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A COMPARISON OF SOLUTE CONCENTRATIONS OF STREAMS DRAINING DIFFERENT ROCK TYPES IN TWO AREAS OF UPLAND BRITAIN

by

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SUMMARY

To determine how widely applicable were the findings from a long running catchment study in mid Wales, eight upland streams in northern England were sampled. The streams were selected to ensure that their catchments were entirely underlain by one of three rock types which contrasted with the rock types of the Welsh catchments. Water was collected at approximately five week intervals over a period of 16 months. Samples from both areas were analysed for 13 ions, including the major nutrients, using the same laboratory methods. pH and Dissolved Total Organic Carbon were also determined. Concentrations of a number of ions were low compared with more intensively managed land but some seasonal trends were identified. Association between streams, in terms of solute concentration, was examined using Principal Component Analysis. Component values were related to physical characteristics of the catchments and it was concluded that of the physical characteristics examined, rock type had the greatest influence on stream water chemistry. It is recommended therefore that rock chemistry be taken into account when applying the findings from the Welsh study to other catchments.

INTRODUCTION

Catchment studies are widely used in element cycling research. The solute chemistry of a stream is the result of many processes occurring in its catchment, and drainage water has been identified as the most important medium for element export from non-arable ecosystems (Harrison, 1985). Topics examined in catchment studies include chemical weathering (eg Crabtree & Trudgill, 1984), effects of different land uses (eg Caporali et al., 1981) and the effects of particular land management activities (eg Likens et al. 1970).

The value of a catchment study does not usually lie in advancing the understanding of the processes occurring solely in the catchment studied. Usually the aim is to establish principles which may be applied in a wider context. However catchment studies are frequently based on only a very limited number of catchments. Seldom are results presented which indicate how the catchments studied relate to other catchments, and therefore, how widely applicable findings may be.

The aim in this study was to establish if the findings, from an extensive catchment study (Hornung et al., 1985) are relevant to another area, where rock types and other catchment characteristics differ.

Some of the elements exported in streams (eg silicon and calcium) are principally the products of weathering of the mineral material in the catchment (White et al., 1971). In addition, the amounts of some elements derived in this way influence the activity of soil (Williams & Gray, 1974) and stream (Sutcliffe & Carrick, 1973) organisms and therefore the export of other ions (eg nitrate). Thus, rock and soil type are likely to have a major influence on the solute concentrations of streams. Some ions in stream water (eg chloride and sulphate) are, at least in part, deposited on the catchment from the atmosphere (White et al., 1971). Thus the location of the catchments, relative to sources of these elements (principally the sea and centres of human population) will also be important in determining stream water concentrations. Because of physical, chemical and biological processes occurring in the soil and in the stream, characteristics such as stream size and altitude may also influence solute concentrations.

In this study, the parameters which may influence solute chemistsry have been related to mean solute concentrations, with the aid of Principal Component Analysis.

THE CATCHMENTS

The catchments studied by Hornung et al., (1985) are headwaters of the River Wye, on Plynlimon in mid-Wales. Five catchments were investigated all of which had the same land use, namely upland sheep grazing. However the catchments differed in land management, two having been agriculturally improved while the others had not. To simplify comparisons only data from the three unimproved Plynlimon catchments are presented here. One of the unimproved catchments differed in lithology from the others. Rock types were (Breward & Reynolds, pers comm):-

1. Frongoch formation. Mainly pale grey mudstones from the Llandovery series of the Silurian period.

2. Gwestyn formation. Grey to black shales and mudstones with some siltstones. Highly pyritic but of the same series as the Frongoch.

Eight catchments in the Lake District (northern England) were studied (Fig 1). Only catchments used for upland sheep grazing were considered. Catchments with visible evidence of land improvement or development of any kind were avoided. To minimize the influence of alien minerals on stream solute chemistry, catchments were also avoided if there was substantial glacial drift, evidence of mineralization or more than one rock type. The Lake District catchments covered three rock types (Moseley, 1978 and Taylor _et al_., 1971):-

1. Ennerdale Granophyre. A variable, intrusive rock composed mainly of quartz and feldspar.

2. Rocks of the Skiddaw Group. The group is made up of mudstones, siltstones and greywacke - sandstones of Ordovician period.

3. Rocks of the Borrowdale Volcanic Group. The group consists of lavas, tuffs and agglomerates of the Ordovician period.

The physical characteristics of all the study catchments are given in Tables 1 and 2 and the chemical composition of the bedrock types in Table 3.

SAMPLING AND ANALYSIS

Sampling of the Lake District streams began in June 1980 and continued until the end of September 1981. As only broad trends between rock types were being investigated sampling was at approximately 5 week intervals. To minimize variability related to stream discharge, periods of peak flow were avoided for sampling. The maximum interval between samplings was 56 days and the minimum 30 days. The Plynlimon streams were sampled weekly but only data for those dates closest to the Lake District samplings have been used here. There was never more than 2 days difference between Lake District and Plynlimon samplings and in 8 cases, samplings took place on the same day.

To ensure compatibility between Lake District and Plynlimon results, solute analysis was performed in the same laboratories using the same methods. Prior to analysis samples were filtered through 0.45 μm membrane filters. Sodium, potassium and aluminium were determined by flame emission spectrophotometry and calcium, iron, manganese and magnesium by flame atomic absorption spectrophotometry. Nitrate-N, ammonium-N, phosphate-P, silicon and chloride were determined colorimetrically using a continuous flow analyser, and sulphate-S by the barium chloride tubidimetric method. Dissolved total organic carbon (DTOC) was measured on a Carlo-Erba analyser. pH was determined on un-filtered water using a combination electrode. Samples were stirred, then allowed to settle for one minute before reading. Detailed descriptions of the analytical methods are given in Allen _et al_., (1974) and Reynolds (1981).

RESULTS

The Lake District catchments were sampled 13 times, but for the purpose of calculating solute means (Table 4) the first and last samplings were discarded, leaving a period of one year. Principle Component Analysis (Hope, 1968) of mean annual solute concentrations was used to examine relationships between catchments. Seasonal patterns were examined graphically.

Discharge. No discharge data are available for the Lake District streams studied. As a surrogate for discharge data, rainfall at Grange-over-Sands (National Grid reference SD409796), on the southern edge of the Lake District is given in Figure 2. The rainfall was totalled for the 3 days prior to the Lake District samplings. Discharge for one of the Plynlimon catchments is given in Figure 2. These data were recorded from a V notch weir at the time of sampling. The marked discrepancy between the rainfall and discharge data in January 1981 results from precipitation falling as rain at Grange-over-Sands but as snow on higher ground. Other deviations reflect localized rainfall, time differences between Lake District and Plynlimon samplings and the rapid response of upland streams to rainfall.

pH. Throughout the sampling period pH was markedly higher on the Borrowdale Volcanic series and Skiddaw series than on the Granophyre and the two Plynlimon rock types (Fig 3). On three occasions streams in Granophyre catchments had anomolous pH values. With the exception of these catchments, variation through the year was small.

Nitrate. In all catchments concentration peaks in late winter, when differences between rock types are most marked (Fig 4). The Borrowdale Volcanic catchments have the highest annual means. The Plynlimon catchments have the lowest annual means, reflecting that during the summer months concentration was below the detection limit (0.01 mg l^{-1} NO_3-N).

Ammonium. In the first 9 samplings, in all catchments, the concentration was below the detection limit (0.5 mg l^{-1} NH_4-N) so determination was discontinued.

Phosphate-P. Concentrations were again below the detection limit (0.02 mg $l^{-1}PO_4$-P) in the first nine samplings so determination was also discontinued.

Potassium. For the Lake District catchments, mean concentration of K reflects the proportion of K in the rocks (Tables 3 and 4); the Granophyre catchments being markedly higher than the others. However the Plynlimon rock types do not conform to this pattern. Both have K levels almost as high as the Granophyre but solute concentrations are much lower than all catchments in the Lake District. There is no consistent seasonal pattern in concentration, Standard Errors associated with annual mean concentration ranging from 0.01 to 0.03.

Calcium. Rocks of the Borrowdale volcanic group have a calcium content 12 times that of any of the other rocks (Table 3), and this is reflected in the higher concentrations in two of the Borrowdale volcanic streams (B1 and B2, Table 4). However mean annual concentration for B3 falls within the range of the other rock types. Variability through the sampling period is small, particularly for those streams where concentration is lowest (Fig 5). Mean calcium concentration is paralleled by mean pH.

Magnesium. Mean magnesium concentration is at a maximum in catchment B1 and a minimum in catchment B3 (Table 4), both these catchments being on the Borrowdale volcanic group. These rocks have the highest magnesium composition of the five included in this study.

Manganese. Individual concentrations were generally close to, or below the detection limit of 0.01 mg l^{-1}. Catchment W was the only catchment where the concentration was consistently above this level.

Iron. Despite significant quantities in all rocks, stream concentrations were generally below the detection limit (0.02 mg l^{-1}) except for the last 2 samplings in 1980. Catchment W had an annual mean higher than all other catchments.

Silicon. Despite having only a slightly higher silicon content, Granophyre releases significantly more silicon into stream water than the other four rock types. No seasonal pattern was detected, Standard Errors ranging from 0.03 to 0.62.

Aluminium. In the first nine samplings, in all catchments, the concentration was at or below the detection limit (0.1 mg l^{-1}) so determination was discontinued.

Sodium. All stream concentrations fell between 2.2 and 4.1 mg l^{-1}. There was no marked effect of rock type but concentrations were generally higher on Granophyre and lower on Borrowdale Volcanics. Granophyre has the highest sodium content.

Chloride. The dominant feature of the chloride data is a marked winter peak which was found for all catchment (Fig 6). All values fell between 2.0 and 8.1 mg l^{-1}, with much overlapping of the ranges between rock types.

Sulphate-S. No clear patterns with time or rock type were detected but the Plynlimon catchments were generally lower in concentration.

Dissolved Total Organic Carbon (DTOC). This determination was discontinued after the ninth sampling. No consistent effects of season or rock type were detected.

Principal Component Analysis. PCA is a statistical technique for examining relationships among multivariate data. The main value of PCA in this study was to indicate association between catchments. Mean annual solute concentration and pH were analysed, elements being excluded if dominated by zeros. Three significant components were identified, accounting for 46%, 39% and 9% of variance. Table 5 indicates the important variables in each component and their weightings. To indicate association between catchments component values for component 1 were plotted against those for component 2 (Fig 7). As these 2 components together account for 85% of variance, the closeness of catchments on Figure 7 indicates association in terms of the solute data analysed.

DISCUSSION

The solute concentrations presented here are all close to, or well below concentrations for rivers and streams draining more intensively managed land. For instance in southern England, Webb and Walling (1985) found daily mean concentrations of nitrate-N ranging between 1.0 and 4.5 mg l^{-1}, and of magnesium ranging between 6 and 12 mg l^{-1}, in a 46 km^2 catchment used mainly for dairy farming. In central Scotland, Harriman (1978) found weekly concentrations of phosphate-P between 0.02 and 3.0 mg l^{-1} in upland streams draining fertilized commercial forests.

Some seasonal variation has been identified. The most dramatic is the nitrate peak in late winter. This has been widely reported from other sites (eg Likens, 1985). Taylor et al. (1982) attributed the peak to the mineralization of proteins derived from soil microorganisms killed by frost. In contrast Edwards et al. (1985) atttributed it to high precipitation inputs coinciding with low plant uptake. The late winter peak in chloride may result from the release of dry deposited ions at snow-melt, but a corresponding peak in the other dominant sea derived element, sodium, was not found. All concentrations will have been influenced, to some degree, by patterns of stream discharge, despite peak discharge having been avoided. Perhaps the most important feature of the seasonal trends of nitrate and chloride is that the same general effect was encountered on all catchments, both in the Lake District and on Plynlimon.

The relationships between different solutes can be examined with the PCA component weightings. The first component was equally dominated by calcium and magnesium with pH, nitrate and sulphate also being important. This component principally represents rock and soil derived, elements. The second component was dominated by sodium, with potassium, silicon and chloride also being important. This component principally represents marine elements, with the exception of silicon, and to some extent potassium (see later in discussion). The third component accounts for only 9% of the variance and reflects the second component.

By relating the physical characteristics of the catchments (Table 1 and 2) to the plot of component values (Figure 7), factors influencing the relationships between catchments may be identified. Altitude, catchment area (an index of stream order and annual discharge) and distance to sea do not appear important. Ranker and peat cover relate weakly to component 2. However rock type is an important determinant in the overall pattern of variability. The granphyre catchments group together as do the Skiddaw catchments. All 3 Plynlimon catchments group together, with the Frangoch catchments closer to each other than to the Gwestyn catchment. The Borrowdale volcanic catchments are widely spread along component 1 ("rock/soil") but closer along component 2 ("marine").

Calcium and magnesium, the two dominant ions in the first component, are present in soil mainly as inorganic compounds, but significant amounts are associated with organic material. Hornung et al. (1985) attributed differences in calcium levels between Plynlimon streams to the proportion of peat in the catchments, and mineralization. In this wider comparison the differences in calcium content of the rocks are more marked and many of the catchments have no peat cover. Thus the calcium content of the streams reflects the calcium content of the rocks. The marked differences in calcium and magnesium concentrations within the Borrowdale Volcanic catchments is the product of the lithological variability within the group and is reflected in the wide spread of these catchments in component 1.

Calcium and magnesium strongly influence pH, which is also important in the first component. Over the eleven streams in this study, significant correlations were found with calcium and pH ($r = 0.812$, $0.001 < P < 0.01$) and magnesium and pH ($r = 0.659$, $0.01 < P < 0.05$). pH in turn markedly influences biological processes in soil, such as nitrification. Thus differences in the biologically derived nitrate (also important in the first component) can be indirectly attributed to rock chemistry. (Correlation between pH and nitrate 0.743, $0.001 < P < 0.01$).

The precursor of nitrate is ammonium, which was not detected in any of the streams. Ammonium is retained in the soil by adsorption onto soil colloids and is thus unlikely to reach streams before oxidation to nitrate. Richey et al. (1985) have demonstrated that ammonium which does reach a stream could be transformed to nitrate in the water. However it should be noted that, in this study, the detection limit for ammonium-N was higher than nitrate-N.

The absence of detectable phosphate in any of the streams indicates the very small amounts available in these catchments. Any that is released by the mineralization of organic material or weathering of rocks will be rapidly assimilated by plant roots and soil organisms, or adsorbed by the mineral fraction of the soil.

Sulphate, the fifth important ion in the first component, is released into drainage water from rocks or soil, but larger quantities are deposited from the atmosphere (White et al., 1971), principally from the burning of fossil fuels (Overrein, 1983). The lack of a clear pattern emerging with time or rock type is attributable to the interaction of these various sources. The lower concentrations detected in the Plynlimon catchments results from their greater isolation from centres of human population. It is noteable that the pyrite in the Gwestyn formation does not result in higher concentrations of sulphate in catchment W.

Iron and manganese are strongly influenced by redox conditions in the soil. Despite appreciable quantities in the rocks, the iron in all catchments will be largely held in the soil in the insoluble, reduced form.

Reynolds et al. (1984), working on the Plynlimon catchments, examined the chemistry of precipitation. Two ions were identified as entirely derived from marine sources, sodium and chloride. These are important in the second component of the PCA of this study. However the issue for the present study is the extent to which precipitation derived water is modified by its passage through the soil and its parent material. Sodium and chloride are not in great biological demand, nor are they readily adsorbed by the mineral fraction of the soil, and thus pass through the soil into drainage water. (Clearly concentrations will change as a result of evapotranspiration).

The granophyre streams have the highest concentrations of sodium, chloride and potassium as well as silicon. The high concentrations of silicon originate in the high proportion of silicon in the readily weathered feldspars in Granophyre. The presence of silicon in the second ("marine") component results, at least in part, from sodium and potassium, also released from the feldspars, augmenting marine derived sodium and potassium. Thus all three ions would correlate. Potassium also occurs in large quantities in plant material, from which it is readily released. Potassium concentration of stream water is correlated with the percentage of ranker in the catchment ($r = 0.781$, $0.001 < P < 0.01$). This implies that the slow growing vegetation of these poorly developed soils releases less potassium.

The lack of relationship between solute chemistry and distance to coast reflects the fairly narrow range of distances in this study, all catchments receiving heavy inputs of marine derived elements. Altitudes of catchments are also unimportant, indicating that over the range covered here, altitude does not influence temperature and moisture regimes sufficiently to effect rates of weathering and other processes. Catchment area, however, covers a very wide range and is still unimportant. Water collected from large catchments has had longer groundwater residence and has travelled a greater distance in the stream. The lack of importance of catchment size indicates that processes occurring in the stream itself are also unimportant, compared with rock chemistry.

With the exception of precipitation input, the many interactive processes which control stream solute chemistry could be expected to be strongly influenced by rock chemistry. Rock chemistry, as given in Table 3, disguises the fact that rocks are assemblages of minerals which weather at different rates. The range of minerals, even in a single rock type can be wide and some of the catchments discussed here are actually on rock groups. The rate at which a mineral weathers depends on its composition, grain size, crystallinity and environment. Despite these complexities some differences in solute chemistry can be attributed to rock chemistry and rock chemistry should therefore be taken into account when assessing the relevance of individual catchment data to wider areas.

CONCLUSIONS

Within the range of rock types and geographic locations investigated, rock type has the dominant role in influencing elements cycling, as indicated by stream solute chemistry. While some seasonal trends occur on all catchments, processes can be identified which occur on different rock types to different degrees. Thus broad conclusions derived from catchment studies on Plynlimon could be applied to the Lake District, particularly in relation to seasonal variations, but allowance would have to be made for different geologies, when interpreting concentration data.

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Table 1. The physical characteristics of the eleven catchments

Rock Type	Catchment Code and name	National Grid Reference of sampling point	Area (ha)	Altitude (m) min-max	Distance to sea (km)
Ennerdale Granophyre	G1 Starling Dodd Gill	NY 145150	18	330-580	17
	G2 Silvercove Tributary	NY 130130	8	220-520	15
	G3 Silvercove Beck	NY 130130	225	210-680	14
Skiddaw Group	S1 Sail Beck	NY 188181	327	210-840	21
	S2 Second Gill	NY 188182	38	210-660	21
Borrowdale Volcanic Group	B1 Blind Beck	NY 364082	21	275-610	33
	B2 Rydal Beck	NY 365082	536	260-860	33
	B3 Birkside Gill	NY 329125	99	300-880	32
Frongoch formation	F1 Unimproved mudstone catchment*	SN 818841	4	400-510	22
	F2 Unimproved mineralized mudstone catchment*	SN 817842	9	390-530	22
Gwestyn formation	W Unimproved shale catchment*	SN 817863	6	490-535	21

* Names used in Hornung *et al* (1985)

Table 2. The soils of the catchments (% cover). For the Lake District catchments data were recorded from a reconnaissance soil map (V.C. Bendelow, pers. com.) using a digital planimeter. For the Plynlimon catchments (codes F1, F2, W) data were derived from auger sampling at the intersections of a 33 m grid. The soil classification follows Avery (1973) and the units used are Soil Groups.

Code	Ranker	Brown Podzolic Soil	Stagnopodzol	Stagnohumic gley	Raw Peat	Rock
G1	68	0	32	0	0	0
G2	58	42	0	0	0	0
G3	60	14	0	0	0	26
S1	56	41	3	0	0	0
S2	11	28	61	0	0	0
B1	54	46	0	0	0	0
B2	40	18	22	0	20	0
B3	22	23	0	0	32	23
F1	0	0	55	0	28	0
F2	0	0	50	17	15	0
W	19	0	22	15	43	0

Table 3. The median percentage chemical composition (w/w) of the five rock types (N. Breward pers. com).

	K	Ca	Mg	Fe	Si	Na
Ennerdale granophyre	3.8	0.12	0.06		32	2.2
Skiddaw group	2.4	0.32	1.3		31	1.2
Borrowdale volcanic group	1.6	4.0	2.0	5.8	28	1.3
Frangoch formation	3.3	0.03	1.3	5.9	29	
Gwestyn formation	3.2	0.007	1.4	6.0	30	

Table 4. Mean concentrations for 13 ions, pH and Dissolved Total Organic Carbon for the 11 catchments. Unless marked with an asterisk, means are for 11 samplings distributed over one year.

Catchment	pH	NO_3-N mgl^{-1}	NH_4-N* mgl^{-1}	PO_4-P* mgl^{-1}	K mgl^{-1}	Ca mgl^{-1}	Mg mgl^{-1}	Mn mgl^{-1}	Fe mgl^{-1}	Si mgl^{-1}	Al* mgl^{-1}	Na mgl^{-1}	Cl mgl^{-1}	SO_4-S mgl^{-1}	DTOC* mgl^{-1}
G1	6.0	0.17	0	0	0.41	0.65	0.87	0	0.01	2.1	0	3.8	5.4	1.8	0.93
G2	5.1	0.06	0	0	0.30	0.9	0.70	0.02	0.01	1.5	0.1	3.4	5.5	1.9	1.04
G3	5.9	0.18	0	0	0.33	1.08	0.81	0.01	0.01	1.6	0	3.4	5.6	1.8	1.47
S1	6.4	0.08	0	0	0.16	1.84	0.91	0	0.01	0.9	0	3.3	5.4	1.8	0.99
S2	6.7	0.08	0	0	0.22	2.69	0.92	0	0	0.7	0	3.2	5.2	1.8	1.10
B1	7.2	0.33	0	0	0.21	6.71	1.94	0	0	1.0	0	3.0	4.6	2.5	1.32
B2	7.0	0.37	0	0	0.18	4.56	1.19	0	0.01	1.1	0	2.8	4.2	1.9	1.26
B3	6.7	0.18	0	0	0.14	2.50	0.53	0	0.01	1.0	0	2.4	3.7	1.5	1.53
F1	5.4	0.06	0	0	0.09	1.05	0.67	0.01	0.02	0.8	0	3.0	4.8	1.4	1.83
F2	5.8	0.06	0	0	0.08	1.57	0.62	0	0.01	0.8	0	2.9	4.5	1.4	1.17
W	4.7	0.04	0	0	0.04	0.62	0.59	0.04	0.06	0.8	0	2.8	4.5	1.2	2.64

Table 5. Component weightings for stream solutes. Only weightings within 75% of the largest in the component are included.

	Components		
	1	2	3
pH	-.42		
NO_3-N	-.44		
Ca	-.45		
Mg	-.45		
SO_4-S	0.44		
K		-.48	
Si		-.45	-.56
Na		-.51	
Cl		-.47	.46

Fig. 1. Catchments sampled in the Lake District (●) and the distribution of the three rock types.
Inset: The location of the Lake District and Plynlimon within England and Wales.

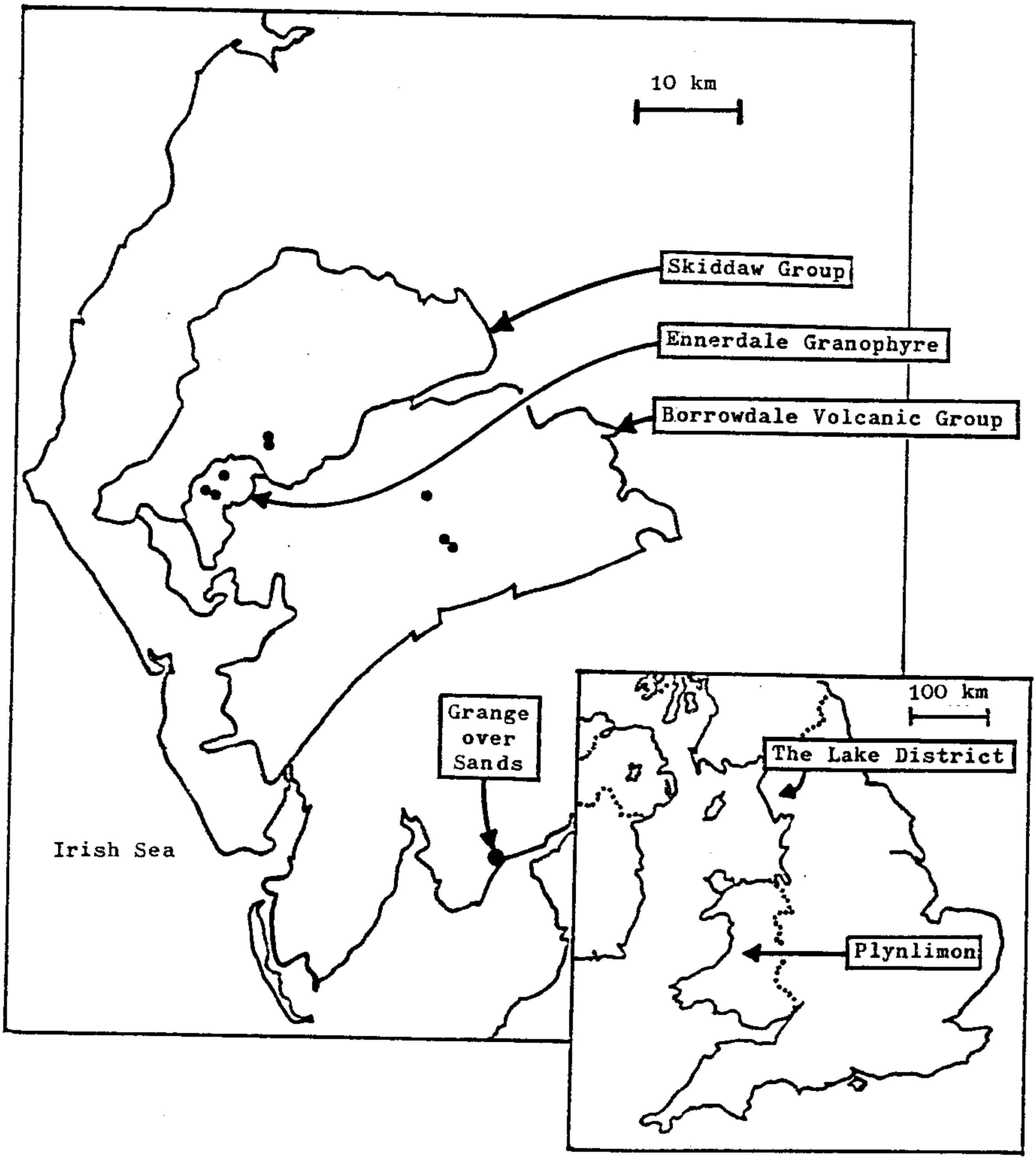


Fig. 2. Discharge, Plynlimon catchment F1 (solid bars) and precipitation, Grange-over-Sands (open bars). Discharge was recorded at the time of Plylimon sampling. The precipitation was totalled for the three days prior to the Lake District sampling. Each pair of bars is centred on the sampling date.

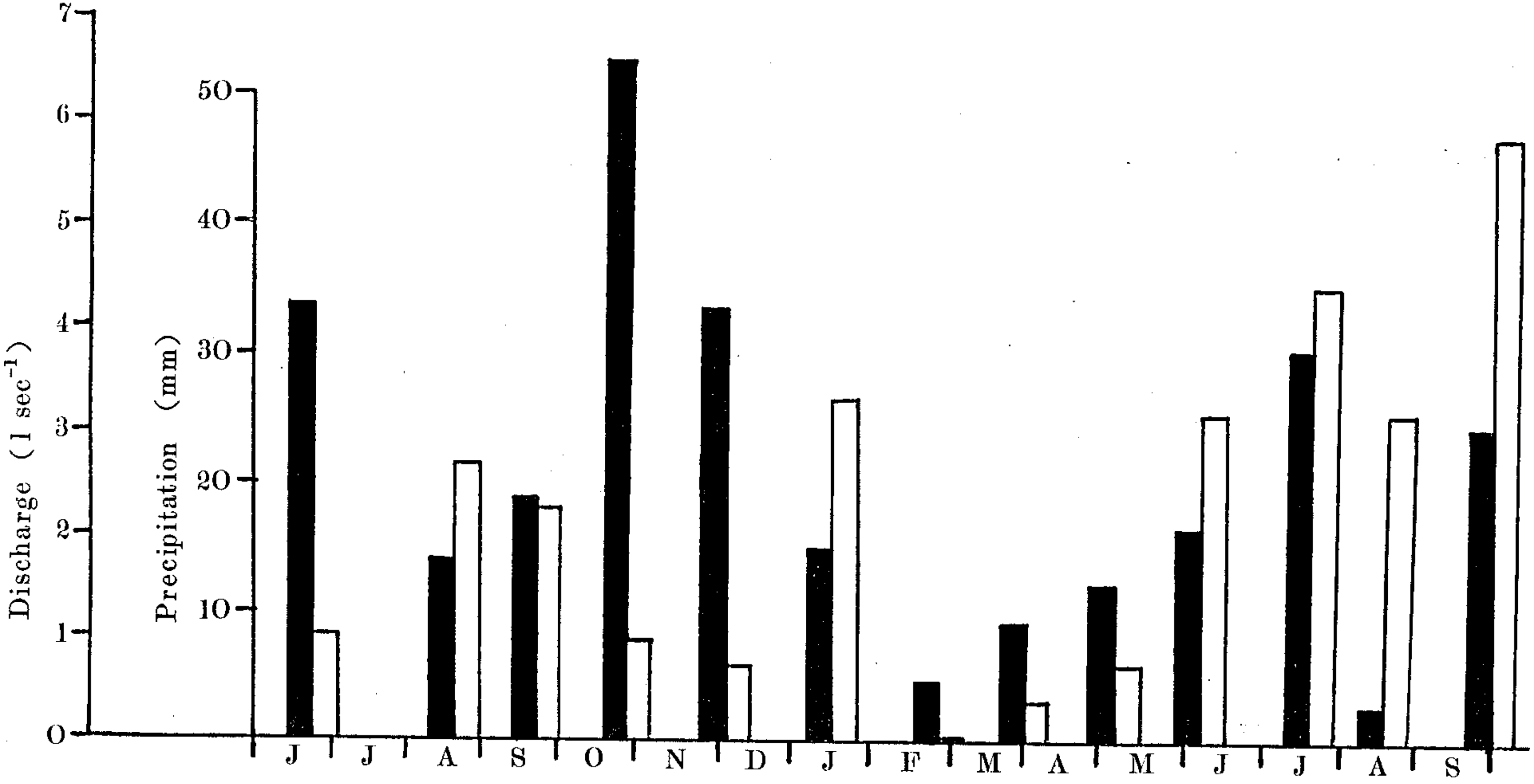
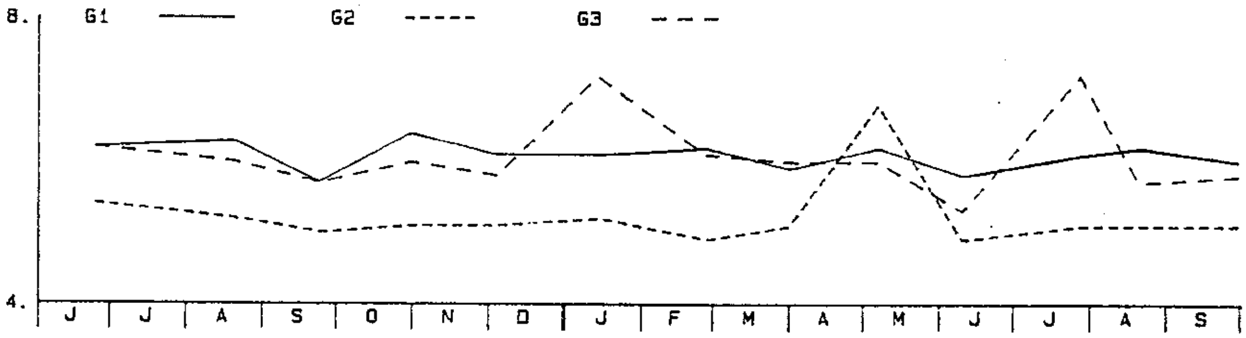
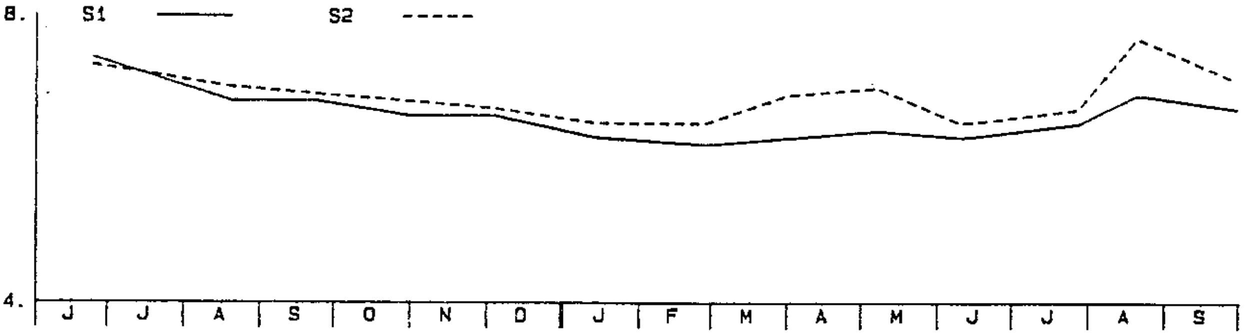


Fig. 3. pH of stream water, 1980-1981.

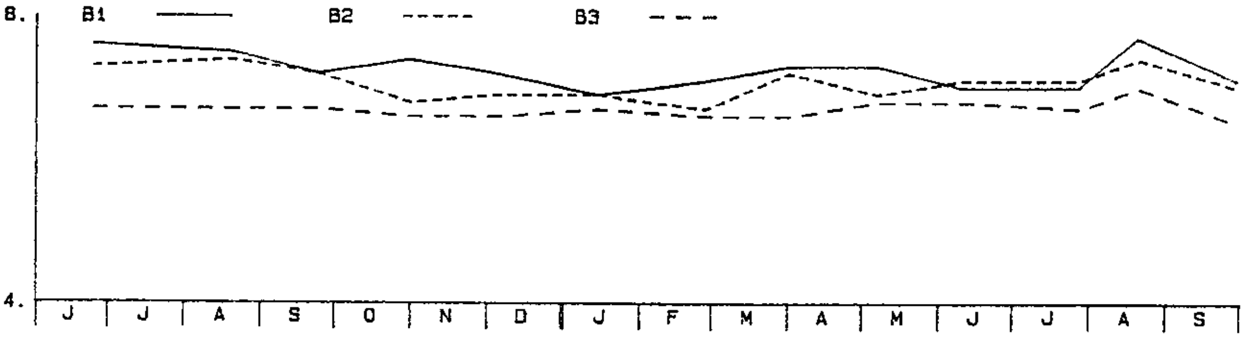
Ennerdale Granophyre streams



Skiddaw Group streams



Borrowdale Volcanic Group streams



Plynlimon streams

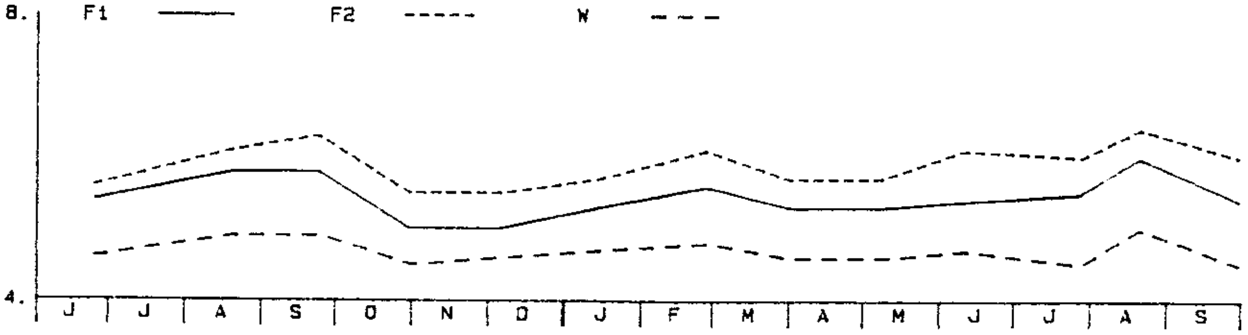
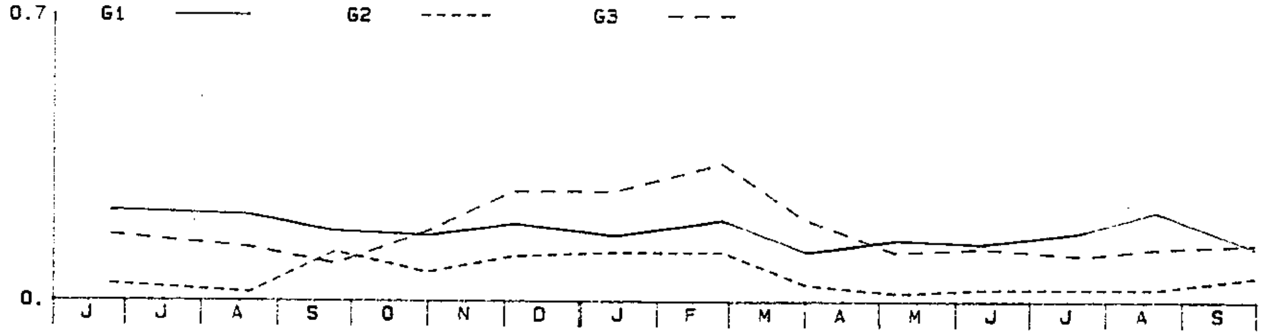
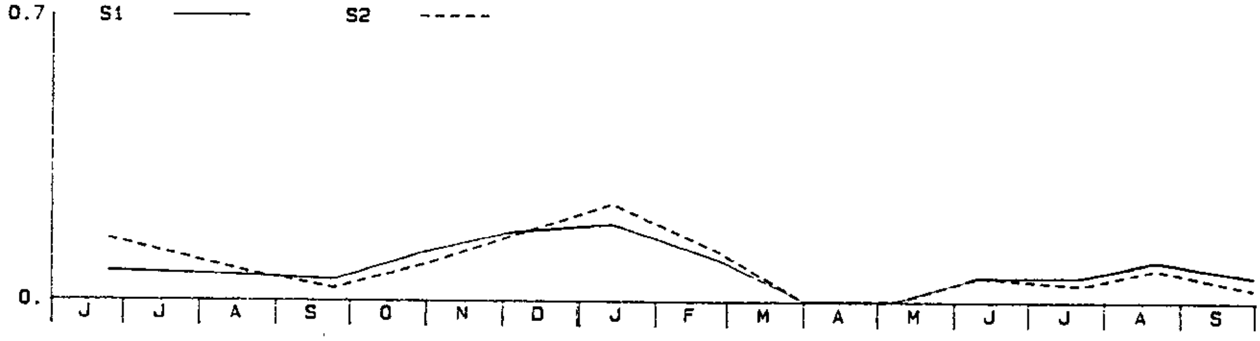


Fig. 4. Concentration of nitrate-N (mg l^{-1}) in stream water, 1980-1981.

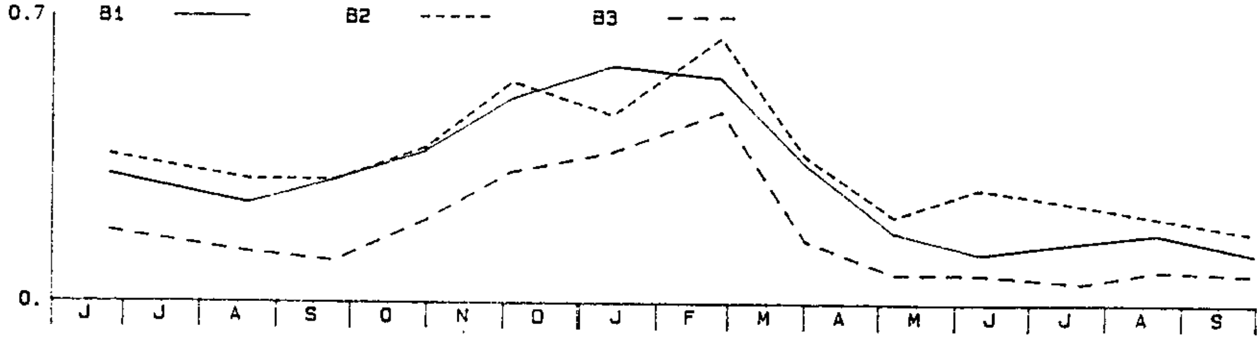
Ennerdale Granophyre streams



Skiddaw Group streams



Borrowdale Volcanic Group streams



Plynlimon streams

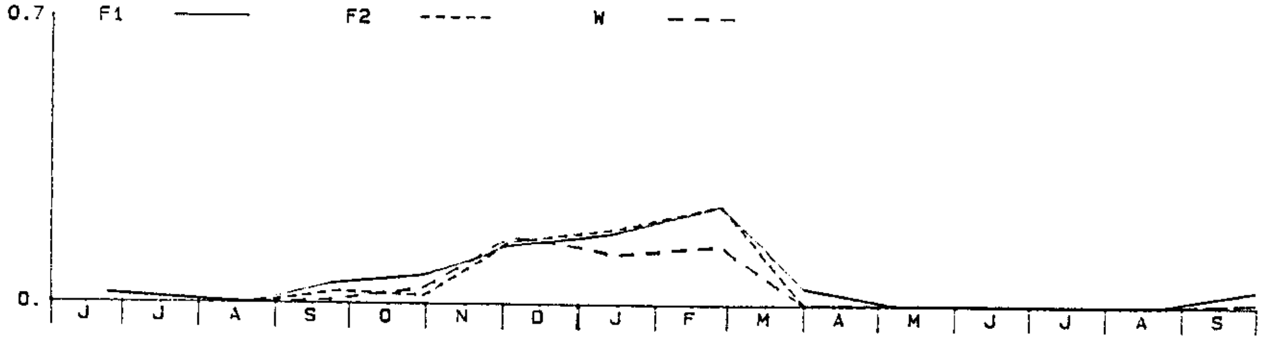


Fig. 5. Concentration of calcium (mg l^{-1}) in stream water, 1980-1981.

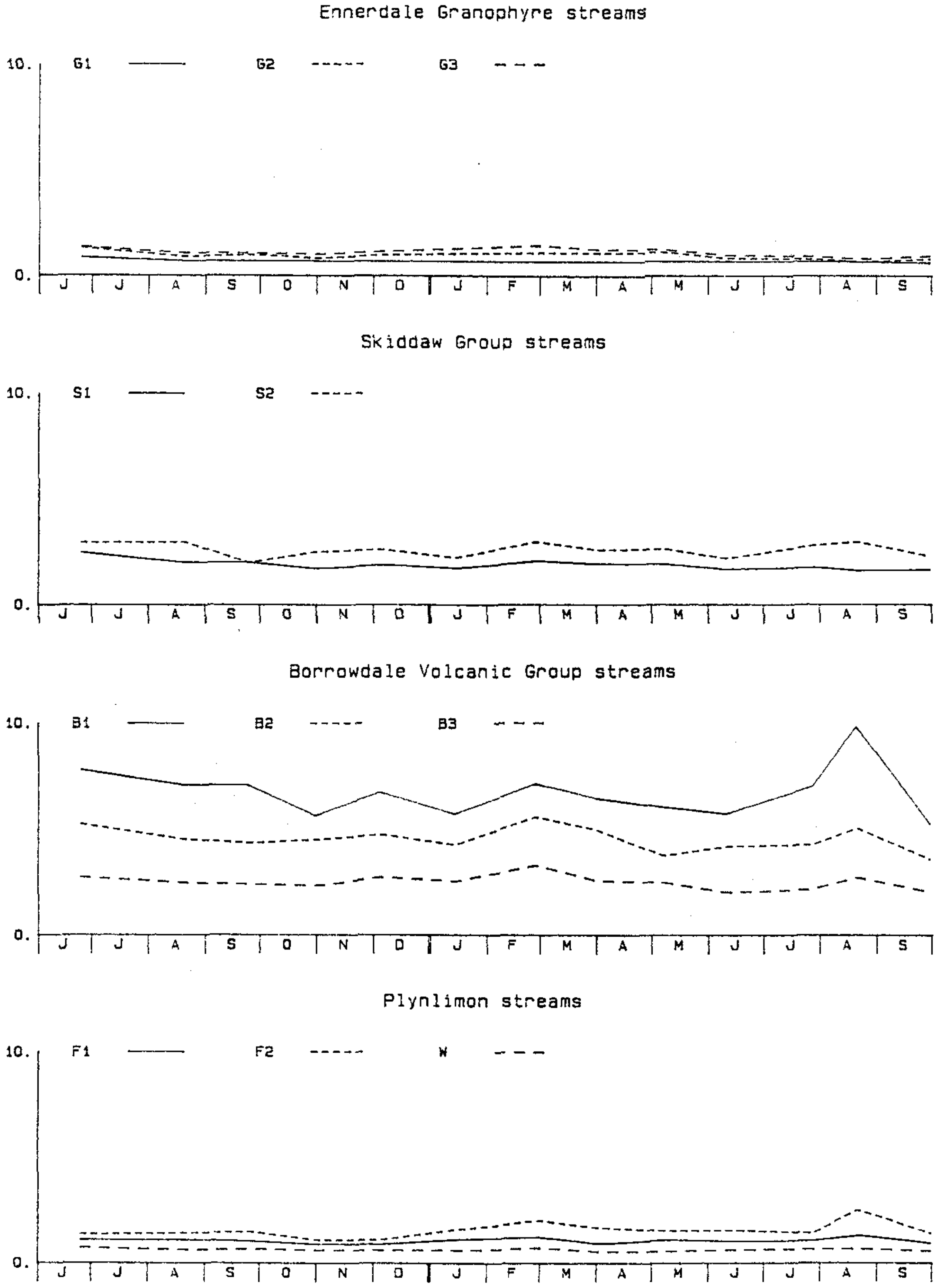
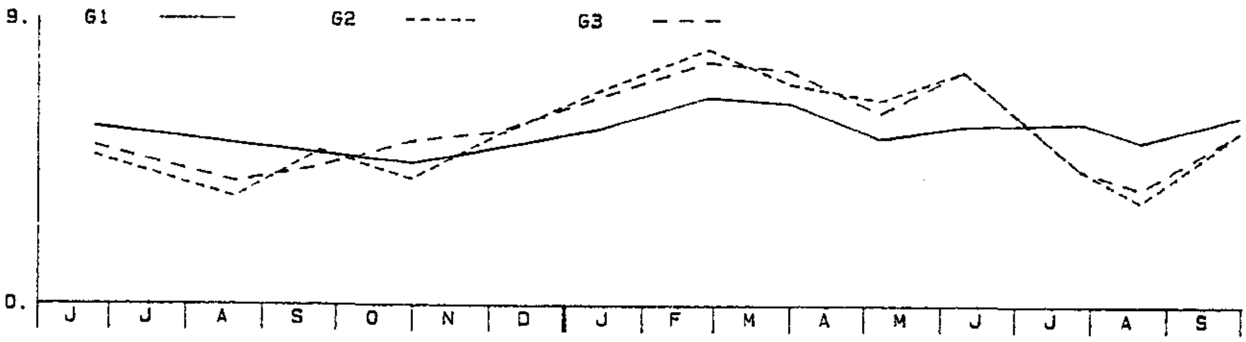
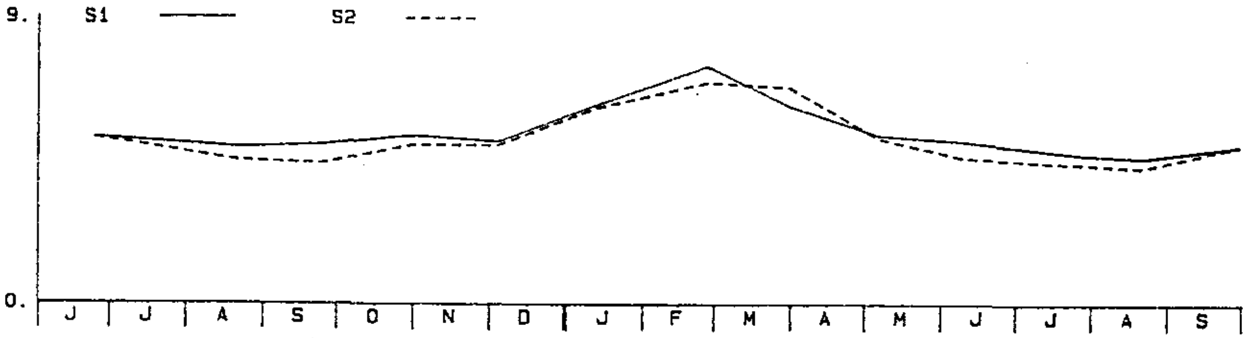


Fig. 6. Concentration of chloride (mg l^{-1}) in stream water 1980-1981.

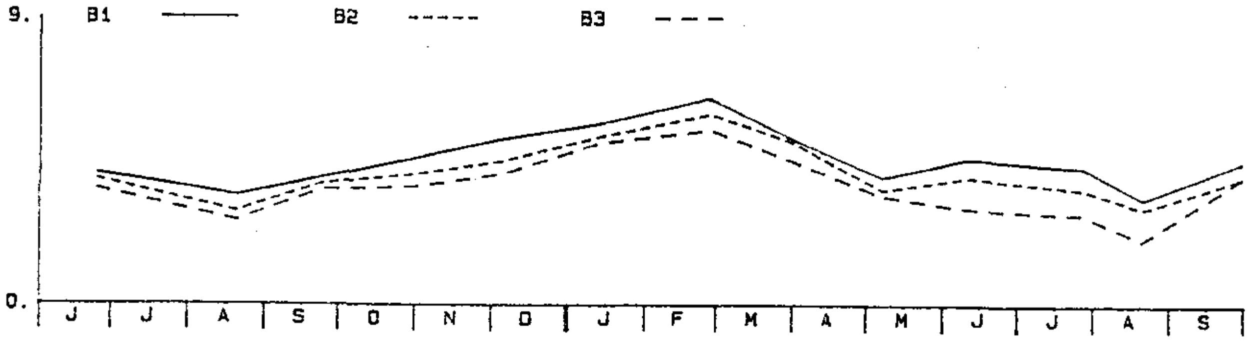
Ennerdale Granophyre streams



Skiddaw Group streams



Borrowdale Volcanic Group streams



Plynlimon streams