



**Institute of  
Hydrology**

**Forestry Impact on Upland  
Water Quality**

**NRA PROJECT 114 (G/NRA1)**

**Project Review September 1989**

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## FORESTRY IMPACT ON UPLAND WATER QUALITY.

A report to the National Rivers Authority on project 114 (DoE ref G/NRA1). C. Neal, C.J. Smith and M. Neal.

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### SUMMARY

Results of a 7 year hydrochemical study of the effects of conifer harvesting and acidic oxide deposition on stream water quality for a 25 to 45 year old sitka spruce plantation at Plynlimon, mid-Wales, are described. The data relates to an extensive monitoring of major, minor and trace element variations in rainfall, throughfall, stemflow and stream water.

Rainfall chemistry is very variable owing to the influence of both a maritime input (Na, Mg, Cl, Br etc) and a pollutant input ( $H^+$ ,  $SO_4$ ,  $NO_3$ , Al, Zn). Stemflow and throughfall chemistry shows a very similar behaviour although the concentrations are, in general, higher due to enhanced mist and dry deposition onto the vegetation as well as cycling through the vegetation. Stream chemistry varies for different chemical components but is not correlated with the rainfall, stemflow and throughfall chemical signals. Nitrate, iodine and total organic carbon show seasonal oscillations. Aluminium, calcium, alkalinity, pH, silicon all vary as a function of flow. Manganese and cobalt remain constant except under very dry conditions when concentrations are reduced by up to an order of magnitude.

Stream water chemistry is determined primarily by hydrological and chemical reactions in the surface organic soils and the underlying inorganic soils/bedrock. Reactions in the organic horizons involve the generation of acidic conditions and the mobilization and transport of easily hydrolysable transition metals. Biologically mediated soil breakdown processes determine, to a large part, the hydrochemical behaviour of dissolved organic carbon, bromide, iodine and the nutrients. Reactions in the inorganic zones involve hydrogen ion consumption together with calcium and magnesium release. Bicarbonate ions are generated from the breakdown of soil organic matter, from carbon dioxide supplied from the tree roots and from decomposition of calcium carbonate within the bedrock.

The initial effects of clearfelling are reflected in the doubling of nitrate and potassium concentrations over a three year period and a marked decline in baseflow alkalinity (25  $\mu\text{Eq/l}$ ). With felling, chloride concentrations have progressively declined by 20% and this reflects reductions in evapotranspiration and reduced atmospheric scavenging of mist and dry deposited materials. Only a small decline in stream sulphate concentrations is observed, above background variation, even though atmospheric inputs will have reduced dramatically following tree harvesting. This indicates that sulphate is being released from the soils.

The application of a simple chemical mixing concept to split the hydrograph, based on the use of acid neutralizing capacity

as a conservative water quality tracer, is highlighted. The results suggest that groundwater contributes a significant component (>20%) to stream flow even during stormflow conditions. The importance of soil water and groundwater mixing processes are highlighted. Groundwater and zones of groundwater and soil water mixing have not been identified or monitored. Consequently important information on the mobilisation, precipitation and transport of chemicals through the Plynlimon catchments, is missing.

#### BACKGROUND

Large tracts of the British uplands have soils, overlying base poor bedrock, which are acidic and acid sensitive. Many of these areas have suffered declines in stream water quality and reduced fish stocks over the past 30 years. This deterioration has been attributed to the effects of acidic deposition and/or the development of conifer plantation forestry. However, their relative effects have not been sufficiently well established. Since many of the plantations now have mature trees there will be a further effect on water quality as harvesting commences and replanting occurs: it remains unclear as to what the effects of this added constraint will be.

In 1983, the project reported on here was instigated to develop an understanding of the importance of land use change in the British uplands by studying water quality changes in forest streams before, during, and subsequent to a deforestation

programme. Two main subcatchments of the headwaters of the River Severn in the Hafren forest were selected for study. This area was chosen since (1) a deforestation programme was planned for one of the two subcatchments, (2) detailed hydrological data for these catchments is available since they comprise an integral part of the Institute of Hydrology's water balance studies and (3) complementary chemical studies within the area were being undertaken by staff of the Institute of Terrestrial Ecology (Bangor).

The aims of the project were and continue to be:-

- (1) the production of a wide ranging hydrochemical data set to establish the natural variation in stream chemistry and the overall consequences of tree harvesting on water quality.
- (2) the development of a model describing the movement of key conservative and non-conservative elements through the catchments under varying hydrological conditions and during land disturbance from tree harvesting.
- (3) the estimation of element residence times.
- (4) the identification of the dominant hydrogeochemical processes determining stream water quality.
- (5) the examination of the potential of "natural" chemical tracers in "fingerprinting" the sources and amounts of components

which make up the storm hydrograph.

Here a report is provided to give a general overview of the work so far together with an account of the developments since NRA funding.

#### STUDY AREA

The work described here relates to two streams, the Afon Hafren and the Afon Hore, forming the main head water drainage of the River Severn in mid-Wales (Figure 1).

Rainfall levels average about 2500 mm/yr with evapotranspirational losses typically amounting to 500 and 650 mm/yr for the Afon Hafren and Afon Hore respectively. Being adjacent to each other, of similar altitude range (360 - 470 m), and similar size (about 340 ha) the streamflow responses to storm events are similar and in phase for the two sub catchments: the hydrograph response to storms is both rapid and "flashy"; flows vary between 0.01 and 4.5 m<sup>3</sup>/s.

Bedrock geology consists of lower Palaeozoic mudstones, greywackes, sandstones and grits. This is covered by a relatively thin soil, typically 70 cm thick, with organic-rich "L" and "O" horizons (3 to 10 cm). The lower soils consist of a leached "E" horizon (10 to 20 cm), and a fine textured podzolic "B" horizon (about 40 cm thick) merging into a stone "C" horizon. The predominant soil is a stagnopodzol, but peat, brown earth and

# PLYNLIMON CATCHMENTS

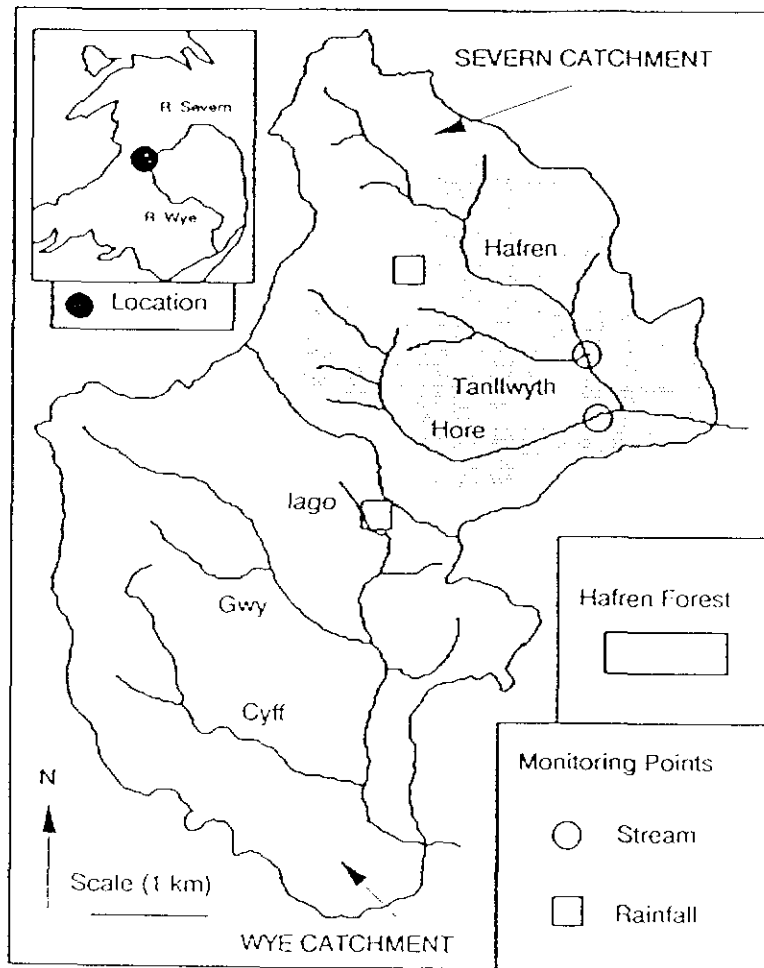


Fig. 1. Location of the Plynlimon catchments.

stagno-gley soils also occur within the two sub-catchments. At the top of both sub-catchments acid grassland is dominant, mainly *Nardus* and *Agrostis* species; *Eriophorium* species predominates on the peat. In the lower parts of the two sub-catchments, plantation forestry (predominantly Sitka spruce, *Picea sitchensis*) was introduced in various phases between 1937 and 1964, onto acid moorland. The areal coverage of the forest amounts to 50 % and 77 % for the Afon Hafren and the Afon Hore respectively.

#### SAMPLING STRATEGY

Since May 1983 stream water and rainfall samples have been collected on a weekly basis. Bulked rainfall was collected for 2 gauges spanning the catchment altitude range. Grab samples were used for stream water collection. From the onset, 2 stream water samples were collected on the lower portions of the Afon Hafren and Afon Hore (Figure 1, Table 1). The Afon Hafren site was chosen to provide a "control" to set against changes in the Afon Hore following deforestation. The Afon Hore site was chosen at a point just downstream of the main area to be deforested. However, as the project developed additional monitoring was introduced (Table 1):-

(1) stemflow and throughfall samples were collected to allow a more complete assessment of atmospheric inputs to the catchment.

(2) important chemical differences were found between the Afon



Table 1. Collection start dates.

	Weekly sampling		Continuous pH and conductivity monitoring	
Atmospheric Inputs				
Rainfall	May	1983	August	1988
Stemflow	February	1989	August	1988
Throughfall	February	1984	August	1988
Mist	February	1984	August	1988
Stream Outputs				
Upper Hafren	May	1990	Being installed	
Lower Hafren	May	1983	April	1989
Upper Hore	September	1984	August	1989
Lower Hore	May	1983	August	1989
Hore streamlet (Hore South 2)	April	1988	Not started	

Hafren and Afon Hore streams due to the higher levels of calcite veining in the bedrock of the Afon Hore. Consequently, Afon Hore stream water was collected at a sampling point upstream of the felling area to provide a more representative "control".

(3) Afon Hafren stream water was collected upstream of the forest area to provide hydrochemical data on an acid moorland stream. This would provide data for comparison with lower Afon Hafren stream chemistry following future felling.

(4) a tributary of the Afon Hore was sampled to provide information on the chemical variations occurring prior to, during and post felling, for an area essentially draining forest soils with minimum groundwater inputs.

(5) fine mist was collected near the top of the Severn catchment, using a system designed by the Institute of Terrestrial Ecology (Edinburgh) to allow assessment of occult deposition.

(6) continuous pH and conductivity monitors were introduced at the upper and lower stretches of both the Afon Hafren and Afon Hore to allow assessment of short term chemical variations.

#### CHEMICAL ANALYSIS

In all cases the samples were treated in the same way for chemical analysis. Samples were filtered (0.45  $\mu\text{m}$ ) at the time of collection. pH, acidity and alkalinity measurements were made

within 2 hours of sampling: reagents, electrodes and water samples were maintained at field temperature to minimise interferences: CO<sub>2</sub> degassing was minimised by keeping the samples in well stoppered, filled, glass bottles prior to analysis. In the acidity titration case, analysis was performed with reactants and titrants being kept in a nitrogen atmosphere to eliminate atmospheric CO<sub>2</sub> contamination. Samples were stored in chromic acid washed glass and hydrochloric acid washed polypropylene bottles prior to chemical analysis for major, minor and trace elements. For the trace metal analysis (inductively coupled plasma optical emission spectroscopy: ICPOES) the waters were acidified (to 1% vv) with concentrated nitric acid to minimise adsorption effects onto the polypropylene containers: samples were concentrated 20 fold by evaporation prior to analysis. Automated colourimetry was used for the analysis of F, Cl, Br, I, NO<sub>3</sub>, PO<sub>4</sub>, NH<sub>4</sub>, and Si.

For the continuous pH and conductivity measurements, pHOX systems were installed. These monitors were calibrated weekly. Additional readings were taken at the time of stream water collection to allow rigorous quality control checking.

## RESULTS

### Atmospheric Inputs

Being only 20 miles from the sea, the rainfall chemistry is, in part, dominated by maritime influences: chloride and other sea

salt components (sodium, magnesium, bromide) are both highly variable in concentration and highly correlated. The effects of industrial sources are also seen: enhanced levels of nitrate and sulphate occur (Figure 2); the rainfall is more acidic than under pristine conditions (Table 2).

Stemflow and throughfall chemistry variations reflect those observed in rainfall. In general, concentrations of the major, minor and trace elements are in the order stemflow > throughfall > rainfall (Table 2). Superimposed on top of the maritime and industrial inputs, element cycling is also observed. This is particularly pronounced for components such as manganese and dissolved organic carbon which have highly enhanced levels in the stemflow and throughfall.

#### Stream water

Stream water quality varies to different degrees and in several contrasting ways for different groups of elements. These variations, or lack of significant variation, together with an account of the underlying reasons for the salient features are described below.

As the Plynlimon catchments experience rainfall with very variable "sea-salt" components, one might anticipate that during storm events, since the streams exhibit a "flashy" flow response to rainfall inputs, large variations in stream water concentrations for these components will occur. This is not the

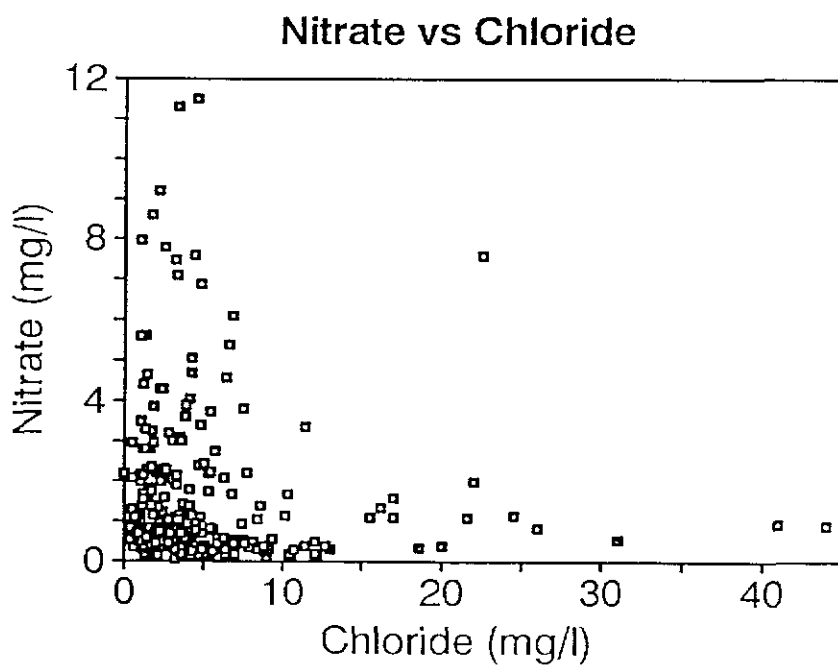
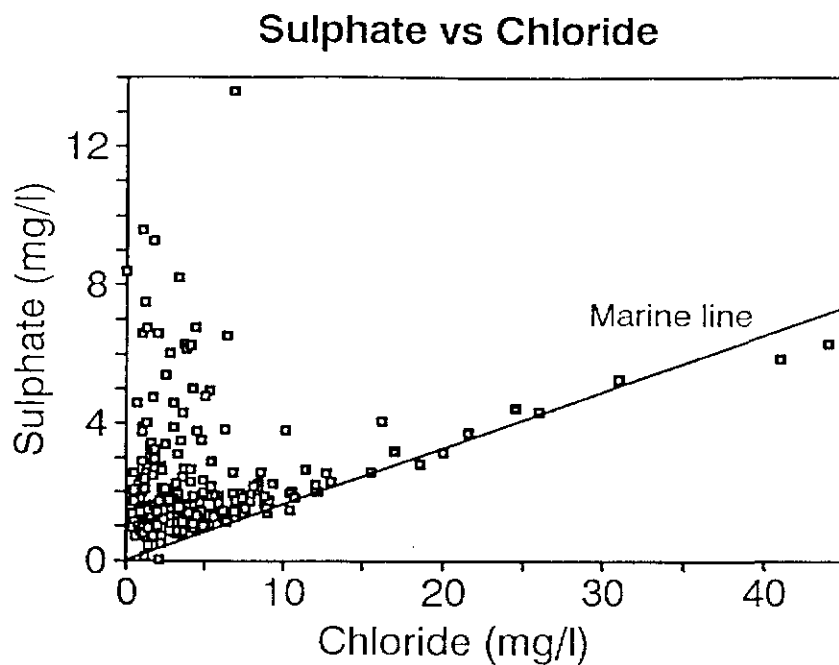


Fig. 2. Sulphate and nitrate variations with chloride for Plynlimon rainfall.

Table 2a. Rainfall, throughfall and stemflow chemistry for the major elements.

	RAINFALL	THROUGHFALL	STEMFLOW
Na	2.45 (0 - 23.6)	12.76 (0 - 81.7)	14.69 (2.1 - 59.0)
K	0.14 (0 - 0.9)	5.40 (0 - 24.7)	8.32 (0.21 - 63.5)
Ca	0.24 (0 - 1.79)	2.04 (0 - 12.4)	3.25 (0.19 - 22.3)
Mg	0.31 (0 - 2.98)	2.79 (0 - 25.2)	3.53 (0.2 - 28.1)
SO <sub>4</sub>	2.15 (0 - 13.6)	17.2 (0 - 170.5)	30.0 (2.7 - 203.9)
Si	0.21 (0 - 3.95)	0.19 (0 - 0.55)	0.23 (0 - 1.25)
DOC	0.43 (0 - 2.4)	10.3 (0 - 214)	16.9 (0 - 98)
NO <sub>3</sub>	1.21 (0 - 11.3)	4.38 (0 - 45)	5.67 (0 - 48)
NH <sub>4</sub>	0.41 (0 - 2.7)	1.14 (0 - 9.4)	1.32 (0 - 10)
PO <sub>4</sub>	0.04 (0 - 0.92)	0.18 (0 - 1.4)	0.19 (0 - 1.6)
F	0.04 (0 - 0.23)	0.10 (0 - 0.33)	0.12 (0 - 0.47)
Cl	4.69 (0.3 - 44.0)	27.2 (0 - 194)	31.0 (3.4 - 144)
pH	4.97 (3.68 - 6.67)	4.54 (3.10 - 5.60)	3.86 (3.15 - 4.47)
Alkalinity	-13.1 (-129 - 201)	-36.7 (-251 - 47)	-169.2 (-708 - 117)
H <sup>+</sup>	19.4 (0.21 - 208)	37.1 (4 - 251)	168.7 (34 - 169)

All units are mg/l except for alkalinity and hydrogen ion which is in  $\mu\text{Eq/l}$ : pH is dimensionless. Ranges are given in brackets.

Table 2b. Rainfall, throughfall and stemflow chemistry for the trace elements.

	RAINFALL	THROUGHFALL	STEMFLOW
B	3.7 (0 - 80)	33.8 (0 - 169)	38.8 (0 - 103)
Li	0.04 (0 - 1.9)	2.1 (0 - 2.1)	4.3 (0 - 4.3)
Sr	2.1 (0 - 14.2)	12.6 (0 - 81.9)	18.9 (1.2 - 127)
Y	0.01 (0 - 0.3)	0.01 (0 - 0.2)	0.02 (0 - 0.3)
Ba	2.7 (0 - 90)	5.6 (0 - 98)	6.7 (0 - 58)
Mn	2.6 (0 - 43)	741. (0 - 9162)	1594. (39 - 10902)
Cu	2.2 (0 - 27)	572. (0 - 2230)	50. (0.5 - 2944)
Fe	11. (0 - 104)	184. (0 - 184)	70. (0 - 410)
Co	0.1 (0 - 3.5)	1.7 (0 - 8.9)	1.7 (0 - 13.9)
Zn	14.9 (0 - 185)	309. (0 - 1087)	89. (6.0 - 942)
Al	19.5 (0 - 603)	87.1 (0 - 588)	127.6 (10 - 1010)
Br	17.6 (0 - 128)	107. (0 - 600)	148. (24 - 475)
I	1.6 (0 - 12)	5.8 (0 - 62)	9.6 (1.4 - 96)

All units are  $\mu\text{g}/\text{l}$ . Ranges are given in brackets.

case even for components such as chloride and  $^{18}\text{O}$ , which are chemically unreactive (Figure 3). This feature shows that the catchments, with or without land disturbance due to tree harvesting, have the ability to smooth the rainfall's variable chemical imprint to a very considerable degree. In other words, rainfall does not pass directly through the catchment to provide the major volume of water in the stream during the hydrograph response.

In spite of the insignificant relationship between rainfall quality and stream chemistry, large fluctuations in several chemical species occur as a consequence of hydrological variations. Baseflow waters have higher calcium and silicon concentrations and alkalinities than the corresponding stormflow waters (Table 3). Stormflow waters, in contrast, have higher aluminium, yttrium and hydrogen ion concentrations than their baseflow counterparts (Table 3). At a qualitative level, this difference can be considered as reflecting the large chemical gradients within the catchment. The soil zones, being organic and aluminium oxide/hydroxide rich, produce acidic and aluminium rich soil water solutions. The bedrock, consisting of weatherable and acid-soluble inorganic components such as calcite and layer lattice silicates (chlorite and illite), has the capacity to neutralise these acid waters, which, after  $\text{CO}_2$  degassing, are of the type observed under baseflow conditions. During storm events, when the catchment soils have wetted up and groundwater tables are high, a greater proportion of water entering the stream is derived from the soil zone. Under baseflow conditions, water



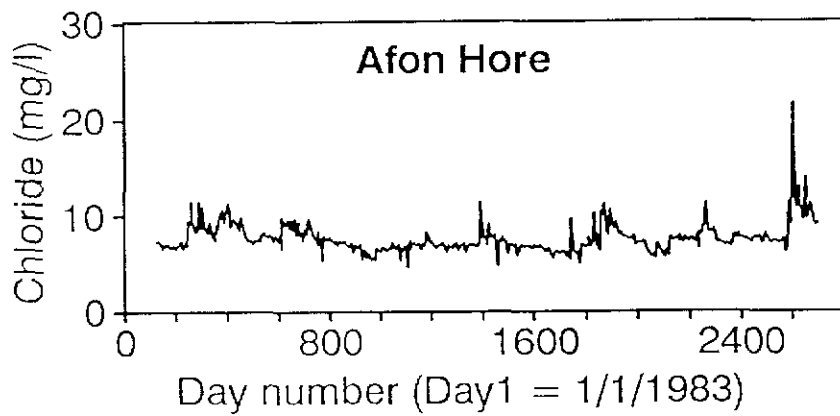
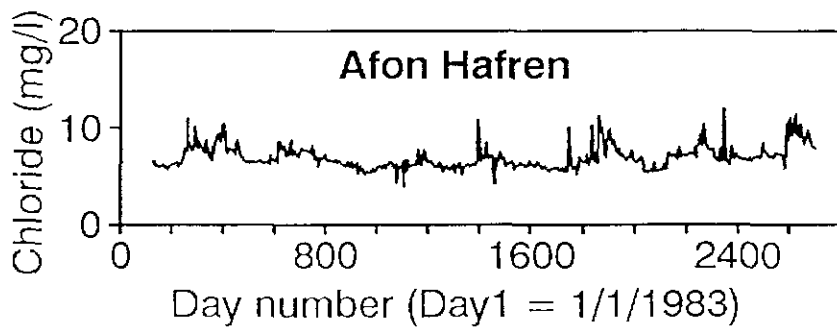
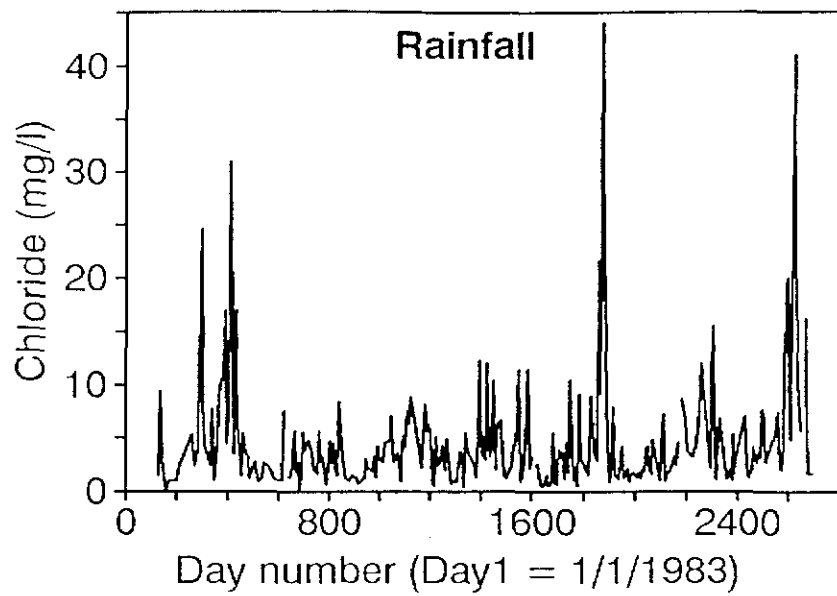


Fig. 3. Chloride concentrations in rainfall and stream water.

Table 3. Mean concentrations of major and trace elements in Hafren forest stream waters.

	Baseflow			Stormflow		
	Hafren	Hore Upper Lower		Hafren	Hore Upper Lower	
Major Elements						
Na	3.9	3.7	4.2	3.9	4.0	4.2
K	.14	.10	.18	.21	.14	.27
Ca	1.1	3.2	3.4	.76	.78	1.0
Mg	.83	.88	1.21	.76	.65	.80
SO <sub>4</sub>	3.7	3.2	4.9	4.8	4.3	5.0
Si	2.3	1.9	2.4	1.2	1.0	1.1
DOC	.8	1.0	.8	2.2	1.9	1.8
NO <sub>3</sub>	.8	.8	1.0	1.8	1.2	2.3
NH <sub>4</sub>	.01	.02	.01	.03	.01	.03
PO <sub>4</sub>	.11	.06	.09	.07	.02	.08
F	.04	.05	.06	.06	.06	.07
Cl	6.6	6.7	7.4	7.4	7.7	8.1
pH	6.4	7.1	7.1	4.6	4.8	4.8
Alkalinity	32.	147.	137.	-29.	-18.	-19.
H <sup>+</sup>	.4	.1	.1	27.	22.	19.
Trace elements						
B	4.4	4.4	6.2	4.0	3.5	4.3
Li	1.9	1.7	1.8	1.9	1.6	2.0
Sr	5.4	5.9	7.7	5.4	4.3	5.2
Y	0.1	0.1	0.1	0.4	0.3	0.3
Ba	1.7	2.1	2.3	3.9	3.2	5.4
Mn	18.7	18.6	23.1	44.2	22.7	38.6
Cu	1.2	1.4	1.4	3.2	2.8	3.8
Fe	47.9	86.9	75.9	112.5	93.5	88.0
Co	0.8	0.9	0.7	2.4	1.9	2.6
Zn	9.0	7.3	10.2	19.7	29.1	42.0
Al	43.0	68.2	56.8	428.1	442.3	480.5
Br	21.3	22.3	23.5	23.5	23.1	23.8
I	1.0	0.9	1.0	1.1	1.0	1.0

All major and minor element concentrations are given in mg/l and  $\mu$ g/l units respectively. Alkalinity is expressed in  $\mu$ Eq/l units: pH has dimensionless units.

drains essentially from the groundwater areas. Soil structure consistency and bedrock variability (i.e. degree of calcite and low temperature vein mineralisation) between the Afon Hafren and Afon Hore catchments explain why baseflow waters differ far more greatly than stormflow waters in their chemistry for these two catchments.

From the autumn of 1982 to the autumn of 1984, abnormally dry periods were encountered with the consequence that base flows were particularly low during the summers of 1983 and 1984. This was reflected in the stream water chemistry (Figure 4): pH values and calcium concentrations were at their highest while manganese and cobalt were anomalously low (by a factor of about 5). These results indicate the input of a water source with a long residence time within the bedrock areas: it constitutes a second groundwater component. This is only identifiable by chemical fingerprinting.

Under baseflow conditions, the stream water is saturated with dissolved  $\text{CO}_2$  and under stormflow conditions, oversaturated by up to a factor of 8. Since the soil water and groundwaters will be oversaturated 20 to 200 fold, major degassing must occur when the soil water and groundwater emerge into the stream. Under baseflow conditions water volumes are sufficiently low and slow moving for equilibrium to be reached: during stormflow conditions no equilibrium is attained.

Several of the nutrients plus some trace elements show, in

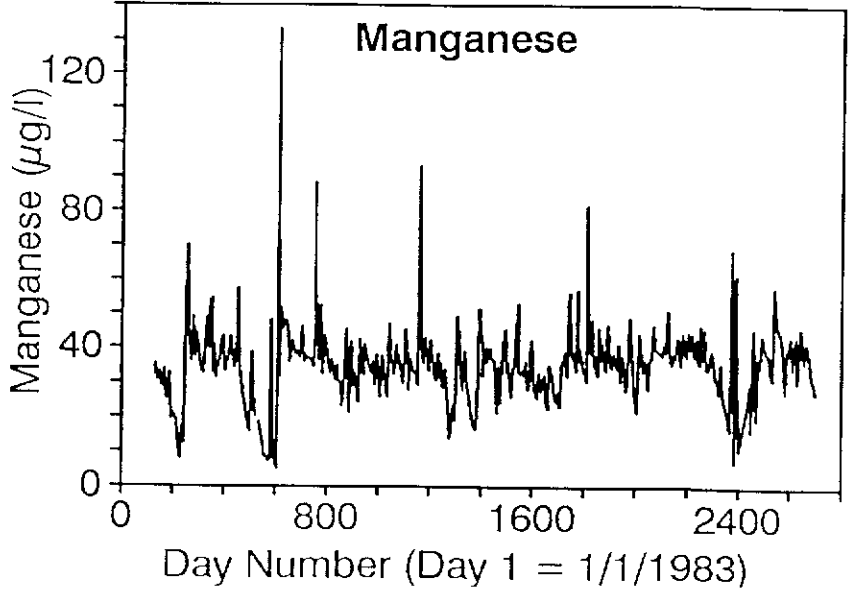
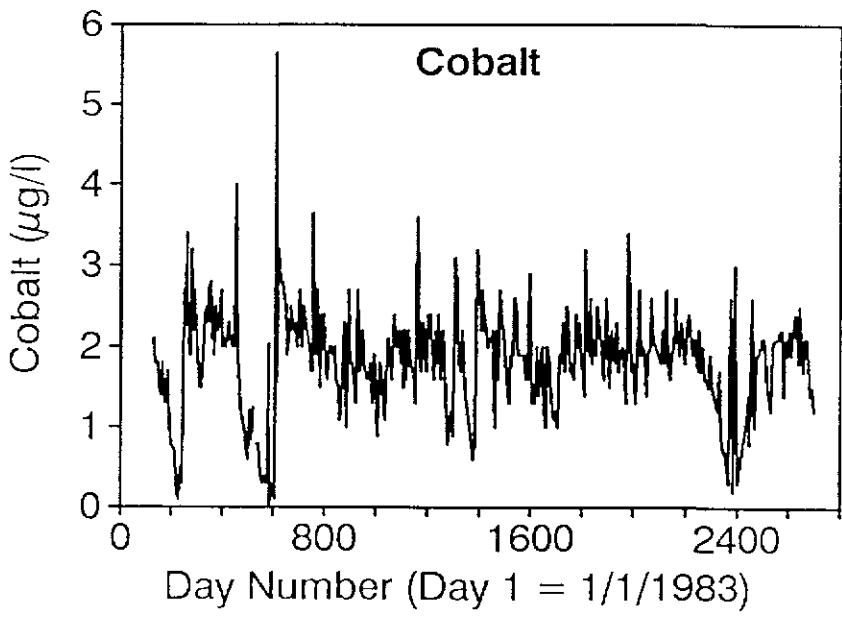
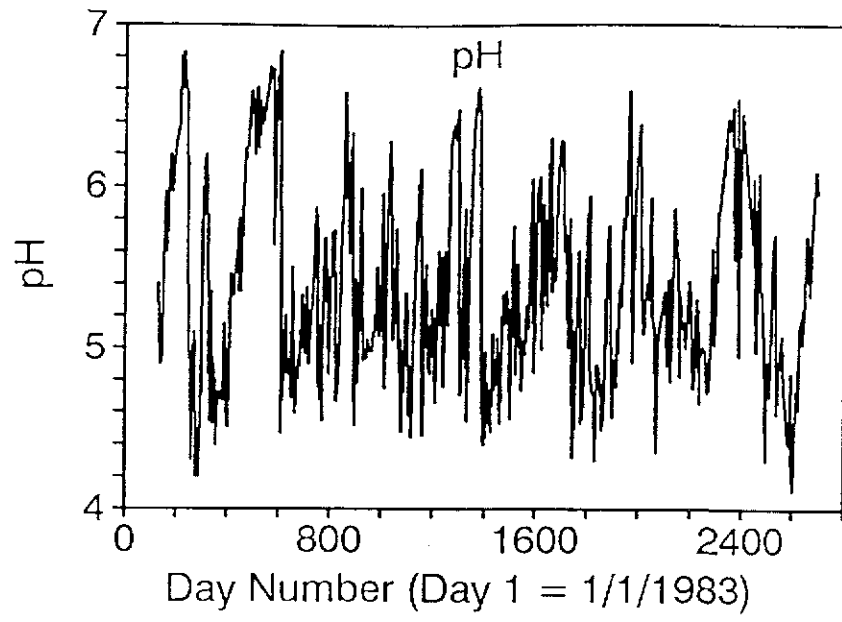


Fig. 4. pH, cobalt and manganese concentration variations with time for Afon Hafren stream water.

part, broad seasonal variations (Figure 5). In some cases (e.g. nitrate, dissolved organic carbon and potassium) the changes have been well described previously in terms of temperature induced biological responses (tree growth, micro-organism, and organic matter decomposition/build-up). In other cases (e.g. bromide and total iodine) the seasonal variations were not anticipated although again the phenomenon can be related to organic breakdown processes releasing constituents to solution. Three major points need to be noted. First, there is large and systematic scatter about the seasonal pattern for most of the biologically mediated elements. For example, nitrate has anomalous peak values during storm events while bromide and total iodine exhibit predominantly the seasonal oscillations. The scatter reflects the interactiveness of the biological and hydrological processes in determining stream water quality for this class of element: data scatter is far outside the analytical error for most of the elements described. Second, although there are seasonal trends, these trends differ for different components: the phases vary between different elements; peaks and troughs occur at different times each year even for individual elements. This illustrates that the rates of generation and consumption of the various elements varies and that no single reaction can describe all the changes occurring. Third, while the seasonal patterns for nitrate and potassium persist for all the streams there is a gradual increase in the concentrations for the lower Afon Hore. This reflects the effects of tree harvesting which was confined to the Afon Hore catchment. This exemplifies the importance of land use change effects on stream water quality via the perturbation of the

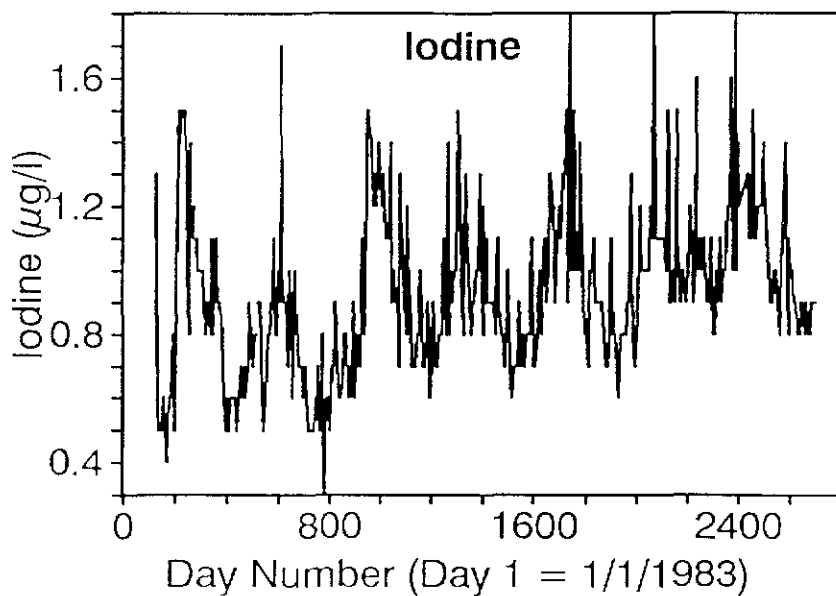
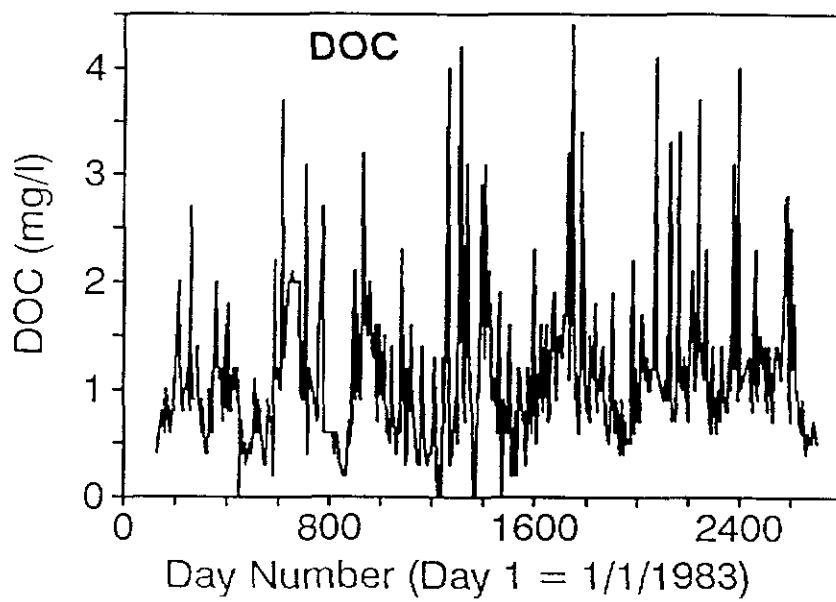
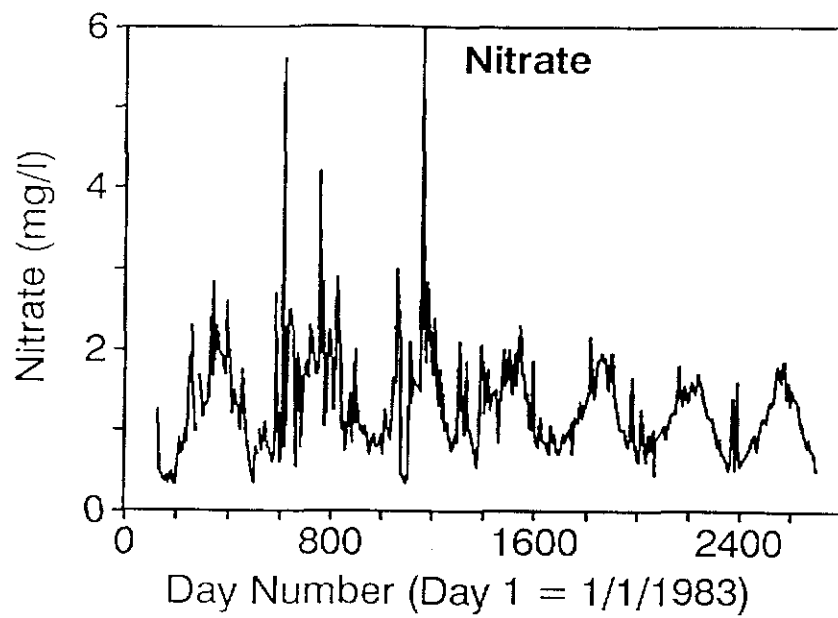


Fig. 5. Nitrate, DOC and total iodine concentration variations with time for Afon Hafren stream water.

biological system. It also underlines the fact that the biological modifications vary for different components: different responses are observed for different elements in this class.

#### The effects of tree harvesting on stream water quality

At a gross level, the main effect of tree harvesting on stream water quality is to enhance the concentrations of nitrate and potassium (Figure 6) as mentioned above. Since the upper Afon Hore represents a very good control site, more detailed evaluation of the forestry effect can be made using the following scheme.

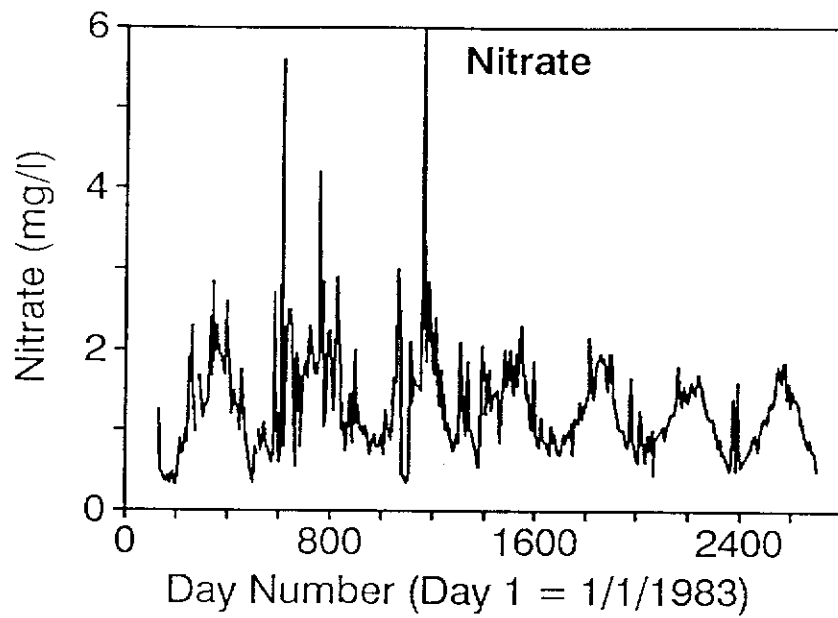
During both high flow and low flow conditions about 30% of the water collected from the lower Afon Hore site is derived from a region upstream of the upper Hore sampling point. For a given chemical component,  $c$ , of concentrations  $c_u$  and  $c_l$  at the upper and lower stream sampling points, respectively, the concentration of water draining the forested/harvested area can be assessed using the equation

$$c_{\text{forest}} = (c_l - 0.3c_u)/0.7$$

The change in the chemical concentrations in the stream with time,  $c_c$ , can be expressed as the difference between  $c_{\text{forest}}$  and  $c_u$ .

For most chemical components no changes are observed before, during and subsequent to felling,  $c_c$  being constant. In general,

### Afon Hafren



### Afon Hore

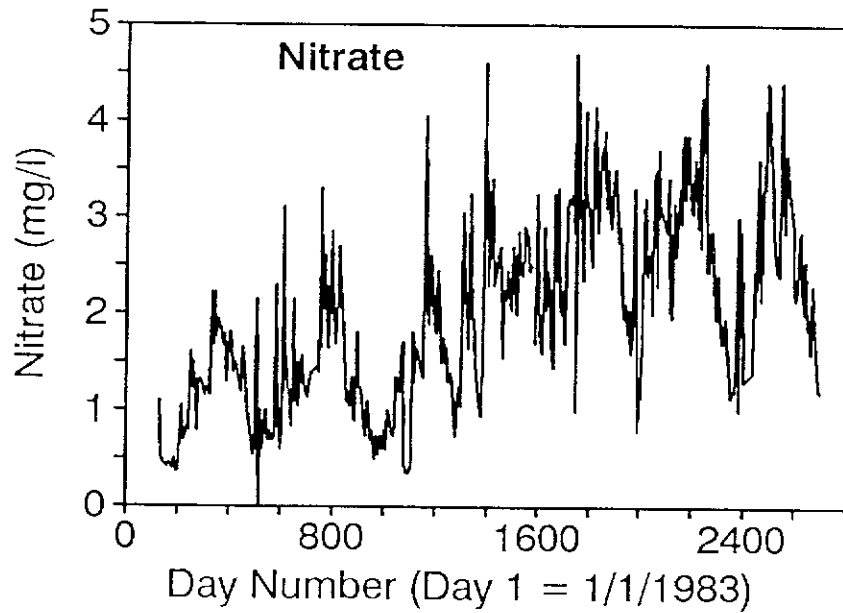
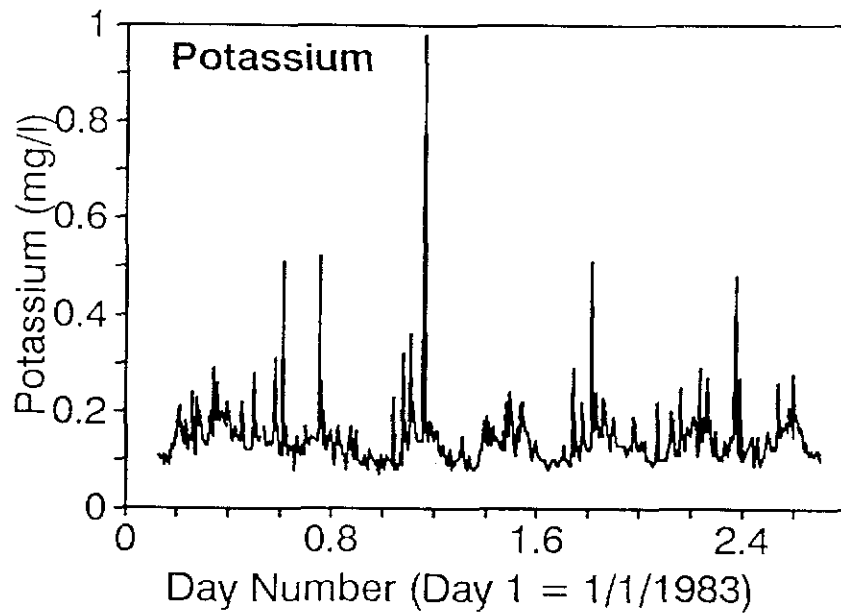


Fig. 6a. Nitrate concentration variations with time for the Afon Hafren and the Afon Hore stream water.



### Afon Hafren



### Afon Hore

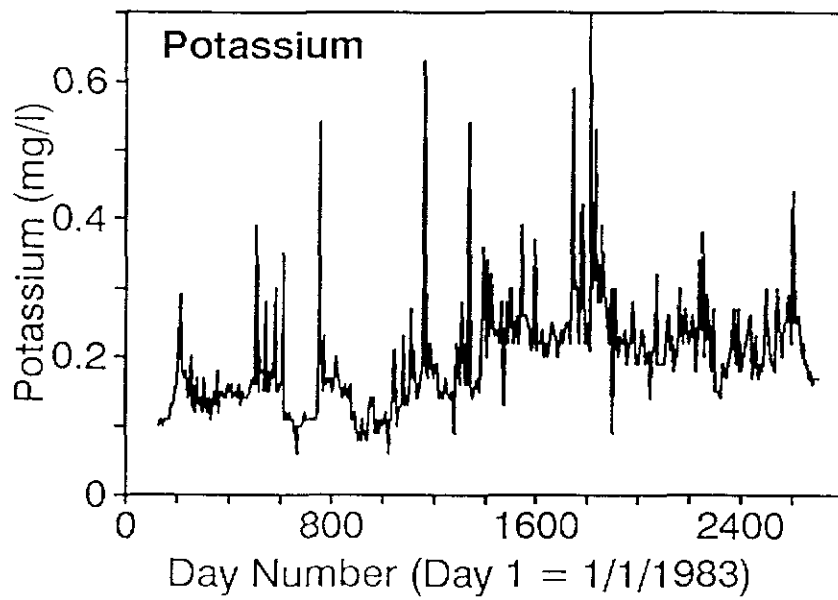


Fig. 6b. Potassium concentration variations with time for the Afon Hafren and the Afon Hore stream water.

nitrate and potassium releases to the stream, following harvesting, have progressively increased (Figure 6, 7), the largest increases in  $c_c$  occurring under stormflow conditions. With harvesting,  $c_c$  for chloride has steadily reduced (Figure 8) due to the reduction in the atmospheric inputs (the atmospheric scavenging by the vegetation declines) and the reduced evapotranspiration: this change corresponds to a 20% reduction in concentration following tree harvesting. Although there has been only a small reduction in stream  $SO_4$  concentration, a major decline in the  $SO_4$  input will have occurred due to the reduction in dry and mist deposition following harvesting. This implies that desorption of  $SO_4$  from soil constituents is counterbalancing this atmospheric reduction. Surprisingly there has been a decline in alkalinity. The greatest declines in alkalinity occur during baseflow conditions: it remains relatively constant during stormflow periods. The change in alkalinity is matched by a small decline in calcium level.

#### ASSESSING THE IMPORTANCE OF WATER SOURCE CONTRIBUTIONS TO STREAMFLOW

Water mixing relationships are difficult to assess for the streams. Although a neutral bicarbonate bearing groundwater component is inferred from the stream data, such an endmember has not been sampled. Most chemical components which exhibit response to flow are chemically reactive and hence conservative mixing formulations cannot be used. Nonetheless, basic inferences can

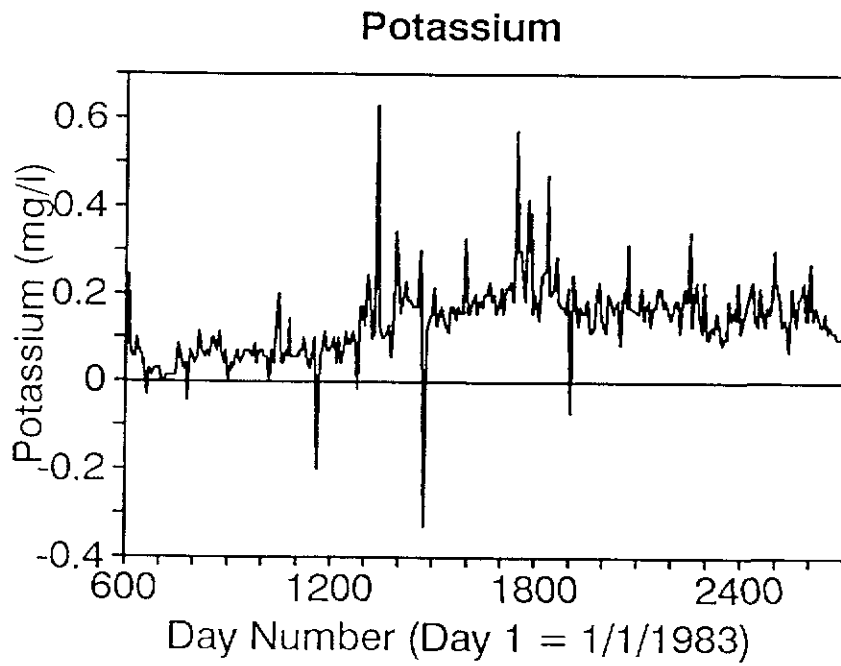
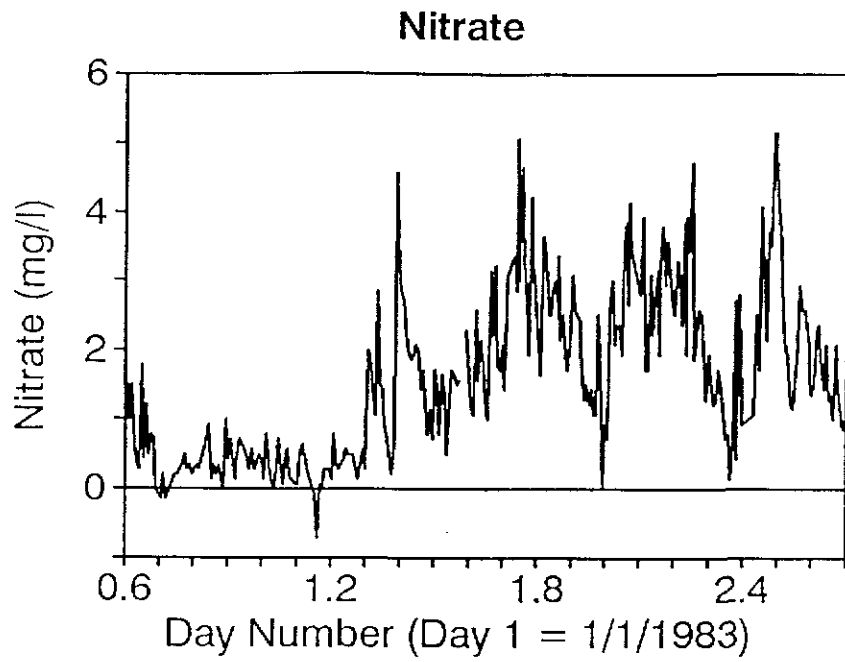


Fig. 7. Difference in nitrate concentrations and potassium concentrations between the upper and lower Afon Hore.

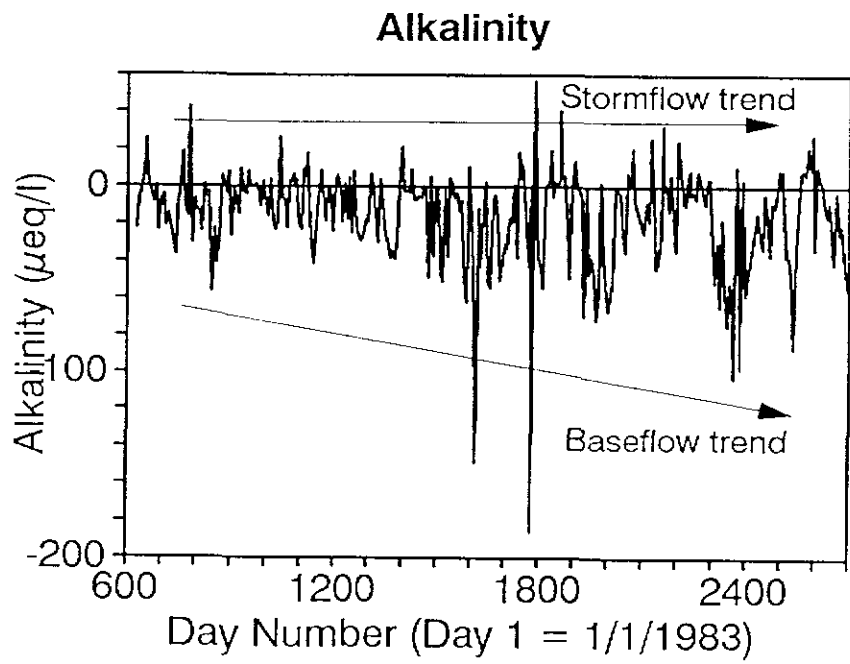
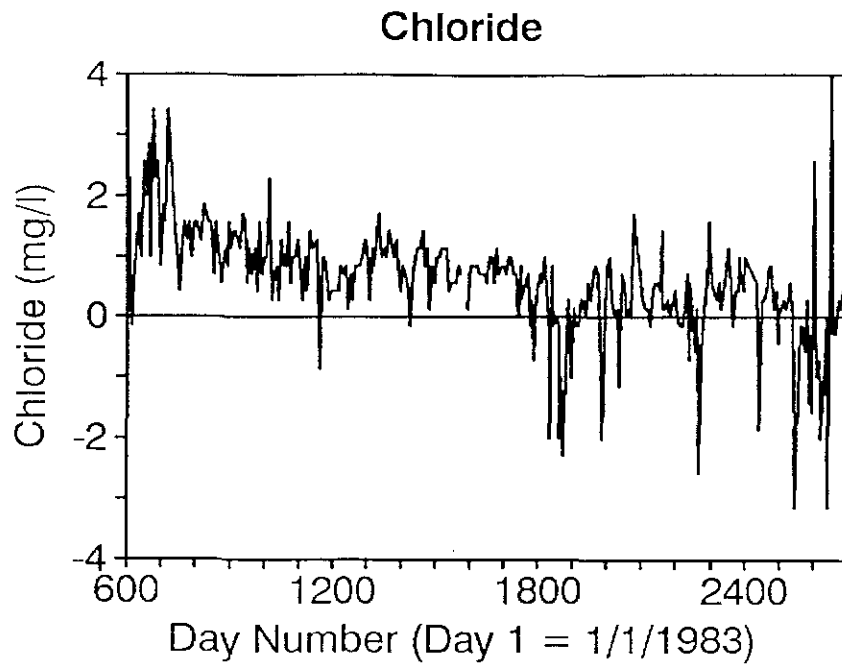


Fig. 8. Difference in chloride concentrations and alkalinities between the upper and lower Afon Hore.

be made which provide some insight into the nature of the hydrological processes operating. The starting point for this evaluation is the application of simple mixing relationships to the most variable but chemically conservative tracer, acid neutralisation capacity (ANC:- the difference, in  $\mu\text{Eq/l}$ , between the concentrations of the unhydrolysed cations and the unhydrolysed anions in solution). The ANC equals numerically the Gran titration alkalinity ( $\mu\text{Eq/l}$ ) minus three times the inorganic aluminium concentration ( $\mu\text{M}$ ).

Taking the baseflow to be represented by low flow chemistry, ranges of groundwater ANC can be considered which span all conditions: 20,80  $\mu\text{Eq/l}$  for the Afon Hafren; 100,200  $\mu\text{Eq/l}$  for the Afon Hore. Within the soil zones, mean ANC is invariant throughout the soil zones and has a value around -200  $\mu\text{Eq/l}$ . Under such circumstances the % groundwater ( $\%_{\text{gw}}$ ) in a water sample of measured ANC ( $\text{ANC}_m$ ) can be estimated from a simple mixing equation:

$$\%_{\text{gw}} = 100(\text{ANC}_m - \text{ANC}_s)/(\text{ANC}_g - \text{ANC}_s)$$

where  $g$  and  $s$  denote groundwater and soil water values respectively.

Results for this exercise show two main features. First, as flow increases the contribution of soil water from the hillslope increases. The rate of increase in soil water contribution is greatest for the moderately low flow region, values levelling off

under intermediate and high flow conditions (Figure 9). This feature corresponds to the behaviour as described above: during storm water conditions, as groundwater levels rise, progressively more water is supplied from the more acidic low ANC, soil zones. Second, even under high flow conditions the groundwater component forms a very significant contribution to the total flow (20 to 60%).

Under low flow conditions the contribution of water from the various soil horizons cannot be directly assessed because no suitable conservative species is available for water mixing calculations: at least two groundwater sources are implied from the baseflow chemistries during dry and wet years, as mentioned above (Ca, pH, Mn, Co variations with time). However, under high flow conditions some assessment can be made since aluminium will behave conservatively: the soil horizons have distinct aluminium concentrations in their pore solutions. On this basis, under stormflow conditions, the "O" horizon soil waters contribute 29 to 86 % of the total soil water component.

#### WIDER DISCUSSION AND COMMENTS

Stream chemistry variations show consistency and regularity of pattern which qualitatively can be related to well recognised underlying hydrogeochemical, hydrological and biological processes operating within the catchment. The study of the wide range of elements described here has highlighted the importance of these processes in a way not achievable with detailed plot

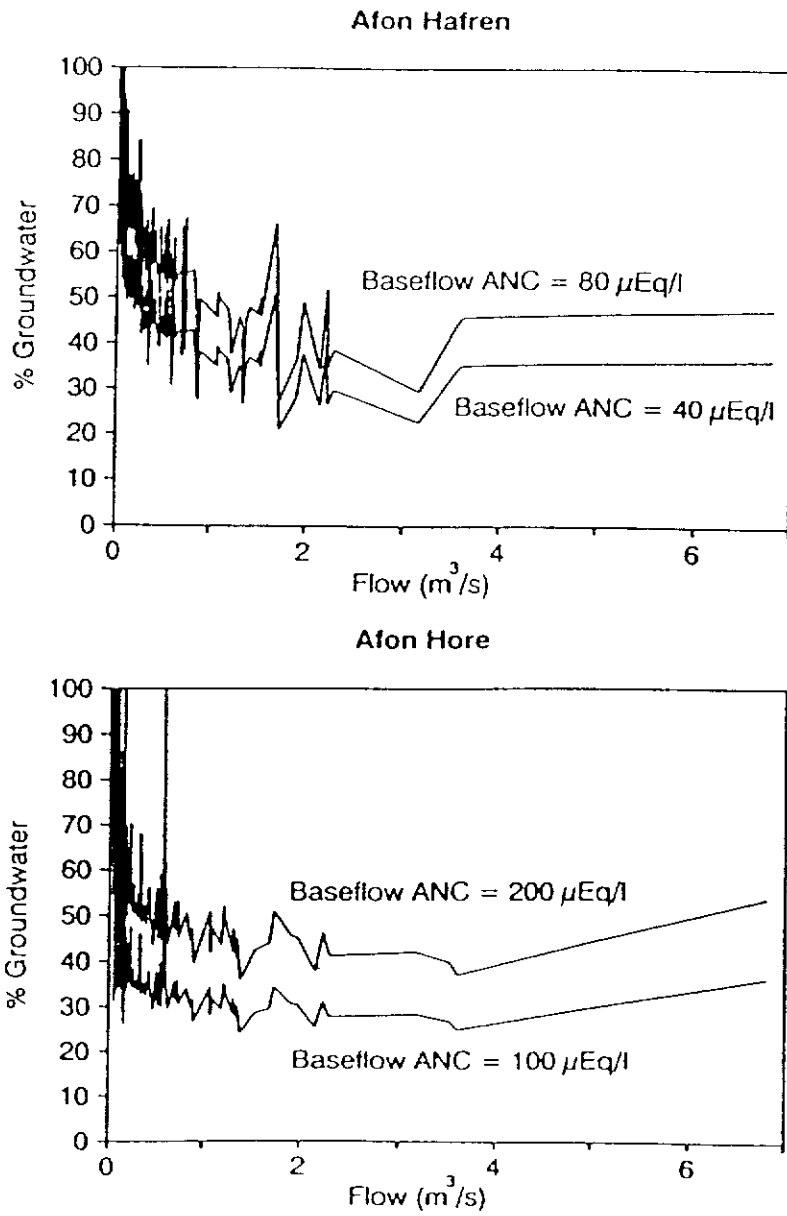


Fig. 9. Estimated groundwater proportions as a function of flow for the Afon Hafren and the Afon Hore.

scale and laboratory simulations.

In practice one needs to quantitatively assess the importance of each process to obtain reliable estimates of the effects of changing land use practice and reductions in the acidic oxide emissions to the atmosphere by industry. In this context the importance of groundwater and bank side processes is emphasised from the above results owing to the high significance of one or both of these components even during stormflow conditions. Further, there is urgent need for a more thorough understanding of the chemical processes operating in the various soil zones. Since these waters have not been sampled and uncertainty remains over the nature of the chemical processes operating, the results point to the need for further field studies to look at water and reaction pathways: if one does not know the fluxes of elements through the various soil and ground water regions then assessment of the hydrogeochemical changes that determine environmental impacts becomes impossible.

#### THE WORK PROGRAMME OVER THE PAST 12 MONTHS.

The main effort has focused on the continuation of the monitoring programme together with the interrogation of data with subsequent publication in the scientific literature. Effort spent may be summarized as follows:-

- 1) over 400 stream, rain, stemflow, and throughfall waters have been analyzed for major, minor and trace elements: full analysis



from the monitoring programme is now complete up to the end of May this year.

2) analytical work has been extended to capitalise on the recently commissioned inductively coupled plasma mass spectrometer (ICPMS). From 1986, samples preconcentrated for ICPOES analysis have been stored. These samples are now being analyzed using the ICPMS to determine ultra low levels of elements, such as caesium and uranium, which were previously at undetectable levels.

3) a method has partially been developed for analyzing inorganic and organic aluminium levels in stream waters. It is hoped that this method will be employed routinely at Plynlimon within the next 6 months.

4) an occult deposition collector has been installed near the top of the Hafren catchment to allow a more complete assessment of atmospheric inputs of elements to the catchment.

5) a continuous monitor for pH and conductivity has been installed on the upper Afon Hafren.

6) new procedures for testing the reliability of the pH electrodes in the continuous monitors have been introduced. Detailed analysis of the continuous data has revealed the limitations of the electrodes used. A new calibration technique has been introduced to allow for electrode drift.

7) throughout the research programme, major effort has been placed on interrogation of data and the publication of the findings. To date, 43 papers which directly or indirectly relate to the Plynlimon study have either been published or accepted for publication (appendix 1). Over the past 12 months six papers have been accepted for publication.

8) the most active research developments over the past 12 months relate to the development of the mixing concepts described above and in particular to the use of ANC to split the hydrograph. The work has been extended to examine data for the NRA's study at Llyn Brianne and one paper covering this aspect has just been published. Close links have been maintained with the IH modelling group with the consequence that the mixing concept is now being used to predict, for the first time, both long term and episodic variations in stream water chemistry.

#### FUTURE WORK: STRATEGIC NEEDS.

Assessment of environmental impacts on the British uplands is hard to gauge since there is incomplete information on the complex and interactive hydrological, chemical and biological processes operating. A basic need is the maintenance of field studies to monitor the long term changes in stream water quality following changes in land use and atmospheric pollutant inputs. This need arises for three reasons. First, the rates of build up or depletion of chemicals in the various catchment stores can be relatively slow. For example in the Plynlimon case, after 3 years

of felling activity, sulphate levels in the stream have only declined a little due to depletion of sulphate from the catchment soils: estimation of rates of depletion are important in assessing how quickly improvements in stream water quality will occur. Second, long term information is required to accommodate the variations associated with yearly fluctuations in climate. At Plynlimon, for example, the three dry years over the past 7 years of monitoring have all affected the observed stream water trends. Third, in the case of plantation forestry, the uplands are now subject to felling and replanting. While data on the effects of deforestation are now emerging, the affects of reafforestation remain obscure. On this basis studies such as those described here are of strategic importance.

Despite the large investment of time and effort over the past decade in the assessment of the impacts of atmospheric deposition and land use change for acidic and acid sensitive systems, major uncertainties remain (see appendix 2). The present study has led to the identification of five important areas for new research initiatives:-

- 1) the importance of groundwater supplies in generating stream water quality has now been established and yet these groundwater supply areas have not been sampled.

- 2) mixing of ground and soil waters are important in generating the observed stream water chemistry and yet the areas of mixing have not been studied.

3) despite the known importance of elevated inorganic aluminium concentrations in reducing fish survival, the processes controlling aluminium mobility remain obscure.

4) while it is well established that cation exchange and weathering reactions are important in determining soil and hence stream water chemistry, the detailed reactions depicting them remain incomplete.

5) knowledge of the input of pollutants to catchments is critical to the assessment of the effects of atmospheric deposition and land use change. Unfortunately, the net input of pollutants cannot be accurately gauged from the data presently collected: it is extremely difficult to separate the materials impacting a catchment from those being cycled through the vegetation.

6) all the predictive hydrochemical models assume that the soil water has a constant chemical composition in each horizon at a given time. However, field studies show large spatial variability. Further work is required to characterise this variability and to integrate it with more representative model formulations.

APPENDIX 1

1) International peer reviewed publications.

Neal, C., and Thomas, A.G., 1985. Field and Laboratory Measurement of pH in Low-Conductivity Natural Waters. *Journ. Hydrol.* 79, 319-322.

Neal, C., and Thomas, A.G., 1985. The measurement of pH in low conductivity waters: a case for the reappraisal of the techniques used. *Inst. of Water Poll. Control, Maidstone*, 1-13.

Whitehead, P.G., Neal, C., Seden-Perriton, S., Christophersen, N., and Langan, S., 1986. A Time-Series Approach to Modelling Stream Acidity. *Journ. Hydrol.* 85, 281-303.

Neal, C., Smith, C.J., Walls, J., and Dunn, C.S., 1986. Major, Minor and Trace Element Mobility in the Acidic Upland Forested Catchment of the upper River Severn, mid-Wales. *Quart. Journ. Geol. Soc., London*, Vol. 143, 635-648.

Neal, C., Whitehead, P.G., Neale, R., and Cosby, B.J., 1986. Modelling the Effects of Atmospheric Deposition and Conifer Afforestation in the British Uplands. *Journ. Hydrol.*, 86, 15-26.

Whitehead, P.G., Neal, C., and Neale, R., 1986. Modelling the Effects of Hydrological Changes on Stream Water Acidity. *Journ. Hydrol.*, 84, 353-364.

Neal, C., Reynolds, B., Stevens, P.A. and Hornung, M., 1986. Factors influencing stream water chemistry in the Welsh uplands; examples from Plynlimon. Welsh Soils Discussion Group, 1-26.

Neal, C., Skeffington, R.A., Williams, R., and Roberts, D.J., 1987. Aluminium Solubility Controls in Acid Waters: the need for a reappraisal. *Earth and Planetary Science Letters*, 86, 105-112.

Reynolds, B., Neal, C., Hornung, M., and Stevens, P.A., 1987. Baseflow Buffering of Streamwater Acidity in five mid-Wales Catchments. *Journ. Hydrol.*, 87, 167-185.

Whitehead, P.G., and Neal, C., 1987. Modelling the effect of acid deposition in upland Scotland. *Trans. Royal Soc. (Edinburgh): Earth Sci.*, 78, 385-392.

Reynolds, B., and Neal, C., 1987. A comment on the use of acidimetric titrations for the estimation of the alkalinity and bicarbonate content of acid upland surface waters. *Sci. of the Total Env.* 65, 155-161.

Hornung, M., Reynolds, B., Stevens, P.A. and Neal, C., 1987. Acidification and Water Pathways. The Norwegian National Committee for Hydrology in co-operation with Unesco and WMO, the IHP National Committees of Denmark, Finland and Sweden. Bolkesjo, 4 - 5 May 1987, vol. 1.

Neal, C., 1988. Bicarbonate estimation from alkalinity determinations for neutral to acidic low alkalinity natural

waters: theoretical considerations. Hydrol. Sci. Bull., 33, 619-624.

Neal, C., Christophersen, N., Neale, R., Smith, C.J., Whitehead, P.G., and Reynolds, R., 1988. Chloride in Precipitation and Streamwater for the upland Catchment of the River Severn, mid-Wales; some consequences for hydrochemical models. Hydrological Processes, 2, 156-165.

Neal, C., and Whitehead, P.G., 1988. The Role of CO<sub>2</sub> in Long Term Stream Acidification Processes: a modelling viewpoint. Technical note in Hydrol. Sci. Bull., 33, 103-108.

Neal, C., 1988. Determination of Dissolved CO<sub>2</sub> in Upland Streamwater. Journ. Hydrol., 99, 127-142.

Neal, C., and Williams, R.J., 1988. Towards Establishing Aluminium Hydroxy Silicate Solubility Relationships for Natural Waters. Journ. Hydrol. 97, 347-352.

Neal, C., 1988. Aluminium solubility relationships in acid waters; a practical example of the need for a radical reappraisal. Journ. Hydrol., 104, 141-159.

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. Water, Air and Soil Poll., 38, 55-70.

Neal, C., Reynolds, B., Stevens, P., Hornung, M., and Brown, S., 1988. Hydrological controls for inorganic aluminium in Welsh soil and stream waters. *Acidification in Wales*. Kluwer Academic Publishers (Dordrecht), 173-188.

Whitehead, P.G., Bird, S., Hornung, M., Cosby, B.J., Neal, C., and Paricos, P., 1988. Stream acidification trends in the Welsh uplands - a modelling study of the Llyn Brianne Catchments. *Journ. Hydrol.*, 101, 191-212.

Whitehead, P.G., Reynolds, B., Hornung, M., Neal, C., and Paricos, P., 1988. Modelling long term stream acidification trends in upland Wales at Plynlimon. *Hydrol. Proc.*, 2, 357-368.

Neal, C., 1988.  $p\text{CO}_2$  variations in streamwaters draining an acidic and acid sensitive spruce forested catchment in mid-Wales. *Sci. of the Total Environment*, 76, 279-283.

Neal, C., Whitehead, P.G. and Jenkins, A., 1988. Are present UK  $\text{SO}_2$  emission declines sufficient to reverse the long-term stream acidification in the British Uplands. *Nature*, 334, 109-110.

Christophersen, N., and Neal, C., 1989. A rational approach to the assessment of aluminium solubility controls in freshwaters. *Sci. of the Total Environment*. 84, 91-100.

McMahon, R., and Neal, C., 1989. Aluminium dis-equilibrium solubility controls in Scottish acidic catchments. *Hydrol. Sci. Journ.*, 35, 21-28.



Neal, C., 1989. Aluminium weathering/ion exchange for acid impacted systems: The Achilles heel of predictive models ? Int. Symp. Water Rock Interactions, Malvern, U.K., August, 1989. Miles (ed.), Balkema, Rotterdam, 515-519.

Neal, C., Reynolds, B., Stevens, P. and Hornung, M., 1989. Hydrogeochemical controls for inorganic aluminium in acidic stream and soil waters at two upland catchments in Wales. Journ. Hydrol., 106, 155-175.

Neal, C., Musgrove, T., and Whitehead, P.G., 1989. Predicting the long term variations in stream and lake inorganic aluminium concentrations for acidic and acid sensitive catchments. Sci. Tot. Envir., 80, 205-211.

Neal, C., and Christophersen, N., 1989. Inorganic aluminium - hydrogen ion relationships for streams; the role of water mixing processes. Sci. Tot. Envir., 80, 195-203.

Neal, C., 1989. Fluorine variations in Welsh stream and soil waters. Sci. Tot. Envir., 80, 213-223.

Neal, C., Smith, C.J., Walls, J., Billingham, P., Hill, S., and Neal, M., 1990. Comments on the hydrochemical regulation of the halogen elements in rainfall, stemflow, throughfall and stream waters at an acidic forested area in mid-Wales. Sci. Tot. Envir., 91, 1-11.

Neal, C. and Rosier, P., 1990. Chemical studies of chloride in

conifer afforested and moorland Britain. *J. Hydrol.*, 115, 269-283.

Neal, C., Smith, C.J., Walls, J., Billingham, P., Hill, S. and Neal, M., 1990. Hydrochemical variations in Hafren forest stream waters, mid-Wales. *Journ. Hydrol.*, 116, 185-200.

Robson, A. and Neal, C., 1990. Hydrograph separation using chemical techniques: An application to catchments in Mid-Wales. *Journ. Hydrol.*, 116, 345-364.

Fiebig, D.M., Lock, M. and Neal, C., 1990. Riparian zone groundwater as a source of carbon for a headwater stream. *Journ. Hydrol.*, 116, 217-238.

Neal, C., Mulder, J., Christophersen, N., Ferrier, R.C., Harriman, R., Neal, M., McMahon, R. and Anderson, H.A., 1990. Ion-exchange and solubility controls in acidic systems: a comparison of U.K. and Norwegian SWAP sites. *S.W.A.P.* In press.

Neal, C., Mulder, J., Christophersen, N., Neal, M., Waters, D., Ferrier, R.C., Harriman, R. and McMahon, R., 1990. Limitations in the understanding for acidic Welsh, Scottish and Norwegian sites. *Journ. Hydrol.*, 116, 11-24.

Christophersen, N., Neal, C., Seip, H.M. and Stone, A., 1990. Hydrochemical models for simulation of present and future short term changes in stream chemistry: development and status. *S.W.A.P.* In press.

Christophersen, N. and Neal, C., 1990. Linking hydrochemical, geochemical and soil chemical processes on the catchment scale: an interplay between modelling and field work. *Water Resources Res.* In press.

Christophersen, N., Robson, A., Neal, C., Whitehead, P.G., Vigerust, B. and Henriksen, A., 1990. Evidence for long term deterioration in stream water chemistry at the Birkenes catchment, southern Norway. *Journ. Hydrol.*, 116, 63-76.

Christophersen, N., Neal, C. and Mulder, J., 1990. Reversal of stream acidification at the Birkenes catchment in southern Norway: predictions based on potential ANC changes. *Journ. Hydrol.*, 77-84.

Christophersen, N., Neal, C., Hooper, R.P., Vogt, R.D. and Andersen, S., 1990. Modelling streamwater chemistry as a mixture of soil-water end members - a step towards second generation acidification models. *Journ. Hydrol.*, 116, 307-320.

Lundquist, D., Christophersen, N. and Neal, C., 1990. Towards developing a new short term model for the Birkenes catchment - lessons learned. *Journ. Hydrol.*, 116, 391-402.

Neal, C., Robson, A., and Smith, C.J., 1990. Acid neutralization capacity variations for the Hafren forest streams, mid-Wales: inferences for hydrological processes. *Journ. Hydrol.*, in press.

2) Editorial.

Neal, C., and Hornung, M.H.: editors, 1990. Transfers of Elements Through the Hydrological Cycle. Journ. Hydrol., special issue, 116, 1-420.

3) Conference publications.

Neal, C., 1985. Hydrochemical Balances in the Spruce Forested Afon Hafren and Afon Hore Catchments: Plynlimon, mid-Wales. Muskoka Conference, Int. Symp. on Acidic Precipitation, 245-248.

Whitehead, P.G., Neal, C., and Neale, R., 1985. Modelling Stream Acidification in Catchments in Scotland and Wales. Muskoka Conference, Int. Symp. on Acidic Precipitation, 244-245.

Christophersen, N., and Neal, C., 1987. Some results important for further development of hydrochemical models describing freshwater acidification. Geomon (International workshop on geochemistry and monitoring in representative basins). Surv., Prague, 139-142.

Lundqvist, D., Christophersen, N., and Neal, C., 1989. The development of a new model for the Birkenes catchment. Annales Geophysicae, special issue, 151.

Neal, C., 1989. Hydrogeochemical variations in streams draining the Hafren forest, mid-Wales. Annales Geophysicae, special issue, 153.

[3]

## LIMITATIONS TO THE UNDERSTANDING OF ION-EXCHANGE AND SOLUBILITY CONTROLS FOR ACIDIC WELSH, SCOTTISH AND NORWEGIAN SITES

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### ABSTRACT

Neal, C., Mulder, J., Christophersen, N., Neal, M., Waters, D., Ferrier, R.C., Harriman, R. and McMahon, R., 1990. Limitations to the understanding of ion-exchange and solubility controls for acidic Welsh, Scottish and Norwegian sites. *J. Hydrol.*, 116: 11-23.

A summary of soilwater and streamwater data from acidic catchments in Wales, Scotland and Norway is presented. It is concluded that insufficient detail has been established to describe quantitatively the ion-exchange and weathering processes in determining streamwater chemistry: such a description is required before reliance can be placed on mathematical models describing short- and long-term changes. The need for manipulative studies is highlighted, emphasis being placed on minimizing perturbation of the system from field conditions. An appeal is made for the use of a standardized method for determining the exchangeable cations. The studies provide overwhelming evidence showing the incorrectness of the commonly used modelling assumption that  $Al(OH)_3$  solubility determines inorganic aluminium levels in the soil and streams. The importance of simple mixing of soil and ground water, in explaining streamwater aluminium-hydrogen ion relationships, is emphasized.

### INTRODUCTION

Predicting the consequences of atmospheric deposition and land-use changes such as conifer afforestation/harvesting, for acidic and acid sensitive systems, requires a thorough understanding of the major chemical, biological, and hydrological processes operative. Mathematical models depicting streamwater and lake water chemistry behaviour are well established and have successfully depicted short-term 'event' streamwater data and historical acidification patterns for lake water (Christophersen et al., 1982, 1984; Cosby et al., 1985; Whitehead and Neal, 1987; Neal et al., 1989a). Amongst the hydrochemical mechanisms depicted in these models, emphasis is placed, correctly, on ion-exchange and weathering reactions. However, simple and unproven mathematical formulations have been used to describe them. Over the past

decade, numerous field studies have been undertaken which now allow a more thorough assessment of the nature of these underlying mechanisms. Here, data from the Royal Society's Surface Water Acidification Programme (SWAP), as well as catchment studies funded by the Natural Environment Research Council and the Department of the Environment, are highlighted to provide such an assessment as a prelude to the development of the next generation of acidification models and to capitalize on recently developed chemical mixing models.

## REACTIONS IN THE STREAM, SOIL, AND GROUNDWATER ZONES

### *Reactions within the stream*

Stream chemistry variations are typically associated with variations of flow (Neal et al., 1989b; Seip et al., 1989). In catchments with mean pH < 6, stormflow waters are acidic and aluminium bearing whereas baseflow waters are impoverished in both these components and enriched in base cations. Stream water can thus be considered as a mixture of soil water and deep percolating 'ground' water components (Robson and Neal, 1990, this volume; Christophersen et al., this volume; Hooper et al., this volume; Neal et al., 1990c, this volume). Baseflow water is derived, essentially, from the groundwater areas where aluminium and hydrogen ion concentrations are low and base cation concentrations are high. Stormflow water is essentially characterized as a mixture of ground water and acidic and aluminium-bearing waters derived from within the soil layers (see Harriman et al., 1990, this volume) and Vogt et al. (1990) for very exceptional cases where baseflow and low flow event waters have mean pH > 6) i.e. as the catchment wets up a greater proportion of water is derived from the upper soil areas. In detail the supply of water comes from a complex hydrological system (e.g. wetting up areas may be greatest near the stream bank, macropore movement may be important etc.). These changes fit in well with simple mixing relationships where soilwater and groundwater end-members mix and aluminium hydroxide is allowed to precipitate either in the stream or the soil zone, should oversaturation occur (Neal and Christophersen, 1989; Neal et al., 1989b). Variations of the trends observed for all the catchments relate to the composition of each of the associated end-members. For example, at a pristine (and more base-rich) site, Hoylandet in mid Norway, preliminary investigations suggest that the soil waters are low in aluminium and are of moderate acidity with the consequence that the stormflow waters are not particularly acidic and aluminium bearing ( $Al_i < 1 \mu M$ ,  $H^+ < 20 \mu M$ ; Christophersen et al., 1990b,c). For catchments receiving greater anthropogenic sulphur inputs ( $6 g S m^{-2} year^{-1}$ ), the stream waters are particularly acidic and aluminium bearing like their soil water counterparts. For the Birkenes catchments in southern Norway,  $Al_i$  rises to 24 and  $4 \mu M$  at sites B1 and B2, the corresponding  $H^+$  maxima being 65 and  $25 \mu M$  (Christophersen et al., 1990b): B1 represents acidic soils underlying spruce vegetation; B2 represents deciduous

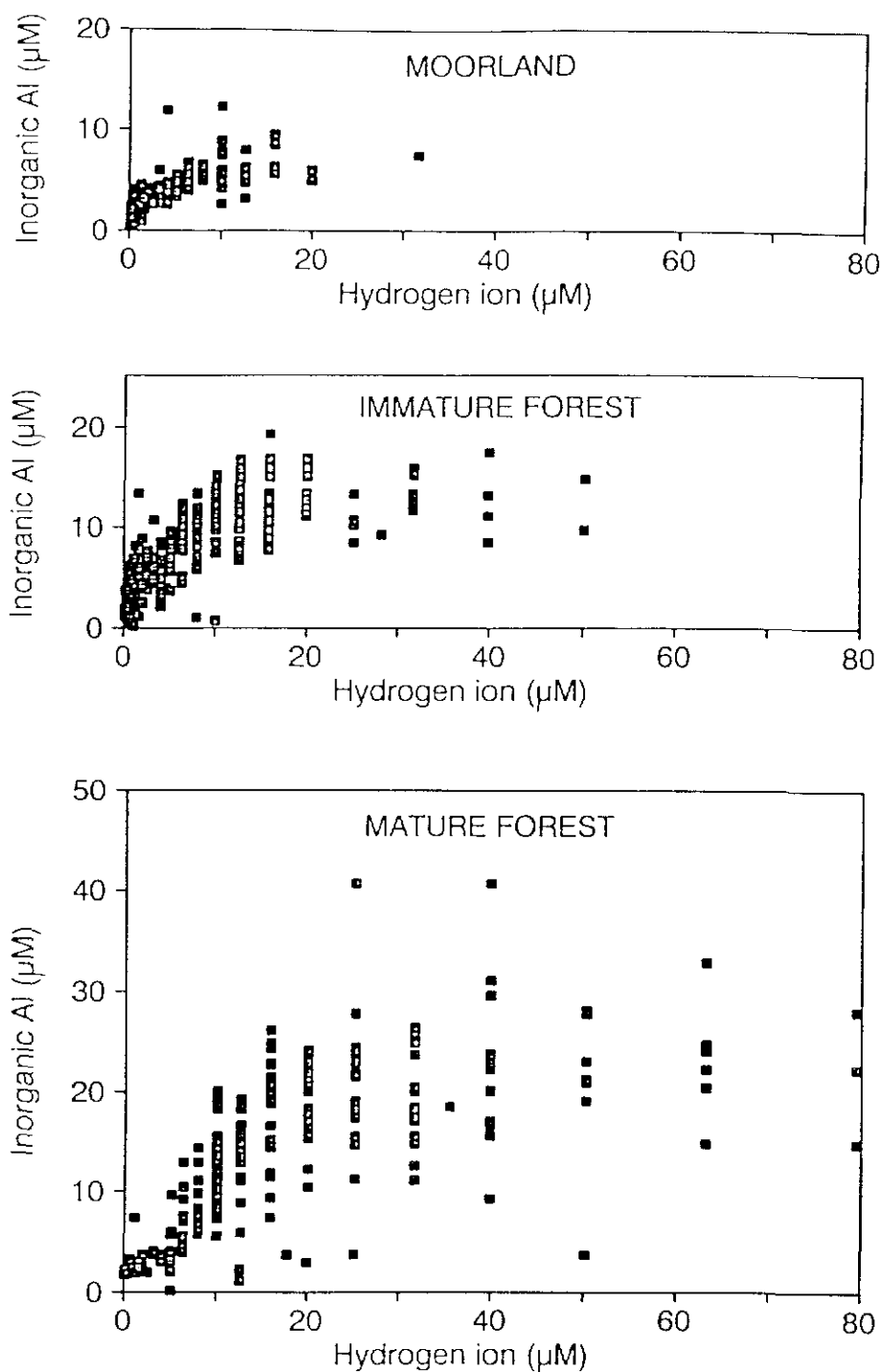


Fig. 1. (a) Inorganic aluminium vs. hydrogen ion concentration plots for moorland (LI6), (b) immature spruce forest (LI8) and (c) mature spruce forest (LI1) sites in the Llyn Brianne area.

vegetation with less-acidic soils and more basic bedrock. At Plynlimon in Mid-Wales,  $Al_i$  and  $H^+$  rise to 27 and 80  $\mu M$ , respectively for the spruce forest streams whereas corresponding values are lower for grassland sites: 5  $\mu M$   $Al_i$  and 30  $\mu M$   $H^+$  (Neal and Christophersen, 1989; Neal et al., 1989b, 1990a). At

Brianne in the southern part of central Wales, a variety of responses is seen which re-emphasizes the important differences between moorland and forest regions with similar bedrock and pollutant deposition seen at Plynlimon; the highest concentrations of inorganic aluminium and hydrogen ion concentrations increase in the following order: moorland,  $12 \mu\text{M Al}_i$ ,  $32 \mu\text{M H}^+$ ; immature spruce forest,  $19 \mu\text{M Al}_i$ ,  $50 \mu\text{M H}^+$ ; mature spruce forest,  $41 \mu\text{M Al}_i$ ,  $79 \mu\text{M H}^+$  (Fig. 1; D. Waters, unpublished data; Robson and Neal, 1990, this volume). Transitional moorland sites such as the Allt a' Mharcaidh in mid Scotland show intermediate, moorland response ( $4 \mu\text{M Al}_i$ ,  $10 \mu\text{M H}^+$ ; McMahon and Neal, 1990; Harriman et al., this volume). In general, the stream waters are undersaturated with respect to aluminium hydroxide for the most acidic waters but saturated to oversaturated under less acidic to alkaline conditions (Neal, 1988; Seip et al., 1989; McMahon and Neal, 1990). Similar behaviour is observed for the survey of 1000 lakes in Norway (Seip et al., 1990, this volume): the waters are roughly saturated with respect to some form of  $\text{Al}(\text{OH})_3$  phase in the higher pH range, whereas at lower pH undersaturation occurs, the degree of undersaturation increasing as pH declines (see also Hooper and Shoemaker (1985) for an example from the U.S.A.). It should be noted that generally within the modelling work, aluminium hydroxide solubility has been assumed to apply in the stream waters throughout the pH range (Christophersen et al., 1982, 1984; Cosby et al., 1985).

#### *Reactions within the soil zone*

The acidic soils of concern here (podzols, gleys, brown earths, etc.) have organic-rich surface horizons and lower horizons volumetrically dominated by inorganic components (sand-, silt- and clay-sized primary minerals plus secondary components such as complex low-crystallinity aluminium/iron oxide/hydroxide/organic materials and clay minerals). The organic layer provides not only a large cation store, partly bound in organic tissue, which is exchangeable with cations in solutions, but also release of acidic humic substances to solution. In the inorganic layers the dominant reactions involve the breakdown of oxide/hydroxide and silicate phases by weathering reactions and cation exchange reactions involving inorganic surfaces and organic surface coatings (it should be noted that although the term inorganic layer is used as a general description, the importance of the small amounts of organic coatings for controlling cation exchange reactions cannot be overstressed; cf. Mulder et al., 1989).

Within the organic and inorganic layers of the soil the ion exchange reactions have, for modelling purposes, been described in terms of simple ion-exchange reactions involving an insoluble material of constant cation exchange capacity (Neal et al., 1989b, 1990a), using equations of the type



for cations M and N with respective charges  $m+$  and  $n+$ , where an



equilibrium, selectivity, constant ( $K_{MN}$ ) is defined with fractions of exchangeable cations,  $\text{Ads}()$ , such that

$$K_{MN} = \text{Ads}(N)^m \times (M^{n+})^n / \text{Ads}(M)^n \times (N^{m+})^m$$

For the situation where the cation exchange store is large compared with the throughput of ions in the soil water (over the time considered) the adsorbed ion ratio,  $\text{Ads}(N)^m / \text{Ads}(M)^n$  remains constant and hence the solution ion ratio,  $(N^{m+})^m / (M^{n+})^n$  also remains constant (cf. the mobile anion concept, Reuss and Johnson, 1986; Neal et al., 1989b). For example, in the case of  $\text{Al}^{3+}$  exchange with  $\text{H}^+$ , the relationship is cubic whereas for  $\text{Ca}^{2+}$  exchange with  $\text{Na}^+$  the relationship is squared.

Examination of soilwater data for both acidic moorland and spruce forest indicates that this simple cation-exchange equilibrium formulation is inappropriate for both the inorganic and the organic soils:  $K_{MN}$  varies as a function of the concentrations of M and N, for constant temperature. This lack of a relationship has been most completely documented with regard to aluminium/hydrogen ion where a cubic relationship has not been encountered. Results of the various studies are presented in the next paragraph to illustrate the general inapplicability of the simple ion-exchange formulations.

Linear relationships occur between inorganic aluminium and hydrogen ion for organic soils from moorland and forest soils in Mid-Wales and South Wales; the relationship is characterized by a power of 1–2 (Neal et al., 1989b, 1990a). Preliminary examination reveals that for the major cations, a similar lack of thermodynamic equilibrium exists within all the soil layers; linear relationships occur both between the various major cations and between the individual major cations and the sum of the anions. In the case of three Scottish catchments, no relationship is observed between inorganic aluminium and hydrogen ion concentration as the data are highly scattered (McMahon and Neal, 1990). At one of these sites, Allt a' Mharcaidh, preliminary analysis of the soil water data revealed sodium, magnesium and the sum of the major anions to be linearly correlated, whereas calcium shows no relationship with these other variables (Neal et al., 1990b). At sites in Canada and the Netherlands, gradients in the  $\text{pAl}^{3+}$  versus pH graph vary from 0 to 3 in the various soil layers (Mulder, 1987). For the soil data at Birkenes, spatial variability of trends is observed and evidence for or against specific ion-exchange reactions is unclear (Christophersen et al., 1990, this volume). For this site, a laboratory desorption experiment provides a power term varying from 2 to 3 (Andersen et al., 1990).

Although there is insufficient information on the spatial variability of soil water chemistry, it is clear that hydrological and mixing processes come into play within the soil zone and produce a complex variety of responses. As a consequence of this, it cannot be conclusively stated that a simple exchange reaction is occurring. Rather, the results can be viewed as representing simple equilibrium in the micropores and simple conservative chemical mixing in the free draining water supplying the soil solution samplers. For the ion-exchange

materials of concern, many of the exchange sites result from ionization of OH groups and the assumption of a constant cation-exchange capacity is therefore very dubious (Walker et al., 1990). Formulations have been developed which allow for change in the cation-exchange capacity (Tipping and Hurley, 1988). Potentially such models can explain deviations in the power relationships (Andersen et al., 1990); however, these models have not been sufficiently developed or tested to show how much improvement can be achieved by their use. Alternatively the models we use may be totally inadequate: do we really have enough information on local flow routes and fluxes, temperature variations, competing ionic species, biological interactions etc.?

Within the inorganic soil zones, weathering reactions are also important and although gross weathering rates have been established (Aaberg et al., 1989), it remains unclear as to the formulations of the kinetic reactions required for short-term modelling purposes. For example, current estimates of plagioclase weathering rates are 1–3 orders of magnitude higher for laboratory compared with field estimates; complex interactions involving strained surfaces, defect dislocations, surface layers, adhered particles, etc. can all account for the differences (Velbel, 1986). It has been widely assumed that inorganic aluminium concentrations are regulated in these soils by a thermodynamic equilibrium involving aluminium hydroxide. However, work from all the soil studies mentioned above disproves such a contention: the waters are typically undersaturated with respect to gibbsite; saturation is approached in the lower inorganic horizons but here data show too great a scatter for this thermodynamic equilibrium to be deemed operative (Neal, 1988; Seip et al., 1989; McMahon and Neal, 1990). This is best demonstrated at one of the Scottish sites: no thermodynamic equilibrium is observed even though it is one of the very few areas where gibbsite has been found within the soil (McMahon and Neal, 1990).

Preliminary comparisons between pristine (Hoylandet, mid Norway), transitional (Allt a' Mharcaidh, Scotland) and impacted sites (Birkenes, southern Norway; Plynlimon and Brianne, Wales) suggest that the relative proportion of exchangeable aluminium to exchangeable hydrogen increases with the degree of impactation, although there are large variations in pattern owing to the effects of vegetation type and hydrological and geological factors (Christophersen et al., 1990b). Therefore, it is difficult to come to any major conclusions as to the variations of the exchangeable cations for different regions: several methods of analysis have been used together with various pretreatments of samples (e.g. drying and sieving soils prior to extraction with unbuffered or buffered salt solutions of various ionic strengths); cf. Walker et al. (1990).

#### *Reactions within the groundwater zone*

Despite the stream waters possessing aluminium and hydrogen ion concentrations lower than the associated soil waters, in very few cases have

sampling programmes been established to assess from where the more alkaline water derives and, quantitatively, the nature of the reactions involved. In the exceptional cases at the Allt a' Mharcaidh in Scotland (Harriman et al., 1990, this volume), the Birkenes catchment in southern Norway (Christophersen et al., 1990, this volume) and Panola, Georgia, U.S.A. (Hooper et al., 1990, this volume), less-acidic waters have been found under the hillslope soils or in stream bog areas. These waters, of  $\text{pH} \geq 6$ , contain bicarbonate and alkaline earth metals and are inorganic aluminium depleted. Therefore, in this zone, not only is the acidic water from the overlying soils partially neutralized by weathering and possibly reduction reactions but either aluminium is removed from solution as aluminium hydroxide/silicate minerals (the waters are in approximate equilibrium with gibbsite and quartz; Neal et al., 1987) or the underlying soils produce only organic aluminium. The kinetics of inorganic-organic aluminium interconversions within the soil matrix and soil solution remains uncertain. Detailed evaluation of the nature of the reactions cannot be made given the sparsity of the information available.

## DISCUSSION

### *Integrating soilwater and streamwater information*

Integrating the soilwater and streamwater data has highlighted the importance of water mixing processes and has provided a simple qualitative way of describing, on the catchment scale, some of the processes that are complex and poorly understood on the plot scale. The results point to the limitations of present modelling efforts that assume 'simple' equilibrium processes are operative. They also highlight the need for more elaborate models describing ion-exchange reactions and the identification of those areas where waters from the various soil and deeper zones mix and weathering reactions predominate. There is a need to assess the representativeness of the various soil water samplers and the delineation between those areas within the soil where chemical and physical mixing reactions take place; the nature of the interactions of aluminium and TOC remains unclear and thus equations linking inorganic and organically bound aluminium in solution also remain uncertain.

### *The relative effects of atmospheric deposition and conifer afforestation*

Since the mid-1970s there has been very active debate over the relative importance of atmospheric deposition and conifer afforestation in acidifying systems. Although the debate has generally focused on Norway (Rosenqvist, 1990, this volume) emphasis is now shifting to the British uplands where extensive afforestation of acid moorland by spruce and pine has occurred over the past 60 years (Ormerod et al., 1989). The results presented above show, in general, that, in a given area (e.g. Plynlimon and Brianne; Fig. 1), streams

draining forested catchments are more acidic and aluminium bearing than their moorland counterparts. This is best seen with the Welsh Waters regional survey (113 catchments) where strong positive correlations are found between inorganic aluminium, hydrogen ion and percentage forest cover (Ormerod et al., 1989). The results fit in very well with both the mobile anion concept used in describing catchment acidification from 'acid rain' and the forest development models usually set against it (Reynolds et al., 1988; Rosenqvist, this volume, 1990b). With the mobile anion concept, the trees can be viewed as enhancing the salt and atmospheric pollutant inputs by atmospheric capture of fine particles owing to the trees high surface area. The tree also increases evapotranspiration thereby increasing the soil ionic strength. For the forest development model, tree growth not only increases the organic, acidic, upper soils, but also depletes the soil of base cations which accumulate in the biomass. As yet it remains unclear as to which of these two processes control the observed differences of stream chemistry; under pristine conditions stream acidification may or may not occur with forestry development, the evidence is contradictory (Battarbee, 1989; Harriman, 1989; Rosenqvist, 1990b). Consequently, a new challenge for U.K. environmental research is an assessment of the relative importance of these two processes. Whatever the mechanism, the planting of conifers on acid soils with base-poor bedrock, will lead to a deterioration of streamwater quality that is best avoided on ecological grounds.

*The need for more appropriate information on soil exchange processes*

Soil acidification has primarily been viewed by modellers in terms of the displacement of bases from cation exchange sites in the soil and the incorporation of either exchangeable hydrogen or exchangeable aluminium, but not both. However, as known by soil scientists for decades, the results suggest that acidic soils occur in both pristine and polluted areas (Rosenqvist, 1990, this volume) and that both exchangeable hydrogen and aluminium make up a large proportion of the cation-exchange sites (Thomas, 1982). On this basis and given the lack of a simple ion-exchange reaction within acidic soils, the models need modification, possibly along the lines of Tipping and Hurley (1988), before any reliance can be placed on them.

There is considerable need for improving laboratory experimentation describing the ion-exchange characteristics within the soil zones. Too often the soils have been viewed in terms of simple inorganic reactions, rather than as a living and physically complex system with organic coatings: little allowance has been made for biological and physical processes that confound the issue. On this basis recommendations for standardized and appropriate schemes of soil analysis are presented here.

Drying clay mineral components in soil leads to the fixation of ions such as  $\text{Al}^{3+}$  whereas drying organic soil components can lead to mineralization reactions and the release of ions to solution. After collection in the field, increasing the temperature of the soil to the laboratory level, and removing

any vegetation cover, can cause biological reactions to come into play: dissolved nitrogen increases (cf. Skeffington and Brown, 1986); with storage of the order of weeks anoxic conditions may even develop. This can be a major hindrance if say one wishes to determine selectivity coefficients and adsorption isotherms from laboratory measurements. The recommendation made here is that adsorption experiments should only be carried out as near to field conditions as possible: the samples must not be dried, temperature must be kept at field temperature, and the experiment should be performed as soon after collection as possible (hours rather than days, weeks or years as is often the case); manipulations in the field with minimal disturbance is particularly recommended (e.g. Vogt, 1989).

Assessment of the cation-exchange complements is important in light of the overall modelling objective. However, the plethora of methods used and the lack of identification as to what the method should be measuring, confounds the issue. New information is required to understand the nature of the soil's cation-exchange complements in the light of the more advanced cation-exchange theory. It is now clear that the problem needs addressing in terms of organic and inorganic adsorption sites of variable charge: the field information required must therefore be of use with variable charge models, for example, of the type described by Tipping and Hurley (1988). Such an approach requires information of a type not collected previously: not only do the amounts of the easily exchangeable base cations need assay but so do the amounts of the weak and more strongly bound aluminium and hydrogen ion components. This requires three extractions: two involving unbuffered and buffered salt solutions, the other a salt solution with a cation that strongly binds to organic surfaces and displaces more strongly bound aluminium. Here, a flag is raised for such a standardized scheme, following the developments made within the soil science field over the past 30 years or more. The extractions are, respectively: (1) 0.1 M barium chloride (Hendershot and Duquette, 1986), (2) 0.1 M barium chloride buffered to Ph 8.2 (Thomas, 1982) and (3) 0.5 copper nitrate (Cronan et al., 1986). In the case where adsorbed sulphate is significant, after extraction (1) the exchangeable barium will need a further assay to allow for barium sulphate precipitation: here a 0.025 M  $\text{MgSO}_4$  salt solution can be considered (Hendershot and Duquette, 1986). In all cases, the technique should be applied (1) immediately or as soon as possible after collection, (2) for undried soils, (3) for the optimum period required to extract the exchangeable cations but minimise other chemical processes, and (4) at field temperature.

#### *The need for more appropriate testing of chemical equilibrium*

For many years thermodynamic stability diagrams have been used for describing the equilibrium status of waters with respect to particular mineral phases (e.g. Garrels and Christ, 1965). In the 'acid rain' field, of overriding use has been a plot of  $p\text{Al}^{3+}$  vs. pH to test for  $\text{Al}(\text{OH})_3$  solubility controls. However, recent evidence suggests that such an approach is of dubious merit (Neal et al.,

1987; Neal, 1988): log activities are used, masking data scatter; the axes are dependent and spurious correlations can result. On this basis a new procedure was introduced which utilized axes with less dependency (Neal, 1988). This led to the use of simple (non-derivative) plots (Neal, 1988; Neal et al., 1990a,b) and further extension by the introduction of Null hypothesis testing with appropriate error evaluation and temperature correction (Christophersen and Neal, 1989). Although such techniques are new it is important that they, rather than conventional techniques, are used for objective assessment of equilibrium.

There remains a predilection for describing waters in terms of the degree of saturation with particular forms of  $\text{Al}(\text{OH})_3$ . For the acid systems of concern in this report, saturation with respect to  $\text{Al}(\text{OH})_3$  is the exception rather than the rule. It is therefore incorrect to continue to describe the waters, thermodynamically, in this blinkered way. With the development of thermodynamic programs, such as WATEQ (Truesdell and Jones, 1974) and ALCHEMI (Schecher and Driscoll, 1987), the degrees of saturation for many minerals associated with the soil can easily be assessed. By using this information, tables listing saturation indexes can valuably be used to describe the thermodynamic status of the water: in this case error assessment is also required owing to the large variations of the thermodynamic constants for many of the solid phases of concern. The use of this technique also overcomes 'data scatter' problems, owing to temperature variation affecting the equilibrium constants, prevalent with most other approaches. Unlogged values of the degree of saturation should be used in this assessment.

## CONCLUSIONS

Throughout this presentation the importance of the interactiveness of the hydrochemical, hydrological, biological processes operative is recognised: an integrated picture of how catchments respond to anthropogenic influences is required. To achieve this objective an interdisciplinary approach is required and it is insufficient simply to use, adhoc, ideas and methods from the parent disciplines (hydrology, biology, soil science, chemistry etc.) (Christophersen et al., 1990, this volume). This has been achieved as new information has accumulated within the surfacewater acidification programme (SWAP) and allied research. At the same time, these projects have highlighted gaps in our understanding. For example, the case considered here shows a surprising lack of detailed knowledge of aluminium mobilization, given that the importance of this component in acidification impacts was known over 10 years ago. To capitalize on the field and modelling work over the past decade a new initiative is required to characterize the cation exchange and weathering reactions. On this basis, process-oriented models along the lines of Tipping and Hurley (1988) deserve encouragement although they must be supported with more rigorous analytical procedures and tests for chemical equilibrium as outlined above.

## REFERENCES

- Aaberg, G., Jacks, G. and Hamilton, P.J., 1989. Weathering rates and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios: an isotopic approach. *J. Hydrol.*, 109: 65-78.
- Andersen, S., Christophersen, N., Mulder, J., Seip, H.M. and Vogt, R.D., 1990. Aluminium solubility relationships in various soil horizons of an acidified catchment. SWAP Final Conference, Royal Soc., (London) (in press).
- Battarbee, R.W., 1989. The acidification of Scottish lochs. Patterns of surface water acidification in Scotland; Symp. Proc., 8 Nov., 1988. Scottish Development Dept., Environ. Protection Division, Edinburgh, pp. 104-110.
- Christophersen, N. and Neal, C., 1989. A rational approach to the assessment of aluminium controls in fresh waters. *Sci. Total Environ.*, 84: 91-100.
- Christophersen, N., Seip, H.M. and Wright, R.F., 1982. A model for stream water chemistry at Birkenes, Norway. *Water Resour. Res.*, 18: 977-996.
- Christophersen, N., Rustad, S. and Seip, H.M., 1984. Modelling streamwater chemistry with snowmelt. *Philos. Trans. R. Soc. London, Ser. B*, 305: 427-439.
- Christophersen, N., Neal, C., Hooper, R.P., Vogt, R.D. and Andersen, S., 1990a. Modelling streamwater chemistry as a mixture of soil-water end-members — a step towards second generation acidification models. *J. Hydrol.*, 116: 307-320.
- Christophersen, N., Neal, C., Vogt, R.D., Esser, J. and Andersen, S., 1990b. Aluminium mobilization in soil and stream waters at three Norwegian catchments with differences in acid deposition and site characteristics. *Sci. Total Environ.* (in press).
- Christophersen, N., Vogt, R.D., Neal, C., Anderson, H.A., Ferrier, R.C., Miller, J.D. and Seip, H.M., 1990c. Controlling mechanisms for streamwater at the pristine Ingerbekken site in mid Norway. Some implications for acidification models. *Water Resour. Res.* (in press).
- Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N., 1985. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and stream water chemistry. *Water Resour. Res.*, 21: 51-63.
- Cronan, C.S., Walker, W.J. and Bloom, P.R., 1986. Predicting aqueous aluminium concentrations in natural waters. *Nature*, 324 (6093): 140-143.
- Garrels, R.M. and Christ, C.L., 1965. *Solutions, Minerals and Equilibria*. Harper, New York, 450 pp.
- Harriman, R., 1989. Patterns of surface water acidification in Scotland. Acidification in Scotland; Symp. Proc., 8 Nov., 1988. Scottish Development Dept., Environ. Protection Division, Edinburgh, pp. 72-79.
- Harriman, R., Gillespie, E., King, D., Watt, A.W., Christie, A.E.G., Cowan, A.A. and Edwards, T., 1990. Short-term ionic responses as indicators of hydrochemical processes in the Allt a' Mharcaidh catchment, western Cairngorms, Scotland. *J. Hydrol.*, 116: 267-285.
- Hendershot, W.H. and Duquette, M., 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *J. Soil Sci. Am.*, 50: 605-608.
- Hooper, R.P. and Shoemaker, C.A., 1985. Aluminium mobilization in an acidic headwater stream: temporal variations and mineral dissolution-disequilibrium. *Science*, 229: 463-465.
- Hooper, R.P., Christophersen, N. and Peters, N.E., 1990. Modelling streamwater chemistry as a mixture of soilwater end-members — an application to the Panola mountain catchment, Georgia, U.S.A. *J. Hydrol.*, 116: 321-343.
- McMahon, R. and Neal, C., 1990. Aluminium dis-equilibrium solubility controls in Scottish acidic catchments. *Hydrol. Sci. Bull.*, 35(1): 21-28.
- Mulder, J., 1987. The aluminium chemistry of spodosols, impacted by strong acid. In: B. Moldan and T. Paces (Editors), *International Workshop on Geochemistry and Monitoring of Representative Basis (GEOMON)*. Geological Survey, Prague, pp. 95-98.
- Mulder, J., van Breeman, N. and Eijck, H.C., 1989. Depletion of soil aluminium by acid deposition and implications for acid neutralization. *Nature*, 337 (6204): 247-249.
- Neal, C., 1988. Aluminium solubility relationships in acid waters — a practical example of the need for a radical reappraisal. *J. Hydrol.*, 104: 141-159.

- Neal, C. and Christophersen, N., 1989. Inorganic aluminium-hydrogen ion relationships for acidified streams: the role of water mixing processes. *Sci. Total Environ.*, 80: 195-203.
- Neal, C., Skeffington, R.A., Williams, R. and Roberts, D.J., 1987. Aluminium solubility controls in acid waters: the need for a reappraisal. *Earth Planet. Sci. Lett.*, 86: 113-119.
- Neal, C., Musgrove, T. and Whitehead, P.G., 1989a. Predicting the long term variations in stream and lake inorganic aluminium concentrations for acidic and acid sensitive catchments. *Sci. Total Environ.*, 80: 205-211.
- Neal, C., Reynolds, B., Stevens, P. and Hornung, M., 1989b. Hydrological controls for inorganic aluminium in acidic stream and soil waters at two upland catchments in Wales. *J. Hydrol.*, 106: 155-175.
- Neal, C., Reynolds, B., Stevens, P., Hornung, M. and Brown, S.J., 1990a. Dissolved inorganic aluminium in acidic stream and soil waters in Wales. In: R.W. Edwards, A.S. Gee and J.H. Stoner (Editors), *Acid Waters in Wales*. Kluwer, Dordrecht, pp. 173-188.
- Neal, C., Mulder, J., Christophersen, N., Ferrier, R.C., Harriman, R. and McMahan, R., 1990b. Ion exchange controls in acidic systems, a comparison of U.K. and Norwegian sites. SWAP Final Conference, Royal Soc. (London) (in press).
- Neal, C., Smith, C.J., Walls, J., Billingham, P., Hill, S. and Neal, M., 1990c. Hydrogeochemical variations in Hapren Forest stream waters, mid-Wales. *J. Hydrol.*, 116: 185-200.
- Ormerod, S.J., Donald, A.P. and Brown, S.J., 1989. The influence of plantation forestry on the pH of upland streams: a re-examination. *Environ. Pollut.*, 62: 47-62.
- Reuss, J.O. and Johnson, D.W., 1986. Deposition and the acidification of soils and waters. *Ecol. Stud.*, 59: 1-119.
- Reynolds, B., Neal, C., Hornung, M., Hughes, S. and Stevens, P., 1988. Impact of afforestation on the soil solution chemistry of stagnopodzols in mid Wales. *Water, Air Soil Pollut.*, 38: 55-70.
- Robson, A. and Neal, C., 1990. Hydrograph separation using chemical techniques: an application to catchments in Mid-Wales. *J. Hydrol.*, 116: 345-363.
- Rosenqvist, I.Th., 1990a. From rain to lake: pathways and chemical changes. *J. Hydrol.*, 116: 3-10.
- Rosenqvist, I.Th., 1990b. Preindustrial surface water acid periods in Norway. SWAP Final Conference, Royal Soc. (London) (in press).
- Schecher, W.D. and Driscoll, C.T., 1987. An evaluation of uncertainty associated with Al equilibrium calculations. *Water Resour. Res.*, 23: 525-534.
- Seip, H.M., Andersen, D.O., Christophersen, N., Sullivan, T.J. and Vogt, R.D., 1989. Variations in concentrations of aqueous aluminium and other chemical species during hydrological episodes at Birkenes, southernmost Norway. *J. Hydrol.*, 108: 387-405.
- Seip, H.M., Andersen, S. and Henriksen, A., 1990. Geochemical control of aluminium concentrations in acidified surface waters. *J. Hydrol.*, 116: 299-305.
- Skeffington, R.A. and Brown, K.A., 1986. The effect of five years acid treatment on leaching, soil chemistry and weathering of a humo-ferric podzol. *Water, Air Soil Pollut.*, 31: 891-900.
- Thomas, G.W., 1982. Exchangeable cations. *Methods of Soil Analysis: part 2, Chemical and Microbiological Properties*. Agronomy, 9(2): 159-165.
- Tipping, E. and Hurley, M.A., 1988. A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances. *J. Soil Sci.*, 39: 505-519.
- Truesdell, A.H. and Jones, B.F., 1974. WATEQ, a computer program for calculating chemical equilibria of natural waters. *J. Res., U.S. Geol. Surv.*, 2: 233-248.
- Velbel, M.A., 1986. Influence of surface area, surface characteristics and solution composition on feldspar weathering rates. In: J.A. Davis and K.F. Hayes (Editors), *Geochemical Processes at Mineral Surfaces*. Am. Chem. Soc. Symp., Ser., 323: 615-930.
- Vogt, R.D., 1989. An experimental approach to aluminium mobilization and flow pathways at the Birkenes Catchment in southern Norway. *Cand. Scient. Thesis, Chem. Inst., dep C., Univ. Oslo*, 93 pp.
- Vogt, R.D., Andersen, D.O., Andersen, S., Christophersen, N. and Mulder, J., 1990. Streamwater, soilwater chemistry and water flow paths at Birkenes during a dry wet hydrological cycle. SWAP Final Conference, Royal Soc. (London) (in press).



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- Walker, T.A.B., Anderson, H.A., Hepburn, A., Ferrier, R.C., McMahon, R.G., Smith, B.F.L. and Millar, J.D., 1990. Inorganic and organic soil processes and their influence on percolating waters. SWAP Final Conference, Royal Soc. (London) (in press).
- Whitehead, P.G. and Neal, C., 1987. Modelling the effect of acidic deposition in upland Scotland. Trans. R. Soc. Edinburgh, 78: 385-392.