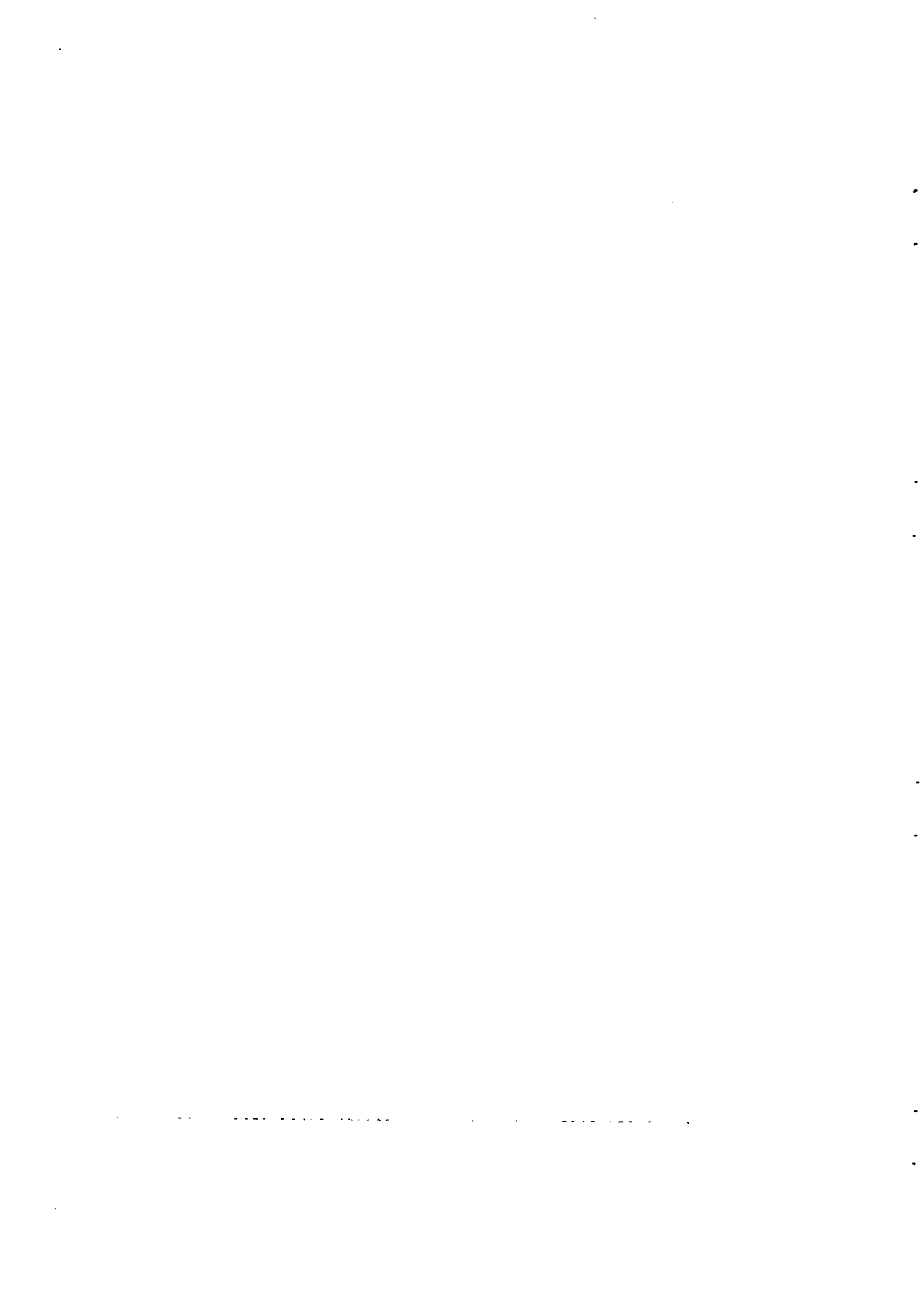


Appendix 1c: time series plots of physical components.

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Water Quality Trends at an Upland Welsh Site.

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Abstract

Ten years of detailed upland stream and rainfall water quality data from Plynlimon, mid-Wales, are examined for trend. The analysis of the data focuses on the use of graphical presentation, smoothing techniques and robust statistical tests. For rainwater, a steady increase in DOC is observed over the ten years and there is a possible rise in ammonia. For the stream waters, there have been increases in DOC, iodine and bromide, suggesting an increase in the rate of organic decomposition in the soils. For most other chemical determinands, any changes are masked by the effects of year to year variations in rainfall volume and chemistry. These variations appear to be caused by random fluctuations in the weather patterns at Plynlimon. The effect is most marked for marine derived elements such as chloride, but is also seen for a number of other determinands. Much longer time series of data will be required before trend can be concluded for any of the species affected by weather variation. The 10 years of data presented here may well not be enough to make any sensible statements about any of the determinands.

1.0 Introduction

There continues to be much concern over the long term impacts which anthropogenic pollution has on upland environments. Analyses of long records of data may provide clues about what will occur in the future. Here, time series of stream water chemistry data are presented for Plynlimon, an upland acidic and acid-sensitive site in Mid-Wales. The Plynlimon records are long and detailed in comparison to many upland sampling programs (UK Acid Waters Monitoring Network, 1991; Hornung et al., 1990). Measurements have been taken weekly for the last 10 years for stream and rain waters and include an exceptionally wide range of major, minor and trace determinands (Neal et al., 1992). Here, the Plynlimon stream and rain water data is examined for evidence of long term change.

Within this paper, a highly graphical approach is used with the objective of presenting data clearly, so that others may form their own judgements and interpretations of what is occurring. Emphasis is placed on examining the observed stream water changes in relation to rainfall inputs, flow variations and catchment processes. Robust statistical tests are applied for some data series - but only where visual inspection suggests that there is a steady monotonic change underlying the observations.

1.1 Trend and context

Here, a time series is loosely defined to have trend if there is a low-frequency component of the time-series response that shows monotonic drift. It is desirable to separate out this drift from the other higher-frequency variations caused by factors such as the season, rainfall, climate and flow. When examining data sets for trend, it is often the underlying cause of change that is of primary interest; the value of trend analysis is that it may provide evidence of changes that are taking place within the system. A consequence of this is that it becomes very important to look at trend (1) in the context of the processes from which the data arise, and (2) with reference to a suitable time scale of concern. The use of such an approach will

make it more likely that persistent changes, in this case changes that will continue into the coming decade or decades, can be differentiated from temporary effects

In the context of upland stream water chemistry, there are many scales at which change can be observed. Over hours and days, episodic storm-induced variations are dominant (Davies et al., 1992), while over a year, there are seasonal variations. With a few years data, the effect of meteorological variations, over and above the seasonal variation, become apparent. And, over a long enough timescale, there may be evidence of change within catchment, e.g. depletion of cations in the soils or accumulation of anions such as sulphate. Here, only ten years of data are available.

At Plympton, primary concerns are the potential effects of acidic wet and dry deposition and of plantation forestry (Neal et al., 1992). The thin acid soils provide little buffering capacity against continued acidic inputs and, with likely deforestation and reafforestation in the future, the system may become yet more acidic. The period of concern is potentially quite long, given that a forest cycle is around 40 years. Clearly it will not be possible to make projections this far forward until much longer data sets have been collected. A decadal trend seen today, may later emerge as part of a longer term fluctuation - just as a trend seen during a period of a few months may simply be part of a seasonal variation. For the 10 year data set considered here, observed changes may at most be expected to provide insight as to what will occur during the coming decade.

It is important when looking at trends to place them in the context of catchment processes and rainfall input variations. For example, consider the question of whether catchment acidification, i.e. a build up of acidity and a loss of base cations from the soil exchange sites, is occurring at Plympton. A likely result of acidification would be a decline in stream water base cations and an increase in hydrogen and aluminium concentrations (UK Acid Waters Review Group, 1988). However, catchment acidification may not be the only cause of such changes. A reduction in rainfall pollutant loads could cause similar decreases because of the reduced number of ions moving through the system. Thus, it is necessary to investigate what is occurring in the rainfall and in the stream before the problem of acidification at Plympton can be addressed. It may also be necessary to consider other factors such as effects of

seasonal and flow related variation if stream water quality is to be properly understood.

2.0 The Plympton catchments

2.1 Catchment Description

The Plympton site is located 24 miles inland of the west coast of mid-Wales and is typical of much of the UK uplands. Bedrock consists of lower Palaeozoic mudstones, shales and grits, whilst soils are acidic and range from peats and podzols to gleys. The Afon Hafren (catchment area 347 ha; altitude 350-690 m) is the main headwater tributary to the river Severn. The upper half of the Hafren catchment drains acidic semi-natural moorlands and peats. The lower half is densely planted with conifers which date from between 1937 and 1964. Plympton has a cool wet maritime climate; annual rainfall is about 2400 mm/year with average evaporational losses of 400-600 mm/year. More extensive descriptions of the Plympton area are given in Kirby et al., 1991 and in Newson, 1976.

As part of the Plympton program, rainfall and stream water samples from the Afon Hafren have been collected at approximately weekly intervals since 1983. A wide range of chemical analyses have been carried out on these samples including pH, conductivity and major, minor and trace elements. Further methodological details, with descriptions of the chemical nature of the catchment, are detailed elsewhere (Neal et al., 1992). For several minor elements, the method of analysis was changed in 1992 so the last year of data has not been used in this analysis.

2.2 Primary catchment chemical processes.

The processes influencing stream water chemistry are multiple and complex and are extensively documented elsewhere (Neal et al., 1986, 1990a, 1992; Robson, 1993). Here a brief overview is provided as a background to the interpretation of the data series that follow.

Rainfall, a major chemical input to the system, is very variable and has substantial effects on stream water chemistry. Rainfall chemical variations are highly complex but are linked in part to meteorological conditions (UK Review Group on Acid Rain, 1990). Storms high in marine salts (eg chloride and sodium, and part of the sulphate, magnesium and calcium) are associated with Atlantic frontal systems and are most common during the winter months. Pollutant components (eg ammonia, nitrate, heavy metals and the remainder of the sulphate, calcium and magnesium) are often highest in summer storms or in smaller storms. Pollutant components are very variable as they derive from long range transport from a variety of sources (eg various industrial and agricultural activities; UK Review Group on Acid Rain, 1990).

Rainfall chemistry has only a small direct impact on stream water quality except during the larger storm events. The largest storms represent a substantial flux of water but part of this water may only be in the catchment for hours or days and thus will have a relatively limited chemical interaction with the catchment. Rainfall from smaller storms is likely to remain in the catchment for some time since it displaces water which is already in the catchment to the stream. Substantial variations in rainfall chemistry are typically mapped into a longer-term, damped, alteration of stream chemistry (Reynolds and Pommeroy, 1988; Neal and Rosier, 1990). This reflects the importance of chemical storage within the catchment. Modelling of residence times suggests that a proportion of the input may remain in the catchment for a very long time, months to years, even for conservative species such as chloride (Robson, 1993).

Once rainfall enters the catchment, it is modified by chemical interaction with the soils and water stores within the catchment. There are marked differences in the chemical characteristics of the upper and lower soils and the groundwater areas (Reynolds et al., 1986) and these result in strong chemical gradients within the catchment. The main hydrochemical processes occurring in these zones are summarized below.

Upper soils: These have a high organic content, giving soil waters which are enriched in humic acids and which are typically strongly acidic (pH's of about 3.5 to 4). This part of the soil is biologically active and there are major adsorption-desorption and organic decomposition controls. Such controls are particularly important for the nutrients (phosphate,

nitrate and potassium) and bromide and iodine. Cation exchange processes are also important in the upper soils: hydrogen and aluminium ions in the soil are exchanged for base cations in rain water. Acid rain may cause the soil exchange sites to become depleted of base cations and may affect the controls on the release and consumption of the humic acids. These humics in turn affect soil pH and aluminium concentration and speciation. Afforestation makes depletion of soil exchange sites more likely as there is an uptake of base cations into the tree biomass.

Lower soils: The main components of the lower soils are the weathering products of the inorganic aluminosilicate bedrock. Acidic waters from the upper soils partly dissolve these substances producing solutions bearing aluminium and transition metals. The soil solutions are typically in the pH range 4 to 4.5. In this zone, humic acids are flocculated and some decomposition occurs.

Groundwater/bedrock zone: In this region, aluminosilicate bedrock minerals are present and weathering reactions predominate. This weathering is promoted by the entry of acidic soil water and it causes the release of base cations (mainly calcium plus some magnesium). During this process, hydrogen ions are consumed and the pH rises so that aluminium and transition metals are precipitated. Alkalinity also increases and bicarbonate ions become an important part of the anion charge.

Stream water chemistry is typically highly dependent on the flow. This dependency reflects the marked chemical gradients described above and the alteration of hydrological flow pathways during storm events. The contribution of waters from the upper and lower soils is largest during storm flow; thus storm flow waters are acidic and enriched in transition metals and aluminium. In contrast, baseflow waters derive from the groundwater zones and are calcium and bicarbonate rich and provide the most ecologically favourable conditions in the stream.

On a longer time scale, stream water chemistry is strongly influenced by both the prevailing and the historical hydrological conditions. A dry year will show an average chemistry typified by the calcium and bicarbonate rich baseflow waters. A wet year will produce more

aluminium, hydrogen and bear less calcium and bicarbonate. Not only this, but a wet year immediately following on from a dry year may yield higher than normal chemical fluxes (Durand et al., 1994).

Thus, the stream water chemistry may be viewed as the result of rainwater which is chemically modified by the soils and bedrock, stored in the catchment for variable periods, and is finally released to the stream via episodically altering flow pathways.

3.0 Methodology of trend analysis

Most of the trend analysis presented in this paper is based on direct presentation of the data and on the use of smoothing techniques. Smoothing allows an impartial guidance to looking at the broader characteristics of change. Here, smoothing is achieved using a locally weighted regression smoother called loess (Chambers and Hastie, 1992; Cleveland, 1979) within the Splus programming environment (Becker et al., 1988). With this technique, the smoothed curve at any point is derived by fitting a local quadratic polynomial between the predictors and the dependent variable. For any value of the predictors, a weighting function is applied to nearby points, and least squares optimisation is used to fit the local curve. In this application, a robust bilinear weight function has been used which is suited to cases where errors are symmetrically distributed, i.e. the data need not follow a normal distribution. Flow and stream water quality data are highly skewed at Plympton, and for positive data series a log transformation of the data was found to improve the symmetry of the data considerably. Where possible, smoothing was therefore applied to log transformed data and the result was back-transformed for plotting. Zero-values in the data were assigned a value of half the detection limit for these log transformations. The use of this transformation reduces the influence of the highest data points (extreme values). For several graphs, a further loess curve is presented in addition to the loess curve fitted to the concentration data. This is weighted for flow (or volume in the case of rainfall) and is used to emphasize changes at high flow, and thus changes in load. A loess curve weighted towards low flow data was also investigated but generally paralleled the other curves and is therefore not shown. The degree of

smoothness used in fitting the curve may be adjusted and here it is selected to emphasize the general drift in the data rather than the seasonal or shorter term changes. It should also be noted that the accuracy of the curve is reduced at the start and end of each data series (in these regions fewer data points can be used in the smoothing functions).

The loess plots were used to screen the data for determinands which may contain trend. In examining a loess curve for trend, we have considered whether a change has been consistently seen throughout the period. For example, would the same 'trend' have been deduced if any of the five year subsets of the data had been used. Cross comparison between the different determinands has also formed an important part of the process. For example, close relationships between many determinands suggest the changes seen in loess curves are rooted in the marine variation. Large year to year differences in the weather appear to cause substantial annual variations in many rainwater and stream water quality determinands. By screening the data series, we hope to eliminate 'false' trends which are an artefact of weather variability. Trends which do not appear to be substantially affected by annual variability are identified and formally tested here. In other words, visual inspection is being used as a tool which can help distinguish between trends which are weather driven (and not of substantial interest here), and trends which may be symptomatic of a change within the catchment.

For those determinands with a possible trend, further investigations were undertaken. Initially, the time series were decomposed into seasonal, trend and residual components using the loess based STL routine of Splus (Statistical sciences, 1993; Cleveland et al., 1990). In this decomposition, no transformation of the data was used because of the difficulty of subsequently interpreting the components. However, the robust bilinear weight function was still used in the curve fitting. In addition, for stream water quality determinands, the effect of flow induced variation was also considered by looking at the trends at low, medium and high flows. Each of the flow groupings was selected so as to contain the same number of sample points, with 25% of the points in one regime also overlapping into the next regime. Scatter plots and loess curves were used to see how response varied over the ten-year period at different flow levels. This is important because almost all determinands show some form of relationship with flow due to the chemical gradients in the catchment (see earlier section). The exercise was aimed at detecting whether any of the 'trends' arise because of uneven flow

distribution. This is particularly important in view of the exceptionally dry period which occurred towards the start of the sampling program.

The selected screened data sets were also formally tested for trend. A number of these data series were highly non-normal and contained a number of extreme values - though it must be emphasized that these 'outliers' are believed to be 'real' values and not measurement error. Because of this, robust statistical tests were used to test for trend. The tests used included the seasonal Kendall test and a robust linear regression method. The seasonal Kendall test is an adaptation of the non-parametric Kendall test and tests for trend in data with seasonality and autocorrelation (Hirsch and Slack, 1984; Hirsch et al., 1982). The seasonal Kendall test statistic is robust to outliers because it uses ranked data in its calculations. A seasonal Kendall slope estimator (based on the Sen estimate of slope) is used. This estimate should also be robust to extreme values since it is constructed by calculating all pairwise slopes within a season, and taking the median of all these values over all the seasons. For comparison, a robust regression method, least trimmed squares regression, was also used, although this does not allow for autocorrelation in the data. This selects the linear regression coefficient which minimises the sum of the smallest half of the squared residuals.

4.0 Application to Plynilimon

4.1 Trends in rainfall chemistry

Rainfall time series graphs have been plotted for all detectable determinands in rainfall and a selection of these graphs are shown in Fig. 1 a,b. For species which have marine and pollutant sources, excess concentrations (the non-marine component as estimated from the chloride concentration) were also examined. The smooth loess curves are used to help summarise the information contained in these graphs. For each chemical species a pair of graphs is presented. The left-hand graph shows the entire data series, whilst on the right-hand graph the y-axis scale is expanded to enhance the resolution. The thick black marks shown on the y axis of the left-hand graphs show the extent of the restricted range that is used on

the right-hand graphs. For rainfall, this range was chosen to eliminate the top and bottom 5% of data points.

The time series plots were screened by eye for trend. The loess curve has been used as the primary guide, with allowance made for lower certainty at the start and end of the record, especially at the start of the record which was very dry. Dry periods may affect rainfall chemistry because dry deposition makes a proportionally larger contribution to the open rainfall collectors at such times. Note that the volumes shown on Fig. 1a are only marked for weeks where it rained (and for which a chemical analysis was carried out); the loess curve shown on this plot is not fully representative as it takes no account of completely dry periods.

The data have been grouped into determinands which do and which do not show some evidence of trend. Yttrium, cobalt and lithium, which are detectable in stream waters, were at or near the detection limit for rainfall and are not included. The results are summarized and commented on below.

4.2 Rainfall species showing no overall evidence of trend

Chloride, sodium, calcium, strontium, sulphate, magnesium, potassium, bromide, iodine, pH, alkalinity, conductivity, zinc, aluminium, barium, manganese, iron, chromium, nitrate.

Chloride and sodium are a major input to the catchment and derive from marine sources. The rainfall data indicate that the time-distribution of seasalt input has been very uneven over the 10 year sampling period (Fig. 1a). The time variance in these inputs shows no evidence of overall upwards (or downwards) trend. The variation is partially linked to meteorological based fluctuations in rainfall volume. For example, dryer than average years, such as 1985 to 1987 and 1992/1993, show lower than average seasalt inputs, whereas the wetter years have the higher seasalt loads.

Rainfall sea salt fluctuations have important consequences for stream water chemistry. Chloride, which dominates the marine input, is one of the major anions moving through the catchment. Increases in chloride concentration result in cation concentrations in the stream also being increased (by charge balance considerations). The variations in marine salt inputs are seen here as system noise since they are weather dependent (as are rainfall volume

variations). Any stream water quality trends of real interest, eg. evidence of long term acidification, must be distinguished from this background noise. It is evident from the graphs that this noise is considerable.

Sulphate, calcium, magnesium, potassium, strontium, bromide, iodine and conductivity show a time variance which roughly follows the chloride variation but some (eg. calcium and magnesium) exhibit other features as well. Where there is some drift, it is generally observed either near the beginning or end of the record and these effects are generally much reduced when volume weighting is used. In the case of calcium, an upward trend at the end of the period remains even with volume weighting. However, the loess curve has probably been strongly influenced by two abnormally high points towards the end of the record. Magnesium shows some slight evidence of decrease, especially in the last two years - but this recent decrease roughly parallels the marine input and is an unconvincing trend. By way of confirmation, excess magnesium is examined and shows no sign of decrease. Examination of excess concentrations for those other species for which the marine component is important gives no indication of trend. Most of these still show a fluctuation in excess concentration which parallels/mirrors the marine component. There is therefore little evidence of any change in the pollutant flux over this period for these species.

Rainfall aluminium, zinc, barium, manganese and iron show similar changes to one another over time, suggesting that they have sources in common. The pattern of fluctuation for these species is distinct from the marine variations, and loess curves do not suggest trend. Chromium has a very distinctive time variance with a large 'bulge' between 1986 and 1989 - it is not known why this has occurred (Fig. 1b). This change seems to have been short lived and in more recent years chromium concentrations have returned to much lower levels. Fluctuations in pH, alkalinity, nitrate and iodine are observed but show no clear relation with anything else.

4.3 Rainfall species showing possible trend

DOC, ammonia, copper

DOC and Ammonia show a rise in concentration over the 10 years of data, whilst there is a

possible decline in copper (Fig. 1b). For these data series, the seasonal Kendall test was used to estimate the magnitude and significance of the suspected trends. For DOC, the trend is highly significant (P-value = 0.002; gradient = 0.07 mg/lyr) and the estimated change over the 10 years is as large as the mean DOC concentration (0.65 mg/l). A second estimate of change was calculated by robust regression. This gave a lower gradient of 0.04 mg/lyr which still represents a big proportional change. For ammonia, the seasonal Kendall statistic is only just significant (P-value = 0.07; gradient = 0.018). The robust linear regression estimate of gradient is similar to the seasonal Kendall gradient and both gradients are considerable when compared the mean concentration (0.51 mg/l). Copper did not give a significant trend when tested using the seasonal Kendall test (P-value = 0.127).

The above time series were decomposed into seasonal, trend and residual components (Fig. 2). These graphs illustrate that (1) the trend and the seasonal effects are small compared with the residual variation, ie there is lot of variation left unexplained, (2) the seasonal variation is important for DOC and ammonia but is small for copper, (3) there is autocorrelation in the residuals, (4) there are extreme values with heavy residuals, and (5) there has been a increase in the frequency of extreme values during the period for DOC and ammonia. The effect of these extreme values on the fitted loess curves was investigated and was found to make only a slight difference to the fit. For ammonia, the decomposed series shows a fall in the last 4 years which suggests that the observed overall upward trend may be a result of a high annual variation and an insufficiently long sampling period. For copper, the downward trend seems mainly a result of the high observed concentration in the first year; any decrease following this initial period is very small.

It therefore appears that there have been increases in the deposition of organic species over the last decade. However, it is not yet known exactly what constituents are contributing to the rainfall DOC or what the sources of DOC in rainfall are. The chemical reactions which take place in the atmosphere are very complex and are not fully understood (Seip, 1990; UK Review Group on Acid Rain, 1990). For ammonia, the main source of emissions is thought to be from farmland (livestock emissions and fertilizer application; UK Review Group on Acid Rain, 1990).

4.4 Summary

In summary, the rainfall data indicates that there have been rises in DOC and ammonia but that only DOC looks like it is continuing to rise. There are large time variations in many of the other chemicals in rainfall, in part these relate to fluctuations in weather conditions, in particular the marine inputs. Treating such fluctuations as background noise leads to the conclusion of there being no trend in the remaining rainfall determinands.

5.0 Stream water chemistry

In this section, water quality parameters for the Halfen stream waters are examined for trend. Stream water data are presented in Fig. 3a, b using a similar format to that used for the rainfall data. For these graphs, the restricted y-axis on the right hand plots eliminates the top and bottom 2% of the data points. As with rainfall, both marine and excess concentrations are examined and the data have been screened by eye for trend.

For those species with possible trend, decomposition into trend and seasonal components has been carried out (Fig. 4). The effect of flow on water quality was investigated using plots in which trends in chemical response are segregated into 3 flow regimes:- low, medium and high flows (Fig. 5). Note, again, that very low flows occurred during the first summer and have not occurred since then. This may account for some of the distinctive behaviour seen in early years so that changes seen at this time are not necessarily evidence of long term trend.

5.1 Stream water species showing no overall evidence of trend.

Chlorine, sodium, calcium, strontium, magnesium, potassium, sulphate, conductivity, pH, alkalinity, ammonia, nitrate, aluminium, lithium, yttrium, barium, manganese, iron, copper, chromium, zinc, cobalt.

Stream chloride shows a very strong sinusoid-like time variation which is notable for the fact

that the scatter about this variation is relatively small when compared to the other stream determinands (Fig. 3a). The chloride variations reflect the year to year changes in rainfall chloride inputs to the catchments (with some lagged effect: eg compare the peak in rainfall in 1990 with that of the stream in 1991). A number of the other stream water determinands show a component of variation which is comparable to that of chloride, eg conductivity, sodium, calcium, magnesium, potassium and strontium. Sulphate also shows a sinusoidal variation - but, surprisingly, this is out of phase with the chloride. Potassium shows some possible decrease, but closer examination suggests that this mainly occurred in the early dry years after which the trend follows chloride. Excess concentrations were also examined for calcium, magnesium, sulphate and strontium but showed no evidence of trend. Excess magnesium comes closest to showing a slight decrease but a rather strong inverse link with chloride remains and suggests it is still not independent of the marine salts and cannot be linked to cation store depletion.

Many other stream water determinands show variation, but with no evidence of trend and no obvious links with rainfall contributions or with chloride. These include lithium, barium, manganese, copper, iron, yttrium, aluminium, nitrate, ammonia and pH. Of these, only aluminium and nitrate showed similarities in their time variance. Zinc and chromium stream water variations appear to be directly related to the zinc and chromium in rainfall. So for example, the 'bulge' seen in the rainfall chromium inputs is translated into a 'bulge' in stream water concentrations (Fig. 1b, 3b). Ammonia also shows a bulge part way through the period but it is not known why - there is no obvious link with rainfall although the stream water bulge has a similar timing to the peak in the rainwater loess curve.

5.2 Species showing possible trend

DOC, iodine, bromide

DOC, iodine and bromide show fairly clear evidence of trend (Fig. 3b). As with rainfall, the seasonal Kendall test is used to test for the magnitude and significance of the trend. All three time series are significant, and have a sizeable gradient relative to the mean concentration (Table 1). Decomposition into seasonal, trend and residual components again shows that the residuals are very large compared to the trend and seasonality (Fig. 4). The effect of flow

regime on response is examined (Fig. 5). An increasing trend is observed at all flow levels, and, for DOC and iodine, this trend is greatest for high flows. This is in accordance with the likely origin of DOC; the upper soils are organic rich and these contribute most to the stream at high flows.

It is notable that the gradients of the increases in stream and rainwater DOC are remarkably similar (both 0.07 mg/l/yr as estimated from the seasonal Kendall test). However, different types of organics are present in the stream and rainfall. The stream waters are coloured because they contain fulvic and humic acids. Rain waters are clear (and therefore do not contain these components) - although their precise composition has not yet been established. One explanation for the stream water DOC rise could be that some of the organics in rainwater are transferred to the stream without uptake by the catchment, i.e. the trend in stream water simply follows from the trend in rainfall. However, this reasoning does not explain why iodine and bromide have also risen.

The concurrent rise in iodine and bromide reflects their similar hydrogeochemical properties and suggests a common source from the organics in the system. Iodine and bromide from rainfall are taken up into the biomass and/or they react with organic compounds in the soils. They are then later released during organic decomposition (Neal et al. 1994b). The rise in stream water DOC therefore suggests that there has either been an increase in organic decomposition, or that changing soil conditions have led to the increased solubility of humic and fulvic acids. At present we have no explanation for why this may be occurring and it is not known whether this is related to acidification.

5.3 Summary of observed stream water changes

- (1) There have been fairly steady increases in DOC, iodine and bromide in the stream waters.
- (2) There are strong sinusoidal variations in chloride. Many of the other determinands show a variation which follows this pattern.
- (3) There is no evidence of trend for the remaining stream water determinands.

6.0 Discussion

Study of the Plympton data has highlighted the extent to which year to year variations in weather conditions affect the rainfall inputs and the stream water quality. A simple but clear example of this is the large, near-sinusoidal fluctuation in stream chloride seen over the sampling period (Fig. 3a). Many of the other water quality determinands show similar variations to chloride, or suggest highly damped relationships with rainfall inputs or links with flow regime. For all of these substances, the non-uniformity in weather is a dominant factor in the smoothed year to year variations in stream water quality. Similar findings have been made for air quality measurements; the difficulty in identifying trends because of these climatological effects is recognized for this type of data (UK Review on Acid Rain, 1990). The experience from Plympton suggests that caution, relating to the effects of weather variability, must be exercised when upland stream water quality data is examined for trend. This means that much longer time series of data will be required before trend can be concluded - unless the trend is very pronounced. It is also clear that *artificial* trends will be apparent if shorter time series of data are examined - this indicates that there is very little point in examining water quality data for trend with less than 10 years data. The 10 years of data presented here may well not be enough to make any sensible statements.

In this paper, a simple approach, relying primarily on graphical presentation of the data, has been deliberately adopted. The use of smoothed trends allows some appreciation to be gained of how much year to year fluctuation there is relative to any overall decline, and allows scientists to make their own judgements. This is important because of the very interrelated nature of chemical data; a crucial step in assessing trends is to understand the data and the underlying processes. The analysis presented here suggests that it is pointless examining stream water data without allowing for climatological variations and without some knowledge of rainfall inputs.

The study of the Plympton data has emphasized some other important features of the data. It has been seen that there is autocorrelation, large residual scatter, even after allowing for seasonal and trend effects, and that the data is non-normal (containing a number of extreme

values) with complex inter-dependencies between the determinands. Further, more detailed investigation which incorporates some of these properties is clearly possible. Ideally, factors such as rainfall dependency, flow dependency and the impact of long meteorological variation would need to be included. A step in this direction would be to incorporate some flow variation by further use of loess smoothing techniques (Hirsch et al., 1991). To include more explicit accounting for rainfall and flow dependency is highly complex and probably requires use of hydrochemical catchment models. Sophisticated time series techniques such as fractional differencing might help to describe the nature of the variations induced by the long term weather variations (Haslett and Raftery, 1989). However, these developments are beyond the scope of this paper. Given the inherent problems arising from the year to year fluctuations in the inputs to the catchments, there is a limit to how much further understanding can be progressed through more detailed analysis.

The ten years of rainfall data are showing no significant changes in the wet deposited pollutants usually associated with acid deposition (sulphate and nitrate), although there has been a possible increase in ammonia. The stream chemistry changes observed at Plynlimon are on the whole small. This contrasts with several studies showing declines in base cations in both rain and stream waters (Christophersen et al., 1990; Driscoll and Likens, 1993; Kirchner, 1993). The Plynlimon data are showing potentially important increases in atmospheric pollution by organic substances, and these changes have not been observed elsewhere.

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List of Figures

Figure 1a,b Rainfall timeseries plots. For each measurement two graphs are shown. The left hand plot shows the full concentration range. The right hand plot shows an enlargement after removing the top and bottom 5% of the data. The thick vertical mark on the right hand axes shows the range used in the left hand graph. Loess curves are shown, the solid line is fitted to the raw data whilst the dotted lines have been flow weighted.

Figure 2 Decomposition of rainfall timeseries into trend, seasonal and residual components using loess techniques. The vertical bars shown beside each set of graph each represent the same distance and can be used to compare scales. In each case, the trend and seasonal components are small relative to the residual noise.

Figure 3a,b Stream water timeseries plots. For each measurement two graphs are shown. The left hand plot shows the full concentration range. The right hand plot shows an enlargement after removing the top and bottom 2% of the data. The thick vertical mark on the right hand axes shows the range used in the left hand graph. Loess curves are shown, the solid line is fitted to the raw data whilst the dotted lines have been flow weighted.

Figure 4 Decomposition of stream water timeseries into trend, seasonal and residual components using loess techniques. The vertical bars shown beside each set of graph each represent the same distance and can be used to compare scales. In each case the trend and seasonal components are small relative to the residual noise.

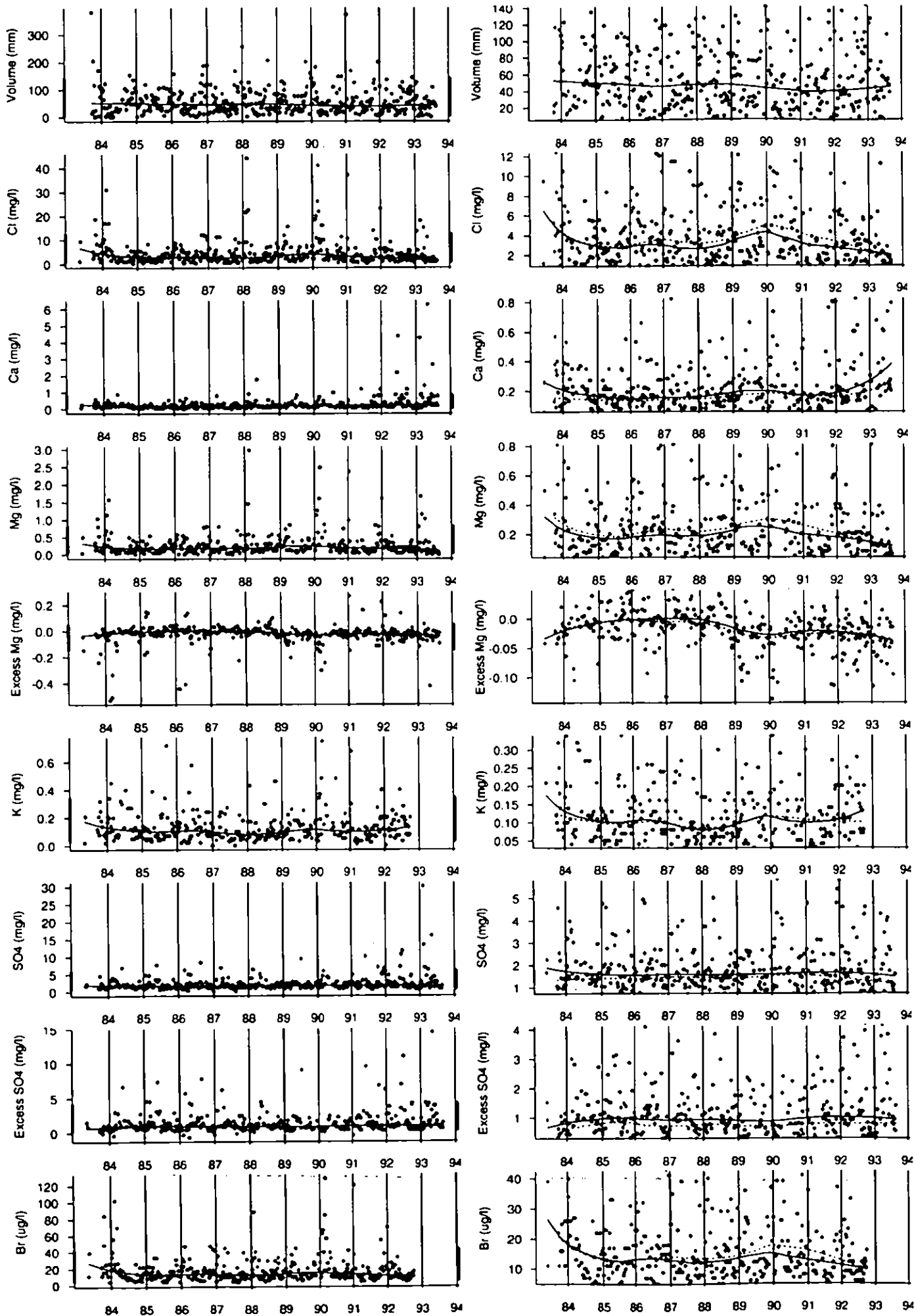
Figure 5 Effect of flow regime on stream water quality. For each determinand, four graphs are shown. The first three show the data for low, medium and high flows (see text) together with a loess curve which has been fitted to the data. The fourth graph shows the three loess curves together. Aluminium and chloride graphs are shown for comparison. Note that for chloride the variation becomes progressively damped and delayed as flow decreases.

Table 1

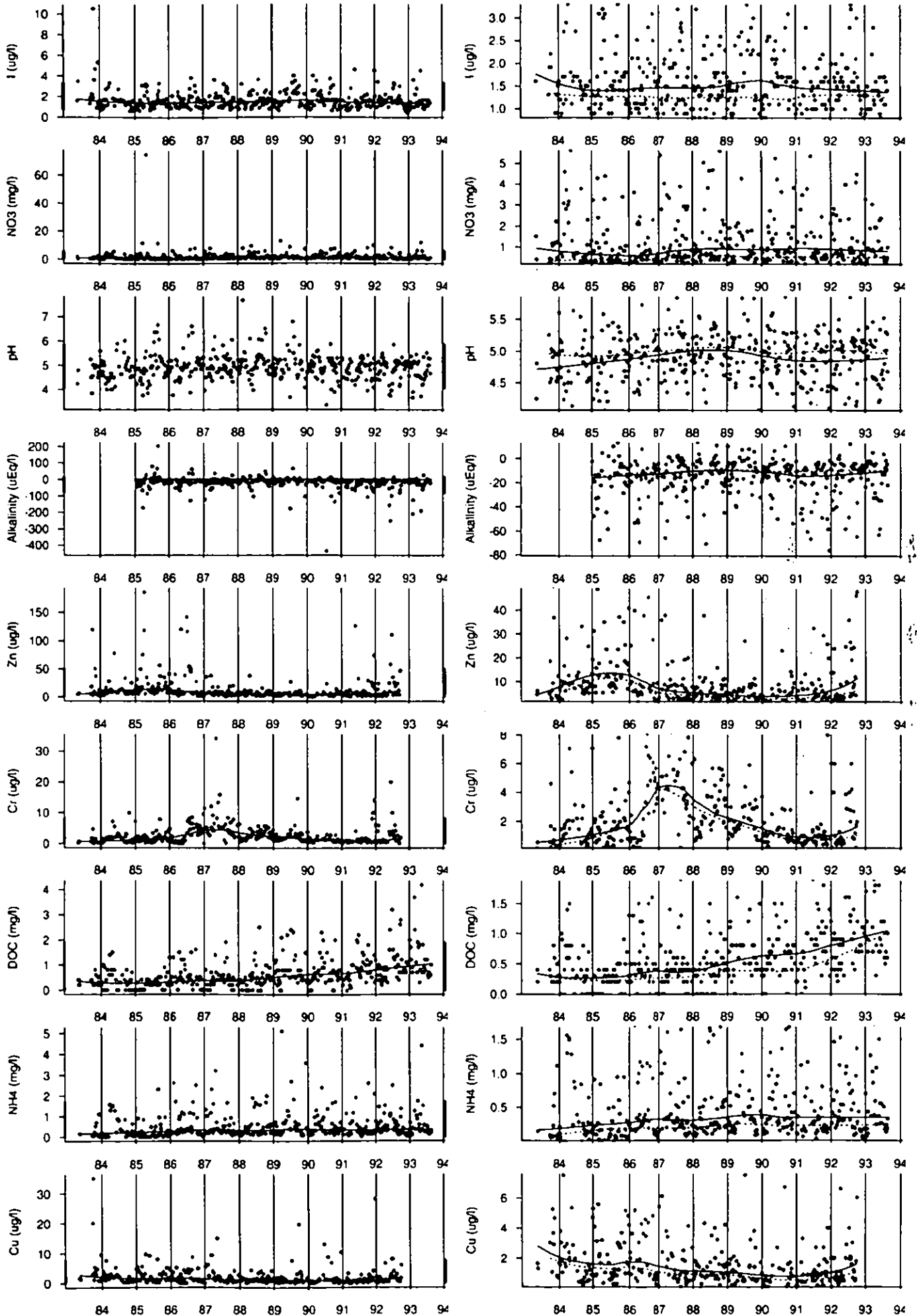
Trend statistics for stream water data. Units are mgCl for DOC and $\mu\text{g/l}$ for iodine and bromide.

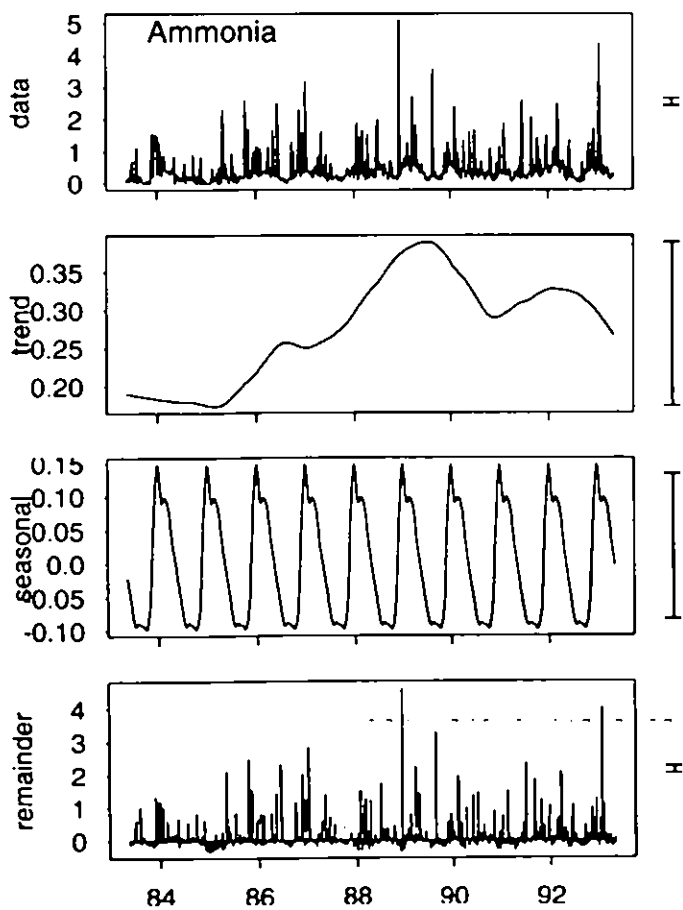
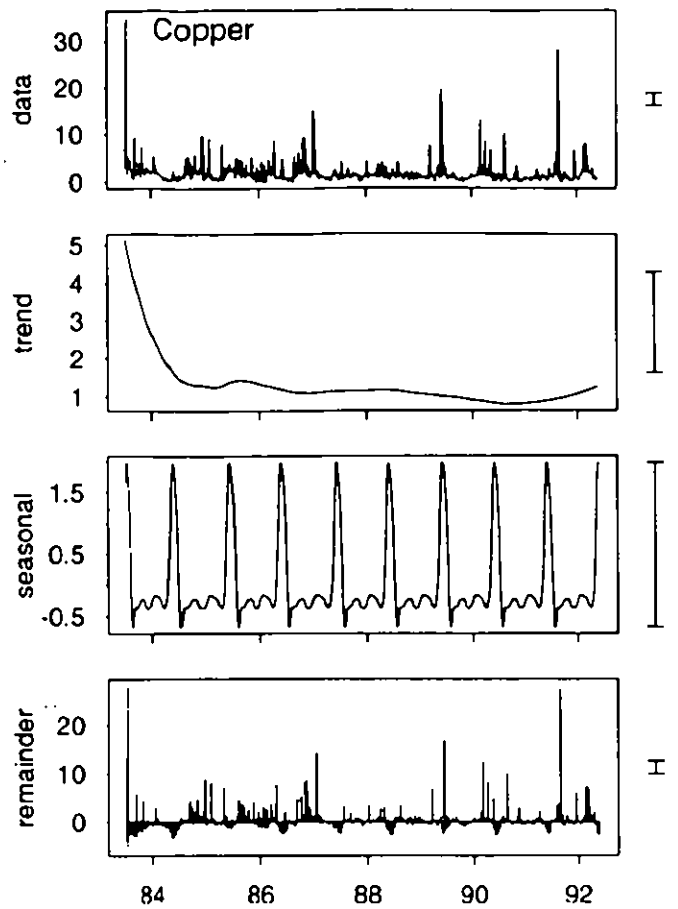
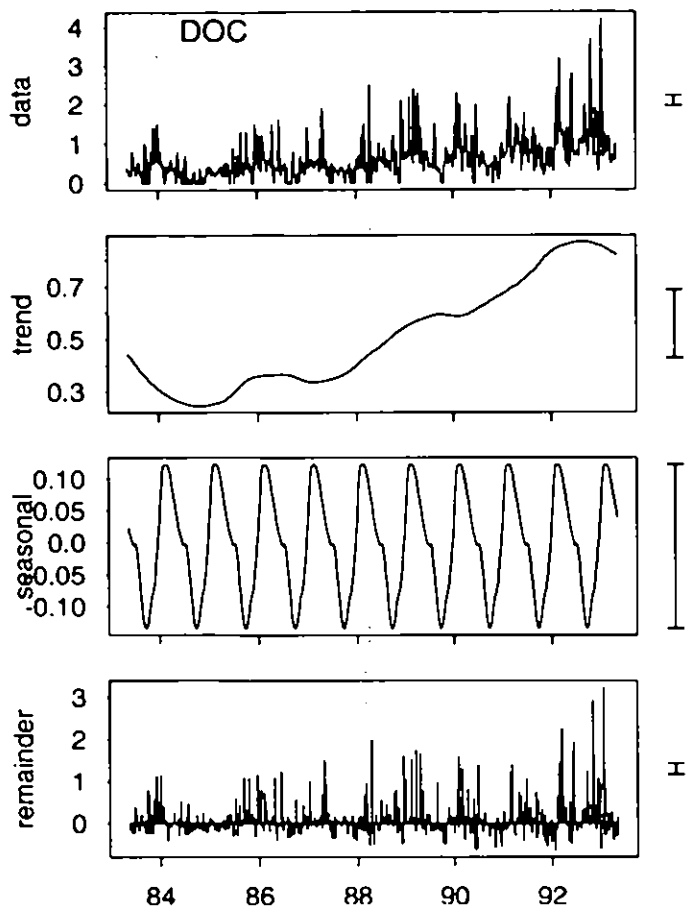
	Mean	Seasonal Kendall P-value	Seasonal Kendall Gradient	Robust Regression Gradient
DOC	1.25	0.004	0.07	0.02
I	0.98	0.003	0.03	0.05
Br	21.4	0.004	0.4	0.5

Rainfall

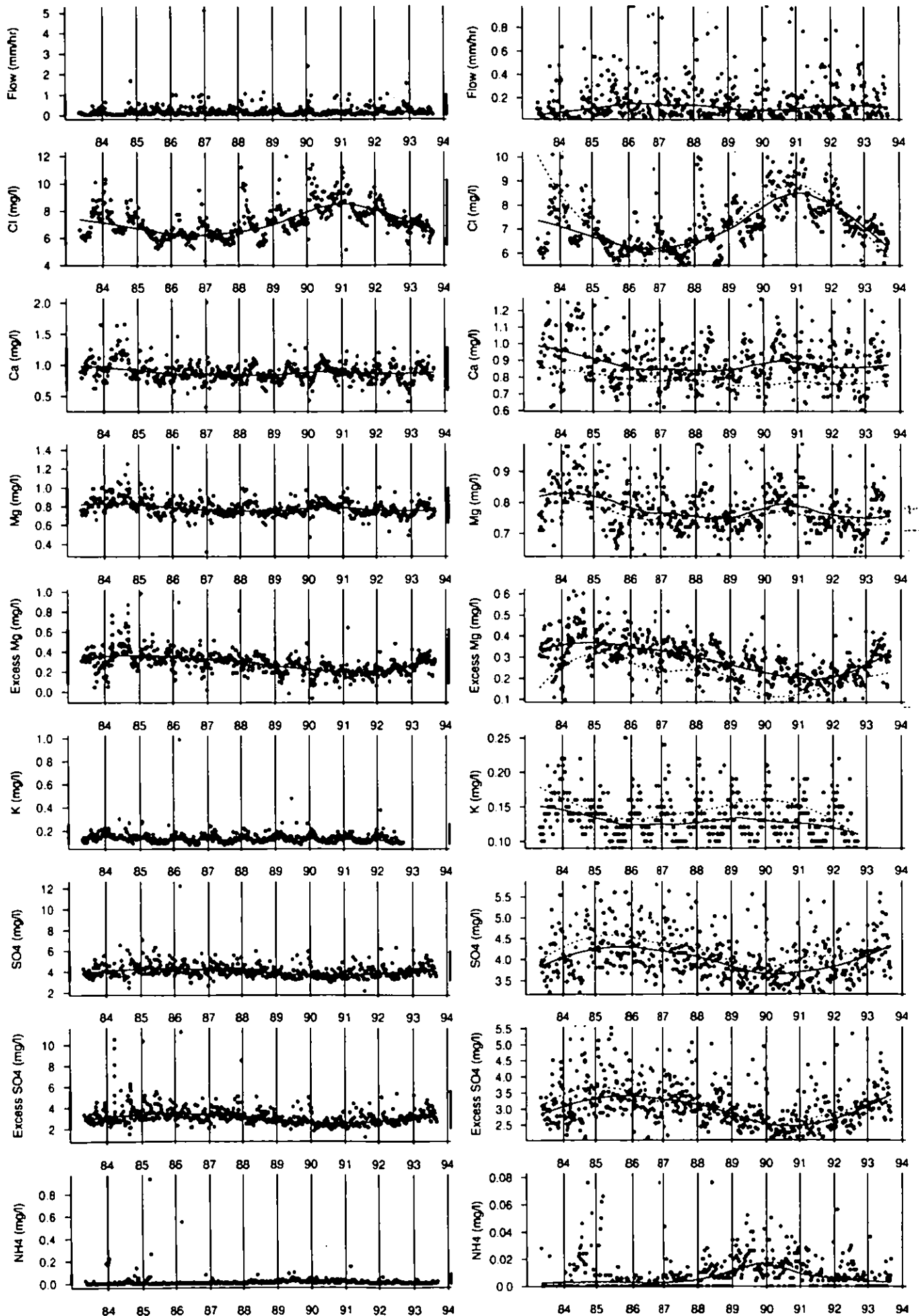


Rainfall

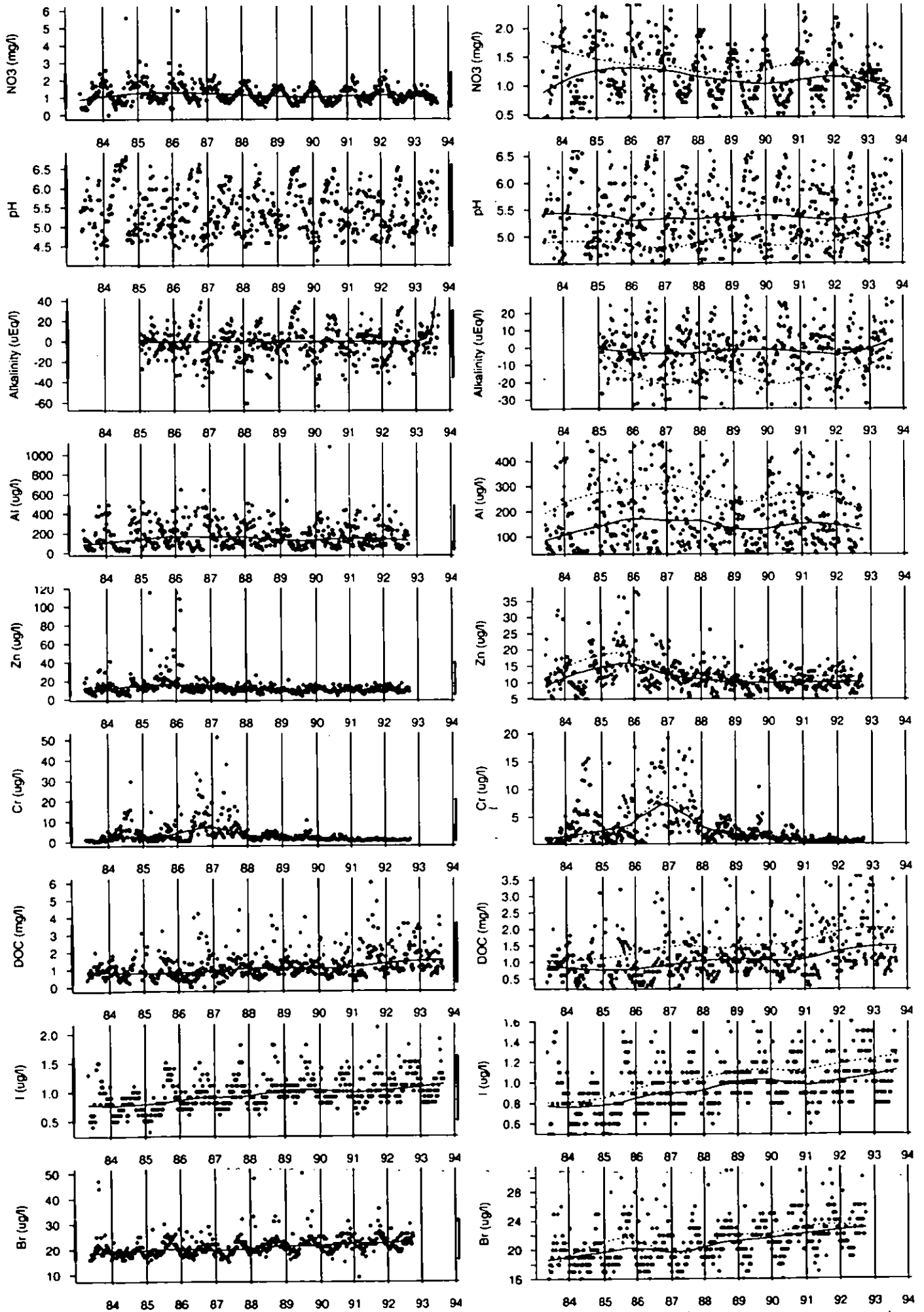


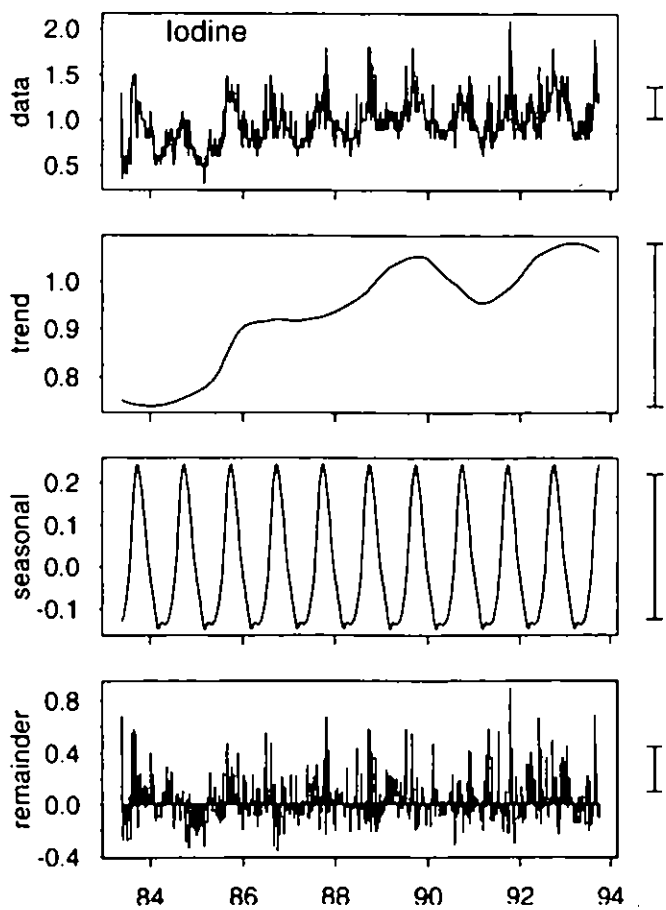
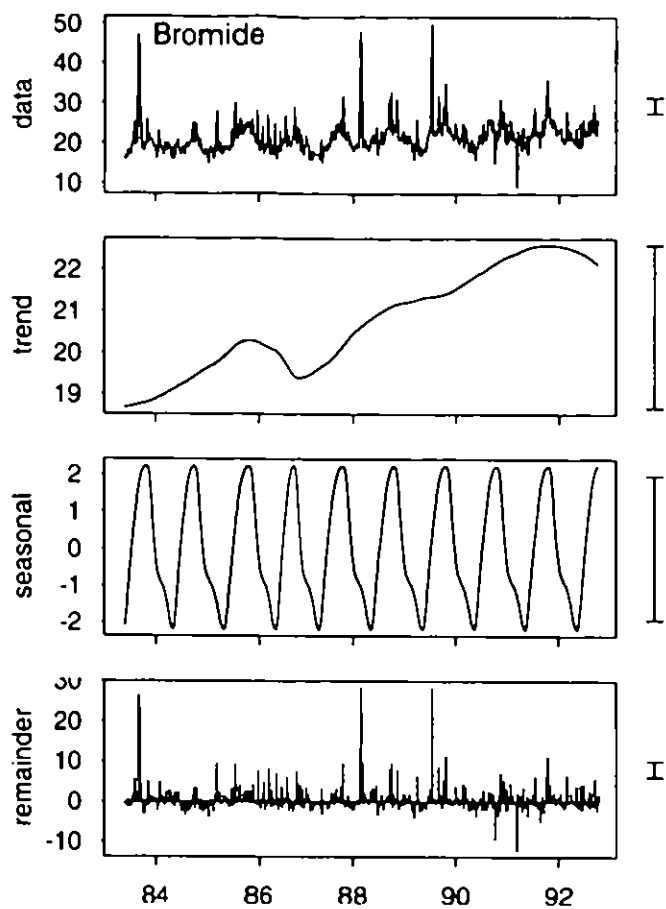
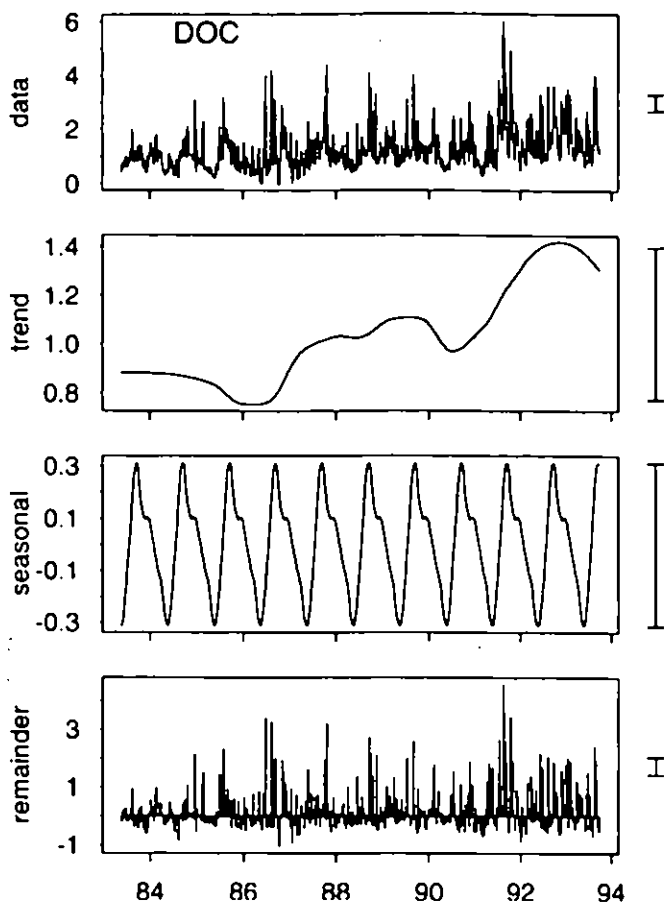


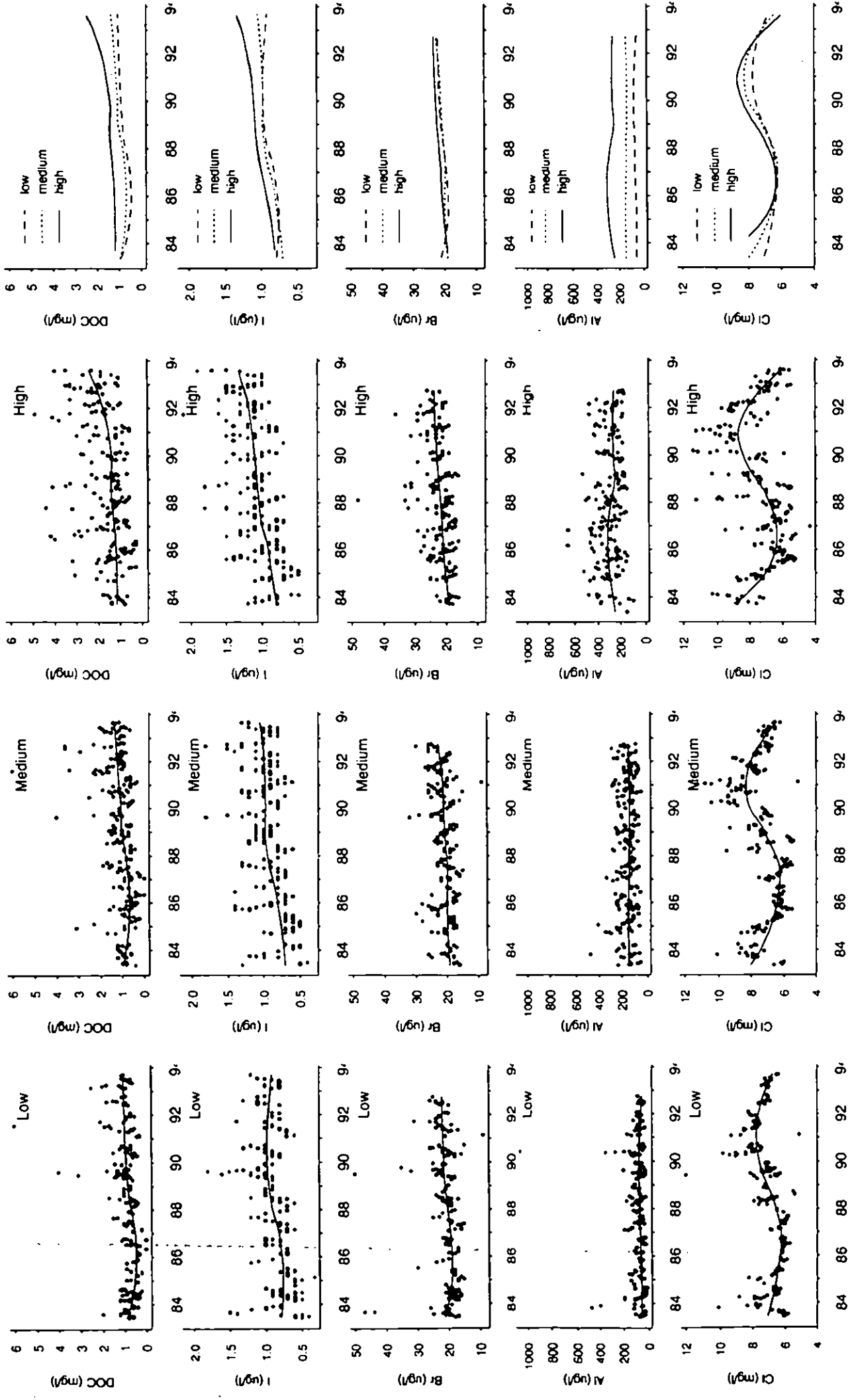
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**STREAM CHEMISTRY IMPACTS OF CONIFER HARVESTING
IN WELSH CATCHMENTS**

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Abstract.

Hydrochemical data have been collected for between 6 and 9 years from forest harvesting experiments in small catchments (<10 ha) at Plynlimon and Beddgelert, Wales, UK. Felling resulted in rapid increases in nitrate and potassium concentrations at both sites. A maximum of 3.2 mgN L⁻¹ was observed at Plynlimon about one year after the start of felling. Concentrations declined to control stream values (0.5 mgN L⁻¹) after 5 years. At Beddgelert, nitrate concentrations in the manipulated catchments remained above those in the unfelled control catchment for three years, before declining below control values. The nitrate pulse was related to increased rates of mineralisation and nitrification in the soil after felling. The initial increase in potassium concentration after felling at Plynlimon was followed by a slow decline but concentrations were still above those in the control stream after 5 years. From four to eight years after felling at Beddgelert, potassium concentrations fell below and then generally remained lower than control values.

The nitrate pulse after felling at Plynlimon sustained inorganic anion concentrations above those in the control stream for the first 18 months after felling. As the nitrate pulse declined, inorganic anion concentrations decreased to below those in the control stream about four years after felling. At Beddgelert, the smaller increase in nitrate concentrations had less effect on inorganic anion concentrations which decreased after felling relative to values in the control stream. The increase in nitrate was associated with temporary streamwater acidification in the felled catchments due to the increased rates of nitrification and nitrate leaching. At Plynlimon, streamwater aluminium concentrations declined after felling, but controls on aluminium behaviour are complex and not explained by simple equilibrium relationships with Al(OH)₃ or by variations in inorganic anion concentrations. At Beddgelert, felling had no effect on stream water Al(tot) concentrations.

Felling at Plynlimon led to a large reduction in streamwater chloride, sodium and sulphate concentrations. At Beddgelert reductions in sulphate and 'sea salt' ion concentrations were less clear, reflecting the smaller proportions of the catchments which were harvested.

Felling had no deleterious effects on water quality, apart from a temporary slight further decline in stream pH at Beddgelert. Increases in nitrate were short-lived and well below drinking water standards. Aluminium concentrations were already higher than statutory standards, but were not increased or decreased through felling.

Keywords:- Clearfelling; clearcutting; forest harvesting; stream chemistry; water quality.

1. Introduction

Upland areas of the UK are predominantly composed of a mosaic of agriculturally-unimproved moorland and grassland on a range of mainly acidic soil types. Since the 1930's, commercial forest plantations have been widely established, consisting of a variety of exotic conifers, especially Sitka spruce (*Picea sitchensis*). Establishment of conifer plantations has resulted in increased stream water concentrations of several major ions (e.g. Harriman and Morrison, 1982; Stoner *et al.*, 1984; Stoner and Gee, 1985; Reynolds *et al.*, 1986; 1989). In particular, concentrations of ions derived from marine sources and air pollution, such as Cl, Na, Mg and SO₄ are usually higher in forest streams, which may also be more acid. Evaporative concentration resulting from rainfall interception by the tree canopy may explain between 20% and 40% of the increased concentrations of ions derived from atmospheric sources (Reynolds *et al.*, 1988). The remainder is generally attributed to enhanced dry and cloudwater deposition to forest canopies, compared with moorland vegetation (Fowler *et al.*, 1989). Of greater concern for water quality, however, is that aluminium concentrations are often higher in forest streams, and at concentrations greater than specified water quality standards (Commission of the European Communities, 1980; Howells *et al.*, 1990).

Large areas of these conifer plantations have now reached maturity and are being felled. In the UK, clearfelling is normal practise, involving removal of entire stands of trees, but generally only stems are harvested and other tree components such as branches and needles remain on site to decompose. The effects of clearfelling have been extensively studied, primarily in North America, and documented in bibliographies, (Blackie *et al.*, 1980; Gaskin *et al.*, 1983), conference proceedings (eg. Leaf, 1979) and accounts of specific sites such as Hubbard Brook (Bormann and Likens, 1979; Likens *et al.*, 1977) and Coweeta (Swank and Crossley, 1987). Responses to clearfelling in the UK may therefore be anticipated, resulting in changes in soil water and stream chemistry as follows:-

1. Decreased rainfall interception, increased water yield, dilution of solutes and increased

leaching through soils (Anderson *et al.*, 1990; Rosén, 1984)

2. Reduced dry and cloudwater deposition of SO₂, NO_x, NH₃, NaCl etc. as a result of canopy removal (Adamson *et al.*, 1987; Adamson and Hornung, 1990; Fuller *et al.*, 1987; Mitchell *et al.*, 1989)
3. Removal of the vegetation 'sink' for nutrients, at least until natural re-vegetation and replanting result in a significant plant cover. Most commercial conifer plantations have non-existent or sparse ground vegetation cover at felling (in the UK, larch - *Larix* spp. - is the exception). Available nutrients in the soil may be leached if no other 'sink' is available (Johnson and Todd, 1987; Knighton and Stiegler, 1981; Stevens and Hornung, 1988; 1990).
4. Losses of nutrients from felling debris and the accumulated forest floor, exacerbated by the lack of a vegetation sink (Fahey *et al.*, 1991a, 1991b; Neal *et al.*, 1992a; Titus and Malcolm 1991; 1992)
5. Increased soil temperature and moisture resulting in faster rates of mineralisation of soil organic matter and accumulated forest floor litter (Emmett and Quarmby, 1991; Emmett *et al.*, 1991a, 1991b; Rosén and Lundmark-Thelin, 1987)
6. Changes in hydrological pathways through the soil, resulting from increased water fluxes, changes in soil structure and water infiltration etc. If a larger proportion of the water reaching streams is channelled through acid, aluminium-bearing upper soil horizons, there will be less opportunity for buffering from deeper soil horizons and bedrock contact (Neal *et al.*, 1992b; Reynolds *et al.*, 1992)

The net result of these processes is therefore a scenario in which reductions in streamwater concentrations of Na, Cl, Mg, SO₄ and possibly inorganic-N occur as a result of reduced atmospheric inputs and dilution. These effects should be accompanied by a decrease in Al concentration associated with this reduction in soil water anion concentration. In contrast, elimination of root uptake and release of nutrients from felling debris should result in

increased K, P and possibly inorganic-N concentrations.

Data from the small number of clearfelling studies in the UK have generally confirmed these predictions (eg. Adamson *et al.*, 1987; Adamson and Homung, 1990; Neal *et al.*, 1992a, 1992b; Reynolds *et al.*, 1992). Exceptions have been the variable response of aluminium and the consistently large pulse of nitrate after felling. The latter has been widely observed in streams draining clearfelled areas in temperate regions of the world (eg. Bormann and Likens, 1979) and is the result of increased rates of nitrification in the soil after felling. The behaviour of aluminium is less easy to understand, and is the subject of active research.

Published data from UK felling studies present a comparatively short-term view of the effects of felling. Most felled areas are replanted in order to establish a second rotation plantation. The process of felling, restocking and re-establishment of a second rotation crop takes 10 to 12 years, and data so far available encompass only the immediate post-felling period. Since model simulations of the effects of second rotation forestry predict increased soil and stream water acidification (Jenkins *et al.*, 1990), availability of stream chemistry throughout the phase of establishment and development of the second rotation is of considerable significance.

This paper presents the results of analyses of stream water samples collected over periods of 9 and 10 years respectively, including 6 and 8 years after felling, at two experimentally clearfelled sites in Wales, Hafren forest (Plynlimon) in Powys and Beddgelert forest in Gwynedd.

2. Sites and Methods

The sites used for this study have been described in detail in previous papers (Reynolds *et al.*, 1986, 1988, 1992 for Plynlimon and Stevens *et al.*, 1989 for Beddgelert) so only outline descriptions will be given here.

The two catchments studied at Plynlimon are about 6 ha in area and contain a mosaic of acid upland soils overlying lower Palaeozoic mudstones and shales. They were both entirely planted with Sitka spruce in 1949. One catchment (A4) was completely clearfelled (stem-

only harvested) between the beginning of July 1986 and the end of April 1987. The other (B2) has remained as an unfelled control catchment unaffected by forestry operations during the eight year period of observation. The stream draining the felled catchment is a tributary to the Afon Hore whilst the control stream drains into the Afon Hafren. These rivers rise on the eastern flanks of Plynlimon approximately 24 km from the west Wales coast and form a part of the headwaters of the River Severn. The catchments are located at about 380 m above sea level and receive an average of 2480 mm of rain annually.

Since the spring of 1982, streamwater chemistry has been monitored at Beddgelert forest in three small catchments located in a north-east facing, former glacial cwm 12 km from the north Wales coast. Catchment D3 (4.7 ha) has remained as an unfelled control throughout this period, but felling of 62% and 28% respectively of the catchments of the other streams, D2 (1.4 ha) and D4 (6.1 ha), took place in September and June 1984 respectively. The catchments at Beddgelert have a similar geology and range of soils to those at Plynlimon and were planted with Sitka spruce in the 1930's. The catchments are at an altitude of approximately 400 m and receive an average annual rainfall of 2600 mm.

At both sites, the unfelled control catchments remained as closed-canopy spruce plantations throughout this study, with no ground flora apart from scattered ferns and bryophytes. No forest management took place in these control catchments during this period.

The streams at Beddgelert forest were sampled weekly and gauged with V-notch weirs from which flows at the time of sampling were calculated. The Plynlimon streams were ungauged and stream water samples were initially collected at fortnightly intervals and then every four weeks for the last eighteen months of the study.

In the laboratory, sample pH was determined prior to filtration through Whatman GF/F filters for samples from Beddgelert and 0.45 μm pore size membrane filters for those from Plynlimon. Up to September 1984, nitrate, sulphate and chloride were determined by continuous flow autoanalyser using standard methods (Allen *et al.*, 1974; Rowland *et al.*, 1984). Subsequently these ions were measured using ion chromatography. The old and new methods were run concurrently for several months to ensure comparability. Total filtrable

aluminium (Al(tot)) in samples from Beddgelert was measured by atomic absorption spectrophotometry. At Plynlimon, labile monomeric aluminium (Al(inorg)) was determined following the speciation scheme of Driscoll (1984). In most cases, Al(inorg) accounted for more than 85% of the total filtrable aluminium in the streamwater samples.

3. Results

Prior to felling, the streamwater chemistry of the two Plynlimon catchments was broadly similar although some differences were apparent (years -2 and -1 in Tables I and II). For example, stream water at A4 had a higher pH than B2 and contained more nitrate, sodium, chloride and magnesium. Larger Al(inorg) concentrations were observed in stream B2. At Beddgelert, the chemistry of the three streams before felling was also broadly similar, although sodium and chloride concentrations were higher in stream D2 (1982 and 1983 in Table III). Stream D3 had higher calcium concentrations and lower Al(tot) and nitrate-N concentrations.

The effects of felling on annual mean stream water chemistry at Plynlimon are shown in Tables I and II, and for Beddgelert in Table III. Trends in stream chemistry are shown in Figures 1 to 6.

3.1 INORGANIC NUTRIENTS

At both sites ortho-phosphate and ammonium-N were below detection limit in the stream water samples. Data for the major inorganic nutrients are therefore restricted to nitrate-N and potassium.

Clearfelling of catchment A4 at Plynlimon resulted in an immediate increase in streamwater potassium and nitrate concentrations (Figures 1a and 1b). The former reached a maximum of 1.8 mg L⁻¹ in the first year after felling with concentrations decreasing towards, though remaining above those in the control catchment B2 after 5 years. Nitrate concentrations increased to a maximum of 3.2 mgN L⁻¹ about one year after the start of felling but declined rather more slowly than potassium to reach concentrations similar to those in B2 after 5 years.

However, since 1989, streamwater nitrate and potassium concentrations in the unfelled catchment have been steadily increasing. The reason for this is unclear, but may relate to the increasing age of the forest (Stevens *et al.*, in press) or to the effects of dry summers in 1989 and 1990 (Reynolds *et al.*, 1992).

At both Plynlimon and Beddgelert, stream water concentration data displayed wide seasonal variations, short term storm event variability and fluctuations in response to changing atmospheric inputs. These variations tend to obscure the effects of felling, especially at Beddgelert where only parts of the catchments of D2 and D4 were felled. To clarify the effects at Beddgelert, the time series plots are presented in such a manner that the results from the two streams which drain clearfelled areas (D2 and D4) are 'normalised' with respect to the 'control', unfelled stream D3. This simply means that concentrations from D2 and D4 were subtracted from D3 values for each sampling occasion. If the figures obtained from this exercise are positive, they indicate that concentrations in D2 and D4 were higher than in the control, and lower than the control if negative.

The most dramatic effect of felling on stream water chemistry at Beddgelert was an increase in K concentration (Figure 2a), although at no point did this exceed 1.7 mg L^{-1} . A slight increase in the potassium concentrations in D2 immediately before felling was probably due to preparatory clearance of access routes into the catchment, but for four years after felling, K concentrations were significantly higher in D2 and D4. The effect was greater in D2, but 62% of this catchment was felled and only 28% of the D4 catchment. Between four and five years after felling, potassium concentrations in the 'felled' streams dropped below those in the control catchment and in general have remained smaller for up to eight years after felling.

In the 'felled' streams at Beddgelert, streamwater nitrate concentrations were greater than those in the control stream for three years after felling. Amounts of nitrate then declined and have been lower than control stream values since (Figure 2b). At no point did nitrate-N concentrations exceed 2.4 mgN L^{-1} and were normally well below 1.5 mgN L^{-1} . These values are well below the EC Surface Water Directive standard of 11.3 mgN L^{-1} .

3.2 SEASALTS AND SULPHATE

The confounding effects of climatic variability on the stream response to felling are clearly demonstrated in the data for chloride at Plynlimon. Stream water chloride concentrations increased in the unfelled B2 catchment over the period of study (Table II; Figure 3a), probably as a result of large seasalt inputs during the winter of 1988-89 and a succession of dry summers in 1989 and 1990. A similar, but more damped response was observed in stream A4 where, after felling, streamwater concentrations were consistently lower than in B2. Streamwater sodium concentrations followed a similar pattern to those of chloride but the responses for magnesium and calcium were less obvious. Prior to felling, calcium and magnesium concentrations in stream A4 were generally larger than those in the reference stream B2 (Figure 4). This is believed to reflect inputs of base rich groundwater similar to those encountered elsewhere in the Plynlimon catchments (Neal 1993, unpublished data). However, three to four years after felling, there was an increase in magnesium and, to a lesser extent, calcium concentrations in the reference stream B2 reflecting the effects of winter 1988-89 seasalt inputs and the 1989 and 1990 dry summers referred to above. In the manipulated stream calcium and magnesium concentrations remained relatively unchanged compared to pre-felling values.

Streamwater sulphate concentrations at site A4 declined relative to those observed in B2, becoming lower than those measured prior to felling (Table II and Figure 3b). In the Beddgelert streams, chloride, sodium, magnesium and sulphate concentrations declined slightly after felling, but the trends were not as marked as at Plynlimon.

The overall effect of the individual anion variations on the total inorganic anion (TIA) concentrations is seen in Figures 5a and 5b. The nitrate pulse after felling in the catchment of A4 at Plynlimon sustained TIA concentrations at around the same level, or above those in control catchment B2 for the first 18 months after felling. As the nitrate pulse declined, TIA concentrations also decreased at site A4, diverging substantially from those observed in B2 about four years after felling. A similar response was observed at Beddgelert (Figure 5b), but the smaller increase in nitrate concentration after felling had only a small effect on TIA concentrations, which decreased immediately after felling relative to values in the control stream.

3.3 ALUMINIUM AND ACIDITY

The effects of felling on aluminium concentrations are partly obscured by the high degree of variability in the data and the missing information for the control site at Plynlimon. Mean streamwater aluminium concentrations at Plynlimon were larger in the control catchment prior to felling and remained so throughout the study (Table I). However, the difference between the two sites as a percentage of the mean concentration at B2 steadily increased after felling from 23% in year 2 to 67% in year 5. This compares with differences of 16% and 15% prior to felling.

Concentrations of Al(tot) in all three streams at Beddgelert increased from around 0.4 to 0.9 mg L⁻¹ in 1982-83 (before felling) to 0.9 to 1.2 mg L⁻¹ in 1986 (two years after felling in catchments D2 and D4), but the changes were not attributable to felling. This is despite a slight decrease in stream pH for five years after felling, an eventual increase in stream pH six to eight years after felling (Figure 6), and a general decline in total inorganic anion concentration (Figure 5). Clearly, some other factor is exercising significant control over stream Al concentrations, and this is masking any effect of felling. Concentrations of Al at these levels are clearly unacceptable for water supply (EC Drinking Water Directive for Al is less than 0.2 mg L⁻¹) and fisheries (recommended standard for soft waters less than 0.1 mg L⁻¹ - Howells *et al.*, 1990).

Annual mean streamwater pH in the harvested catchment A4 at Plynlimon was consistently higher than that in B2 (Table I). Maximum pH values in A4 (c. pH 6) were about one unit higher than in B2 although minimum values were similar in both streams (c. pH 4.5). In the two years after felling, however, the stream pH response in A4 was damped, with few peak values exceeding pH 5. Four to five years after felling the streamwater pH of the felled catchment increased, whilst in B2 stream water became more acid. The pH decline in B2 reflects the increase in nitrate concentrations and may relate to the increasing age of the forest (Stevens *et al.*, in press).

After felling at Beddgelert, pH dropped in the 'felled' streams by around 0.1 of a unit with respect to the control stream, and remained at this level for five years (Figure 6). Subsequently, pH gradually recovered in the 'felled' streams, and was higher than the control

by around 0.1 pH unit eight years after felling. This recovery in pH may indicate that the decline in stream pH with increasing plantation age observed in Welsh forests (Hughes *et al.*, in press) is at least partly reversible after felling.

Statistical analyses of the effects of forest harvesting were investigated using the technique of Randomised Intervention Analysis (RIA). This procedure was originally described by Carpenter *et al.* (1989) and its application to paired catchment water chemistry data is discussed by Uddameri *et al.* (this volume). The RIA uses paired data points from a manipulated and a reference catchment to test statistically the null hypothesis that changes observed in the manipulated catchment have occurred at random. Rejection of this null hypothesis indicates that a non-random change has occurred, although this does not necessarily mean that the manipulation caused the change. The RIA was performed on approximately 115 data pairs from Plynlimon and nearly 400 paired data points from Beddgelert forest. These included more than two years pre-manipulation data and up to 8 years post-manipulation data.

The results of the RIA are shown in Table IV. At Plynlimon, sodium, potassium, magnesium, nitrate-N, sulphate-S and chloride have rejection limits above 99%. Calcium has a rejection limit of 97.5%, aluminium 75% and pH 42%. This implies that the null hypothesis can be rejected with certainty for most solutes, but the rejection is uncertain for aluminium and improbable for pH. For stream D2 at Beddgelert, the rejection limit of the null hypothesis is above 99% for all solutes except pH (95%) and aluminium (75%). For stream D4, rejection of the null hypothesis is "certain" (99%-95%) for sodium, potassium, chloride, pH and nitrate-N. Rejection is uncertain for calcium and magnesium (75%) and very improbable for aluminium and sulphate-S (30%). These RIA results indicate that felling at Plynlimon has had little or no effect on stream water aluminium concentrations and pH. At Beddgelert, the RIA indicates that felling probably had little effect on aluminium concentration in either stream. Sulphate concentrations were also relatively unchanged after felling in the D4 catchment.

Loss of nutrients from soil is an inevitable consequence of forest harvesting. The loss of nutrients in streams after felling is an additional loss which can be quantified at Beddgelert.

For each year from two years before felling (year -2) to seven years after felling (year +7), stream water K and NO₃-N fluxes were calculated as the product of the annual discharge-weighted mean concentration and the total stream discharge for the year. To obtain fluxes per hectare from the felled areas of streams D2 and D4, it was assumed that the K and NO₃-N fluxes from the unfelled areas of these two catchments were equal to the fluxes from the unfelled control catchment.

Stream K fluxes increased immediately after felling and were greatest in the second year after felling in both D2 and D4 (Table V). Six years after felling, K fluxes had returned to values similar to those in the control stream D3. In the latter, K fluxes remained fairly constant throughout. Stream nitrate-N fluxes increased in the year immediately after felling and remained higher for three and two years respectively for streams D2 and D4. A slow decline then occurred, such that control stream values were reached four years after felling.

4. Discussion

The felling technique used at Plynlimon ('windrowing') created lines of thick brash (felling debris) separated by bare ground. The latter revegetated gradually, whilst the brash piles remained free of vegetation until four or five years after felling. The felled catchments at Beddgelert included areas which were harvested conventionally (CH; stem only removed, debris left on site) and areas of whole tree harvesting (WTH; all above ground material removed). Related soil studies at both sites showed that potassium was rapidly leached from the felling debris and passed through the soils in to the streams. The pulse of potassium lasted for approximately three years, and immobilisation in the re-establishing vegetation and second rotation tree crop was one of the major sinks for this nutrient (Fahey *et al.*, 1991a). At Beddgelert, detailed analysis of soil exchangeable potassium indicated that almost 50% of the potassium leached from the brash was retained in the soil, although this only represented a small overall increase in the soil pool (Goulding and Stevens, 1988).

The pulse of nitrate-N in streams draining clearfelled areas has been widely observed in temperate regions of the world (eg. Likens *et al.*, 1977; Bormann and Likens, 1979; Vitousek

et al., 1979) including the UK (Adamson and Hornung, 1990; Neal *et al.*, 1992a), despite earlier predictions that felling of conifers in the British uplands would result in only small increases in stream water nitrate concentrations (Heal *et al.*, 1982). The mechanisms responsible for the nitrate pulse have been studied in detail at Beddgelert (Emmett *et al.*, 1991a, 1991b; Emmett and Quarmby, 1991; Stevens and Hornung, 1988, 1990). Disruption of the nutrient cycle by removing the trees will make more inorganic nitrogen available for leaching, irrespective of the effects of soil nitrogen transformations. The brash was a net sink for inorganic-N for three years after felling at Beddgelert, which was the period when the nitrate pulse occurred, and was therefore not directly the source of the additional leached N. The brash may have been a source of dissolved organic-N which, after mineralisation and nitrification, could have generated the observed nitrate pulse. Decomposition of woody fine roots after felling has also been suggested as a further source of nitrogen after felling (M. Hornung, pers. comm., 1992).

Lysimeter experiments at Beddgelert forest indicated that the presence of brash induced microclimatic conditions favourable to organic matter mineralisation and nitrification (Emmett, 1989). Similarly in Sweden, maintenance of a more constant, higher moisture content beneath the brash was identified as a particularly important microclimatic factor leading to increased rates of nitrogen mineralisation and nitrogen leaching beneath the brash piles (Rosén and Lundmark-Thelin, 1987).

In areas of bare ground, microclimatic conditions are also more favourable for nitrogen transformations compared with the pre-felling situation (Emmett, 1989). Since nitrate is a very mobile anion leaching takes place, unless there is denitrification or uptake by vegetation. The rapid re-establishment of vegetation on the whole tree harvest (WTH) plots at Beddgelert, compared with those harvested conventionally (CH), was a major factor in reducing the duration of the nitrate pulse in the WTH plots (Stevens and Hornung, 1990; Emmett *et al.*, 1991b), and may have been an important control on nitrate leaching losses from the bare ground between the brash piles at Plynlimon. Vegetation also played an important role in the Swedish study, as root uptake was much reduced under the brash piles, compared with clear areas (Rosén and Lundmark-Thelin, 1987).

The studies of nitrogen transformations at Beddgelert were conducted on the dominant, freely drained podzol soils in which nitrification was active. These were also the dominant soils at Plynlimon, which were actively nitrifying prior to felling (B. Emmett, pers. comm., 1993). Both sites contain areas of less well drained peaty gley soils, and evidence from clearfelling studies on peaty gley soils in northern England (Kielder forest) suggests that these would have responded very differently to felling (Titus and Malcolm, 1992). The soils at Kielder did not nitrify freely, and much of the runoff occurred laterally below the forest floor, especially after felling when the water table rose. Ammonium-N dominated the inorganic-N losses at this site for at least 7 years after felling (Titus and Malcolm, 1992). In gley soils at Plynlimon, soil water ammonium and nitrate concentrations in the surface organic horizon increased after felling, suggesting that nitrification was active. The presence of ammonium may indicate that nitrification was periodically inhibited by waterlogging and anaerobic conditions resulting from the rise in water table following felling (Reynolds *et al.*, 1992). The Kielder site remained virtually free of vegetation throughout the study period. In contrast, vegetation cover was plentiful after only two years at Beddgelert in both CH and, in particular the WTH areas, despite the absence of ground flora before felling. At Plynlimon, the rate of re-vegetation was slower, particularly on the gleyed soils and this may account for the more prolonged release of nitrate from this site.

Nitrification releases H ions (Reuss and Johnson, 1986), and this will have contributed to the observed temporary increase in stream acidity following felling. At Plynlimon, the acidification of stream A4 was limited by an input of base-rich water from an unidentified groundwater source. In the absence of any buffering inputs, a more pronounced acidification was observed at Beddgelert. A similar response was observed at Hubbard Brook, where increased rates of nitrification following clearcutting resulted in stream acidification and larger concentrations of aluminium (Lawrence *et al.*, 1987).

The behaviour of aluminium in soil waters has been linked in earlier work to the variations in total inorganic anion concentrations through the 'mobile anion' concept (Reynolds *et al.*, 1988, 1992). However, this simple relationship is not transferred to the streams. In common with earlier findings (Neal *et al.*, 1989) and despite significant correlations between stream water Al(inorg) and hydrogen ion concentrations (eg. A4: $r = 0.691$, $P < 0.01$; B2: $r = 0.498$,

$P < 0.01$), simple $\text{Al}(\text{OH})_3$ solubility relationships do not hold. At high pH (low H ion concentration) the waters are approximately saturated with respect to amorphous $\text{Al}(\text{OH})_3$ and oversaturated with respect to crystalline $\text{Al}(\text{OH})_3$ (Neal *et al.*, 1989). At larger H ion concentrations, the waters are undersaturated with respect to all but the most crystalline forms of $\text{Al}(\text{OH})_3$. There is large uncertainty in the analytical determination of aluminium at low concentrations which affects the reliability of the calculated saturation values. However, as the data do not fall on any single line at any range of pH, it appears that $\text{Al}(\text{OH})_3$ solubility controls do not operate in these streams. This highlights the complexity of aluminium chemistry in acid upland catchments where concentrations are influenced by factors such as mixing of waters from different sources (Neal *et al.*, 1989) and interactions with suspended sediments (Goenaga and Williams, 1990) and streambed material (Tipping and Hopwood, 1988). The data from Beddgelert also illustrate the difficulty in separating the effects of felling from the underlying variability due to other factors.

The reductions in the concentrations of sulphate and the 'sea salt' ions (Na, Mg and Cl) can be ascribed partly to dilution by the larger water flux through the catchments following felling and partly to a reduction in atmospheric inputs caused by the removal of the forest canopy. The less marked changes at Beddgelert reflect the smaller proportions of the catchments which were felled. In addition, the exposure of a longer forest edge in the Beddgelert catchments may have increased sea salt deposition, offsetting the effects of canopy removal.

In the manipulated stream at Plynlimon, only relatively small changes in calcium and magnesium concentrations were observed following felling. However, this does not mean that felling had no effect on these solutes as comparison with the reference stream indicates. It is probable that the increased seasalt deposition in 1989/90 and the successive dry summers offset the anticipated decline in divalent base cation concentrations following felling. It is also possible that changes in hydrological pathways resulting from tree removal and increased water fluxes, may have increased the groundwater contribution to the manipulated stream although this cannot be substantiated.

Adsorption / desorption reactions in the soils have been proposed as an important control on

stream water sulphate concentrations (Reuss and Johnson, 1986), whereby desorption in order to re-equilibrate with reduced inputs, would delay any decline in the amounts of sulphate in stream water. This does not appear to have happened at Plynlimon, where a very rapid decrease in concentration was observed. There is evidence from Hubbard Brook that soil water acidification due to increased nitrification can lead to greater sulphate adsorption on to protonated variable charge surfaces (Fuller *et al.*, 1987; Mitchell *et al.*, 1989). In the gley soils, sulphur may have been immobilised as sulphides under the anaerobic conditions induced by the rise in water table.

5. Conclusions and Management Implications

In general, the effects of felling on stream water chemistry at both sites were as predicted. However, the scale of the change was not as extreme as might have been expected, especially with regard to those solutes derived from atmospheric sources, eg. sulphate, chloride, sodium etc. From the management standpoint, harvesting had no notable deleterious effect on water quality. Increases in NO₃-N concentrations were short-lived and were well below drinking water standards. Concentrations of aluminium were already above recognised standards and were not substantially changed by felling.

At Plynlimon, the results from the study of the small subcatchments A4 and B2 confirm and amplify findings from the investigation in the main Hore catchment at Plynlimon. At A4, maximum monthly concentrations of nitrate (3.2 mgN L⁻¹) were more than double and potassium (1.8 mg L⁻¹) approximately three times those reported for the main Hore outflow (Neal *et al.*, 1992c). The effects of felling were also less apparent in the Beddgelert catchments compared with A4. At the former site, felling effects were less pronounced (lower peak concentrations) in stream D4, where a smaller proportion of the catchment area was felled compared with D2. These results may simply reflect differences in the environmental conditions between the sites but it seems that the proportion, rather than the size, of the catchment area felled is a significant factor.

The complete felling of subcatchment A4 represents a 'worst case' scenario. Comparison with the main Hore outflow and Beddgelert indicates that dilution by runoff from unfelled and/or moorland parts of the catchment can ameliorate harvesting impacts. Future harvesting

strategy should take account of this and seek to limit the proportion of the catchment felled at one time so that water quality impacts are minimised.

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Table I. Arithmetic annual mean pH and cation concentrations (mg L^{-1}) in streams draining unfelled control (B2) and clearfelled (A4) catchments at Plympton. ¹ Years before and after start of felling. Felling occurred during year zero.

Year ¹	Catchment	Na	K	Ca	Mg	Al	pH
-2	B2	5.9	0.06	1.74	1.13	0.43	4.80
	A4	6.4	0.06	1.68	1.23	0.36	4.93
-1	B2	4.6	0.02	1.33	0.89	0.72	4.90
	A4	5.5	0.05	1.67	1.10	0.61	5.11
0	B2	5.0	0.08	1.37	0.90	--	4.81
	A4	5.1	0.68	1.53	1.05	0.44	4.85
+1	B2	5.1	0.07	1.34	0.92	--	4.79
	A4	5.0	0.48	1.56	1.18	0.47	4.82
+2	B2	5.7	0.06	1.49	0.94	0.47	4.81
	A4	4.4	0.35	1.67	1.12	0.36	4.92
+3	B2	6.0	0.10	1.99	1.06	0.44	4.79
	A4	4.4	0.23	1.93	1.07	0.28	4.94
+4	B2	7.2	0.12	1.69	1.11	0.76	4.68
	A4	4.6	0.29	1.57	1.01	0.36	4.95
+5	B2	6.4	0.16	1.53	1.10	0.54	4.66
	A4	4.3	0.25	1.57	1.04	0.18	5.05

Table II. Arithmetic annual mean inorganic anion concentrations (mg L⁻¹) in streams draining unfelled control (B2) and clearfelled (A4) catchments at Plynilimon. ¹ Years before and after start of felling. Felling occurred during year zero.

Year ¹	Catchment	NO ₃ -N	SO ₄ -S	Cl
-2	B2	0.39	2.81	10.6
	A4	0.49	2.60	11.1
-1	B2	0.27	2.54	7.1
	A4	0.36	2.37	8.5
0	B2	0.32	2.50	8.2
	A4	1.00	2.39	7.7
+1	B2	0.26	2.61	9.1
	A4	2.10	1.85	7.0
+2	B2	0.30	2.62	11.0
	A4	1.94	1.72	6.9
+3	B2	0.38	2.65	11.6
	A4	1.25	1.74	7.7
+4	B2	0.56	2.45	15.1
	A4	1.00	1.68	8.7
+5	B2	0.68	2.61	11.5
	A4	0.68	1.85	7.1

Table III. Annual flow-weighted mean concentrations (mg L⁻¹) in streams draining felled catchments (D2 and D4) and control catchment D3 at Beddgelert forest. Felling in the catchments of streams D2 and D4 took place during 1984.

Year	pH			Na			K		
	D2	D4	D3	D2	D4	D3	D2	D4	D3
1982	4.21	4.24	4.29	7.0	5.4	5.9	0.21	0.21	0.24
1983	4.37	4.33	4.35	7.1	6.2	6.7	0.27	0.25	0.30
1984	4.41	4.38	4.45	8.1	6.7	7.2	0.22	0.18	0.17
1985	4.46	4.48	4.58	6.1	4.5	5.1	0.42	0.35	0.17
1986	4.54	4.58	4.69	6.3	5.1	6.5	0.73	0.37	0.20
1987	4.61	4.64	4.72	4.7	4.3	5.0	0.41	0.21	0.16
1988	4.62	4.59	4.65	5.8	5.0	6.2	0.25	0.15	0.19
1989	4.58	4.61	4.66	6.9	5.5	7.4	0.29	0.19	0.22
1990	4.62	4.61	4.62	8.4	7.9	9.9	0.17	0.15	0.21
1991	4.62	4.51	4.58	8.0	6.9	8.8	0.12	0.15	0.27

	Ca			Mg			Al		
	D2	D4	D3	D2	D4	D3	D2	D4	D3
1982	0.86	0.96	1.82	0.81	0.76	0.93	0.9	0.6	0.4
1983	0.83	0.97	1.65	0.85	0.74	0.87	0.8	0.9	0.7
1984	0.81	0.84	1.48	0.94	0.81	0.92	1.0	0.9	0.7
1985	0.83	0.87	1.46	0.84	0.72	0.80	1.1	0.9	0.7
1986	0.81	0.90	1.59	0.88	0.75	0.90	1.2	1.0	0.9
1987	0.72	0.74	1.45	0.69	0.64	0.79	1.0	1.0	0.9
1988	0.83	0.82	1.56	0.76	0.66	0.83	0.7	0.8	0.7
1989	0.88	1.00	1.80	0.69	0.63	0.94	0.7	0.7	0.7
1990	0.95	1.21	1.77	0.98	0.87	1.21	0.7	0.7	0.7
1991	0.79	0.83	1.64	0.89	0.84	1.15	0.5	0.5	0.6

	NO ₃ -N			SO ₄ -S			Cl		
	D2	D4	D3	D2	D4	D3	D2	D4	D3
1982	0.39	0.57	0.70	2.8	2.5	2.6	15.0	9.9	10.6
1983	0.64	0.93	0.89	2.5	2.3	2.3	11.7	9.8	10.3
1984	0.70	0.89	0.81	2.1	2.0	2.2	14.0	11.9	12.5
1985	1.01	1.17	0.84	2.0	2.0	2.2	10.3	7.3	8.4
1986	1.11	0.87	0.72	2.0	2.2	2.3	10.8	9.4	11.0
1987	0.80	0.71	0.66	2.0	2.1	2.3	7.5	7.2	8.4
1988	0.55	0.65	0.66	1.7	1.9	2.2	10.9	9.2	11.3
1989	0.62	0.82	0.81	1.7	1.8	2.6	13.5	10.6	13.4
1990	0.41	0.79	0.93	1.6	1.7	2.1	20.6	16.8	19.4
1991	0.34	0.74	0.94	2.0	1.9	2.6	13.8	11.7	16.1

Table IV. Results from randomised intervention analysis (RIA) on stream water data from Plynlimon and Beddgelert.

Solute	Probability (%) of rejection of null hypothesis		
	Plynlimon Stream A4	Beddgelert Stream D2	Beddgelert Stream D4
Na	99	99	99
K	99	99	99
Ca	97.5	99	75
Mg	99	99	75
Al	75	75	30
NO ₃ -N	99	99	95
SO ₄ -S	99	99	30
Cl	99	99	99
pH	42	95	99

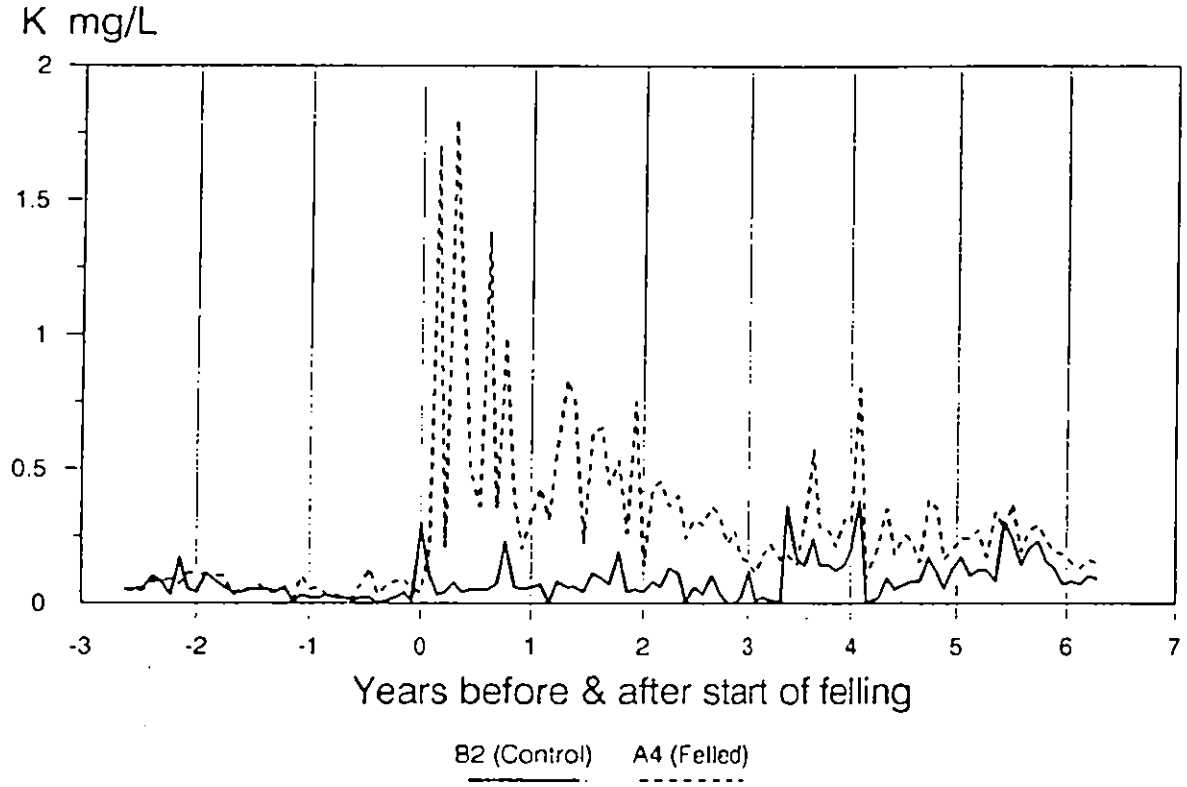
Table V. Stream water K and NO₃-N fluxes (kg ha⁻¹ year⁻¹) for two years before felling and seven years after felling. The catchment of stream D2 was 62% felled and D4 28% felled. Data are expressed per hectare of the felled area. Stream D3 drained the unfelled control catchment. N.a. not available.

Year	K			NO ₃ -N		
	D2	D4	D3	D2	D4	D3
-2	5.8	5.2	6.1	11.8	16.4	15.7
-1	1.7	2.6	2.9	6.7	11.4	10.9
+1	15.1	6.4	3.8	39.2	27.1	24.3
+2	29.2	11.6	3.3	35.7	27.8	12.7
+3	19.2	7.5	4.1	38.4	19.7	18.0
+4	6.5	3.8	3.1	11.5	12.1	12.7
+5	6.2	1.7	2.7	13.6	11.4	10.6
+6	3.3	1.4	2.0	7.1	10.6	11.3
+7	N.a.	1.0	4.4	N.a.	10.5	17.2

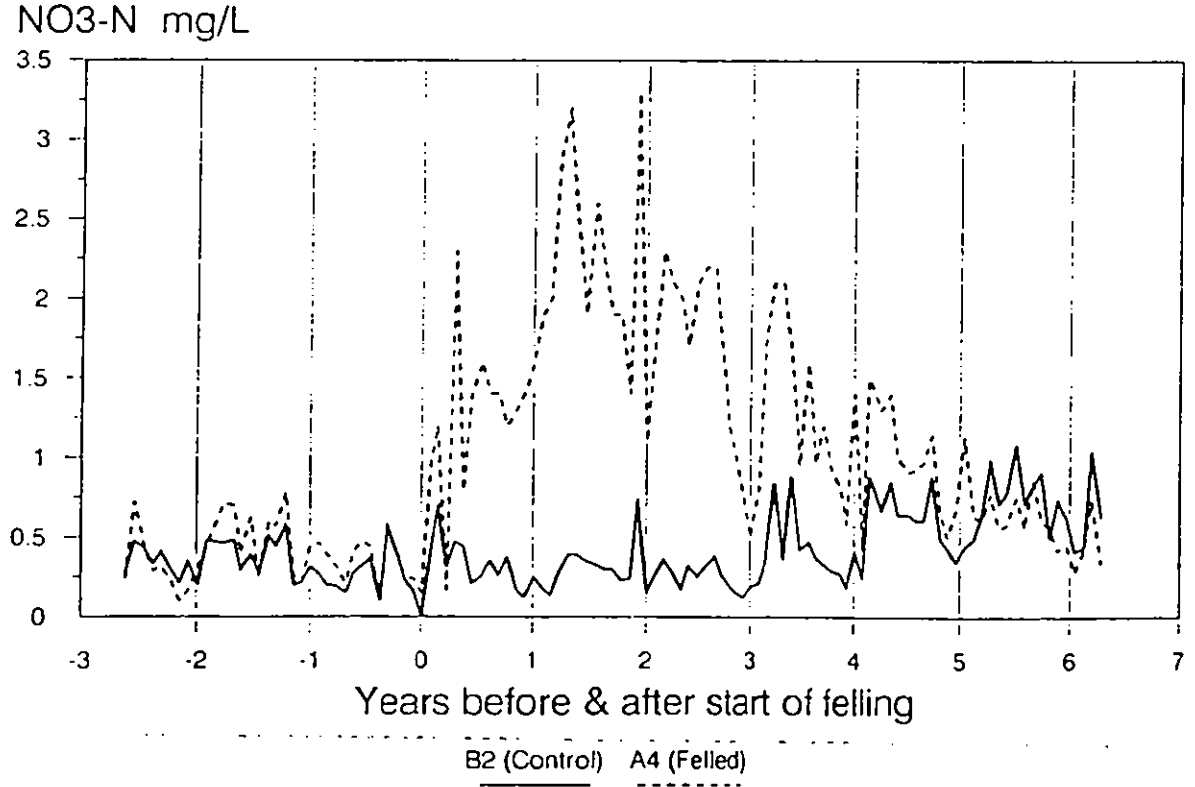
Figures

- Fig. 1 Concentrations (mg L^{-1}) of a) potassium and b) nitrate-N in streams at Plynlimon.
- Fig. 2 Concentrations (mg L^{-1}) of a) potassium and b) nitrate-N in streams at Beddgelert. Data from stream D2 (catchment 62% felled) and D4 (catchment 28% felled) have been 'normalised' with respect to stream D3 (control catchment, no felling).
- Fig. 3 Concentrations (mg L^{-1}) of a) chloride and b) sulphate-S in streams at Plynlimon.
- Fig. 4 Concentrations (mgL^{-1}) of a) calcium and b) magnesium in streams at Plynlimon. Data from stream A4 (clearfelled) have been 'normalised' with respect to the control stream B2.
- Fig. 5 Total concentrations of inorganic anions ($\mu\text{eq L}^{-1}$) in streams at a) Plynlimon and b) Beddgelert. Data for Beddgelert are normalised as described in caption to Fig. 2.
- Fig. 6 Stream water pH at Beddgelert. Data are normalised as described in caption to Fig. 2.

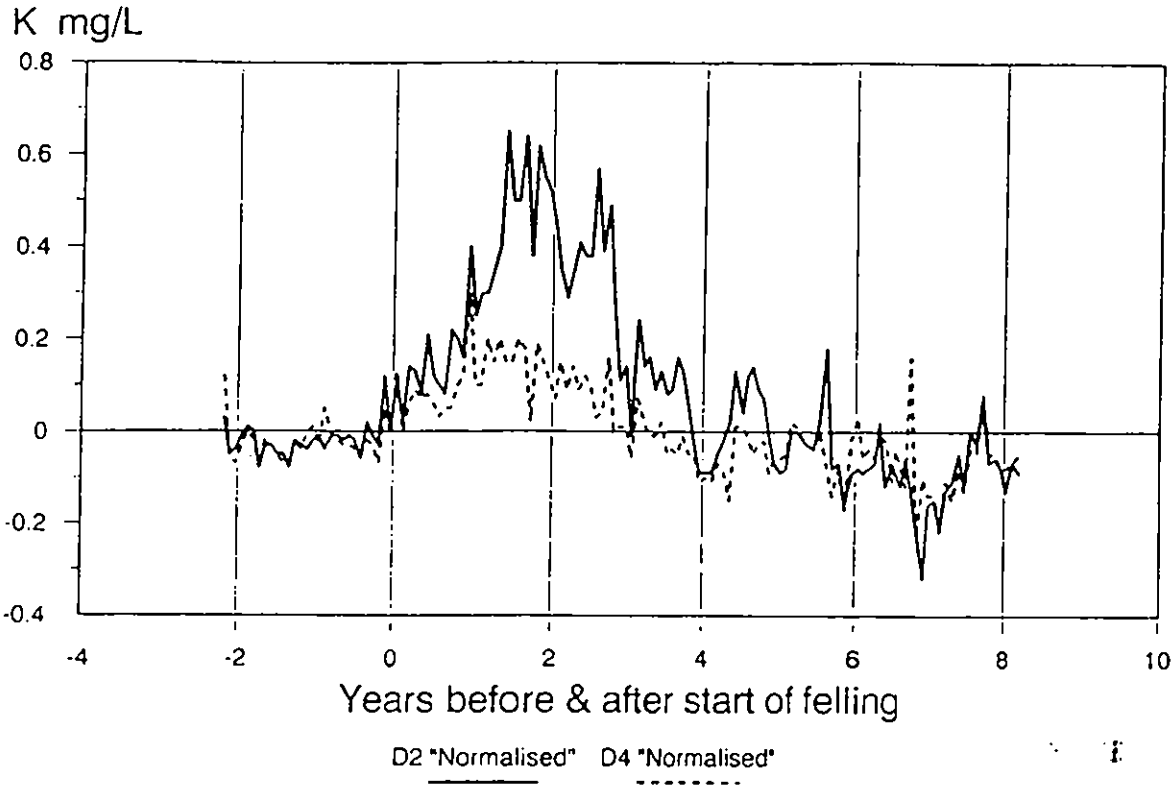
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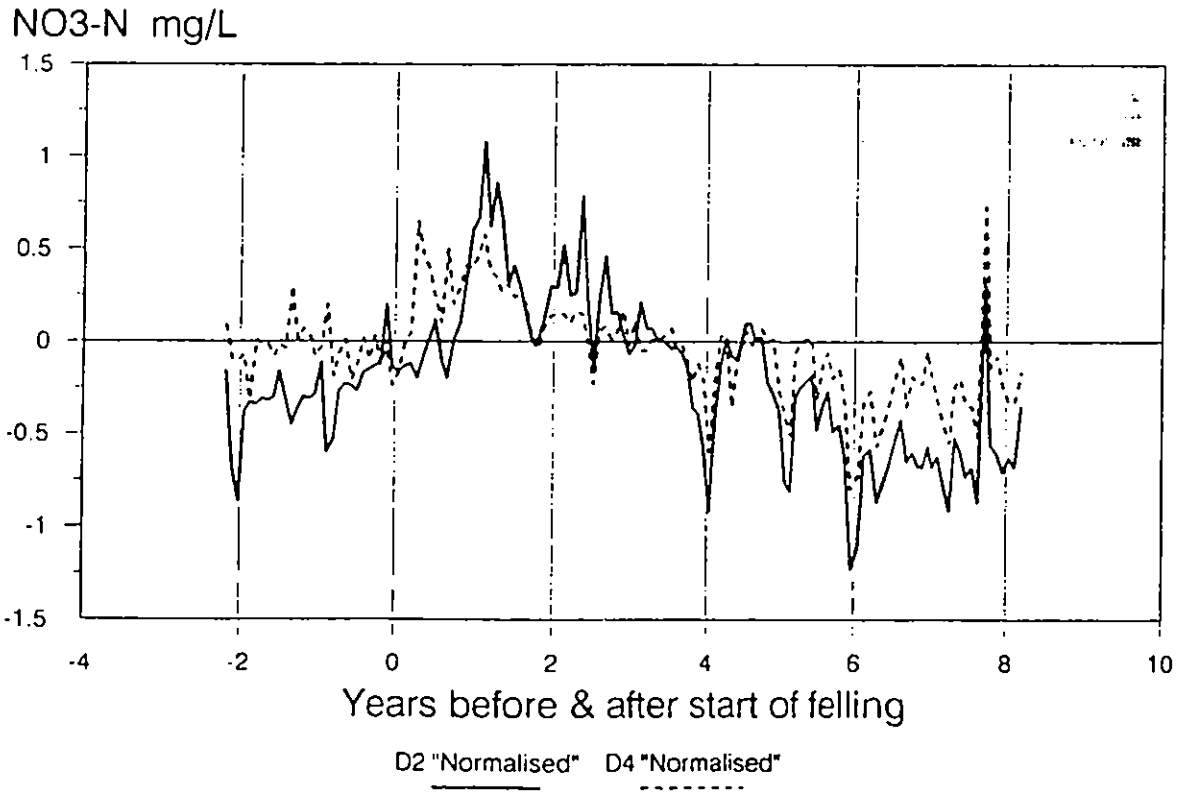
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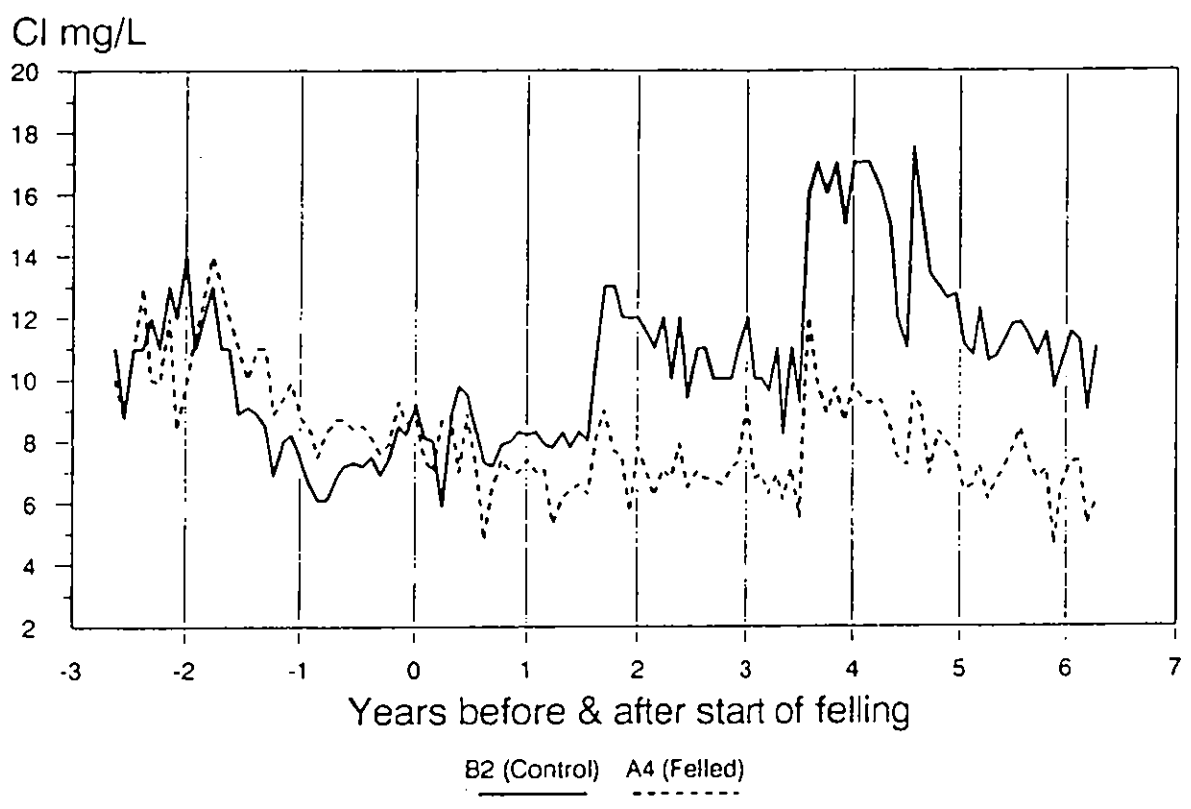
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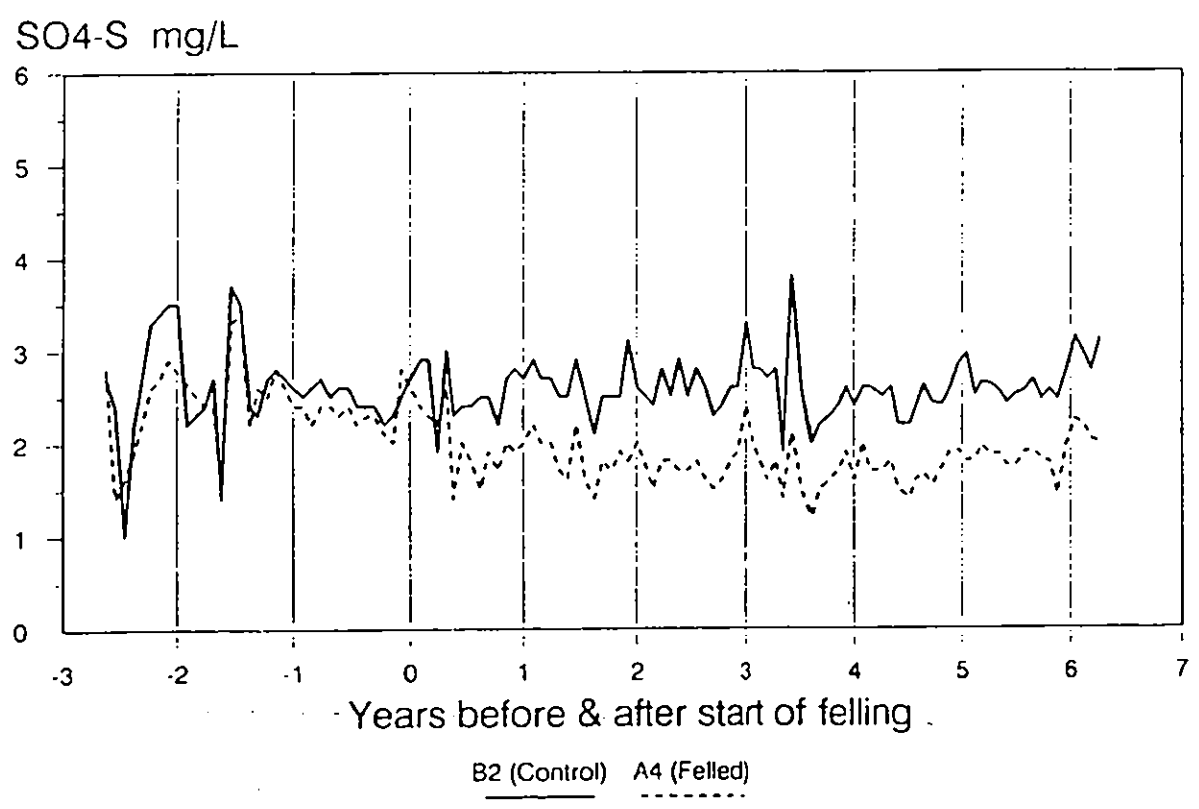
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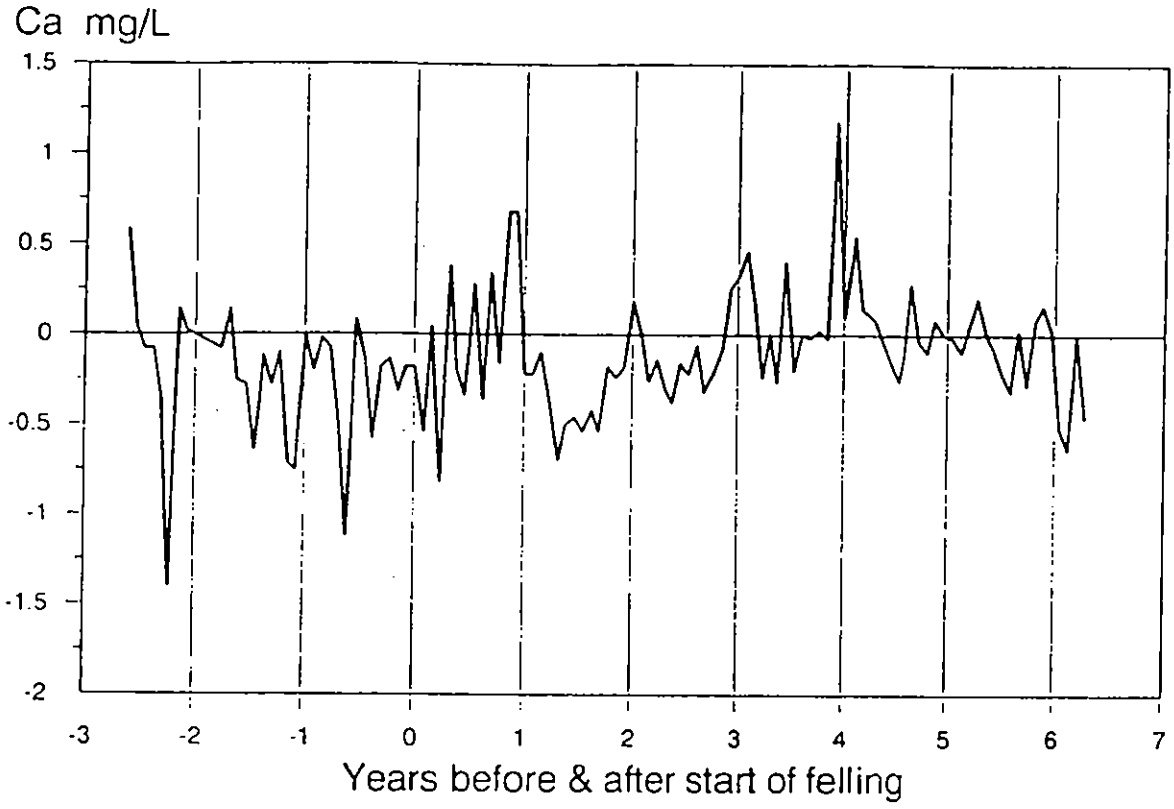
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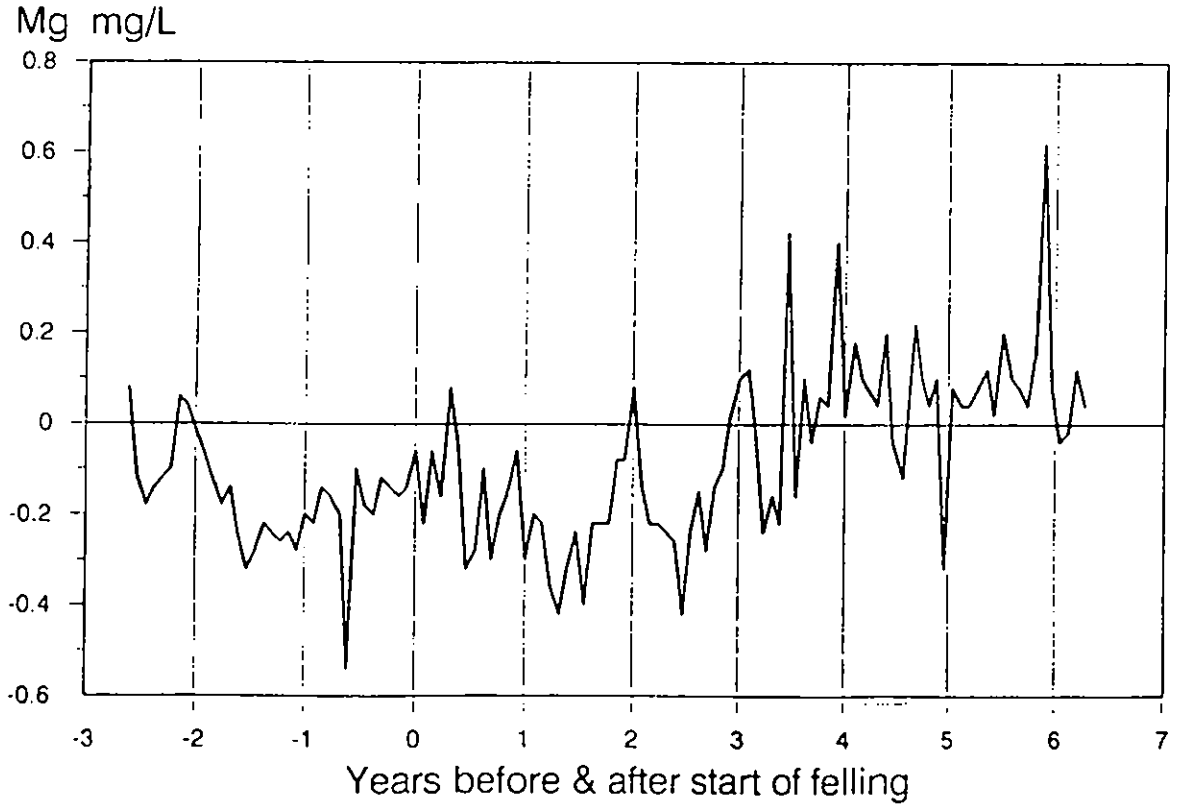
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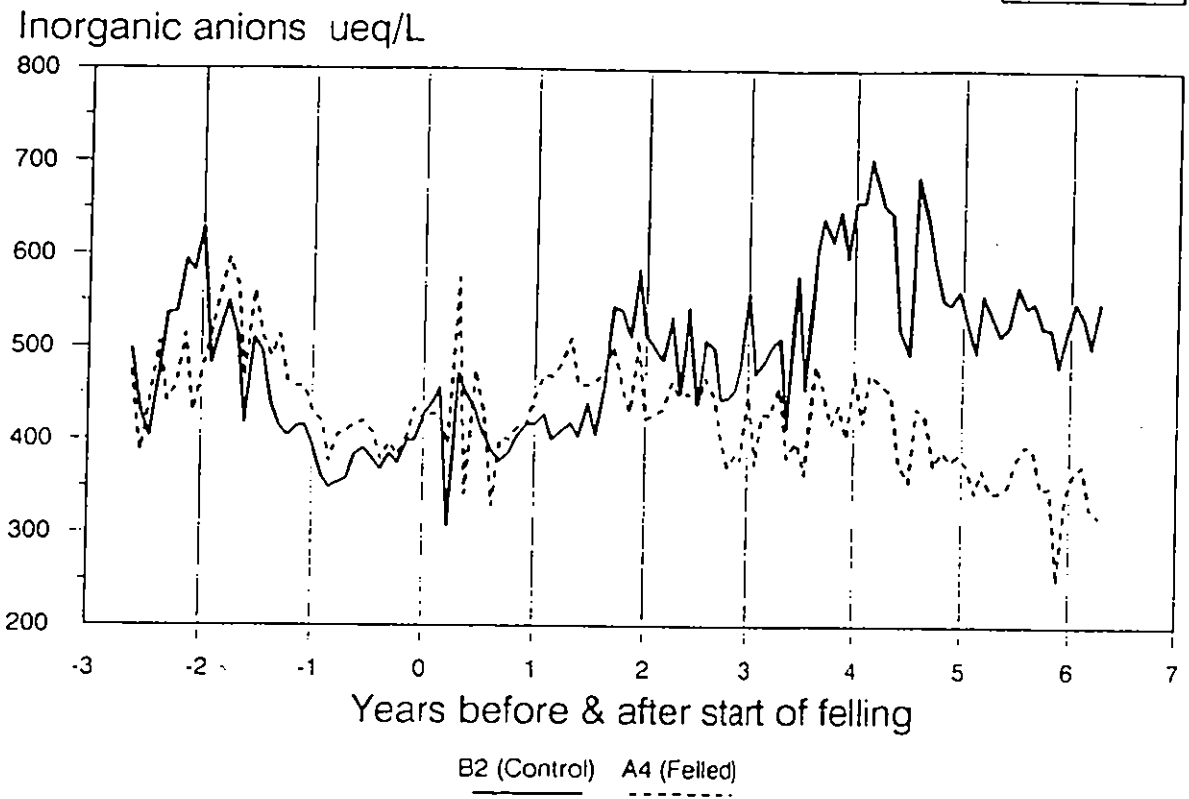
4a



4b



5a Plynlimon



5b Beddgelert

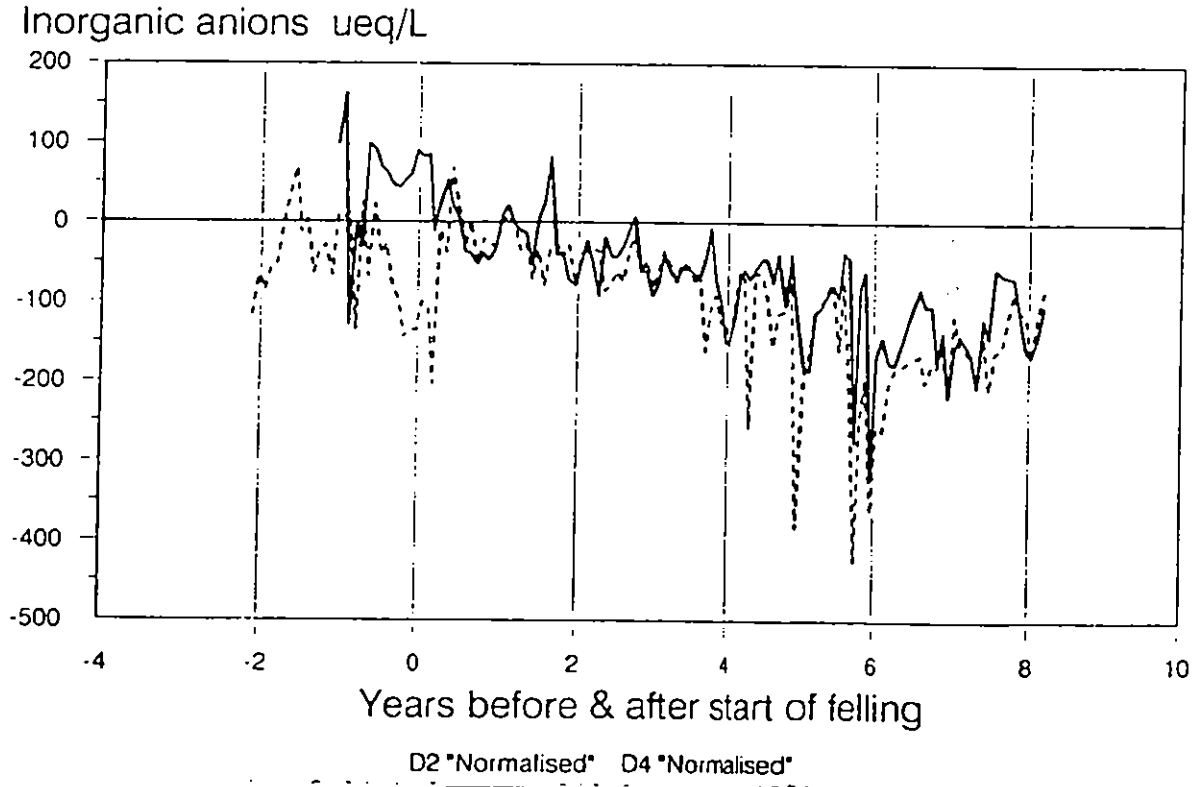
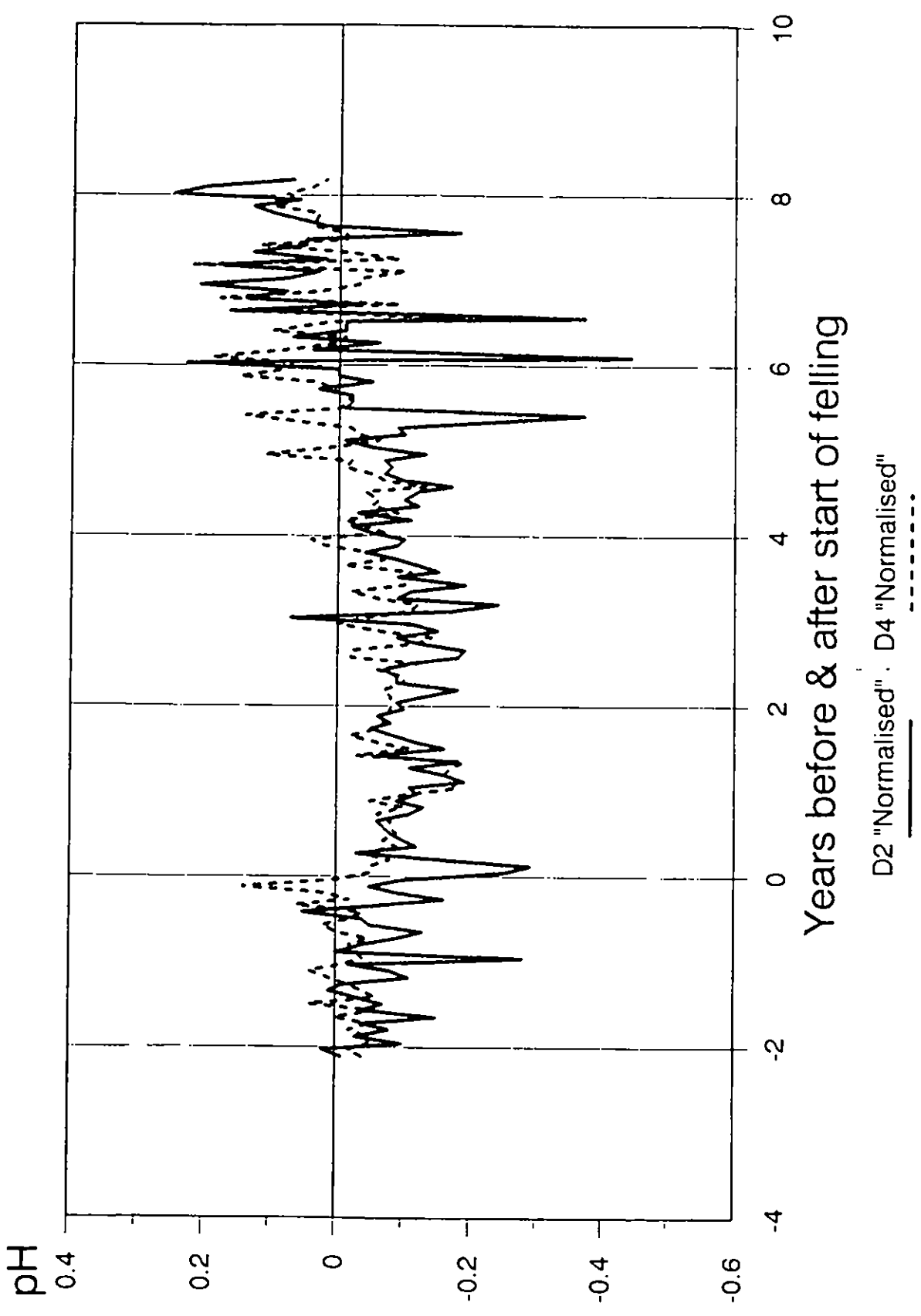


Fig 6



Years before & after start of felling

D2 "Normalised" : D4 "Normalised"

