INSTITUTE
OF
HYDROLOGY

HYDROCHEMICAL BUDGETS OF CONIFEROUS FOREST: A PROGRESS REPORT

by

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ABSTRACT

Seasonal changes in major, minor and trace elements in two afforested catchments, the Afon Hore and the Afon Hafren in the Upper Severn river basin, have been monitored since 1983 to ascertain the natural variations in stream water chemistry prior to clear felling of the trees. This interim report presents data obtained so far and discusses their interpretation in the context of both hydrological and hydrogeochemical budgets.

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INTRODUCTION

Acidic deposition is widely believed to be responsible for the acidification of soils and stream waters which causes major adverse ecological effects in Northern America and Europe. Areas particularly at risk are the uplands where soil cover is thin and natural buffering mechanisms are swamped or bypassed. It is now recognised that stream acidification, often accompanied by the release of ecologically toxic elements, is in part the consequence of inappropriate land use. While the fluxes of hydrogen ion and sulphur dioxide to catchments may represent a major contribution to stream acidity, in many other cases the disturbance or build up of organic rich soils with extremely high acid content, coupled with changes in hydrology, can also be a major factor. However the relative importance of land use practices in affecting the environment has not been fully established and remains controversial.

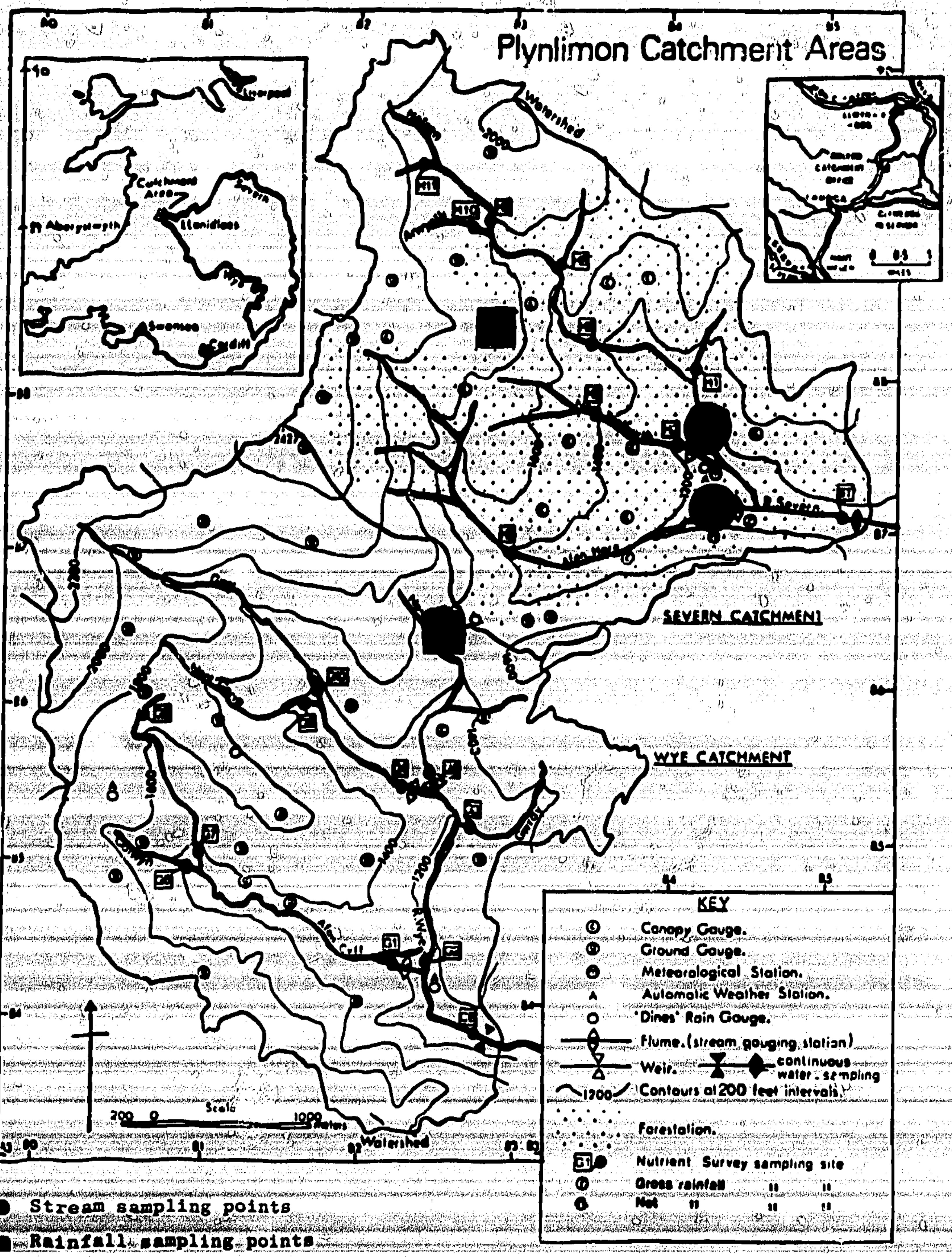
To develop an understanding of the importance of land use change in controlling stream water quality in upland areas the present project was initiated, in spring 1983, to study water quality changes in forest streams before, during and after a deforestation programme. Two main subcatchments of the headwaters of the River Severn in the Hafren forest, at the eastern edge of Plynlimon, Mid Wales, were selected for study. This area was chosen because a deforestation programme was planned for one of the two subcatchments, detailed hydrological data for these catchments is available since they comprise an integral part of the Institute of Hydrology's water balance studies, and complementary chemical studies within the Plynlimon area are being undertaken by the Institute of Terrestrial Ecology. Details of the catchment characteristics of these sites are shown in Table 1 and Figure 1.

Table 1. Hafren and Hore Catchment Characteristics

	Area	Altitude Range	Rainfall (yearly)	Evapotranspiration (yearly)**	Stream Flow rate	Vegetation Forest*	Grass/Peat
	(ha)	(m)	(mm)	(mm)	(m^3s^{-1})	(% area)	
Hafren	347	361-740	1600-2800	24-55	0.01-4.62	50	50
Hore	335	370-625	1600-2800	24-55	0.01-[illegible].47	77	23

* Forest soils gleys and podsols
Tree types mainly Norway and Sitka
spruce, but also some pine and larch;
these having been planted from
1937 to 1964

** Values for the Upper Severn



● Stream sampling points

■ Rainfall sampling points

FIGURE 1 The Plynlimon catchments

The aims of the project are:

(1) to produce a comprehensive baseline hydrochemical data set for detailed comparison with data gathered following the Hore deforestation programme of autumn 1985 in collaboration with the Institute of Terrestrial Ecology (ITE) and the British Geological Survey (BGS).

(2) to develop a model describing the movements of key conservative and non-conservative elements through the two catchments under varying hydrological conditions

(3) to use the model (2) to estimate element residence times;

(4) to identify the dominant hydrogeochemical processes aided by mineral equilibrium models;

(5) to determine the relative importance of atmospheric, geological and biochemical sources of a wide range of elements within the two catchments making use of, and linking directly with, the ITE's detailed studies in Plynlimon on plot and catchment scale experiments;

(6) to examine the potential of "natural" tracers for assessing the component of rapid runoff in streamwater, linked with IH studies of flood runoff using "artificial" tracer techniques.

Results are presented to show the progress made during the first 12 months and the directions in which the continuing studies will develop.

SAMPLING AND ANALYSIS

Weekly sampling of rain and stream waters was initiated in May 1983 at the sites shown in Figure 1. Stream water samples were also collected during periods of high flow. At the streamwater sampling sites two samples of water were taken and immediately filtered, one through a 0.45 µm cellulose membrane, the other through a 1 µm glass fibre filter, the samples being stored in polythene and glass bottles respectively. The samples in the polythene bottles were acidified to 1% v/v with "Aristar" hydrochloric acid. Two rainfall samples were collected, one at the Gwy, the other at the Carreg Wen rainfall monitoring sites. These samples were taken to the Plynlimon laboratory where they were bulked together to give an average chemistry for the altitude range of the catchments. The bulked sample was then split, filtered and put into polythene and glass bottles in the same way as for the streamwaters.

The stream water and rainfall samples were analysed for 38 determinands which are listed, together with the analytical methods usedfor their determination, in Table 2. Conductivity, alkalinity, pH and bicarbonate were analysed at the Plynlimon laboratory within two hours of sample collection to avoid changes that might occur during storage. The other 34 determinands were analysed at the Wallingford laboratories.

Table 2. Chemical analysis

Element	Storage	Pretreatment	Analysis
Na K Ca Mg	Polythene	0.45 µm filtration	
B Li SO_4 Sc	bottle	with cellulose membrane	
Sr Y Ba Mn		Sample acidified with	Inductively
Cu Fe V Cd		aristar HCl to 1% v/v	Coupled Plasma
Zr Co Zn La		Samples preconcentrated	Emission
Cr Ni Mo Al		by a factor of 20 by	Spectrograph
Pb		evaporation	
NO_3 NH_4 PO_4	Glass	1 µm glass fibre filtration	Colourimetric
(F) Br I Cl	bottle		
Si			
DOC	Glass	1 µm glass fibre filtration	Phase sep/flame
	bottle		ionisation
			(Tocsin II)
Alkalinity, pH	Glass	1 µm glass fibre filtration	Titrimetric
and HCO_3	bottle		
Conductivity	Direct measurement in field for		
	stream water, glass bottle storage		Conductivity meter
	for rain water.		

RESULTS

Rainfall

The rainfall chemistry presents large variability in the concentrations of virtually all of the determinands, the range of values being up to an order of magnitude (Table 3, Figure 2). Of 25 samples analysed 21 show high correlations between the major ions Na, K, Ca, Mg, SO_4, Sr, Br, Cl and element ratios to Cl are similar to sea water ratios indicating the maritime influence (Table 4, Figure 2); the low concentrations of major, minor and trace elements and the moderate acidity in these samples are taken to reflect natural rainfall concentrations. The remaining samples are anomolously acidic (pH ~4) and are enriched in SO_4, NO_3, Cu, Zn, Ba, Mn, Fe, Al (Figure 2) indicating that for part of the year pollutant inputs are significant.

Table 3. Rainfall and Stream Water Chemistry

Element	Rainfall		Hafren Stream Water		Hore Stream Water	
	mean	range	mean	range	mean	range
Major components (concentrations in mg l^{-1})						
Na	3.62	2 - 15	4.09	3- 5	4.18	3 - 5
K	0.17	0.05- 0.50	0.16	0.07- 0.27	0.14	0.07-0.27
Ca	0.25	0.1 - 0.6	0.91	0.6 - 1.6	1.81	1 - 4
Mg	0.46	0.2 - 1.6	0.80	0.7 - 1.0	0.91	0.8 - 1.3
SO_4	2.05	1 - 5	4.22	3 - 6	4.79	3 - 6
Si	.03	.02 - .05	2.01	1 - 3	1.90	1.5 - 5.0
DOC	0.34	0.2 - 0.8	1.05	0.5 - 2.5	1.01	0.5 - 2.5
HCO_3	-	-	2.75	1 - 8	5.33	2 - 17
NO_3	0.88	0.2 - 3.0	1.31	0.3 - 3.0	1.18	0.5 - 2.5
Cl	6.96	2 - 25	7.42	7 - 12	8.31	7 - 11
Minor and trace element components (concentrations in µg l^{-1})						
B	3.13	2 - 9	3.21	2 - 7	4.21	3 - 15
Li	0.00	0.00	2.51	1.6 - 2.8	2.03	1.3 - 2.3
Sr	1.32	0.1 - 9.0	5.49	4 - 7	5.70	4 - 8
Y	0.00	0.00	0.25	0.1 - 0.6	0.19	0.1 - 04
Ba	1.32	0.8 - 4.0	1.99	1 - 6	2.99	2 - 8
Mn	2.28	0.2 - 9.0	35.5	10 - 70	28.0	10 - 45
Cu	6.26	1 - 40	1.45	1 - 6	2.86	1 - 40
Fe	7.36	0 - 30	71.6	50 - 150	63.7	10 - 120
Co	0.00	0.00	1.73	1 - 4	1.64	1 - 3
Zn	18.3	10 - 120	13.6	5 - 30	20.6	5 - 30
Al	12.9	0 - 100	219.	25 - 600	140.	25 - 600
Br	24.7	10 - 80	20.9	15 - 45	20.8	10 - 32
I	2.71	2 - 10	0.98	0.5 - 1.5	0.80	0.5 - 1.5
Acidity (concentration in µM l^{-1})						
H^+	24.1	10-150	14.8	1 - 60	10.3	1 - 50

Elements analysed but less than the detection limits of the analytical methods used were Sc (0.05), La (0.5); V, Cd, Zr, Cr (1.0); Ni, Mo (5.0); Pb (10.0).

NH_4 and PO_4 values not included due to uncertainties in the stream water mean concentrations (many values being less than the detection limit) and the large range in rainfall values.

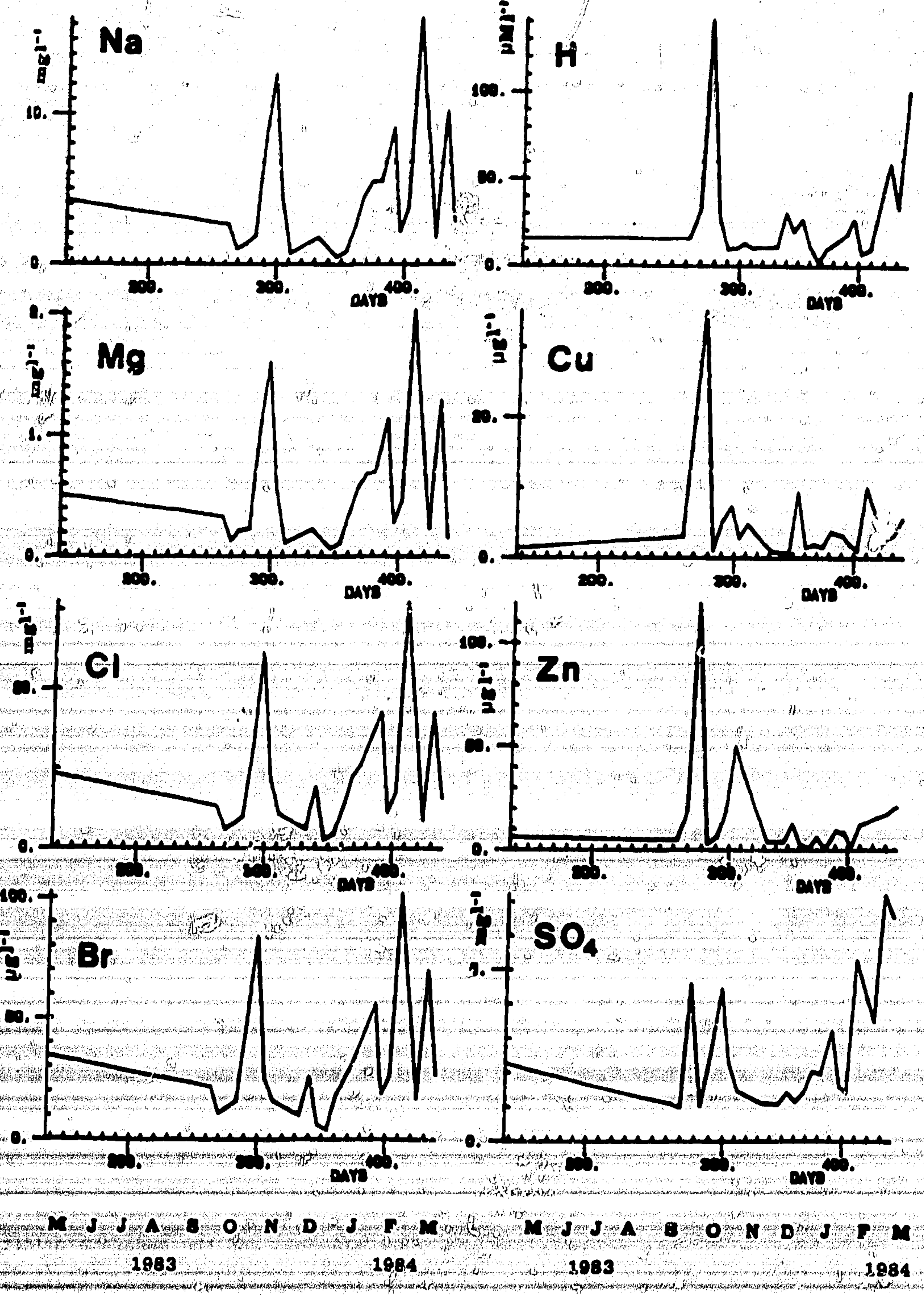


FIGURE 2 Variations of Na, Mg, Cl, Br, H^+, Cu, Zn and SO_4 concentration in rainfall with time for the period May 1983–March 1984

TABLE 4 Rainfall correlations for the major and trace elements, and element ratios for Cl for the "sea salt" components

Correlations for a confidence level 99%

(a) CORRELATED GROUPS FOR ALL RAINFALL SAMPLES ANALYSED

Group 1 Na, K, Mg, Sr, Br, Cl
Group 2 Weekly rainfall intensity for the Hore and Hafren catchments

Element ratios to Cl (mg/l)*

	Na	K	Ca	Mg	B	SO_4	Br	I	Sr
Rainfall	0.52	0.024	0.036	0.066	0.45×10^{-3}	0.28	0.0036	0.39×10^{-6}	0.40×10^{-3}
Sea water	0.56	0.021	0.021	0.066	0.23×10^{-5}	0.14	0.0033	0.003×10^{-6}	0.41×10^{-3}

(b) CORRELATED GROUPS FOR ALL RAINFALL SAMPLES ANALYSED EXCLUDING ANOMALOUS ACIDIC SAMPLES

Group 1 Na, K, Ca, Mg, SO_4, Sr, Br, Cl
Group 2 Weekly rainfall intensity for the Hore and Hafren catchments

Element ratios to Cl (mg/l)*

	Na	K	Ca	Mg	B	SO_4	Br	I	Sr
Rainfall	0.52	0.024	0.036	0.066	0.45×10^{-3}	0.28	0.0036	0.39×10^{-6}	0.40×10^{-3}
Sea water	0.56	0.021	0.021	0.066	0.23×10^{-5}	0.14	0.0033	0.003×10^{-6}	0.41×10^{-3}

* Mean concentrations used to determine ratios (data not rainfall intensity rated)

TABLE 5 Hafren stream chemistry correlations (May 1983–February 1984)

Correlations 99% confidence limit)

(1) CORRELATED GROUPS FOR SUMMER LOW FLOW PERIOD (May–Aug 1983)

Group 1* Ca, Mg, Sr, pH, HCO_3, Li, NO_3, Na
Group 2* H, Al, Mn, Y, Zn, Ba
Group 3 K, DOC

(2) CORRELATED GROUPS FOR AUTUMN STORM PERIOD (September=983-February 1984)

Group 1* Ca, Mg, Sr, pH, Si, HCO_3
Group 2* H, K, SO_4, Y, Fe, Co, AP, DOC, I, Ca, Mn, NO_3 flow
Group 3 Cl, Br

(3) CORRELATED GROUPS FOR SUMMER AND AUTUMN PERIOD (May 1983–February 1984)

Group 1* Ca, Mg, HCO_3, Sr, pH
Group 2* K, Li, SO_4, Y, Ba, Mn, Ca, Fe, Co, Al, DOC, NO_3, B, flow
Group 3 Na, Mg, SO_4, Cl
Group 4 Sr, Mg

Element ratios to Cl (Mg/l)**

	Na	K	Ca	Mg	B	SO_4	Br	I	Sr
Stream-water	0.55	0.021	0.113	0.108	0.43×10^{-3}	0.57	0.0028	0.13×10^{-6}	0.74×10^{-3}
rainfall	0.52	0.024	0.036	0.066	0.45×10^{-3}	0.28	0.0036	0.39×10^{-6}	0.40×10^{-3}
sea water	0.56	0.021	0.021	0.066	0.23×10^{-5}	0.14	0.0033	0.003×10^{-6}	0.41×10^{-3}

* Groups 1 and 2 are inversely related

** Mean concentrations used to determine ratios (data not flow weighted)

Afon Hafren

The stream chemistry is variable, the range of values differing for the various determinands (Table 3, Figure 3); the main "sea salt" components show only a two fold variation while many of the minor and trace elements show variations of up to an order of magnitude. Hydrogen ions and several of the major and trace elements are strongly related to flow (Table 5, Figure 3); they fall into two groups (Table 6) one having moderate acidity and relatively high concentrations of Ca, Sr, Mg and HCO_3 at low flows, the other having relatively high acidity and relatively high concentrations of Li, SO_4, Y, Ba, Mn, Cu, Fe, Co, Al, DOC, NO_3 and B at high flows Despite this broad relationship, for several elements the link between flow and concentration is complex and linear correlations do not describe the relationships well (Figure 4). For example Li, Mn and Co all show higher concentrations during the autumn storm period while total iodine shows increased concentrations during long periods of recession and variations in Si concentration show a strong relationship with the occurrence or absence of storms (Figure 5)although the magnitude of the change is not directly related to flow intensity. A seasonal variation is observed for Na, Cl, K and NO_3, concentrations increasing from May 1983 to February 1984 (Figure 3), although an increase in concentration is observed during the first storm flush period of the autumn for Na, Cl and NO_3.

Afon Hore

The Afon Hore shows similar behaviour to the Afon Hafren and hence only a brief description of the results is given. Thus:

(1) the stream chemistry varies with time, the range of concentrations differing for the various determinands (Table 3, Figures 6 and 7); the sea salt elements Na and Cl showing only two fold variation while many of the minor and trace elements (Al, Y, H, HCO_3, NO_3, B, Mn, Zn, NH_4 Br, I) show up to an order of magnitude range.

(2) Hydrogen ions and several of the major and trace elements are strongly linked to flow (Table 6 and 7, Figure 6); they fall into two groups (Table 6) one having moderate acidity and relatively high concentrations of Ca, Mg, Sr, Si, Fe, HCO_3 and I, the other having relatively high acidity and relatively high concentrations of Y, Ba, Co, Zn, Al, DOC, NO_3 and Mn at high flows.

(3) The link between flow and element concentration is complex and in most cases linear correlations do not describe the relationships well (Figures 4 and 7).

(4) A seasonal variation is observed for Na, Cl and NO_3, although again high concentrations are linked with the early autumn storm events.

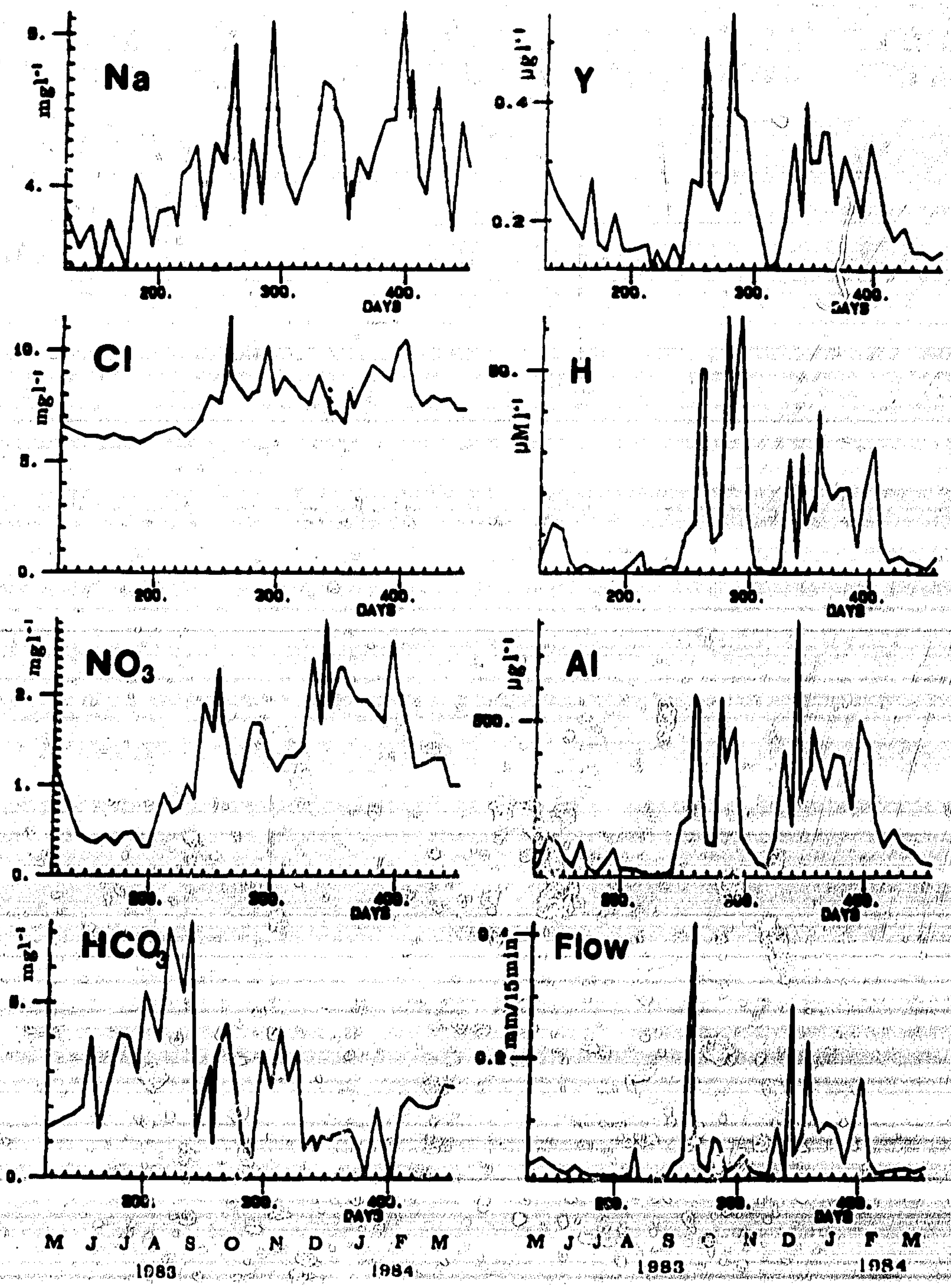


FIGURE 3 Variations of Na, Cl, NO_3, HCO_3, Y, H^+, Al concentrations and flow with time for the Afon Hafren during the period May 1983-March 1984

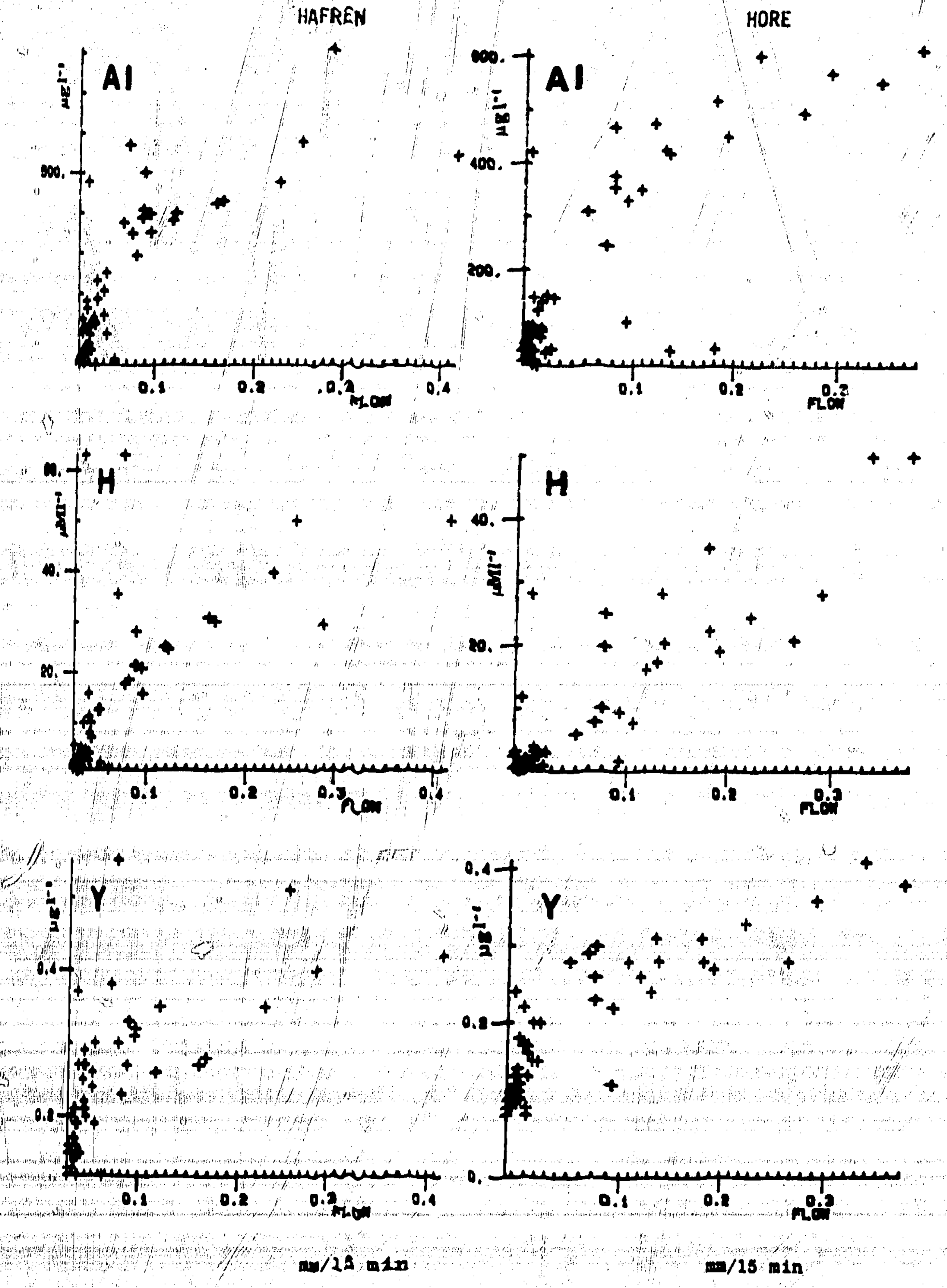


FIGURE 4 Plots of Al, H and Y concentrations versus flow for the Afon Hafren and Afon Hore

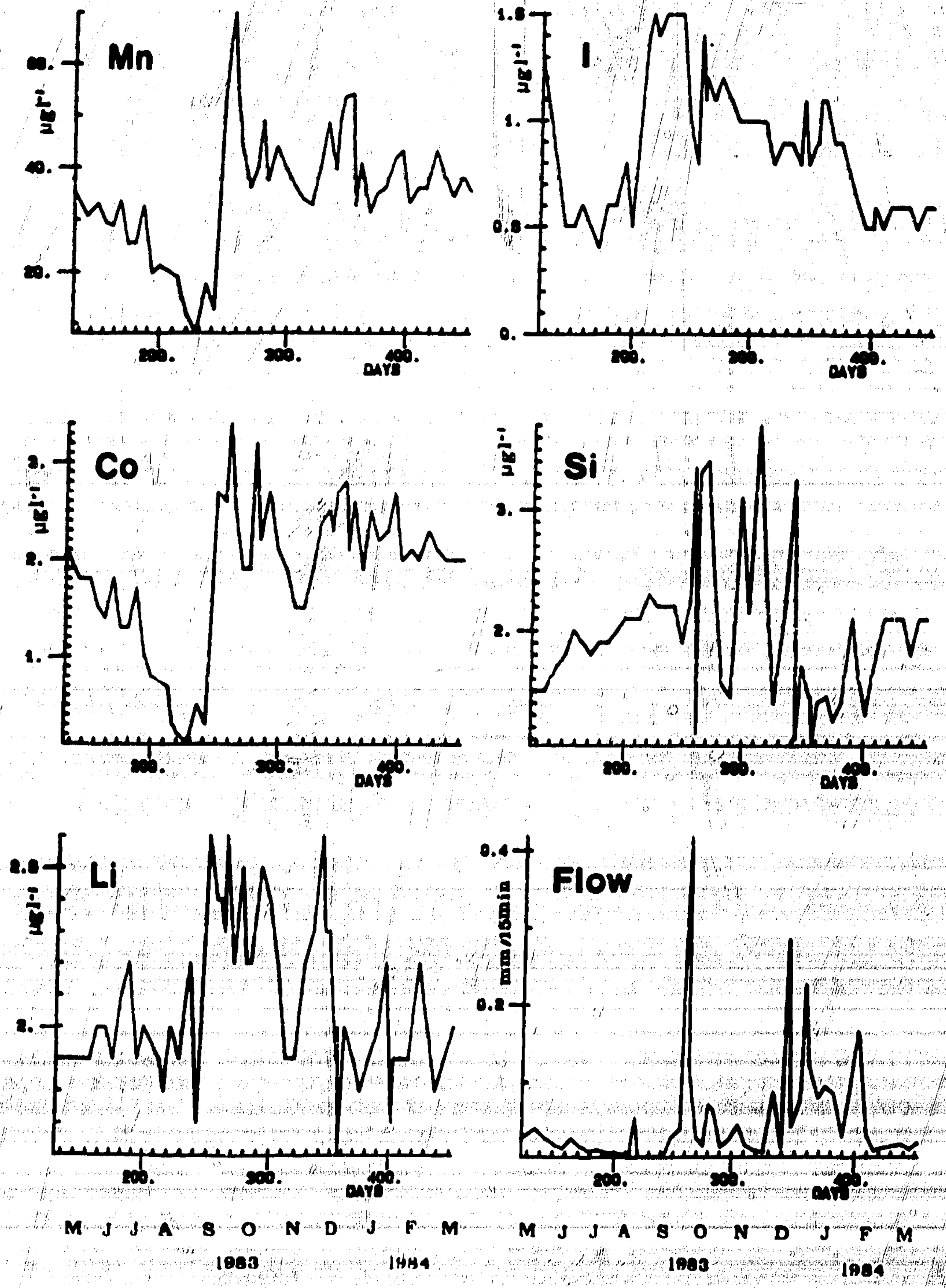


FIGURE 5 Variations of Mn, Co, Li, I, Si, concentrations and flow with time for the Afon Hafren during the period May 1983-March 1984

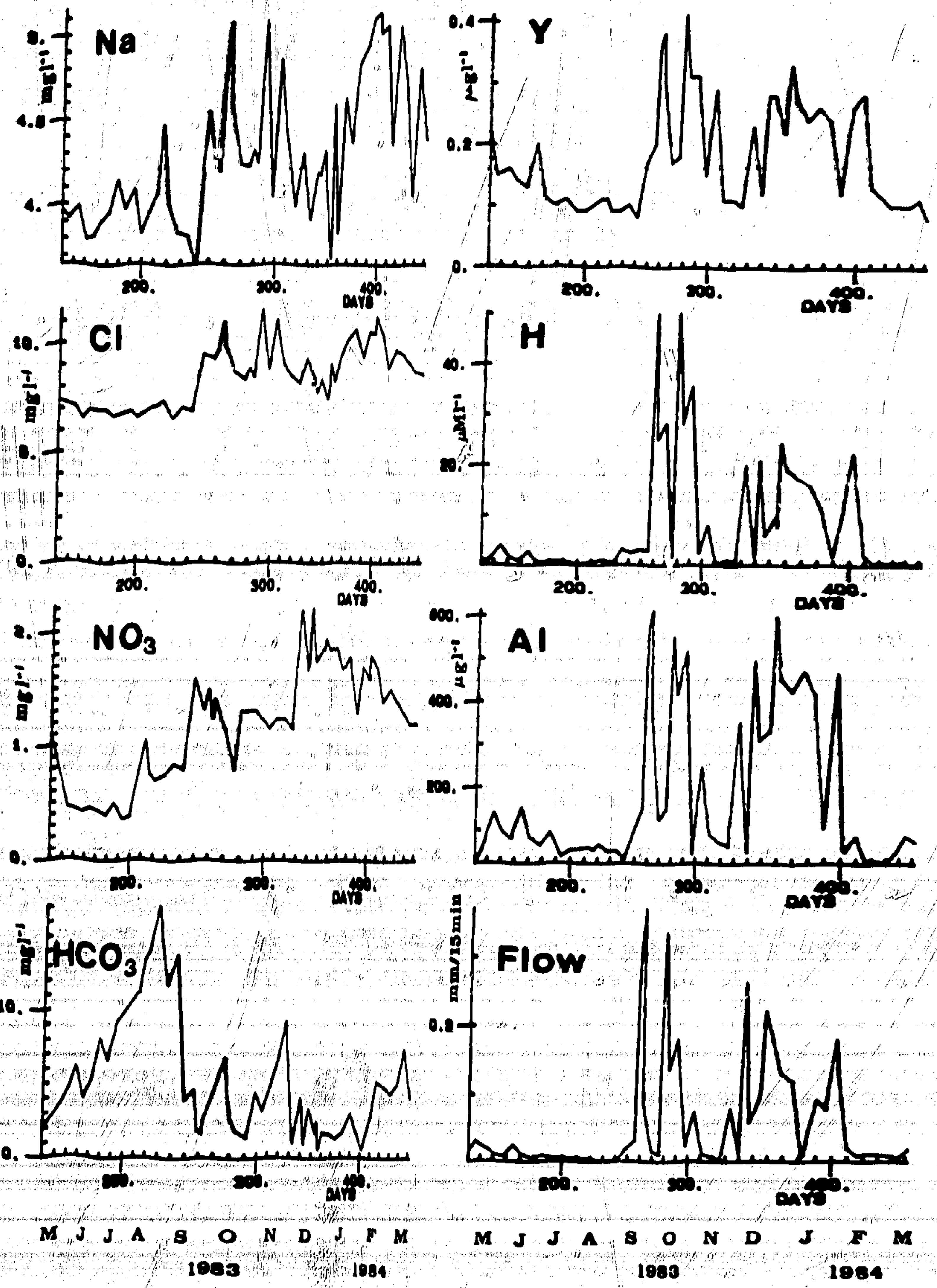


FIGURE 6 Variations of Na, Cl, NO$_3$, HCO$_3$, Y, H$^+$, Al concentrations and flow with time for the Afon Hore during the period May 1983 - March 1984

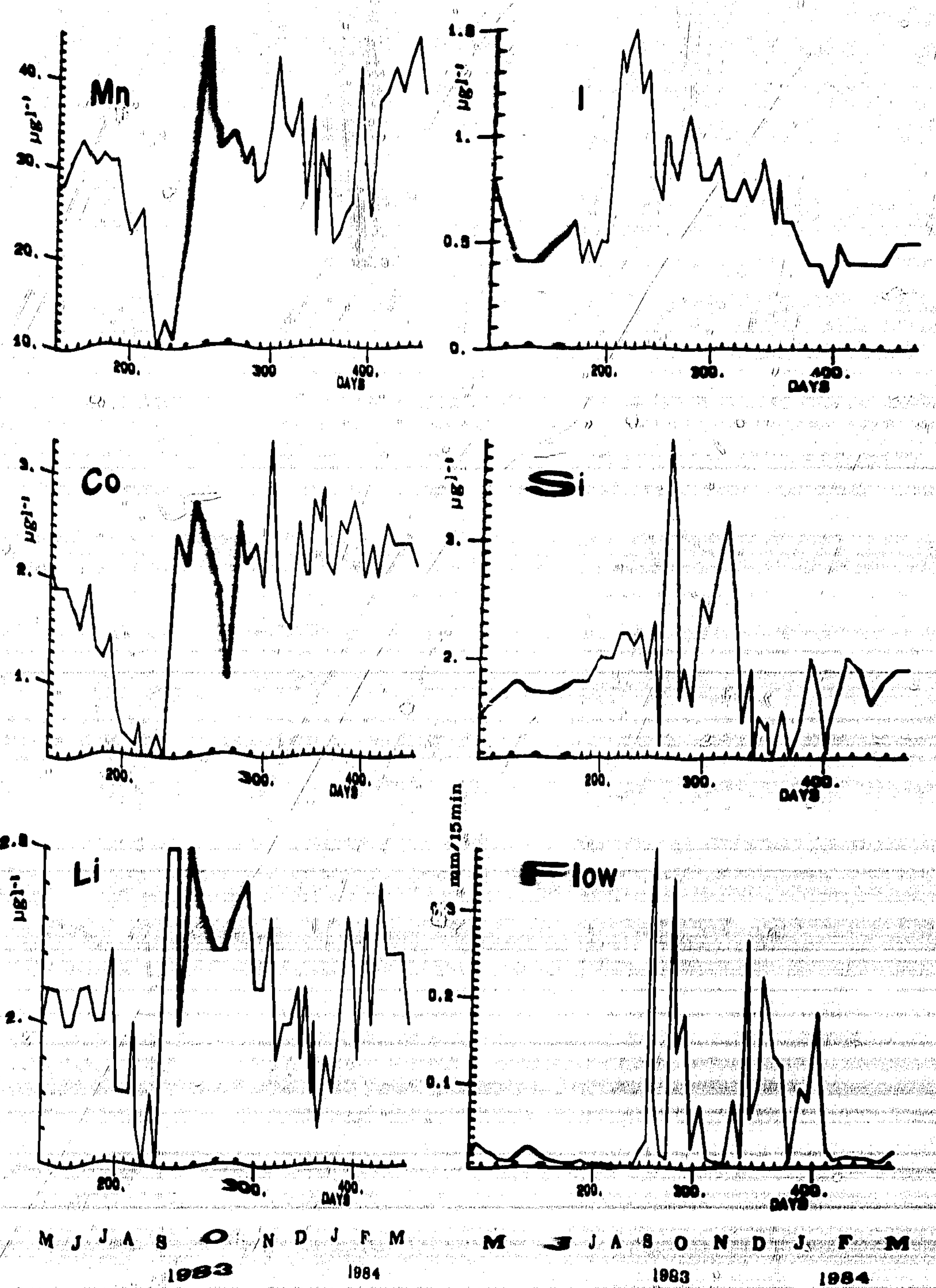


FIGURE 7 Variations of Mn, Co, Li, I, Si concentrations and flow with time for the Afon Hore during the period May 1983 - March 1984

Table 6. Mean concentrations of major, minor and trace elements in baseflow and stormflow waters for the Afon Hafren and Afon Hore.

Element	Baseflow flow < 0.01 mm 15 min^{-1} Hafren	 Hore	Stormflow flow > 0.10 mm 15 min^{-1} Hafren	 Hore
Major components (concentrations in mg l^{-1})				
Na	3.97	4.15	4.48	4.56
K	0.156	0.166	0.224	0.149
Ca	1.05	3.01	0.706	0.836
Mg	0.817	1.13	0.782	0.749
SO_4	3.67	4.80	4.61	4.83
Si	2.06	2.11	1.76	1.43
DOC	1.05	0.954	1.60	1.32
HCO_3	5.23	10.3	1.23	1.47
NO_3	0.782	0.878	2.13	1.66
Cl	6.48	7.58	9.01	10.5
Minor and trace element components (concentrations in µg l^{-1})				
B	2.88	4.62	3.99	4.07
Li	1.98	1.89	2.10	2.01
Sr	5.34	7.11	5.30	4.83
Y	0.152	0.109	0.355	0.307
Ba	0.362	1.09	3.66	5.91
Mn	18.7	24.0	42.1	27.4
Cu	1.18	1.42	2.49	5.75
Fe	54.2	79.8	96.7	63.5
Co	0.687	0.969	2.49	2.32
Zn	7.05	11.0	16.4	29.8
Al	56.6	85.8	506.	427.
Br	27.6	23.2	19.6	20.8
I	1.19	0.923	1.01	0.754
Acidity (concentrations in µM l^{-1})				
H^+	1.9	1.8	35.0	26.2
pH	5.80	6.08	4.47	4.62

NH_4 and PO_4 values not included due to uncertainties in these estimates (many values being less than the detection limit) and the large range in rainfall values.

Table 7 Hore stream chemistry correlations (99% confidence limit)

(1) Correlated groups for summer low flow period (May-August 1983)

Group 1*	Ca, Mg, Sr, Fe, HCO_3, I, K, Si, pH
Group 2*	Y, Ba, Co, Zn, Al, Mn, Li, H, flow
Group 3	Na, Cl
Group 4	Cl, Li, Zn, NO_3

(2) Correlated groups for autumn storm period (September 1983 - February 1984)

Group 1*	Ca, Mg, Sr, HCO_3, Si, pH
Group 2*	H, Y, Al, DOC, Ba, Zn, Co, Fe, K, flow
Group 3	Na, Cl

(3) Correlated groups for summer-autumn period (May - February)

Group 1*	Ca, Mg, Si, Sr, Fe, HCO_3, I, pH
Group 2*	Y, Ba, Co, Zn, Al, DOC, NO_3, Li, Na, Cl, Mn, flow
Group 3	K, Fe, DOC, Br, I

Element ratios to Cl (mg l^{-1})**

	Na	K	Ca	Mg	B	SO_4	Br	I	Sr
Stream-water	0.50	0.017	0.218	0.110	0.51×10^{-3}	0.58	0.0025	0.96×10^{-6}	0.69×10^{-3}
Rainfall	0.52	0.024	0.036	0.066	0.45×10^{-3}	0.28	0.0036	0.39×10^{-6}	0.40×10^{-3}
Sea Water	0.56	0.021	0.021	0.066	0.23×10^{-5}	0.14	0.0033	0.003×10^{-6}	0.41×10^{-3}

* Groups 1 and 2 are inversely related.

** Mean concentrations used to determine ratios (data not flow weighted)

DISCUSSION OF RESULTS

Rainfall-runoff relationships

The large variation in the concentrations of the "sea salts" in the rainfall are not reflected in the subsequent patterns of stream water chemistries. For example the range of concentrations of chloride in rainfall is 2 to 25 mg l^{-1} and in the streamwater is only 6 to 12. Similarly, the variation in the concentrations of the trace elements in the rainfall is not reflected in the streamflow. The concentrations of many of these trace elements are occasionally very high and are associated with high acidity as well as enhanced levels of SO_4 and NO_3 (Table 4). Apart from these anomalous rain events, the variations and mean concentrations of the trace elements in rainfall are smaller than those in the streamwaters.

Stream Water Relationships for the Afon Hore and Afon Hafren

The concentrations of the chemical species in the streamwater vary either seasonally or are related to hydrological change and are not due to variation in the rainfall chemistry. This relationship between chemistry and hydrological change takes three forms:

(1) Direct flow response where the concentration increases and decreases as flow increases and decreases.

(2) Damped flow response where the concentration increases (or decreases) in the autumn-winter period when high flows prevail and decreases (or increases) when flows return to the low level in the spring and summer.

(3) Compound flow response where the variations in concentration are related to hydrological changes though their relationships with flow are complex.

Figures 3 and 6 provide examples of "direct flow response". They show that during storm events, H, Al and Y increase by an order of magnitude while HCO_3 decreases. Figures 5 and 7 provide examples of "damped flow response". They show that Li, Mn and Co increase markedly at the onset of the autumn storms while I increases during long periods of baseflow. Seasonal variations and "compound flow response" are shown for Na, Cl and NO_3 (Figures 3 and 6) and Si (Figures 5 and 7) respectively.

The variations in chemical concentrations between the two streams are remarkably similar with high correlation coefficients for several elements (Na, K, Ca, SO_4, Si, Y, Ba, Mn, Co, Al, NO_3, Cl) as shown in Table 8 and examples provided in Figure 7. Despite these similarities differences between the streams occur in four respects:

(1) while Mg and Sr are correlated for each stream (Figure 9) poor correlations are observed between the two streams.

(2) Fe concentrations in both streams behave in a similar manner toeach other except during the summer baseflow period when its concentration increases in the Afon Hore but not in the Afon Hafren; values differing by a factor of 3.

(3) The concentrations of Ca, HCO_3, Ba and Zn are approximately twice the values

on the Afon Hore compared with the Afon Hafren; differences being greatest during periods of baseflow for Ca and HCO_3 (Table 6).

(4) Ba, B, Cu, DOC and SO_4 are not correlated; SO_4 concentrations behave like Co and Mn in the Afon Hafren but not in the Afon Hore.

In addition to the variation in chemical concentrations some mention must be made of an apparent difference in the hydrographs for the two catchments (Figure 10). While flows in the two catchments are in general highly correlated (as expected given their close proximity) for two storm events little flow increase is shown in the plotted data for the Afon Hafren even though the ions associated remain correlated for the two streams (Figures 8 and 10); detailed (15 min.) data show the storm events. This apparent difference in the two hydrographs illustrates the rapidity of the flow response of the catchments to rainfall and the danger of using weekly flow data; it results from a sampling

Table 8. Correlations between the Hore and Hafren stream chemistries

	Summer	Autumn-Winter	Summer-Winter
Na	.381	.410	.489 ++
K	.899 ++	.494	.457 ++
Ca	.497 +	.596 ++	.589 ++
Mg	.069	.481 +	.185
B	.380	.310	.250
Li	.620 ++	-.086	-.021
SO_4	.613 ++	.477 +	.465 ++
Si	.923 ++	.706 ++	.718 ++
Sr	.008	.232	-.023
Y	.773 ++	.717 ++	.805 ++
Ba	.985 ++	.224	.844 ++
Mn	.644 ++	.625 ++	.600 ++
Cu	.347	.201	.104
Fe	- .051	.108	.241
Co	.962 ++	.917 ++	.908 ++
Zn	.663 ++	.596 ++	.548 ++
Al	.660 ++	.765 ++	.430 ++
DOC	.544 +	.782 ++	.731 ++
HCO_3	.910 ++	.689 ++	.877 ++
NO_3	.985 ++	.906 ++	.973 ++
NH_4	.359	- .164	- .166
PO_4	.453 +	- .469 +	- .303 +
Br	.524 +	.598 ++	.533 ++
±	.944 ++	.629 ++	.889 ++
Cl	.919 ++	.898 ++	.844 ++
pH	.600 ++	.853 ++	.866 ++
Flow	.663 ++	.789 ++	.835 ++
Peak flow	.912 ++	.976 ++	.940 ++
H^+	.570 ++	.874 ++	.908 ++
Peak flow intensity	.991 ++	.479 +	.629 ++

++ 99% Confidence limit
\+ 95% Confidence limit

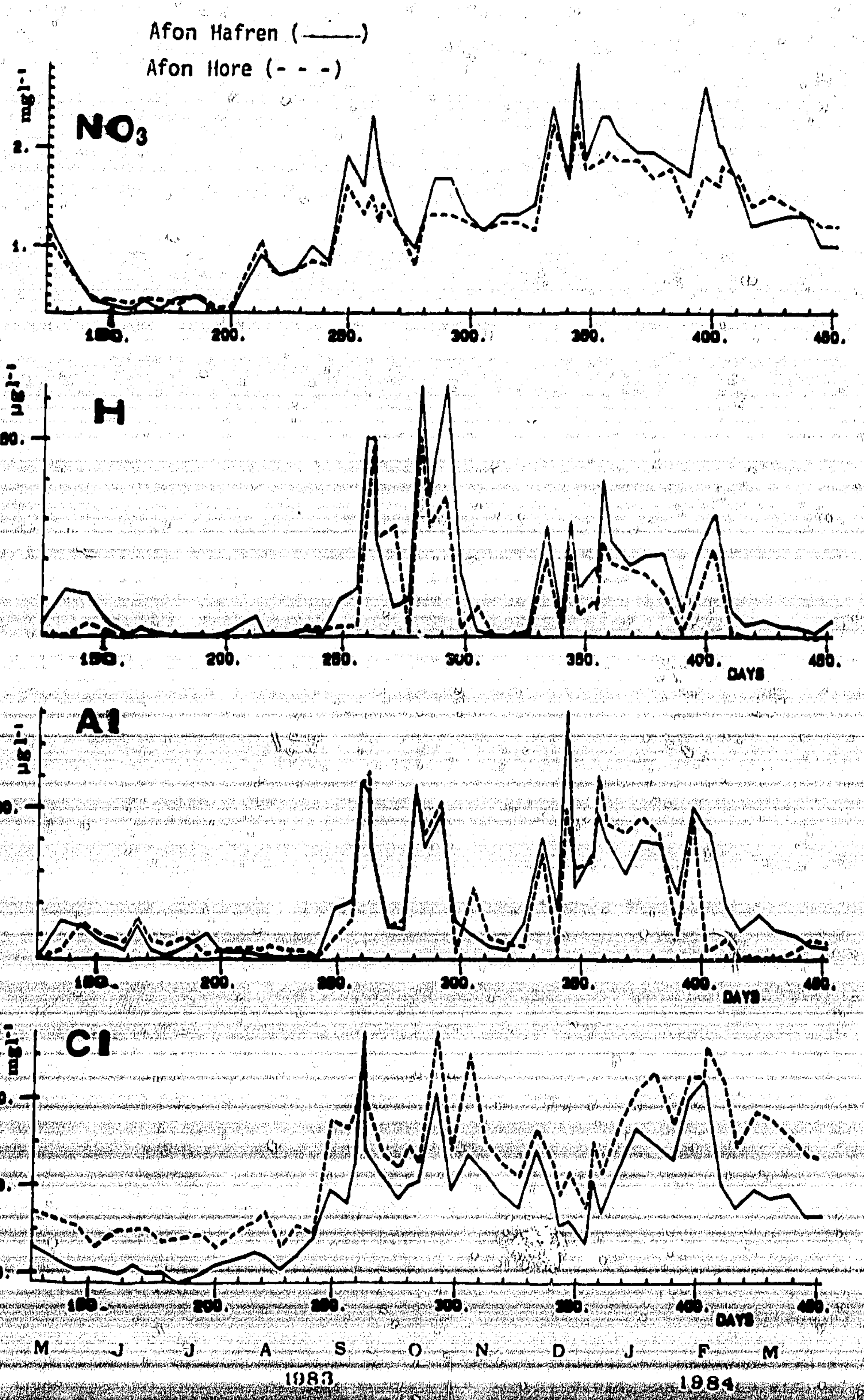


FIGURE 8 Variations in NO$_3$, H+, Al and Cl concentrations in Afon Hafren and Afon Hore stream water for the period May 1983-March 1984

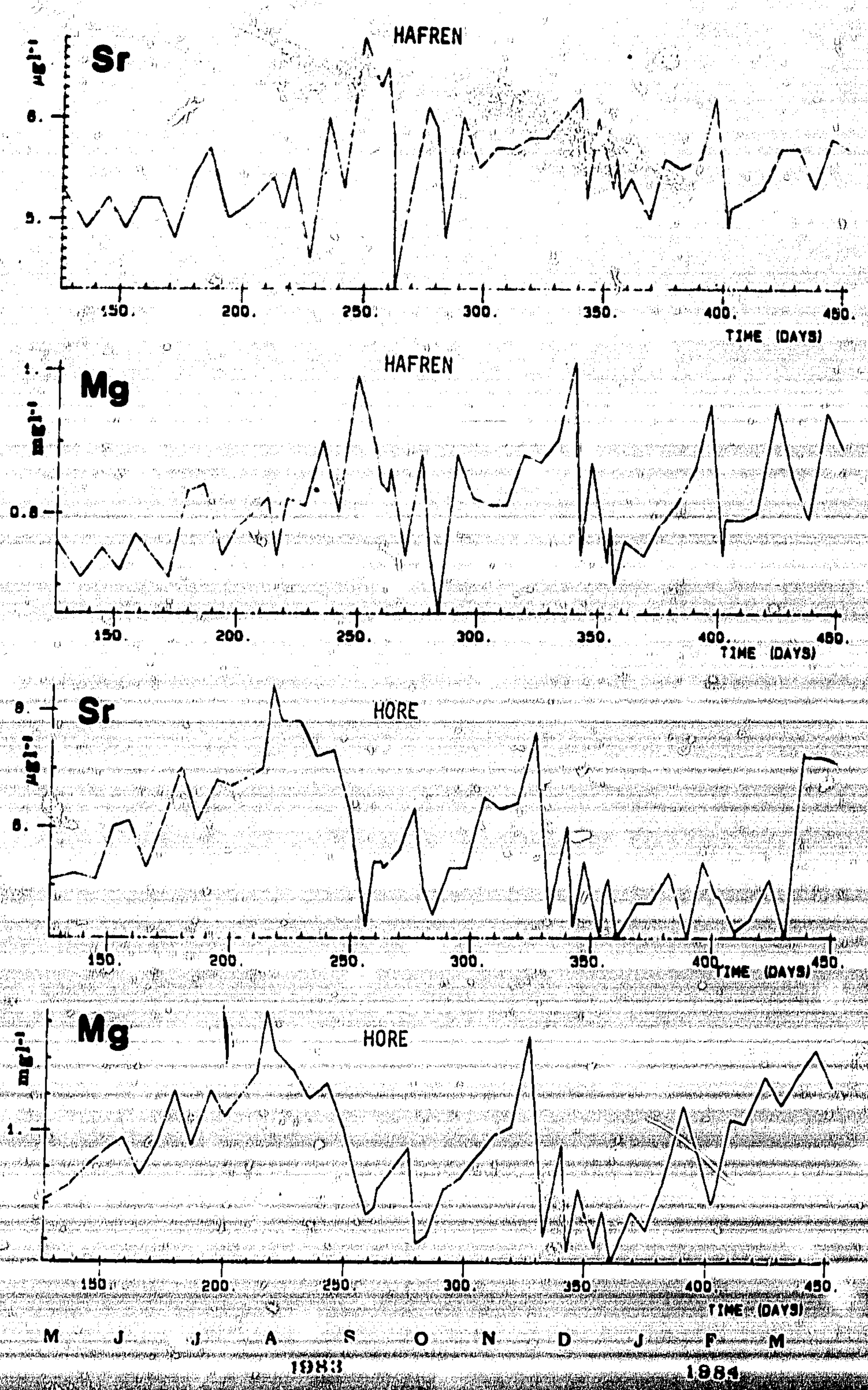


FIGURE 9 Variations of Sr and Mg concentrations with time for the Afon Hafren and the Afon Hore for the period May 1983-March 1984

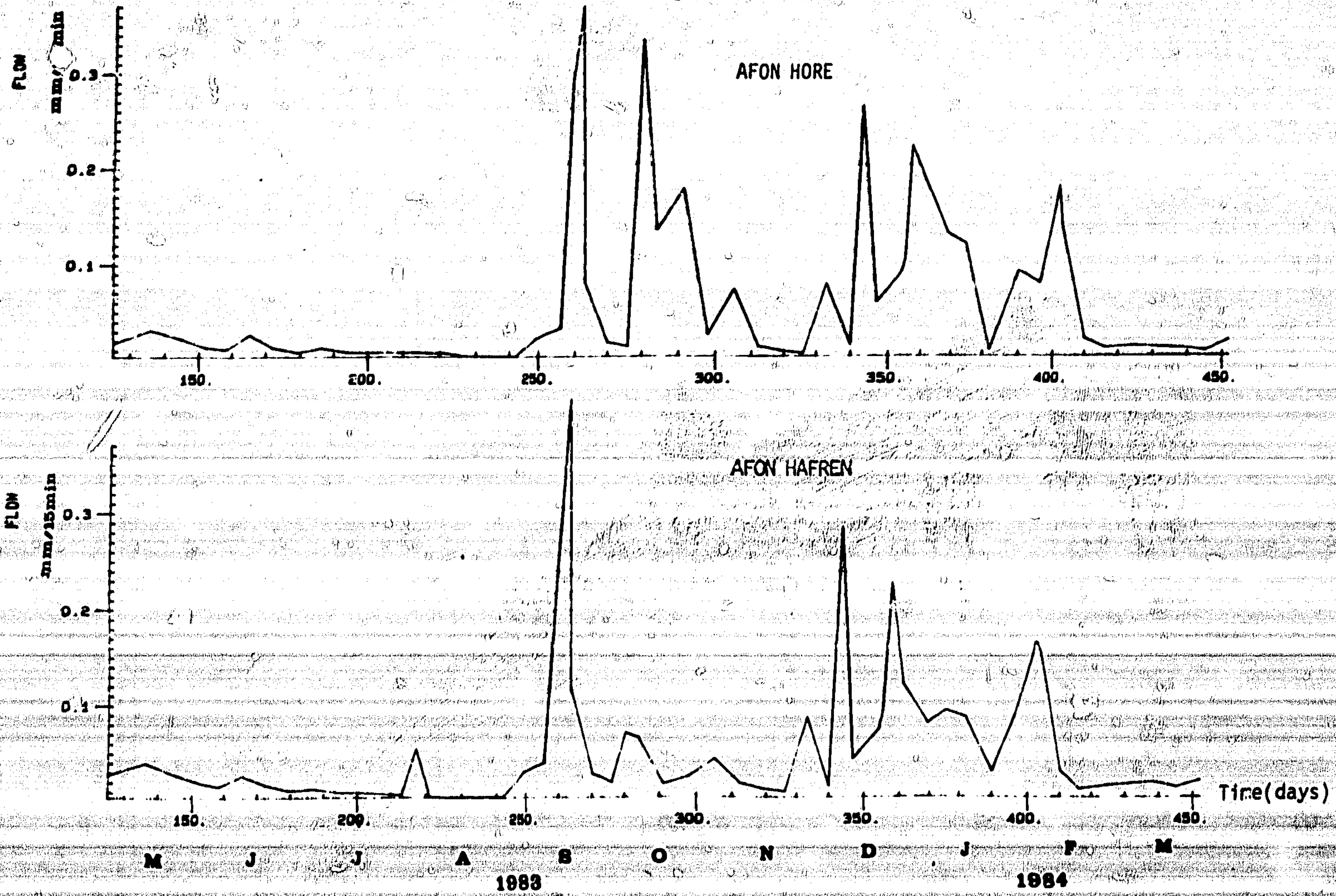


FIGURE 10 Variations in flow with time for the Afon Hafren and Afon Hore for the period May 1983-March 1984

time separation of only 5 hours during which time flow decreases significantly, stream acidity did not.

Hydrogeochemical and Hydrological Processes

The hydrochemical and hydrological factors determining stream water chemistry are interlinked and the distinction between their controls is not sufficient for them to be referred to in isolation. It is likely that similar hydrogeochemical reactions are occurring in the saturated and unsaturated zones, but the residence time and the extent of water-rock contact are important in determining the hydrochemistry. The heterogeneity of the hydrological system, including the water level fluctuations and preferred flow-routing, will add to the complexity, resulting in the mixing of waters having different chemical compositions. In general though, baseflow is characterised by low acidity, Ca-HCO_3 bearing, stream waters and stormflow is characterised by high acidity, Al and transition metal bearing, waters.

In essence the processes determining stream chemistry can be described in terms of the flushing and mixing of waters from the near surface organic and the underlying inorganic horizons. Dry deposition washed from the trees together with the products of organic matter decomposition result in acidic conditions (pH 4) in the near surface horizons. This produces mobilisation of the easily hydrolysed transition metals, a process enhanced by organic complexation and sometimes by reducing conditions in the podsol and gley horizons. Reactions in the inorganic horizons involve the hydrolysis of silicate minerals, clay transformations of chlorite to vermiculite and dissolution of carbonates resulting in the release of Ca, Mg and Si to solution together with the consumption of hydrogen ions. As a consequence of this hydrogen ion consumption, these near surface waters lose their Al and most easily hydrolysed transition metals and losses of these metals from the catchment are limited under low flow conditions. Superimposed on these reactions are biological processes producing release/consumption of NO_3, HCO_3 and K. The stream water composition thus reflects a combination of mixing processes, mineral and organic reactions and flushing out of the different water types from the various horizons. Under summer low flow conditions the soil moisture deficit is high and water is supplied from the inorganic horizons. During the autumn storm period the soil moisture deficit decreases and the stream water is supplied from both matrix and macro pore flow, mainly from the upper organic horizons.

Several observations imply that not all of the processes can be described simply by the main controls cited above. For example :

(1) Rapid, damped and compound flow response are observed for different chemical elements. This must indicate that the chemical reaction rates are different for the different mineral phases in the different soil horizons, that several hydrogeochemical processes (mineral dissolution, adsorption and redox reactions) are operating and that there are complex hydrological flow routes.

(2) Cl concentrations in the stream waters are highest during the autumn and winter storm periods when soil moisture deficits are at a minimum. This can only mean that evapotranspiration has produced high concentrations of Cl in the near surface horizons during the spring and summer months.

flows the main supply of water in the Upper Hafren is from the peat areas and is derived from gravel aquifers.

(4) Sr and Mg are highly correlated in both the Hafren and the Hore streams. However the variation in the concentration of these elements with changes in flow is different for the two streams. This shows that even when the geological and vegetation types are similar, different hydrochemical controls can operate.

(5) The large variation in the concentration of major maritime elements in rainfall is not reflected in the stream water. This shows that either rapid mixing of the rain inputs with the stored water occurs or that there is a large water storage volume in the catchment.

(6) During winter storm recessions, concentrations of Al, H ion and HCO_3 return to baseflow levels even though the soil moisture deficit is low and the saturated zone extends to the organic horizons. This illustrates the importance of macropore flow and of the inorganic horizons in the low flow process since micropore flow would continue to give streamwater chemistries characteristic of the upper organic zone.

(7) Increases in Cl concentration in the stream water are not fully matched by increases in the Na concentrations (Figure 11). Since both Cl and Na are from a "maritime" source and Cl is a "conservative" element Na is being lost to the catchment.

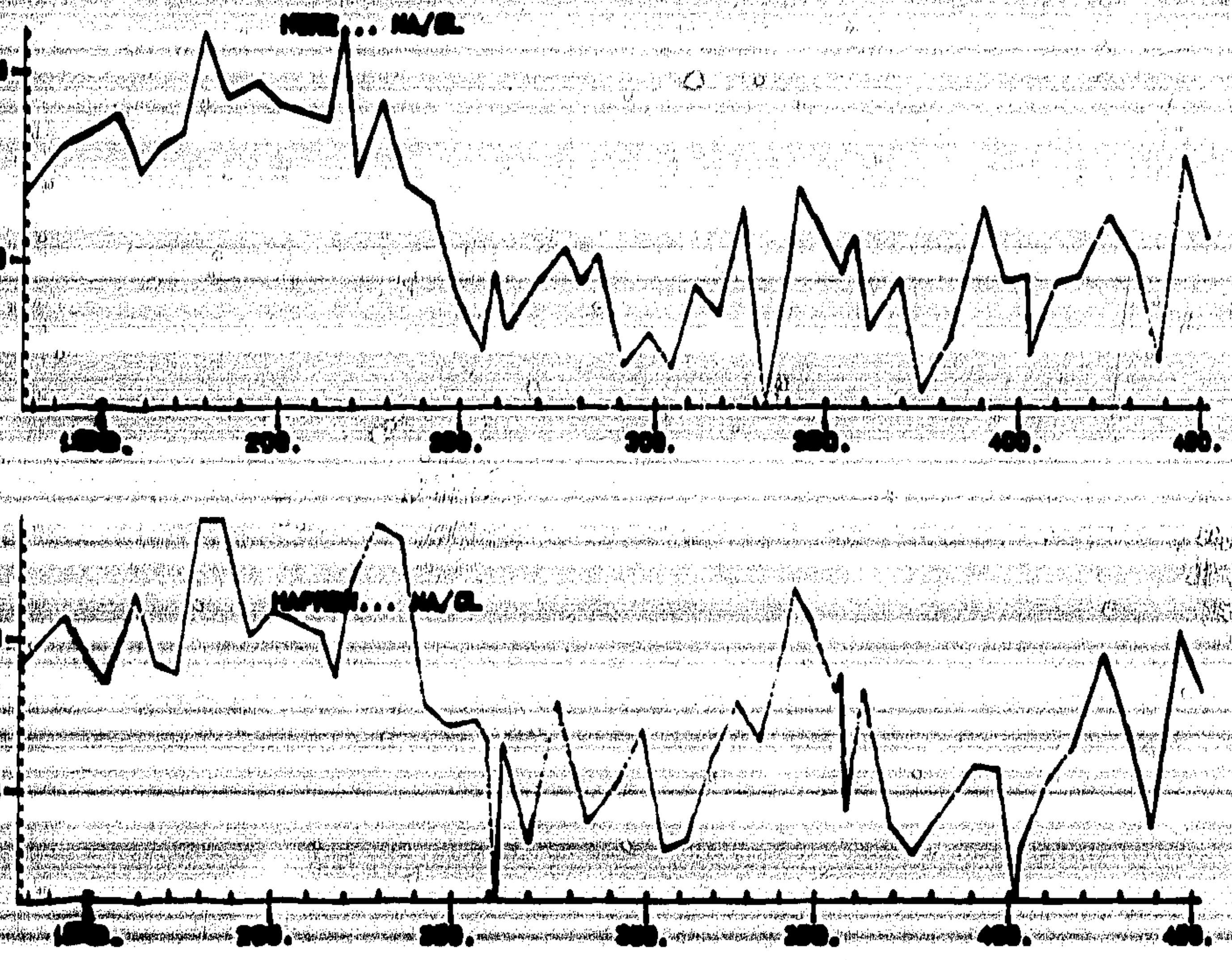


FIGURE 11 Variations in Na/Cl ration with time for the Afon Hore and Afon Hafren

HYDROCHEMICAL BUDGETS

Uncertainties in the determination of input-output budgets for these catchments are large due to difficulties in obtaining representative wet and dry input levels of elements using standard rain collectors, the arbitrary division between dissolved and suspended matter (determined by filtration) and the accuracy of the available hydrological data (flow, rainfall). To reduce this uncertainty, and, hopefully, to provide realistic values for most dissolved chemical elements, it is initially assumed that Cl is attenuated within the catchment due to physical, rather than chemical, processes and that dry deposition of the various elements are in the same proportion to Cl as those in wet precipitation.

Dissolved load budgets show that the elements being lost from the two catchments are Ca, Mg, SO_4, NO_3, DOC, HCO_3, Li, Sr, Y, Ba, Mn, Fe, Co, Al, Zn, Si while those being gained by the catchments are Na, K, Cu, Br and I. (Table 9).

Table 9 Afon Hafren and Afon Hore Catchment Budgets°

Element	Rainfall Estimates++		Runoff+		Catchment Loss	
	Afon Hafren	Afon Hore	Afon Hafren	Afon Hore	Afon Hafren	Afon Hore
Major Elements (kg ha^{-1} yr^{-1})						
Na	71.7	78.1	65.4	68.0	- 6.3	- 10.1
K	3.07	3.34	3.05	2.24	- 0.02	- 1.10
Ca	3.98	4.2	11.9	15.3	8.0	11.1
Mg	9.0	9.8	11.9	11.9	2.9	2.1
SO_4	34.4	37.5	68.0	73.1	33.6	35.6
Si	3.5	3.9	26.1	23.6	22.6	19.7
DOC	7.5	8.1	21.3	19.4	13.8	11.3
HCO_3	0.0	0.0	23.9	31.7	23.9	31.7
NO_3	12.0	13.1	28.8	23.3	16.8	10.2
Cl	129.	141.	129.	141.	0.0	0.0
Minor and Trace Elements (g ha^{-1} yr^{-1})						
B	76.9	83.8	61.7	63.3	- 15.2	- 20.5
Li	0.0	0.0	31.5	30.9	31.5	30.9
Sr	56.8	61.9	82.5	75.3	25.7	13.4
Y	0.0	0.0	4.92	4.32	4.92	4.32
Ba	19.7	21.5	53.1	82.7	33.4	61.2
Mn	34.2	37.3	626.	444.	592.	407.
Cu	63.4	69.1	32.9	65.4	- 30.5	- 3.7
Fe	214.	233.	1320.	974.	1110.	741.
Co	0.0	0.0	35.7	35.0	35.7	35.0
Zn	150.	163.	237.	429.	87.0	266.
Al	255.	278.	6200.	5900.	5950.	5620.
Br	475.	517.	297.	318.	- 178.	- 199.
I	31.7	34.6	14.5	11.6	- 17.2	- 23.0
Acidity (M ha^{-1} yr^{-1})						
H^+	379.	413.	423.	357.	44.	- 56.

° Values are all rainfall/flow weighted

\+ An average value of 1500 mm yr^{-1} runoff is used in the calculation

++ Dry deposition of sea salts allowed for by assuming Cl conservative in catchments; values probably underestimated for dry deposition of non sea salt component

Hydrogen ion shows an approximate balance between input and output from our determinations. However our determinations do not include stemflow measurements which are known to have pH's one unit lower than that sampled by a standard rainfall collector. Since up to 20% of the total rain input in these forested catchments occurs as stemflow the catchments may well be removing a significant amount of the hydrogen ion input. Furthermore, adsorption of atmospheric SO_2 and NO_2 in the tree canopy and loss of N_2 from the catchment make S and N budgets difficult to ascertain; these SO_2 and NO_2 inputs provide additional problems for the H ion budget.

Regarding the sulphate budget, previous estimates of the sulphur dry deposition rates are of the order of 30 kg SO_4 ha^{-1} yr^{-1} and this corresponds very well well with the differences between the input and output values for the Afon Hafren and Afon Hore catchments (33.6 and 35.6 kg SO_4 ha^{-1} yr^{-1} respectively). Consequently if allowance is made for dry deposition of sulphur there is a net balance for the catchments. Assuming the dry deposited sulphur occurs as SO_2, this corresponds to an additional rainfall input of 625 M ha^{-1} yr^{-1} of hydrogen ion with the consequence that 625 M ha^{-1} yr^{-1} of hydrogen ion acidity is gained by the catchment (ie 60% of the total acid input).

Despite the similarities in gains and losses of elements by the two catchments, losses of Ca, Ba, Zn and HCO_3 are greater for the Afon Hore than the Afon Hafren while losses of Mg, Si, Sr, Mn, Fe, Al, DOC and NO_3 are greater for the Afon Hafren than the Afon Hore. Correspondingly gains of Na, K and I are greater for the Afon Hore, while the Afon Hafren shows only a greater gain for Cu.

Regional baseflow survey

In addition to the Hafren forest studies, baseflow surveys of streams throughout the Plynlimon area have been undertaken. Preliminary results (not detailed in this report) show that the major hydrochemical variations are related to mining activity and land improvement (liming/fertilizer application) rather than vegetation type. The main hydrochemical anomalies are observed in the upper River Wye catchment where high concentrations of Zn, Pb, Cd, SO_4, HCO_3 and B are found in the tributaries where lead-zinc mining has been carried out and unexplained high Cu and Al concentrations are observed in the River Wye and its tributaries below the Afon Cyff.

HYDROLOGICAL BUDGETS

The conservative behaviour of Cl in rainfall, soil and stream waters and the lack of Cl-bearing bedrock allows calculation of the evapotranspiration rates for the catchments using the formula:

$$\%\,\text{evapotranspiration} = \left(\frac{Cl_s - Cl_R}{Cl_s}\right) \times 100$$

where Cl_s and Cl_R are the Cl concentrations (volume weighted means) in the stream water and rainfall respectively. This calculation yields evapotranspiration losses of 28 and 34% for the Afon Hafren and Afon Hore respectively compared with hydrological estimates for the Upper Severn of 35%. The variation in these values reflects the differences in the extent of forestation in the catchments (the order being Upper Severn Afon Hore > Afon Hafren) and is in agreement with the hydrological data from the Plynlimon water balance experiments. A simple mass balance calculation using the evapotranspirational estimates above and the fractional areas grassed and forested, for the Afon Hafren and Afon Hore, yield evapotranspiration values of 17 and 39% for the grassed and forested portions of the catchments respectively. This compares extremely well with hydrologically determined evapotranspiration estimates of 15% (Upper Wye) and 35% (Upper Severn), remembering that the latter estimate is an underestimate for the Hafren forest since the Upper Severn is partly grassed; correcting for the grassed area gives anevapotranspirational estimate based on the hydrological data of 42%.

There results are provided to illustrate a potential use of chemical data for limited/not available or of questionable accuracy (for ungauged catchments flow proportional stream water samplers or some crude measurement of flow is required). This method however needs validating using a much longer chemical data set to allow for seasonal and yearly variations in hydrological conditions and stream/rainfall chemistry.

INTERIM CONCLUSIONS AND FUTURE WORK

The chemistry of Plynlimon stream waters is determined primarily by chemical reactions in the surface organic rich soils and underlying inorganic soils and bedrock and the complex hydrology. Reactions in the organic horizons involve the generation of acidic conditions and the mobilisation of the hydrolysable transition metals while reactions in the inorganic horizons involve hydrogen ion consumption, release of Ca, Mg and HCO_3 and the immobilisation of the hydrolysable transition metals. Rainfall chemistry is dominated by the maritime influence although occasionally, pollutant inputs are important. Baseflow chemistry is determined by inorganic reactions; for the Afon Hore the dominant influence is the lead-zinc mineralisation with the dissolution of carbonate and sulphide phases; for the Afon Hafren, baseflow chemistry is determined by reactions in the peats and underlying gravel deposits at the headwaters. Storm water chemistry is determined by flushing of waters from the organic horizons.

To date the work has centred on studies of natural variations in major, minor and trace element concentrations in rainfall and streamwaters to provide "baseline" values for comparison with results following the deforestation phase beginning summer 1985. By June 1985, two years baseline data will exist and by November 1985 this first phase of the programme will be complete. During the second and final phase of the work (June 1985-December 1987) several aspects will be considered, and these include:

(1) Hydrogeochemical studies on the effects of deforestation; this requires a further 2 years data collection on the same scale as the baseline study.

(2) Determination of the dominant hydrogeochemical processes operating in the catchment; this requires new analyses of soil waters collected from the ITE monitoring sites in the forest.

(3) Modelling and mineral equilibrium studies to describe the variations in stream water chemistry.

(4) Determination of element fluxes through the tree canopy to establish the effects of dry deposition and pollutant inputs. As with (2) this requires additional analyses of stemflow and throughfall waters collected from the ITE monitoring site in the forest.

(5) Continuation of the regional baseflow studies to explain the Cu, Al and other anomalies.

(6) Detailed surveys of stream chemistry during storm events to determine short term fluctuations and "lag times" for chemistry - flow response including stable isotope work.

(7) Studies of organic, nutrient and trace metal transfers across the stream sediment-water interface. This forms a major component of a CASE studentship with Bangor University, the field programme beginning in spring 1985.