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Stream solute sources and variations in a temperate granite drainage basin

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ABSTRACT Bulk precipitation and stream water samples were analysed to determine a chemical budget (February 1977-February 1978) for a small granite basin on Dartmoor, southwest England. Seventy per cent of the solute load was derived from external sources, the remaining 30% coming from internal sources. Principal components analysis (PCA) was employed to examine variations in and controls of the solute chemistry from selected pathways. Solute variations in bulk precipitation were dominated by sodium, chloride and magnesium derived from marine sources, and seasonal trends were related to prevailing weather conditions. The solute chemistry of springs was also found to depend mainly on the influence of marine derived ions. PCA was used to isolate groupings of springs, and the effect of the sitka spruce forest was identified. Annual solute variations in the stream were mainly a function of changes in the concentration of sodium, chloride and magnesium, pH and silica. Stream water chemistry is controlled mainly by processes in the atmosphere, but weathering in the soil is also important.

Origine et variations des matières dissoutes dans un cours d'eau d'un bassin granitique tempéré

RESUME On a analysé des échantillons d'eau de pluies et de rivière pour établir le bilan chimique pendant une année (février 1977 à février 1978) d'un petit bassin granitique (Dartmoor sud-ouest de l'Angleterre). 70% de la charge en matières dissoutes est d'origine extérieure au bassin. Une analyse des composantes principales a permis d'examiner les variations de la nature chimique des matières dissoutes suivant les différentes voies de transport ainsi que les facteurs qui la gouvernent. Les variations des matières dissoutes dans les précipitations portaient en grande partie sur le sodium, le chlore et le magnésium, d'origine marine. Pour ces ions les tendances saisonnières ont été mises en évidence ainsi que leur relation avec les conditions atmosphériques dominantes. On a trouvé aussi que la constitution chimique des sources dépendait surtout de l'influence des ions d'origine marine. L'analyse des composantes principales a permis de classer par groupes les différentes sources et de mettre en évidence l'influence de la forêt de *Picea sitchensis*. La variation annuelle des matières dissoutes dans le cours d'eau porte essentiellement sur la concentration en sodium, chlore, magnésium, silice et sur le pH. La chimie du cours d'eau est donc régie en grande partie par les processus atmosphériques, bien que le sol joue aussi un rôle important.

INTRODUCTION

This paper presents a hydrochemical budget for the Narrator basin, Dartmoor, southwest England, for the period of one year (February 1977-February 1978) and also analyses the principal sources of ions discharged in the stream water. Changes in solute chemistry were monitored in precipitation, throughfall, litterflow, interflow, springs and the river. The chemical characteristics of four interflow pathways have been previously identified and discussed by Williams *et al.* (1983). Principal components analysis (PCA) was utilized as a method of examining sources of variation. The technique is discussed by Davis (1973) and Johnston (1978), while its application to water quality data has been shown by Mahloch (1974). The related technique of factor analysis has been applied to solute chemistry data by Ashley & Lloyd (1978) and Reid *et al.* (1981), although the underlying nature of the factor analysis model differs from that of principal components analysis. PCA was undertaken using the CLUSTAN 1C computer program (Wishart, 1982) in the Q mode, so that similarities between water samples from the various points along the hydrological pathways collected within the study period could be investigated.

THE NARRATOR BASIN

The Narrator drainage basin is located 17 km northeast of Plymouth on the southwest margin of Dartmoor, southwest England (Fig.1). The basin has an area of 4.75 km^2 and a relief of 232 m, but most of the research was conducted within the lower valley. The prevailing climate is cool and wet, since the region is exposed to southwesterly maritime influences. Depressional activity from the Atlantic is experienced for more than half the year and accounted for a significant proportion of the 1904 mm of rain received in the study period. The Narrator basin is entirely located on the porphyritic granite of the Dartmoor pluton. Quartz is the most abundant mineral (40%) and there is also a high proportion of plagioclase (19.6%) and potash (25.3%) felspars. The solid granite is overlain by a variable thickness of decomposed granite. From borehole evidence, this is known to be at least 35 m thick in the valley bottom. The soils are dominated by gleyed stagnopodzols (Orthods) on the moorland plateau and by brown podzolics (intergrades between Ochrepts and Orthods) on the hillslopes (Ternan & Williams, 1979). The major vegetation communities are sitka spruce forest *(Picea sitchensis)*, sited in the lower basin, acid grassland extensively invaded by bracken *(Pteridium aquilinum)* located on the valley sides and blanket bog dominated by *Molinia caerulea* which is found over the upper part of the basin (Kent & Wathern, 1980).

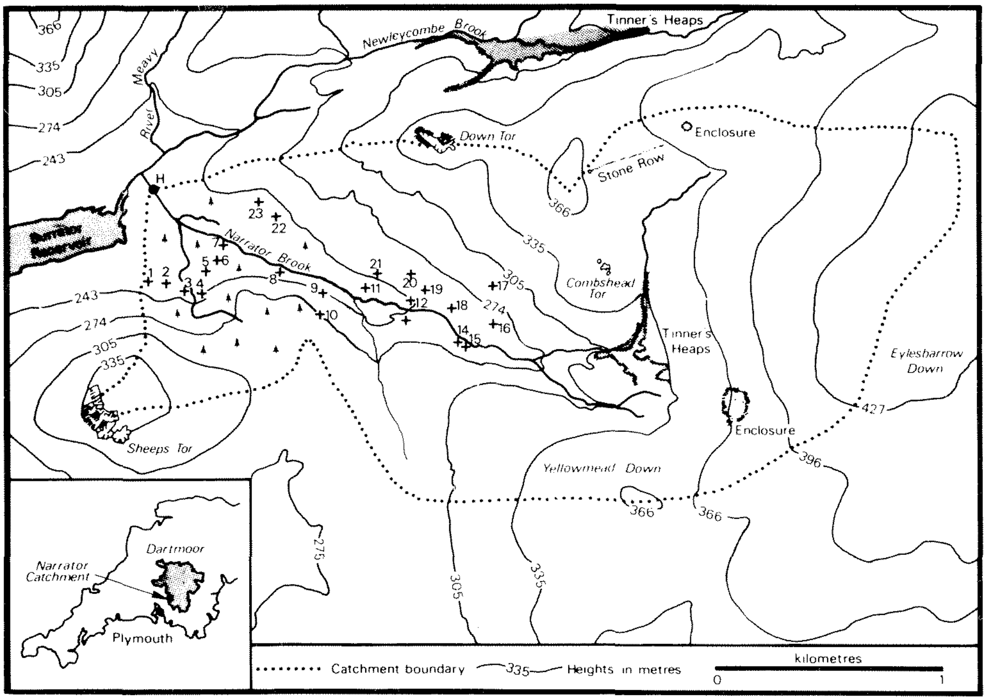

FIG.1 The Narrator basin showing the network of spring sites (+).

GEOCHEMICAL BUDGET

The geochemical budget was computed from the atmospheric inputs and losses in the stream (Table 1). Solute inputs in bulk precipitation were calculated on a weekly basis as the product of the concentration of each element in the collector and the amount of precipitation. The input totals include an estimation of the amount of dry deposition, assuming that there is no source of chloride in the basin and therefore no excess in the balance. Following Claridge (1970), the net input of other ions in dry deposition was calculated as the ratio of the ionic concentrations in dry fallout, a technique also adopted by Reid *et al.* (1982). When the amount of dry deposition is taken into account, Table 1 shows the dominance of sodium and

TABLE 1 Geochemical budget (kg $ha^{-1} year^{-1}$) for the Narrator basin (14 February 1977-13 February 1978)

	H	Na	K	Ca	Mg	SiO_2	Cl
Output	0.05	103.1	13.5	19.5	14.0	92.7	151.4
Input	1.05	96.4	10.4	8.2	11.7	0.1	151.4
Balance	-1.00	6.7	3.1	11.3	2.3	92.6	0.0

chloride, which together account for 90% of the incoming solute load.

The output in the stream was calculated as the product of the solute concentration of a stream water sample and total discharge for the day. These daily outputs were summed for the year to determine total loss from the basin. The greatest annual losses were for sodium (103 kg $ha^{-1}year^{-1}$) and chloride (151 kg $ha^{-1}year^{-1}$), comprising 26% and 38% of the total load respectively. Not surprisingly, silica losses were high (93 kg $ha^{-1}year^{-1}$) because the basin is underlain by granite, which consists of more than 70% SiO_2 by weight.

BULK PRECIPITATION

The importance of the atmospheric supply of solutes to stream chemistry is well documented (Eriksson, 1955; Gorham, 1961; Douglas, 1972; Reid *et al.* 1981). For example, studies in the Hubbard Brook have shown that approximately 70% of the total stream load may be atmospherically derived (Likens *et al.* 1977). Four bulk precipitation collectors were used in this study, and each consisted of a 12.7 cm diameter funnel draining into a 1-litre polythene bottle. The collectors were open continuously and therefore the water samples contained both dissolved material in wet precipitation and water soluble material from dry fallout, these two components being termed bulk precipitation by Whitehead & Feth (1964). The collectors were installed at sites from the valley floor to the moorland plateau and water samples were collected at weekly intervals. No significant differences between the solute concentrations as a result of altitudinal changes were detected.

The ions in wet precipitation and dry fallout originate from a variety of sources. Eriksson (1960) compared the ionic ratios of bulk precipitation with those of sea water in order to distinguish between oceanically and terrestrially derived ions. In the Narrator basin sodium and chloride were present in bulk precipitation in the ionic ratio of 1:1.56, which is similar to that found in sea water (Table 2) and demonstrates a predominantly marine origin for sodium and chloride. The Na:Cl ratio in bulk precipitation showed a seasonal change from 1:1.61 in winter to 1:1.36 in summer. The winter maximum is due to the large number of depressions passing across the area carrying aerosols derived from oceanic spray. The ionic ratios of magnesium to sodium and magnesium to chloride were identical to those found in sea water (Table 2), also indicating a marine source for magnesium. Potassium and calcium ratios to those of sodium and chloride were, however, greatly in excess of those monitored in sea water (Table 2). This demonstrates the predominantly

TABLE 2 Ratios of mean solute concentrations in bulk precipitation (February 1977-February 1978) and sea water

	Na/Cl	*Na/Mg*	*Na/K*	*Na/Ca*	*Cl/Mg*	*Cl/K*	*Cl/Ca*
Bulk precipitation	*1.56*	*0.12*	*0.10*	*0.09*	*0.07*	*0.07*	*0.06*
Sea water	*1.80*	*0.12*	*0.04*	*0.04*	*0.07*	*0.02*	*0.02*

terrestrial sources of these salts. A possible source is wind blown dust from cultivated fields and limestone quarries 12 km to the south.

Principal components analysis of bulk precipitation chemistry

The concentration of each solute included in Table 1, together with conductivity for every sample collected for one year, was subjected to PCA. The first three components explained 83% of the variance, with all three components possessing eigenvalues greater than 1.0. Investigation of the loadings for these components (Table 3) shows that component I, which explains 45% of the variance, is dominated by chloride, **magnesium** and sodium, and demonstrates the dominance of the marine derived ions in the annual variation of bulk precipitation chemistry. Components II and III, which together explain 38% of the variance, are observed to have high loadings for potassium, silica, pH and calcium. This implies the influence of terrestrially derived ions.

TABLE 3 Highest component loadings on the first three principal components of bulk precipitation chemistry

COMPONENT I	*Variance explained*	*45%*
Chloride		*0.494*
Magnesium		*0.485*
Sodium		*0.483*
COMPONENT II	*Variance explained*	*24%*
Potassium		*0.585*
Silica		*0.493*
pH		*0.381*
COMPONENT III	*Variance explained*	*14%*
pH		*0.732*
Conductivity		*0.374*
Calcium		*0.311*
Total variance explained		*83%*

The component scores on axes I and II have been plotted on a scattergram and classified by month of collection (Fig.2). This facilitates study of changes in the variables affecting the chemical composition of bulk precipitation over the year and points on the scattergram may also be examined for clusters or groups. The closer points are to one another, the greater the degree of similarity between them in terms of their chemical characteristics. Figure 2 reveals that the majority of points are grouped towards the lower left corner and represent samples with low concentrations of both marine and terrestrially derived ions due to offshore winds in May and August. Samples to the right with higher component I scores have concentrations close to the averages of the eight variables. Samples which were collected when cyclonic weather prevailed, with depressions bringing in marine derived aerosols, are found in the lower right corner with high component I scores. These samples contained high chloride and sodium concentrations and were associated either with periods of very unsettled weather bringing storms and high winds during winter or with washout effects associated with low rainfall events and long periods of dry weather. Component II scores were generally low, but samples with high component II scores were collected in summer. The maximum score was attained in July, when a warm moist tropical air mass brought 22 mm of rain following three dry weeks. The rain washed out the dust which had accumulated in the atmosphere and caused high concentrations of potassium and silica.

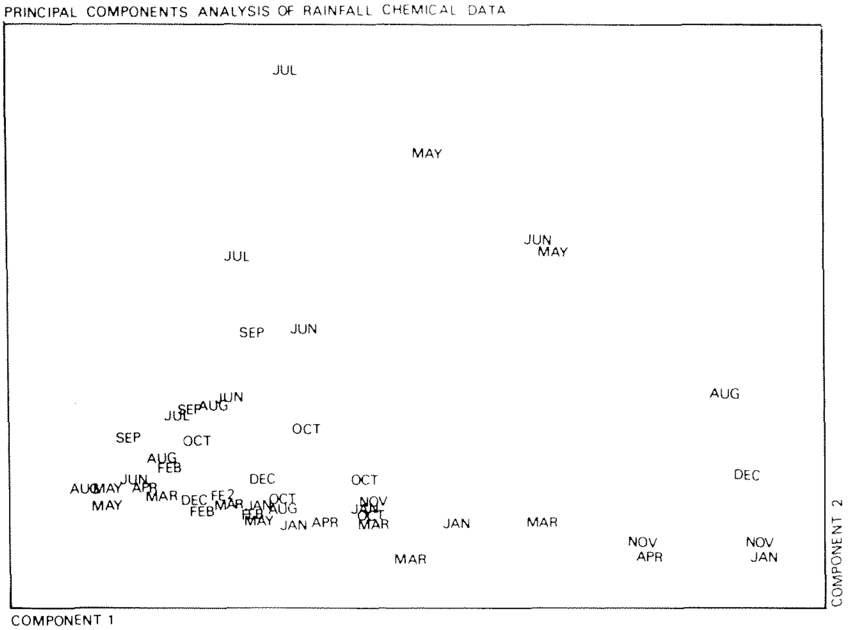

FIG.2 Scattergram for the first two axes of principal components analysis for bulk precipitation chemistry.

SPRING WATERS

Much of the stream water is supplied by numerous springs and seepages, and a network of 23 sites was selected for study (Fig.1). Ninety-five per cent of the stream water may be classified as delayed flow, with only 5% attributable to quickflow. Much of the stream water, therefore, is derived from rain which has percolated through the soil to the springs and seepages. The springs are primarily located in the lower part of the basin and in most cases they appear to emerge in distinct groups, although some isolated springs such as spring 8 (Fig.1) do occur. Occurrence of springs is governed by a number of factors including position of the water table, topography and presence of joints and fissures. Several springs emerge in the valley floor and their location is governed by local height of the water table (springs, 7, 11, 18, and 19). Other springs are located on the valley sides (springs 1, 2 and 3), issue at one level and then lose water into their stream beds. These are probably supplied by perched saturated zones, and the presence of clay lenses within the decomposed granite regolith support this explanation. A further set of springs is located in hillslope hollows at sites favourable to the generation of interflow (springs 4, 14 and 15), and these are fed by water from both shallow and deep sources.

Measurements of variability of spring water temperature reveal a continuum of springs ranging from those supplied from shallow sources to those emerging from greater depth. Shallow springs and those emerging from subsurface pipes (spring 16) have the highest temperature variability, whilst those from depth have the lowest. Comparison with annual temperature variation of water recorded in boreholes suggests that the majority of springs in the study basin emerge from depths in excess of 20 m. A significant positive correlation ($P = 0.01$) was obtained between the mean sodium, magnesium and chloride concentrations from the springs and temperature variability. The shallower springs have a higher concentration of marine derived ions as a result of water being lost from the system by evapotranspiration. No relationship was observed between the concentration of ions derived from weathering and temperature variability.

The seasonal variation in the concentration of ions in spring water, when compared with the stream, may facilitate an understanding of the flow routes which operate. Unfortunately, such variation in the study basin is low and difficult to detect, and the standard deviation of ionic concentrations in springs is generally less than 0.5 mg l^{-1}. The silica concentration at most springs, however, rose slightly in summer. This trend may be related to hydrological, biological and weathering controls and in particular to the decreased amount of water passing through the system. Sodium levels also rose while chloride levels remained stable, which indicates that increased weathering was occurring. This was possibly due to increased biological activity resulting in the generation of more carbon dioxide for hydrolysis.

Principal components analysis of spring chemistry

PCA was employed to isolate groupings of springs with respect to their chemistry. The data set was systematically subsampled in order to reduce the number of data points and so clarify the scattergram. Eight chemical parameters were again subjected to PCA and the first two components explained 73% of the variance (Table 4). Component I, which explains 53% of the variance and is dominated by conductivity, sodium, magnesium and chloride, again reflects the importance of the marine derived salts. Component II accounts for 20% of the variance and has high loadings for pH, silica and potassium, which suggests that it is influenced by weathering.

The first two sets of component scores were plotted on a scattergram in order to identify possible groupings of springs. Each point represents the chemical characteristics of a water sample from a spring at one instant in time (Fig.3), and the distance between the points is again an approximation of the degree of similarity between samples. Points on the scattergram can be subjectively divided into

TABLE 4 Highest component loadings on the first two principal components of springflow chemistry

COMPONENT I	*Variance explained*	*53%*
Conductivity		*0.459*
Sodium		*0.439*
Magnesium		*0.431*
Chloride		*0.407*
COMPONENT II	*Variance explained*	*20%*
pH		*0.672*
Silica		*0.573*
Potassium		*0.309*
Total variance explained:		*73%*

three groups. The greatest variation is along the first axis, hence the springs are grouped in terms of conductivity and the concentrations of sodium, magnesium and chloride. Firstly, there is a group of springs to the left of the scattergram with low component I scores, which on the basis of temperature variability data may be supplied by either shallow or deep sources. Secondly, there is a group of springs (6, 7, 8, 9, 10 and 23) with high component I scores (Fig.3) which are located within the sitka spruce forest (Fig.1). The relatively high conductivities, in excess of 70 μS cm^{-1} at 25°C, and high concentrations of chloride in these springs may be due to the entrapment of chloride aerosols by spruce needles (Eriksson, 1955). Spring 10, which plots at the extreme right of the scattergram, is an example of a spring supplied from shallow sources within the forest which only functions during floods. High ionic concentrations are related to the flushing of accumulated salts during each storm

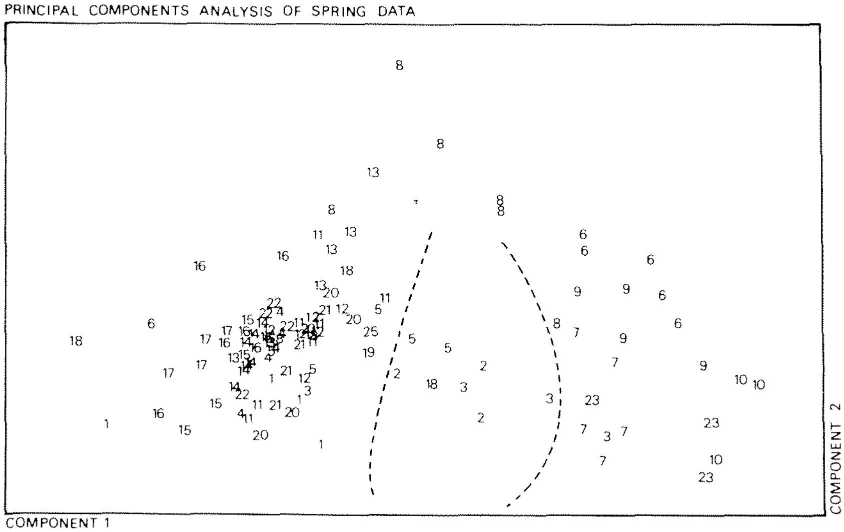

FIG.3 Scattergram for the first two axes of principal components analysis for springflow chemistry.

event. Finally, there is a third group of springs (2, 3 and 5), sited within the forest, which is transitional between the other two.

There is little variation along the second axis of the scattergram, the majority of points plotting in the lower half. Only springs 8 and 13 have high component II scores and these are related to high silica concentrations which were always greater than 9.5 mg l^{-1} at these sites. The grouping of the springs seems therefore to depend on the vegetation through which the water has passed. In particular, the forest springs have higher conductivities and concentrations of sodium, magnesium and chloride as a result of greater evapotranspiration and enhanced atmospheric entrapment.

STREAM WATER CHEMISTRY

Study of the interactions between solute sources and runoff dynamics is fundamental to an explanation of the variation in stream chemistry. Delayed flow, the slow movement of water through the regolith, is the dominant process by which water moves to the stream in the study basin and is responsible for baseflow which predominates for most of the year. The quickflow component makes only a minor contribution to flow in the Narrator basin, ranging from 2% in summer to 10% in winter. Seasonal variation in the stream chemistry can be related to the interaction of solute and runoff processes acting throughout the year. River chemistry is determined by the quantity of salts derived from atmospheric and weathering sources and the extent to which these inputs are diluted by the volume of discharge.

Sodium levels in the stream were higher in the summer although the atmospheric inputs were at their lowest. The high concentrations reflect less water moving through the system and a higher rate of weathering of plagioclase in the summer months. At this time, chloride levels reach a minimum similar to the concentration in bulk precipitation. Silica exhibited a pattern of increasing concentration through the year, reaching a peak in late August/early September, which coincides with the rise in silica in the springs. As in the case of sodium, this trend may be ascribed to long residence time and high weathering rates in summer. A secondary peak was monitored in December/January and was also present in a number of springs. This feature may be related to higher silica concentrations in quickflow and also may reflect the expansion of wet areas on the plateau and in the valley and the subsequent leaching of silica from the decaying litter layer.

Principal components analysis of stream chemistry

PCA was used to summarize the major sources of variation in the stream chemistry. The data set of 365 samples taken from the exit of the drainage basin was subsampled systematically and reduced to 52. The seven chemical measures for stream water (Table 1) plus conductivity were subjected to the analysis. The first three components explained 60% of the variance (Table 5). Investigation of the loadings reveals that components I and II, which explain 44% of the variance are dominated by sodium, magnesium and chloride. Temporal variation in stream chemistry is therefore mainly the result of

TABLE 5 Highest component loadings on the first three principal components of stream water chemistry

COMPONENT I	*Variance explained*	*24%*
Sodium		*0.579*
pH		*0.551*
Chloride		*0.316*
Magnesium		*0.309*
COMPONENT II	*Variance explained*	*20%*
Chloride		*0.571*
Silica		*-0.473*
Magnesium		*0.438*
COMPONENT III	*Variance explained*	*16%*
Conductivity		*-0.646*
Calcium		*0.476*
Silica		*0.361*
Total variance explained:		*60%*

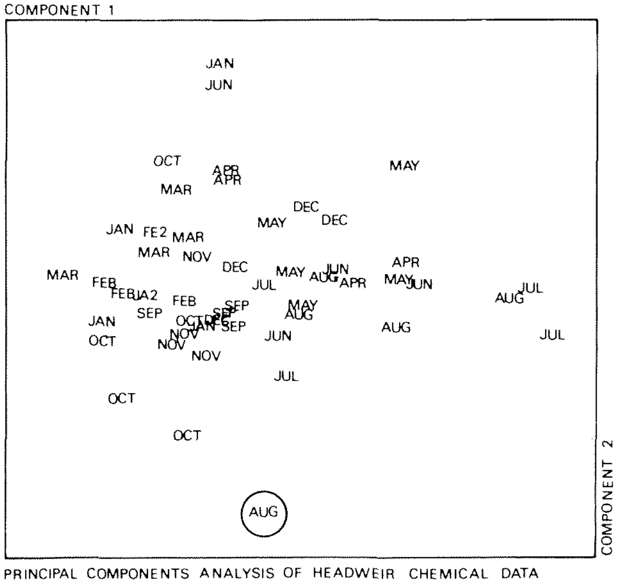

FIG.4 Scattergram for the first two axes of principal components analysis for stream water chemistry.

changes in marine derived ions. In addition, hydrogen is highly loaded in the first component and silica in the second, which suggests that weathering processes are also fundamental. Component III has high loadings for conductivity, silica and calcium. Conductivity is significantly correlated with the marine derived ions, whereas silica and calcium are both weathering derived. Component III, therefore, is also infuenced by solutes from both sources, and solute variation in the Narrator Brook is the result of seasonal trends in both internally and externally derived ions.

The results of the PCA are presented in Fig.4 which plots the component scores on axes I and II, classified according to season, as a scattergram. Component I scores are a measure of sodium, pH, chloride and magnesium, and values were high in summer (July and August) when precipitation inputs were low and the residence time for the water was high. Conversely, dilution by more water moving rapidly through the system and the greater amount of precipitation directly entering the channel resulted in low component I scores during winter months. Samples associated with high component II loadings such as those collected in January, possessed high chloride and magnesium concentrations but low silica levels. In winter months, high rainfall inputs from depressions crossing the study area imported large amounts of chloride and magnesium but diluted silica levels. Anticyclonic weather in the summer period was associated with a decline in chloride levels but a rise in silica concentrations. These trends were exacerbated by the occurrence of summer storms, such as the event of 29 August 1977 circled on Fig.4, when the increase in silica, for example, was the result of flushing of accumulated salts as various wet weather pathways came into operation.

CONCLUSIONS

In the study period, 90% of the solute load entering the study basin from the atmosphere was derived from marine sources and only 10% had a terrestrial origin, which reflects the proximity of the Narrator Brook to the sea. In terms of stream output, the proportions of solute load contributed from marine and terrestrial sources change to approximately 70% and 30% respectively. Silica is an important component of the load derived from terrestrial sources, and despite the very low amounts of calcium present in the granite bedrock (0.55% as CaO), this ion represents 10% of the weathering loss and is highly mobile.

The method of PCA has proved useful in determining the factors controlling solute composition and has also facilitated the identification of groups of points with similar characteristics. The relationship between PCA and other related methods of factor analysis, as applied by Reid *et al.* (1981), is to be investigated further.

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