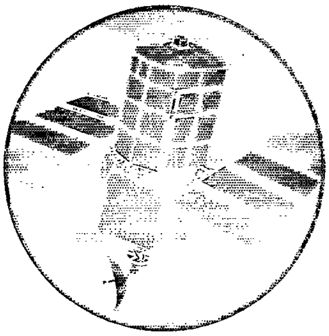
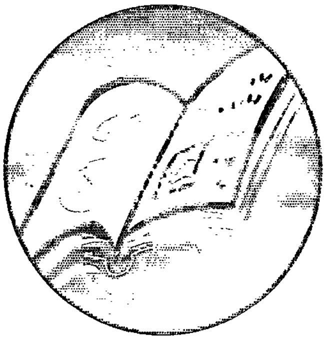
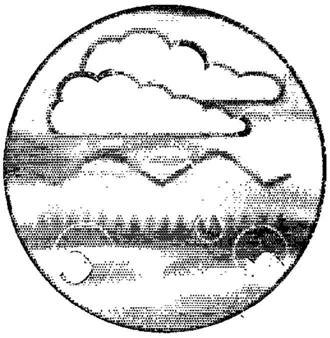
The Impact of Conifer Harvesting and Replanting on Upland Water Quality







Research and Development
Technical Report
P211

ENVIRONMENT AGENCY

The Impact of Conifer Harvesting and Replanting on Upland Water Quality

Technical Report P211

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Research Contractor:
Institute of Hydrology

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This report describes a five year investigation into the effects of conifer harvesting and replanting on the upland aquatic environment. It establishes links between environmental measurement, scientific understanding and forest management, formulating methodologies for environmental impact assessment and proposing improved forest management practices. The findings of the study will influence the future development of the Forests and Water Guidelines and other forest management policy and guidance. It will mainly be of interest to Water Quality, Fisheries and Conservation staff concerned about the effect of forestry activities within their river catchments.

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R&D Technical Report P211

CONTENTS

EXECUTIVE SUMMARY

Many parts of the UK uplands have acidic and acid sensitive soils reflecting the inability of the bedrock to weather at a sufficient rate to counteract both the acidity generated within the soils, and the impacts of acidic atmospheric pollution. These upland areas have also been a major focus for the development of conifer plantations since the turn of the century. It is believed that conifers can enhance the capture of atmospheric acid and other pollutants, thereby increasing their impacts on soils and fresh waters, although the scale of the increase remains uncertain. Many upland plantation forests are now reaching the age for harvesting and replanting and the amount of such activities will increase over the next decade.

Harvesting and replanting practices may lead to an increased acidification of stream water from:

1. Accelerated nitrate leaching from felled sites during the first 1 to 3 years post felling caused by disruption of the nutrient cycle accompanied by enhanced rates of organic matter mineralisation and nitrification.

2. Export of base cations in harvested products and uptake in to the replanted forest leading to soil base cation depletion on the decadal to centennial timescale. The magnitude of this particular impact on water quality is hard to gauge as there are poorly quantified mechanisms which can partially or wholly offset the acidification. These include an increase in base cation weathering beneath the trees and enhanced atmospheric base cation inputs due to scavenging by the forest canopy.

The environmental importance and vulnerability of upland aquatic ecosystems in the UK, the lack of detailed scientific understanding of the effects of harvesting and the imminence and scale of harvesting and replanting operations, means that the actual impacts need to be assessed urgently. This report contains the findings of an extensive five-year research project designed to meet this need. Its remit was "to assess the impacts of conifer harvesting and replanting on upland stream water quality with a view to identifying best practice ameliorative management strategies and the development of a model and guidelines for environmental impact assessment".

The project has been extensive, covering a large spectrum of detailed water quality information from paired catchment manipulation experiments, a regional survey, long-term monitoring and a synthesis of the findings from other UK studies of forest harvesting impacts. The results show that with harvesting there is a disruption of the biogeochemistry of the forest ecosystem and a change in the physical characteristics of each site which results in water quality changes across a range of timescales. The initial biogeochemical response to felling may last for up to three years and is manifest by variable increases in stream water concentrations of nitrate (typically from less than one up to ten mg-NO_3/l) and potassium (typically from less than one up to about two mg/l) together with, at the small scale, phosphate (typically from less than 0.02 up to 0.06 mg-P/l) and ammonium (typically from less than 0.2 up to about 0.6 mg-NH_4/l) for catchments with gley soils. The physical response to felling is seen in 1) a reduction in aerosol capture leading to reduced sea salt and pollutant loads to catchments, and 2) an increase in runoff because of reduced evapotranspiration losses. The duration and intensity of the changes are determined by the proportion of the catchment area felled, the method of harvesting, the rapidity of re-vegetation and the soil type.

Detailed statistical analysis reveals that the biogeochemical and physical changes associated with forest harvesting affect acidity, aluminium and base cation levels within the soil solution due to their interaction with the soil matrix. In the upper soils where aluminium is tightly bound, the interaction involves base cations and hydrogen ions. However, in the lower soils, aluminium leaching and cation exchange reactions linked to weathering of base cations are involved. Across all the scales of catchment monitoring, there is a balance between increased stream acidification due to nitrate generation following felling and decreased stream acidification because of reductions in strong acid anion concentrations (and possibly increased base cation concentrations due to enhanced weathering associated with carbon dioxide production). This is probably the most important finding of the project. Thus:

> in the vast majority of cases, when set against other temporal variations in water quality, the net acidification effect of felling is hard to discern at the catchment level.

The only potential cause for concern lies with acidity and aluminium production following felling and even here only a very limited number of cases are involved. Apart from small (5-10 ha) first order catchments, Acid Neutralisation Capacity (ANC) changes in response to forest harvesting are usually much less than 30 μEq/l, even where the entire catchment has been felled. Thus overall, the felling responses for these and the twenty or more trace elements measured in this study do not pose a water quality problem in relation to statutory limits as, except perhaps at the very local scale, the concentrations are too low. Potentially, there are other considerations beyond the scope of this project such as chemical thresholds to protect biodiversity and conservation interests and the development of more appropriate and representative environmental diagnostics for assessing the biological impacts of acidification and land use change.

Regional predictions of water quality sensitivity based on maps of soil and geological attributes are already available with regards to stream acidification and forest planting strategies. It therefore seems reasonable to use these as templates for determining vulnerable areas with regards to felling. However, an analysis of observed catchment hydrochemistry in relation to acid sensitivity predictions has identified a large number of outlier values at both high and low stream water ANCs. This results from the highly heterogeneous nature of upland catchments. In order to capture this variability and improve predictions at the appropriate catchment scale, an interim modification to the existing Environment Agency Wales map is recommended, whereby the sensitivity classification is extended to incorporate the areas of intermediate sensitivity containing a high proportion of the low ANC outliers. For the longer term, our firm recommendation is to use regional acid sensitivity maps based on direct measurements of water quality and biology as the current alternatives are too crude a representation at the scale of interest for assessing the potential impact of forest harvesting operations.

As ANC changes in response to forest harvesting are usually much less than 30 μEq/l, even where the entire catchment has been felled, this value can be used as a precautionary threshold to separate sensitive from nonsensitive areas. As with other approaches, the threshold value should be applied relative to the minimum values observed in the stream rather than the average. With the introduction of more sophisticated GIS systems it is appropriate that harvesting impacts should be judged in relation to the proportion of a catchment felled rather than to coup size as at present.

Practical ways of minimising potential water quality impacts associated with forest harvesting are essentially contained within the Forests and Water Guidelines (FC, 1993) and other "good practice" manuals (e.g. Nisbet *et al.*, 1997). The following are highlighted for consideration specifically in relation to forest harvesting:

1. Early re-vegetation of the site should be encouraged to minimise the nitrate pulse and the associated potential acidification.

2. The effects of felling should be diluted out by phasing the felling operations within a catchment. This will be effective because: a) there will be dilution by runoff from the standing crop remaining in the catchment and b) where there are areas felled two or more years previously, these will contribute less acidic water than both the remaining standing crop and the recently clearfelled area.

3. Care should be taken a) to minimize the impacts of extreme events associated with high flows and b) to prevent localised forestry activities introducing intermittent point sources of pollution.

In these respects, we endorse the consistent application of the existing guidelines.

The longer term impacts associated with the introduction of second and subsequent generations of plantation forestry are linked to the overall balance between (1) base cation losses from biomass export; (2) accelerated base cation leaching losses at harvesting and (3) base cation inputs from the atmosphere and soil/bedrock. Indeed, this aspect may well provide the critical determining factor over the sustainability of repeated forestry cycles both in terms of nutritional requirements and water quality impacts. An analysis of calcium cycling within mature forest stands and a dynamic water quality modelling study indicates that the calcium budget is finely balanced, lying within the errors of many of the measured parameters; whole tree harvesting will deplete the base cation store to a greater extent than stem-only harvesting. Thus, the long term impacts of forestry cycles cannot be assessed accurately and this aspect remains a major upland environmental management issue requiring further research.

Within our study, the end product has been straightforward, practical solutions to issues of great scientific complexity. However, the benefits of good environmental management ultimately depend on forward looking co-operation between forestry interests and the environmental regulators. All parties should be encouraged to combine their considerable practical expertise and experience in addressing the environmental issues related to commercial plantation forestry in the uplands. The value of this approach can be gauged by the success of this project.

KEY WORDS

Water quality, rivers, uplands, acidification, aluminium, ANC, alkalinity, trace metals, forestry, harvesting, replanting, conifers.

1. INTRODUCTION

Considerable evidence has been accumulated which shows that acidification of the UK upland environment has occurred. The first phase of soil acidification may have started up to ten thousand years ago with the development and subsequent loss of birch, hazel, alder and oak forests (Dimbleby, 1952; Taylor, 1974; Pennington, 1984). The deforestation occurred during the Neolithic and Bronze ages as a result of climatic change about 2700 years ago and local deforestation by man from 5000 years ago up to present day. As a consequence of this, thin acidic moorland soils developed supporting acid grassland vegetation and these semi-natural grassland ecosystems are characteristic of much of the UK uplands today. In waterlogged areas, where reducing conditions ensured limited breakdown of organic matter, a very acidic environment developed and peat deposits accumulated. Set against this long term change in the upland environment, further acidification has occurred during the past one hundred years with consequent adverse effects on upland ecology. This later phase of acidification has been associated with the increased emissions of acidic oxides following the industrial revolution. Indeed sulphur emissions accelerated rapidly from 1940 onwards, reached a peak in the 1970s and have subsequently declined. While sulphur provided about two thirds of acidic inputs to catchments, the remaining third was associated with nitrogen compounds during the peak years of the 1970s and subsequently, in contrast to sulphur, the emissions of oxidised and reduced nitrogen species (NO_2 and NH_3 in particular) have increased through the 1980s and now are only starting to show a decline for example with the introduction of catalytic converters on cars (UKRGIAN, 1994).

From the late 1960s, concerns were raised over whether the atmospheric deposition of industrially emitted acidic oxides (SO_x in particular) was adversely affecting stream and lake ecology. The acid sensitive areas were those which possessed acidic soils overlying base-poor bedrock. Indeed, the main problem of acidification rests with the lack of weathering reactions of primary rock minerals, to release base cations and promote bicarbonate production from biogenic CO_2 within the soils and groundwater, to neutralise the acidic inputs. The concerns generated heated political debate across Europe and led to considerable scientific research to characterise the nature of the acidification process and to identify potential remedial treatments. Even from the onset, there was much debate over the relative importance of acidic deposition and changing land use. Nowadays, the importance of atmospheric pollution is generally recognised on a continental scale, with, for example, acidification problems being identified across Europe and North America. Major concern has been raised over the deterioration in stream water quality in the UK uplands associated with this second and ecologically potent phase of acidification. However, despite all the research, major question marks remain over the nature of the determinative hydrochemical processes, the likely impacts and the extent of recovery (Renner, 1995).

In the UK, the relative importance to acidification of acidic deposition and land use change remains a major issue especially in the uplands (land over 300 m altitude) which comprise about a third of the UK land area (Roberts *et al.*, 1994). By far the most important land use change in the uplands over the last century has been the widespread afforestation with exotic conifers. Although it is widely agreed that acidic oxide deposition has been the major driving force, conifer planting has also been implicated as a factor in soil and freshwater acidification (Stoner and Gee, 1985; UKAWRG, 1988; Whitehead *et al.*, 1988a,b, Jenkins *et al.*, 1990). Both may lead to the generation of more acidic and aluminium bearing stream water and conditions unhealthy for stream biota. Acidification has occurred in extensive tracts of the uplands without tree cover although conifers enhance the capture of acid pollutants (Milne *et al.*, 1988; Fowler *et al.*, 1989), thereby increasing their impacts. Nonetheless, the relative importance and the degree of interaction between the two factors still needs clarifying (Hornung *et al.*, 1989; Miller, 1985; Jenkins *et al.*, 1990; Rosenqvist, 1978, 1990; Nisbet, 1990; Krug, 1991). For example, under pristine conditions there is evidence both for and against the deleterious effects to stream water of conifer development. In a modelling study of afforestation, Jenkins *et al.* (1990) comment that "afforestation in the absence of acidic deposition, has had a lesser effect on surface water acidification even though the nutrient demands of forest growth have caused significant soil acidification". The key issue as to whether forestry causes acidification in its own right relates to the balance between base cation inputs from the atmosphere, cation exchange pools and weathering versus losses in stream water and harvested biomass. This balance has not been satisfactorily resolved.

Many of the earlier coniferous plantations have already reached the felling stage and these practices could themselves lead to further deterioration in water quality over a range of time scales. Statistics (Forestry Commission, 1997) show that, for the years 1990 to 1997 (inc.), the average annual area of restocking was 15,000 hectares. This can be regarded as a lower limit of the amount of forest clear-felled per annum. This figure for the UK is likely to increase as more of the older plantations approach felling age.

Clear felling represents an abrupt and dramatic end to the 30-60 year period of forest crop development with its comparative lack of disturbance both in relation to water quality (Hudson *et al.*, 1997a) and sediment yield (Marks and Rutt, 1997; Marks and Leeks, 1998). Complete disruption of the nutrient cycle occurs as removal of the tree crop effectively eliminates root uptake while decomposition of large quantities of felling debris and accompanying leaching may result in a pulse of nutrients through the soil. Mature spruce plantations are characteristically devoid of ground vegetation and revegetation following clear felling is often slow because of the presence of brash limiting ground cover development, while tree growth from juvenile planting is comparatively slow. As a result of the absence of a root sink, mobile nutrients such as potassium and nitrate will be leached from the soil and into streams; less mobile nutrients, for example phosphorus, will generally remain in the soil. Within the soil, nitrification rates may also increase after felling accompanied by increased nitrate leaching with acidification of streams and shallow groundwater.

Crop removal allows substantially more water to reach the soil; interception and transpiration by the trees having been eliminated. Greater water throughput will have a dilution effect on solute concentrations in soil and stream waters. Removal of the tree canopy also reduces scavenging of marine, pollutant and other terrestrially-derived particulate and gaseous material, and reduces the inputs of these to soils.

Timber removal from the site at felling may lead to long-term nutrient depletion and this will be particularly significant with whole tree harvesting (Reynolds *et al.*, 1999). In particular, the export of base cations in harvested products together with uptake into the developing forest may lead to a further and possibly more important acidification phase.

It is with these national environmental issues relating to water quality and catchment land-use in mind that the present programme was instigated in 1993 to build on the detailed hydrochemical studies of the Institutes of Hydrology and Terrestrial Ecology at the Plynlimon catchments in mid-Wales.

2. STUDY SITES AND METHODS

2.1 Site descriptions and sampling programmes

The primary data presented in this report come from catchment studies in mid Wales (Plynlimon and Vyrnwy catchments: Neal *et al.*, 1992a-d; Neal *et al.*, 1997a-d). This is supplemented by parallel information for catchment studies in north Wales (Beddgelert Forest; Stevens *et al.*, 1989; Stevens *et al.*, 1993; Reynolds *et al.*, 1995a-c) and northern England (Kershope Forest: Adamson *et al.*, 1987, 1990; Adamson and Hornung, 1990)) and a survey of small streams across Wales. Twenty one sites have been examined for this report: these have been described in detail within the literature in terms of catchment attributes, management, sampling regime, chemical analysis and water quality variations. Background information, including soil and vegetation types, length of record etc are provided in Table 2.1 for the catchment studies and Table 2.2 for the Welsh regional study. A brief summary of the information for each area is as follows.

Table 2.1. Catchment summary information for the key IH and ITE monitoring sites in Wales and Northern England. Key: SS=Sitka Spruce; G=Gley; P=Podzol; M=Acid Moorland; Pe=Peat; BE=Brown Earth; Y=Yes, 100% fell unless indicated otherwise; N=No, 0% fell.

Site	Area	Soil type	Vegetation	Fell	Sampling	Data run
BD2	2-4	P	SS	Y62%	26	15
BD3	2-4	P	SS	N	26	15
BD4	2-4	P	SS	Y28%	26	15
KD1	2	G	SS	N	52	5
KD2	2	G	SS	Y	52	5
KD3	2	G	SS	Y	52	5
KD4	2	G	SS	Y	52	5
SE1	2-4	P	SS	Y	26	3
SE3	2-4	P	SS	N	26	3
TanN	<2	G	SS	N	26	3
TanS	<2	G	SS	Y	26	3
Vn1	2-4	BE	SS	N	26	3
Vn2	2-4	BE	SS	N	26	3
S2H	3-6	P	SS	Y	52	9
Tan	51	G	SS	Y50%	52	7
UHa	117	M/Pe	M	M	52	14
UHoB	178	M/P/G	SS	N	52	14
UHoS	178	M/P/G	SS	N	52	14
Ha	347	M/P/G	SS	Y<25%	52	14
HoB	335	M/P/G	SS	Y	52	14
HoS	335	M/P/G	SS	Y	52	14

Table 2.2 **A summary of data coverage for the Welsh regional survey catchments with differing soil types.**

Soil type	Number of sites	Felling periods
Bog	8	0 to 5
Brown earth	10	0 to 9
Gley (PG)	32	0 to 9; 12 to 14; 47
Gley (SWG)	8	0 to 4; 14 to 16
Podzol (IIP)	8	0 to 9
Podzol (PIP)	9	0 to 7

2.1.1 Plynlimon and Vyrnwy (mid Wales)

Two types of monitoring site are present in the Plynlimon and Vyrnwy areas which are all underlain by base-poor Lower Palaeozoic mudstones, shales and grits. Firstly, for the Plynlimon area, there are long term monitoring sites for the main tributaries of the head-waters of the River Severn. These drain a hill top plateau moorland region and, lower in the catchment, the Hafren Forest (catchment areas vary from about 50 to 300 ha). The moorland and forest catchments represent a mixture of upland acid soil types dominated by peaty podzols with subsidiary peaty gley, deep peats are also important in the moorland plateau area. In total, there are five streams regularly monitored, one moorland (upper Hafren) and four mainly forested streams (lower Hafren including the moorland drainage from the upper Hafren, the entirely forested Tanllwyth, the upper Hore and the lower Hore). Of these, the forest area in the lower Hore catchment was clearfelled during the mid 1980s while for the other sites some localized felling has taken place over many years to thin and in some cases harvest small areas of the crop: about a half of the Tanllwyth catchment has been felled over the past two years. Hafren Forest comprises mainly Sitka spruce with some Norway spruce (*Picea abies*), larch (*Larix* spp) and lodgepole pine (*Pinus contorta*) planted in various phases between the mid 1940s and 1960s. A variety of harvesting techniques have been used, but in most areas only the tree stem has been removed from site leaving the felling debris (stumps, branches and needles) behind.

Secondly, there have been a series of eight small catchment studies (< 15 ha) explicitly examining the interaction between soil type and forest harvesting on water quality. In most cases a paired catchment approach has been applied with control and wholly manipulated forested catchments. Six of these sites are located within Hafren Forest at Plynlimon and represent two of the main soil types of concern, peaty podzols (S2H, Se1, Se2, Se3) and peaty gleys (Tan-N, Tan-S). The other two sites are located close to Llyn Vyrnwy some 40 km to the north of the Plynlimon area. The Vyrnwy sites provide information on the other main type of soil of concern, brown earths (Vn1 and Vn2): no suitable brown earth sites were available for study in the Plynlimon area. The manipulated sites at Plynlimon are: S2H, Se2, Se3, Tan-N.

Across the Hafren catchments, a series of exploratory (13) and monitoring (6) boreholes was drilled to monitor groundwater chemistry and water levels in April 1994. The exploratory boreholes were spread throughout the Hafren catchment to examine upper plateau, intermediate slopes and flat near river areas to cover a range of geomorphological environments and were monitored for one year on a monthly basis. The six monitoring boreholes were established since 1994 near the paired catchments to provide an assessment of groundwater quality changes at felling and control sites. The sampling has been ongoing on a fortnightly basis.

2.1.2 Beddgelert Forest (north Wales)

Bulk precipitation and stream water chemistry from streams draining three catchments in Beddgelert Forest have been monitored on a fortnightly basis since 1982. The catchments comprise two sites (BD2 and BD4) where 50 year old Sitka spruce (*Picea sitchenis*) was harvested using a mixture of stem only and whole tree harvesting techniques in 1984: the third site (BD3) was left as a forested control. About 62% of BD2 and 28% of BD4 were felled, the remaining areas comprising standing Sitka spruce forest and acid grassland vegetation. In 1994, two boreholes were established, one down-slope of the felled catchment D4 and the other below D3 and fortnightly sampling for chemical analysis proceeded from then on. All the sites relate to small catchments (about 2 to 4 ha in area) draining extremely acidic peaty-podzol soils underlain by base-poor Lower Palaeozoic slates and shales.

2.1.3 Kershope Forest (northern England)

Data from four plots on peaty gley soils (each of about 2 ha area) are available from earlier studies within the Institute of Terrestrial Ecology (Merlewood). These comprise one control plot planted with Sitka spruce in 1948 (KD1) and three similar plots clearfelled in 1983 (KD2, KD3 and KD4). The plots are underlain by a clay-rich till developed from the underlying Carboniferous geology. The till, which was originally calcareous, has been decalcified to a depth of between 75 and 150 cm. Water samples were collected from the main ditch issuing from a network of open forestry drains on each plot.

2.1.4 Welsh regional study

The rationale behind the regional sampling programme was to obtain soil/hillslope drainage "endmember" chemistries representative of a variety of soil types in order to describe how the chemical composition of the major inputs to streamflow generation change with forest clearfell. The focus on soil drainage chemistry is justified because under highflow conditions in the stream, when these inputs predominate, the main problems of stream acidity occur (Neal and Christophersen, 1989). Small discrete catchments were chosen (a) to provide an integrated measure of soil drainage water chemistry (very heterogeneous behaviour is observed at smaller scales such as within the soil pores; Neal, 1996) and (b) to minimise groundwater inputs which are more prevalent as baseflow discharge to the main streams. Drainage water samples were taken at both baseflow and highflow extremes so as to identify the range of responses. The regional extent of the survey and the intermittent nature of the hydrological extremes meant that an innovative campaign approach had to be used. This involved opportunistic high and low flow sampling by Forest Enterprise field staff. Sampling was "triggered" by central assessment at the Institute of Hydrology, Wallingford, of suitable weather patterns and the alerting of the sampling teams for each of the Forest Enterprise (FE) regions. The timing of low flow sampling was judged on the basis of dry weather conditions being maintained for a minimum of three weeks. High flow sampling was initiated to coincide with rainfall from particular frontal weather systems. It was left to the judgement of the field staff exactly when to sample, the criteria being that rainfall prior to the sampling was sufficient to fully 'wet up' the catchment and that flow from runoff had to be particularly high. Seasonality was incorporated into the experimental design: autumn storm flush and winter and spring stormflow periods were sampled as were spring, summer, autumn and winter baseflow periods. The campaigns covered the period autumn 1995 to spring 1998.

Of over 200 sample sites initially considered across Wales, a subset was selected to have (a) a catchment area between 2 to 5 ha, (b) a definable catchment boundary (c) a first order stream draining a single soil type and single site management regime, (d) available site information such as felling and replanting dates, (e) available FE staff for opportunistic sampling and (f) to be either fully forested or completely harvested (and in some cases replanted) at single stages in the past. By this process, 51 clear felled/replanted and 16 standing forest sites were selected from all the FE districts in Wales where representative catchments were available (Table 2.2, Figure 2.1).

2.2 Chemical analysis and determination of gran alkalinity and ANC

2.2.1 General analytical methods

A wide variety of major, minor and trace elements have been determined on filtered samples. The filtration was mainly undertaken either in the field or within a few hours after return to the laboratory. For trace metal analysis, samples were 0.45 μm membrane filtered and then acidified to 1% vv with ARISTAR grade concentrated nitric acid and stored in acid washed polyethylene bottles. For the anions and nutrients, these were filtered through either 0.45 μm membrane filters or 0.7 μm glass fibre filters and then stored in chromic acid washed glass bottles. The samples were stored at 4°C in the dark. A combination of standard instrumental techniques including automated colorimetry, atomic-emission, atomic-absorption and inductively coupled plasma optical emission and mass spectrometry, ion chromatography were used. Acid titration and electrometric methods were used to determine pH and alkalinity on unfiltered samples. These methods are described in detail in the relevant papers quoted above. For the Plynlimon study an interference in the phosphorus analysis was observed due to silica (Neal *et al.*, 1999) and this was corrected for using the regression relationship

$$SRP_{\text{new methodology}} = (1.02\pm0.07)*SRP_{\text{old methodology}} - (0.030\pm0.002)*\{Si\} + (0.002\pm0.019) \quad [2.1]$$

where N= 125 and $R^2 = 0.886$.

2.2.2 Standardization of approaches to gran alkalinity and ANC determination

There are two differences in approach between the measurements for mid-Wales and for the other sites. For the mid-Wales sites, Gran alkalinity (Alk-G) has been directly measured by titration and

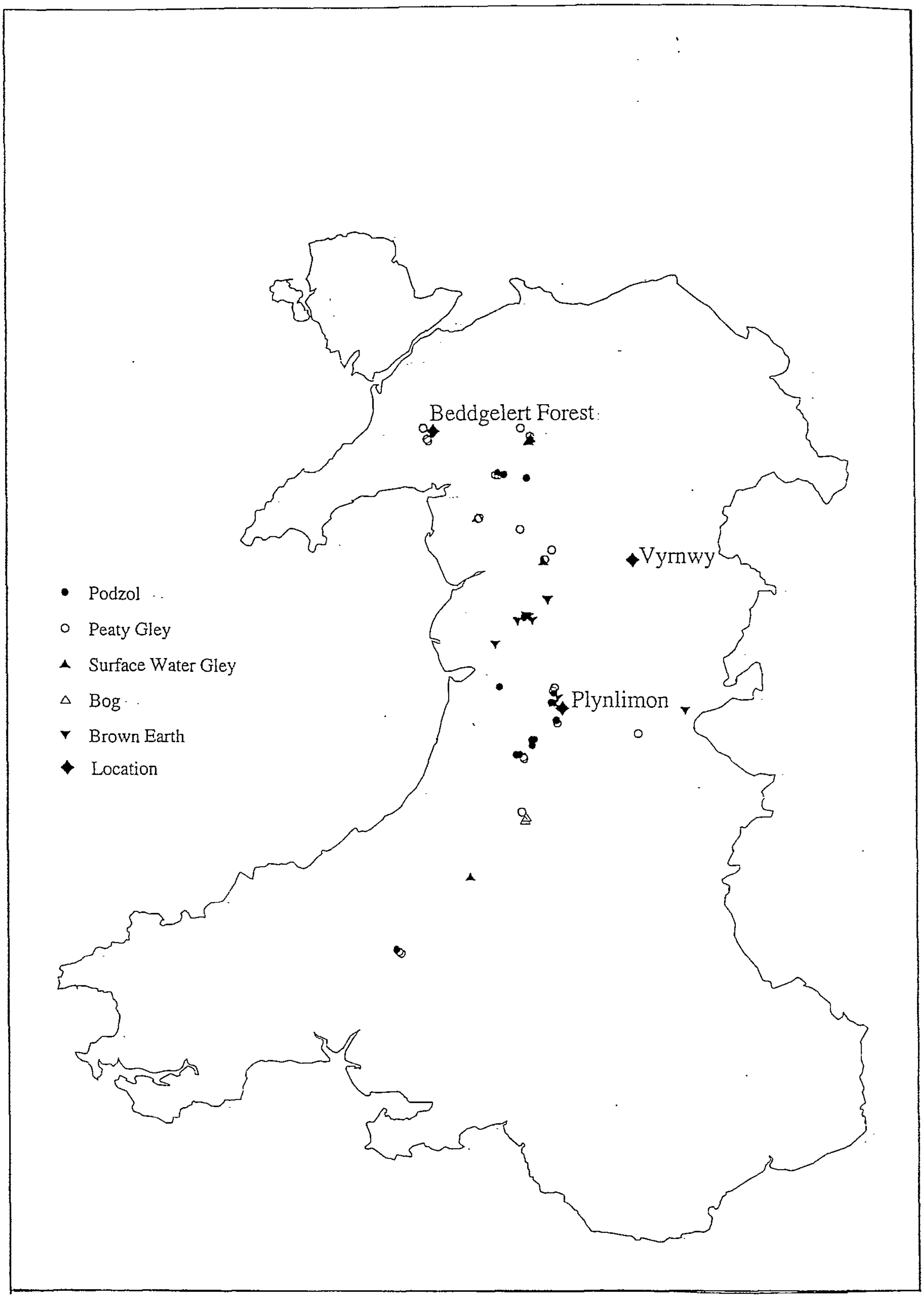


Figure 2.1 **Location of Plynlimon, Beddgelert forest, Vyrnwy and Welsh regional survey sites**

acid neutralisation capacity (ANC) is subsequently estimated (ANCest) using information on Alk-G, total dissolved aluminium (T-Al) and dissolved organic carbon (DOC) concentrations using the formula of Robson (1993) developed from charge balance considerations and thermodynamic relationships derived from the ALCHEMI program of Schecher and Driscoll (1988):

$$\text{ANCest} = \text{Alk-G} - 3*[\text{T-Al}] + 0.054*[\text{DOC}] \qquad (2.1)$$

where Alk-G is in μEq/l units while [T-Al] and [DOC] are both in μM/l units.

For the other sites, Gran alkalinity was not measured and ANC was calculated directly from the charge balance (ANCcb) as:

$$\text{ANCcb} = [\text{Na}] + [\text{K}] + 2*[\text{Ca}] + 2*[\text{Mg}] - [\text{Cl}] - [\text{NO}_3] - 2*[\text{SO}_4] \qquad (2.2)$$

where the concentrations of all components are in μM/l units and ANCcb is in μEq/l units.

Gran alkalinity has been subsequently estimated (Alk-G.est) as

$$\text{Alk-G.est} = \text{ANCcb} + 3*[\text{T-Al}] \qquad (2.3)$$

in μEq/l units. The approximation is based on Eqn1, but, as with many studies, without the small correction term for organic anions: no DOC data are available for these sites.

The two methodologies of ANC calculation agree well from an analysis of the mid-Wales data where both techniques have been used. Thus, linear regression for the full mid-Wales ANC data set gives -

$$\text{ANCcb} = 0.94(\pm 0.02)*\text{ANCest} + 12(\pm 30) \qquad (2.4)$$

$N=983$, $r^2=0.924$.

As the constant is not significantly different from zero, it can be eliminated from the regression equation to give -

$$\text{ANCcb} = 1.00(\pm 0.02)*\text{ANCest} \qquad (2.5)$$

$N=983$, $r^2=0.880$.

in μEq/l units, where the ± term in brackets represents twice the standard error.

Hence, ANCcb can be considered as equalling ANCest to a high degree of statistical significance. For the Kershope sites, there are anomalous features as described below that indicate additional anionic components may be present that are currently not considered within the formulation of equations (1) and (2). Dealing with this aspect is beyond the scope of the present study but it does not significantly affect the findings presented within this report.

There are many aspects to the measurement of alkalinity and ANC which are beyond the scope of this Technical Report, but are central to environmental measurement and regulation of acidification. We refer the reader to the companion Project Record (R&D Project Record P2/067/1; 1999).

3. LONG TERM VARIABILITY IN RAINFALL AND STREAM WATER CHEMISTRY

3.1 Plynlimon

3.1.1 Atmospheric inputs

Plynlimon rainfall is derived from a variety of sources and therefore it has a chemical composition that is highly variable (Table 3.1). Being close to the Irish sea and the North Atlantic Ocean, westerly winds provide rainfall enriched with sodium, magnesium, strontium, bromide and chloride: they are transferred from the sea to the atmosphere as sea-spray and the ratios of their concentrations remain close to those of sea-water. In contrast, winds from other directions bring air that has passed over agricultural land and industrial areas. This air provides rainfall low in sea salts but enriched with lithogenic (e.g. silica) and pollutant (heavy metals, sulphate, nitrate and ammonium) components. For the non-sea salt components, rainfall concentrations are highly variable and they have low inter-element correlations due to their diverse sources: only ammonium, aluminium and iron are correlated. Concentrations increase with decreasing volume of catch for most of the pollutant components. However, there is no corresponding systematic concentration variation for the marine components. For components that have both maritime and industrial sources (e.g. calcium, sulphate and potassium) two linear trends are observed when their concentrations are plotted against chloride: one trend corresponds to the marine line while the other has a much steeper gradient (Neal *et al.,* 1992e). Both concentrations and loads of sea-salts deposited on the Plynlimon catchments show marked seasonality. Their values peak in the autumn and winter, coinciding with high rainfall volumes associated with the progression of low pressure systems from the Atlantic. The annual variations in catchment wet deposition loadings of Ca, SO_4 and K are complicated by the dual sources of these constituents and variability in annual weather patterns. Sulphate loads at Plynlimon correlate with south-westerly and westerly winds; the highest rainfall volumes also coincide with these wind directions resulting in high sulphur loadings from marine sources, whereas the highest sulphur concentrations in rainfall are non-marine in origin.

While there is high data scatter, there are longer term patterns in inputs for sea-salts, chromium, lead, and zinc but there is no general trend with time (Wilkinson and Jenkins, 1996 and Robson and Neal, 1996). For zinc, the higher concentrations occur for years of relatively low sea-salt inputs and this probably reflects the relative importance of Atlantic frontal systems and complex air masses that have travelled over the industrial centres of Wales and England. However, it seems that there has been a major increase in rainfall concentration over the past few years for lead.

The concentrations of pollutant sulphate, nitrate and ammonium in precipitation are relatively low compared to less remote parts of the UK, although the high annual rainfall volume means that the fluxes entering the catchment are relatively high (1.02 gm-S m^{-2} yr^{-1}; 0.61 gm-NO_3-N m^{-2} yr^{-1}; 0.6 gm-NH_4-N m^{-2} yr^{-1}). Examination of the rainfall chemistry shows that at least 60% of the sulphate in wet deposition can be accounted for by anthropogenic rather than sea-salt sources. Trace metal concentrations in rainfall at Plynlimon are low compared with many areas of the UK (Cawse, 1981) due to the lack of heavy industry and predominance of marine inputs from the south-west although there are exceptions (zinc and chromium in particular); loadings of the marine components are large compared to other UK sites. In mist, concentrations of most determinands

Table 3.1 **Major, minor and trace element summary for rainfall and cloudwater.**

		Rain Min	RainMax	RainAvg	CloudMin	CloudMax	CloudAvg
Na	mg/l	0.00	23.60	2.07	1.3	1034.2	40.9
K	mg/l	0.00	1.95	0.13	0.1	44.0	1.9
Ca	mg/l	0.00	4.60	0.29	0.2	107.1	4.3
Mg	mg/l	0.00	2.98	0.26	0.1	130.5	5.0
NH_4	mg/l	0.00	4.10	0.45	0.1	49.0	6.2
Cl	mg/l	0.30	44.00	4.13	1.7	740.0	56.1
SO_4	mg/l	0.00	15.90	2.00	0.9	510.4	25.9
NO_3	mg/l	0.00	11.30	1.28	0.5	180.0	23.1
F	mg/l	0.00	0.23	0.02	0.00	0.9	0.1
DOC	mg/l	0.00	3.90	0.69	0.00	0.7	0.1
PO_4	mg/l	0.00	1.22	0.03	0.00	23.0	2.9
Si	mg/l	0.00	3.95	0.11	0.00	0.9	0.1
Al	µg/l	0	176.4	11.7	0.00	5891.6	162.1
B	µg/l	0	99.4	4.4	0.00	4930.0	116.3
Ba	µg/l	0	246.5	8.0	0.6	298.9	13.7
Be	µg/l	0	0.2	0.00	0.00	1.5	0.1
Br	µg/l	1.0	128.0	15.5	6.0	2300.0	176.5
Co	µg/l	0	4.1	0.1	0.00	15.7	0.5
Cr	µg/l	0	41.7	2.5	0.00	86.2	1.7
Cu	µg/l	0	30.0	2.0	0.2	427.4	12.9
Fe	µg/l	0	136.9	9.5	0.00	2332.0	109.9
I	µg/l	0.4	5.2	1.5	0.8	40.0	10.9
Li	µg/l	0	2.2	0.1	0.00	64.8	1.4
Mn	µg/l	0	27.6	1.9	0.00	1130.0	33.1
Ni	µg/l	0	18.6	0.8	0.00	234.7	5.4
Pb	µg/l	0	1206.6	28.5	0.3	3384.1	47.4
Sr	µg/l	0	19.0	2.2	1.0	2506.0	45.7
Y	µg/l	0	0.2	0.00	0.00	19.3	0.2
Zn	µg/l	0	185.6	13.6	2.2	7156	128.6
pH		3.4	7.0	4.9	2.7	6.9	4.6
Alk	µeq/l	-436.5	201.1	-18.6	-2089	734	-112.1

are large compared to rainfall and there is a similar subdivision between marine and pollutant components (Table 3.1; see also Wilkinson *et al.*, 1997). Concentrations of the non marine constituents generally decrease with increasing volume of catch, however, mist provides an important source of chemicals to the catchment alongside dry deposition. For example, cloud water provides about 40% of the sea salts and 35% of the total wet deposited sulphate for the forested catchments at Plynlimon. For the moorland areas these values are around 15% and 10%, respectively (Wilkinson *et al.*, 1997). Including cloud water, total wet deposition of trace metals to both moorland and forested areas of Plynlimon (Wilkinson *et al.*, 1997) are low compared with many areas of the UK.

3.1.2 Chemical variations in streams draining undisturbed forest

Not only do the Plynlimon catchments experience very variable rainfall chemistry, but the streams also exhibit a "flashy" flow response to rainfall inputs. Therefore, one might expect large variations in stream water concentrations that mirror the rainfall signal. This is not usually the case even for components such as chloride and ^{18}O, which are essentially chemically inert (Sklash and Farvolden 1979; Rodhe 1981; Bonnell *et al.*, 1990; Neal and Rosier, 1990; Neal *et al.*, 1992b; Durand *et al.*, 1993; Neal, M. *et al.*, 1996). This shows that the catchments have the ability to damp out the rainfall's variable chemical imprint to a very considerable degree. In other words, rainfall does not usually pass directly through the catchment to provide the major volume of water in the stream during the hydrograph response. However, this feature is partly overcome under two circumstances. Firstly, during very large storm events, the rainfall signal sometimes influences the stream response and affects the response for the next few events. This has been shown by (1) studies of continuous conductivity measurements in Plynlimon rainfall and Afon Hafren stream water (Robson, 1993) and (2) by major, relatively short lived sea-salt deposition episodes at Plynlimon which produce a large stream response followed by an exponential decline to concentrations approaching the mean value. Secondly, where there are longer term, more systematic changes in atmospheric inputs, the rainfall signal can be broadly observed in the stream. For example, the effects of rainfall patterns are very marked for marine derived elements such as chloride. With regards to zinc, the patterns follow that for sulphate. In this case, the primary zinc flux to the catchment comes from wet deposition while for sulphur, the major atmospheric source comes from mist and dry deposition. For zinc, total and non marine sulphate, the stream water variations are the inverse of that for chloride (Robson and Neal, 1996). These features strongly indicate that mist and dry deposition of sulphur vary with weather conditions: high when the air masses come from the land and low during periods when weather systems are predominantly frontal and laden with sea salts. Chromium concentrations exhibit stream variations which parallel the rainfall concentration patterns (Neal *et al.*, 1996). In this case, consistent rainfall-stream water patterns occur only during the 1980s. During the 1990s, high rainfall chromium concentrations are not matched by high stream water concentrations. The high rainfall concentrations during this later period correspond to low rainfall volumes and no correlation would be expected.

In spite of the generally weak relationship between rainfall quality and stream chemistry, large fluctuations in many chemical species occur in the stream. These variations correspond to changes in hydrology and season.

In general, baseflow waters have relatively high calcium, silicon and alkalinity levels and stormflow waters have relatively high aluminium, some trace metals (yttrium, manganese, cobalt, nickel, beryllium) and hydrogen ion concentrations (Table 3.2). The major changes in concentration occur at relatively low flows: at intermediate to high flows, concentrations remain either constant or decline as flow increases. This difference reflects the large chemical gradients within the catchment. The soil zones, being organic and aluminium oxide/hydroxide rich, produce acidic soil water rich in aluminium and transition metals. The bedrock, consisting of weatherable and acid-soluble inorganic components such as calcite and layer lattice silicates (chlorite and illite), has the capacity to neutralize these acid waters and precipitate the easily hydrolysable transition metals and aluminium. Such reacted water degasses carbon dioxide on its passage to the stream and produces the characteristic low acidity, calcium and silica rich but aluminium and transition metal depleted base flow chemistry. During storm events, when the catchment soils have wetted up and groundwater tables are high, more of the water entering the stream is derived from the soil zone. With intense and long duration storms, more of the stormflow water is derived from the upper and most acidic soil layers and this change accounts for declining concentrations of beryllium and aluminium at very high flow values. Under baseflow conditions, water drains mainly from near the stream bank and from the groundwater areas. Variations in the bedrock composition lead to differences in the stream water chemistries of the Afon Hafren and Afon Hore (Reynolds *et al.*, 1986). The presence of calcite and lead/zinc sulphides in the Hore catchment leads to high calcium concentrations and measurable lead and zinc concentrations in the stream (a factor of four or more difference between the two streams: the Tanllwyth chemistry is similar to that for the Hafren). Other differences in bedrock composition lead to contrasting behaviours for strontium and magnesium between the Hore and the other two catchments. Concentrations of lead and zinc in the Afon Hore are lowest under baseflow conditions. This is particularly surprising as these components come from vein minerals within the bedrock. This suggests that either there is mine waste associated with the soil zone or that these elements are being cycled and mobilised within the soil.

Manganese and cobalt are two constituents whose concentrations rise with flow and the amount of these constituents reaching the stream is purely determined by wetting and drying of the chemically reduced gley layers within the soil and the transition from immobile to mobile forms. The concentrations of manganese and cobalt rise sharply at low to intermediate flows and then plateau and may decline at even higher flows. This pattern may again result from physical aspects of the catchments; gleyed areas tend to lie at the stream margins in valley floor areas; these are zones of hydrological convergence and will tend to be the first areas to wet-up. Once wetted-up, the supply of new source areas for these species will be relatively small. Aluminium, however, is derived more generally from the soil system and its rise in concentration with flow is more gradual and continues up to high flows. With intense and long duration storms, at the very highest flows, there may be infiltration excess or saturation excess run-off resulting in a dilution of the soil derived constituents and the declining concentrations of aluminium and other species.

Chemical components associated with seasonal patterns include many of the nutrients (nitrate, potassium, boron, bromide and total-iodine) which are actively cycled between the soil and the trees. In the spring and summer, plant uptake reduces the amount of loss and the concentrations observed in the streams are lower. Boron, bromide, total-iodine and DOC also show seasonal variations and the changes occurring in the stream are associated with both organic matter breakdown and microbial uptake processes within the soil and perhaps longer term break-down of deep peats on the upper areas of the catchments. For phosphorus, very little cycling is observed

Table 3.2 **Baseflow and stormflow chemistries for the Afon Hafren, upper Afon Hore and Afon Hore (prior to felling).**

		Lower Hafren		Lower Hore		Upper Hore	
		Base	**Storm**	**Base**	**Storm**	**Base**	**Storm**
Na	mg/l	4.1	3.8	4.2	3.9	3.8	3.6
K	mg/l	0.1	0.2	0.2	0.3	0.1	0.1
Ca	mg/l	0.9	0.7	1.8	0.8	1.6	0.5
Mg	mg/l	0.8	0.7	0.9	0.7	0.7	0.6
SO$_4$	mg/l	4.1	4.5	4.9	4.5	3.7	3.8
Si	mg/l	1.7	1.0	1.6	0.9	1.4	0.8
DOC	mg/l	1.3	2.8	1.2	2.5	1.1	2.2
NO$_3$	mg/l	1.2	1.5	1.7	1.9	1.1	1.1
NH$_4$	mg/l	0.0	0.0	0.0	0.0	0.0	0.0
PO$_4$	mg/l	0.0	0.1	0.0	0.0	0.0	0.0
F	mg/l	0.0	0.1	0.1	0.1	0.1	0.1
Cl	mg/l	7.2	7.1	7.6	7.3	7.0	7.3
pH		5.4	4.5	5.9	4.6	6.0	4.5
Acid	μEq/l	126.5	217.6	129.5	172.6	134.7	200.3
Alk	μEq/l	0.2	-33.6	33.6	-23.1	37.0	-34.2
Cond	μS	41.9	49.5	47.9	48.3	41.9	48.8
Mn	μg/l	36.0	43.6	33.1	36.0	22.8	20.1
Fe	μg/l	76.4	127.1	65.1	106.6	77.0	87.1
Li	μg/l	2.0	1.8	2.1	1.9	1.8	1.5
Be	μg/l	0.1	0.1	0.1	0.1	0.1	0.1
B	μg/l	5.2	5.8	5.6	5.8	4.9	4.8
Al	μg/l	174.0	416.3	189.3	474.9	195.1	463.9
Cr	μg/l	2.6	2.5	2.6	1.8	4.3	4.4
Ni	μg/l	2.0	2.4	2.4	2.8	1.6	1.6
Co	μg/l	1.7	2.0	1.8	2.0	1.6	1.6
Cu	μg/l	1.7	3.3	2.0	3.2	1.9	2.8
Zn	μg/l	14.1	20.0	20.7	27.0	13.9	17.0
Sr	μg/l	5.3	4.8	5.8	4.5	4.8	3.7
Y	μg/l	0.3	0.4	0.2	0.4	0.2	0.3
Ba	μg/l	3.0	4.7	4.4	5.8	2.8	3.1
Pb	μg/l	1.6	1.7	4.1	8.7	5.4	12.1
Br	μg/l	21.6	24.5	23.4	25.0	21.0	22.1
I	μg/l	1.0	1.3	0.9	1.3	0.9	1.1

even though this represents an important possibly limiting nutrient within the upland environment. In this case, the low phosphorus inputs to the catchments coupled to the high bio- and fine sediment reactivity ensures minimal leaching to stream courses. For most determinands, any trends in response to long term changes in the rainfall signal are masked by the year to year variations in the quantity and quality of the rainfall. Nonetheless, time series data (Robson and Neal, 1996) indicate that there are clear trends in DOC, total-iodine, bromide and iron, which increase over time, presumably due to increased breakdown of organic materials within the catchment. This increase may be a more general feature of many acidic upland catchments as the longer term information being obtained within the United Kingdom Acid Waters Monitoring Network is beginning to reveal.

3.1.3 Chemical variations in streams draining disturbed forest

The results from the two components of the study of the effects of conifer harvesting and replanting on stream water quality at Plynlimon are described separately below. The data from the relatively large scale clearfelling for the Hore catchment are presented first, whilst the second component describes the effects of harvesting on runoff from the small hillslope subcatchments A4 and South2Hore. This second component examines the changes in drainage chemistry for what essentially represents a soil water component.

Hore / Upper Hore

Felling began in 1985 within the Hore catchment. Here, the lower half of the catchment was totally felled over a three year period. Originally it was planned that a direct comparison between the Hafren and the Hore would be made with the Hafren acting as a control site for the Hore harvesting programme. However, as discussed above, the higher rates of weathering due to mineralization of the bedrock in the Hore meant that the Hafren provided a poor control site and for this reason the control was changed to the upper portion of the Hore which (a) was partly forested, (b) was not subject to clearfelling and (c) had a similar chemistry to that of the lower Hore prior to felling. The major changes occurring are as follows.

The most marked changes in stream water chemistry associated with felling in the Hore catchment were increases in concentrations of nitrate and potassium (Figure 3.1). Such increases commonly last for 3 to 5 years after which concentrations return to background levels. In the Hore, the extended period of felling operations meant that the increased nutrient concentrations persisted for 8 years. Increased nutrient concentrations following tree felling result from a combination of processes. Firstly, the decomposition of brash and stumps releases potassium (and dissolved organic carbon) with either a decrease or an increase in nitrate depending upon circumstances. Secondly, there is a break in the nutrient cycle as there is no longer uptake by the trees; this leads to more potassium and nitrogen being available for leaching. Thirdly, there is increased mineralization of organic matter leading to the soil water being supplied with additional dissolved organic carbon and organic nitrogen. Nitrate supplies also increase due to the nitrification of ammonium, and the breakdown of the brash is not sufficiently rapid to remove nitrate by fungal and microbial processes. The presence of brash on the catchment also limits development of vegetation which would take up nutrients. A further less obvious change is in the timing of the peak nutrient concentrations. Prior to felling, nitrate and potassium concentrations peaked in mid to late winter and after felling in early to mid-winter (a phase shift of 1 to 2

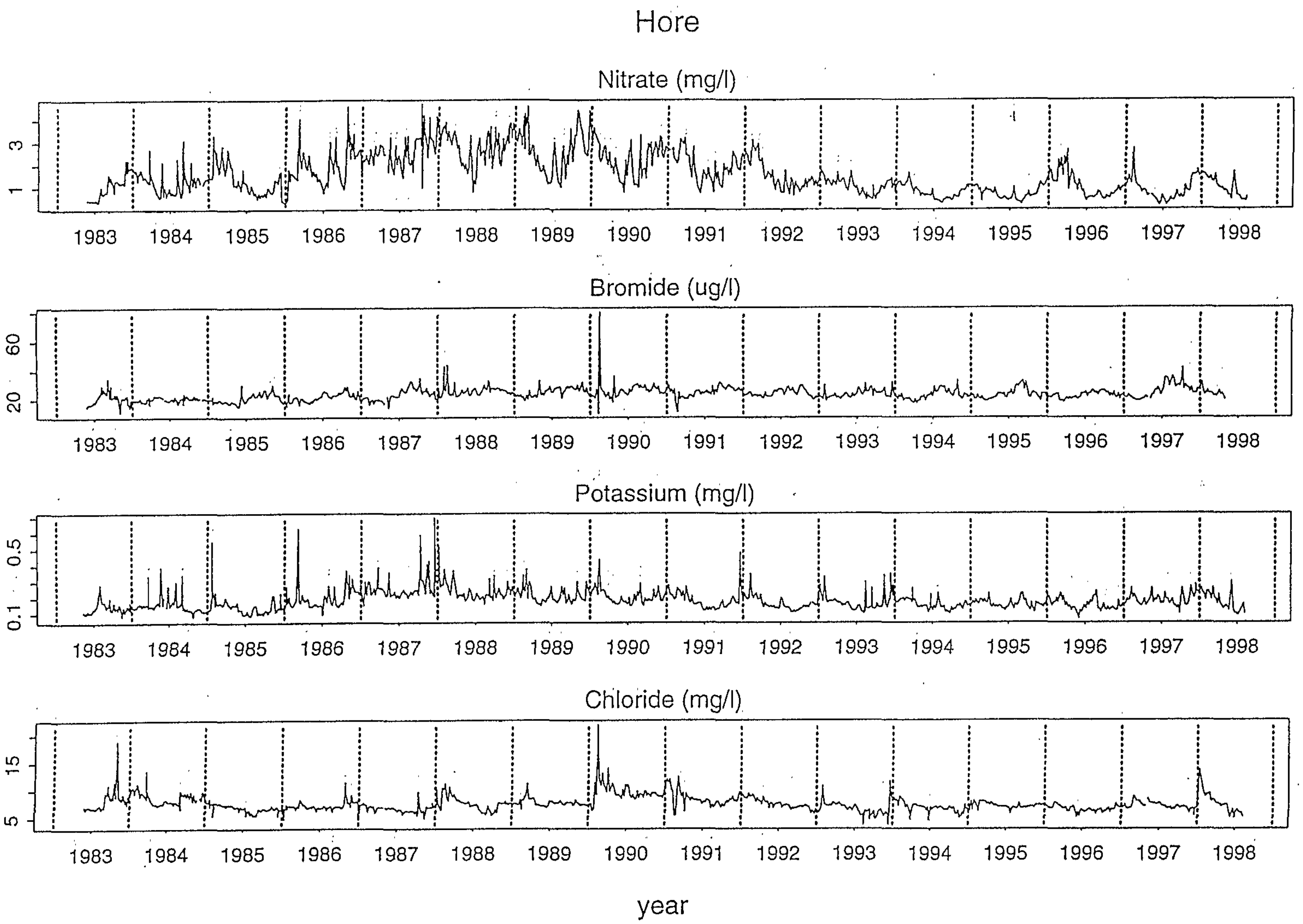


Figure 3.1 **Afon Hore time series for nitrate, bromide, potassium and chloride concentrations.**

months). This was not the case for bromide whose concentrations peak in late summer to autumn; the elevated concentrations are more likely to result from the rewetting of the upper soil layers resulting in enhanced organic matter breakdown (Hughes *et al.*, 1996).

Other changes in chemistry are more subtle and may be summarized as:

> *A reduction of solute capture from mist and dry deposition.* The concentration of solutes whose major source is deposition undergo a fall in concentration following felling. Chloride concentrations prior to felling were greater in the lower forested part of the catchment compared to the partly moorland covered upper Hore. After felling, the chloride concentration in the Hore dropped to that in the upper Hore, eventually (after 8 years) falling below that of the upper Hore. The absence of the rough forest canopy reduces capture of chemicals from mist and dry deposition compared to the control stream (see Wilkinson *et al.*, 1997): a reduction of around 25% for both sea-salts and pollutants. This part of the catchment also lies at a lower altitude further reducing the potential to capture mist and dry deposition. The time delay between felling of the catchment and the reduction of chloride concentrations below those in the upper Hore is probably due to long-term storage in the catchment and the time taken for the system to equilibrate to the reduced input of chloride.
>
> *Dissolved organic carbon concentrations increased slightly with felling.* The general disturbance of the land leads to greater solution of organic components; hydrological conditions changed so that more water is supplied from the organic-laden upper soil layers. The micro climate changed with felling, with the loss of tree shade increasing soil temperature (up to 3°C higher in summer) and thus increasing the rate of organic matter decomposition (Hughes *et al.*, 1990). This change has persisted throughout the period of record following felling. Detailed time series analysis based on smoothed data for upstream and downstream of the felling revealed an increase from 1.0 to 1.3 mg-C/l with 100% of the forest felled (Neal *et al.*, 1992a) although data scatter was high.
>
> *Transient acidification and enhanced aluminium leaching.* The amplitude of the seasonal cycles of aluminium in the Hore was enhanced for the first 2 years following harvesting; the main increases occurred during the winter period when aluminium concentrations were at their highest (from about 250 to 350 μg/l with 100% forest coverage: Neal *et al.*, 1992a,b). This indicated that the release of aluminium from the soils was due to increased nitrate concentrations displacing aluminium from exchangeable cation sites and leaching hydrous phases in the soil. The increase in aluminium, like nitrate, was only transient; concentrations have now fallen below those from the upper part of the catchment and this may again reflect the reduced capture of acidic deposition. There was also a reduction in the concentration of calcium and alkalinity in the Hore for the first few years after felling Neal *et al.*, 1992a,b). This recovered briefly then declined again, merging with the concentration in the upper Hore towards the end of the period of record. There are a number of factors that may explain why the aluminium concentration was only briefly elevated. Firstly, the reduction of base cation capture from the atmosphere, combined with the nitrate release, has a doubly acidifying effect. From 1991 onwards, the aluminium concentration in the Hore decreased to below that in the upper Hore, calcium concentrations were higher in the Hore during this period and nitrate concentrations began to fall towards those in the upper Hore. Thus, the acidifying phase of felling was complete

by 1991. The continuation of lower calcium concentrations in the Hore may reflect a reduction in calcium inputs from dry and mist deposition as well as a reduction in acidic inputs and a concomitant reduction in weathering. The details of these changes are discussed in much more detail later in the report. With regards to pH, the main changes with felling are observed under baseflow conditions, where pH reduces by about 0.5 of a unit: this change persists for about two years post felling.

There are few clear effects of felling on the trace metals. The clearest pattern of change is for manganese which peaks for about a three month period probably after the time when harvesting equipment directly disturbed stream bank/stream-bottom sediment.

Subcatchments A4 and B2

Prior to felling, the streamwater chemistry of subcatchments A4 and B2 was broadly similar although some differences were apparent. For example, stream water in A4 had a higher pH than B2 and contained more nitrate, sodium, chloride and magnesium. Larger Al(inorg) concentrations were observed in stream B2. For both subcatchments phosphate and ammonium were below detection limit in the stream water samples.

Clearfelling of catchment A4 resulted in an immediate increase in streamwater potassium and nitrate concentrations. The former reached a maximum of 1.8 mg/l 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 14.2 mg-NO_3/l 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.*, 1994) or to the effects of dry summers in 1989 and 1990 (Reynolds *et al.*, 1992). Apart from these clear changes, other felling responses are confounded by climatic and hydrological variability.

South2Hore

The South2Hore stream has run-off characterised by acidic and aluminium-bearing waters with a variable major, minor and trace element chemistry (Table 3.3) which is similar to the main Hore under high flow conditions. This is anticipated as the first order streams are expected to primarily drain the soil zones which supply the principal water source to the main channel under high flow conditions. Clear felling in autumn 1989 led, in the following June-July, to an increase in nitrate concentration to about 4 mg-NO_3/l from a background of 1 mg-NO_3/l (Figure 3.2). This increase continued through the winter months and declined to about 2 mg-NO_3/l the following spring and then increased during the following summer and autumn to peak values of about 8 mg-NO_3/l with further declines thereafter. Within the first two years of felling, concentrations of K, H^+, the major elements and Al also increased while alkalinity declined. After these two years postfelling, the water quality reverted to pre-felling values and then changed further: the major anions and cations as well as aluminium and many of the trace elements have lower concentrations than pre felling levels four or more years post felling while there are corresponding increases in pH, alkalinity and ANC. These results fit well with the findings for the Hore in that clearfelling leads to disruption of the biogeochemical functioning of the catchment (releasing nitrate and potassium and acidifying the soil water). However, for nitrate and potassium the magnitude of the changes

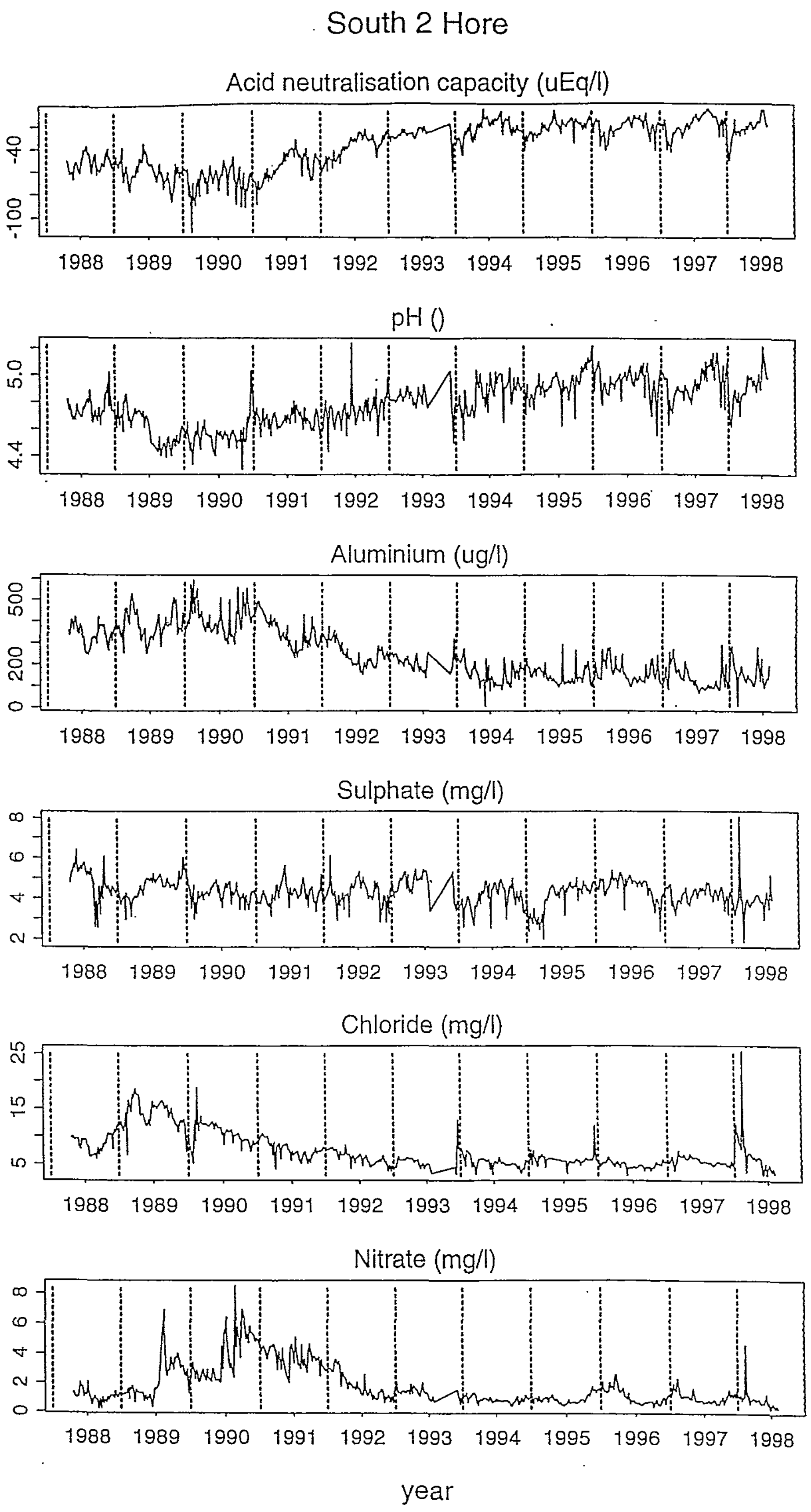


Figure 3.2 **Time series for ANC, pH, aluminium, sulphate, chloride and nitrate for the South2Hore site.**

observed are higher for South2Hore than the Hore since the South2Hore catchment (a) was initially totally forested then totally clearfelled over a month (as opposed to 50% of the Hore over three years) and (b) is predominantly supplied by water from the soil zone where harvesting effects are maximal. The longer term improvement in water quality following felling observed in the South2Hore stream is not clearly reflected within the main Hore. This difference occurred due to the longer felling period, the reduced area felled and the greater fluctuation in stream water quality within the main river owing to the mixing of soil and groundwaters. The major element changes for South2Hore 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 aluminium, dissolved organic carbon, bromide and total-iodine are less than would be anticipated based on results for the main Hore drainage area.

Table 3.3a The major element chemistry for the south2Hore catchment. Three sets of values are presented to describe the felling effects at this site: (1) pre felling and pre nitrate pulse (May 1988 to August 1989), (2) nitrate pulse (September 1989 to August 1992) and (3) post nitrate pulse (September 1992 to May 1998). The units are in mg/l (as the element in all cases except mg-NH_4/l, mg-NO_3/l, mg-SO_4/l, mg-PO_4/l, pH which is dimensionless and Alkalinity and ANC which have units of μEq/l).

	Pre NO_3 pulse Avg	**Pre NO_3 pulse min**	**Pre NO_3 pulse max**	**NO_3 pulse Avg**	**NO_3 pulse min**	**NO_3 pulse max**	**Post NO_3 pulse Avg**	**Post NO_3 pulse min**	**Post NO_3 pulse max**
Na	**4.55**	3.44	5.21	**5.01**	2.51	8.30	**3.41**	2.06	16.57
K	**0.22**	0.17	0.28	**0.49**	0.17	1.16	**0.29**	0.10	0.96
Ca	**0.75**	0.37	0.98	**0.67**	0.16	1.22	**0.59**	0.21	0.88
Mg	**0.86**	0.57	1.03	**0.84**	0.41	1.28	**0.67**	0.24	1.86
NH_4	**0.02**	0.00	0.06	**0.02**	0.00	0.26	**0.02**	0.00	1.72
Cl	**8.29**	6.00	9.90	**9.77**	4.10	18.80	**5.50**	2.90	25.50
NO_3	**1.15**	0.25	2.10	**2.84**	0.25	8.50	**1.02**	0.35	4.60
SO_4	**5.24**	2.59	6.39	**4.30**	2.56	6.12	**4.21**	1.85	8.07
PO_4	**0.00**	0.00	0.00	**0.00**	0.00	0.29	**0.00**	0.00	0.04
Si	**1.40**	0.85	1.70	**1.27**	0.00	1.80	**1.18**	0.00	1.90
DOC	**0.89**	0.50	1.70	**1.59**	0.30	5.60	**1.76**	0.50	6.90
pH	**4.75**	4.65	4.89	**4.64**	4.30	5.24	**4.90**	4.50	5.21
Alk	**-18.81**	-31.90	-12.59	**-24.61**	-52.16	-10.50	**-12.83**	-35.58	-3.84
ANC	**-52.23**	-66.78	-36.93	**-57.32**	-111.13	-23.22	**-22.98**	-60.21	-5.47

Table 3.3b The trace element chemistry for the south2Hore catchment. Three sets of values are presented to describe the felling effects at this site: (1) pre felling and pre nitrate pulse (May 1988 to August 1989), (2) nitrate pulse (September 1989 to August 1992) and (3) post nitrate pulse (September 1992 to May 1998). The units are in µg/l (as the element).

	Pre NO_3 pulse Avg	Pre NO_3 pulse min	Pre NO_3 pulse max	NO_3 pulse Avg	NO_3 pulse min	NO_3 pulse max	Post NO_3 pulse Avg	Post NO_3 pulse min	Post NO_3 pulse max
Al	336.75	248.00	420.00	358.62	155.00	595.50	162.72	6.66	318.99
B	8.68	4.10	67.30	6.55	2.50	24.00	5.00	1.52	45.97
Ba	9.34	4.41	22.27	6.10	1.06	11.59	3.85	2.00	12.00
Be	0.07	0.04	0.13	0.05	0.01	0.11	0.06	0.00	1.14
Br	24.50	19.00	29.00	29.73	16.00	45.00	27.13	14.00	66.00
Cd	0.18	0.00	0.60	0.18	0.00	0.90	0.07	0.00	1.07
Ce	0.69	0.02	4.89	0.08	0.01	1.74	0.05	0.01	1.01
Co	1.73	0.46	2.54	1.76	0.35	3.53	0.75	0.09	1.38
Cr	2.05	0.58	4.90	1.43	0.20	9.88	0.17	0.01	1.07
Cs	0.02	0.00	0.03	0.04	0.01	0.30	0.04	0.00	1.38
Cu	2.33	0.54	9.31	1.57	0.73	12.54	1.91	0.36	66.64
F	0.05	0.03	0.06	0.04	0.00	0.11	0.02	0.00	0.06
Fe	46.82	24.00	141.80	47.77	22.40	153.00	68.45	15.80	861.70
I	0.87	0.70	1.20	1.16	0.70	2.60	1.41	0.70	6.40
La	0.05	0.01	0.30	0.03	0.00	0.12	0.02	0.00	1.05
Li	1.78	0.62	2.47	2.19	0.85	5.26	1.46	0.25	2.36
Mn	93.48	32.75	128.95	86.89	22.25	153.00	61.99	5.70	94.00
Mo	0.25	0.00	1.00	0.35	0.00	2.00	0.02	0.00	1.00
Ni	1.86	0.55	2.54	2.10	0.80	7.26	1.43	0.79	5.09
Pb	0.73	0.21	1.39	1.12	0.25	6.43	2.63	0.14	291.08
Pr	0.01	0.00	0.03	0.01	0.00	0.03	0.01	0.00	1.09
Rb	0.41	0.08	0.54	0.84	0.21	3.56	0.47	0.19	1.54
Sb	0.21	0.03	0.48	0.07	0.04	0.24	0.15	0.00	1.74
Sc	0.07	0.00	0.16	0.04	0.00	0.16	0.46	0.01	1.05
Sr	4.33	1.26	5.15	4.88	1.69	8.34	3.35	1.04	36.99
Th	0.01	0.00	0.04	0.02	0.00	0.09	0.04	0.00	0.61
U	0.01	0.00	0.02	0.01	0.00	0.03	0.00	0.00	1.08
Y	0.07	0.03	0.10	0.08	0.04	0.36	0.08	0.01	1.04
Zn	15.09	5.03	32.52	11.10	5.75	27.02	15.16	1.06	132.54

Nant Tanllwyth

The Nant Tanllwyth provides the most acidic of the main Hafren and Hore tributaries. For example the average pH and ANC is 5.3 and -27.4 μEq/l respectively while the corresponding ranges are 4.1 to 6.9 and -151 to +225 μEq/l. In 1997, the introduction of a borehole near the stream resulted in an influx of calcium bearing water which changed the chemical nature of the stream. Subsequently, monitoring was undertaken upstream and downstream of the borehole to record the water quality differences.

With regards to felling, the water quality has shown only small changes involving increases in potassium (from about 2 to about 3 mg/l), rubidium (from about 0.3 to about 0.4 μg/l) nitrate (from about 2 to about 2.5 mg-NO_3/l) and phosphate (from less than detection levels to about 0.05 mg-PO_4/l) and for all these determinands a higher range of values is observed post felling (Figure 3.3). The only other noticeable changes are for (a) chloride which shows a marked decline from January to July 1998 (from 16 to 5 mg/l) and (b) ANC which has much fewer positive values in 1998.

3.1.4 Input-output budgets

In order to compute input-output budgets, a simplified scheme has been developed following the more detailed work of Durand *et al.* (1994) for the Plynlimon catchments. To do so, the long term flow weighted chemical data for rainfall, cloud-water and stream water have been compared, based on an average cloud-water input of chloride of 20% of the rainfall figure (Table 3.4; cf Durand *et al.*, 1994). From this, the percentage retention of the atmospheric input or net gain from the catchment has been determined for the streams based on the assumption that there is a net chloride input-output balance (Table 3.4).

Six broad groups of chemical determinands can be distinguished:

1. Determinands which are strongly retained by the catchment: ammonium, total-iodine and lead. For these determinands, ammonium acts as a fertilizer to the vegetation and is easily converted to nitrogen in higher oxidation states such as nitrate (Miegroet and Johnson, 1993). Iodine is easily assimilated into organic matter both by inorganic and organic processes (Neal, 1990a,c). Lead is unusual in that, as discussed earlier, it has only entered the catchment in significant concentrations in recent years. It is not clear what the form of this lead is, but lead is rapidly adsorbed by vegetation and organic rich soils (Salmons and Forstner, 1984). The net uptake of lead is much higher for the Hafren compared to the Hore and this is because of the within catchment supplies in the Hore from the bedrock mineralization, as already noted.

2. Determinands which are partially retained by the catchment: phosphate, boron, barium, bromide and nitrate. Apart from barium, these determinands are nutrients and some retention by the catchments would be expected as with the first case (Lindsay, 1972; Price *et al.*, 1972). In the case of nitrate, there is a net release from the Hore catchment and this reflects the effects of felling as discussed earlier. The pattern for barium is unexpected and it seems that the properties of this element differ from the other divalent base cations.

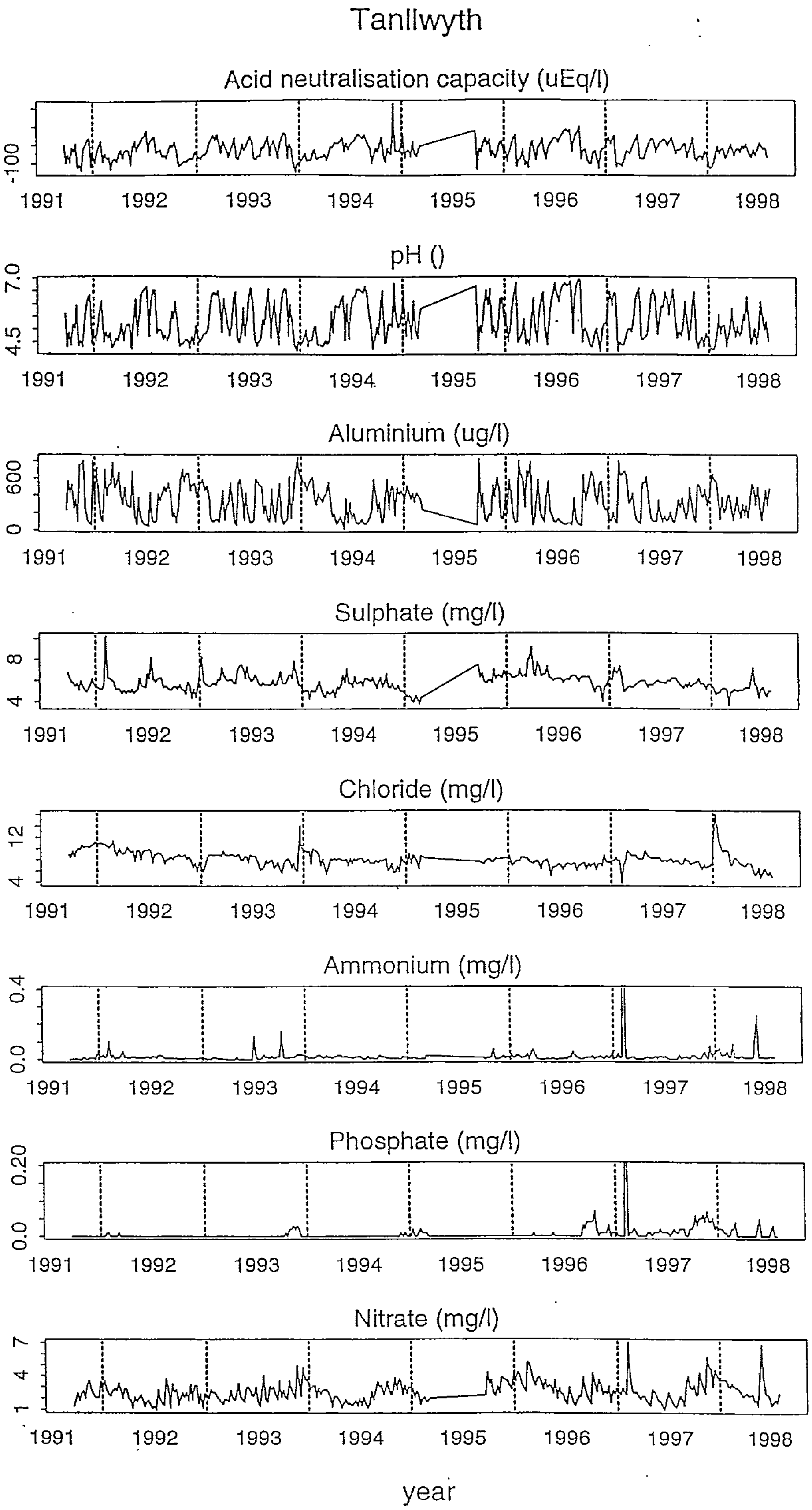


Figure 3.3 ANC, pH, aluminium, sulphate, chloride, ammonium, soluble reactive phosphate and nitrate time series for the Tanllwyth upstream of the borehole.

Table 3.4 Input-output data and catchment water quality percentage balances for the Lower Hafren and Upper and Lower Hore.

	Rain	Cloud	Input	Lower Hafren	Upper Hore	Lower Hore	Lower Hafren	Upper Hore	Lower Hore
	Major elements mg/l						Percentage balance		
Na	2.30	26.69	2.92	3.84	3.99	4.10	3	-2	-3
K	0.12	1.11	0.14	0.19	0.12	0.30	3	-67	30
Ca	0.19	1.86	0.24	0.72	0.92	1.12	58	64	70
Mg	0.28	3.15	0.35	0.69	0.63	0.81	35	22	38
NH_4	0.29	3.39	0.37	0.01	0.01	0.02	-3103	-5468	-2084
Cl	4.33	45.88	5.39	6.91	7.52	7.76	0	0	0
SO_4	1.57	14.20	1.90	4.21	3.94	4.70	42	33	42
NO_3	0.77	11.41	1.04	1.32	0.98	2.69	-1	-48	45
PO_4	0.02	0.04	0.02	0.03	0.01	0.02	-5	-96	-44
F	0.02	0.04	0.02	0.05	0.05	0.06	51	48	54
DOC	0.48	1.72	0.52	2.26	1.89	1.65	71	62	55
Si	0.10	0.07	0.10	1.20	0.98	1.13	89	86	87
	Trace elements µg/l						Percentage balance		
Al	6.2	45.2	7.3	311.0	336.0	428.0	97	97	98
B	3.2	80.1	5.0	5.2	4.6	5.3	-23	-51	-35
Ba	4.9	5.3	5.0	4.5	4.1	6.4	-44	-70	-14
Be	0	0	0	0.1	0.1	0.1	85	85	89
Br	16.4	142.6	19.7	23.4	21.5	24.3	-8	-28	-17
Co	0.00	0.20	0.00	1.9	1.6	2.4	97	96	97
Cr	1.6	0.5	1.7	2.5	2.0	3.7	14	-19	36
Cu	1.5	5.2	1.6	2.8	2.6	2.9	26	14	21
Fe	5.8	39.1	6.7	110.0	88.2	88.2	92	89	89
I	1.2	8.6	1.4	1.2	1.0	1.0	-43	-82	-88
Li	0.1	0.6	0.1	2.0	1.8	2.2	94	93	94
Mn	1.1	9.5	1.3	40.2	20.3	39.7	96	91	95
Ni	0.5	2.1	0.5	2.2	1.8	2.8	71	61	74
Pb	13.7	12.6	14.0	1.5	10.8	7.7	-1073	-81	-162
Sr	2.0	21.4	2.5	4.9	4.2	5.4	35	16	33
Y	0	0.1	0	0.4	0.3	0.3	96	95	95
Zn	8.6	57.8	9.9	17.6	16.0	25.2	28	13	43
Alk_{Gran}	-12.7	-45.5	-13.7	-21.0	-7.8	-10.3	16	-145	-91

3. Determinands showing a net input-output balance: chloride (by definition), sodium and possibly chromium. Sodium and chloride are, chemically, relatively unreactive in the catchment and a long term net input-output balance would be expected. For chromium, the situation is more complex as it occurs in two oxidation states, one having low chemical reactivity (CrVI in the form of chromate) and the other (CrIII) which is adsorbed by the soil. A detailed discussion of this element is given in Neal *et al.* (1996) and it seems that throughout the 1980s the main input has been as CrVI and for the last few years CrIII has predominated and has co-varied with lead pollution in rainfall.

4. Determinands showing a net output which is modest and up to 70% of the input: calcium, magnesium, sulphate, fluoride, DOC, copper, strontium and zinc. For these determinands, there are relatively important atmospheric and within catchment sources and sinks. For example, magnesium, calcium and strontium have maritime sources and they are derived from major base cation weathering sources as both carbonates and silicate minerals within the bedrock (Neal *et al.,* 1997a,f,g). For DOC, the main catchment sources are from breakdown of organic matter and the generation of humic and fulvic acids. In the case of sulphate, the input-output balance is more complex to determine as there are significant gaseous inputs to the catchment from acidic oxides (SO_x). Indeed, there may well be a net balance if the gaseous term is included (cf Durand *et al.,* 1994; Reynolds *et al.,* 1997a; Wilkinson *et al.,* 1997).

5. Determinands showing a major net output (>70%): aluminium, silicon, beryllium, cobalt, iron, lithium, manganese, nickel and yttrium. These determinands represent two distinct hydrochemical groupings. First, silicon and lithium are derived from the weathering of the bedrock. Second, the remaining determinands are metals which exist as highly charged or complexed species in solution and which are easily hydrolysed in the environment. These metals occur predominantly within the hydrous-oxides and oxides within the soil and they are mobilized under acidic conditions (Salmons and Forstner, 1984).

6. Determinands showing a variable response: potassium and alkalinity. Potassium is a major plant nutrient and exists as a weatherable source within micaceous minerals in the soil and bedrock and enters the catchment from atmospheric deposition. For the Hafren there seems to be a net balance between biological uptake and weathering release, while for the upper Hore the biological uptake predominates. For the lower Hore there is a net release, but this would be anticipated given the disruption of the biological cycle with felling. For alkalinity, there is a high net production by the catchment for the upper and lower stretches of the Hore and this is characteristic of the effects of the higher bedrock weathering rates for this catchment. For the Hafren, where easily weatherable minerals are less abundant, there is a much closer balance between input and output although it must be borne in mind that no allowance has been made for the acidity within the input associated with gaseous acidic oxides which would increase the estimate of net alkalinity production.

3.1.5 Summary

Despite the apparent distance from industrial areas, the Plynlimon catchments experience atmospheric pollution by both acidic oxides and heavy metals. The extent of this pollution varies according to air mass trajectories and the patterns of change seem to be cyclical in nature. Load calculations based on bulk deposition at Plynlimon show no reduction in the deposition of acidic pollutants despite reduced industrial production and greater emission controls over the last 20 years. In the case of metals such as chromium and lead, unexpected atmospheric pollution episodes were observed. In the case of chromium, concentrations were highest in the mid 1980s and this timing does not tally with the other industrial pollutants and the source of this pollution remains unknown. For lead, the increases in concentration of the last few years may well prove to be associated with increased car rallying on adjacent land (Wilkinson and Jenkins, 1996) and possibly increased forest-vehicle activity in the area.

In the streams, the patterns of water quality variation match three dominant hydrobiogeochemical controls as well as a composite pattern.

1. Weathering and inorganic leaching. The components which fit into this group have the largest catchment supplies (as indicated by the input-output balances) and they show the greatest variations with flow. The components divide into two groups (1a and 1b). Firstly, there are several base cations (Ca, Sr, Li), silica and bicarbonate (as represented by high alkalinities) which have highest concentrations under baseflow conditions (group 1a). These components are derived from reactions occurring within the bedrock and groundwater zones. Secondly, there are several transition metals (Co, Fe, Mn, Ni) and beryllium, aluminium and yttrium which have their highest concentrations at intermediate to peak flows (group 1b). This second group comprise elements which are readily hydrolysable, are mobilized under acidic conditions and precipitate under more basic conditions. They are essentially derived from the breakdown of oxides and hydroxides within the acidic soil zones and in some cases the leaching rate and stability in solution may be augmented by complexation with fluorides, hydroxyl ions and organic acids. In terms of the input-output relationships, the second group show the highest percentage catchment sources due to the increased flux contribution at high flows.

2. Biological mediation. The components which fit into this group are the nutrients (ammonium, nitrate, phosphate and boron) the halides (bromide and total-iodine). With the exceptions of phosphate and ammonium, all of these components show a strong seasonality and accumulate-in or leak-from the catchment. There is no significant ammonium supply within the bedrock and only small supplies of phosphorus and it seems that virtually all these components are retained within the biomass, or, in the case of ammonium, are converted to other forms of nitrogen.

3. Physical controls. This group comprises the components which have a predominantly atmospheric source and little within catchment reactivity. The main elements in this group are the marine components sodium and chloride. However, chromium (for the 1980s) and sulphate are members of this group even though they have a predominantly pollutant signal. For this group, there is little

relationship between concentration and flow and a net input-output balance is observed (except for sulphate where an additional gaseous input has not been allowed for).

4. Composite controls. This group consists of zinc and lead where there are significant atmospheric inputs which are partially retained (for zinc) or almost completely retained (for lead) by the catchment. But, at the same time, they are also generated within the catchment to augment stream water concentrations. For both of these transition metals, stream water concentrations are highest under storm flow. This would be expected as their hydrochemical properties are similar to the group 1b elements described above.

With forest felling, the disruption of the biological system has increased the supply of nutrients to the stream and sometimes led to a transient increase in aluminium concentrations. These results are good news for forestry management in terms of upland water quality in that the effects of even a major clear-felling programme are not long lived and, apparently no major environmental problems are caused.

3.2 Beddgelert Forest

At Beddgelert, the chemistry of the three streams before felling was broadly similar, although sodium and chloride concentrations were higher in stream D2 (1982 and 1983 in Tables 3.5 and 3.6). Stream D3 had higher calcium concentrations and lower total aluminium and nitrate concentrations. In all subcatchments, phosphate and ammonium were at or below detection limit in the stream water samples (< 0.05 mg-NH_4/l & <0.005 mg-P/l respectively).

Stream water concentration data displayed wide seasonal variations, short term storm event variability and fluctuations in response to changing atmospheric inputs. These variations obscure the effects of felling, especially as only parts of the catchments of D2 and D4 were felled. The most dramatic effect of felling on stream water chemistry was an increase in potassium concentration although at no point did this exceed 1.7 mg/l. 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, potassium concentrations were significantly higher in D2 and D4. The effect was greater in D2, but 62% of this catchment was felled compared with 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 have remained lower up to 1996 (12 years after felling). An increase in potassium concentrations in D2 from 1996 onwards may indicate renewed felling activity in the top part of the catchment.

Stream water nitrate concentrations responded more slowly than potassium, reaching a peak in the felled streams about two years after felling. At no point did nitrate concentrations exceed 10.6 mg-NO_3/l and were normally well below 6.6 mg-NO_3/l. The relative amounts of nitrate generated in the felled catchments during the first three years corresponded to the proportion of each catchment that was felled, with more nitrate in D2 (62% fell) compared with D4 (28% fell) even though the absolute area felled in D2 (0.87 ha) was about half that felled in D4 (1.71 ha). By 1987 (3 years post-felling), nitrate in the streams draining the felled catchment had declined to values

Table 3.5 **Annual geometric mean pH and geometric mean concentrations (mg/l) of sodium, potassium, calcium, magnesium and aluminium 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	4.30	4.43	4.39	6.7	5.4	6.1	0.23	0.22	0.25
1983	4.55	4.62	4.64	7.6	6.3	6.8	0.22	0.20	0.24
1984	4.52	4.62	4.65	9.3	7.1	7.9	0.20	0.18	0.17
1985	4.56	4.59	4.69	4.9	4.7	5.3	0.41	0.28	0.15
1986	4.60	4.65	4.73	5.8	5.1	6.4	0.60	0.29	0.13
1987	4.66	4.70	4.77	4.5	4.3	5.1	0.36	0.18	0.16
1988	4.64	4.68	4.72	5.5	4.7	6.2	0.18	0.10	0.18
1989	4.68	4.75	4.76	6.1	5.3	7.0	0.13	0.12	0.15
1990	4.60	4.66	4.61	9.8	7.9	11.1	0.11	0.13	0.19
1991	4.66	4.62	4.60	8.0	6.9	8.7	0.09	0.11	0.25
1992	4.79	4.75	4.74	6.3	5.7	6.9	0.06	0.09	0.14
1993	4.78	4.85	4.77	5.7	5.3	6.6	0.04	0.07	0.14
1994	4.90	4.78	4.77	5.0	4.8	5.7	0.03	0.06	0.15
1995	4.80	4.75	4.72	6.0	5.5	7.1	0.06	0.10	0.17
1996	4.82	4.77	4.72	5.6	5.5	6.4	0.20	0.12	0.16
1997	4.76	4.68	4.69	5.9	5.8	6.9	0.22	0.09	0.15
1998	4.76	4.72	4.67	6.7	6.1	7.4	0.15	0.09	0.16
	Ca			Mg			Al		
	D2	D4	D3	D2	D4	D3	D2	D4	D3
1982	1.13	1.37	2.17	0.88	0.80	0.95	0.73	0.40	0.37
1983	1.12	1.48	2.15	0.92	0.86	0.96	0.45	0.49	0.38
1984	1.44	1.70	2.54	1.18	0.99	1.14	0.77	0.47	0.46
1985	1.00	1.22	1.82	0.82	0.79	0.85	1.05	0.85	0.75
1986	0.94	1.15	1.78	0.84	0.77	0.91	1.16	0.83	0.75
1987	0.85	1.06	1.66	0.67	0.65	0.79	0.78	0.74	0.61
1988	0.89	1.09	1.80	0.74	0.69	0.88	0.72	0.64	0.66
1989	1.13	1.43	2.09	0.73	0.71	0.89	0.64	0.54	0.56
1990	1.17	1.36	2.21	0.86	0.77	1.26	0.59	0.56	0.62
1991	0.86	0.99	1.62	0.93	0.89	1.20	0.46	0.53	0.56
1992	0.86	1.17	1.74	0.84	0.86	1.05	0.43	0.47	0.53
1993	0.85	1.28	1.72	0.72	0.76	0.95	0.39	0.42	0.45
1994	0.71	0.79	1.42	0.64	0.68	0.85	0.32	0.42	0.42
1995	0.95	1.12	1.84	0.82	0.83	1.09	0.41	0.44	0.47
1996	0.95	1.27	1.92	0.81	0.84	1.05	0.36	0.41	0.45
1997	0.93	1.18	1.73	0.83	0.84	0.98	0.41	0.46	0.47
1998	0.94	1.07	1.68	0.98	0.89	1.09	0.49	0.56	0.55

Table 3.6 **Annual geometric mean concentrations (mg/l) of nitrate, sulphate, chloride, manganese, silicon and dissolved organic carbon (DOC) 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	NO$_3$-N			SO$_4$			Cl		
	D2	D4	D3	D2	D4	D3	D2	D4	D3
1982	0.33	0.62	0.68	8.40	6.66	7.47	15.00	9.94	11.09
1983	0.45	0.72	0.74	7.71	6.69	7.26	12.71	11.00	11.94
1984	0.68	0.83	0.80	7.20	6.36	8.22	17.39	13.37	14.82
1895	1.24	1.09	0.75	6.48	6.45	7.44	7.68	7.93	8.74
1986	0.94	0.70	0.61	5.94	6.33	7.02	10.01	9.72	11.18
1987	0.67	0.60	0.60	6.06	6.30	7.29	7.15	7.13	8.38
1988	0.29	0.48	0.55	5.37	5.61	6.72	10.63	9.21	11.83
1989	0.24	0.49	0.59	5.28	5.40	6.87	11.86	10.14	13.39
1990	0.17	0.53	0.84	5.10	5.43	6.87	20.17	16.56	22.15
1991	0.32	0.73	0.93	5.67	5.70	7.53	14.51	12.72	16.60
1992	0.21	0.52	0.73	5.76	6.00	7.26	11.68	10.77	13.36
1993	0.09	0.31	0.47	5.28	5.85	7.29	10.45	10.09	12.34
1994	0.04	0.26	0.57	5.04	5.88	6.84	8.50	8.39	9.96
1995	0.08	0.32	0.64	4.26	5.37	6.39	10.41	9.40	13.97
1996	0.31	0.43	0.66	4.92	5.76	7.14	10.00	10.24	12.03
1997	0.31	0.43	0.63	4.56	5.40	6.54	11.06	11.20	13.11
1998	0.40	0.69	0.83	4.20	5.10	6.12	13.27	11.65	14.13

Year	Mn			Si			DOC		
	D2	D4	D3	D2	D4	D3	D2	D4	D3
1982	--	--	--	1.10	0.86	0.92	--	--	--
1983	0.21	0.21	0.25	1.16	0.97	1.00	--	--	--
1984	--	--	--	1.08	1.04	1.07	0.93	0.46	0.61
1985	0.22	0.20	0.18	1.03	0.99	0.03	1.05	0.48	0.65
1986	0.22	0.20	0.19	0.94	0.92	1.00	1.12	0.70	0.77
1987	0.15	0.15	0.16	0.85	0.92	1.02	1.22	0.75	0.84
1988	0.16	0.15	0.18	0.77	0.86	0.98	1.12	0.67	0.78
1989	0.17	0.16	0.19	0.76	0.85	1.02	1.24	0.78	0.93
1990	0.20	0.18	0.26	0.73	1.04	1.00	1.44	1.01	1.16
1991	0.15	0.18	0.22	0.83	0.85	0.96	1.77	1.55	
1992	0.14	0.14	0.16	0.66	0.85	0.97	1.39	0.91	0.57
1993	0.12	0.10	0.15	0.89	0.93	1.04	0.85	0.63	0.71
1994	0.12	0.12	0.15	0.88	0.93	0.98	1.27	0.73	1.16
1995	0.13	0.11	0.18	0.93	0.96	1.01	1.40	1.21	1.29
1996	0.11	0.11	0.15	0.98	0.99	1.03	1.10	0.75	0.92
1997	0.12	0.12	0.16	0.97	0.94	1.00	1.38	0.87	1.20
1998	0.15	0.14	0.17	0.89	0.88	0.93	1.43	1.18	1.44

seen in the control, and were lower than control stream concentrations from 1989 onwards. Presumably this reflects uptake of nitrogen by the new, vigorously growing crop. In all streams, the dry summers in 1990 and 1995 caused elevated nitrate concentrations during the following two to three winters. From late 1997 onwards, there is an indication that nitrate concentrations in D4 are approaching those seen in the control catchment (D3).

The initial stream water responses for sodium, magnesium and chloride are complex possibly reflecting climatic influences of large seasalt inputs. However, the pronounced separation in the time series plots between control and felled catchments from 1990 onwards strongly suggests that felling has reduced sodium, magnesium and chloride concentrations to below what they would otherwise have been. In contrast to nitrate, the differences in sodium, magnesium and chloride do not reflect the proportion of catchment felled. Other factors, such as the location of the remaining standing forest and the amount of new forest edge have probably influenced the response. From 1986 onwards, stream water sulphate concentrations in the felled catchments declined steadily and they progressively separated from the control stream. Eight years after felling, in 1992, the time series for the two felled catchments split apart and then run in parallel from 1995 onwards. The progressive stream response to the removal of the forest and hence to a stepwise reduction in inputs suggests that there is some capacity within the catchments to buffer sulphate concentrations. This is consistent with desorption of sulphate stored in the mineral soil until a new equilibrium is reached with the reduced inputs (Reuss and Johnson 1986). There is no clear explanation for the differential response between the felled catchments after 1993.

Calcium at Beddgelert is derived predominantly from weathering, although there are significant atmospheric inputs. There has been no effect of felling on stream water calcium concentrations, although there is evidence that the dry summers of 1984, 1990 and 1995 had a pronounced effect on calcium trends.

During the first five to six years following felling (1984-1990), the large amount of variability in the data makes it difficult to discern trends in pH, aluminium and ANCcb which can be unequivocally related to felling. It is clear that concentrations of total aluminium in all three streams at Beddgelert increased from around 0.4 to 0.9 mg/l in 1982-83 (before felling) to 0.9 to 1.2 mg/l in 1986 (two years after felling in catchments D2 and D4). However from being the most consistently acid and aluminium-rich of the streams, after 1990 stream D2 becomes the least acidic with generally the highest pH and ANCcb but lowest aluminium concentration. This period coincides with some of the largest declines in sulphate and nitrate concentrations in D2. The pattern is less clear for stream D4 presumably because a smaller proportion of that catchment was felled.

Following the discovery of groundwater at each of the boreholes drilled at Plynlimon, investigations were undertaken further afield to ascertain whether the results at Plynlimon were in any way anomalous compared to other parts of Wales underlain by similar strata. Two boreholes were drilled at Beddgelert Forest in the autumn of 1994 and sampling commenced in November 1994. Chemical data from the boreholes contrast markedly with those from the streams. The waters are circumneutral, with high, positive alkalinities and contain little inorganic aluminium. With the exception of sodium in BG1, the borehole waters are enriched in base cations, silicon, chloride and sulphate compared to streams, but depleted in aluminium and manganese. The BG1 and BG2 boreholes are, respectively, approximately 18 and 8 times oversaturated with respect to atmospheric carbon dioxide. This means that on degassing the waters will have a degassed pH which averages about, respectively, 1.0 and 0.7 units higher than the undegassed pH. These waters are unlike any of the soil waters sampled at the site which have been consistently acidic and aluminium rich (see e.g. Stevens *et al.*, 1988; Neal *et al.,* 1990b).

3.3 Kershope Forest

Prior to felling the run-off chemistry from the four plots was remarkably similar. Nitrate in run-off from two of the felled plots increased immediately after felling relative to the control (Figure 3.4). At the third felled plot there was a years delay before nitrate concentrations rose, this was the least well drained site. Nitrate concentrations peaked in the second year after felling and then gradually returned to pre-felling values in the fourth year. Aluminium and pH in run-off from the felled plots were generally lower than from the control plot subsequent to felling. Sulphate, sodium and chloride concentrations fell immediately after felling and remained at the reduced levels throughout the rest of the study due to the loss of atmospheric scavenging. Potassium and phosphate rose gradually after felling peaking as nitrate, in the second year after felling. Concentrations of both solutes remained elevated through-out the remaining years of study. Phosphate at the third felled site, whose nitrate concentration rose slowly, was far higher than the other felled sites.

The observed increase in nitrate is similar to that seen in the studies at Plynlimon and Beddgelert. The rise in nitrate was attributed to increased mineralization and the elimination of root uptake. The modified temperature and moisture regime following felling, probably resulted in greater decomposition and hence mineralization in the organic soil layers (Adamson *et al.,* 1987; Adamson and Hornung, 1990). These authors also cite the results of Likens *et al.* (1978) who studied the effects of felling in the Hubbard Brook in eastern North America. Re-vegetation was prevented at this site for three growing seasons and it was concluded that the gradual reduction in nitrate levels was due to the exhaustion of readily available nutrients and substances for decomposition.

The pronounced seasonal cycles in potassium following felling may have resulted from the invasion of the plots by a perennial herb (*Chamaenerion augustifolium*). Autumn leaf-fall would release potassium during the winter period, spring/summer growth causing rapid uptake and hence lower summer concentrations in drainage water (Adamson and Hornung, 1990). Phosphate and iron variations are related to soil moisture. A rise in water table resulting from the elimination of root uptake and canopy evaporation caused extended periods of anaerobic conditions, leading to iron reduction and mobilisation: phosphorus which is frequently bound to iron being released at the same time.

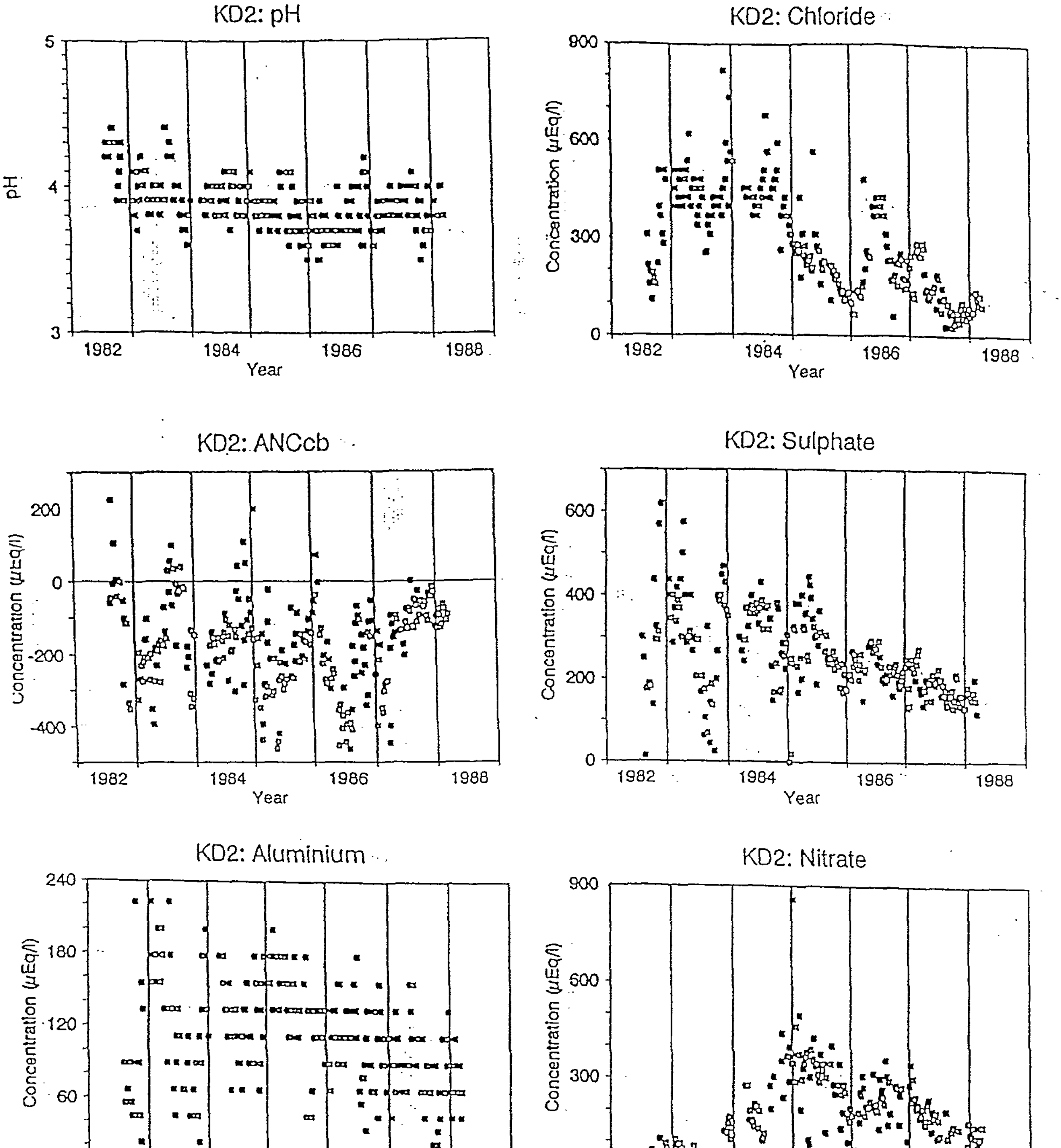


Figure 3.4 **ANC, pH, aluminium, sulphate, chloride and nitrate time series for site KD2.**

4. ANALYSING WITHIN-CATCHMENT CONTROLS ON STREAM HYDROCHEMISTRY AND THE RESPONSE TO FOREST HARVESTING: PART 1, ESTABLISHED SITES.

4.1 Hydrograph separation

All the earlier results have indicated the presence of two contrasting water types within the streams: an acidic, aluminium-bearing water at high flow which is characteristic of observed soil waters and a low acidity, bicarbonate and base cation bearing water observed at low flows which is associated with weathering reactions within the bedrock. Over several years the relative contributions of these two water types have been examined using chemically conservative indicators of mixing and a methodology known as chemical hydrograph separation (cf. Bonnell *et al.*, 1990; Neal *et al.*, 1990c; Hooper *et al.*, 1990; Christophersen and Neal, 1990; Christophersen *et al.*, 1990; 1993). For the Plynlimon streams, these relationships have been examined for the most variable but chemically conservative tracer, acid neutralisation capacity (ANC).

For the Plynlimon streams, ANC decreases with increasing flow. Under baseflow conditions, stream waters are bicarbonate bearing, of low acidity and contain base cations mainly derived from weathering reactions involving aluminosilicate and carbonate minerals within the bedrock. Under stormflow conditions, a much higher proportion of stream water comes from the soil zone where acidic aluminium bearing conditions apply and where base cation concentrations are low due to (a) the lack of weatherable bedrock components or (b) an insufficiently long residence time or (c) a combination of both (Neal *et al.*, 1990c; Robson *et al.*, 1990). Given a knowledge of the groundwater and soilwater "endmember" ANC concentrations within a catchment, the percentage groundwater within surface runoff can be determined by a two component mixing analysis based on the equation

$$\% \text{ groundwater} = 100*(\text{ANC}_{\text{streamwater}} - \text{ANC}_{\text{soilwater}})/(\text{ANC}_{\text{groundwater}} - \text{ANC}_{\text{soilwater}}) \qquad (4.1)$$

In order to split the hydrograph, the two end members used were the average soil water chemistry and the baseflow chemistry (stream baseflow). The results of this analysis show that with increasing flow the predominant water source within the streams is soil water. Nonetheless, an integrated response indicates that perhaps 30% of the total flow comes from groundwater. There are four features to this: 1) the groundwater seems to be a volumetrically important component of stream flow generation, 2) previous conceptualisation of stream flow generation within the catchments contained no component of groundwater and groundwater had not been measured in the catchments up to that time, 3) the soil water endmember was an average and actual measurements of soil waters within pores were extremely variable and there were major problems of measuring this variability, 4) it was certain that the measured fine pore soil waters were actually representative of waters entering the stream at high flows. For these reasons, three separate experiments were undertaken and these are discussed below. Firstly, there was the issue as to whether groundwaters actually existed within the catchments; this required installation of exploratory boreholes. Secondly, there was a question as to the chemical composition of the soil water end members and this required sampling from ephemeral streams where, at least in principle, it would be expected that the main drainage would be from the soils. Thirdly, there was the issue of how both surface and groundwaters would chemically respond to forest harvesting

4.2 The Plynlimon groundwater study

A network of exploratory boreholes across the Hafren catchment revealed widespread groundwater. Typically, the water table was at about 5 m below ground level, but depths varied both in space and time. None of the boreholes dried up during the summer months and all but the shallowest boreholes showed rapid response to rainfall, with levels varying by up to 4 metres. Two of the boreholes were artesian during most of the winter months. The main findings of the work are as follows.

a) With the exception of two very shallow holes which probably intercept surface/soil runoff, the waters have positive alkalinities. The waters from the deeper holes have pHs in the range 7 to over 8 after degassing. These pHs and alkalinities are high enough to explain values observed within the stream during baseflow.

b) Chloride shows systematic variations from site to site with lowest values occurring for sites in forest clearings or sites outside the forest: i.e. areas where atmospheric scavenging of sea salts will be less effective and where lower evapotranspiration might well be expected.

c) One borehole, near the Hafren meteorological site, had a notably high alkalinity (up to almost 5000 μEq/l) during the summer months for the first year of sampling. During the subsequent winter months the alkalinity decreased markedly to around 100 μEq/l, but for the following summer the very high alkalinities did not recur. For this location, the high alkalinity is associated with high weathering, the generated alkalinity being counterbalanced by the production of calcium, magnesium and sodium cations. It seems that this high alkalinity store might be of small volume given the difference in alkalinities between subsequent summer months and the rapid flushing of the water during the winter periods.

d) During the air-flush drilling of one site near the Tanllwyth stream a fracture route to the stream was opened up. This resulted in major increases in calcium, pH, alkalinity and ANC particularly under baseflow within the Tanllwyth (e.g. Figure 4.1). The change persists for low to moderate flows; pH has increased by about 0.5 units (except at very high flows) and baseflow calcium concentrations have increased up to five fold. A survey along the stream indicated that the abrupt 0.5 pH unit change occurred close to the borehole; this confirms that the local groundwater input was the source of the change and that the process of drilling and flushing had augmented the transmissivity of the aquifer by removing chemical precipitates and fine grained sediment.

e) All the above indicate that, even with a relatively impermeable bedrock, there is a hydrologically and chemically active shallow groundwater system. This groundwater system is very variable on a local scale. The study confirms the findings of the ANC hydrograph splitting studies for Plynlimon.

Public Drinking Water Abstraction Points: The following criteria apply under EC legislation (75/440/EEC) at designated abstraction points for public water supply. The criteria quoted are for sources requiring the minimum level of treatment (Simple physical treatment and disinfection).

pH	6.5-8.5 (Guideline value)
Nitrate	25 mg-NO$_3$/l (Guideline value); 50 mg-NO$_3$/l (Mandatory value which may be waived under certain meterological or geographical conditions)

Drinking Water Supplies 'at Tap' (Public and Private): The following criteria apply under EC legislation (80/778/EEC) relating to the quality of water intended for human consumption (i.e. 'at tap').

pH	6.5-8.5 (Guideline value); 9.5 (Maximum admissible concentration (MAC))
Aluminium	50 µg/l (Guideline value); 200 µg/l (MAC)
Nitrate NO$_3$ mg/l	25 mg-NO$_3$/l (Guideline value); 50 mg-NO$_3$/l (MAC)
Manganese mg/l	50 µg/l (MAC: Drinking Water Regulations 1989)

Fish Farms: It is assumed that criteria to protect salmonids (above) would also be appropriate for fish farms

SSSIs/SACs/BAPs etc: In most cases freshwater SSSIs/SACs are designated in part due to their salmonid populations. Therefore criteria set above should also be adequate for these sites. However in some cases other species may be of importance, or salmonids may not be present due to impassible barriers to migration. In such cases advice should be sought from the relevant conservation body, but criteria to protect salmonids will be used as a default.

With regards to the biological impacts of felling due to acidification effects, limits or defined controls on felling should be linked to the short term impacts (1 to 3 years following felling) where ANC can very occasionally decrease by about 30 µEq/l as noted in Chapter 8. Further work and negotiation between the Environment Agency and Forestry Commission is required before standards can be set. From the previous chapter, it is clear that Gran alkalinity can provide a more convenient measure of vulnerability compared to ANC according to the choice of range presented in chapter 8. For the critical ANC range, Gran alkalinity can be considered as being relatively chemically inert and the same type of calculation can be used as ANC for assessing dilution effects.

4.3 Paired catchment studies

To characterise water quality changes with harvesting across a spectrum of representative soil and geological types over time, the water quality of runoff from adjacent sampling sites has been determined. One of these sites represents a control and the other a manipulated area to be felled within the study period. Ephemeral streams draining small areas (<10 ha) were chosen to obtain an integrated measure of the soil water chemistry without the influence of groundwater inputs. Surface runoff has been 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. At each site, boreholes were introduced to obtain representative groundwaters from below the soil zone and to allow endmember mixing analysis to proceed.

The main soil types being studied are podzol, gley and brown earth. Of these, podzol and gley sites were established at Plynlimon. There were no suitable brown earth sites at Plynlimon, these were established at Llyn Vyrnwy where EA could undertake the sampling.

The study sites and research findings are presented for each soil type below. To avoid repetition, linkages between rainfall and stream and groundwater chemistry are not covered as the features are essentially the same as those for all the catchments described so far as (a) water storage damps down the atmospheric sea-salt inputs to the catchment by the time they reach the stream and (b) chemical processes linked to water mixing processes within the catchment effectively determine highflow and lowflow chemistry (e.g. for, ANC, alkalinity, aluminium, calcium and pH).

4.3.1 Podzol

Initially several sites were monitored and these showed large site to site differences in pH and alkalinity, even though the sites were very close together. They fall into two groups; one of fairly low alkalinity (average about -4.9 and range -10.5 to 3.1 μEq/l)with a pH averaging about five (range 4.8 to 5.4), and the other of higher alkalinity (average about 32 and range -9 to 101 μEq/l) with pH averaging about 6.3 (range 4.9 to 6.8). The higher alkalinity sites have been examined for the effects of felling with site SE3 as control and SE1 as the felled site; the other sites were felled prematurely. Boreholes were also established adjacent to SE1 and SE3. Their chemistry has a positive alkalinity (averaging 69 and 416 μEq/l with ranges of -8 to 341 and 2.9 to 570, respectively), while pH, after degassing, averages 6.4 and 7.5 respectively. These pH's are about one unit higher than the undegassed values owing to the high partial pressures of carbon dioxide within the waters collected (31 and 16 times the atmospheric value, respectively). The borehole waters have higher alkalinity and base cation concentrations and higher pH (on degassing) than the surface waters indicating, as expected, a higher degree of chemical weathering in the bedrock zone compared to the soil. For SE1 borehole, relatively large changes in chemistry are observed. In essence, the higher alkalinities occur during the summer baseflow or at a time of flow recession. The chemistry of the borehole moves towards lower pH and alkalinity as flows increase. The large variation in borehole chemistry over time reflects the varying contributions of water from the soil and ground water areas.

In general, higher concentrations are observed in the groundwaters relative to surface waters for most chemical determinands including the base cations and minor elements. Broadly, this reflects the greater degree of chemical weathering. The exceptions are for hydrogen ion, aluminium, DOC and nitrate, where concentrations are higher in the surface waters and this difference reflects the greater acidity and DOC of the soil waters compared to groundwaters and the mobilization of aluminium under acid conditions and precipitation under more basic conditions.

With felling, by far the greatest change in water quality observed within the stream is for nitrate: concentrations increase from about 2.4 to 12 mg-NO_3/l (Figure 4.2). The increase does not take place immediately after felling, but occurs during the following September-October when the catchment wets up. No seasonal pattern is observed for nitrate and the high values following felling have persisted for over one year and they continue to persist. Within the stream there have been some increases in rubidium, iron, bromide and potassium after felling. However, the increases start before the post-felling nitrate peak and in most cases the changes are much smaller than for nitrate. After the nitrate peak there may also be small declines in sodium, chloride and sulphate: there are no other visually discernable changes in stream water quality. For the boreholes, clearfelling has also led to an increase in nitrate concentration from background levels of about 2 mg-NO_3/l although the concentrations vary considerably over time dependent upon groundwater level and hydrological fluctuations. Following felling, nitrate concentrations vary between about 1 and 11 mg-NO_3/l and there is no other clear variation in groundwater chemistry.

4.3.2 Gley

Gley sites have been located within the Tanllwyth catchment at Plynlimon. The stream control and felling sites TanN and TanS were established for small ephemeral streams/ditches associated boreholes have been drilled and sampled. TanS was felled in February 1996 while TanN has remained an unfelled control. As with the other Plynlimon sites, harvesting practice followed current clearfelling techniques appropriate to the site conditions.

The TanN and TanS stream waters show very acidic waters with pH around 4, low alkalinities, around -80 μEq/l and high dissolved organic carbon (up to 3.6 mg-C/l) and aluminium (up to 1.2 mg/l) although on one occasion at TanN, the pH rose to a value of 6.1. This abnormal value corresponded to a period where the stream had virtually dried up and stagnant conditions prevailed. In contrast, the borehole waters are of much higher alkalinities and pH, with high partial pressures of carbon dioxide as well as most major, minor and trace elements, but lower dissolved organic carbon and aluminium. The TanS borehole water exhibits the highest alkalinities and pH's, with values, respectively, averaging 1435 μEq/l and 8 (after degassing). The alkalinity and pH does vary with time but to a limited degree, while borehole level varies by about 3.5 m. For the TanN borehole, the groundwater has a much lower alkalinity (average about 9 μEq/l) and pH after degassing (5.9): level varies by about 2.5 m. Although the two boreholes have different chemistries, there is little time related variation in pH and alkalinity at each site.

With felling, the main change in stream water quality is associated with the release of nutrients in October 1996 when the catchment wetted up (Figure 4.3). The main increases are for nitrate (0.6 to 4.4 mg-NO_3/l) potassium (0.3 to 1.9 mg-K/l), ammonium (0.02 to 0.17 mg-NH_4/l), soluble reactive phosphate (0.0 to 0.2 mg-PO_4/l) and rubidium (0.5 to 2.7 μg-Rb/l): the bracketted values represent averages. Of these nutrients, all have remained at elevated concentrations up to present with the exception of nitrate and ammonium which has now declined to background levels some 12 months after the onset of felling. The effects of felling are also observed for DOC, barium and

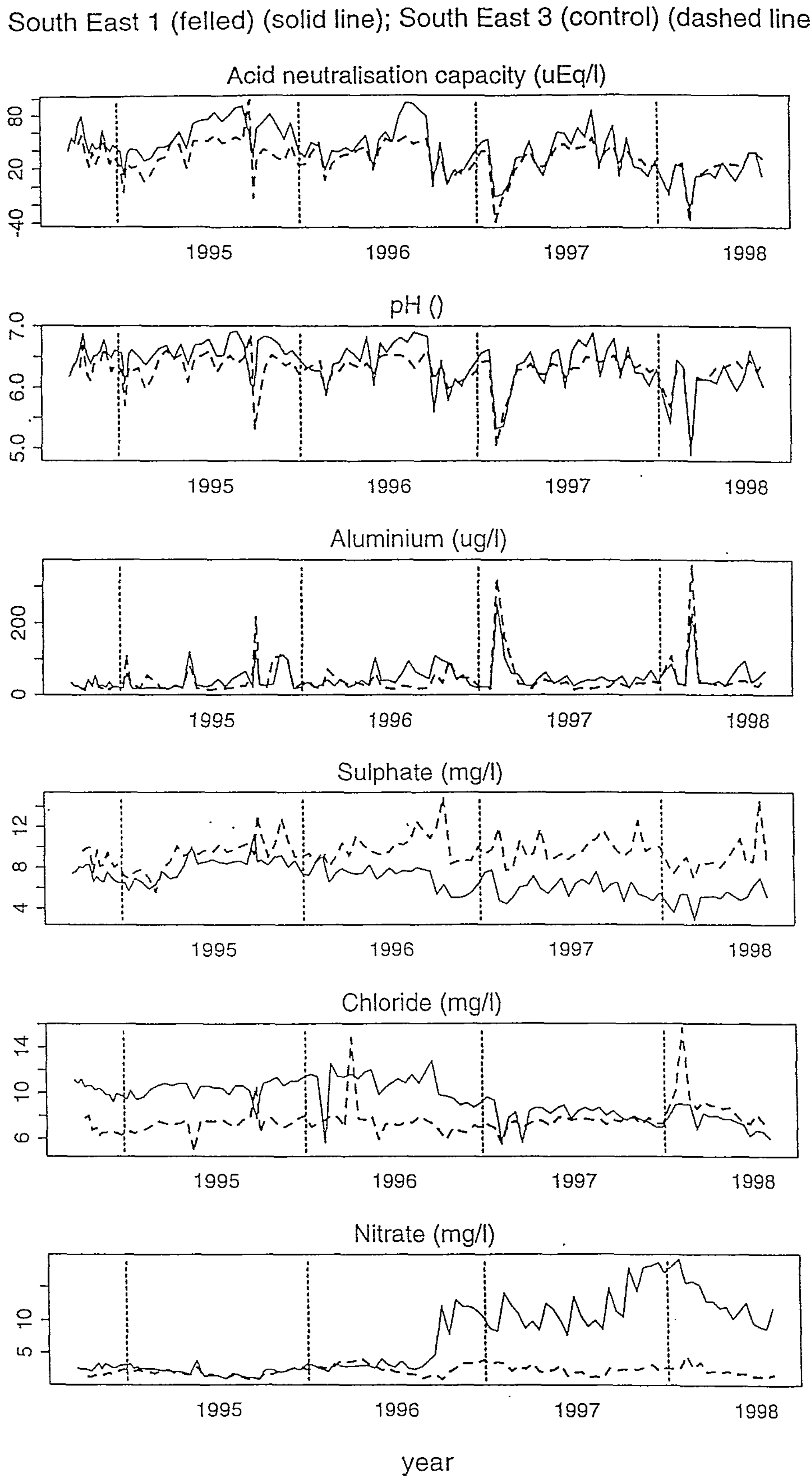


Figure 4.2 **ANC, pH, aluminium, sulphate, chloride and nitrate time series for site SE1 and SE3 streams.**

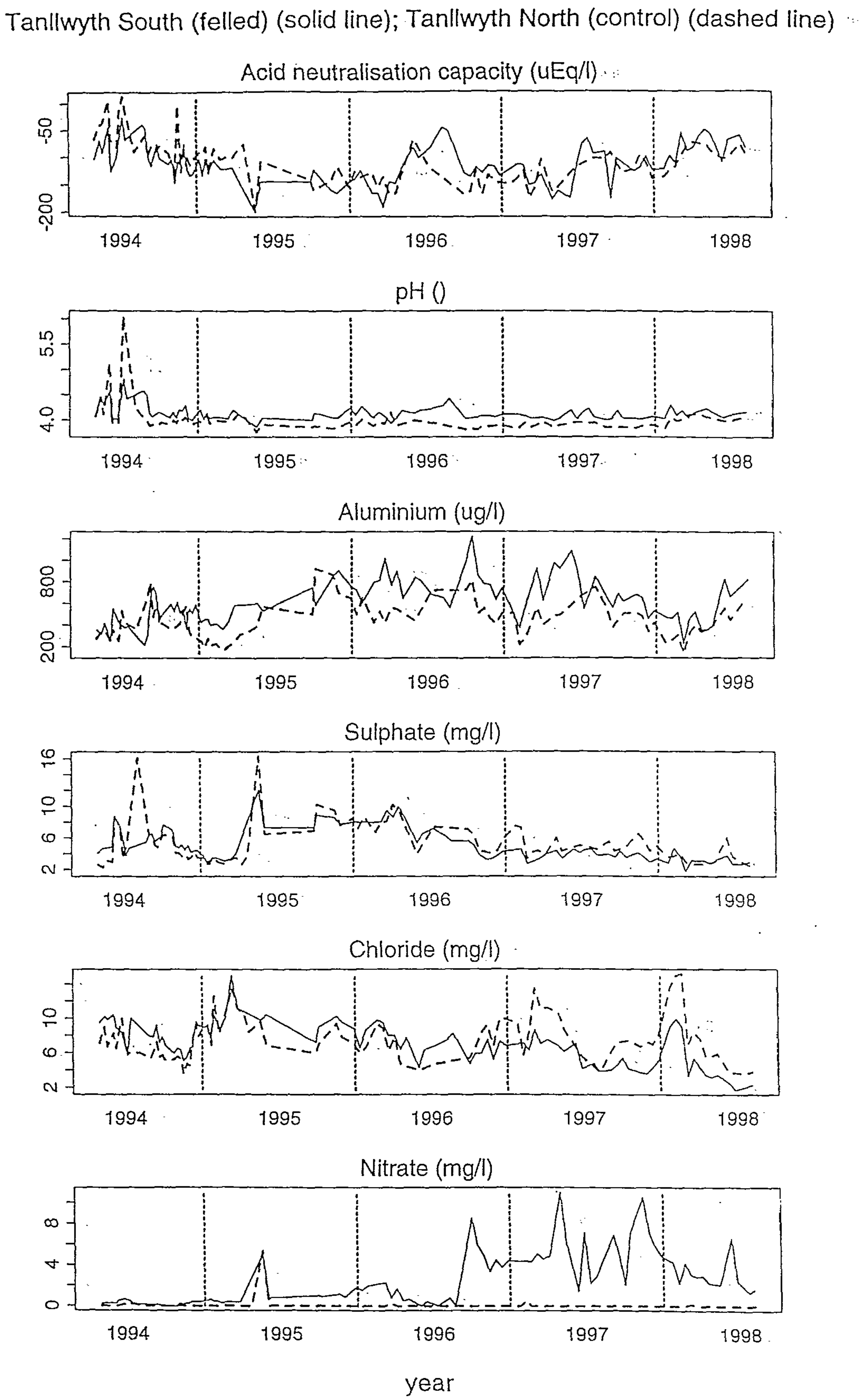


Figure 4.3 **ANC, pH, aluminium, sulphate, chloride and nitrate time series for site TanS and TanN streams.**

boron which increase in concentration, while sodium and chloride decline in concentration. However, these changes are of relatively small magnitude and for DOC, the changes are short lived. There are also small to moderate increases in metal mobility about the time of the initial nitrate pulse following felling in the cases of manganese (15 to 40 μg-Mn/l), iron (700 to 2000 μg-Fe/l) and nickel (5 to 10 μg-Ni/l), and these are short lived. Within the boreholes, some increase in nitrate and ammonium has occurred at the felled site but these increases are erratic and are of much smaller amplitude than observed within the stream

4.3.3 Brown earth

Felled and control sites were established by Lake Vyrnwy for both stream water (VN1 and VN2 respectively) and associated groundwaters. Felling took place during April 1997 at the VN1 site using techniques appropriate to the specific requirements of the site. The control site is a small steep, perennial stream flowing into the southern margin of the lake. The felling site is located on a moderately steep, perennial stream.

The surface waters have positive alkalinities (about 60 μEq/l) and moderately high pH's (about 7 after degassing) and are approximately two times oversaturated with respect to atmospheric carbon dioxide. The ground waters are of similar pH to each other after degassing (averaging about 7.5) and are of higher average alkalinities and base cation concentration (e.g. alkalinities averaging 455 and 243 μEq/l for VN1 and VN2 boreholes, respectively) than the stream waters. The borehole at the felling site (VN1) has a much higher carbon dioxide partial pressure than the atmospheric value (69 times higher than atmospheric), while the other is only four times the atmospheric value: this difference does not however reflect the effects of felling as the same differences were observed both pre- and post- felling. Also, at the felling site the borehole water is enriched in nitrate even prior to felling.

In general, higher concentrations are observed in the groundwaters relative to surface waters for most chemical determinands including the base cations and minor elements, reflecting the greater degree of chemical weathering. The exceptions are for hydrogen ion and aluminium, where concentrations are higher in the surface waters reflecting the greater acidity of the soil waters.

With felling, by far the greatest change is for nitrate, where concentrations increased on average from about 1.2 to 4.7 mg-NO_3/l (Figure 4.4). The increase occurred in August 1997 when the catchment wetted up. Within the boreholes, the felled site shows changes in nitrate mirroring those of the stream except that there is a delay of about 2 months in the timing of the peak. There is no other clear water quality change for any of the other chemical determinands in either the stream or borehole with felling except for small increases in sodium and calcium in the stream.

4.4 Synthesis of results from Plynlimon, Beddgelert Forest and Kershope Forest

The results from all the experimental sites show that felling effects are manifest mainly by an increase in nitrate during the summer and early autumn periods following felling irrespective of soil type. The gley sites show the greatest variability in response with clear increases in potassium, ammonium and phosphate together with limited increases in several trace elements.

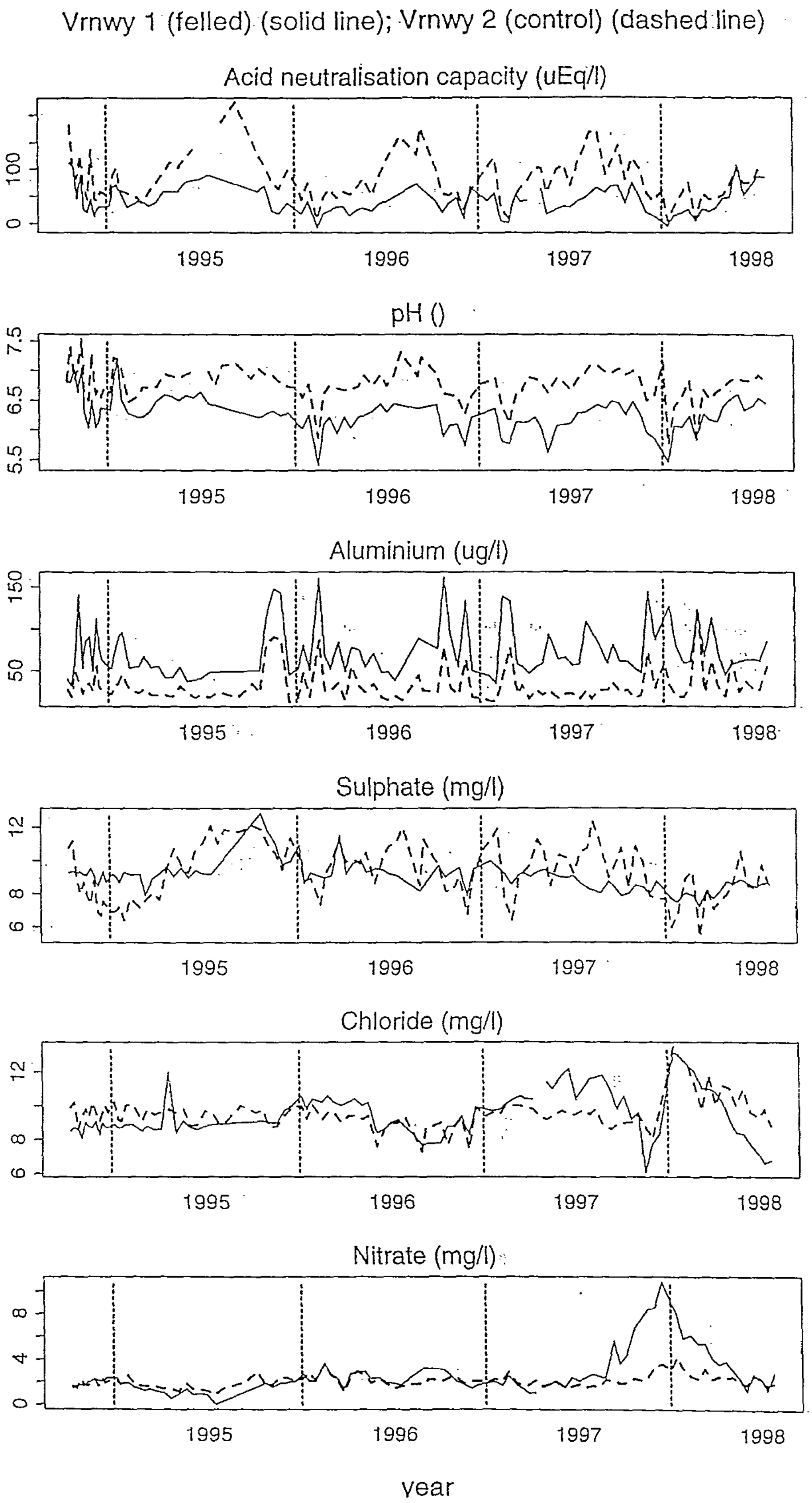


Figure 4.4 ANC, pH, aluminium, sulphate, chloride and nitrate time series for site VN1 and VN2 streams.

For many determinands the changes are within experimental error. For most determinands the changes involved are of limited environmental significance. However, in the case of acidification, at marginal sites with ANC values around zero relatively small changes in pH and ANC potentially can have significant biological impacts. Consequently, a more detailed assessment of the factors determining acidification changes and the potential scale of the changes associated with felling and climatic variability has been undertaken using data from all the catchments and across all scales and soil types.

4.4.1 Definitions and strategy

The analysis is focused on five main determinands central to describing the effects of acidification in freshwaters (calcium, pH, Gran alkalinity, ANC and aluminium; cf Reuss and Johnson, 1986): here termed the acidification indices.

Calcium. This is a major base cation derived from within the catchment, primarily from the weathering of aluminosilicate and, in some cases, carbonate minerals as well as from cation exchange reactions.

pH. This is the negative logarithm of the hydrogen-ion concentration (more strictly the hydrogen-ion activity) in solution. It represents a measure of hydrogen-ion generation, a primary factor for biological deterioration under acidic conditions (Harriman *et al.*, 1990) and a major control on aluminium and heavy metal solubility (Stumm and Morgan, 1970).

Gran alkalinity. There are several operational definitions of alkalinity (Neal, 1988a; Reynolds and Neal, 1989). Here, the term is based on an acidimetric titration in the pH range 4 to 3. The methodology used, following the work of Gran (1952) (hence the term Gran alkalinity), provides a measure of the balance between weak acid buffers (mainly bicarbonate, humates and fulvates) and hydrogen-ions: positive values represent bicarbonate bearing waters with pH > 5.6 while negative values represent acidic waters (pH < 5) which are bicarbonate depleted.

ANC. This represents the charge balance between the acid neutralizing buffers (mainly bicarbonate and organic-acid anions) and the products of acidification (hydrogen-ions and aluminium). It is formally defined as the difference between the strong bases (Na + K + Ca + Mg) and the strong acid anions ($Cl + SO_4 + NO_3$) where all the concentrations are in μEq/l units (Reuss and Johnson, 1986). This is the primary integrated measure of stream and soil acidification and an ANC of zero is taken as a "broad brush" threshold for the acid-induced deterioration of aquatic biological populations (Jenkins *et al.*, 1997a).

Aluminium. This is one of the most important products of acidification as it is harmful to freshwater biota (Edwards *et al.*, 1990). It is generated within the catchment soils by a combination of acid leaching of secondary minerals (clays, aluminium hydroxides) and cation exchange. In addition, there may be inorganic aluminium solubility controls and organic complexation reactions that modify its release, transport and fate within the soils and streams. In particular, within the streams, aluminium may precipitate when acid, aluminium bearing soil waters encounter more alkaline groundwaters and the solubility product is exceeded (Neal and Christophersen, 1989).

Of these acidification indices, only ANC provides a truly chemically conservative indicator of the balance between weathering and acidification. For example, on the mixing of acidic soil-water with more alkaline groundwater, pH changes in a highly non-linear fashion due to the confounding influences of (1) bicarbonate buffering with carbon dioxide degassing (2) aluminium precipitation/dissolution reactions and (3) a logarithmic concentration term. For Gran alkalinity, there will be a less complex response than for pH with the non-linearity primarily related to aluminium solubility controls, which is often of second order importance. Calcium, behaves in a chemically conservative manner on mixing, but the dominant control is associated with weathering reactions.

The core strategy of the analysis rests with linking, for each catchment, the five acidification indices listed above with variations in the components which lead to an acidification/neutralization response, namely the strong acid anion concentrations, nitrate, chloride and sulphate, which can all make up a significant proportion of the anion charge in solution, and with flow. For the analysis, each anion and flow is considered separately as each represent different inputs and behaviours. Thus,

> *Chloride*: the variability is determined by atmospheric inputs mainly for maritime sources (there are no significant within-catchment sources) and physical storage within the catchment which damps the large variation observed in rainfall deposition. Chloride is a major component of the strong acid anion sum. It needs to be considered as potentially a driving variable within cation exchange - an increase in sea salt concentrations in the catchment soils from wet and dry deposition (Reynolds *et. al.*, 1997; Wilkinson *et. al.*, 1997) plus the effects of evaporative concentration within the soil should, from theory, lead to displacement of base cations, hydrogen-ions and aluminium from the cation exchange complex in the soil (the mobile anion effect).
>
> *Sulphate*: this has both atmospheric and within catchment sources. The former come both from maritime and pollutant sources while the latter include mineralization and oxidation of soil organic matter and metal sulphide oxidation within the bedrock. Sulphate influences cation exchange controls (the mobile anion effect) and weathering (from the leaching of bedrock).
>
> *Nitrate*: this also has atmospheric and within catchment sources. However, for the study sites, the dominant term is the within catchment generation of nitric acid as a product of organic matter mineralization and oxidation following felling. Also of importance is the in-catchment and in-stream removal of nitrate as this represents a one-to-one μEq/l acid neutralization process plus the contribution of nitrate to the cation exchange process within the soil (the mobile anion effect). Within stream mineralization of organic nitrogen followed by oxidation to nitrate can also occur.
>
> *Flow*: this represents a term describing the mixing of acidic soil- and more alkaline ground- waters. It also represents a separation between acid generation and acid consumption through weathering. Many studies have shown that changes in base cations

and Gran alkalinity/ANC are directly linked to the logarithm of flow (Kirchner *et al.*, 1993; Hill and Neal, 1997).

4.4.2 Spatial and temporal variability

The water quality of the sites is summarised in Figure 4.5 where average and ranges of chemistries are plotted in a sequence north-Wales, northern-England, mid-Wales and progressively from small to large catchment areas. The water quality varies markedly from site to site and over time at each site and a wide range of concentrations are encountered. However, for part of the time at least, at most sites the waters are acidic and aluminium bearing and they have alkalinities and ANCs which are negative. The water quality of these sites is typical of the range of compositions in the acidic and acid sensitive UK upland areas (Edwards *et al.*, 1990). Across the sites, the chemistry varies both in terms of averages and ranges of concentration. The variety of responses for the various acidification indices and strong acid anions are:-

> *Gran alkalinity and ANC.* The small sites, with the exception of SE1, SE3, VN1 and VN2, have the lowest average and minimum alkalinities and ANCs and they show the most variable range in values from site to site. The alkalinities and ANCs generally follow a systematic pattern with flow, with low flows having the highest values. These features reflect not only the dominance of acid, soil-derived runoff, particularly at high flow, but also a residual component of the ground-water input at low flows. In the case of the small SE1, SE3, VN1 and VN2 catchments and the larger streams, Gran alkalinity and ANC are still variable and decrease with increasing flow, but the spread of values is less than for the other streams, reflecting a larger ground-water component.
>
> *Aluminium.* Some of the small streams (the Beddgelert and Kershope sites in particular) have the highest average and maximum concentrations of aluminium reflecting the predominance of high acidity soil water components. The lower aluminium concentrations in the small, less acidic streams (SE1, SE3, VN1 and VN2) and in the larger streams occur because they have a greater ground-water component and because aluminium precipitation can occur at these higher pH values (Neal and Christophersen, 1989).
>
> *pH.* The large streams and the small streams which receive more ground-water have higher pH values as would be expected from their higher alkalinities and ANCs. However, the Gran alkalinity/ANC and pH responses differ in two ways. Firstly, there is a much greater spread of pH values in the larger streams. This feature reflects the effect of bicarbonate buffering and possibly the influence of aluminium precipitation on modifying the hydrogen-ion concentration in the larger streams (Neal and Christophersen, 1989 and Neal *et al.*, 1990a-d). Secondly, for the Kershope Forest sites, high maximum values of Gran alkalinity and ANC are not matched by the equivalent high maximum pH values probably due to the influence of intermediate strength acid anions as discussed later in this paper.
>
> *Chloride, sulphate and nitrate.* The small streams at Beddgelert and Kershope exhibit the widest range of strong acid anion concentrations but for chloride and sulphate, differences in the average values between the small and large streams are relatively small. This shows

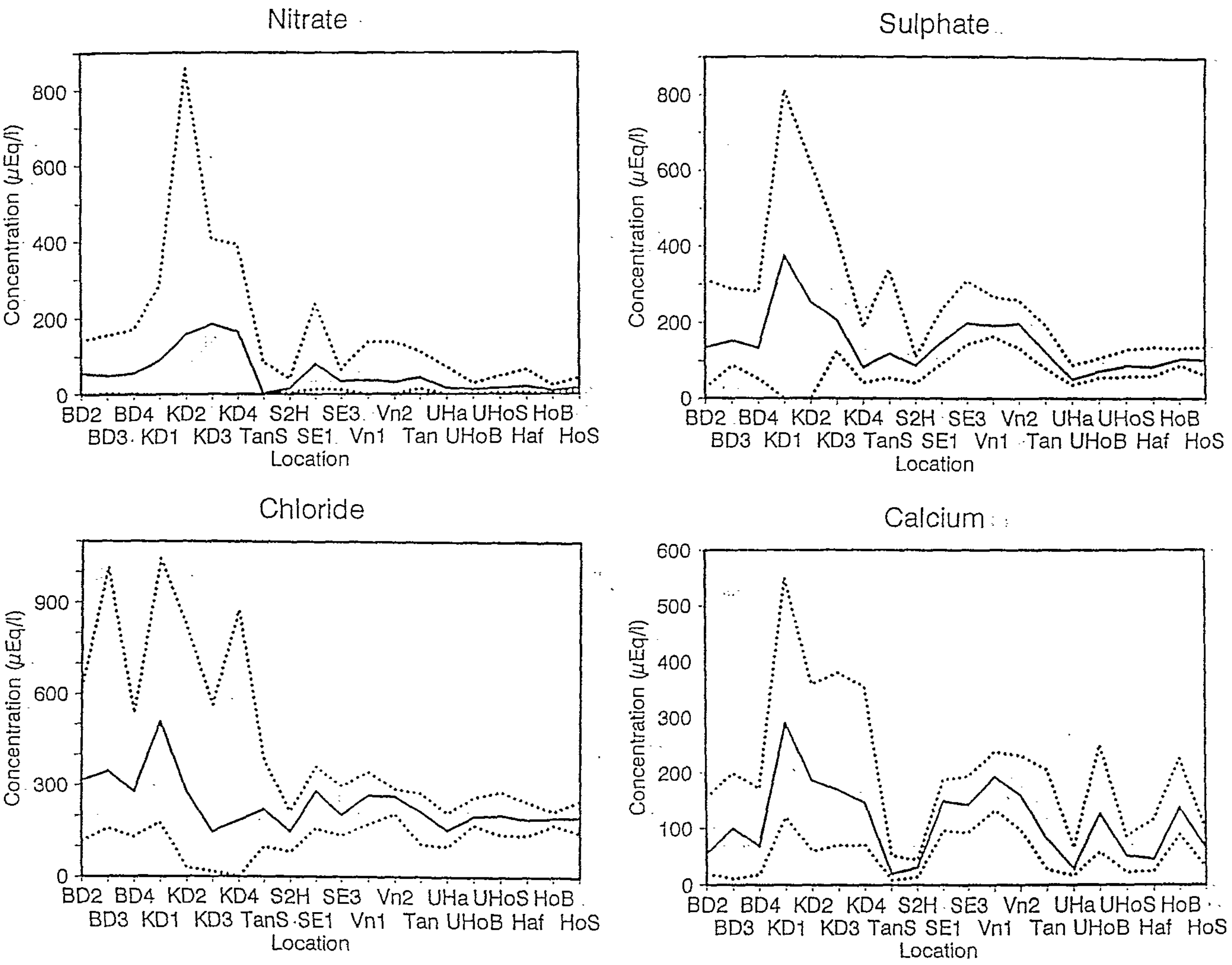


Figure 4.5a Plots of averages (solid line) and minima and maxima (dashed lines) concentrations for nitrate, sulphate, chloride and calcium across the experimental sites. Within the plots, the locations are separated from left to right between small (BD2 to VN2) and large (Tan to Ho) catchment areas.

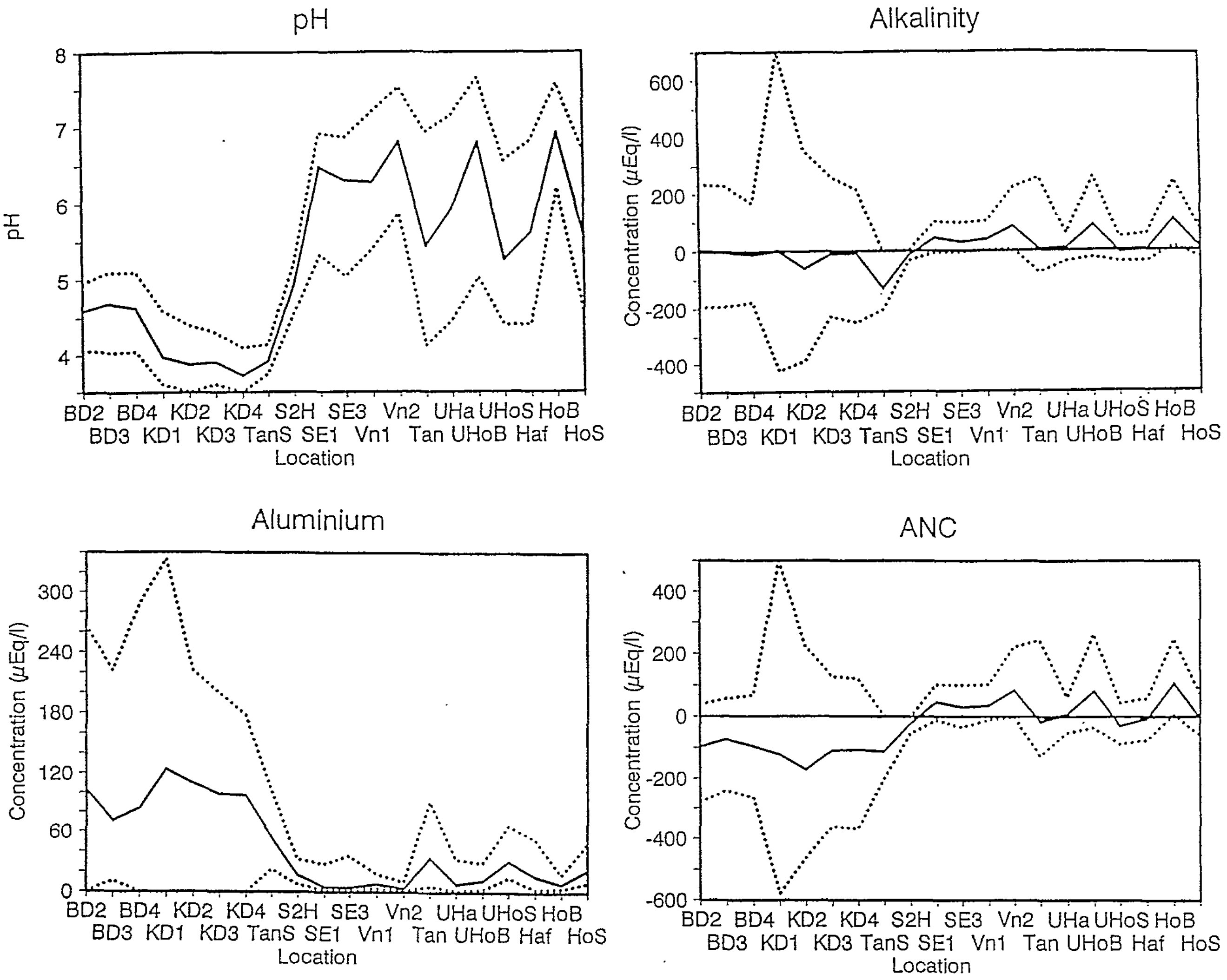


Figure 4.5b **Plots of averages (solid line) and minima and maxima (dashed lines) for pH and concentrations of alkalinity, aluminium and ANC across the experimental sites. Within the plots, the locations are separated from left to right between small (BD2 to VN2) and large (Tan to Ho) catchment areas.**

clearly a general feature of catchments in which the variable rainfall signal is progressively damped with increasing catchment size for these components, reflecting an increasing storage/residence-time effect. For nitrate, a similar pattern is observed, but for the Kershope Forest sites, the effects of felling are evidenced by the highest average and maximum concentrations.

> *Calcium*. There is little pattern to the variations in calcium concentration across the sites in relation to catchment size. However, the highest values occur at the Kershope Forest sites both in terms of average and maximum values. This presumably reflects the influence of the underlying calcareous till but clearly other factors come into play at these sites (cf. comments made above in the section on pH).

4.4.3 The effects of felling on stream water quality: difficulties in assessing the effects of strong acid anion concentrations on the acidification indices

One of the main problems in determining the effects of felling on the important parameters associated with stream acidification/acid-neutralization is that (a) the strong acid anions show large variations in concentration and (b) there is a confounding influence of varying soil- and ground- water inputs to the stream associated with the variability of stream flow (Neal and Christophersen, 1989). Current cation exchange theory predicts that as the sum of the strong acid anion concentrations increase/decrease there will be a corresponding increase/decrease in acidity. So, if the concentration of one strong acid anion increases while the others decrease, the acidification response will be less than if all the strong acid anions increased together. Indeed, from theory, if the net change in strong acid anion concentration is to a more dilute water, there could even be a net reduction in acidity (i.e. an increase in Gran alkalinity and ANC). The variability in response is illustrated below for two streams, SE1 and KD2, which have been monitored to assess the effects of clear-felling on water quality.

> *The Plynlimon SE1 site*. Changes in nitrate, chloride, sulphate, aluminium and ANC concentration and pH occur with time at SE1 (Figure 4.2). In response to felling, nitrate shows a marked increase while chloride and sulphate concentrations gradually decline. For aluminium, pH, Gran alkalinity and ANC, there is considerable variability and visually there are no clearly distinct signals corresponding to the felling other than perhaps, a decrease in pH, Gran alkalinity and ANC. Nonetheless, an acidifying effect of clearfelling becomes discernable for pH, alkalinity and ANC when the values are plotted against flow and points before and after felling are identified. This is illustrated in Figure 4.6 for ANC where felling seems to have resulted in a decline, particularly at high flows, of about 30 μEq/l. Prior to felling ANC was positive for all high flow events, while after felling, zero to negative values are observed at high flows. Note that flow was not directly measured at this site, rather data from the Hafren flume are used. If flow has increased post-felling, as might be expected, then there should be a shift in the post-felling data towards higher flows. However, the observed separation, pre- and post-felling will remain, particularly at high flows. The corresponding plot for the forested control site shows no such time dependent separation of values (Figure 4.2, 4.6).

> *The Kershope Forest KD2 site*. Even larger changes in water quality occur at KD2 than at SE1 (Figure 3.4). In response to felling, nitrate shows a marked increase in

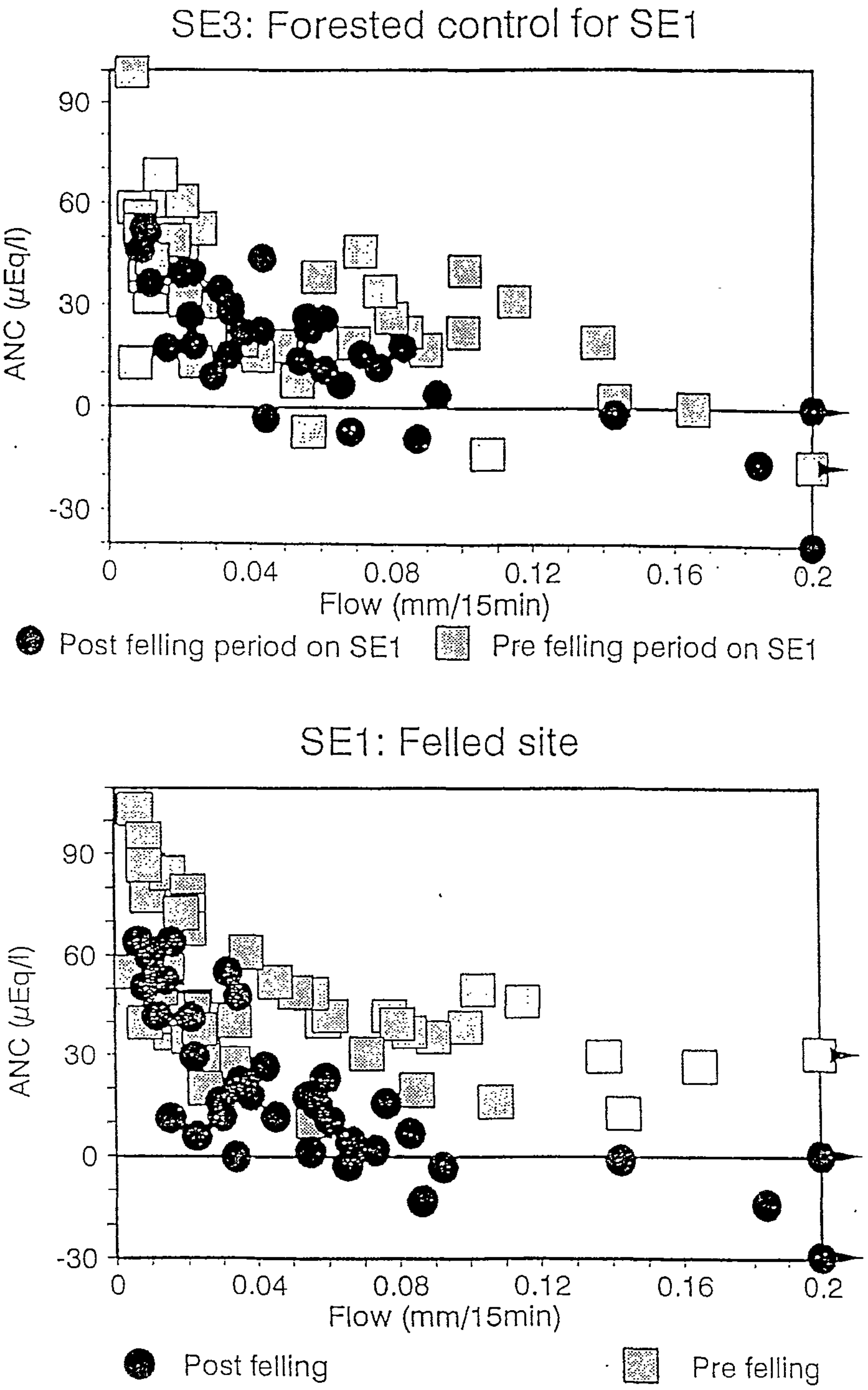


Figure 4.6 **ANC plots with flow for felled site SE1 and the associated forested controls SE3. The circle and square symbols used refer to the times before and after felling, respectively, for the felling site. The same symbols are used for the control site to depict the corresponding period to that of felling at the other sites. The arrows at the right hand side of the plots indicate points with larger flow values; the scales have been expanded to show the underlying data structure.**

concentration although, after one to two years, the concentration declines as the new vegetation is reestablished (at SE1 this is not observed because of the shorter monitoring period). Chloride and sulphate concentrations decline gradually after felling as at SE1 although the changes are bigger (again probably due to the longer data record). For aluminium, pH, Gran alkalinity and ANC, there is considerable scatter in the time series patterns and visually there are no clearly distinct signals corresponding to the felling other than perhaps, a decrease in pH, Gran alkalinity and ANC for the first two years following felling. Further, unlike for SE1, an acidifying effect of clearfelling is not discernable when pH, alkalinity and ANC values are plotted against flow. The clearest indication of a change in acidity comes from a contour plot of the frequency of ANC values against time (Figure 4.7). The plot illustrates that after felling ANC declines initially, but that in the later years ANC tends towards values which are higher than those prior to felling. Thus, it seems that acidification has increased and then decreased after felling although it must be borne in mind that the data spread is particularly high.

4.4.4 The rationale for multiple regression analysis

The large variations in strong acid anion concentrations, as well as flow, means that a novel approach is required to "tease out" how the individual strong acid anions affect the acidification indices and ANC in particular. Here, a multiple regression analysis has been used to separate hydrological and chemical factors following the pioneering work of Kirchner *et al.* (1993). The underlying rationale is two fold. Firstly, in order to change the concentration-flow relationship for the acidification indices from curves to straight lines, a transformation of flow is undertaken. In this case, the degree of linearization differs for the individual components. However, for this analysis, emphasis is placed on linearizing those acidification indices which behave relatively conservatively on mixing of soil- and ground- water in the stream (calcium and ANC and to a lesser extent Gran alkalinity). For this purpose a logarithmic transformation of flow has been used following the approach of Kirchner *et al.* (1993). Preliminary analysis of our data revealed linear ANC-log(flow) relationships in many cases although, as would be expected, data scatter can be high when the influence of the strong acid anions becomes large. For the upper and lower Hore sites, two straight lines rather than one were found: one from base to moderate flows, the other from moderate to high flows. For the Hore, calcium and alkalinity values are high at low flows due to both the occurrence of vein carbonate within the bedrock and upstream drainage from derelict mine adits (Neal *et al.*, 1986b; Reynolds *et al.*, 1986). At particularly low flows, calcium and alkalinity enriched waters may well come from mine water storage. Because of the potential for two baseflow sources, the upper and lower Hore data have been split into two linear ANC-log(flow) categories which have been analysed separately. Secondly, deviations away from this straight line are examined to see if the differences are related to the individual strong acid anion concentrations. In this part of the analysis, the concentrations have not been transformed as a direct linear relationship would be predicted between the strong acid anions, Gran alkalinity and ANC due to the potential stoichiometric reactions involved. By undertaking a multiple linear-regression analysis for individual anions and the logarithm of flow, the direct influence of these components on the acidification indices can be identified systematically. In the case of aluminium and pH, non-linear features are to be expected as these components are not chemically conserved during mixing of soil- and ground- water in the stream. Nonetheless, the multiple regression analysis is still useful for revealing the directions of change in the acidification indices with change in the individual strong acid anions. For example, acidification theory predicts that if cation exchange reactions are important then increasing concentration of any individual strong

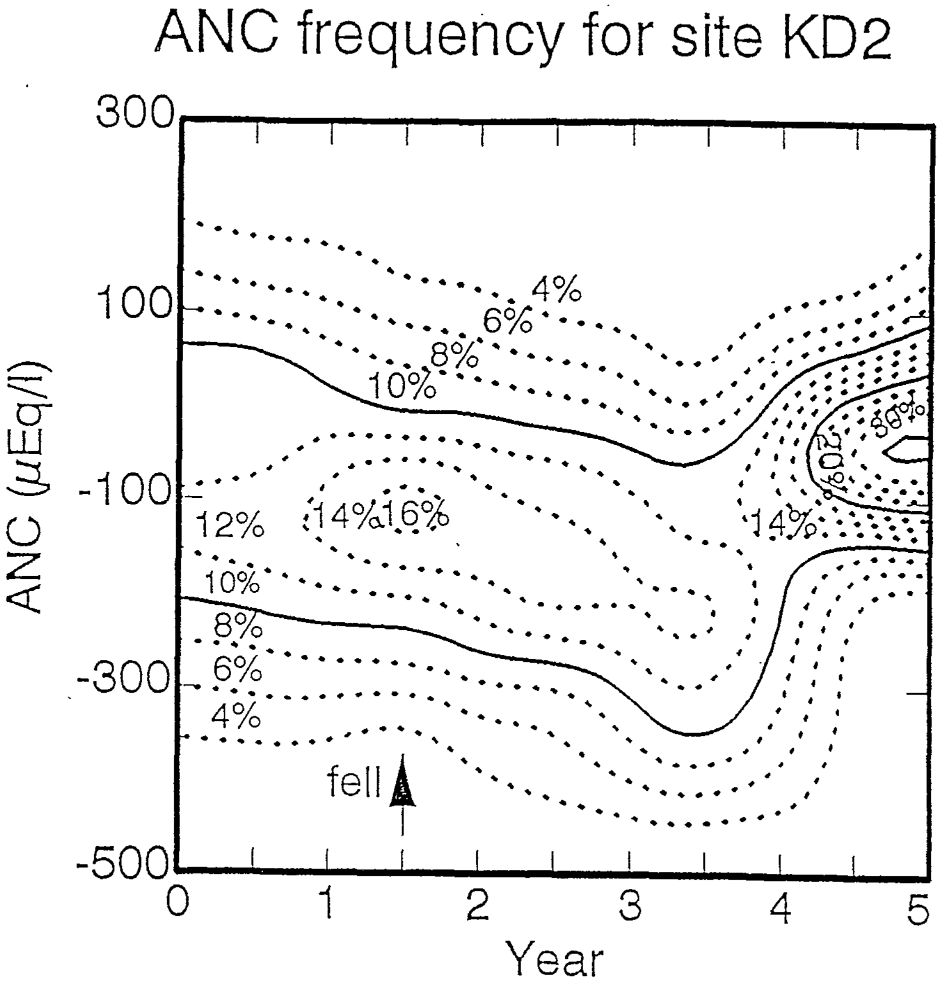


Figure 4.7 **A contour plot of the percentage frequency of ANC values for stream waters at site KD2 as a function of time and ANC. Solid lines represent frequencies of 10 and 20%, while the dashed lines indicate 2% incremental steps.**

acid anion should result in an incremental decrease in pH and an incremental increase in aluminium concentration for that individual anion. For this theory, it is assumed that the cation exchange stores remain of relatively constant composition and weathering rate remains constant over the period of study (Christophersen *et al.*, 1982, 1984; Reuss and Johnson, 1986). The multiple regression analysis thus provides a semi-quantitative test for this theory but applied to each strong acid anion individually.

The multiple regression equation employed here for each acidification index (AI) takes the form

$$\{AI\} = a^*\{Cl\} + b^*\{SO_4\} + c^*\{NO_3\} + d^*\log(flow) + e \qquad (4.2)$$

where {} denotes concentration in μEq/l while "a", "b", "c" and "d" are the regression coefficients and "e" is a constant. Within equation 4.2, the "a", "b", "c" and "d" terms all represent the rates of change of AI with respect to each independent component of the regression. For the analysis, each concentration has been expressed on a μEq/l basis so that direct charge comparisons can be made. Thus, for example, the regression coefficient "c" represents the rate of μEq/l change of AI per μEq-NO_3/l. In the case of all the AIs, other than pH, the "a", "b" and "c" regression coefficients have dimensionless units while "d" has a unit of $1/\mu$Eq since log(flow) is dimensionless: for pH, the first three regression coefficients have the units of $1/\mu$Eq and "d" is dimensionless. For all cases, except ANC, regression of independent variables is undertaken. The same is true for ANC when it is calculated from Gran alkalinity data, but not when charge balance is used. For the ANCcb case, the results must be interpreted with caution and regression coefficients for chloride, sulphate and nitrate will be biassed towards values of -1.

4.4.5 Multiple regression analysis results

The results of the multiple regression analysis are presented in graphical form where the sulphate, chloride and nitrate regression coefficients are plotted, with statistical error estimates (twice the standard error), for all the acidification indices for each location. They cover the full monitoring period even though at some sites the catchments were felled and in some cases replanted during the period. Initial analysis of the longer term time series indicates that the same patterns of behaviour occur on a shorter (yearly) timescale, within statistical error, even for the "manipulated" sites. For compactness, only the longer term regression analysis is presented in this paper.

The results show a variable but generally highly statistically significant set of regressions. The highest r^2 values, typically greater than 0.5 (N usually greater than 100 and often several hundred), occur for calcium and ANC since they are the most chemically conservative of the acidification indices. The highest r^2 values for all the AIs occur for the larger streams: this would be expected given the larger range in concentrations. Correspondingly, aluminium shows the poorest multiple regression fits, as would be expected from its chemical reactivity in the stream. The individual regression coefficients vary in size and they are in most cases statistically significant, although standard errors can be fairly high and site VN1 shows particularly low r^2 values (generally <0.3). The variations in the regression coefficients are described below in more detail and their statistical significance is related to twice the standard error.

For all three strong acid anions, the regression coefficients are generally positive for calcium and aluminium but negative for Gran alkalinity and ANC, as well as pH, whilst the modulus of the regression coefficients lies in the range 0 to 1. This conforms with general acidification theory in two ways. Firstly, increasing anion concentrations should be accompanied by calcium and aluminium release together with an increase in acidity (i.e. a decline in pH, Gran alkalinity and ANC). Secondly, the stoichiometric balance should not exceed 1 and would generally be expected to be less than 1 since the acidity generated is partially neutralized by base cation production. The regression coefficient for nitrate is more positive for aluminium and more negative for Gran alkalinity and ANC, compared to chloride (Figure 4.8). Thus, nitrate is having a disproportionate influence on stream acidification and aluminium generation compared to chloride. In the case of sulphate, the patterns of behaviour show wider variability due to the added degree of complexity from several additional processes (as discussed below). However, excluding the extremes of behaviour, sulphate exhibits an intermediate degree of acidification to chloride and nitrate. These features are inconsistent with the standard model representation of the mobile anion effect in which the soil is taken simply as a single uniform environment where the total rather than the individual strong acid anion concentration is what matters: all the anions should change the acidity to the same degree per μEq of charge. Indeed, for chloride, there is virtually no corresponding aluminium response whereas it is sulphate which exerts a disproportionate influence on calcium. In this case, sulphate is partly derived from the bedrock where it contributes to weathering and augments calcium release.

Within the general patterns, there is large variability for individual sites. The more specific variations for the acidification indices are as follows.

> *Gran alkalinity and ANC.* The patterns are similar for Gran alkalinity and ANC, except that the ANCs have lower values: ANC is the difference between the Gran alkalinity and a positive number, the aluminium concentration. For ANC, the regression coefficients are negative except for three outliers: KD1 for nitrate, SE3 for chloride and VN2 for sulphate. For Gran alkalinity, the coefficients remain negative for both chloride and nitrate (within two standard errors except for chloride at SE3), although there is a small, but significant positive coefficient for nitrate at site KD1. However, for sulphate, there is a much greater degree of variability and the averages range between +1 and -1. In this case, only three sites show positive coefficients within or close to two standard errors (VN2, KD3 and KD4); a groundwater source of sulphate seems to be particularly important in these streams. Excluding the high coefficients for sulphate, the remaining values are much closer to those for nitrate (about -0.2 to -0.6). Thus, in the majority of cases, the two major anions directly associated with acidification (sulphate and nitrate) exert a similar influence in contrast to chloride which shows a weaker influence on acidification.
>
> *Aluminium.* The individual strong acid anions show different effects for aluminium. In the case of nitrate, all the regression coefficients are positive and there is no clear divide between the small and the large catchments. For chloride, the regression coefficients have small values and they are randomly distributed about zero: aluminium does not seem to be affected to any significant degree by this anion. For sulphate, most of the regression coefficients are positive. However, the values are close to zero or slightly negative for the Beddgelert sites. This differing pattern may reflect a limiting process such as hydroxy-aluminium-sulphate precipitation and complex surface adsorption processes (Mulder and

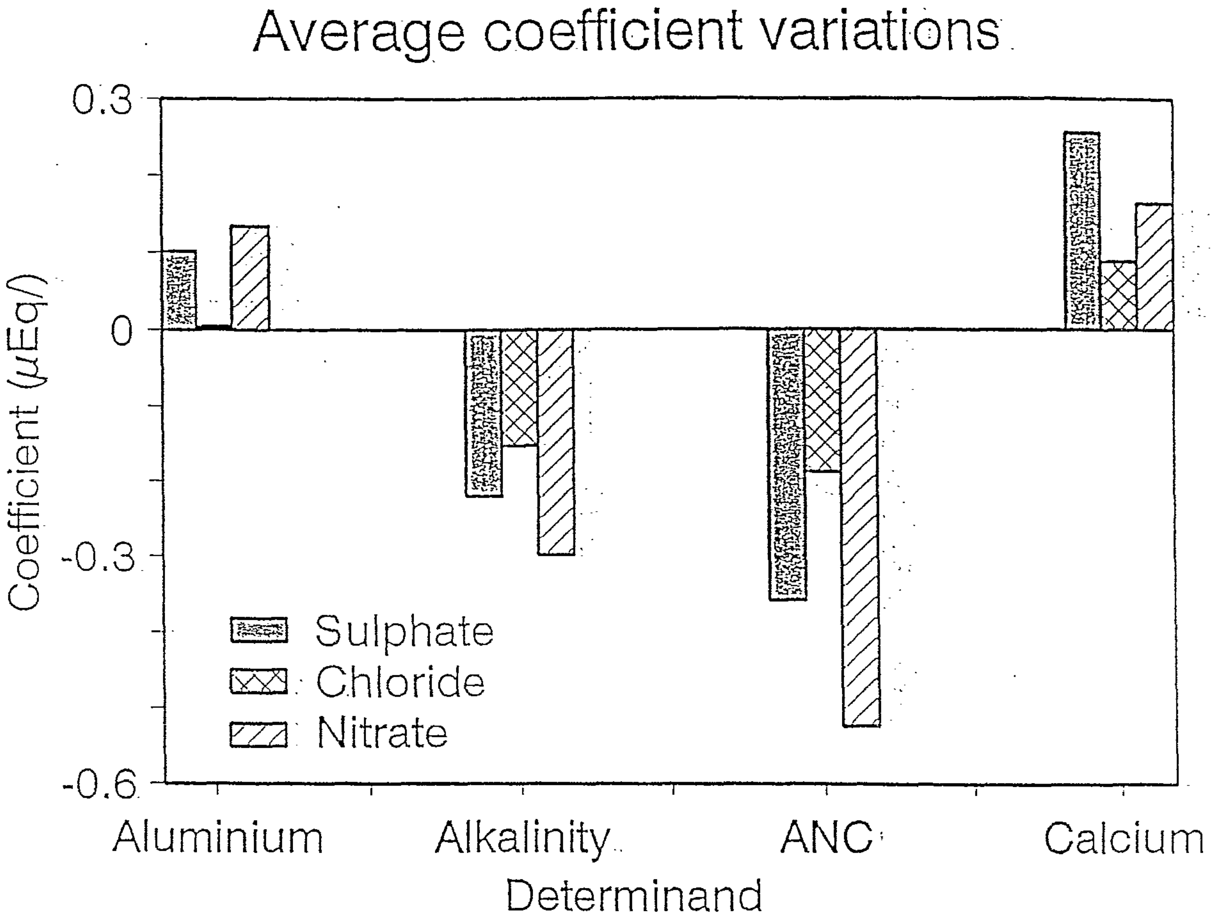


Figure 4.8 **Average regression coefficients for aluminium, alkalinity, ANC and calcium across the sites.**

Cresser, 1994) which could occur under the acidic aluminium and sulphate rich Beddgelert environment.

> *pH*. The regression coefficients are negative or close to zero within two standard errors with the exception of sulphate at two sites. However, there is a marked contrast between the small and large catchments where gradients are about -0.001 and -0.005 respectively. These values are all very low, but the difference may well reflect the higher pH values encountered at the larger sites. There are two reasons for this. Firstly, a logarithmic expression is used for hydrogen-ion (e.g. a 0.1 pH unit change at pH 5 and pH 7 would correspond to a change in hydrogen-ion concentration of 2 and 0.02 μEq/l, respectively). Secondly, aluminium precipitation may occur in the less acidic waters leading to a corresponding one-to-one release of hydrogen-ions although in part this will be balanced by bicarbonate buffering. Note for the Kershope sites, there is the added complexity of pH buffering by intermediate strength organic acids.
>
> *Calcium*. The regression coefficients are all positive or close to zero (within two standard errors). However, particularly high values (0.8 to 1.5) occur for sulphate at five sites (KD3, KD4, VN1 and VN2 as well as the Hore under baseflow conditions). This further indicates a groundwater sulphate source at some of these sites.

4.4.6 Discussion

While data scatter is high, simple multiple regression analysis provides a valuable interrogative tool for teasing out key hydrochemical processes associated with acidification. The results broadly conform to acidification theory but not in detail as the response of varying strong acid anion concentrations on the acidification indices varies from site to site and in different ways.

Nitrate shows a marked acidification effect for individual sites and probably the simplest emergent patterns. On average, for every μEq increase in nitrate, Gran alkalinity declines by about 0.3 μEq leaving about 0.7 μEq to be consumed by weathering and aluminium generation (Figure 4.8). The corresponding decline in ANC is about 0.5 μEq/μEq-NO_3. About 0.1 μEq of the hydrogen-ion formed when nitric acid is generated within the catchment is consumed by aluminium release and about 0.5 μEq by weathering reactions releasing base cations. With regards to the weathering component, the 0.5 μEq/μEq-nitrate change is only partially balanced by calcium (0.2 μEq/μEq-NO_3) and clearly other base cations are involved. The main base cation fulfilling this role is probably magnesium as this is known to provide a significant within-catchment source: sodium in contrast is primarily associated with sea-salt sources and it is relatively unreactive within the system (Neal *et al.*, 1997e). The overall changes probably reflect reactions occurring in two geochemically distinct zones within the soil: the upper organic-rich and the lower mineral horizons. In the upper soils, nitrate generation will result in hydrogen-ion production. Some of these hydrogen-ions will be leached to the lower horizons whilst others participate in reactions with base cations; there are limited supplies of mobile aluminium in the upper horizons. The main pool of available aluminium resides in the lower mineral soils on cation exchange sites and as poorly ordered oxides/hydroxides. This aluminium will be mobilised in response to both hydrogen leaching from surface organic horizons and nitrate production in the lower mineral soil itself. The acidification and aluminium enrichment of the stream rests with the balance between these two processes in the soil combined with the modifying influence of groundwater and within-stream and within-catchment nitrate consumption.

For chloride, increasing/decreasing concentrations appear to lead to a relatively small acidification/acid-neutralization effect at each site. Nevertheless, there is virtually no significant effect on aluminium while the Gran alkalinity and ANC declines are almost equal. Because of this, it seems that the chloride acidification term for each site relates primarily to hydrogen-ion gain and bicarbonate consumption (about 0.2 μEq/μEq-Cl loss of Gran alkalinity). Consequently, the mobile anion effect for chloride seems to be primarily linked to the interactions between base cations and hydrogen-ions which is probably characteristic of cation exchange reactions in the upper organic soils: aluminium would probably also act as a cation exchanger, but its influence will be small as it is strongly bound to organic matter and concentrations are low in the upper soils (Stevens, 1987; Reynolds *et al.*, 1988; Neal *et al.*, 1990a). The lack of any significant chloride-aluminium response may well indicate that aluminium leaching in the lower soil from hydrogen-ions generated by chloride in the upper soils is not significant compared with net acid production in the lower soil itself. A major portion of the chloride variance is explained by a charge counterbalance with sodium and the movement of chloride ions through the soil is largely related to near-conservative transport of rainfall inputs of sea-salts. Nonetheless, time series analysis of sodium and chloride variations in one of the Plynlimon streams does indicate a small underlying cation-exchange signature (Neal *et al.*, 1986b).

Clearly, sulphate acts as an acidifying component often to a similar degree to nitrate for individual sites. Sulphate in rainfall and stream waters contains a dominant non-seasalt component associated with acid deposition. However, there seem to be additional factors linked to groundwater sources and possibly controls such as hydroxy-aluminium-sulphates as mentioned earlier. While the regression analysis has raised process-based issues that need to be addressed, they cannot be resolved within this paper.

With regards to ANC, components not normally considered in the charge balance may be important at a few sites. This is most clearly illustrated for the Kershope sites where initial calculations based on the method of Neal *et al.* (1997c) indicate that if the high alkalinities at KD1 and KD2 were primarily related to bicarbonate then the partial pressure of carbon dioxide would have to be extremely high to induce such a low pH. For example, the samples with the ten highest pH values observed at KD2 have alkalinities ranging between -22 and +224 μEq/l with an average of +82 μEq/l. This yields corresponding carbon dioxide partial pressures of 450 to 6700 times the atmospheric level and an average value of 2000; for KD1 the average value is 6000 and the maximum exceeds 11000 times the atmospheric level. These values are several orders of magnitude higher than those normally encountered within surface waters in both upland and lowland areas (Neal and Hill, 1994; Neal *et al.*, 1997b). Similar features are observed for all the Beddgelert Forest sites. As commented above, the estimate of Gran alkalinity for these sites is based on ANCcb and aluminium concentration values and does not include a term for organic acids. For the organic acids to account for this Gran alkalinity difference, DOC concentrations would have to be around 56 mg-C/l. This estimate is far too high as, for example, the waters are relatively clear and DOC concentrations would only be expected to be a few mg-C/l. It is therefore inferred that there is an additional anion component which is currently not incorporated within the ANCcb calculation. The nature of this additional component cannot be resolved in this report as there is no further information available for these sites: however, intermediate strength organic acids may be important.

One of the major purposes of our study was to attempt to determine the effects of forest harvesting on stream water acidity. Clearfelling leads to both nitrate production and declines in sulphate and chloride concentrations as shown in this report and elsewhere (Neal *et al.*, 1992a,c; Neal *et al.*, 1997e,g). In the context of our findings and earlier theory, the processes are mutually opposing. Acidification of stream water will be most extreme when nitrate production is particularly high or under abnormal circumstances where nitrate and the other strong acid anions concentrations are all large. Correspondingly, acidification will be reversed when nitrate concentrations return to background levels two or three years after felling and when sulphate and chloride concentrations are low. The variable nature of the response is illustrated by three different examples of small felled catchments: SE1 and KD2 - the sites where strong acid anions and ANC have been plotted earlier in the paper - and South2Hore (S2H) which has one of the longest water quality records in relation to felling.

> *The Plynlimon SE1 site.* Here, chloride and sulphate have declined by about 100 and 50 μEq/l with felling, respectively, while nitrate has increased by about 200 μEq/l. From the regression analysis for this site, only the nitrate term is statistically significant and has a value of about -0.14 μEq/μEq-NO_3 when the sulphate and chloride terms are set to zero. Thus, the net effect of the felling is a decrease in ANC of about 28 μEq/l which is about the difference observed within the ANC time series and the ANC-flow plots before and after felling. While this change seems relatively large in environmental impact terms (e.g. for critical loads and long term acidification changes: Jenkins *et al.*, 1997a,b), it is relatively small when compared to the ANC fluctuations over time (-30 to +95 μEq/l). Thus, the inferred acidification due to felling corresponds to only about 25% of the total data scatter and about 40% of the scatter prior to felling. In terms of the processes operative, two comments need to be made. Firstly, the lack of a chloride and sulphate signal implies that cation exchange processes may not be significant at this site. This may well be the case as the higher pH values at this site indicate that groundwater sources are particularly important and ANC variations are primarily related to weathering mechanisms. Secondly, aluminium has not increased significantly with acidification at this site because aluminium solubility controls come into play at the observed pH values (Neal and Christophersen, 1989).
>
> *The Kershope Forest site KD2.* Here, chloride and sulphate have shown declines while nitrate has shown an increase and a subsequent decrease in concentration with time compared to pre-felling values. The regression analysis provides gradients for these three strong acid anions of -0.06, -0.61 and -0.45 μEq/μEq, respectively. Consider two contrasting periods: 1985, when the felling effect was greatest for nitrate and 1987 when all the strong acid anions had declined following felling. For 1985, nitrate increased by about 300 μEq/l while sulphate and chloride declined by about 50 and 200 μEq/l following felling. This corresponds to a change in ANC of about -135, +31 and +12 μEq/l for nitrate, sulphate and chloride respectively. Thus, the net ANC change is computed to be about -92 μEq/l. However, the ANC range for this site is -450 to +210 and the net change represents only about 14% of the full range. Indeed, it is hard to discern visually any significant change in ANC. For 1987, the net concentration change is an increase in nitrate of about 100 μEq/l and declines in chloride and sulphate of about 400 and 150 μEq/l, respectively compared to pre-felling values. This corresponds to respective components of ANC change of -45, +24 and +92 μEq/l and a net gain in ANC of 71 μEq/l. In this latter case a partial reversal of acidification has occurred which is both

clearly visible as the data scatter has been reduced and almost completely balances the earlier acidification change. Note that for this example, the computed ANC changes may be artificially high due to the autocorrelation discussed above.

The South2Hore site. Here, the early phase of harvesting resulted in an initial increase in nitrate and other strong acid anions as the felling debris was burnt on site. This was followed by a subsequent and ongoing decline as described earlier in the report and by Neal *et al.*, (1992a;c) and illustrated in Figure 3.2. The net effect of these changes is to decrease ANC by about 20 μEq/l and increase aluminium by about 10 μEq/l for the first two years and then to increase ANC by about 30 μEq/l and decrease aluminium concentrations by about 20 μEq/l from pre-felling values thereafter (Figure 3.2).

The implications of these findings are discussed later in this report after discussion of the results of a regional survey of felling so that an integrated evaluation can be made.

5. ANALYSING WITHIN-CATCHMENT CONTROLS ON STREAM HYDROCHEMISTRY AND THE RESPONSE TO FOREST HARVESTING: PART 2, REGIONAL SURVEYS

5.1 General features of water quality patterns

Water quality across the region varies from acidic and aluminium bearing to circumneutral waters containing calcium with relatively high alkalinity and ANC values (Table 5.1). For example, pH varies between about 4 and 7.2 for both standing forest and felled sites. Correspondingly, most ANC values lie in the range +200 to -200 μEq/l but there are also a small number of higher and lower values. For waters with particularly high ANCs (>+200 μEq/l), the main ions are (a) bicarbonate which is mainly balanced by base cations (calcium in particular) and (2) chloride which is mainly counterbalanced by sodium (Table 5.2). Under more acidic conditions where ANC values are particularly low (<-200 μEq/l), hydrogen-ions and, especially, aluminium become important to the cation charge: the balancing anions are sulphate, chloride and, most particular in the case of felled sites, nitrate. Under these acidic conditions, sodium and chloride are also major components of the charge balance and they approximately counterbalance each other. Waters with intermediate ANCs have compositions which lie between these two extremes: the neutralization of the more acidic drainage waters by groundwaters ensures linear features for the chemically conservative base cations, strong acid anions and ANC, but more complex behaviour for the non-conservative components such as bicarbonate and aluminium which are influenced by chemical processes across the pH range. Statistical analysis of the entire data reveals no significant difference across the regions or between stormflow and baseflow conditions. Further, a statistical analysis for all the individual sites separately is not appropriate given the limited number of collections for many sites. However, for the few sites with the most samplings (six), statistical analysis reveals no significant difference between stormflow and baseflow conditions either for forested or felled sites.

5.1.1 Water quality patterns: within and across catchment variability

There are clear site to site differences and these are illustrated in Figures 5.1 and 5.2 where the mean and ranges in nitrate, aluminium and ANC concentration together with pH are plotted for the individual sites. In the diagrams, the sites are organized in a sequence of soils from left to right, bog (B), brown earth (BE), gley (PG, peaty gley; SWG, surface water gley) and podzol (PIP, peaty iron pan; IIP, intergrade iron pan). For each soil grouping, the sites are listed in a sequence left to right of increasing time between felling and sampling. The dashed lines represent the minimum and maximum values and the solid line the average. There are two points to note in light of the variation in the number of samples collected at each site. Firstly, a very limited number of samples have been taken: indeed some sites are represented by only one sample and hence the minimum, maximum and mean values are the same. Clearly the plots do not reflect the full range of variability. Secondly, the plotted sequence of time between felling and sampling is an average in some cases (e.g., the sampling period can cover up to two years). More detailed assessment of the influence of felling age must come later when individual points are plotted.

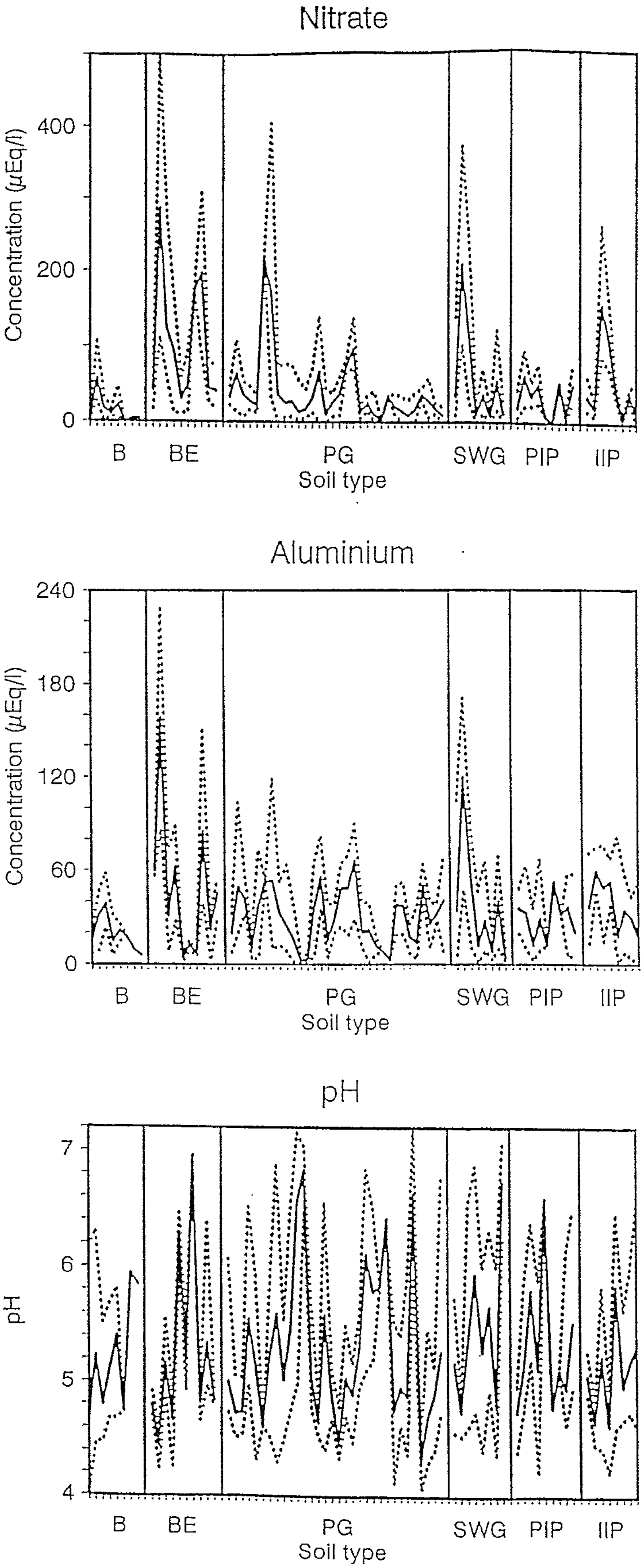
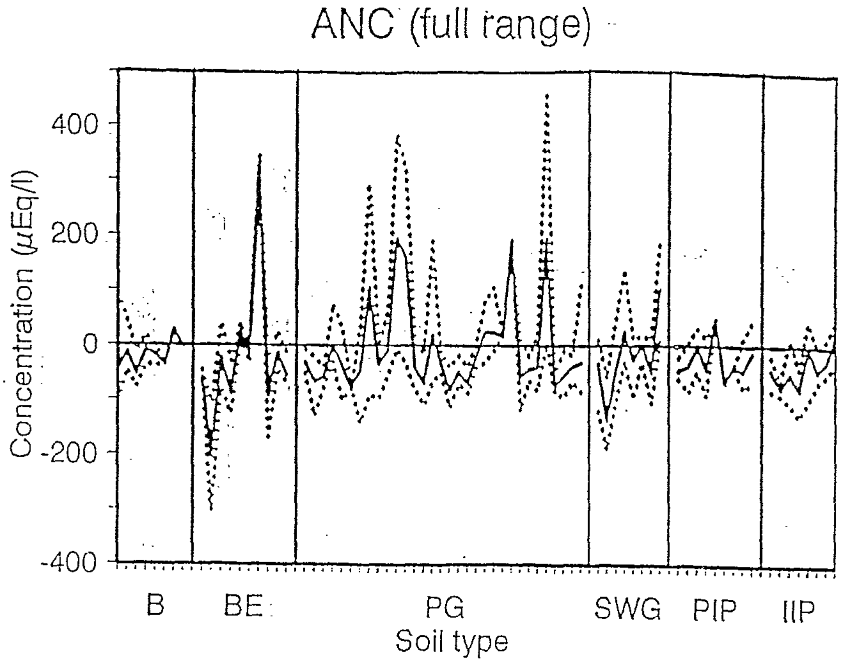


Figure 5.1 Variations in average, minima and maxima for nitrate and aluminium concentrations and pH across the survey sites.



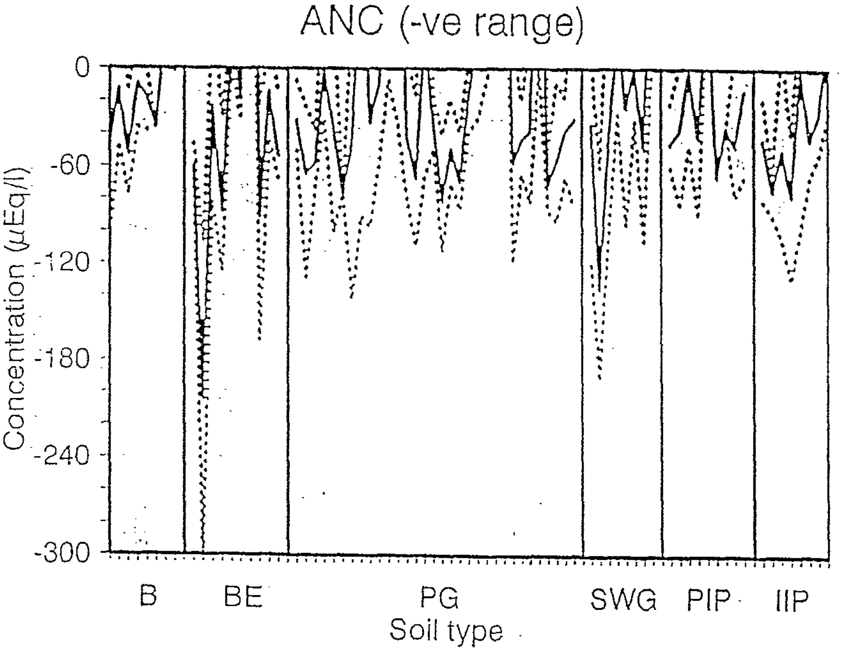


Figure 5.2 Variations in average, minima and maxima for ANC across the survey sites. Two plots are provided, one covers the full range of concentrations while the other focuses in on the more acidic conditions where negative values occur. Note that at one brown earth site (the seventh point in the sequence), a very high ANC value (>1000 μEq/l) was observed which distorted the results: this point was not included in the plot and the computed average does not include this value.

Table 5.1 **A summary of the water quality of the forested and clearfelled survey sites. All the concentrations are expressed in μEq/l units except for pH which is dimensionless and DOC which is μM/l.**

Forested sites		**Average**	**Median**	**Minimum**	**Maximum**
Na	μEq/l	232.92	210.43	134.35	393.48
K	μEq/l	9.08	6.92	2.31	50.00
Ca	μEq/l	71.35	67.25	20.50	171.00
Mg	μEq/l	80.93	75.72	27.98	169.55
Al	μEq/l	32.32	25.18	2.74	104.96
SO_4	μEq/l	129.46	125.94	68.54	356.88
Cl	μEq/l	259.02	229.90	126.94	473.91
NO_3	μEq/l	36.23	29.44	0.00	216.13
pH		5.00	4.88	4.04	6.54
G-alk2	μEq/l	-5.34	-6.88	-90.45	96.02
ANC	μEq/l	-39.51	-40.34	-128.33	92.20
DOC	μM/l	209.42	125.00	0.00	975.00

Felled sites		**Average**	**Median**	**Minimum**	**Maximum**
Na	μEq/l	216.77	210.43	115.22	454.78
K	μEq/l	8.26	6.41	0.00	56.92
Ca	μEq/l	104.00	75.00	20.50	1460.00
Mg	μEq/l	83.16	74.90	27.98	476.54
Al	μEq/l	29.37	23.16	0.92	229.76
SO_4	μEq/l	132.21	128.75	56.67	436.67
Cl	μEq/l	231.84	222.85	107.19	499.29
NO_3	μEq/l	41.23	24.19	0.00	500.00
pH		5.35	5.03	4.07	7.18
G-alk2	μEq/l	25.21	-1.13	-89.46	1499.83
ANC	μEq/l	-5.14	-28.71	-305.08	1496.11
DOC	μM/l	228.12	150.00	0.00	1400.00

Table 5.2 **An illustration of the chemical composition of three distinct water types within the survey: low ANC (site C41), near zero ANC (site A25) and high ANC (site B3).**

	C41 μEq/l Cations	C41 % Cations	A25 μEq/l Cations	A25 % Cations	B3 μEq/l Cations	B3 % Cations
Na	208	29	129	50	203	30
K	57	8	2	1	4	1
Ca	66	9	55	21	363	54
Mg	108	15	51	20	97	15
Al	230	32	17	7	3	0
H	58	8	6	2	0	0
	Anions	**Anions**	**Anions**	**Anions**	**Anions**	**Anions**
NO_3	500	64	0	0	12	2
SO_4	104	13	76	29	119	18
Cl	152	20	147	56	178	27
HCO_3	0	0	21	8	357	53
DOC	23	3	16	6	5	1

5.1.2 Water quality variability: linkages with time since felling

In order to establish patterns of water quality change with felling, a simple data interrogation scheme was introduced where determinand concentrations were plotted against time between felling and sampling using data-labels corresponding to the different soil types. For many of the determinands, the data broadly show two main features with time since felling. Firstly, for over 80% of the post felling samples, concentrations are within the range observed for the standing forest sites and, given the scatter to the data, trends are absent or very poorly defined for this main data swarm. Secondly, concentrations are much higher for the remaining samples. Further, even for the periods since felling where high concentrations occur they constitute only a fraction (often <50%) of the total number of samples taken during that time. These two patterns become clearer when the frequency of concentrations are compared for different time since felling bands. This is illustrated for nitrate in Table 5.3.

For the majority of samples, the analysis cannot be taken further because of the confounding nature of the interactions between distribution of soil types, flow regime etc. For example, examination of the time series data for two key water quality indices, nitrate and ANC shows the following.

> *Bog soils.* There is no clear pattern with time since felling and all values lie within the range of the standing forest. However, the key period of 0.5-3 years post-felling has not been sampled.

Table 5.3 **Frequency distribution of nitrate concentrations with time since felling for the regional survey data.**

NO_3 (μEq/l)	Year	Year	Year	Year	Year	Year	Year
	0	.5-2	3-4	5-6	7-8	9-16	47
0	6	2	4	13	11	12	11
10	8	9	30	28	32	16	44
20	16	12	18	15	13	28	11
30	20	21	12	10	3	28	22
40	14	6	6	15	21	4	11
50	20	7	9	5	11	8	0
60	2	9	1	5	8	0	0
70	3	6	0	3	0	4	0
80	1	4	5	5	3	0	0
90	1	2	6	0	0	0	0
100	2	3	0	0	0	0	0
110	3	2	1	0	0	0	0
120	0	2	0	0	0	0	0
130	0	2	2	0	0	0	0
140	0	0	1	0	0	0	0
150	1	0	1	0	0	0	0
160	0	0	1	0	0	0	0
170	0	3	0	0	0	0	0
180	0	0	0	0	0	0	0
190	0	0	1	0	0	0	0
>190	1	9	1	0	0	0	0

Brown earths. A clear nitrate signal is observed between 0.5 and 3 years after felling but most values fall within the range corresponding to standing forest sites. However, years 5 and 6 post-felling are missing. For ANC the data are highly scattered although there are some high and low values during the first three years after felling. A much more extensive data set is required to clarify the response.

Podzols and gleys. These show similar features and cover a wide time span in relation to felling. The data show a combination of responses for nitrate which broadly fit into three patterns: (a) the majority of points have low nitrate concentrations irrespective of time since felling, (b) a decline with time since felling in the maxima for the higher density data swarm and (c) anomalous peak 0.5 to three years following felling. This feature is illustrated in Table 5.3 where nitrate frequencies are presented for the entire dataset: the podzols and gleys constitute the majority of the data. For ANC there is no clear pattern at all.

The high concentration outliers, which fall into four groups of determinands, have been investigated further:

Nitrate, aluminium, potassium. The highest concentrations were observed during the first 2-4 years since felling at a few sites mainly associated with brown earth soils but other acid soil types were also represented. For example, there are fourteen data points where nitrate concentrations exceed 160 μEq/l (10 mg-NO_3/l) and these represent 10 locations and about a third of the total number of data points for these sites. Correspondingly, there were 8 relatively high values for aluminium and potassium at four sites.

Calcium, alkalinity and ANC. These show a varied response. In the case of alkalinity and ANC, low values (<-50 and <-100 μEq/l, respectively) occurred during the first four years after felling. Within this time span, sites draining brown earth soils covered a wide range of ANC and alkalinity response. For both alkalinity and ANC, there were eight samples with relatively high values (>300 and >200 μEq/l, respectively). However, about 70% of all the data points had negative values for alkalinity and ANC and there were about 11 outliers with values of <-50 and <-100 μEq/l, respectively.

Iron, manganese and DOC. Elevated concentrations of these determinands were observed during the ten year period following felling at some of the 32 sites on peaty gley soils: four had iron concentrations >10 μEq/l, eight had manganese concentrations >6 μEq/l, and six had DOC concentrations >900 μM/l on at least half of the sampling occasions. It appears that the more mature second rotation sites are on peaty gley soils. For this reason, it is not clear that any inferences can be drawn over whether or not the patterns relate to felling, soil type or a combination of both.

Trace elements. At four sites, there are anomalously high values for several trace elements. Two types of pattern emerge in this category. Firstly, cadmium, zinc and lead are all enriched for one peaty iron pan site where concentrations reach about 6, 1800 and 70 μg/l, respectively, against corresponding background levels of <0.5, <100, and <2 μg/l. Secondly, there is enrichment in some lanthanides and actinides together with yttrium and uranium (and possibly nickel) at three sites which have peaty gley and intergrade iron pan soils. The high values and corresponding background values (presented in brackets) are; La, 3.2 (1.0); Pr, 0.8 (0.2); Ce, 13 (2); Y, 3.0 (<0.6); U 0.16 (<0.03 μg/l). There are a further two sites where lanthanum and praesodymium are also enriched. It is not clear if the patterns observed for either group of sites correspond to felling activities. However, in both cases, the sites are in areas with known vein ore-mineralization and this, rather than felling, is likely to be the primary factor.

5.2 Identifying concentration interrelationships associated with felling: graphical and statistical approaches

The concentrations of those determinands which showed changes with felling age were plotted against nitrate, the primary strong acid anion response with felling, to identify underlying patterns (Figure 5.3). Two main patterns emerged. Firstly, plots of aluminium, potassium and barium against nitrate gave positive relationships but with high data scatter. Two linear features were observed for barium: (a) a steep barium to nitrate gradient is mainly for one brown earth site,

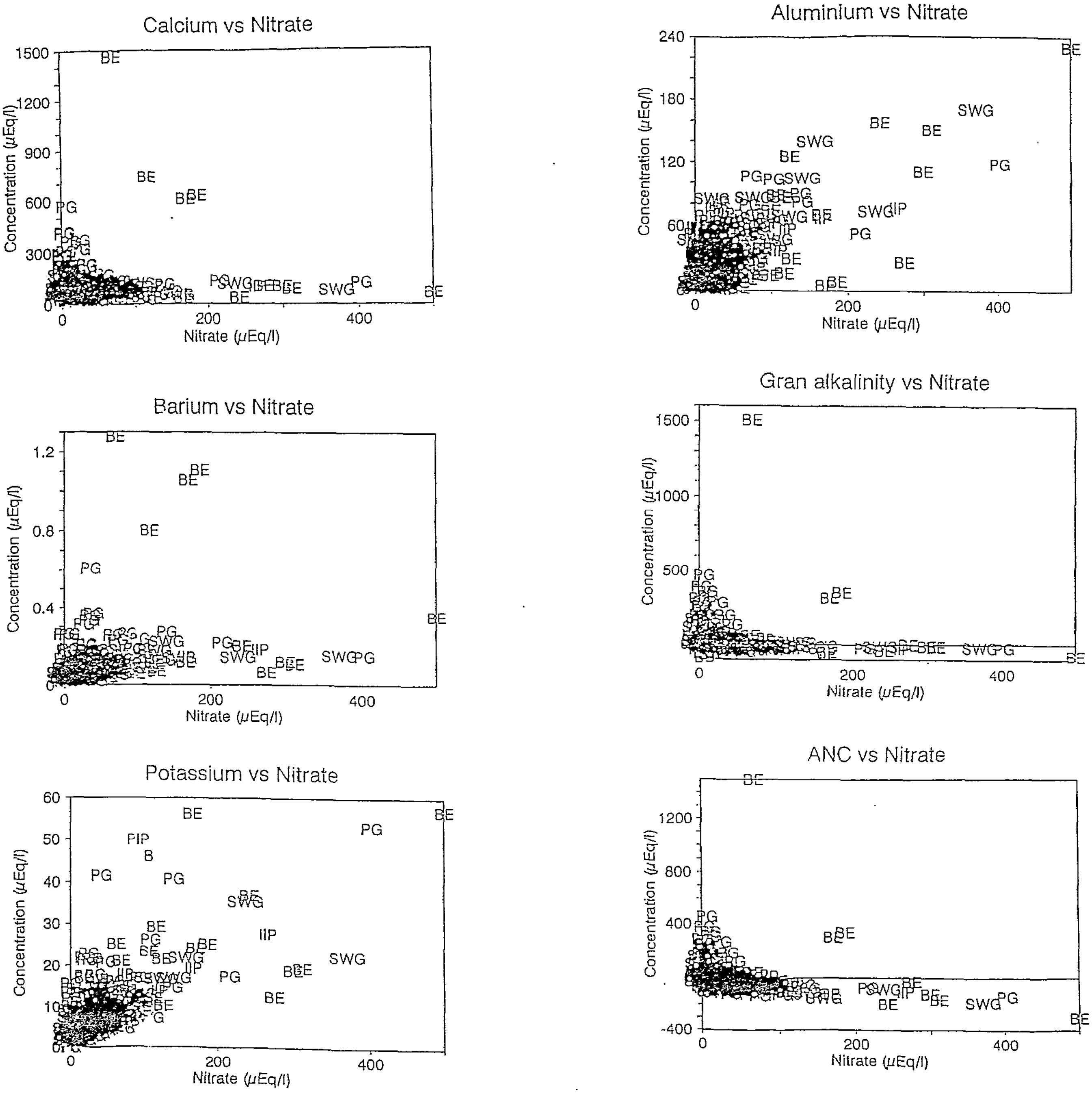


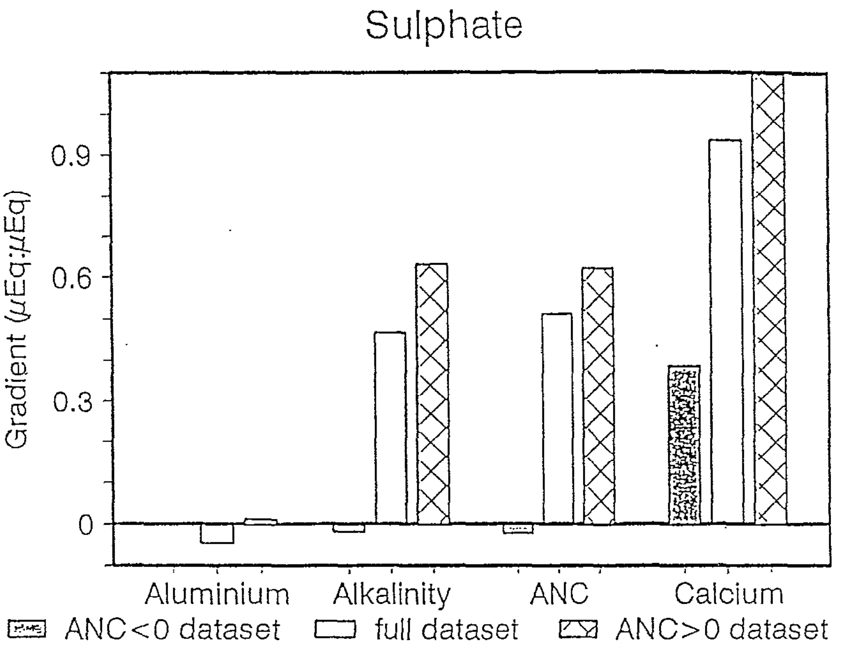
Figure 5.3 Plots of the concentrations of calcium, barium, potassium, aluminium, alkalinity, and ANC against nitrate.

although a peaty gley site is also represented and (b) a shallow barium to nitrate gradient for a series of observations and a range of sites. A more complex relationship was identified between nitrate, alkalinity and ANC. At intermediate to high nitrate concentrations, both alkalinity and ANC had negative values: in the case of ANC an approximately linear and negative relationship occurred but with high data scatter. At low nitrate concentrations, no pattern emerged other than for alkalinity and ANC: both had mainly positive values and these values were either near-to or well-above the nitrate trend line observed at higher nitrate concentrations.

To examine the influence of the major anions on stream acidity, a linear multiple regression analysis has been performed along the lines discussed in the previous chapter. However, lithium and silica have been used as surrogates for weathering controls. Lithium and silica were chosen on the basis of data from Plynlimon which show that these elements are almost exclusively derived from within-catchment sources; the inverse relationships observed with flow indicate an essentially bedrock weathering source (Neal *et al.*, 1997g).

As there were very contrasting situations with both alkaline and acidic waters involved, the analysis was undertaken for these distinct water types (the data being divided on the basis of ANC=0) and for the full dataset to see if there were clear differences corresponding to contrasting hydrochemical provenance. The regressions for the full and ANC<0 and ANC>0 datasets provide respective r^2 values of 0.39 (N=390), 0.45 (N=285) and 0.49 (N=105) which are statistically highly significant ($p<0.001$). The coefficients obtained for sulphate and nitrate with aluminium, alkalinity, ANC and calcium are shown Figure 5.4. In the case of chloride, no statistically significant coefficients were obtained for any of the AIs for the ANC<0 and ANC>0 data sets, possibly due to the relatively small ranges in concentration. However, for the full dataset, a statistically significant relationship with ANC was observed with a regression coefficient of -0.22 μEq-ANC/μEq-Cl: because of this lack of a clear pattern, little further comment is made for this anion in the remaining text.

> *Sulphate*: there are clear, statistically significant positive relationships for alkalinity, ANC and calcium for the full and the positive ANC datasets, but no statistically significant results for the ANC<0 dataset other than with calcium. The overriding control of sulphate on these three AIs is one of weathering of the bedrock which leads to parallel increases in calcium and bicarbonate (as expressed as a positive term for alkalinity and ANC): cation exchange should give a negative relationship. There is no statistically significant effect for aluminium. At ANCs>0, more alkaline conditions pertain and aluminium would not be an important component in solution owing to aluminium hydroxide solubility controls (cf. Neal and Christophersen, 1989) while at low ANCs, sulphate concentration variations are sufficiently small to negate statistical identification of a cation exchange mechanism.
>
> *Nitrate*: there are statistically significant relationships for aluminium, calcium and ANC for the ANC<0 and the full datasets. In the case of aluminium, the relationship is a positive one, while for ANC, it is negative to the same degree as aluminium is positive. In contrast, alkalinity does not show a corresponding change to ANC. This pattern is consistent with increased acidity associated with nitrate generation being linked to aluminium solution (with concomitant ANC decline) and increased calcium. For the positive ANC data set, as nitrate varies alkalinity, ANC and calcium show corresponding changes. While this pattern is consistent with cation exchange theory for calcium, it is



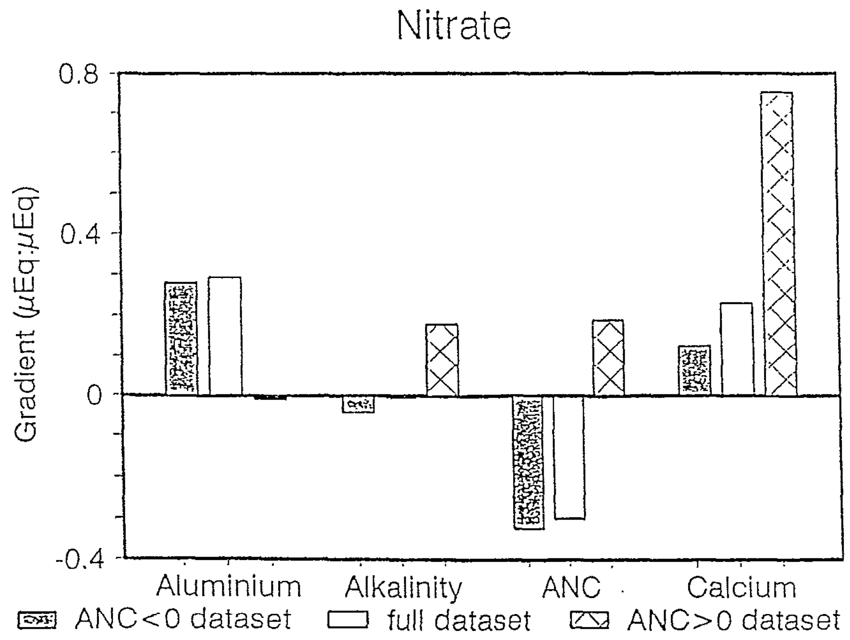


Figure 5.4 **Plots of average regression coefficients for aluminium, alkalinity, ANC and calcium against sulphate and nitrate.**

incompatible with theory for alkalinity and ANC. However, with nitrate generation and organic matter decomposition, carbon dioxide is also generated. This, in turn, will cause increased base cation weathering under less acidic to alkaline conditions and the promotion of bicarbonate generation within the water. It is probably this process which gives rise to the anomalous result.

5.3 Discussion

The survey results suggest that an alkaline groundwater component seems to be present even at the small catchment/hillslope scale. Thus, runoff chemistry is less acidic than might be expected from the analysis of waters directly extracted from the soil. This is consistent with the more recent findings at the Plynlimon catchments and they conclusively show a general characteristic and not simply a local anomaly. The results confirm that there is a high degree of variability in the chemistry of runoff from catchments draining apparently similar bedrock and soil types. Further, the results show that it is difficult to predict where groundwater will or will not provide an important source of alkaline inputs to either drainage waters or streams. For example, alkaline waters are observed at acid peaty gley sites even though intuitively, such an input would not be expected due to the supposedly impermeable nature of the lower soils. Further, more extreme high and low acidity waters occur at sites with more freely drained brown earth soils. In this case, it is extremely difficult to predict whether acid or alkaline conditions will prevail or even what an average case might be.

The results provide important clues on the importance of particular processes of which groundwater inputs is only one. For example, changes in ANC within catchments and associated runoff are linked to strong acid anion variations (nitrate, sulphate and chloride). Increases in any of these strong acid anions without a balancing increase from base cation weathering lead to increases in soil water acidity (Reuss and Johnson, 1986). Similarly, decreases in strong acid anions without compensating changes in base cation levels will lead to reduced acidity (Neal *et al.,* 1998a,b). In the present study, the main strong acid anion change with felling is nitrate and ANC also shows significant declines. However, the large nitrate increases only occur at about a sixth of the sites and for only a third of their values (ie about a fifth of the total number of samples collected). Correspondingly, ANC shows particularly low values at only six sites and for a total of ten values (ie about 5% of the data points). In contrast, chloride and sulphate show only small or non systematic variations in concentration across the sites. Thus, in its extreme, a nitrate pulse dominates the net strong acidification response to changing total strong acid anion concentrations but at some sites, the weathering term is sufficiently high to counteract the acidity generated with nitrate release. The multiple regression results show that increasing nitrate concentrations lead to aluminium release and ANC decline by about 0.3 μEq/μEq-NO_3, the remaining charge balance probably being linked to base cation release. This value is lower than that observed in a companion paper where a value of about 0.5 μEq/μEq-NO_3 was obtained. It seems that for the highly acidic sites monitored in the regional survey, greater nitrate production and acidity generation is taking place in the lower soils where aluminium is primarily available for leaching and cation exchange. In the case of sulphate, the positive link with alkalinity, ANC and calcium indicates the importance of sulphate weathering sources. Indeed, this result for sulphate may well have ramifications for long term acidification modelling associated with acidic deposition, where the sulphate weathering term is usually ignored: all sulphate being assigned to atmospheric sources.

With regards to the other determinands, the availability of certain trace metals such as cadmium, lead, zinc, actinides and lanthanides in the bedrock and iron, manganese and barium in the soils from particular localities within the region, does raise an issue of metals mobility. For the few detailed studies, such as at Plynlimon, where trace metal mobilization has been studied in upland areas, bedrock mineralization can lead to metal enrichment in the soils and release to the streams during highflow periods (Neal *et al.*, 1992e; 1997g). In the case of iron and manganese, soil disturbance can lead to releases to the stream for example in relation to DOC generation which complexes and stabilizes these reactive metals in solution.

The results of this study indicate that in many cases there is an insignificant hydrochemical response to felling. In exceptional cases, increased nitrate and potassium concentrations corresponding to those seen at several other sites are observed (Bormann and Likens, 1994; Hornung *et al.*, 1989; Reynolds *et al.*, 1995b; Neal *et al.*, 1998a,b): a small increase in barium concentrations in drainage water with felling is in line with observations for an area in the Hafren Forest at Plynlimon, mid-Wales (Neal *et al.,* 1992a,c). In the case of nitrate, preliminary examination of the site details of the survey catchments revealed that at the few sites with nitrate concentrations exceeding 160 μEq/l (10 mg-NO_3/l) most were those where (a) replanting and natural re-vegetation of the ground had not occurred following felling and/or (b) early autumn storm events had been sampled. This is in agreement with previous theoretical, laboratory and field based studies (Stevens and Hornung, 1988; 1990, Emmett *et al.*, 1991a,b) all of which have indicated that rapid re-vegetation of harvested areas is a major factor in reducing the duration of the nitrate leaching pulse.

In the case of the more alkaline situations (i.e. higher weathering regimes) the increased biological activity associated with nitrate generation may even promote ANC production due to the increase in carbon dioxide induced weathering. Indeed, simple calculations based on alkalinity and pH measurements (cf Neal *et al.*, 1997c,d) indicate that the higher alkalinity waters have carbon dioxide pressures two to ten times atmospheric levels. While this is relatively low for upland soil and groundwater situations, stream values should and usually are close to equilibrium with the atmosphere due to the high degree of degassing (Neal *et al.*, 1988a; 1997c). This weathering aspect may be of wider importance to acidification studies in that often the rate of weathering is taken as being constant, which, as some recognise (Sverdrup and Wafvinge, 1988; 1993; Sverdrup, 1996), it clearly need not be.

At sites where a nitrate felling response is seen, there is often a near balance between nitrate generation leading to increased stream acidification and reduction in strong acid anions (and possibly increased base cation concentrations due to enhanced weathering associated with carbon dioxide production) leading to reduced stream acidification and when set against other temporal variations in water quality, the net effect is often hard to discern. Indeed, if the average data for the survey are examined then it appears that the felled areas have a higher ANC than the forested sites: i.e. on average, acidity is reduced following felling (standing forest ANC averages -40 μEq/l and clearfelled sites average -5 μEq/l: Table 5.1): these differences are not statistically significant because of the high variability. The average behaviour is nonetheless precisely what acidification modelling predicts if the enhanced "nitrate signal" and carbon dioxide driven weathering is not incorporated (Neal *et al.*, 1986a). However, as with all aspects to this study, the heterogeneous nature of the catchments and the large range in chemical compositions makes quantitative evaluation difficult. For example, if the data are further subdivided with respect to time since felling and the influence of the extreme values is eliminated by using medians, then the following result is observed: ANC for standing forest, the first three years post felling (when nitrate extremes are observed) and greater than three years since fell, give median values and standard deviations (in brackets) of -42 (41), -19 (107) and -35 (74) μEq/l, respectively: none of the medians can be considered as statistically significant yet if these differences are actually representative one must view hydrochemical response in a different way: put bluntly, for all the hydrochemical processes bar nitrate production, the major effect of conifer harvesting is to increase alkalinity. This type of information also raises many fundamental questions: these include: how many samples are required to provide a thorough representation of the spatial variability across catchments and regions? How can one capture the significance of all the interacting chemical and physical processes at a representative level of scaling? How can the nitrogen signal with felling be minimised to ensure harvesting leads to an improvement in water quality?

6. THE NATURE OF WITHIN-CATCHMENT CONTROLS ON STREAM HYDROCHEMISTRY AND RESPONSES TO FOREST HARVESTING

6.1 Heterogeneity of upland systems

The results of this and associated postgraduate studies, when combined with the Plynlimon findings (Hydrology and Earth Systems Sciences, vol. 1(3)) show that the systems under study are highly heterogeneous in their chemical reactivities and water flow pathways. Further, for all the soil types, groundwater can provide an important component of acid neutralization. However, the extent of the chemical reactivity and water flow routing can only be gauged by direct measurement of stream chemistry owing to the apparently random nature of the variability. Indeed, the concept of there being "representative catchments" with predicable runoff chemistry for particular geology/soil/landuse combinations may at best prove elusive and may not even exist in practice. This complexity makes process based field and computer based modelling studies of these upland environments difficult even without the added constraints of other factors such as forestry, climate and atmospheric pollution which can affect soil and groundwater quality.

The highly variable nature of the underlying processes at the catchment and landscape scales has meant that in the analysis of the data contained within this report we have had to move away from the current trend of using catchment characteristics to assess regional water quality variation and land-use/atmospheric-pollution impacts. There remains a need to monitor water chemistry under both high and low flow conditions to determine the actual state of water quality across a region. For future monitoring programmes, we strongly recommend the scheme used in the regional survey as both relevant and cost effective at a range of scales.

6.2 Major anion variations and stream water acidity

Analysis of the data across the sites has revealed that the strong acid anions are affecting stream acidity but in a much more complex way than hitherto suggested by the paradigms used in contemporary environmental impact models. For example, the strong acid anions are not behaving in a uniformly similar manner. Further, it seems that the key acidification processes occurring in the soil reside in two geochemically contrasting layers (the upper and lower soils). In one layer (the upper soils) base cation and hydrogen-ion interactions seem important in relation to cation exchange mechanisms. In the other layer (the lower soils), base cation, aluminium and hydrogen-ion interactions become much more important due to weathering/leaching and possibly cation exchange. These distinct layers need to be considered separately in relation to data interrogation and environmental impact modelling. The differences in the behaviour of the major strong acid anions probably accounts for the mismatch between lumped cation exchange modelling and field observations with regard to the mobile anion concept (Neal *et al.*, 1992a, Neal, 1996). However, it is also clear that further understanding of basic processes is required, to address the issues of (1) unmeasured strong acid anions affecting the ANC, (2) changing carbon dioxide partial pressures on weathering rates, (3) aluminium solubility controls other than aluminium hydroxide and (4) the role of hydrology and element cycling through the vegetation in supplying base cations from the groundwater areas to the soil.

6.3 Stream water response to clearfelling

The results of this study reveal that clearfelling can sometimes lead to stream acidification over the duration of the nitrate pulse. However, the acidification resulting from nitrate generation must be balanced against the reduction in strong acid anion concentrations due to lower evapotranspiration losses (dilution by increased runoff) and decreased atmospheric scavenging. The results also reveal that the changes are small when compared with the scatter in the data. Thus, for example, while nitrate production with clearfelling clearly leads to a net acidification for the SE1 and KD2 sites during the earlier period following felling, the reduction in chloride and sulphate represents an important acid neutralization element that cannot be ignored. This is most graphically demonstrated for South2Hore where an initial acidification due to a nitrate pulse was more than offset by a subsequent increase in ANC when strong acid anion concentrations declined to values less than prefelling. Indeed phased felling within a catchment offers a way of both physically diluting and chemically neutralising the acidification effects of the nitrate pulse.

The net ANC decline during the nitrate pulse is seemingly large (15 to 90 μEq/l for the examples given earlier) in relation to environmental management indices such as critical load thresholds. However, these ANC changes are almost within the noise of the natural variations in the system and visual inspection of the time series data shows hardly any marked perturbation. Indeed, within the main channel of a stream receiving drainage from felled tributaries, the changes are obscured even further by natural water quality variability due to groundwater inputs which dilute and, in part, neutralize soil water runoff. Further, it seems unjustifiable, from visual examination of the time series data to argue that clearfelling has led to any major recognisable deterioration in ANC at any of the deforested sites even though the harvested sites were clearfelled over a short period to maximize the potential changes. The clearest change occurs within the lower Hore under base-flow conditions, but even here graphical smoothing techniques were needed to pick up any clear patterns (Neal *et al.*, 1992a,c; 1997g). Even with more sophisticated statistical and graphical techniques, it remains difficult to assess with any high degree of accuracy what the net changes in acidity will be with harvesting, owing to the highly variable nature of the reactions involved and the difficulty of predicting how the individual strong acid anion concentrations will change over time. Despite all the difficulties and uncertainties, the most problematical time for a deterioration in water quality probably occurs under two circumstances:

1. when the balance between nitrate generation and strong acid anion reduction is weighted towards nitrate production, particularly at times of high flow when acid conditions are most extreme;

2. when the total strong acid anion concentrations are at their highest (after allowance for their differing rates of acidification for the individual anions). This for example could occur in the early autumn after dry periods when evaporative concentration of strong acid anions and nitrate generation will be at its highest and also at times when the atmospheric input of sea-salts is at its highest.

6.4 Soil nitrogen transformations following forest harvesting

Early predictions indicated that felling of conifers would result in only small increases in stream water nitrate concentrations in the British uplands (Heal *et al.*, 1982). However, the pulse of nitrate-N in streams draining clearfelled areas has been widely observed both in the UK (the present study and elsewhere: e.g. Adamson and Hornung, 1990) as well as in other temperate regions of the world (e.g. Likens *et al.*, 1978; Bormann and Likens, 1994; Vitousek *et al.*, 1979).The mechanisms responsible for the nitrate pulse have been studied in detail at Beddgelert forest amongst other places (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 may also be a further significant source of nitrogen after felling.

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 (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 whole tree harvested (WTH) plots at Beddgelert, compared with those harvested conventionally (CH), was a major factor in reducing the duration of the nitrate pulse (Stevens and Hornung, 1990; Emmett *et al.*, 1991a,b). Vegetation also played an important role in the Swedish study, as root uptake was much reduced under brash piles compared with clear and revegetated 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. Contrasting behaviour was evident from clearfelling studies on peaty gley soils in northern England (Kielder forest) which did not nitrify freely and where much of the runoff occurred laterally below the forest floor, especially after felling when the water table rose (Titus and Malcolm, 1992). Ammonium-N dominated the inorganic-N losses at Kielder for at least 7 years after felling during which time the site remained virtually free of vegetation (Titus and Malcolm, 1992) in contrast to Beddgelert. 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 have indicated that nitrification was periodically inhibited by waterlogging and anaerobic conditions resulting from the rise in water table following felling (Reynolds *et al.*, 1989, 1992).

In conclusion, the generation of the nitrate pulse at felling will depend largely on the capability of the soil to nitrify ammonium released from mineralisation of organic-N and on the rate at which vegetation cover develops. Whilst the latter can be controlled by site management and harvesting techniques, the soil nitrification response is an intrinsic site property probably reflecting site nitrogen deposition and land use history. There is evidence from work on atmospheric nitrogen pollution that in freely drained soils, forest floor C/N ratio is a good predictor of the likely nitrate leaching response of soils to incoming nitrogen (Emmett *et al.*, 1993). For stands with a high denitrification potential (poorly drained soils), there is likely to be less nitrate leaching. Thus, in highly sensitive areas, it may be possible to predict the nitrate leaching potential of a site from an analysis of the forest floor and an assessment of the denitrification potential.

6.5 Long term changes in soil base cations stores with repeated harvesting: potential controls on water quality

The overall balance between base cation losses from biomass removal and accelerated leaching losses at harvesting and inputs from atmospheric deposition and weathering are likely to prove crucial to the long-term sustainability of second and subsequent conifer crops growing on acid upland soils.

6.5.1 Assessing soil calcium depletion using a mass balance approach

There is widespread concern over the potential for nutrient depletion following repeated tree harvesting and potential problems have been identified from the tropics (e.g. Bruijnzeel, 1990) and particularly from the United States (Smith *et al.*, 1986; Johnson and Todd, 1987; Johnson *et al.,* 1988; Hornbeck *et al.*, 1990). The significance of nutrient removal in harvest products varies from nutrient to nutrient and with harvesting regime (Morris and Miller, 1994). In the UK, there are unlikely to be any major effects of repeated harvesting on nitrogen status and availability as inputs of nitrogen from the atmosphere more than compensate for losses at harvest (Stevens *et al.,* 1988; 1993; 1995). In contrast, potential problems have been identified with phosphorus, potassium and/or calcium depletion (Carey, 1980; Anderson, 1985; Stevens *et al.*, 1988; Goulding and Stevens, 1988). For calcium, the overall balance between losses from biomass removal at harvesting and inputs from atmospheric deposition and weathering are likely to prove crucial to the long-term sustainability of second and subsequent conifer crops growing on acid upland soils with a low calcium content. Significant depletion of the soil calcium reserve may also have important implications for soil and stream water acidification (Berden *et al.,* 1987).

One approach to the assessment of long-term nutrient depletion is by complete characterisation of the nutrient cycle through a combination of measurement and dynamic modelling (Morris and Miller, 1994; Currie *et al.*, 1996). However, a simpler approach has been adopted here in which a rotation length calcium budget for Sitka spruce growing in the Welsh uplands has been calculated utilising data from a chronosequence of 20 stands ranging in age between 10 and 55 years (Stevens *et al.*, 1994). The calculations have been supplemented by information on tree biomass calcium content taken from the literature (Miller *et al.*, 1993, Carey and O'Brien, 1979). For ease of calculation with respect to the available data, the rotation length has been set at 50 years.

Methods

A simple mass balance approach has been taken in order to assess the effects of forest growth and harvesting on the soil calcium pool. The mass balance has been calculated with respect to inputs and outputs from the soil within the standing forest. In the first rotation, the forest floor is considered as a separate pool distinct from the soil profile in order to evaluate changes in soil calcium status compared to non-forested land. The effects of harvesting and growth of the second rotation crop are considered separately. Thus for the standing forest, the calcium budget for a 50 year rotation can be expressed as a mass balance equation:

$$Ca_{dep} + Ca_{w} + Ca_{veg} - Ca_{bio} - Ca_{ff} - Ca_{le} = \Delta P_{Ca} \qquad (6.1)$$

where:

Ca_{dep} = wet + dry calcium deposition to the forest over 50 years
Ca_{w} = accumulated weathering input of calcium
Ca_{veg} = release of calcium from pre-existing ground vegetation
Ca_{bio} = calcium accumulated in tree biomass at 50 years of age
Ca_{ff} = calcium accumulated in forest floor after 50 years
Ca_{le} = total calcium leaching losses from below the rooting zone
ΔP_{Ca} = change in soil calcium pool over 50 years
Units = kg ha^{-1}

The chronosequence of Sitka spruce stands were located as five groups of four sites in each of Beddgelert, Dyfnant, Dyfi, Hafren and Twyi forest areas in north and mid-Wales. Within each group, precipitation chemistry was sampled at a site on adjacent open moorland using a continuously open collector which was emptied monthly. Each of the forest sites was instrumented with throughfall collectors which were also emptied monthly (Stevens *et al.,* 1994). Calcium deposition to the moorland sites was calculated as the annual sum of the product of monthly bulk precipitation chemistry and monthly rainfall. Total calcium deposition to the spruce canopy of each forest stand was estimated using the simple ratio technique proposed by Sverdrup *et al.* (1990), in which it is assumed that sodium is unaffected by canopy leaching and ion exchange processes, so that a scaling factor for dry deposition can be calculated as the ratio of sodium inputs in throughfall to those in wet deposition. Total deposition of calcium to each spruce stand was estimated by multiplying the wet deposited calcium by the sodium scaling factor (Reynolds, 1996). There is a significant non-seasalt component to calcium deposition in Wales (Donald and Stoner, 1989) so that it is possible that calcium inputs are underestimated by a scaling technique which relies on an ion derived almost entirely from seasalts. The extent of this underestimation is unknown. An alternative estimate of deposition is provided by calcium in throughfall, however this contains an unknown canopy leaching component of calcium cycled through the tree and will thus overestimate deposition inputs. A recent study of 12-year-old Sitka spruce in which atmospheric inputs of calcium were modelled independently indicates that about thirty percent of the calcium in throughfall is derived from canopy leaching (Reynolds *et al.,* submitted).

Analysis of variance of the calcium deposition data showed that there were no statistically significant effects of either age or site location. Therefore the arithmetic mean deposition to the 20 stands was considered to be the best estimate of annual deposition to the trees between 10 and 50 years of age (Table 6.1). Annual deposition from years one to nine was estimated by ramping the average annual deposition to the five moorland sites (Table 6.1) up to the average for the established forest to account for the effect of the increasing forest canopy.

Table 6.1 **Mean (and standard deviation) of calcium deposition and leaching losses for moorland and forest sites in upland Wales.**

	Atmospheric deposition kg ha^{-1} yr^{-1}	Leaching loss kg ha^{-1} yr^{-1}
Moorland	3.97 (0.55)	4.95 (1.66)
Forest	6.35 (1.64)	4.60 (2.84)

It was assumed that the forest calcium cycle would be calculated for trees growing on stagnopodzol soils developed from Lower Palaeozoic greywackes. The input of calcium from weathering was estimated for the soil profile using data from Plynlimon and Beddgelert giving the rate of calcium depletion over the last 10,000 years, relative to the stable mineral components zirconium and rutile (Langan *et al.*, 1996). The figure (0.2 kg ha^{-1} yr^{-1}; Table 6.2) which is based on direct measurement of changes within the soil is very close to the average weathering rate using rainfall and stream water data as predicted by the PROFILE model (Sverdrup and Warfvinge, 1993) but is much smaller than values calculated from catchment mass balance (16.4 kg ha^{-1} yr^{-1}) and from earlier applications of the MAGIC model to Welsh upland catchments (13.7 kg ha^{-1} yr^{-1}). The discrepancy between soil and catchment based estimates is indicative of contributions beneath the soil profile from deeper weathering sources within the drift and bedrock which may, in some cases, be influenced by the presence of rapidly weathering carbonate minerals. This source of weathering has been confirmed by the presence of highly alkaline, base cation enriched groundwater in many upland Welsh catchments underlain by Lower Palaeozoic shales and mudstones (Neal *et al.,* 1997a,b,f).

Table 6.2 **Summary of calcium weathering rates for Lower Palaeozoic mudstones and shales in upland Wales.**

Method	Weathering rate kg ha^{-1} yr^{-1}	Reference
Soil profile element depletion (2 sites)	0.20	Hornung *et al.* 1987; ITE unpublished data
PROFILE model (3 sites)	0.21	Reynolds *et al.* 1995a; Reynolds *et al.* in press
Catchment mass balance (4 sites)	16.37	Reynolds *et al.* 1987; Reynolds *et al.* 1997a
MAGIC model (3 sites + 1984 Welsh regional acid waters survey)	13.67	Whitehead *et al.* 1988a Whitehead *et al.* 1988b Jenkins and Wright 1992 Jenkins *et al.* 1990

The pre-existing moorland vegetation is gradually shaded out as the forest closes canopy and it therefore provides a potential source of calcium to the first forest rotation. The quantity of calcium present in the moorland vegetation was estimated using biomass data from open moorland adjacent to Aber forest in north Wales (Emmett *et al.*, 1997) combined with measurements of calcium content taken from a site with similar vegetation at Llanbrynmair in mid-Wales (Reynolds *et al.*, in press). For the budget calculation, it was assumed that all the vegetation will have decomposed during the 50 years releasing all the calcium.

Calcium data for the above-ground components of fifty year old Sitka spruce have been published by Miller *et al.* (1993) for Scotland and by Stevens *et al.* (1988) for Wales and these results have been used in this budget. Total above ground biomass calcium content measured in the two studies was very similar at 281 and 279 kg Ca ha^{-1} respectively so an average value of 280 kgCa ha^{-1} has been used for this budget. From the two studies, an average of 58% of the above ground biomass calcium is held in the stem (wood + bark) and 42% in needles and twigs (Table 6.3).

Table 6.3 **Calcium held in the various biomass components of 50 year old Sitka spruce. Values calculated from data published by Carey and O'Brien (1979); Stevens *et al.* (1988) and Miller *et al.* (1993).**

Biomass component	Calcium pool (kg Ca ha^{-1})
Stem (wood + bark)	162
Needles & twigs	118
Total above ground	280
Coarse roots	24
Fine roots	11
Total below ground	35
Total tree	315

Few data are available describing nutrient pools in below ground biomass of Sitka spruce. From data published by Carey and O'Brien (1979) for 33 year old, unthinned Sitka spruce, coarse woody roots account for 15% and fine roots about 1% of the total tree biomass on a dry weight basis. The contribution of roots to total biomass probably changes as the stand develops, but as no information is available about this effect it was assumed that the proportions remained constant with age. Assuming that the above ground biomass of 50 year old Sitka spruce is 300 tonne ha^{-1} (Miller *et al.*, 1993), then total tree biomass can be estimated as 357 tonne ha^{-1} of which 53.5 and 3.5 tonne ha^{-1} will be associated with coarse and fine roots respectively. In the absence of any specific calcium data for these components, it was assumed that the calcium concentration in woody roots was the same as that published for stem wood by Miller *et al.* (1993), whilst the calcium content of fine roots was assumed to be similar to that of needles. From this, 24 kg Ca ha^{-1} is estimated to be held in coarse woody roots and 11 kg Ca ha^{-1} in fine roots (Table 6.3).

As the 50 year old forest stands in the chronosequence were all first rotation, the calcium accumulated in the forest floor over the rotation was measured directly by sampling L and F horizon material at each 50 year old site (Emmett *et al.*, 1993). This removed the need to calculate the accumulated calcium as the difference between calcium returned in litter and that mineralised from the forest floor. The forest floor calcium at 50 years represents the net change to this store over the period of forest development and assumes that any calcium mineralised from litter during forest growth is accounted for either by biomass uptake or in leaching losses.

Leaching losses from the forest and moorland sites were calculated as the product of the modelled annual flux of percolating water (Emmett *et al.*, 1993) and the annual volume-weighted average of monthly B horizon soil water calcium concentrations sampled using suction lysimeters (Stevens *et al.*, 1994). Suction lysimeters sample soil solution from the bulk of the soil matrix and this may not be of the same chemical composition as water moving rapidly through macropores in response to storm events. Further, the lysimeters give a time-integrated sample over the measurement period. It is uncertain, therefore, to what extent the suction lysimeter samples represent the chemistry of water freely percolating through the soil. However, the forest soils are very wet for much of the year and there is likely to be good connectivity between the sampled and percolating water.

The flux of percolating water for each forest site was calculated from an evaporation model published by Calder (1990) in which total evaporation was predicted from the sum of interception loss plus transpiration. The transpiration term was calculated from daily Penman evapotranspiration estimates based on climatological data collected in each forest area (Emmett *et al.*, 1993), multiplied by the transpiration fraction (β; Calder, 1990) and the fraction of time for which the canopy was dry (Calder and Newson, 1979). Interception loss was calculated as the difference between rainfall and throughfall measured at each site.

Analysis of variance performed on leaching data from the forest sites showed no statistically significant effects of either forest age or site location. Therefore the arithmetic mean leaching loss for the 20 forest stands was considered to be the best estimate of annual leaching losses from stands between 10 and 50 years of age (Table 6.1). Annual leaching losses from the stands between one and nine years old was estimated by ramping the average annual leaching loss from the five moorland sites (Table 6.1) down to the average for the mature forest.

The total reserves of calcium and the amount held in exchangeable form have been calculated for acid peaty podzol soils beneath Sitka spruce of different ages at sites in north and mid-Wales (Table 6.4). This soil is developed from base-poor Lower Palaeozoic mudstones and shales and is a common forest soil type throughout the uplands of Wales. The soil exchangeable calcium reserves for Plynlimon (Table 6.4) were calculated using chemical data from Reynolds *et al.* (1988) whilst estimates of total soil calcium used unpublished total silicate analyses from the British Geological Survey. For Beddgelert, soil exchangeable and total calcium analyses were from unpublished ITE and INRA (Nancy) sources respectively. Bulk densities and soil depths were measured at the sites using standard techniques (Hodgson, 1976). Soil chemistry, horizon depth and bulk density data for Llanbrynmair and Llyn Brianne were taken from Reynolds *et al.* (in press) and Soulsby (1991) respectively. Total calcium chemistry for each horizon at Llyn Brianne came from Kennedy (1997).

Table 6.4 Calcium reserves in peaty podzol soils planted with Sitka spruce in north and mid-Wales.

Site	Forest age (yr)	Profile depth (m)	Depth to base of B horizon (m)	Total Ca to bottom of profile (kg ha^{-1})	Total Ca to base of B horizon (kg ha^{-1})	Exchangeable Ca to bottom of profile (kg ha^{-1})	Exchangeable Ca to base of B horizon (kg ha^{-1})
Plynlimon	40	0.77	0.37	3660	1591	270	173
Beddgelert	55	0.75	0.46	2299	1389	141	112
Llanbrynmair	12	na	0.65	na	1141	na	na
Llyn Brianne	30	0.81	0.55	2519	1557	278	197
Mean (std dev)		0.78 (0.02)	0.51 (0.10)	2826 (597)	1420 (178)	230 (63)	161 (36)

na: no data available

Results and discussion

The calcium balance sheet with respect to the soil for a 50 year old standing crop of Sitka spruce is shown in Table 6.5. The balance shows that to grow the forest stand and develop the forest floor required depletion of the soil calcium pool by 205 kg Ca ha^{-1}. This is of the same order of magnitude as the exchangeable calcium pool to the base of the C horizon of the stagnopodzol soil to a depth of about 80 cm (Table 6.4) and is equivalent to 7% of the total calcium pool to this depth. However from detailed soil profile descriptions at Plynlimon, Beddgelert Forest and Llyn Brianne, Sitka spruce roots rarely penetrate below the bottom of the B horizon at a depth of about 50 cm (Reynolds *et al.*, 1988, Soulsby, 1991). To this depth, the exchangeable calcium pool is 161 kg Ca ha^{-1}, or 11% of the total calcium (1420 kg Ca ha^{-1}) to the bottom of the B horizon. If the calcium accounted for by soil depletion is derived from the exchangeable cation pool and mineral weathering rates are assumed to be constant at the low value of c. 0.2 kg Ca ha^{-1} yr^{-1}, then a large decline in exchangeable calcium should occur during forest development. However data from Plynlimon indicate that this is not the case, as the exchangeable calcium reserve in the forest soils (173 kgCa ha^{-1}) is only slightly smaller than that measured to the same depth in stagnopodzol soils under unimproved grassland (193 kg Ca ha^{-1}). A similar result was obtained at Beddgelert forest in North Wales, where ITE unpublished data show no differences in exchangeable calcium between stagnopodzols beneath a fifty year old first rotation spruce stand and those under adjacent semi-natural acid grassland. One explanation for this is that the presence of the forest has increased mineral weathering rates above long-term values and those predicted by modelling of soil chemistry, thereby allowing the exchange complex to be maintained whilst calcium is taken up into biomass. In a review of changes in soil chemistry beneath Swedish forests, Binkley and Hogberg (1997) come to a similar conclusion. There are a number of mechanisms by which this could occur including i) the effects of pre-planting cultivation and drainage in breaking up the soil and increasing access for water, ii) changes in the nature and acidity of accumulated organic matter, iii) increases in soil pCO$_2$ accompanying the enhanced rates of organic matter mineralisation in forest compared to moorland soils (Emmett *et al.*, 1997) and iv) increased exploration of the soil by tree roots compared to moorland vegetation. A further possibility is that under dry conditions, trees may cause upward movement of shallow 'groundwater' which is enriched in calcium and there may be lateral movement of such water into down slope sites.

An important caveat attached to the interpretation of mass balance calculations is the size of the possible errors associated with each of the terms. Atmospheric deposition and leaching comprise two of the largest terms in equation 6.1 and both are associated with major uncertainties. Averaged over 50 years, the imbalance in calcium amounts to approximately 4 kg ha^{-1} yr^{-1} which is of the same order as the annual deposition and leaching rates. An estimate of the variation in these is given in Table 6.1. The effect of this variation on the calcium budget can be illustrated by recalculating the mass balance using 'best' and 'worst case' scenarios of the atmospheric deposition plus/minus one standard deviation combined with the leaching loss minus/plus one standard deviation. This gives ΔP_{Ca} values of +5 and -414 kgCa ha^{-1} respectively. Thus, with the largest atmospheric inputs and lowest leaching losses, the calcium budget is approximately in balance.

Stem-only harvesting is the most commonly practised technique in UK upland forests in which branches, needles and roots are left on site whilst only the stem (wood + bark) are removed. Whole tree harvesting, in which all the above ground material is removed from the site, is much less common although it has been used in some Welsh forest districts. Restocking normally follows within two years of whichever harvesting method is used.

Although the removal of calcium in harvest products has been examined in previous UK studies (Stevens *et al.*, 1988; Miller *et al.*, 1993), these have tended to focus on site nutrient depletion and have not fully considered the effects on the soil. Depending on the technique used, several potential sources of calcium remain on site which can offset the drain on the soil reserve caused by growth of the second rotation crop. Following stem-only and whole-tree harvesting, calcium accumulated in the forest floor (44 kgCa ha^{-1}; Table 6.5) and the below ground biomass (35 kgCa ha^{-1}; Table 6.3) is potentially available to the next crop amounting to 79 kg Ca ha^{-1}. If stem-only harvesting is used, this can be supplemented by a further 118 kg Ca ha^{-1} from the twigs and needles left on site (Table 6.3). Assuming that 1) there are no accelerated leaching losses of calcium at harvesting, 2) that the nutrient dynamics of the second crop are the same as those of the first with respect to atmospheric deposition, weathering rates, leaching losses, biomass and forest floor accumulation and 3) that all the calcium accumulated in forest floor, forest debris and below ground biomass are available to the next rotation, then the net change in the soil calcium pool after 50 years of second rotation forest following stem-only harvesting would be -79 kgCa ha^{-1}. Due to the absence of felling debris the net change in the soil pool after 50 years of forest growth following whole-tree harvesting would be -197 kgCa ha^{-1}.

Table 6.5 **Soil calcium balance sheet for a first rotation, 50 year old standing crop of Sitka spruce growing on peaty podzol soils in the Welsh uplands.**

Inputs	**Flux (kg Ca ha^{-1})**
Atmospheric deposition	300
Soil mineral weathering	10
Release from pre-existing ground flora	71
Total input to soil	381
Outputs	
Leaching losses	227
Tree biomass	315
Forest floor accumulation	44
Total output from soil	586
Balance ΔP_{Ca}	-205

These predictions of soil calcium depletion rest crucially upon the stated assumptions. Data from experimental studies at Beddgelert forest (Stevens *et al.*, 1995) provide some insight into the short-term effects of harvesting on the soil calcium economy. Calcium leaching from the felling debris at Beddgelert four years after harvesting (Table 6.6) was equivalent to 31% of the total amount present in brash (128 kgCa ha^{-1} ; Stevens *et al.*, 1995) and it appears that the majority of this calcium was lost from the site. A further 10 kgCa ha^{-1} was lost from the soil to the bottom of the surface organic layer (Oh horizon), presumably from mineralisation of fine roots and / or forest floor material. The re-establishing vegetation retained 9 kgCa ha^{-1} and this would potentially be available to the next crop. In contrast, calcium leaching losses following whole-tree harvesting were only marginally greater than rainfall inputs with only 3 kgCa ha^{-1} being mobilised and lost from the soil organic and litter layers. Re-establishing vegetation retained 14 kgCa ha^{-1}. Thus whilst approximately the same amounts of calcium were mobilised from the soil under the two harvesting treatments, approximately 50% of this calcium was lost from the stem-only harvested site because there was less retention in the re-establishing vegetation. However, at the end of four years, the pool of calcium held in felling debris and re-established vegetation amounted to 97 kgCa ha^{-1} in the stem-only harvest site, compared to 14 kgCa ha^{-1} in the whole-tree harvest site where there was no felling debris present.

Table 6.6 Calcium fluxes to and from the soil over a period of 4 years following harvesting of Sitka spruce at Beddgelert forest (summarised from Stevens *et al.* 1995).

External inputs to soil	Stem-only harvesting kgCa ha^{-1}	Whole tree harvesting kgCa ha^{-1}
Rainfall	29	29
Leached from brash	40	0
Total inputs	69	29
Outputs from soil		
Re-vegetation	9	14
Leaching losses	79	32
Total losses	88	46
Inputs - Outputs	-19	-17

On most upland soils in Wales, crops would generally respond to phosphate fertiliser applied at or around year eight (Taylor, 1991) and rock phosphate is now the main type of fertiliser used. Although the chemical composition is variable, rock phosphate (Gafsa phosphate) typically contains 37% calcium by weight (Edwards, pers comm, 1998). The recommended application rate to supply 60 kg ha^{-1} of phosphorus is 450 kg ha^{-1} of rock phosphate which would add 166 kgCa ha^{-1} to the forest. Thus, as noted by Nisbet *et al.* (1997), rock phosphate provides a relatively large potential source of calcium to the soil, equivalent to about 80% of the depleted calcium in the first rotation, assuming that the fertiliser calcium is completely available. For the second rotation following stem-only harvesting, calcium from rock phosphate would be more than adequate to offset the drain on soil reserves, whilst it would offset about 84% of the depleted calcium following whole-tree harvesting. Whilst the soil calcium mass balance would appear to be satisfied by calcium phosphate additions, the key issue is the extent to which this potential calcium source is actually available to either the growing crop and/or the soil exchange complex. This remains an area of uncertainty which needs to be resolved and it is clear that there are two lines of evidence that indicate that calcium depletion may be low with restocking. Firstly, Forestry Commission records show that no rock phosphate was applied to the parts of Beddgelert forest sampled for soil exchangeable calcium content. In this case, the lack of evidence for depletion in soil exchangeable calcium, inferred from a comparison with adjacent grassland soils, cannot be attributed to calcium from rock phosphate. Secondly, for the regional surveys, one site (B16) comprised a second generation mature forest and yet the stream water quality was very similar to that for the first generation forest.

Conclusions

The simple rotation-length mass balance approach indicates that development of a 50 year old stand of Sitka spruce on acid upland soils in Wales will deplete the soil calcium reserve by an amount approximately equivalent to the exchangeable calcium pool. This amounts to 14% of the total soil calcium reserve to the bottom of the main rooting zone (base of B horizon). For Wales, fertilizer applications are rarely required and hence calcium additions from this source is not significant for the area. Despite these predictions, measurements of exchangeable calcium show no differences beneath mature forest and acid grassland, implying that one or more of the following comments is appropriate: 1) weathering rates in forest soils are greater than long-term estimates or model predictions 2) the trees can access other sources of calcium and 3) there are significant errors in the mass balance. A central uncertainty to the mass balance approach is that it assumes that all sources of calcium are equally available to the crop. This can only be resolved by dynamic modelling of the calcium cycle at the ecosystem scale based on appropriate field measurements.

Forest harvesting techniques have a major influence on the soil calcium balance for the second rotation crop. Assuming that the calcium in the organic remains (roots, forest floor, needles and branches) of the first rotation are fully available to the second crop, depletion of soil calcium by growth of the second crop is much smaller following stem-only harvesting compared to either whole-tree harvesting or the development of the first crop. After the first crop (felled at 50 years), stem-only harvesting would allow a further 18 rotations before depletion of the total calcium reserve to the bottom of the B horizon. Whole-tree harvesting would allow for seven rotations after the first crop. The potential for significant soil acidification, defined as a depletion of the base cation store, is therefore much greater following whole-tree harvesting. In line with current recommendations (Nisbet *et al.*, 1997), this technique should probably be avoided on acidic, nutrient-poor soils unless remedial measures are included to enhance the soil base cation status, for example, by addition of rock phosphate fertiliser.

6.5.2 Long-term dynamic water quality modelling

While the mass balance approach described above can give some indication of the potential changes in cation exchange stores, it does not provide the required information on the effects of these changes on runoff chemistry. Several models have already been produced which can simulate changes in soil and stream water chemistry in response to changing land use and atmospheric deposition scenarios. However, at present (1) the underlying processes are not sufficiently understood for us to provide confidence in the future predictions of forestry impacts and (2) many of these processes are not directly represented within current models. Our concerns, which stem from the findings in the previous section as well as earlier in the report, centre on the lack of knowledge about:

> The actual atmospheric deposition fluxes of base cations, particularly from aerosols and particulate phases, through the forestry cycle;
>
> The differing nature of the cation exchange and aluminium leaching processes in the upper and lower soils;
>
> The nature of base cation cycling: the various fluxes of base cations are poorly defined particularly with regards to groundwater-soilwater interactions, litter organic matter decomposition rates and uptake into the growing biomass;
>
> The heterogeneous nature of the catchment responses: i.e. different parts of catchments as well as different catchments will respond in different ways and generalizations may well be inappropriate;
>
> The nature of the chemical weathering reactions: e.g. weathering rates may well be related to carbon dioxide partial pressures and kinetically mediated according to the pH of the groundwater and soil water systems.

Present modelling using the major approach taken in the UK (the MAGIC model; Cosby *et al.*, 1985a,b; Jenkins and Cosby, 1989; Jenkins *et al.*, 1990, 1997a,b; Whitehead *et al.*, 1988a,b) predicts that forest development can lead to stream acidification with ANC declines in the order of 40 μEq/l as shown for example in Table 6.7. for a simulation for the Hafren forest. The table illustrates one of the strengths of the modelling approach in that it allows an assessment of "what if scenarios" in a dynamic process based framework whose predictions are not easy to envisage by any other means. The simulation in this case shows that baseflow and stormflow chemistry change to differing degrees if base cation uptake into the growing biomass comes from the soil or the groundwater zones. The net effect of reafforestation for high flows, when water quality is most environmentally harmful, is a deterioration; without forest replanting it is predicted that water quality improves in the long term. Nonetheless, the simulations are only as good as the assumptions made in the model and the questions raised above suggest that the present simulations may well represent a worst case scenario for at least one forest rotation. Limitations of a finite pool of calcium in the rooting zone of the soil may provide a more severe acidification after several rotations than the model would predict. However, if weathering rates increase with forest development and base cations can come from the groundwater zones, then it could easily be envisaged that reafforestation would result in no deterioration in water quality. Indeed with replanting of deciduous trees improvements might easily accrue as they are more deeply rooted and have a lower efficiency for scavenging of atmospheric pollutants. Thus, the predicted change with replanting can cover a wide spectrum from major acidification to potential improvement. While the present simulations and speculations provide a guide, it is essential that there are further iterations between process based and modelling studies in order to develop a more convincing representation of these highly heterogeneous systems and hopefully more reliable predictions.

Table 6.7 **Simulations of ANC through a forestry cycle for the Hafren Forest catchment, based on the approach of Jenkins *et al.* (1997) as developed using the MAGIC model in a two-box mode representing soil and groundwater stores. For the simulation, base cations uptake in to the biomass has been supplied separately from the soil and groundwater stores so as to show the range of potential responses. The data provide ANC values in μEq/l for the soil, the groundwater and the flow weighted average stream water. Two scenarios are considered: clearfelling with no replanting and clearfelling with replanting.**

	uptake from soil		**uptake from groundwater**	
	clearcut with no replanting	**clearcut with replanting**	**clearcut with no replanting**	**clearcut with replanting**
		baseflow		
1991	29.9	29.9	26.8	26.8
2001	28.7	28.1	60.4	23.8
2011	27.1	24.0	90.6	-18.5
2021	25.6	20.1	126.7	3.7
2031	23.9	13.8	149.8	10.8
2041	22.7	6.9	168.6	42.0
		stormflow		
1991	-44.8	-44.8	-38.2	-38.2
2001	-44.2	-49.9	-35.5	-38.8
2011	-36.7	-65.9	-28.7	-45.8
2021	-32.9	-70.9	-26.2	-45.8
2031	-29.1	-85.1	-23.9	-53.6
2041	-25.3	-79.7	-21.3	-51.8
		flow weighted average for stream		
1991	-29.0	-29.0	-24.4	-24.4
2001	-29.1	-33.6	-15.7	-25.6
2011	-23.3	-47.1	-3.9	-40.1
2021	-20.2	-51.6	5.5	-35.5
2031	-18.3	-64.3	12.5	-40.2
2041	-15.2	-61.3	18.7	-32.2

7. SCIENTIFIC CONCLUSIONS

The data show that for many chemical determinands, changes associated with fluctuations in atmospheric deposition and climate can be as large as, or even greater than, the impacts of clearfelling. In particular, there are significant decadal scale changes for chloride, anthropogenic sulphur and heavy metals such as zinc both within rainfall and stream runoff which are linked to fluctuating patterns of atmospheric transport from contrasting maritime and industrial sources. In addition, there are surprising atmospheric inputs and stream outputs of chromium and fluorine, clearly of anthropogenic origin, which are of unknown source. For nitrate, there are no systematic changes within rainfall. However, clear increases in nitrate concentrations occur within the streams following extreme dry periods. These increases remain for several years and clearly the dry periods have triggered changes in catchment nitrogen cycling processes. The results indicate that measurement even on decadal scale is far too short to distinguish long-term patterns of climate change from trends associated with atmospheric deposition and land-use change.

For all the larger streams, there is a marked contrast between stormflow and baseflow waters. Under stormflow conditions, waters are mainly derived from the more acidic soil layers and hence runoff is characteristically acidic and aluminium bearing. In contrast, under baseflow conditions, much of the stream flow is supplied from the lower soil and groundwater zones where weathering reactions ensure that part of the acidity generated in the upper soils is neutralized and the waters are therefore more alkaline and bicarbonate and calcium enriched but depleted in aluminium. Exploratory boreholes have confirmed the presence of such alkaline groundwater across the Plynlimon catchments, at Beddgelert Forest in north Wales and at Vyrnwy in north-central Wales. For the smaller streams, water chemistry varies considerably from site to site. Sometimes it is highly acidic, enriched in DOC and aluminium as would be expected in streams dominated by drainage from acidic peaty soils. However, even for surface runoff at small sites there is a high degree of variability in the chemistry of runoff and alkaline conditions are observed at some sites. Thus it seems that even for the small catchment sites where soil water would be expected to dominate the surface runoff, groundwater can provide a significant but erratic contribution. Overall, the results provide a clear picture of the complexity of the hydrochemical functioning of upland catchments and the difficulty of predicting afforestation, clearfelling and reafforestation effects on water quality irrespective of fluctuations driven by climatic variability and patterns of pollutant deposition. This complexity arises not because of the processes themselves, which are inherently simple, but because of their interactions within a very heterogeneous system both in space and time.

Despite the complexity of the interacting hydrochemical and biological processes, some common behaviour can be identified in response to forest harvesting which relates to a disruption of the biological system and a change in the physical characteristics of the site. The biological response within the soil is manifest by the common overriding increase in stream water concentrations of nitrate and potassium at felling together with phosphate and ammonium mobilization with iron for the catchments with gley soils. This increase lasts for a few years (<5) across all scales and the duration and intensity of the changes are determined by the proportion of area of catchment felled, the type of harvesting, the rapidity of revegetation and soil type. Within the biological response, there are associated direct and indirect effects in the soil related to acidification and changes in dissolved organic carbon production. These effects can introduce inorganic aluminium, hydrogen ions and DOC into surface waters, but the response is mainly small, often within the noise of the natural variability. Some of the changes may be hidden when soil chemical variations alone are considered. For example, phosphorus and iron can undergo solutional processes but their high chemical reactivity often results in strong binding to particulate material, precipitation of low solubility minerals and biological uptake, thus immobilizing these elements within the catchment. The physical response of felling is evident in a decrease in the atmospherically derived components, from sea salts to pollutants such as heavy metals and sulphur as well as base cations. This relates to the removal of the aerodynamically rough forest canopy which otherwise enhances the capture of these components when the forest is standing. Also, associated with the removal of the forest canopy is a reduction in interception losses which increases the flux of water through the system, contributing to the dilution of solutes in runoff. The relative magnitude of this effect compared with the decrease in capture of atmospherically derived components cannot be readily assessed at this stage.

While data scatter is high, simple multiple regression analysis provides a valuable interrogative tool for teasing out key hydrochemical processes associated with acidification. Nitrate shows a marked acidification effect for individual sites. On average, for every μEq increase in nitrate ANC declines by about 0.5 μEq and about 0.1 μEq of the hydrogen-ion formed when nitric acid is generated within the catchment is consumed by aluminium release and about 0.5 μEq by weathering reactions releasing base cations. These changes probably reflect reactions occurring in the upper organic-rich and the lower mineral horizons. In the upper soils, nitrate generation will result in hydrogen-ion production as there are limited supplies of mobile aluminium. The main pool of available aluminium resides in the lower mineral soils on cation exchange sites and as poorly ordered oxides/hydroxides. This aluminium will be mobilised in response to both hydrogen leaching from surface organic horizons and nitrate production in the lower mineral soil itself. For chloride, its influence on the acidity of runoff primarily relates to cation exchange reactions in the upper organic soils. As chloride concentrations change, there is a parallel change in hydrogen ions and an inverse change in bicarbonate. Sulphate acts as an acidifying component often to a similar degree to nitrate for individual sites. However, there seem to be additional factors linked to groundwater sources (oxidation of sulphide minerals) and possibly controls such as hydroxy-aluminium-sulphates. With regards to ANC, initial calculations indicate that additional anion components (probably intermediate strength organic acids) not normally considered in the charge balance may be important at a few sites. The overall changes in ANC within catchments and associated runoff are linked to strong acid anion variations and without a balancing increase from base cation weathering increases in drainage water acidity occur. Similarly, decreases in strong acid anions without compensating changes in base cation levels will lead to reduced acidity.

The overall balance between base cation losses from biomass export and accelerated leaching losses at harvesting and inputs from the atmosphere and soil/bedrock are crucial to determining the long-term acidification of upland soils and waters. Indeed, this aspect may well provide the critical determining factor over the viability of a second generation of forestry both in terms of nutritional requirements and water quality impacts. To estimate potential changes, an analysis of calcium cycling within mature forest stands has been undertaken. The results indicate that the Ca budget is finely balanced, lying within the errors of many of the measured parameters. Particular uncertainties involve an accurate assessment of atmospheric inputs throughout the forest cycle and the ability of trees to tap sources of base cations at depth. A dynamic simulation of water quality change indicates that re-afforestation can lead to ANC declines of the order of 40 μEq/l if tree uptake of base cations is from the soil layer, but less than this if the uptake is from the groundwater. However, this probably represents a worst case scenario as increases in weathering, base cation cycling and atmospheric scavenging of the particulate phase have not been incorporated in the model. The uncertainties concerning calcium fluxes probably means that predictions of the effects of re-afforestation lie between an ANC decline of 40 μEq/l to no decline at all, or potentially an improvement. Indeed, there is little field evidence to indicate that calcium is depleted from the soil with tree regrowth.

Across all but the local spatial scales of catchment monitoring, there is often a balance between nitrate generation with felling leading to increased stream acidification and reduction in strong acid anions (and possibly increased base cation concentrations due to enhanced weathering associated with carbon dioxide production) leading to reduced stream acidification. Further, apart from nitrate and potassium the felling responses for other chemical determinands are also small and they do not pose a water quality problem in themselves. Indeed, apart from nitrate and potassium, when set against other temporal variations in water quality, the net effect is often hard to discern.

Overall, our findings indicate that harvesting effects on stream water quality are of relatively short duration and that by reducing the proportion of the catchment felled at any one time, the effects are reduced. Nonetheless, care will need to be taken in relation to the impacts of extreme events associated with high flows and localised forestry activities introducing intermittent point sources of pollution.

7.1 Scientific needs

Long term monitoring of upland water quality shows a complex pattern of variation driven by fluctuations in climate and atmospheric deposition. Many of the changes are surprises and we are aware of no current environmental model that would have predicted them. Indeed, the patterns being observed must lead to new models and the present data must be used to calibrate them. No doubt, the surprises will continue and it is essential that long term records of this type be maintained as decadal and longer timescale changes are involved.

Deciphering the key determinative processes against very erratic changes due to the highly heterogeneous and dynamic nature of the systems being studied is extremely difficult at a representative scale. We do not accept the validity of standard laboratory experimentation to separate out individual processes when the environment is actually responding to a complex set of interactions between the hydrological, chemical and biological components of the ecosystem. Indeed we highlight the value of long term monitoring for assessing ecosystem responses to climatic perturbations. In addition, in assessing the impacts of land use change, as for example with the paired catchment approach to study clearfelling effects, manipulations of ecosystems are being undertaken which are not simply of major applied environmental management value: they are of major scientific value as natural tests for key processes. As many of the catchment stores change over long periods of time, the manipulated sites need to be monitored for many years in order to assess the changes in these stores. This is best illustrated by the South2Hore and Beddgelert felling sites.

One major research need is to determine why the water quality is so variable across sites of apparently similar soil type, geology and geomorphology. In the case of the nutrients, there are major missing gaps relating to felling and it may be possible to use carbon to nitrogen ratios, to explore the nature of the local variability. In the case of the weathering components, a combination of hydrograph separation using ANC and isotopic methods (oxygen and hydrogen) may be of value to determine the nature and size of the catchment stores

There remain question marks over the hydrogeochemistry of base cations within these acidic systems, from uncertainties in atmospheric deposition in particulate forms, the nature of the weathering reactions and the potential base cation sources for tree growth. These aspects are of crucial significance for determining whether or not repeated forest rotations will result in both chronic and acute acidification of surface waters. Work urgently needs to be undertaken to resolve these issues. Novel techniques no doubt will be required and these can include isotopic methods to separate atmospheric and weathering sources of base cations (strontium). Along the vein of catchment acidification due to base cation depletion of the soil with forestry development, there is a need to identify if nutritional changes with tree development precedes or follows on from stream acidification. If nutritional changes come first, then they will automatically be identified by the forest manager and rock phosphate fertilizer application would at least in part restore the calcium balance, before a problem occurred within the stream. However, if stream acidification came first then clearly models are more urgently needed to predict the scale of the impact.

One of the main results of the study has been the identification of the major role the groundwater can play in determining stream water chemistry. While shallow groundwaters seem ubiquitous throughout all the catchments we have examined, we still do not know the size of the groundwater stores or the hydrological and chemical functioning of what is a complex fracture flow routing system. Studies in this area are essential both in relation to understanding hydrological transport and the nature of weathering processes. Further this high degree of heterogeneity potentially allows the opportunity for improving water quality by targeting areas with low groundwater input for both soil and groundwater manipulation. Current modelling does not fully account for, and often ignores this high degree of heterogeneity and groundwater potential. This ultimately is counter productive, as not only is there a lack of process representation but it may well prove that it is because of the heterogeneity that environmental improvements can be achieved. Clearly new environmental modelling and management approaches are required but many uncertainties remain over the nature of the heterogeneity; this also warrants further study.

In undertaking environmental impact studies as in this report, work has centred on assessing deteriorations in water quality which are then equated with perceived biological responses. In practice, there is not a one-to-one match and other habitat factors such as light penetration and temperature can be extremely important. Within this project we have used ANC as a surrogate for the likely biological response. We recognise that this is no more than a pragmatic approach, but we know of no better one at present. Ultimately controls on forestry practice, industrial emissions and other human activities which impact stream water quality will have to be related to ecological responses although regulation will remain focused on water quality and emission standards. A crucial issue for environmental management will be the development of an integrated approach that can link water quality, habitat and biological functioning.

While we fully recognise the major contribution of environmental models to the understanding of hydrochemical systems, we also recognise that models are a simplified representation of reality. Within our studies, we have shown that there is a contrast in hydrochemical behaviour between upper and lower soils and complex groundwater systems. Further, the chemical functioning of these zones differs both in relation to equilibrium and kinetic reactivity. Presently, we do not seem to have a user friendly model which allows us to assess the potential importance of these variables in determining stream water quality, particularly in relation to predicting environmental change. One future need must be to develop more flexible systems that can be used by non-specialists.

8. FROM ENVIRONMENTAL MEASUREMENT AND SCIENTIFIC UNDERSTANDING TO MANAGEMENT PRACTICES: BRIDGING THE GAP

The complex heterogeneous nature of the acidic catchments of concern means that

1. any changes in water quality associated with forestry practice can be masked by natural fluctuations

2. it is extremely difficult to assess forestry impacts on water quality based simply on biogeochemical theory and catchment and forestry harvesting schemes.

Because of these constraints, it is inappropriate to provide detailed process based models to describe water quality changes and environmental management scenarios for forest harvesting and replanting impacts. Rather, the pressing need is to provide, using the biogeochemical insights gained during this project and from earlier studies, simple straightforward practical approaches for effective management of forest harvesting and replanting in relation to environmental water quality needs. The target audience is thus Forest and Environment Agency planners and field managers.

Within this chapter, the linkage between theory and measurement with formulating forestry management practice is examined. Thus, the reasoning behind our suggestions for practical management options are explained as a backdrop to the next chapter dealing with "Formulating improved management practices".

For this chapter, three issues are considered: 1) management of short term responses, 2) management of long-term impacts and 3) regional assessment of acid sensitivity. These issues are discussed separately below.

8.1 Short-term Response

Except for the first few years when a nitrate pulse is observed, conifer harvesting and initial replanting improves stream water quality. Consequently, the main focus of management must be concerned with water quality impacts associated directly with the fell and the subsequent year to five year period. Formulation of practical management strategies requires two issues to be addressed: What are the water quality controls on forest harvesting?; What practical strategies can be adopted to limit the acidification associated with the nitrate pulse?

8.1.1 Water quality controls on forest harvesting

Ultimately, water quality controls on forest harvesting must be linked to biological and water quality criteria. With regards to biological impacts, the primary concern is over acidification and for pragmatic purposes an ANC of zero has been used as the prime water quality criterion. Positive ANC values represent less acidic conditions more favourable to acid sensitive biota. An ANC of zero approximately represents the divide between healthy and acid impacted systems

(CLAG 1995). The experimental and monitoring programmes indicate that apart from small first order catchments, ANC changes are usually less than 30 μEq/l. Hence, at a precautionary level, unless there are specific more local concerns or "knock on" effects further down stream:-

> if the minimum (or bottom 10 percentile) ANC in the stream is greater than 30 μEq/l, then there is much less cause for direct concern even with whole catchment felling.

Note, that as the proportion of catchment felled decreases, there will be an approximately pro-rata decrease in the ANC decline.

8.1.2 Practical strategies to limit the acidification associated with the nitrate pulse

The study shows that to minimise potential acidification impacts of conifer harvesting, increased nitrate production and extremes in nitrate concentration need to be kept in check. Owing to the limitations of within-stream removal of nitrate, particularly at high flow, mitigating strategies must primarily focus on management techniques to (a) encourage rapid vegetation as soon as is convenient after felling, (b) to time felling and replanting to maximise plant uptake of nitrate and minimise nitrate build up in the soil thereby limiting any nitrate 'flush' with the first major autumn rainfall and (c) to focus attention on cases where nitrate generation can be high. However, the effects will be very variable from site to site in linkage with the extent of nitrate production within the first few years of felling, the nature of groundwater supplies and the relative effects of cation exchange and weathering processes. We have highlighted the difficulty in estimating nitrate production for individual soils and point especially to a lack of process and monitoring information on the brown earth soils whose high productivity can sometimes lead to particularly high nitrate production with felling.

Nonetheless, the issue of local deteriorations in water quality following felling must be kept in perspective in relation to (a) the size of the water quality changes in relation to natural variability, (b) the normal scale of commercial harvesting operations, (c) the reduced impacts of partial felling of catchments and (d) the fact that acid events are not simply related to forestry effects (e.g. partial melting of snow and high-sea-salt inputs can also be important: Langan, 1987, 1989; Jenkins, 1989; Mulder *et al.*, 1990). Despite all the variability and lack of detailed process knowledge, it is clear that in many cases drainage water quality will not be significantly affected by felling and that without the nitrate pulse with felling, stream water quality will improve. At larger catchment scales which are more likely to be of concern to environmental managers (i.e. greater than 50 ha: over ten times the size of the survey catchments), local variability could easily be averaged out provided that there is adequate mixing upstream of the areas of environmental concern (to avoid localised inhomogeneities in water quality). With the current emphasis in Forests and Water Guidelines (FC, 1993) and the Forestry standard (FC, 1998) on phased harvesting within catchments, the impacts will be diluted even further. Indeed, current forestry guidelines which ensure good site management and a more "landscape approach" to commercial forestry (FC, 1993, 1994) can clearly overcome or minimise harvesting impacts on water quality.

The results from our main catchment studies show that felling effects are very hard to discern when 20% or less of the catchment is felled within a given year. This occurs for two reasons. Firstly there will be dilution of runoff from the standing crop remaining in the catchment. As already shown, the maximum ANC decline with felling is about 30 μEq/l with complete felling.

Clearly, if a smaller proportion of the catchment is felled there will be a proportionally less of an effect as observed in our measurements. For example, if an area of less than 20% is felled, even in the worst case, then the decline in ANC is not only within the noise level of the natural variability but also close to the analytical error within the measurements. This corresponds to observations both for the main catchment experiments at Plynlimon and for other studies as well (e.g. the Kirkton catchment in Scotland as referred to in the associated Project Record). Secondly, where there are areas felled two or more years previously, these will contribute less acidic water than even the standing crop. For this reason, phased felling is particularly important and it is difficult to envisage that felling at this or lower intensity will have any significant impact at this scale. At smaller scales, the same is true, except for a very limited number of small first order catchments of less than 10 ha where localised variations can produce much higher ANC changes.

8.2 Long-term Impacts

With regards to longer term impacts of harvesting and replanting, there are major uncertainties as outlined earlier due to lack of knowledge of how the base cation inputs and stores will change with the development of second and subsequent forest rotations. The range of possibilities are large but it seems from initial estimates that loss of base cations (calcium in particular) in harvested products may be counterbalanced approximately by standard calcium phosphate fertilizer additions even with the worst case scenarios. This does not necessarily negate continued acidification as there will be enhanced scavenging of atmospheric pollutants as the forest canopy develops. For example, a) acidification may be offset by declining sulphur emissions and increased base cation scavenging as well, b) the nature of the weathering process may be more complex than presently envisaged and c) feedback mechanisms limiting base cation depletion may come into play. Thus the magnitude and timescales of base cation change remain illusive.

8.3 Regional Assessments of Acid Sensitivity

For regional assessment of acid sensitivity, maps derived from soil and bedrock geology have been produced. Within the UK, the first such map allocated map units on the 1:65000 geological map to one of four classes based on the geochemistry and mineralogy of the dominant rock types (Kinniburgh and Edmunds 1986). It was recognised, however, that this map had short comings for the prediction of surface water acidity, in that whilst geology has an important influence on baseflow chemistry, soils are one of the most important factors determining stream water chemistry at high flows. Thus a new map was produced for the UK which combined 1 km square databases of soil information with the geological data (Hornung *et al.*, 1995). In the map, soil mapping units were assigned to one of three acid sensitivity classes according to data for base saturation and soil pH. A GIS overlay procedure was used to combine the resulting sensitivity map of the dominant soil within each 1 km square with a modified version of the Kinniburgh and Edmunds geology map to produce a combined map with five acid sensitivity classes (Table 8.1). In Wales, a simplified version of the UK map was produced for screening new forest planting applications where acid deposition and scavenging are the key issues The revised maps also included a 300 m contour overlay, on the basis that the scavenging effect is most significant above this altitude, thus attention focused on new planting above 300 m (planting below this altitude is not subject to a catchment based assessment). The Welsh map (Figure 8.1) has two classes: non-sensitive (combination of UK map classes 1-3) and sensitive (combination of UK map classes 4 and 5). In terms of felling, the areas of concern are essentially the same as those for planting and potentially these maps can be used for the same purpose. However, it is important to remember that the purpose of the acid sensitivity map was to predict average sensitivity at a resolution of 1 kilometre square whereas for felling impacts much smaller areas are of concern and have been monitored.

Table 8.1 **Surface water sensitivity classes from Hornung *et al.* (1995).**

Sensitivity class	Description (sensitivity)	Prediction
1	Non-sensitive	Acidic waters will not occur
2	Low	Acid waters very unlikely
3	Medium-low	Acid waters unlikely
4	Medium-high	Acid waters likely at very high flows
5	High	Acid waters will occur at all flows

Within this section the potential for using these maps for providing a background resource for assessing the areas of critical concern with respect to felling activities is explored. To do so, the predicted acid sensitivity from the map is compared with the observed ANC in stream runoff using data sets from our Forest Felling Regional Water Quality Survey and the Welsh Acid Waters Survey.

8.3.1 The Welsh Acid Waters Survey catchments

The Welsh Acid Waters Survey catchments provide an opportunity to assess the validity of acid sensitivity predictions across a range of catchment sizes (20 to 5673 ha) and land use types including conifer forestry, semi-natural and agriculturally improved moorland. A statistical analysis of these data reveals that the relationship between stream water ANCcb and the acid sensitivity of the catchment does not depend ($p>0.15$, 1-Way ANOVA) on how the acid sensitivity class is assigned to the catchment, i.e. whether an area-weighted value, a modal value or the value at the sampling point is used (Table 8.2). For the catchment area-weighted sensitivity, statistical analysis of the ANCcb data shows that stream water is significantly less acid ($p<0.001$ 1-Way ANOVA) in the non-sensitive catchments (Table 8.2). However, the analysis also shows that catchments classified as non-sensitive can still have a minimum ANCcb value considerably below zero. Indeed, 46% of non-sensitive catchments mapped according to catchment area weighting had minimum ANCcb values less than zero with 54% having a value less than 20 μEq/l; 92% of the sensitive catchments had ANCcb minima less than zero. For both non-sensitive and sensitive catchments mapped in this way, only one site in each case had a maximum observed ANC less than 20 μEq/l. The Welsh Acid Waters Survey data show that whilst the acid sensitivity predictions are generally upheld for catchments in excess of 20 ha, extremes of acidity which transgress currently accepted biological thresholds are not reliably predicted.

Table 8.2 Summary of the mean (ANC_{mean}), minimum (ANC_{min}) and maximum (ANC_{max}) values of ANC (μEq/l) observed in twelve monthly samples from 102 Welsh Acid Waters Survey catchments classified according to acid sensitivity using three different methods.

Classification method	Sensitivity	Mean ANC_{mean}	se. ANC_{mean}	Min ANC_{mean}	Max ANC_{mean}	No. of sites
Catchment area weighted sensitivity	Non-sensitive	289	67	-22	1592	39
	Sensitive	77	17	-73	910	63
Modal sensitivity	Non-sensitive	337	79	-3	1592	32
	Sensitive	76	16	-73	910	70
Sensitivity at sample point	Non-sensitive	196	39	-73	1592	74
	Sensitive	58	16	-23	331	28

Classification method	Sensitivity	Mean ANC_{min}	se. ANC_{min}	Min ANC_{min}	Max ANC_{min}	No. of sites
Catchment area weighted sensitivity	Non-sensitive	95	43	-171	996	39
	Sensitive	-62	11	-270	217	63
Modal sensitivity	Non-sensitive	105	53	-171	996	32
	Sensitive	-51	10	-270	217	70
Sensitivity at sample point	Non-sensitive	22	25	-270	996	74
	Sensitive	-65	17	-243	180	28

Classification method	Sensitivity	Mean ANC_{max}	se. ANC_{max}	Min ANC_{max}	Max ANC_{max}	No. of sites
Catchment area weighted sensitivity	Non-sensitive	528	101	8	2354	39
	Sensitive	212	38	-1	1794	63
Modal sensitivity	Non-sensitive	622	117	46	2354	32
	Sensitive	201	34	-1	1794	70
Sensitivity at sample point	Non-sensitive	397	63	-1	2354	74
	Sensitive	164	26	21	577	28

One-way ANOVA of the Welsh Acid Waters Survey data in relation to the original five band classification of acid sensitivity, shows that there are no significant differences in mean, minimum and maximum ANCcb between classes 3, 4 and 5 ($p<<0.01$). However, sites in class 2 have significantly less acid chemistry ($p<0.001$) than any of these other classes. There are no Acid Waters Survey sites in class 1.

8.3.2 Forest Felling Regional Water Quality Survey

In the case of this dataset, where small forested and harvested catchments (first order streams) are represented, the large variations in water quality observed are poorly predicted when information determined from the acid sensitivity map is compared with field information (Table 8.3). A statistical assessment of the regional survey data reveals no statistically significant relationship between vulnerability assessed from the mapped acid sensitivity of the catchment sample point and the measured baseflow and stormflow ANC values for the catchments ($p>0.15$, 1-Way ANOVA). This result becomes even stronger when those sites influenced by the post-felling nitrate pulse (nitrate concentrations >= 3 mg/l) are removed ($p>0.3$, 1-Way ANOVA). Furthermore, some extremely acid waters were observed in the non-sensitive catchments even under baseflow conditions. Indeed, of the 26 baseflow samples collected from non-sensitive sites, eight had negative ANC values while a further fourteen had ANC values less than 20 μEq/l. Conversely, under stormflow conditions, some highly positive ANC values were observed in catchments classified as acid sensitive. The results show that the high degree of spatial heterogeneity in the hydrochemistry of small catchments cannot be predicted from relatively coarse scale regional mapping.

8.3.3 Conclusions over the value of acid sensitivity maps for assessing vulnerability.

Clearly there are important shortfalls with the use of acid sensitivity maps based solely on soil and geological type irrespective of the size of the catchment. The reason for this is simply related to the high degree of heterogeneity within catchments and the complexity of soil and groundwater interactions with or without the added complications of forestry felling cycles. In our stream water surveys we were surprised at the high degree of variability: a variability unknown to the producers of the earlier sensitivity maps. Given the new information and the critical assessment of the regional data presented here, we have little confidence in their value for assessing harvesting effects where areas much less than those used for the sensitivity maps are involved. Further, the results of the analysis of the Acid Waters Survey study also lead us to question the validity of the maps even at a relatively coarse scale, since the maps totally fail to represent the extremes. We therefore conclude that while the maps offer a starting point for assessing sensitivity, they provide no more than a very crude indication. Further, the current sensitivity sub-division in to five bands provides an over optimistic description of acid sensitivity. Currently, the EA map is divided into two bands as discussed above. Our cruder subdivision is probably more appropriate, and we propose that the EA 'sensitive class' be revised to include the medium-low category of Hornung *et al.* (1995) as shown in Figure 8.1. In our opinion, a more satisfactory route for assessing sensitivity is to directly use water quality and biological information.

Table 8.3 Mean, minimum and maximum ANC values observed in the regional survey streams classified according to the acid sensitivity of the catchment sampling point for a) all data and b) samples with NO_3 concentrations less than 3 mg/l.

Table 8.3a All data

Flow conditions	Sensitivity	Mean ANC µEq/l	se.	Min ANC µEq/l	Max ANC µEq/l	No. of samples
Baseflow	Non-sensitive	18.0	23.5	-120.9	464.7	26
	Sensitive	-5.8	8.4	-167.7	385.2	99

Flow conditions	Sensitivity	Mean ANC µEq/l	se.	Min ANC µEq/l	Max ANC µEq/l	No. of samples
Stormflow	Non-sensitive	0.6	14.1	-112.4	346.4	47
	Sensitive	-16.6	5.4	-123.8	349.8	173

Table 8.3b Samples with NO_3 <3 mg/L

Flow conditions	Sensitivity	Mean ANC µEq/l	se.	Min ANC µEq/l	Max ANC µEq/l	No. of samples
Baseflow	Non-sensitive	26.9	24.1	-50.0	464.7	20
	Sensitive	4.3	9.4	-100.0	385.2	83

Flow conditions	Sensitivity	Mean ANC µEq/l	se.	Min ANC µEq/l	Max ANC µEq/l	No. of samples
Stormflow	Non-sensitive	0.3	12.7	-109.3	295.2	42
	Sensitive	-10.8	6.5	-104.5	349.8	137

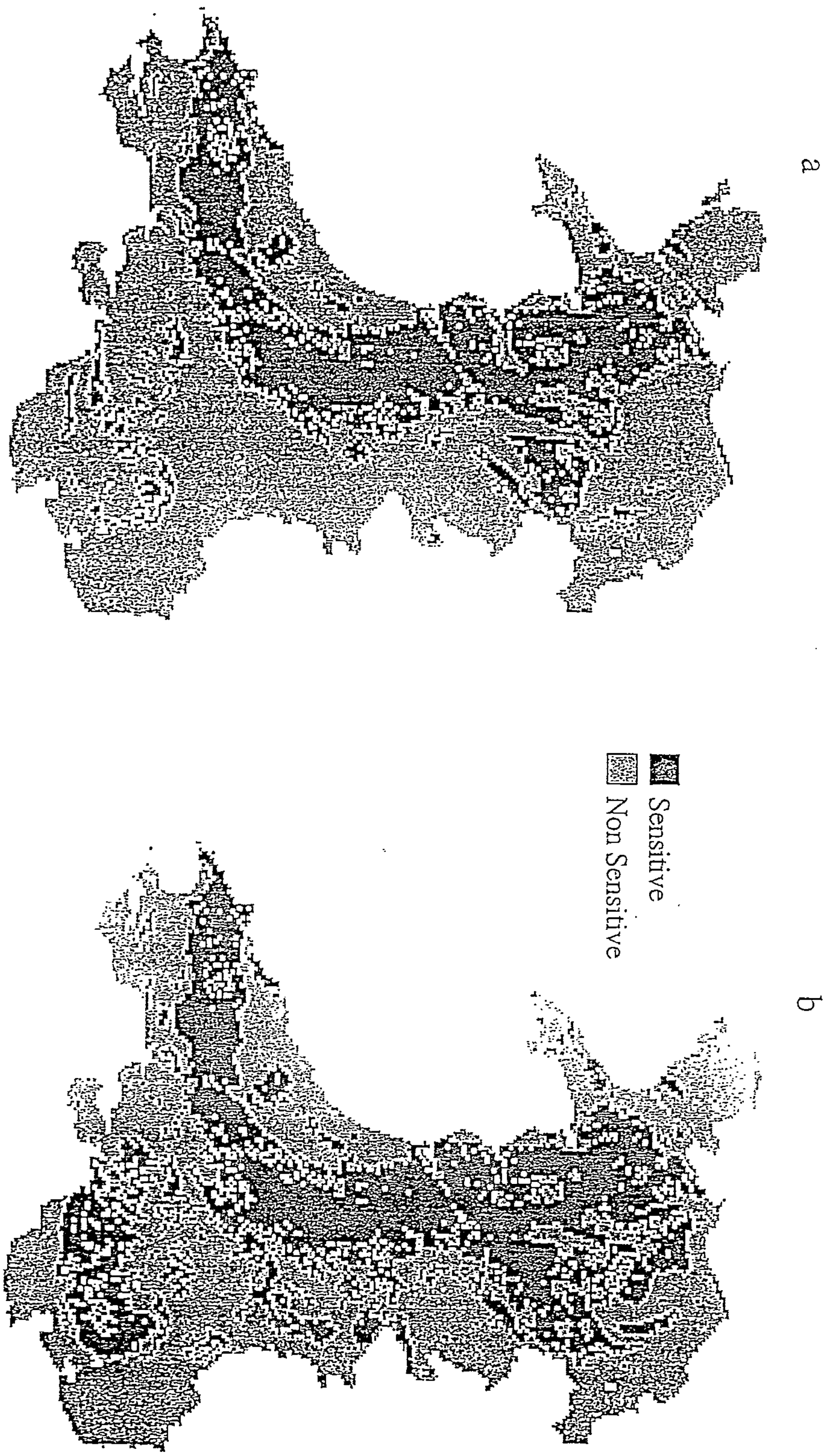


Figure 8.1 Acid sensitivity map for Wales showing a) the current EA classification, and b) our recommended revised classification.

9. FORMULATING IMPROVED FORESTRY MANAGEMENT PRACTICES

9.1 Forestry Regulation

The Government Department responsible for forestry in Great Britain is the Forestry Commission. It implements the regulatory responsibilities, and also comprises two executive agencies: the Forest Enterprise which manages the nationally owned forest estate and Forest Research, which conducts research and development and provides authoritative advice on forestry matters. Planting of new woodlands, tree felling and replanting operations are controlled through approval mechanisms. New planting proposals are approved through the Woodland Grant Scheme, supported with appropriate Environmental Assessment if it is likely that there will be a significant environmental impact.

Felling in private woodlands is permitted by the Forestry Commission by granting a felling licence, approving a Forest Plan, or by approving a plan associated with a grant scheme. Felling licences generally cover a two year period, while Forest Plans are given approval for felling operations over a ten year period. Forest Enterprise gains approval for felling in woodlands under its management by the production of Forest Design Plans which are subject to revision and approval every five years. The Forestry Commission holds a public register of proposals for new woodland or felling which is available for inspection in order for interested parties to comment. Details are also sent directly to local authorities and other statutory bodies, including the Environment Agency, for formal consultation, or to provide opportunities to comment as appropriate. Arrangements are in place for consultation between the Environment Agency and Forestry Commission on new planting in acid sensitive areas.

Deforestation, when restocking does not take place, will be subject to consideration of Environmental Impact Assessment under the proposed changes to the Environmental Assessment (Forestry) Regulations 1998, due in 1999.

9.1.1 The UK Forestry Standard and supporting guidelines

In 1998 the Forestry Commission published the UK Forestry Standard - the Government's approach to sustainable forestry. The purpose of the standard is to set out the criteria and standards for the sustainable management of all forests and woodlands in the UK. These criteria cover the basic resources which can be grouped as physical (soils, air and water); biological (trees and biological diversity); human (workforce and communities) and cultural (heritage and landscape). New planting and felling proposals are required to aim towards incorporating the requirements of the standard.

The national Sustainable Forest Management (SFM) criteria for water resources is:

> "Water quality is protected or improved, water yields are maintained above any critical level and water discharge patterns are disturbed only when unavoidable, and options have been explored."

National level indicators include:

> "Cases where the agreed maximum afforestation rate in a 'Critical Load Exceedance' area has been overstepped; evidence from surveys of freshwater rivers and catchments; hydrological monitoring of afforested catchments; hydrological studies."

Forest management unit indicators require evidence that:

> "Local liaison takes place when appropriate and agreements for water are respected; an acceptable standard of forest design is applied to water margins; opportunities are taken to improve riparian zones in the course of forest operations; all operations are planned and carried out to minimise disturbance to watercourses and to avoid pollution and siltation; emergency pollution control measures are in place when high risk operations are carried out."

Criteria for biological and cultural (landscape) resources may also provide benefits for the physical resources.

The UK Forestry Standard acts as a reference against which good practice can be measured. Standard Notes within the Standard, act as a reference for identifying acceptable options for management, with Standard Note 1 "General Forestry Practice" and Standard Note 4 "Felling and Restocking Planted Woodland" being especially relevant. Practice is also linked to supporting publications, including the Forests and Water Guidelines 3rd Edition, and the Forests and Soil Conservation Guidelines, which are relevant to the impact of felling operations on water quality.

9.2 Best practice issues

It is clear from the present report that in many cases drainage water quality will not be significantly affected by felling and that without the initial nitrate pulse for the first year or so post felling, stream water quality will improve. Emphasis therefore needs to be placed on identifying areas at risk and reducing the threat of acidification by adopting best management practices. Practical ways of minimising potential water quality impacts associated with forest harvesting are essentially contained within the Forests and Water Guidelines and other good practice manuals.

Recommendations to be considered as best management practices fall broadly into three topic areas: (1) Planning Consultation - Individual Felling Applications and Long Term Plans, (2) Site Assessment and (3) Operational Guidance. These aspects are covered separately below.

9.2.1 Planning Consultation - Individual Felling Applications and Long Term Plans

Felling and Restocking Applications are placed on the Forestry Commission's Public Register for 28 days. Lists of applications are sent to Environment Agency Area Planning sections, and criteria can then be used to select applications where further information is required. Arrangements are already agreed for dealing with new planting in acid sensitive areas (Forests and Water Guidelines). Private forestry managers and Forest Enterprise also liaise with the Environment Agency during formulation and review of Forest Plans and Forest Design Plans.

Consultation Triggers

Acid Sensitive Areas Map

Initial screening of any application or plan is needed to identify whether or not the areas to be felled lie within an acid sensitive catchment area. In chapter 8 the applicability of acid sensitivity maps has been investigated and clearly there are major deficiencies at the scale of concern for felling and replanting operations. Indeed, there is a lack of clarity over what is the relevant scale and what the 'real' area of risk is. This issue must form a new topic of active debate and research.

As an interim solution we recommend the following.

> For initial screening of felling applications, an acid sensitivity map based on soil and geology types following the approach used by the EA in Wales, modified as proposed in Section 8.3.3 (Figure 8.1) should be used. Wherever possible, the map should be refined at a more detailed level by making full use of local knowledge and monitoring/survey data to indicate where acid streams actually occur and acidification impacts have been recorded. The modified EA acid sensitivity map for Wales may be used as a template for a similar scheme in England. In Scotland a provisional critical load exceedance map is used to define those areas where individual catchment based assessments of acid sensitivity for new planting are required and this could also be considered for felling. For those catchments lying within exceedance squares, the Henriksen Steady State Water Chemistry equation (CLAG 1995) is used to calculate the critical load for the catchment using water chemistry from a sample taken under high flow conditions and a critical chemical limit of ANC = 0 μEq/l.
>
> As a longer term solution for initial screening of applications, we recommend that water quality and biological sensitivity maps based on field data should be used once the relevant scale has been identified. To infill for missing information, shortfalls in current monitoring programmes could easily be identified. Effectively, we recommend that more use be made of existing water quality data with additional sites being sampled 2-3 times under baseflow and stormflow conditions to determine the minimum ANC. For this purpose an ANC risk threshold would need to be defined perhaps within the region of ANC 0 to 30 μEq/l; the latter being the precautionary ANC limit for felling impacts described earlier.

Felling Area Size and Timescales

Once a felling area or long term plan is identified as lying wholly or partially within an acid sensitive area, it is then necessary to identify whether the scale of the felling operation is of concern. Nevertheless, for practical reasons an interim de minimus size is needed to exclude the very heterogeneous behaviour observed at the local scale which is not of primary concern.

Coupe size guidance relates to sensitivity within landscape, and therefore allows for different sizes of fellings under the UK Forestry Standard. Within Wales the majority of coupe sizes are between 2 - 20 ha, average 13 ha, and only occasionally 50 ha or above. In forests in some upland parts of England, for example Kielder Forest, larger coupe sizes are more common reflecting undistinguishing landform of gently sloping hills and plateau.

The UK Standard encourages greater species and structural diversity of replanting, by incorporating more open space and broadleaved and conifer species in existing plantations, particularly in areas greater than 100 ha in the uplands. However, where single unit plantations are over 30 years old it may not be possible to comply with the standards initially, but redesign of the forest should enable this in future cycles.

It will be necessary to ensure cumulative effects of individual applications in one catchment are considered. This will be facilitated in the future by the use of GIS by the Forestry Commission (and ultimately the EA). Multi-ownership of individual woodlands is being investigated as part of the Forest Plans Pilot project. Consideration of adjacent Forest Design Plans from Forest Enterprise will also be required as outlined in the section dealing with long term plans.

In order to assess cumulative effects, it is necessary to look over longer time periods. A number of time factors need to be considered. Currently, felling licences cover a 2 year time span, Woodland Grants for new planting and restocking cover 5 years, private sector Forest Plans cover 10 years, and Forest Design Plans cover approximately 20 years for felling and restocking, reviewed every 5 years. A recommended minimum of 8 years, or until regrowth reaches 2 m, should be left between felling adjacent coupes in upland areas according to the UK Forestry Standard. Ideally the Forestry Standard of 8 -15 years between adjacent coupes could also be used to influence the timing of felling in adjacent forest management units, under different ownerships, when taking a catchment based approach. The studies within this report, together with others in the UK and elsewhere, show that the impacts of felling last for 1 to 3 years for both nutrients and acidification indicators. However, in the case of ANC and aluminium, an early acidification and aluminium release associated with nitrate production within the first 3 years after felling can be offset by a reduction in acidification and aluminium release thereafter.

Therefore the individual felling applications need to be considered with any others in the same catchment within a 5 year period to ensure cumulative effects are allowed for. Similarly the 5 year timescales used within plans are suitable units to consider the impacts of felling.

Our recommendations are three fold

1. Methods are developed to provide information on felling in relation to the proportion of catchment felled in a given year or a series of years.

2. A mathematically/statistically based study should be undertaken to investigate how forestry management planning at the various timescales translates to the proportions of catchments which will be felled in a given year for different sizes of catchment. This is required as at present it is not clear what the linkage is even from a theoretical standpoint.

3. The relationship between forestry guidelines and practical outworking should be independently audited at the regional level to indicate successes and shortfalls with the current approach and assess (1) compliance with the guidelines and (2) catchment areas actually felled

Receptors

Once a felling area or plan has been identified as being within an acid sensitive area, and of a scale that is likely to be of concern, it is then necessary to establish if there are any sensitive uses or receptors within or downstream of the felling area which may potentially suffer as a result of the activity.

There may be key uses within a catchment which are susceptible to the impacts of acidification and which require protection through the implementation of best practice. These uses can be linked to the most sensitive receptors for which protection criteria can be identified. The receptors may not necessarily be located within the area to be felled, or even the area of forestry, but it is important to protect downstream uses. The identification of the presence of these receptors will normally be carried out by Environment Agency staff during the planning consultation process. Local Environment Agency Plans, or LEAPs will normally identify the presence of these receptors as a guide. In line with the current pragmatic approach used in the EA, we recommend that the following receptors are used noting fully that the definition and location of the receptor within the catchment must be established, particularly within a macro catchment of different land use types.

> *Salmonid fisheries including spawning areas*: As defined in Environment Agency LEAPs, or by liaison with local Fisheries officers if LEAPs have not been completed for the relevant area.
>
> *Public Potable supplies*: Preliminary screening by LEAPs, but this would need to be confirmed by liaison with Water Resources licensing staff to ensure that the most up to date sources are identified.
>
> *Private Potable supplies*: The issue of protection of private supplies would also need to be considered. The Environment Agency would not necessarily have all the relevant details. However, forestry managers should establish if such supplies exist for wider pollution prevention requirements. Dilution would be much lower at such sites, but may be influenced by local groundwaters. The system is far too variable to allow prediction of any changes. Water supplies may need to be monitored in cases where no pretreatment for aluminium and nitrate is presently undertaken. This would fall within the responsibility of the Local Authority Environmental Health department.
>
> *Fish farms*: Again screening could be carried out using LEAPs, local knowledge and confirmation by liaison with Water Resources licensing staff and Fisheries staff.
>
> *Freshwater Sites of Special Scientific Interest (SSSIs); Special Areas of Conservation (SACs), Biodiversity Action Plans (BAPs) etc*: Use LEAPs and details for designated sites to determine if present policy is appropriate through liaison with Conservation staff. For example, this may be important in areas where salmonids are not actually present due to migration barriers.
>
> *Wetland areas, bogs, and pools*: These may also need protection if designated and there are primarily two issues to address: (1) eutrophication of nutrient-poor wetlands and pools due to an increase in nitrate, potassium and, in a limited number of cases, phosphorus in

runoff waters at felling and (2) acidification might occur in small areas of "sensitive" open waters. These issues are unlikely to be a problem for most wetland systems.

Consultation Response

There is a need for the EA and Forestry Commission to discuss ways forward in relation to setting up a de minimus felling area size for consultation, and a procedure for assessing proportions of areas felled and determining critical timescales of felling.

Forest Plans/Forest Design Plans

In addition to the above screening and response, additional factors can be considered within Forest Plans and Forest Design Plans where catchment and sustainability issues can be addressed more effectively.

Sustainability in terms of Base Cation Uptake

The main issue is whole tree versus stem only harvesting, and the effects on soil base cation stores. In Wales only a small proportion (150 ha per year out of 2500 ha felled) of whole tree harvesting is carried out.

Simplifying, whole tree harvesting has a high risk of high impact; while stem only harvesting appears to be low risk of high impact. However, there are large uncertainties in base cation stores, weathering and cycling fluxes within the catchment and with atmospheric deposition inputs. This remains an outstanding issue which cannot be addressed fully within the timescales of this project as discussed in earlier sections.

The method of harvesting may be determined by economic considerations or site conditions such as altitude and topography, and in some cases may not be variable, e.g. skyline practices and whole tree harvesting may be the only option on steep slopes. Harvesting manuals such as the "Guide on Whole Tree Harvesting" (Nisbet *et al.,* 1997), give guidance on selection of appropriate methods to minimise environmental impacts, and this is incorporated into contract specifications.

Tree species may have a bearing on base cations. Broadleaves generally root more deeply than conifers and can thus potentially access base cations from the subsoil and cycle them to the soil surface in falling litter and canopy leachate. However, nitrogen fixers (e.g. Alder) on a significant scale should be avoided in acid sensitive areas. The issue of the use of phosphate fertilisers also needs to be investigated further as the main form of addition is as calcium salts. Indeed, our initial calculations suggest that the calcium supply from these sources may well balance out the effects of calcium depletion from the catchment due to biomass removal at harvesting. Such additions might be used as a standard application for areas deemed to be particularly vulnerable to acidification.

Catchment Boundaries

For assessment, these will be needed on Forest Plans together with watercourses as marked to 1:25000 map. Also reference should be made to adjoining Forest Plans (both Private and FE) which lie within the same catchment, and the timing of felling activities within these areas. This should be considered particularly where the use of GIS systems is being developed for these plans and the need for linking coups felled to the proportions of catchments affected. The development of strategic plans by Forest Enterprise, linking Forest Design Plans within and between districts with similar attributes, would also enable the plans to be considered within a wider environmental context.

Soils mapping

Soil type is important in influencing the extent of the acidifying effects. However, within this report we argue that the water quality must also be linked to groundwater sources and the highly heterogeneous nature of catchments means that direct water quality measurement is of more relevance.

Buffer zones

Throughout our project the question of the value of buffer zones has been raised. There is evidence that following forestry ploughing, vegetated buffer zones can reduce sediment inputs to streams through settlement of particulates: the main controls being flow velocity, slope, width of strip, extent of lateral dispersion of water, type and nature of vegetation. (Swift and Norton 1993). However, even in this case, the effectiveness of the buffer zones can decline as the vegetation decays and is flattened by successive storms. While the importance of riparian management in terms of providing an appropriate physical habitat for aquatic biota is not in doubt (Maitland *et al*,. 1990; Stretton, 1998), there are some questions as to whether open buffer zones along the stream margin, at least in the short term, enhance invertebrate and fish densities (Ormerod *et al.*, 1986; Proctor, 1986). For example, at Plynlimon "the apparent failure of invertebrates to respond to substantial changes in local environmental conditions (clearfelling) may reflect either a lack of understanding of causal links between invertebrates and environmental factors or the overriding influence of the dynamics of recruitment to populations" (Gee and Smith, 1997).

There seems to be little clear evidence for the value of buffer zones in upland forests to reduce solute concentrations in runoff. For example, the work of Swift and Norton (1993) which experimentally investigated the effectiveness of buffer strips for protecting water quality following forestry ploughing and fertilisation was inconclusive with regard to dissolved phases. The water samples were apparently not filtered and the changes in chemical concentrations across the buffer zones were explained in terms of the dynamics of the particulate phase. In contrast, a study of a recently afforested catchment showed reductions in the stream water loadings of dissolved nitrogen, total monomeric aluminium, iron and DOC by 38%, 39%, 54% and 34% respectively as water passed through a small riparian wetland (Emmett *et al.,* 1994); a prolonged period of summer drought reduced the efficiency of the system to retain solutes. There has been considerable research in to the use of buffer zones to control the leaching of excess nutrients from agricultural land in the United States and the UK (see Haycock *et al.,* 1997). However much of this information is not directly applicable to upland plantation forests because of differences in land management and hydrology. For our part, we cannot see how buffer zones will influence the poorest water quality which occurs at high flow runoff in upland forests due to both the large chemical fluxes and the operation of flow by-pass mechanisms particularly for forest systems with established drainage ditches.

Water quality deterioration with felling due to 'within river processes' is probably associated mainly with local and short-lived stream bed and stream-side disturbance of sediments: for example, at Plynlimon, manganese concentrations can rise for a few months with stream bank disturbance at times of felling. This aspect can be very important and it is covered by recent guidelines for controlling sediment erosion.

Our only recommendations with regards to buffer zones are:

1. they are used when appropriate for controlling sediment loss;

2. current guidelines for riparian management are observed and there is a need to determine optimal management of buffer zones for physical (habitat) benefits;

3. they are researched much more thoroughly and systematically in the context of upland forestry in relation to dissolved and particulate chemical transfers.

Current Forest Design Guidelines encourage a trend of bringing down the tree line where appropriate and moving away from replanting source and other high altitude areas where trees grow poorly. Where areas are left as open space there may be opportunities for reinstatement of semi-natural vegetation communities. Particularly for source areas, non-planting would be preferred as consequential drainage and ground preparation may cause water quality deterioration.

9.2.2 Site Assessment

This assessment could be used for individual applications or forest plans once these have been identified as being within a sensitive area through consultation with the Environment Agency and the Forestry Commission.

Locations of receptors need to be identified by the Environment Agency to establish at what point assessment should be carried out. At the small scale heterogeneity dominates, but the effects become integrated and simplified downstream. Therefore the upper headwaters may not necessarily be the receptor areas.

For each receptor, protective criteria are required:

> *Salmonid Fisheries - including spawning* areas: The threshold currently accepted at a national level for Critical Load assessments for Salmonids is that of a critical chemical limit of ANC = 0 μEq/l. The critical load mapping for new planting is based on high flow water chemistry, and this seems particularly appropriate although, the biological significance of this approach for running waters is currently subject to further work within a NERC R&D Project entitled 'The biological significance and uncertainty analysis of critical load exceedance for freshwaters at the catchment scale'. The project is timetabled for completion towards the end of 1999. Until the outputs from this project are delivered, the critical load will be set with respect to high flow chemistry and a critical chemical limit of ANC = 0 μEq/l. This allows for the dynamic nature of water quality changes in rivers compared to the lake regime where much smaller variations occur. Further, the ANC threshold of zero was originally defined using lake data.

Public Drinking Water Abstraction Points: The following criteria apply under EC legislation (75/440/EEC) at designated abstraction points for public water supply. The criteria quoted are for sources requiring the minimum level of treatment (Simple physical treatment and disinfection).

pH	6.5-8.5 (Guideline value)
Nitrate	25 mg-NO_3/l (Guideline value); 50 mg-NO_3/l (Mandatory value which may be waived under certain meterological or geographical conditions)

Drinking Water Supplies 'at Tap' (Public and Private): The following criteria apply under EC legislation (80/778/EEC) relating to the quality of water intended for human consumption (i.e. 'at tap').

pH	6.5-8.5 (Guideline value); 9.5 (Maximum admissible concentration (MAC))
Aluminium	50 μg/l (Guideline value); 200 μg/l (MAC)
Nitrate NO_3 mg/l	25 mg-NO_3/l (Guideline value); 50 mg-NO_3/l (MAC)
Manganese mg/l	50 μg/l (MAC: Drinking Water Regulations 1989)

Fish Farms: It is assumed that criteria to protect salmonids (above) would also be appropriate for fish farms

SSSIs/SACs/BAPs etc: In most cases freshwater SSSIs/SACs are designated in part due to their salmonid populations. Therefore criteria set above should also be adequate for these sites. However in some cases other species may be of importance, or salmonids may not be present due to impassible barriers to migration. In such cases advice should be sought from the relevant conservation body, but criteria to protect salmonids will be used as a default.

With regards to the biological impacts of felling due to acidification effects, limits or defined controls on felling should be linked to the short term impacts (1 to 3 years following felling) where ANC can very occasionally decrease by about 30 μEq/l as noted in Chapter 8. Further work and negotiation between the Environment Agency and Forestry Commission is required before standards can be set. From the previous chapter, it is clear that Gran alkalinity can provide a more convenient measure of vulnerability compared to ANC according to the choice of range presented in chapter 8. For the critical ANC range, Gran alkalinity can be considered as being relatively chemically inert and the same type of calculation can be used as ANC for assessing dilution effects.

9.2.3 Operational Guidance

An extensive range of Forestry Guidance is available - and this is currently being reviewed as part of a separate R&D project. Once this review is complete it will be possible to identify which guidance needs to be reviewed in order to incorporate the recommendations from this study.

The primary guidance will be "Forests and Water Guidelines" (FC, 1993), "Forests and Soil Conservation Guidelines", the "Guide to Good Practice in Whole Tree Harvesting" (Nisbet *et al.*, 1997) and harvesting manuals.

Management practices need to examine the degree of benefit/disbenefit of any operation. An external audit protocol is planned and will be implemented to provide independent auditing of operational performance against the government's commitment to forestry sustainability as set out in the UK Forestry Standard.

Harvesting operations and to a lesser degree ground preparation and restocking operations have the potential to degrade the environment through soil damage, erosion and loss of nutrients. Managers must specify the harvesting regime and ground preparation methods to be used as part of the site felling and restocking plans. Procedures followed to protect the site and minimise sediment loss are likely to be favourable for minimising nutrient, including nitrate, leaching. Critical factors are harvesting regime, brash management, site preparation and, replanting and establishment of ground cover.

Brash Management

Brash consists of all the waste tree, branch and top material, and its management is an important part of harvesting operations. It is used in mats to protect soils from disturbance by machinery, to an extent determined by the harvesting method selected and ground preparation equipment used.

Brash is usually left on site as felling operations progress. However, on steeper sites trees may be harvested using cable crane whole tree harvesting techniques. Increasingly, brash will be left at the roadside. The long term sustainability of utilizing such areas needs to be considered taking into account the soil type. Calcium and other base cations may be depleted if brash is removed from the site. In addition, stored brash by roadsides can lead to leachate problems, which need to be minimised, and measures must be taken to ensure that this does not contaminate watercourses. Further, land disturbance associated with brash removal can also be important.

There is some small scale use of brash for biofuels but this is economically marginal. It is unlikely that there will be a large scale tendency to remove brash for biofuel production: if biofuel becomes popular other sources of biomass will be more economically sustainable, though harvesting residues as part of a mixed intake to biofuel plants will continue to be important in the medium term (5 - 10 years).

The benefits of leaving brash to return base cations and nutrients to the soil needs to be considered with respect to short term peaks in nitrate leaching. The timing and release of calcium from brash with respect to tree growth will have significant effects on base cation levels. The base cation sustainability issue requires further investigation.

Following completion of harvesting operations, brash mats are often disrupted, promoting more rapid regrowth of groundcover vegetation. This recycles calcium back into the soil and results in the uptake of nitrate by regenerating plants. If brash is left as dense mounds or mats, light penetration to ground level may be restricted, and groundcover will be slow to develop.

Many of these issues are addressed within existing and forthcoming Forestry Guidelines.

Site Preparation

Before restocking commences, it may be necessary to carry out preparation work. Ground preparation in the form of ploughing or sub surface treatments is not generally appropriate due to the presence of tree stumps and roots. Therefore the methods used tend to be less disruptive, and measures taken to prevent soil erosion will also reduce nitrate leaching. Opportunities may be taken to improve drainage systems to minimise the occurrence of harmful runoff through the installation of buffer zones.

Replanting/Groundcover

To minimise the effects of nitrate generation and loss, rapid regeneration of plant cover is recommended and foresters have the incentive to reestablish the new tree crop early, before other vegetation (weeds) reestablish themselves. Foresters sometimes need to control weed growth and limit initial competition with trees by the application of herbicides, on for example brown earth soil types. These are used in a 1 m diameter circle around trees. This may represent 25% of total ground cover. However, weeds may be an interim valuable nitrogen sink to reduce leaching. If a good seed pool has developed, natural regeneration of Sitka spruce can rapidly occur. It is then possible to thin this growth down to 2500 stems/ha. Initial high densities of self-seeded stock would also take up nitrate and reduce leaching, and minimal ground disturbance would occur, reducing potential risks to water courses.

Harvesting regimes

Many upland conifer stands are subject to windthrow, and therefore are at risk from large scale thinning. An estimated 86% of Welsh upland stands have the potential to be thinned though difficult ground conditions and limited economic returns may also restrict this activity. Heavy thinning will encourage or maintain groundcover establishment, and reduce nutrient loss although, groundcover will be shaded out as the canopy re-closes. Alternative harvesting regimes can increase the age diversity of stands and effectively maintain continuous forest cover. Very small felling coupes, <0.25 ha, if cleared in a patchwork, would minimise the nitrate pulse associated with felling. However, the small areas which are clear felled are unlikely to significantly reduce scavenging inputs.

10. CONCLUSIONS

The biogeochemical functioning of acidic and acid sensitive catchments is complex and difficult to pin down at the detailed scale. The essential problem is not primarily one of vastly complex hydrological, chemical and biological processes, which can easily be qualitatively described, but rather one connected with the heterogeneous nature of the hydrological, chemical and biological interactions. While the research community may have a sound descriptive grasp of the underlying theory, translating this into environmental management practice at a detailed level is extremely difficult. Indeed, we consider that the primary way forward to identifying management approaches to dealing with water quality issues in relation to land management at present is mainly via environmental measurement and pragmatic generalized approaches.

Clearly the present study provides good news in that under most circumstances, water quality deterioration following harvesting and replanting will be relatively small. Indeed under some circumstances improvement will result. This was not expected at the start of the project although in terms of process understanding the basic theory was in place and the results uphold the theory, apart from the issue of heterogeneity which was previously grossly underestimated.

The essential issue of maintaining and improving water quality rests with practical management "on the ground" rather than through broad theoretical pronouncements. For this to happen, it is vital that 1) the principles described here are communicated to field staff and policy makers and that they are incorporated in to future policy documents and best practice manuals and 2) that new initiatives be developed between Environment Agency and Forestry groups where considerable long term expertise is available. The practical issues at hand for felling and replanting, in the first five years are:

How to minimise land disturbance and nitrate release;

How to dilute water quality deterioration at the local scale for the larger catchments of more pressing concern.

Clearly, contemporary forestry guidelines offer a basis for achieving both goals.

On the longer term, there are issues of forestry cycles potentially leading to stream acidification as a result of base cation uptake into the growing biomass and export from the catchment with the harvested crop. However, there are too many uncertainties to properly gauge what the effects will be and clearly more research is required on this issue. Nonetheless, even here, practical issues that can be addressed are 1) to consider the value of using stem only harvesting methodologies and 2) to explore the use of phosphate fertilizer applications in acid sensitive areas. The latter as a "spin off", provide calcium back to the soils at levels approaching the calcium loss with harvesting and stimulates development of the newly planted trees to remove excess nitrogen.

With regards to scientific issues, it is clear that there is the need for:

1. long and continuing water quality datasets to show how our environment is actually changing, rather than relying excessively on broad generalisations and the theoretical predictions of computer modelling. The only real guide to judging how well we actually

understand climate and land use change is through long-term, uninterrupted, reliable, high quality measurement.

2. more thorough understanding of the heterogeneous nature of catchments and of groundwater-soilwater interactions. This issue may be of major practical importance because of the potential for harnessing the natural variability within catchments to improve our environment. For example manipulations might be considered to improve groundwater routing in areas of catchments which are particularly acidic or acid sensitive to reduce acidification.

3. more thorough understanding of trace metal and base cation cycling through catchments. This is of importance for the former in relation to assessing heavy metal critical loads from atmospheric pollutant sources and for the latter in terms of long-term acidification patterns. There are important 'fertiliser' sources of trace and major nutrients from atmospheric deposition. For many of these elements, a major component of the input is from pollution sources (e.g. sulphur, nitrogen and boron). With changing emission patterns there may be forest health issues relating to nutrient imbalances.

4. more thorough understanding of the link between water quality change and biological impacts. This is a fundamental issue. While water quality changes drive, in part, the biological response to land use and climate change, and water quality is more easily measured and modelled, it is in fact the biological response which is the primary concern.

These issues need to be explored from many perspectives, underpinned by high quality and long-term, focussed environmental measurement to produce the necessary overview for environmental management. In order to achieve this, the various parties concerned with the management of the upland environment need to be brought together so that the breadth and diversity of their experience can be exploited towards a common goal. We believe that the success of this project has demonstrated the effectiveness of this approach and we thank the steering committee for adding breadth and depth to our research. Further, both Environment Agency and the Forestry Commission have a valuable resource of experienced field staff who can facilitate many of the basic measurements. This is illustrated by the regional monitoring programme, which was only achievable by strong support from both the management and staff of Forest Enterprise.

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