HAL open science

Analysis of the impacts of major anion variations on surface water acidity particularly with regard to conifer harvesting: case studies from Wales and Northern England

C. Neal, B. Reynolds, J. K. Adamson, P. A. Stevens, M. Neal, M. Harrow, S. Hill

To cite this version:

C. Neal, B. Reynolds, J. K. Adamson, P. A. Stevens, M. Neal, et al.. Analysis of the impacts of major anion variations on surface water acidity particularly with regard to conifer harvesting: case studies from Wales and Northern England. Hydrology and Earth System Sciences Discussions, 1998, 2 (2/3), pp.303-322. hal-00304547

HAL Id: hal-00304547

https://hal.science/hal-00304547v1

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Hydrology and Earth System Sciences, 2(2–3), *303–322* (1998) © EGS

Hydrology & Earth System Sciences

Analysis of the impacts of major anion variations on surface water acidity particularly with regard to conifer harvesting: case studies from Wales and Northern England

Colin Neal[1], Brian Reynolds[2], John K. Adamson[3], Paul A. Stevens[2], Margaret Neal[1], Martin Harrow[1] and Susan Hill[1]

[1] Institute of Hydrology, Crowmarsh Gifford, Wallingford, OXON, UK, OX10 8BB.
[2] Institute of Terrestrial Ecology, Bangor Research Unit, Deiniol Road, Bangor, Gwynedd, N. Wales, UK, LL572UP.
[3] Institute of Terrestrial Ecology, Merlewood Research Station, Grange-over-Sands, Cumbria, UK, LA116JU.

Abstract

Data on the water quality of streams draining a range of acidic and acid sensitive, mainly afforested, upland catchments in mid- and north-Wales and northern-England are described to investigate the acidification effects of conifer harvesting in relation to natural variability. Most sites show a large range in pH and major cation and major anion concentrations. The waters draining from the smaller catchments are more acidic and aluminium bearing reflecting a higher proportion of runoff from the acidic soils in each area. However, there is often a less acidic component of runoff under base-flow conditions due to ground-water contributions particularly within the larger streams. Higher concentrations of nitrate occur for sites which have been felled although declines in concentration occur several years after felling. Multiple regression analysis reveals the importance of cation exchange and within catchment acidification associated with sulphate and nitrate generation. Sulphate also has a component associated with weathering but the patterns vary from catchment to catchment. Analysis of the influence of changing anion concentrations associated with tree harvesting reveals that the acidification induced by increases in nitrate can be offset or reversed by the lowering of chloride and sulphate concentrations due to decreased atmospheric scavenging by the vegetation, reduced evapotranspiration and increased surface runoff diluting the acidity generated. It is concluded that contemporary UK forestry guidelines with an emphasis on phased harvesting of catchments over several years and careful harvesting methodologies can alleviate most problems of stream acidification associated with felling activities and in some cases can reverse the acidification pattern.

Introduction

Considerable concerns have been raised over the effects of atmospheric deposition of acidic oxides (SO_x in particular) on the water quality and ecological vitality of streams draining acidic and acid sensitive areas of the UK (UKAWRG, 1988; UKRGAR, 1990; Mason, 1990; Edwards *et al.*, 1990: Smith *et. al.*, 1997). Acidic deposition is believed to have depleted base cations within the soil and to have increased the acidity of soil waters. Subsequently, when these waters are transferred to the streams, particularly under high flow conditions, more acidic conditions are induced both in terms of averages and extremes than prior to the onset of acidification (Jenkins *et al.*, 1990; Edwards *et al.*, 1990; Neal *et al.*, 1992a). There are also growing concerns over the additional stresses imposed on these acidic and acid sensitive systems. For example, climate variability and conifer planting and harvesting can generate acidity in the soil and acid flushes into the streams (Neal, 1997; Hudson *et al.*, 1997; Robson and Neal, 1996; Neal *et al.*, 1997a; Reynolds *et al.*, 1997; Langan 1987, 1989; UKRGAR, 1990; Hornung and Newson 1986). Nonetheless, following agricultural improvement, the application of basic slag fertilizers and lime has had a reverse effect by reducing soil and stream acidity (Hornung *et al.* 1986; Adams and Evans 1989; Reynolds *et al.*, 1986). Despite the broad conceptual understanding of acidification processes (Reuss and Johnson, 1986) and the development of catchment and regional scale environmental impact models of water quality for acidic and acid sensitive systems (Cosby *et al.*, 1985a,b; Christophersen *et al.*, 1982, 1984; Gherini *et al.*, 1985; Sverdrup, 1996), detailed quantitative understanding of the relative importance of these factors remains elusive and question marks remain over process representation (Neal, 1997; Neal *et al.*, 1997e, 1998). At the detailed scale of plots and individual small catchments (up to ten hectares in area), huge complexity becomes apparent due to the interactive nature of the processes and the con-

founding heterogeneity of natural systems (Neal *et al.*, 1997b; Hill and Neal, 1997). This is highly significant to many environmental managers dealing with specific issues such as local water quality problems. Up-scaling to larger catchments (100s to 1000s of hectares in area) and to regional levels leads to the emergence of simpler patterns (Neal, 1996, 1997). These patterns are readily captured in broad scale environmental impact models of relevance to national and international scale environmental management and regulation (Jenkins *et al.*, 1997). A discordance remains, therefore, between adequate process representation at the detailed scale and the ease of describing simple patterns of behaviour mathematically at the broad scale where factors such as over-parameterization and uncertainty over lumped process and data representations come into play (Christophersen and Neal, 1990; Neal, 1996, 1997).

Over the past two decades there have been several monitoring programmes examining stream water quality variations for acidic and acid sensitive areas of England and Wales as part of the UK Natural Environment Research Council's (NERC) remit within the environmental sciences under the Centre of Ecology and Hydrology (CEH) grouping. These studies have covered water quality issues at a range of scales varying from small ditches to streams and upland headwater rivers as a part of programmes such as the NERC funded Special Topic on Geochemical Cycling, SWAP (the Royal Society Surface Water Acidification Programme; Mason 1990), and the ENCORE (European Network of Catchments Organised for Research on Ecosystems; Hornung *et al.* 1990) project funded by the European Union. More recently, a joint NERC, Environment Agency and Forestry Commission research project has examined the impacts of forest harvesting and replanting on stream water quality (EA R&D project P2/i502). While considerable advances have been made within catchment science from these endeavours, the data have not been used to test, fundamentally, or examine the underlying processes of acidification except in a few cases (Neal, 1996).

Within this paper, the importance of major anion variations to stream water quality changes are examined using the wealth of UK information available from the above-mentioned studies within the context of Centre of Ecology and Hydrology research of CEH. Forested catchments are focused upon as harvesting leads to a perturbation of the catchment which changes all the major anion species. From the response to this manipulation, the underlying process understanding is tested and the magnitude and variation of the effects are quantified. The information gained is of (1) structural relevance for conceptual, descriptive and prescriptive environmental impact models and (2) practical relevance for the local and regional management of water quality issues related to forestry.

Sample sites

The data presented come from catchment studies in north Wales (Beddgelert Forest; Stevens *et al.* 1989; Stevens *et al.* 1993; Reynolds *et al.* 1995), mid Wales (Plynlimon and Vyrnwy catchments: Neal *et al.*, 1992a–c; Neal *et al.*, 1997a–d) and northern England (Kershope Forest: Adamson *et al.*, 1987; Adamson and Hornung 1990)). Nineteen sites have been examined for this paper: 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 1. A brief summary of the information for each area is as follows.

BEDDGELERT FOREST (NORTH WALES)

Three monitored catchments in Beddgelert Forest were examined. They 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. All the sites are small catchments (about 2 to 4 ha in area) draining extremely acidic peaty-podzol soils underlain by base-poor Lower Palaeozoic slates and shales.

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 gleys: deep peats are also important in the moorland plateau area. Five streams have been 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

Table 1. Catchment summary information. Key: SS=Sitka Spruce; G=Gley; P=Podzol; M=Acid Moorland; Pe=Peat; BE=Brown Earth; Y=Yes corresponds to 100% fell unless indicated otherwise; N=N corresponds to 0% fell.

Site	Area ha	Soil type	Vegetation	Fell	Sampling (per-year)	Data run (yrs)
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

since the mid 1940s and 1960s. A variety of harvesting techniques has 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 has 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 representing 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. At Vyrnwy, harvesting has only recently taken place at the Vn2 site and the data presented here only cover the pre-felling period. For the present analysis, the Tan-N site is not considered as the reducing conditions encountered resulted in nitrate concentrations below the detection limit and hence the data could not be analyzed using the methods described later in this paper. The reason for this difference is not clear from site geomorphology, soil and vegetation characteristics.

KERSHOPE FOREST (NORTHERN ENGLAND)

Data from four plots on peaty gley soils (each of about 2 ha area) are used in this paper. 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.

Chemical analysis and standardization of approaches to gran alkalinity and ANC determination

The methods of chemical analysis involved a combination of standard instrumental techniques including automated colorimetry, atomic-emission, atomic-absorption • and inductively coupled plasma optical emission and mass spectrometry, ion chromatography, acid titration and electrometric determinations. These methods are described in detail in the relevant papers quoted above. However, 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 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 programme of Schecher and Driscoll (1988):

$$\text{ANCest} = \text{Alk-G} - 3*[\text{T-Al}] + 0.054*[\text{DOC}] \quad (1)$$

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:

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

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

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

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

Of these two methods of estimating ANC, ANCest provides the primary reference in this paper because of the nature of the statistical tests presented later in the paper where ANC is regressed against the strong acid anions: ANCest is truly independent of the strong acid anion concentration while ANCcb is not. Nonetheless, ANCcb is used for the analysis when ANCest information is not available: 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:

$$\text{ANCcb} = 0.94(\pm 0.02)*\text{ANCest} + 12(\pm 30): \quad N = 983 \quad r^2 = 0.924$$

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

$$\text{ANCcb} = 1.00(\pm 0.02)*\text{ANCest} : N=983 \; r^2=0.880$$

in μEq/l units, where the $\pm$ 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 Eqns. 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 paper.

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, 1988; 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.*, 1997).

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, aluminum may precipitate when acid, aluminium bearing soil waters encounter more alkaline ground-waters 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 ground-water, 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 represents 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.*, 1996; 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-water. 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).

Results

SPATIAL AND TEMPORAL VARIABILITY

The water quality of the sites is summarised in Figs. 1a and 1b 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 is 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 probably 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

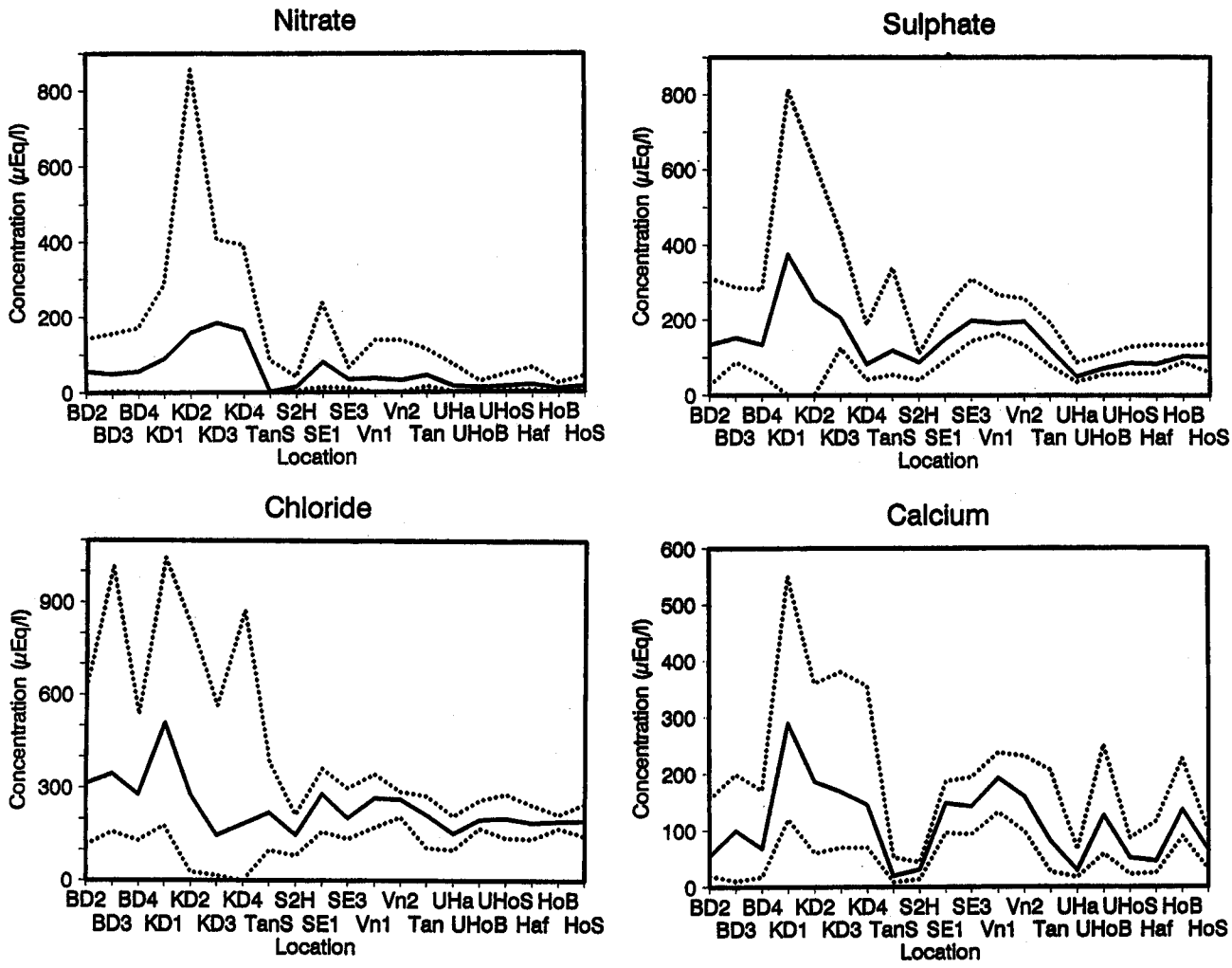


Fig. 1a. *Plots of averages (solid line) and minima and maxima (dashed lines) concentrations for nitrate, sulphate, chloride and calcium across the experimental sites. Within the plots, the locations are separated from left to right between small (BD2 to Vn2) and large (Tan to Ho) catchment areas.*

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.*, 1990). 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 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).

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

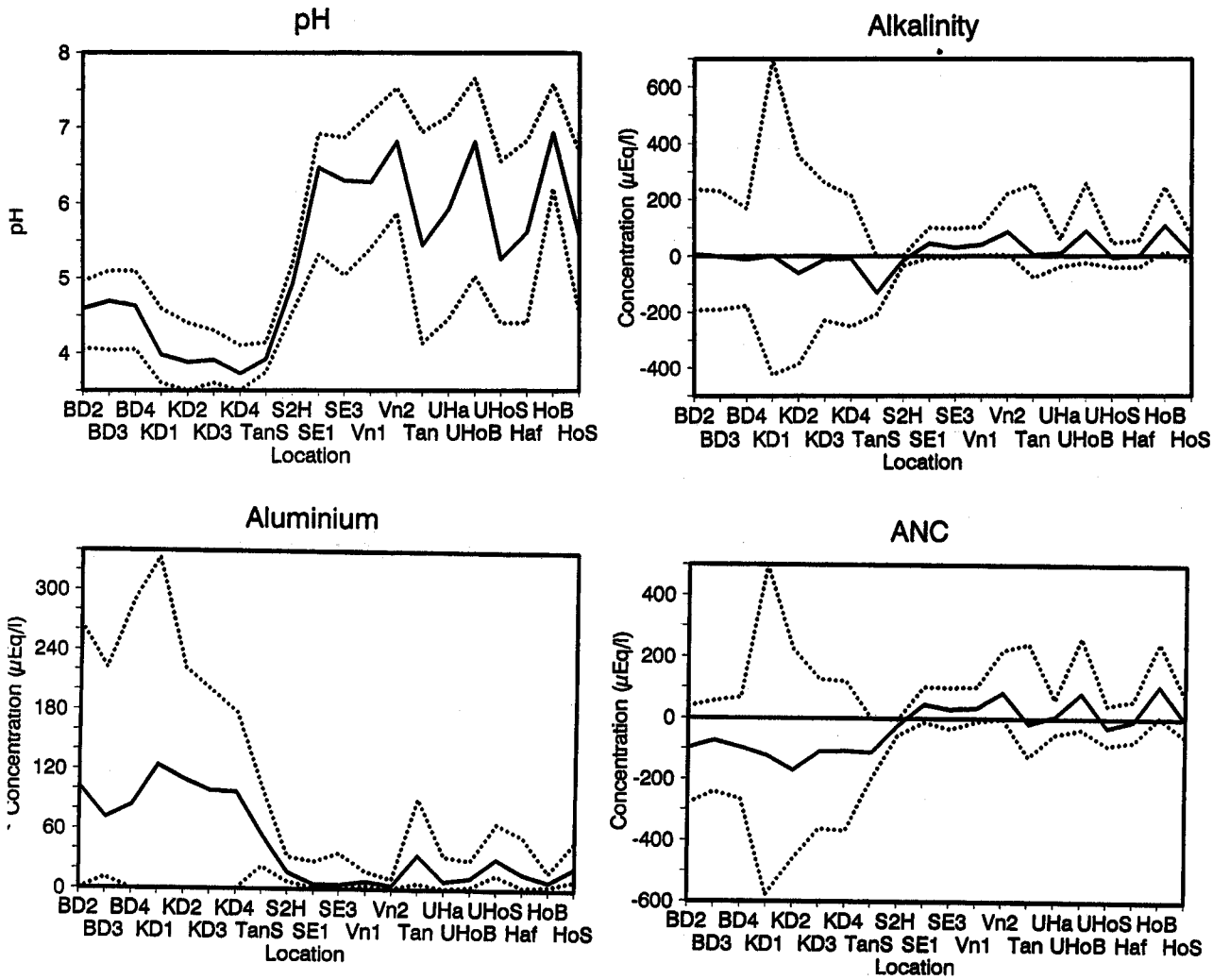


Fig. 1b. *Plots of averages (solid line) and minima and maxima (dashed lines) for pH and concentrations of alkalinity, aluminium and ANC across the experimental sites. Within the plots, the locations are separated from left to right between small (BD2 to Vn2) and large (Tan to Ho) catchment areas.*

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 groundwater 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 increases or decreases there will be a corresponding increase or 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 (ie. 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. Large changes in nitrate, chloride, sulphate, aluminium and ANC concentration and pH occur with time at SE1 (Fig. 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 deforestation 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 Fig. 3 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

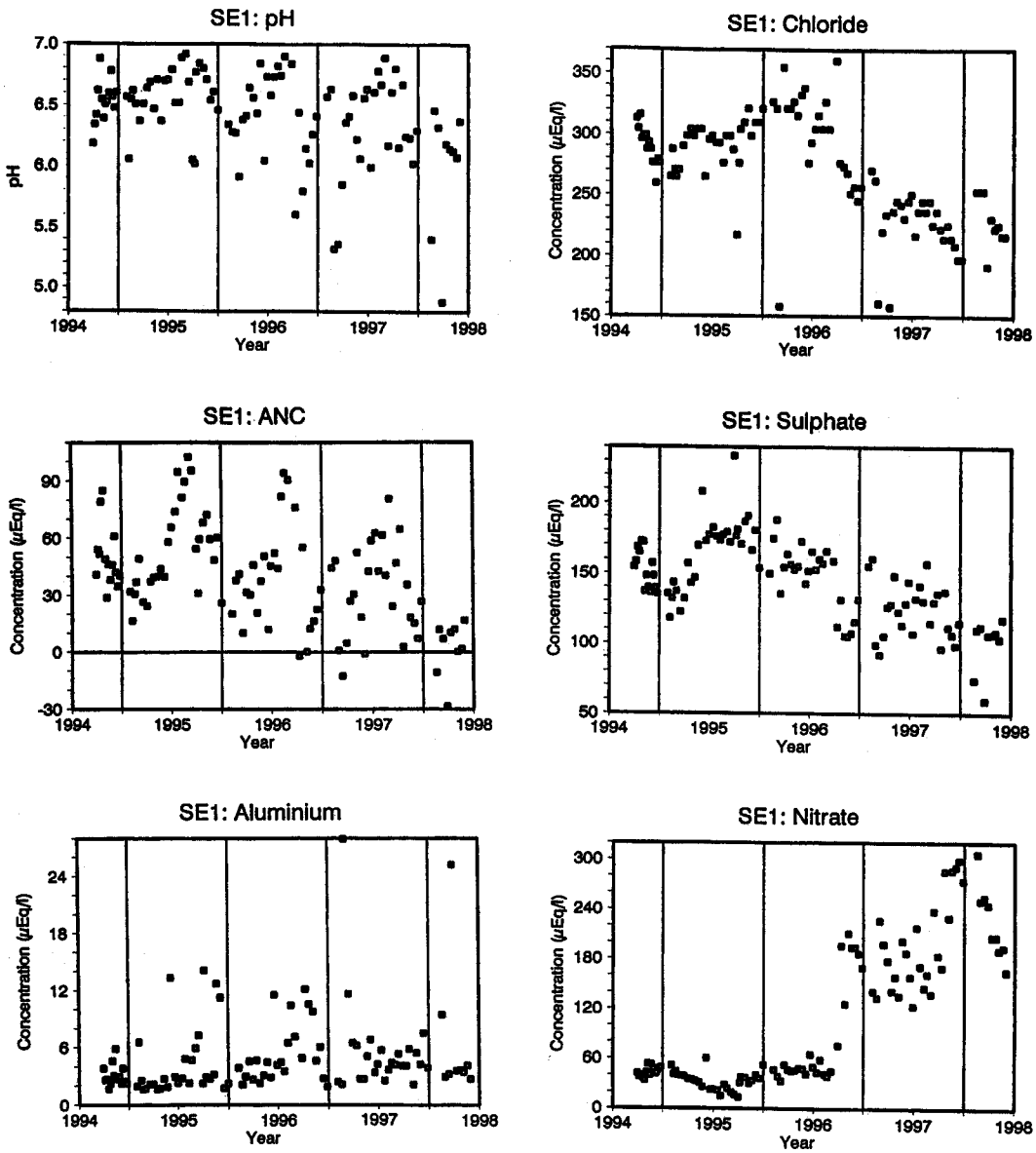


Fig. 2. *ANC, pH, aluminium, sulphate, chloride and nitrate time series for site SE1.*

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 (Fig. 3).

The Kershope Forest KD2 site. Even larger changes in water quality occur at KD2 than at SE1 (Fig. 4). In response to felling, nitrate shows a marked increase in 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 deforestation 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 (Fig. 5). 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

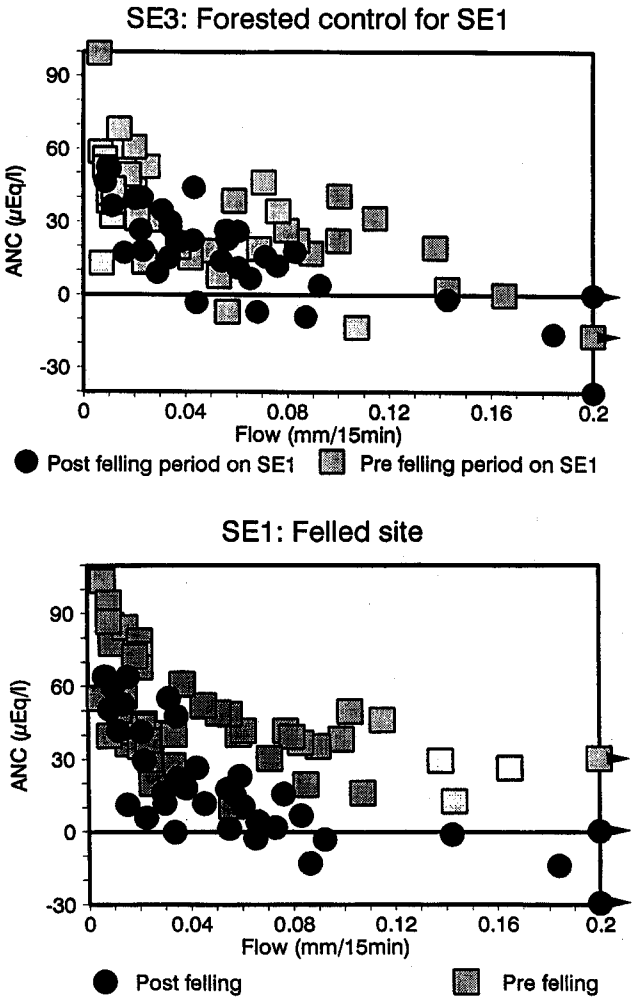


Fig. 3. *ANC plots with flow for felled site SE1 and the associated forested controls SE3. The circle and square symbols used refer to the times before and after felling, respectively, for the felling site. The same symbols are used for the control site to depict the corresponding period to that of felling 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.*

increased and then decreased after felling although it must be borne in mind that the data spread is particularly high.

THE RATIONALE FOR MULTIPLE REGRESSION ANALYSIS

Given 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 (Fig. 6). 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.*, 1986a, 1992a; Reynolds *et al.*, 1986). At particularly low flows, calcium and alkaline 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 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.

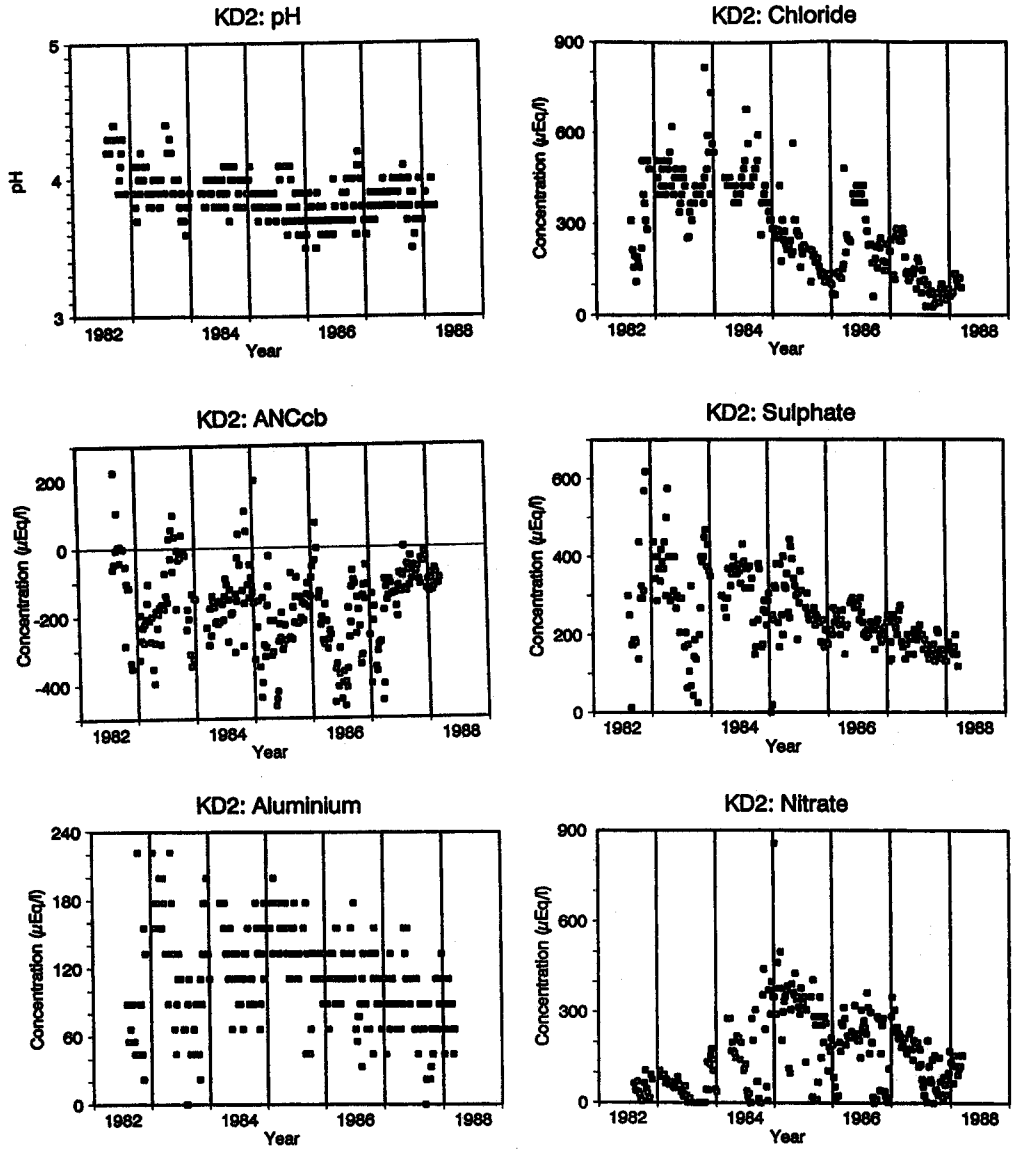


Fig. 4. *ANC, pH, aluminium, sulphate, chloride and nitrate time series for site KD2.*

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

$$\{AI\} = a^*\{Cl\} + b^*\{SO_4\} + c^*\{NO_3\} + d^*\log(\text{flow}) + e \quad (4)$$

where {} denotes concentration in μEq/l while "a", "b", "c" and "d" are the regression coefficients and "e" is a constant. Within the equation, 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 l/μEq since log(flow) is dimensionless: for pH, the first three regression coefficients have the units of l/μEq 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.

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

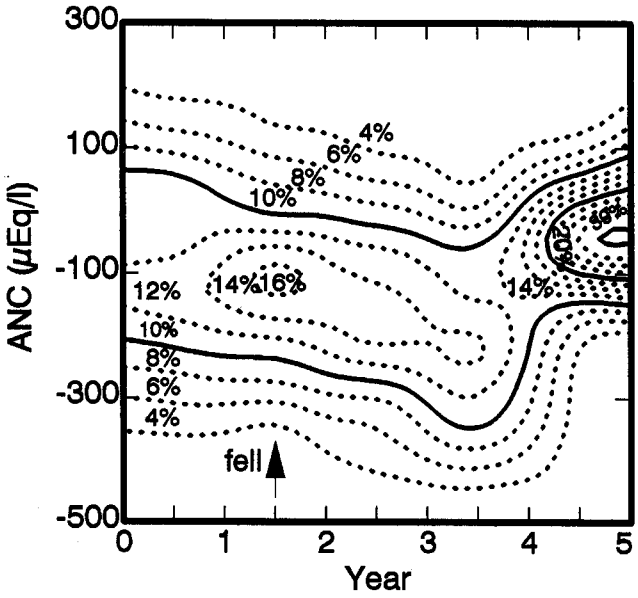


Fig. 5. *A contour plot of the percentage frequency of ANC values for stream waters at site KD2 as a function of time and ANC. Solid lines represent frequencies of 10 and 20%, while the dashed lines indicate 2% incremental steps.*

error estimates (twice the standard error), for all the acidification indices for each location (Appendix 1). 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 (Appendix 1) 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, ANC and pH whilst the

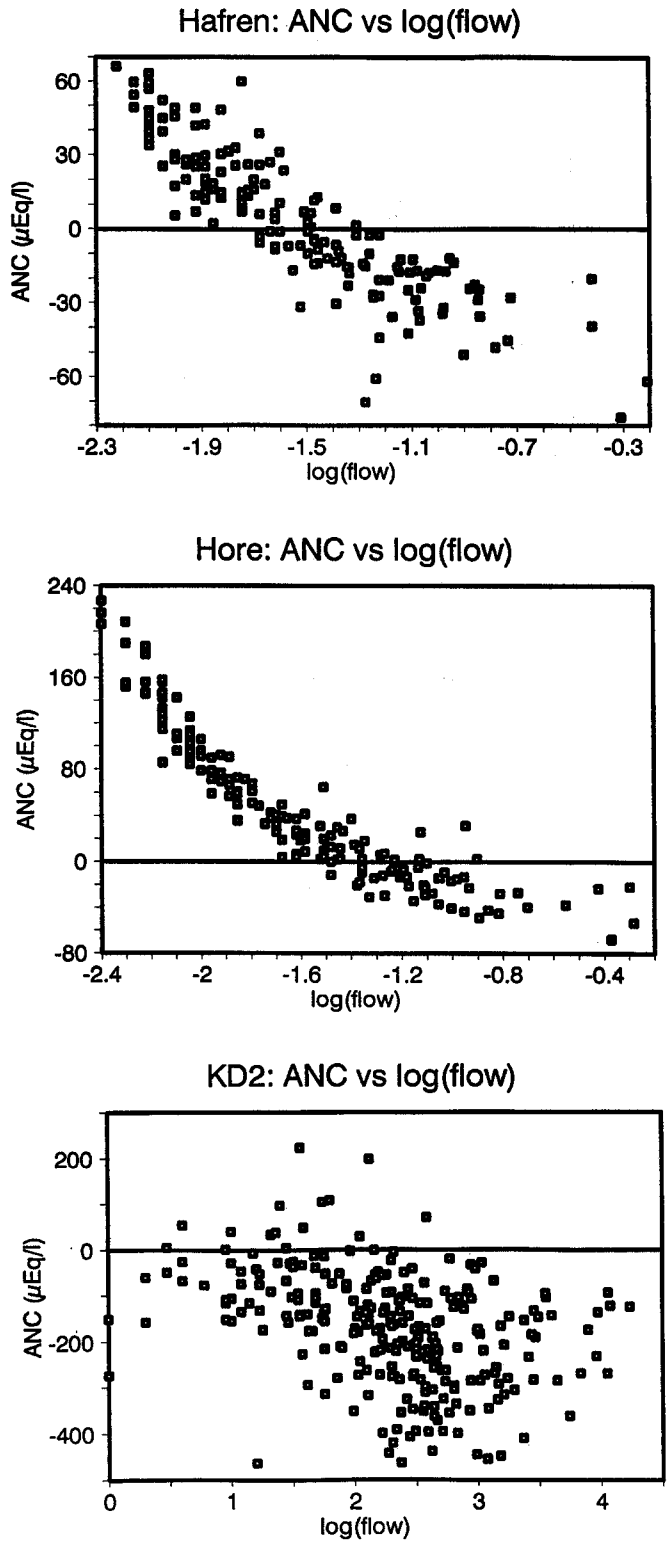


Fig. 6. *Plots of ANC against the logarithm of flow for the lower Hafren, lower Hore and KD2 sites. The single linear pattern observed for the Hafren is characteristic of most sites although the degree of scatter can be high as illustrated with the KD2 example. However, the pattern for the lower Hore follows two linear features and this probably reflects two different groundwater contributions at moderate to low flows.*

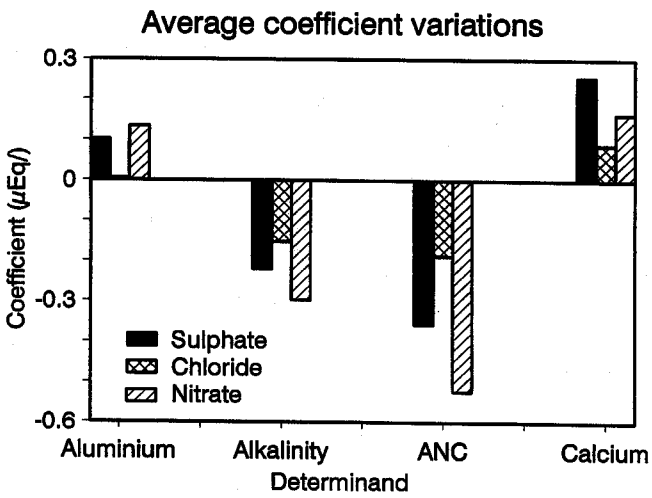


Fig. 7. *Average regression coefficients for aluminium, alkalinity, ANC and calcium across the sites.*

modulus of the regression coefficients lies in the range 0 to 1 (Appendix 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 (Fig. 7). 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 (Appendix 1) 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 (Appendix 1). 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 ground-water 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 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 (Appendix 1). 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, par-

ticularly 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.

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 (Fig. 7). The corresponding decline in ANC is about 0.5 μEq/μEq-NO_3. Thus, about 0.2 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.*, 1997a). 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 ground-water and within-stream and within-catchment nitrate consumption.

For chloride, increasing or decreasing concentrations appear to lead to a relatively small acidification or 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.*, 1990). 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.*, 1986a).

Clearly, sulphate acts as an acidifying component of stream runoff often to a similar degree to nitrate for individual sites. Sulphate in rainfall and stream waters contains a dominant non-sea-salt component associated with deposition of atmospheric pollution. However, there seem to be additional factors linked to ground-water 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.* (1997f) 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.*, 1997g). 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 (cf. Eqn. 1 and Eqn. 3). 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 paper 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. Deforestation leads to both nitrate production and declines in sulphate and chloride concentrations as shown in this paper and elsewhere (Neal *et al.*, 1992a–c; Neal *et al.*, 1997a). 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 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 (Fig. 2 and Fig. 3). While this change seems relatively large in environmental impact terms (e.g. for critical loads and long term acidification changes: Jenkins *et al.*, 1997), 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 chloride and sulphate signals 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 by Neal *et al.*, (1992a,b) and illustrated including more recent data in Fig. 8. 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 (Fig. 8).

Conclusions

The work; (1) shows the value of studying a variety of sites to identify both common and differing patterns of hydrochemical behaviour, (2) confirms the value of multiple regression as a method for initial data appraisal and the identification/verification of key underlying processes, (3) points to the importance of cation exchange and aluminium leaching concepts currently used in acid deposition work at the descriptive level at least, (4) illustrates that the systems under study are highly complex and variable, (5) demonstrates the need for long term monitoring periods to pick up the salient features and (6) shows, by the nature of the hydrochemical variability, that predicting

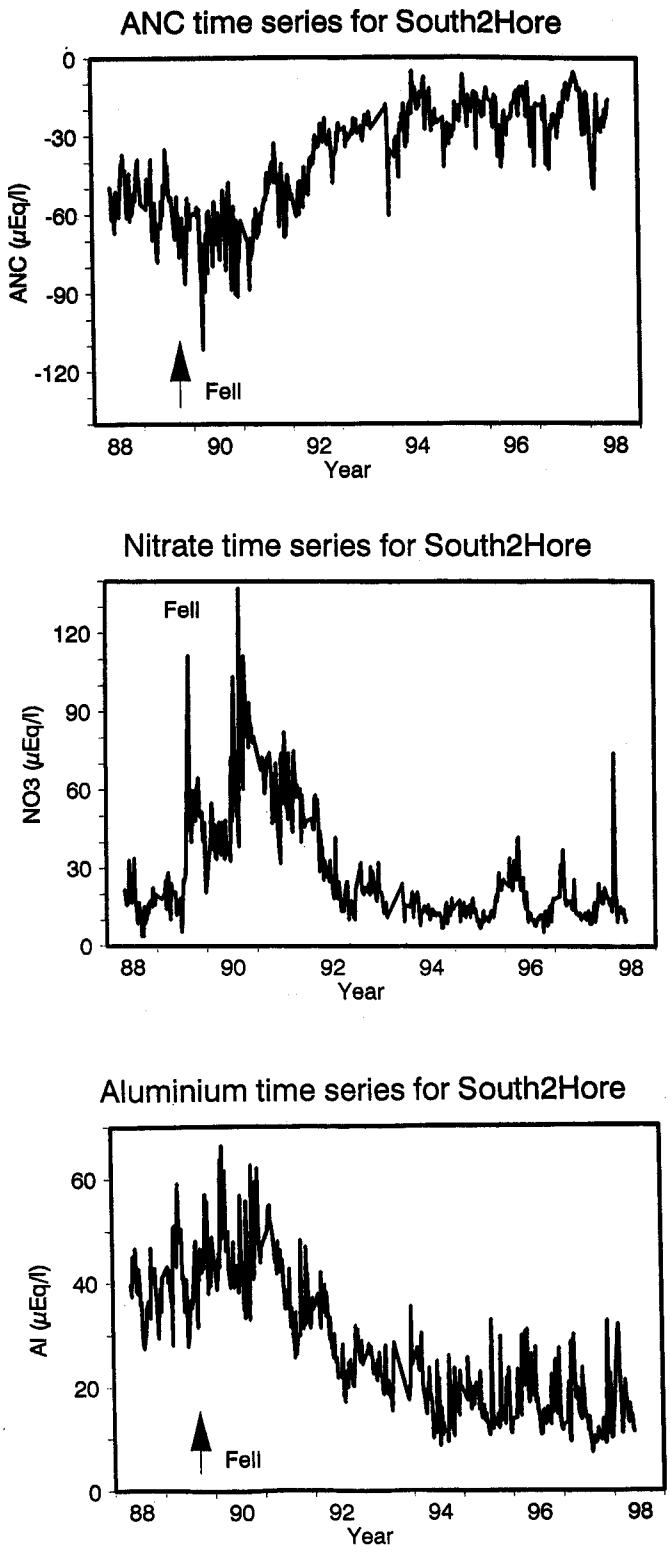


Fig. 8. *Time series for ANC, nitrate and aluminium concentrations for the South2Hore site.*

water quality, both in relation to natural variability and changes associated with felling at a quantitative level, is extremely difficult.

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.*, 1992b, Neal, 1996). However, it is also clear that further understanding of basic processes is required, for example, (1) to address the issue of unmeasured strong acid anions affecting the ANC, (2) the effect of changing carbon dioxide partial pressures on weathering rates and (3) the potential for aluminium solubility controls other than aluminium hydroxide.

The results reveal that deforestation 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 deforestation 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 (Neal *et al.*, 1986b; Reynolds *et al.*, 1988). This is most graphically demonstrated for S2H 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.

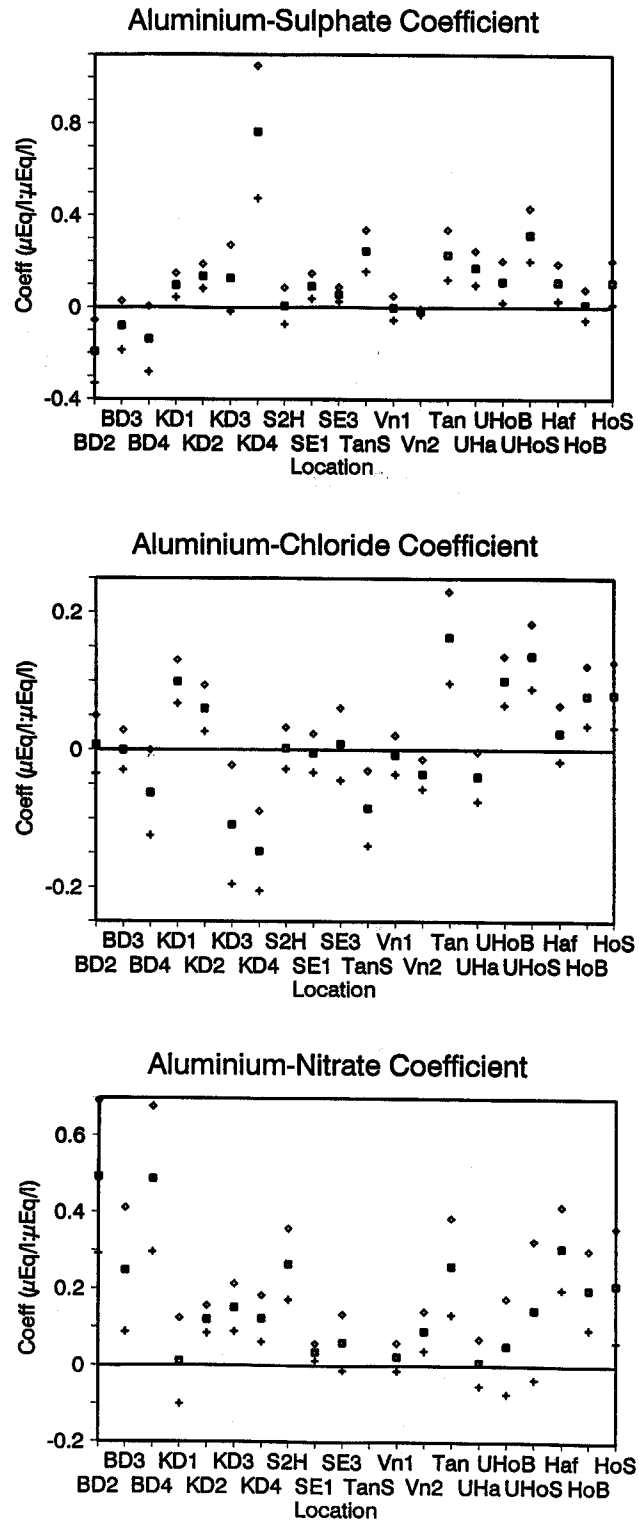
The net stream acidification during the nitrate pulse is seemingly large (i.e. about 30, 90 and 15 μEq/l for the three examples) in relation, for example, to environmental management indices of acidification such as critical load thresholds. However, these ANC changes are almost

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 deforestation 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.*, 1992bc; 1997a). 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:

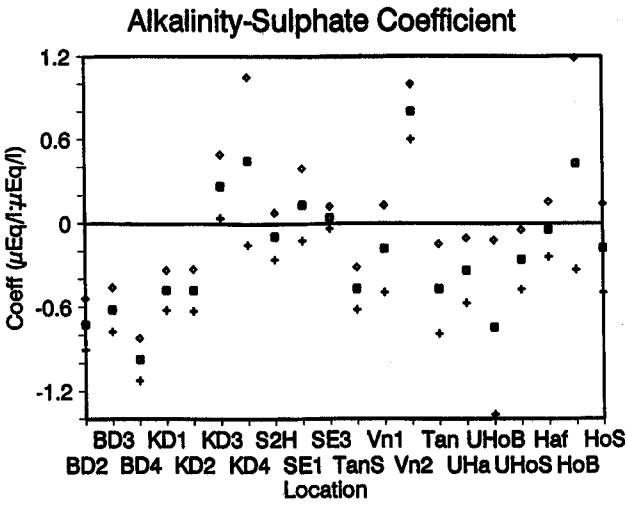
(1) when the balance between nitrate generation and strong acid anion reduction is weighted towards nitrate production, particularly at times of high flow when acid conditions are most extreme;
(2) when the total strong acid anion concentrations are at their highest (after allowance for their differing rates acidification). 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 maritime inputs of sea-salts is at its highest.

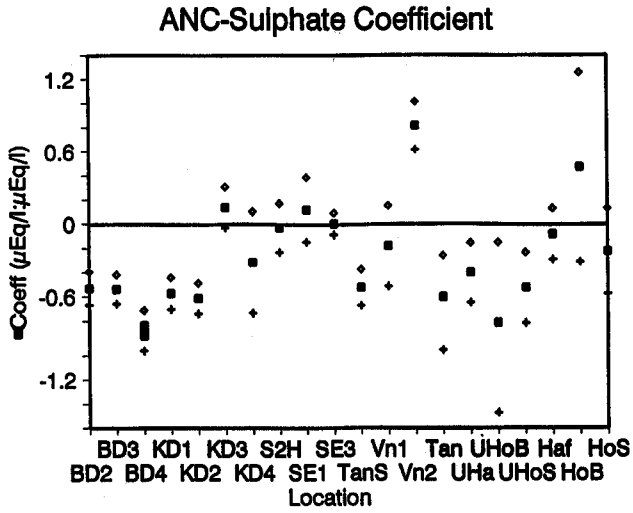
The results illustrate that, to minimise acidification impacts of conifer harvesting, increased nitrate production and extremes in nitrate concentration need to be kept in check. Thus, the onus is to ensure the introduction of new vegetation as soon as possible after felling and completion of felling at the onset of the period when catchment nitrate generation is likely to be minimal. Nonetheless, this issue 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, (d) 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, 1989; Jenkins, 1989; Mulder *et al.*, 1990). Adherence to the contemporary forest management guidelines (FC 1993) and good practice manuals (Nisbet *et al.*, 1997) should ensure maintainenance and improvement of water quality in plantation forests on such acidic and acid sensitive systems.

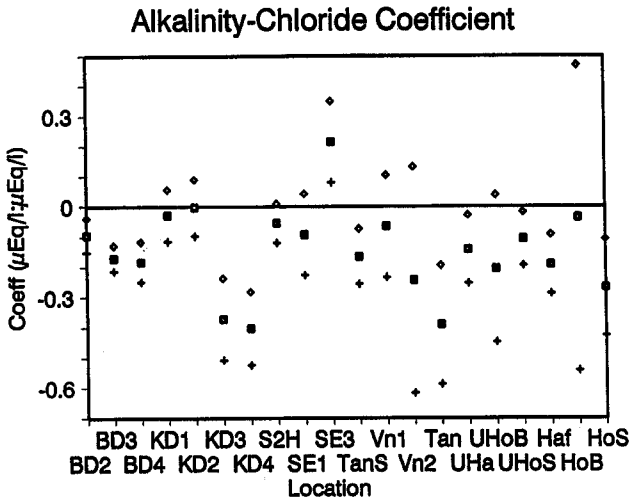
Appendix

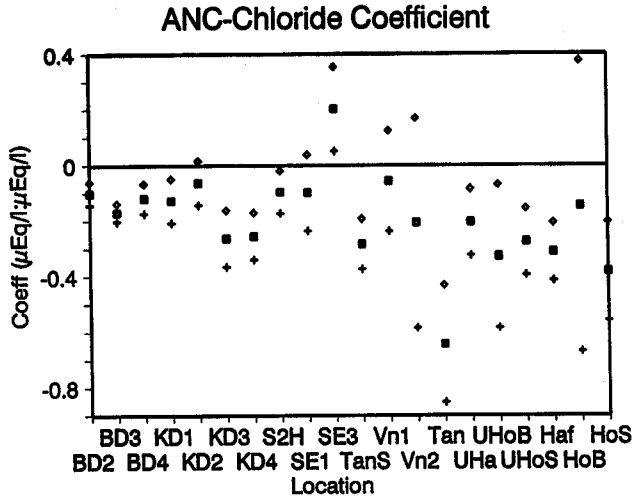


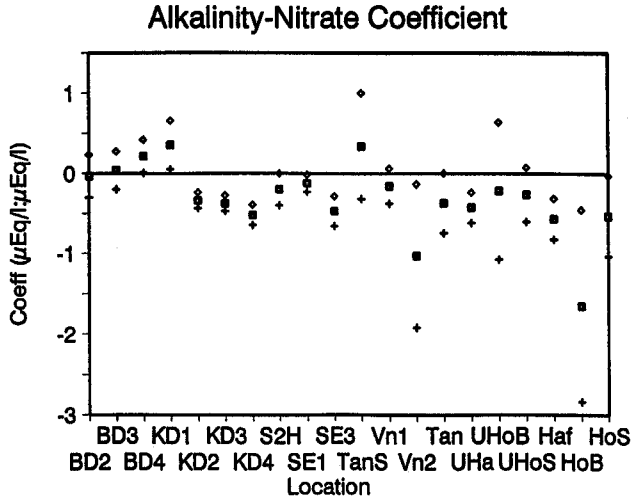
Appendix graph 1a. *Regression coefficients for aluminium with the strong acid anions across the experimental sites. The values plotted include an estimate of error based on ± twice the standard deviation.*

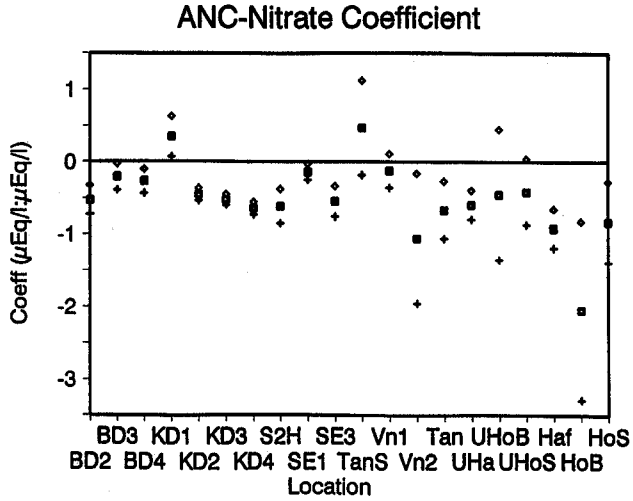






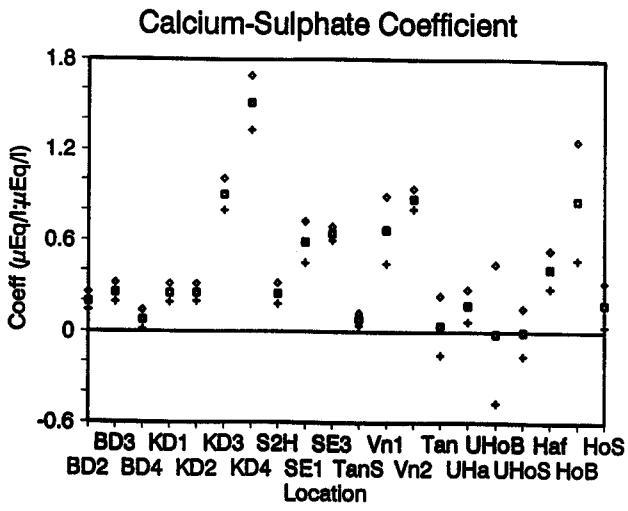


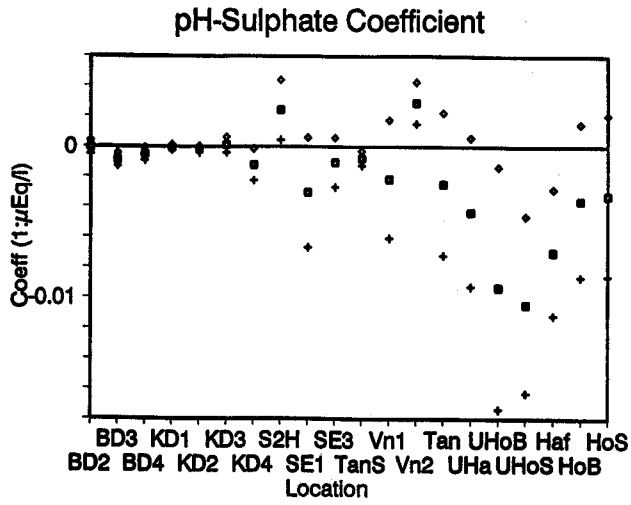


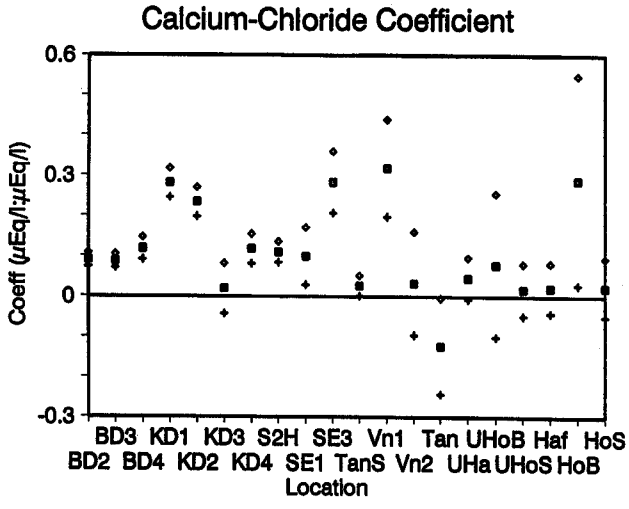


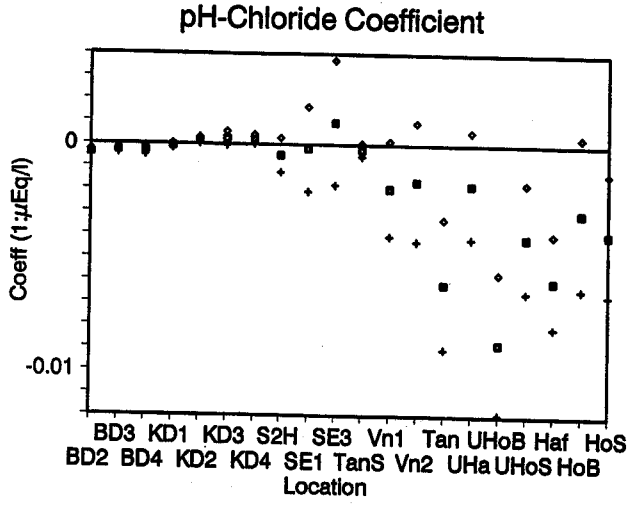
Appendix graph 1b. *Regression coefficients for Gran alkalinity with the strong acid anions across the experimental sites. The values plotted include an estimate of error based on ± twice the standard deviation.*

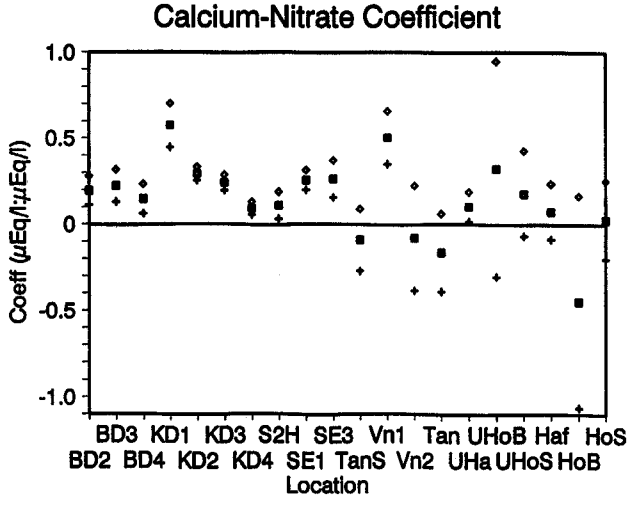
Appendix graph 1c. *Regression coefficients for ANC with the strong acid anions across the experimental sites. The values plotted include an estimate of error based on ± twice the standard deviation.*

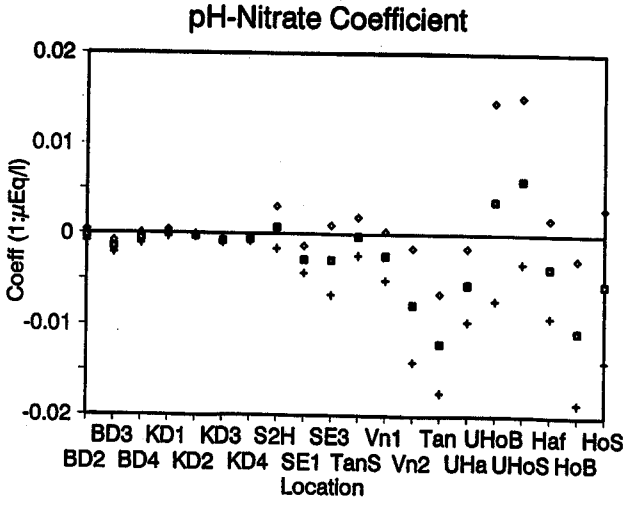












Appendix graph 1d. *Regression coefficients for calcium with the strong acid anions across the experimental sites. The values plotted include an estimate of error based on ± twice the standard deviation.*

Appendix graph 1e. *Regression coefficients for pH with the strong acid anions across the experimental sites. The values plotted include an estimate of error based on ± twice the standard deviation.*

Acknowledgements

We are indebted to the enthusiastic help of Bob Farmer (FE) with the design and implementation of the programme and the reviews by Alan Jenkins (IH), Tom Nisbet (FA) and Graham Rutt (EA) as well as external and other reviewers for their first class critical assessment of the work, which allowed a far superior contribution to be produced.

References

Adams, W.A. and Evans, G.M., 1989. Effects of lime applications to parts of an upland catchment on soil properties and the chemistry of drainage waters. *J. Soil Sci.*, **40**, 585–597.

Adamson, J.K., Hornung, M., Pyatt, D.G. and Anderson, A.R., 1987. Changes in solute chemistry of drainage waters following the clearfelling of a Sitka spruce plantation. *Forestry*, **60**, 165–177.

Adamson, J.K. and Hornung, M., 1990. The effect of clearfelling Sitka spruce (*Picea sitchensis*) plantation on solute concentrations in drainage water. *J. Hydrol.*, **116**, 287–298.

Christophersen, N. and Neal, C., 1990. Linking hydrological, geochemical, and soil chemical processes on the catchment scale: an interplay between modelling and field work. *Wat. Resour. Res.*, **26**, 3077–3086.

Christophersen, N., Seip, H.M. and Wright, R.F., 1982. A model for stream water chemistry at Birkenes, Norway. *Wat. Resour. Res.*, **18**, 977–996.

Christophersen, N., Rustad, S. and Seip, H.M., 1984. Modelling streamwater chemistry with snowmelt. *Phil. Trans. Roy., Soc. London*, ser. B, **305**, 427–439.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N., 1985a. Modelling the effects of acidic deposition: assessment of a lumped-parameter model of soil water and stream water chemistry. *Wat. Resour. Res.*, **21**, 51–63.

Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N., 1985b. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Wat. Resour. Res.*, **21**, 1591–1601.

Edwards, R.W., Gee, A.S. and Stoner, J.H., 1990. *Acid Waters in Wales*. Kluwer (Dordrecht), 337pp.

FC., 1993. *Foresty and Water Guidelines*. Forestry Commission, HMSO, London.

Gherini, S.A., Mok, L., Hudson, R.J.M., Davis, G.F., Chen, C.W. and Goldstein, R.A., 1985. The ILWAS model: formulation and application. *Wat. Air Soil Pollut.*, **26**, 425–459.

Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst*, **77**, 661–671.

Harriman, R., Gillespie, E. and Morrison, B.R.S., 1990. Factors affecting fish survival in Scottish catchments. In: 1990. *The surface water acidification programme* (ed. Mason, B.J.), Cambridge University Press, 343–355.

Hill, T. and Neal, C., 1997. Spatial and temporal variation in pH, alkalinity and conductivity in surface runoff and groundwater for the upper River Severn catchment, Plynlimon, mid-Wales. *Hydrol. Earth System Sci.*, 1(3), 697–716.

Hornung, M. and Newson, M.D., 1986. Upland afforestation: influences on stream hydrology and chemistry. *Soil Use Manag.*, **2**, 61–65.

Hornung, M., Stevens, P.A. and Reynolds, B., 1986. The impact of pasture improvement on the soil solution chemistry of some stagnopodzols in mid-Wales. *Soil Use Manag.*, **2**, 18–26.

Hornung, M., Roda, F. and Langan, S.J., 1990. *A review of small catchment studies in Western Europe producing hydrochemical budgets*. Air Pollution Research Report 28, Commission of the European Communities, Brussels.

Hudson, J.A., Gilman, K. and Calder, I.R., 1997. Land use and water quality issues in the uplands with reference to the Plynlimon study. *Hydrol. Earth System Sci.*, 1(3), 389–398.

Jenkins, A., 1989. Storm period hydrochemical response in an unforested Scottish catchment. *Hydro. Sci.*, **34(4)**, 393–404.

Jenkins, A. Cosby, B.J., Ferrier R.C., Walker T.A.B. and Miller, J.D., 1990. Modelling stream acidification in afforested catchments: an assessment of the relative effects of acid deposition and afforestation. *J. Hydrol.*, **120**, 163–181.

Jenkins, A., Coric, S., Reynolds, B., Curtis, C. and Renshaw, M., 1997. Critical loads for soils and freshwaters: a comparison of methods at the Plynlimon catchments. *Hydrol. Earth System Sci.*, 1(3), 729–742.

Kirchner, J.W., Dillon, P.J. and Lazerte, B.D., 1993. Separating hydrological and geochemical influences on runoff in spatially heterogeneous catchments. *Wat. Resour. Res.*, **29**, 3903–3916.

Langan, S.J., 1987. Episodic acidification of streams at Loch Dee, SW Scotland. *Transactions of the Royal Society of Edinburgh*, Earth Sciences, **78**, 393–397.

Langan S.J., 1989. Sea-salt induced streamwater acidification. *Hydro. Proc.*, **3**, 24–41.

Mason, B.J. (ed.) 1990. *The surface water acidification programme*. a compendium of papers edited by B.J. Mason. Cambridge University Press, 522pp.

Mulder, J. and Cresser, M.S., 1994. Soil and solution chemistry. Chapter 5 in: *Biogeochemistry of small catchments: a tool for environmental research* (eds Moldan, B. and Cerny, J.). John Wiley and Sons (Chichester). 107–131.

Mulder, J., Christophersen, N., Hauhs, M., Vogt, R.D., Andersen, S. and Andersen, D.O., 1990. Water flow paths and hydrochemical controls in the Birkenes catchment as inferred from a rainstorm high in sea salts. *Water Resour. Res.*, **26**, 611–622.

Neal, C., 1988. Determination of dissolved CO_2 in upland streamwater, (Wales, UK). *J. Hydrol.*, **99**, 127–142.

Neal, C., 1996. Towards lumped integrated models of complex heterogeneous environments. *Sci. Tot. Environ.*, **183**, 115–124.

Neal, C., 1997. A view of water quality from the Plynlimon watershed. *Hydrol. Earth System Sci.*, 1(3), 743–754.

Neal, C. and Christophersen, N., 1989. Inorganic aluminium-hydrogen relationships for acidified streams: the role of water mixing processes. *Sci. Total Environ.*, **80**, 195–203.

Neal, C. and Hill, S., 1994. Dissolved inorganic and organic carbon in moorland and forest streams: Plynlimon, Mid-Wales. *J. Hydrol.*, **153**, 231–243.

Neal, C. Smith, C.J. Walls, J. and Dunn C.S., 1986a. Major, minor and trace element mobility in the acidic upland forested catchment of the upper River Severn, mid-Wales. *Quart. Journ. Geol Soc. (London)*, **143**, 635–648.

Neal, C., Whitehead, P.G., Neale, R. and Cosby, B.J., 1986b. Modelling the effects of acidic deposition and conifer afforestation on stream acidity in the British uplands. *J. Hydrol.*, **86**, 15– 26.

Neal, C., Reynolds, B., Stevens, P.A., Hornung, M. and Brown, S.J., 1990. Dissolved inorganic aluminium in acidic stream and soil waters in Wales. In *Acid Waters in Wales* (eds Edwards, R.W., Gee, A.S. and Stoner, J.H.). Kluwer (Dordrecht), 173–188.

Neal, C. Smith, C.J. and Hill, S., 1992a. *Forestry impact on upland water quality*. Institute of Hydrology No. 119. Institute of Hydrology, Maclean Building, Crowmarsh Gifford, Wallingford, OXON, OX10 8BB, UK. 50pp.

Neal, C. Reynolds, B., Smith, C.J., Hill, S., Neal, M., Conway, T., Ryland, G.P., Jeffery, H.A., Robson, A.J. and Fisher, R., 1992b. The impact of conifer harvesting on stream water pH, alkalinity and aluminium concentrations for the British uplands: an example for an acidic and acid sensitive catchment in mid-Wales. *Sci. Total Environ.*, **126**, 75–87.

Neal, C., Fisher, R., Hill, S., Neal, M., Conway, T., Ryland, G.P. and Jeffery, H.A., 1992c. The effects of tree harvesting on stream water quality at an acidic and acid sensitive spruce forested area: Plynlimon, mid-Wales. *J. Hydrol.*, **135**, 305–319.

Neal, C., Robson, A.J., Reynolds, B. and Jenkins, A., 1992d. Prediction of future short term stream chemistry—a modelling approach. *J. Hydrol.*, **130**, 87–103.

Neal, C., Wilkinson, J., Neal, M., Harrow, M., Wickham, H., Hill, L. and Morfitt, C., 1997a. The hydrochemistry of the River Severn, Plynlimon, mid-Wales. *Hydrol. Earth System Sci.*, **1**, 583–618.

Neal, C., Hill, T., Hill, S. and Reynolds B., 1997b. Acid neutralization capacity measurements in surface and ground waters in the Upper River Severn, Plynlimon: from hydrograph splitting to water flow pathways. *Hydrol. Earth System Sci.*, **1**, 687–696.

Neal, C., Robson, A.J., Shand, P., Edmunds, W.M., Dixon, A.J., Buckley, D.K., Hill, S., Harrow. M., Neal, M. and Reynolds, B., 1997c. The occurrence of groundwater in the lower Palaeozoic rocks of upland Central Wales. *Hydrol. Earth System Sci.*, **1**, 3–18.

Neal, C., Hill, T., Alexander, S., Reynolds, B., Hill, S., Dixon, A.J., Harrow, M., Neal, M. and Smith, C.J., 1997d. Stream water quality in acid sensitive upland areas, an example of potential water quality remediation based on groundwater manipulation. *Hydrol. Earth System Sci.*, **1**, 185–196.

Neal, C., Robson, A.J. and Christophersen, N., 1997e. Towards coupling hydrological, soil and weathering processes within a modelling perspective. In: *Geochemical processes, weathering and groundwater recharge in catchments* (eds O.M. Saether and P. de Caritat). A.A. Balkema (Rotterdam), 329–380.

Neal, C., House, W.A. and Down, K., 1997f. An assessment of excess carbon dioxide partial pressures in natural waters based on pH and alkalinity measurements. *Sci. Tot. Environ.*, **210/211**, 173–186.

Neal, C., House, W.A., Jarvie, H.P. and Eatherall, A., 1997g. The significance of dissolved carbon dioxide in major lowland rivers entering the North Sea. *Sci. Tot. Environ.*, **210/211**, 187–204.

Neal, C., Reynolds, B., Wilkinson, J., Hill, T., Neal, M. and Harrow, M., 1998. The impacts of conifer harvesting on runoff water quality: a regional survey for Wales. *Hydrol. Earth System Sci.*, **2**, 323–344.

Nisbet, T., Dutch, J. and Moffatt, A., 1997. *Whole-Tree Harvesting; A Guide to Good Practice*. Forestry Commission, 231 Corstorphine Road, Edinburgh, EH12 7AT.

Reuss, J.O. and Johnson, D.W., 1986. *Acid deposition and the acidification of soils and waters. Ecological studies*, **59**, Springer-Verlag (New York), 119pp.

Reynolds, B. and Neal, C., 1989. A comment on the use of acidimetric titrations for the estimation of the alkalinity and bicarbonate content of acid upland surface waters. *Sci. Tot. Environ.*, **65**, 155–161.

Reynolds, B. Neal, C. Hornung, M. and Stevens, P.A., 1986. Baseflow buffering of streamwater acidity in five mid-Wales catchments. *J. Hydrol.*, **87**, 167–185.

Reynolds, B. Neal, C. Hornung, M. Hughes, S. and Stevens, P.A., 1988. Impact of afforestation on the soil solution chemistry of stagnopodzols in mid-Wales. *Wat. Air Soil Pollut.*, **38**, 55–70.

Reynolds, B., Stevens, P.A., Hughes, S., Parkinson, J.A. and Weatherley, N.S., 1995. Stream chemistry impacts of conifer harvesting in Welsh catchments. *Wat. Air Soil Pollut.*, **79**. 147–170.

Reynolds, B. Fowler, D. and Thomas, S., 1996. Chemistry of cloud water at an upland site in mid-Wales. *Sci. Tot. Environ.*, **188**, 115-125.

Reynolds, B., Renshaw, M., Sparks, T.H., Hudson, J.A., Hughes, S., Brittain, S.A. and Kennedy, V.H., 1997. Trends and seasonality in streamwater chemistry in two moorland catchments of the upper River Wye, Plynlimon, mid-Wales. *Hydrol. Earth System Sci.*, **1**, 571–582.

Robson, A.J., 1993. *The use of continuous measurement in understanding and modelling the hydrochemistry of the uplands*. PhD dissertation, University of Lancaster, Lancaster, Lancashire, UK, 278pp.

Robson, A.J. and Neal, C., 1996. Water quality trends at an upland site in Wales, UK, 1983–1993. *Hydrol. Processes*, **10**, 183–203.

Schecher, W.D. and Driscoll, C.T., 1988. An evaluation of the equilibrium calculations within acidification models. The effects of uncertainty in measured chemical components. *Wat. Resour. Res.*, **24**, 533–540.

Smith, R.I., Cape, J.N., Binnie, J., Murray, T.D., Young, M. and Fowler, D., 1997. Deposition of atmospheric pollutants to the LOIS area. *Sci. Total Environ.*, **194/195**, 71–86.

Stevens P.A., 1987. Throughfall chemistry beneath sitka spruce of four ages in Beddgelert Forest, north-Wales, UK. *Plant and Soil*, **101**, 291–294.

Stevens, P.A., Hornung, M. and Hughes, S., 1989. Solute concentrations, fluxes and major nutrient cycles in a mature Sitka spruce plantation in Beddgelert Forest, North Wales. *Forest Ecology and Management*, **27**, 1–20.

Stevens, P.A., Williams, T.G., Norris, D.A. and Rowland, A.P., 1993. Dissolved inorganic nitrogen budget for a forested catchment at Beddgelert, North Wales. *Environ. Pollut.*, **80**, 1–8.

Stumm, W. and Morgan, J.J., 1970. *Aquatic Chemistry*. Wiley-Interscience (New York), 583pp.

Sverdrup, H., 1996. Geochemistry, the key to understanding environmental chemistry. *Sci. Total Environ.*, **183**, 67–88.

UKRGAR, 1990. *Acid Deposition in the United Kingdom 1986-88*. Third Report of the Review Group on Acid Rain, AEA Technology, Harwell, 1-124.

UKRGAR, 1997. *Acid Deposition in the United Kingdom 1992-94*. Fourth Report of the Review Group on Acid Rain, AEA Technology, Harwell, 1-60.

UKAWRG, 1988. *United Kingdom Acid Waters Review Group, second report*. Acidity in United Kingdom fresh waters. Her Majesty's Stationary Office, London, 1–61.

Wilkinson, J., Reynolds, B., Neal, C., Hill, S., Neal, M. and Harrow, M., 1997. Major, minor and trace element composition of cloud-water and rainwater at Plynlimon. *Hydrol. Earth System Sci.*, **1**, 557–570.