Dissolved Loads of Rivers and Surface Water Quantity/Quality Relationships
(Proceedings of the Hamburg Symposium, August 1983). IAHS Publ. no. 141.

Stream solute behaviour in the River Exe basin, Devon, UK

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ABSTRACT The major findings of a long-term study specifically designed to investigate stream solute levels in the sizable river network (1500 km^2) of the Exe basin, Devon, UK are reported and reveal considerable variability and complexity of behaviour in space and in time. Marked spatial ranges and patterns of baseflow solute levels are apparent, but details of spatial variation and the controlling factors responsible differ between individual solute parameters. Temporal solute behaviour, in terms of annual regime and general response to discharge fluctuations, also exhibits considerable variety between different stations and solute parameters. Detailed monitoring of tributary streams has revealed strong differences in the responses of individual ions both within and between storm events, and complexity of solute behaviour is compounded at mainstream sites by aggregation and transmission processes. Studies of water composition at tributary and main channel stations are thought to offer considerable scope for further understanding of stream solute behaviour in the study basin.

Comportement des matières en solution dans les eaux du bassin de la rivière Exe, Devon, RU
RESUME On rend compte ici des constatations principales faites à la suite de recherches à long terme conçue pour étudier les niveaux de matières en solution dans les eaux du réseaux assez important (1500 km^2) du bassin de la rivière Exe, Devon, RU. Elle révèle une variabilité considérable et une grande complexité dans le temps et dans l'espace. Une répartition spatiale bien marquée et des schémas types de niveaux de concentration des constituants en basses eaux sont bien apparents, mais les détails des variations et les facteurs conditionnels different suivant les divers paramètres de la solution. Le comportement de l'ensemble des matières en solution sur le plan des variations temporelles, en ce qui concerne le régime annuel et la réponse la plus courante aux fluctuations de débits montre aussi une grande variété entre les stations étudiées et les paramètres de l'ensemble des matières dissoutes. La surveillance minutieuse des cours d'eau tributaires à mis en évidence de fortes différences dans les réponses des ions individuels à la fois pendant les averses et entre les averses et la complexité du comportement des matières dissoutes est

combinée aux sites principaux par des processus et cumuls et de transmission. Les études de la composition de l'eau aux stations des tributaires et du cours d'eau principal présente une grande partie pour une meilleure compréhension du comportement des matières dissoutes dans le bassin étudié.

INTRODUCTION

Over the past 30 years interest in stream solute behaviour has grown enormously (Walling, 1980a), and during this period increased efforts have been made not only to document nationwide variations of water chemistry in major rivers (e.g. Brown *et al.*, 1982; Emmeneger, 1982), but also to investigate in research basins the hydrological and other processes controlling stream solute levels (e.g. Likens, *et al.*, 1977; Reid *et al.*, 1981; Johnson & East, 1982). However, in Britain and in many other countries few studies have attempted to link the results from small basin investigations to the findings obtained at mainstream sites. This lack of attention partly reflects a general disparity in objectives set, personnel involved and techniques employed between the work of statutory authorities, which emphasizes routine collection of water quality data for surveillance and monitoring purposes (Rodda, 1980), and the research efforts of universities and other establishments which are often orientated to the testing of specific and detailed hypotheses of solute behaviour but lack continuity in space and time. Furthermore, although solute variations have been researched for sites situated along larger rivers (Miller & Drever, 1977; Oborne *et al.*, 1980), few solute studies have been specifically designed to elucidate the functioning of a river network and to document the integration of tributary and mainstream behaviour.

The Exe basin, Devon, UK, provides an opportunity not only to link the results from small and larger drainage basins, but also to investigate the processes which control solute behaviour in a river network. This study basin (Fig.1) comprises an essentially unpolluted drainage area of approximately 1500 km^2, which exhibits a great variety of geological, topographical, land use and hydrometeorological characteristics, and over the past 10 years a network of monitoring stations has been specifically established to document solute behaviour at tributary and mainstream sites. The programme of research has involved the construction of permanent installations at gauging stations in order to continuously record fluctuations in specific conductance, a general parameter of background solute levels, and also to collect samples at frequent intervals linked to hydrological conditions for subsequent laboratory analysis of major cation and anion content. The latter objective has been effected by the use of purpose-built sampling equipment (Walling & Teed, 1971). In addition, specific exercises of manual river sampling, involving up to 500 sites on small tributaries for a single survey, have been undertaken to investigate spatial variations in solute levels within the Exe Basin as a whole and its sub-units. The aim of this paper is to provide a brief synthesis of the major findings to emerge from this research. Early work in the study basin was aimed to document the general magnitude and pattern of solute variations, whereas more

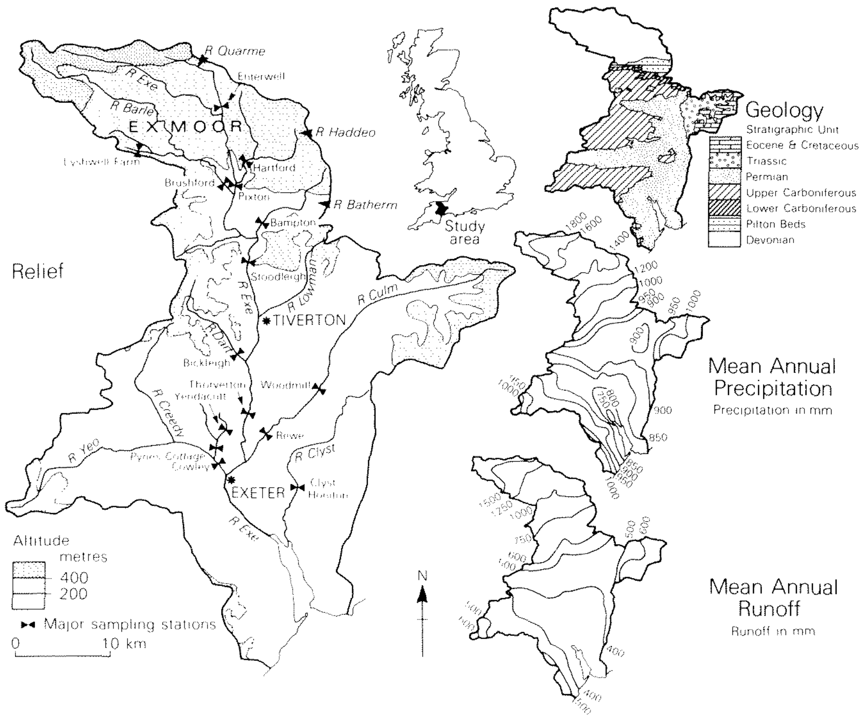

FIG.1 Characteristics of the study basin.

recent investigations have concentrated on detailed solute behaviour in tributaries and at mainstream sites.

MAGNITUDE AND PATTERN OF SOLUTE BEHAVIOUR

Spatial variations

Spatial sampling exercises, conducted over short time periods to ensure stability of flow levels and to avoid the consequences of fluctuating discharge for solute concentrations (Gregory & Walling, 1973), have revealed a large range and clear pattern in the solute levels of tributaries across the Exe basin (Webb & Walling, 1974; Webb, 1976; Walling & Webb, 1981). This finding applies not only to total dissolved solids concentration indexed by specific conductance, and to other parameters of general background water quality, such as pH, but also to the variation in concentration of individual ions. Figure 2 presents results for selected solute parameters which are based on separate spatial surveys completed during two periods of low flows in June 1979 and June 1980, but are also typical of many other sampling exercises undertaken in the study basin. The maps for nitrate reveal very similar patterns for the 1979 and 1980 surveys, and it has been generally found that the range and distribution of low flow solute levels are essentially stable from year to year. Furthermore, it is apparent from Fig.2 that the spatial patterns of pH, total dissolved solids and cation and anion content have many broad similarities, so that acidic waters of low solute concentration are typical of northwestern Exmoor, whereas more strongly alkaline runoff containing greater dissolved material is characteristic of the eastern and southern parts of the basin. In detail, however, there are differences between individual solute parameters in both the range and distribution of stream concentrations. Calcium content,

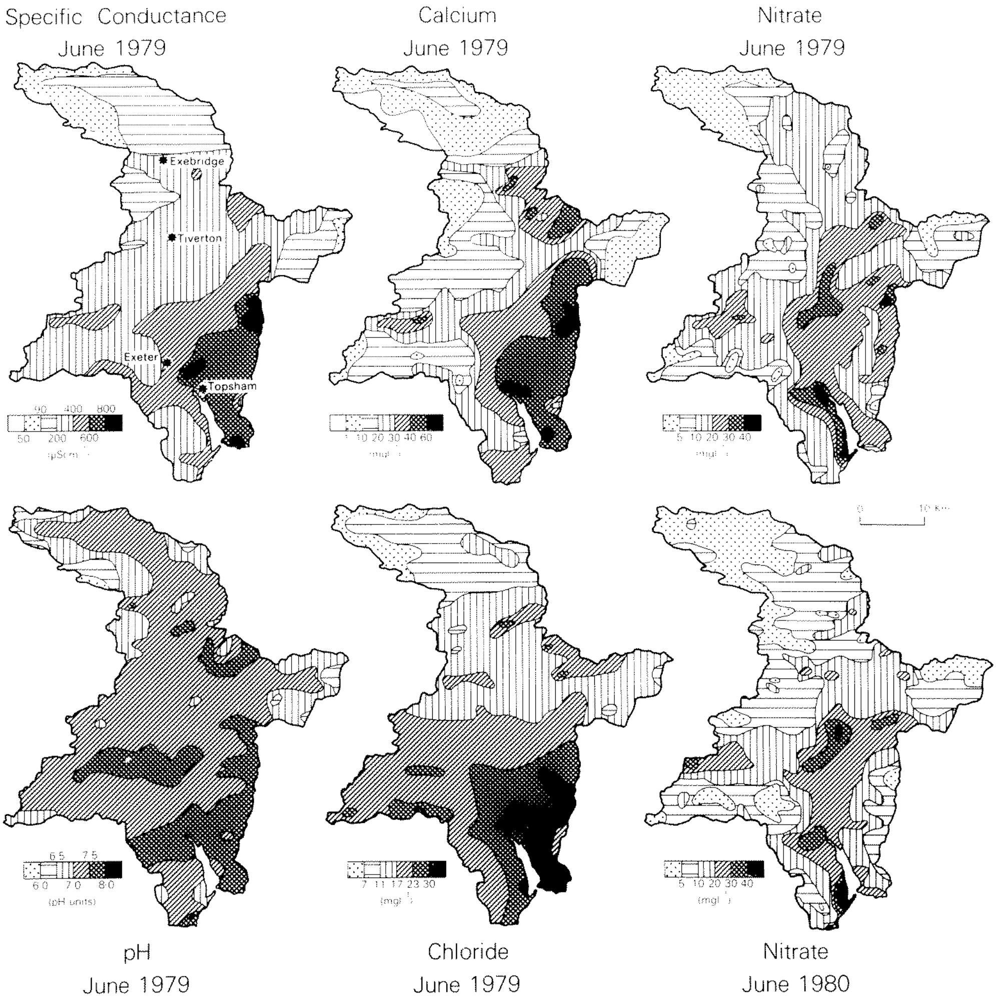

FIG.2 Spatial variation of baseflow solute levels in the study basin.

for example, is more varied than that of chloride, whereas the occurrence of high solute concentrations along the eastern margin of the drainage basin is not so well developed for nitrate as in the case of some other solute parameters (Fig.2).

The general and specific characteristics of solute patterns reflect a number of environmental controls, and in broad terms solute levels in the study basin can be related to geological, land-use, topographical and hydrometeorological conditions (Walling & Webb, 1975; Webb, 1980). Total and individual solute concentrations are lowest in upland areas which are underlain by resistant Devonian slate and sandstone lithologies, carry a cover of grass or heather moorland and experience high annual precipitation and runoff totals (Fig.1). Solute levels generally reach a maximum in lowland agricultural areas which are underlain by post-Carboniferous rock

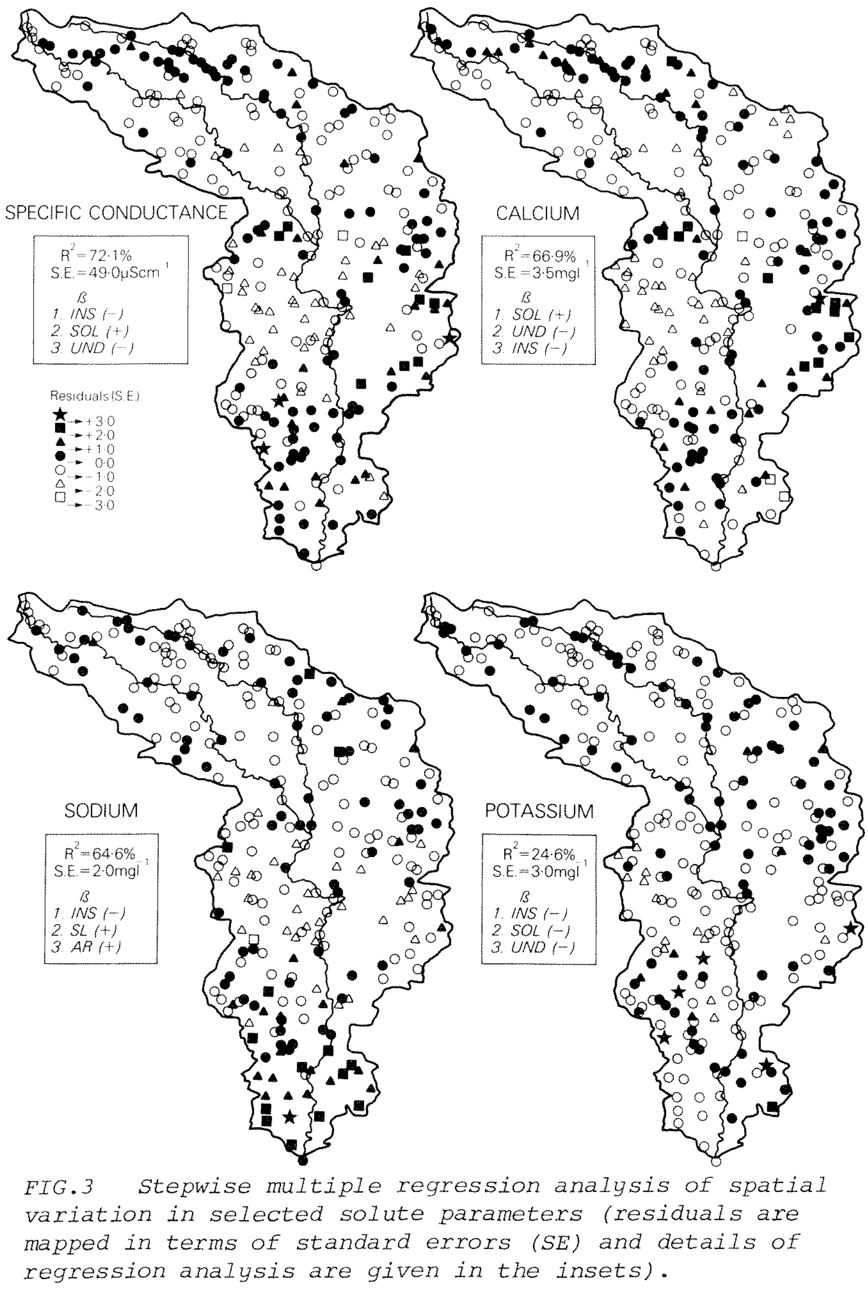

FIG.3 Stepwise multiple regression analysis of spatial variation in selected solute parameters (residuals are mapped in terms of standard errors (SE) and details of regression analysis are given in the insets).

types and have lower precipitation and runoff. Different environmental controls tend to vary simultaneously across the Exe basin and to have a mutually reinforcing influence on solute patterns, but there is also some evidence that individual solute parameters are sensitive to different suites of controlling factors and therefore can be predicted with varying degrees of success from information on drainage basin characteristics (Webb & Walling, 1980; Webb, 1983). Figure 3 summarizes the results from four stepwise multiple regression analyses employed to investigate and predict baseflow levels of total and individual solute content in the middle and upper part of the study basin (601 km^2) above the South West Water gauging station at Thorverton. The dependent variables in these analyses comprise solute data for samples collected from 270 sites during a short lowflow period in September 1973, and information on the percentages of insoluble and soluble rock types and undisturbed and intensive agricultural land uses, on the occurrence of significant urban areas and on area and slope for the drainage basin above each sampling station provides a set of seven independent variables. It is apparent from the values for explained variance (R^2), which range from more than 70% in the case of specific conductance to less than 25% for potassium, that the set of drainage basin characteristics varies in its ability to predict the spatial patterns of the different solute parameters. Consideration of the three most influential independent variables (Fig.3) in each analysis, on the basis of beta coefficients (Davis, 1973), also indicates that different factors are of importance for individual solute parameters, although it is clear that geological and land-use conditions have a greater impact than topographic factors and in turn than the presence of urban areas, which has only a minimal influence in this predominantly rural drainage basin. The signs associated with the independent variables, as might be expected, show that solute concentrations are inversely related to the proportion of relatively insoluble Devonian rock types (INS) in the drainage area, but also indicate an inverse relationship with the percentage of undisturbed land uses (UND), which reflects the absence of soil disturbance and fertilizer application in moorland and woodland areas. An increase in the proportion of Pilton beds, Lower Carboniferous strata or Permian rock types (SOL), which are the most calcareous and soluble major geological units in the Middle and Upper Exe basin, results in higher conductance and calcium levels. Basin slope (SL) and area (AR) are both positively related to sodium concentrations and may reflect respectively the tapping of deeper and more highly concentrated groundwaters in tributaries of greater relief (Ternan & Williams, 1979) and the incidence of more significant pollution at mainstream sites.

Further insight into the controls of spatial variation may be obtained from an analysis of residuals computed for each site in the study basin as the difference between measured solute concentrations and those predicted by the multiple regression equations (Fig.3). The pattern of residuals for calcium, emphasizes the role of rock and soil weathering in the supply of this ion to river waters, since areas of strong positive residuals correspond to the outcrop of particularly calcareous lithologies. In the north of the study basin, a band of positive residuals corresponds to the outcrop of the

Ilfracombe beds, which are a Devonian unit of calcareous slates and limestones, whereas strong residuals near to the confluence of the rivers Barle and Upper Exe and also in the east of the basin reflect the occurrence of limestone units in the Pilton beds and the Lower Carboniferous strata. A somewhat different pattern of residuals exists for sodium and may be related to the influence of atmospheric supply and hydrometeorological conditions on this ion. Chemical analysis of bulk precipitation suggests that much of the sodium content of river waters in the Middle and Upper Exe basin is contributed from the atmosphere and is originally derived from marine sources (Foster, 1979; Webb, 1980). Positive residuals occurring along the interfluve areas of the Exmoor upland may therefore represent preferential input of sodium to high ground which is relatively close to the coast and is in the path of the prevailing winds. The pattern of residuals for sodium also clearly shows a concentration of strong positive residuals in the southernmost portion of the study catchment (Fig.3) which is mainly accounted for by climatic conditions. The ratio of precipitation to evapotranspiration reaches a minimum in the vicinity of the basin outlet and leads to the enhancement of sodium levels in streamwaters as compared to precipitation by a factor of 2.2, whereas the equivalent figure for the northwestern part of the basin is only 1.2. A more random pattern characterises the distribution of residuals for potassium, and it is likely that the spatial variation of this ion in runoff reflects detailed differences of land use and agricultural practice in the drainage area above a sampling station. Very strong residuals occur at a few sites in southern tributaries and may represent contamination from agricultural sources such as slurry waste and the washings from livestock pens. These strong deviations are also apparent in the map for specific conductance (Fig.3), although the pattern of residuals for this parameter is very similar to that of calcium which is the major cation contributing to conductivity in the study area.

Temporal variations

The solute content of rivers not only displays spatial variation across the Exe basin but also exhibits fluctuations through time at individual stations in response to seasonal marches and more short-lived discharge changes (Walling, 1975). However, temporal behaviour is varied between individual parameters at a single station and also between sites for individual parameters. These features are apparent in the annual regime of solute levels, and weekly sampling at the mainstream site of Thorverton (Fig.4), for example, reveals fluctuations for calcium and sodium concentrations to be greater in amplitude than those for magnesium and potassium. These and other data for stations in the study basin (Webb, 1980) indicate that all the major cations have an annual march which, to a greater or lesser extent, is inversely related to the discharge regime. This relationship is most clearly developed for magnesium, but it is somewhat obscured for calcium by the effects of autumn flushing, winter ploughing and spring application of lime; for sodium by seasonal contrasts in the content of precipitation and the winter use of road salt; and for potassium by leaching from autumn leaf fall, biological uptake in the growing season and the random impact of

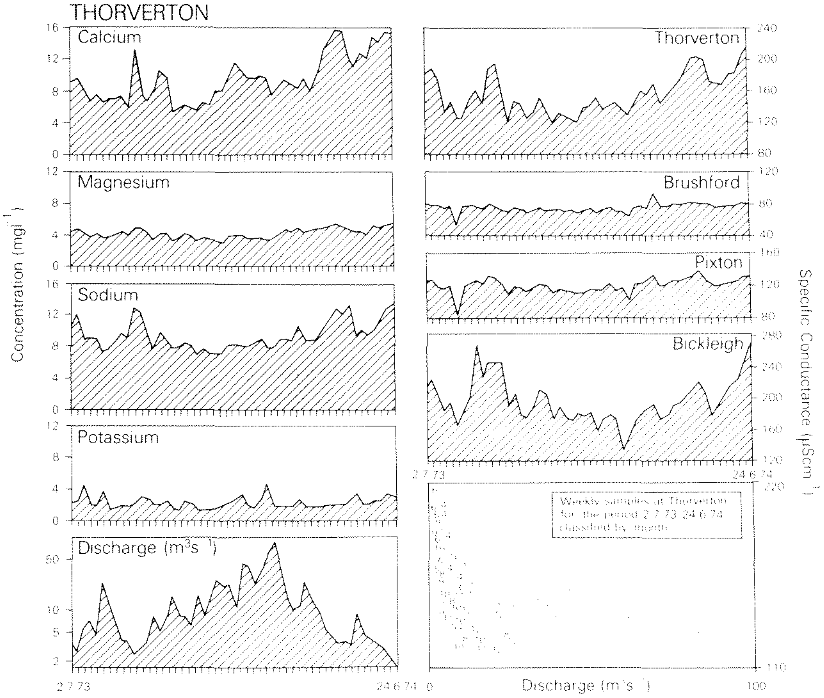

FIG.4 The annual regime of solute levels in the study basin.

storm events. Figure 4 also reveals considerable variation in the annual march of specific conductance levels at four sites in the study basin constructed from weekly samples. The amplitude and regularity of seasonal fluctuations is least marked at the stations of Brushford and Pixton which are situated on northern tributaries characterized by low total dissolved solids content. Higher specific conductance levels are typical of the mainstream at Thorverton and southern tributaries, such as the River Dart at Bickleigh, and produce a much more pronounced annual march in conductivity. Plotting and classification of solute levels against discharge provides no evidence for a clear annual hysteresis in solute content of the sort recognized by some workers in other environments (e.g. Gunnerson, 1967; Carbonnel & Meybeck, 1975), and a trend towards lower solute levels with increasing flow in winter months, as exhibited by specific conductance at Thorverton (Fig.4), is a more typical response in the study basin.

The general reaction of solute levels to flow changes during storm events has been investigated by establishing power function rating relationships between solute levels and discharge based on regular and storm-period sampling. In common with the results of many other investigations (e.g. Buckney, 1977; Feller & Kimmins, 1979), solute levels in streams of the study basin are typically diluted by increasing flows. However, plotting of the range in the slopes of the rating lines for specific conductance and the major cations in the standardized form advocated by Edwards (1973) evidences considerable variation between particular solute species and individual stations (Fig.5(a)). Magnesium concentrations exhibit strongest dilution with increasing flow and this behaviour is related to the occurrence of limited supplies in the soil and the ready leaching and depletion of the ion during storm events (Davies, 1971). In contrast, sodium levels are only weakly diluted in high flows and exhibit a narrow range in the slope of rating relationships across the study area. This response may be explicable by reference to supply of sodium from atmospheric sources which restricts the magnitude of dilution during storm events and to buffering mechanisms in the soil (Johnson *et al.*, 1969) which reduce the maximum concentrations attained under lowflow conditions. Rating lines for calcium

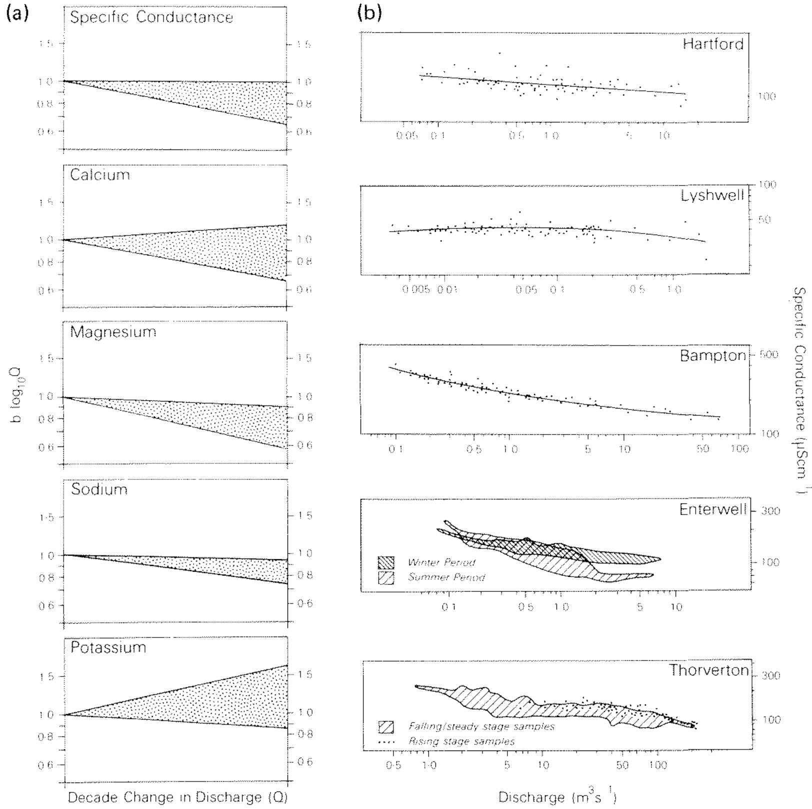

FIG.5 The range in the slope exponent, b, plotted in standardized form for solute concentration-discharge power functions in the study basin (a), and selected examples of more complex rating relationships (b).

vary considerably in slope and at some stations concentrations increase in higher flows. This behaviour is best developed for potassium; it occurs especially in catchments with appreciable moorland land use and is attributable to vegetation leaching by heavy rain and to release of potassium from organic horizons washed by surface flows (Waylen, 1979). Total solute levels, indexed by specific conductance, are generally diluted by increasing discharge

(Fig.5(a)), and although conductivity is affected by the varying behaviour of individual ions, the slope of the specific conductance rating line at individual sites is usually very similar to that of calcium which is the major cation component.

Variation in dilution responses between sites is systematically related to the magnitude of lowflow solute concentrations, since sites with more dissolved material in baseflow provide a greater potential for dilution by dilute storm runoff and, in turn, have steeper rating lines (Webb, 1980). Although concentration-discharge relationships can be generally approximated by a simple power function of the kind constructed for the sampling site at Hartford (Fig.5(b)), at some stations a simple polynomial curve on logarithmic coordinates appears to be more appropriate for taking into account certain features of temporal solute behaviour, such as virtually constant levels in low and moderate flows at Lyshwell and in high discharges at Bampton (Fig.5(b)). There is also clear evidence in some concentration-discharge plots for separate winter and summer rating relationships. At many stations, including Enterwell (Fig.5(b)), the rating line for the summer period is significantly steeper and reflects, amongst several factors, the influence of biological uptake, lower solute concentration in precipitation and flashier runoff response. A tendency for higher solute concentrations in samples taken during rising limbs of storm hydrographs is apparent at Thorverton (Fig.5(b)), and other sites. This effect is promoted by the flushing of previously accumulated soluble material in the early stages of a storm event (Walling, 1974) and was greatly exaggerated during the exceptionally heavy rainfall which ended the severe drought of 1976 (Walling & Foster, 1978; Walling, 1980b). Such phenomena complicate stream solute behaviour, and more recent studies in the Exe basin have focussed on detailed investigation of storm-period solute responses.

DETAILED SOLUTE RESPONSES

Tributary stations

Figure 6(a) presents results from automatic hourly sampling of a storm event in the Jackmoor Brook which in the complexity of solute behaviour is typical of many tributaries in the study basin. The various responses of different ions, which are not readily apparent from the record of specific conductance, include strong dilution of magnesium concentrations and a clear increase in chloride levels. Potassium concentrations exhibit a positive relationship with discharge but there is also evidence of through-storm exhaustion of potassium supplies, since concentrations recorded in the peak flows of 12 March are considerably higher than those associated with the higher discharges of the following day (Fig.6(a)). Responses for different ions are not always in phase with each other or with the storm hydrograph, and during the event at Jackmoor Brook minimum magnesium levels occur later than the discharge peaks and after the troughs in conductance levels. In contrast, nitrate concentrations increase throughout the storm but reach a maximum approximately 24 h after the peak discharge, and this timing reflects the arrival in the stream channel of a delayed throughflow component rich in nitrate (cf. Troake & Walling, 1975). Understanding of solute responses in tributary basins is made more difficult because patterns of behaviour vary between different stations (Walling, 1978) and through time at a particular site (Walling & Foster, 1975). An illustration of these complexities can be found in the nature of nitrate responses recorded at Bickleigh sited on the River Dart. A delayed increase in nitrate concentration (Fig.6(b i)) is typical of storms monitored at Bickleigh during summer and autumn months, but the time between peak flow and the attainment of maximum nitrate

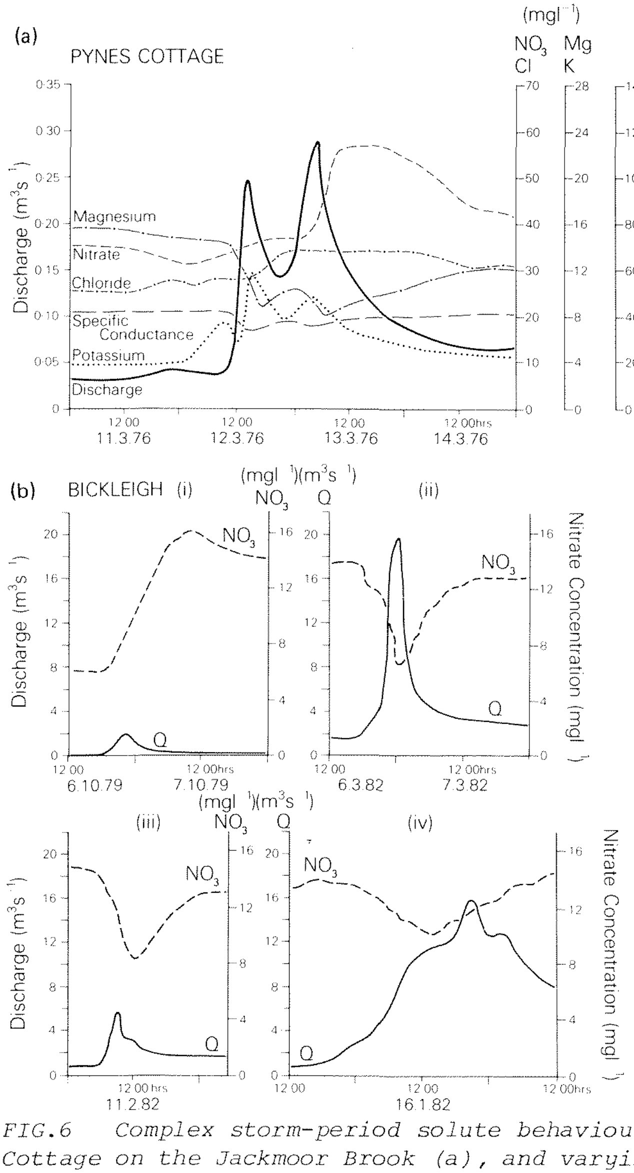

FIG.6 Complex storm-period solute behaviour at Pynes Cottage on the Jackmoor Brook (a), and varying nitrate responses to storm events in the River Dart at Bickleigh (b).

levels tends to be shorter than at Pynes Cottage, and this is tentatively attributed to steeper slopes and greater throughflow velocities in the basin of the River Dart. In the winter and spring period, storm events at Bickleigh exhibit rapid dilution of nitrate concentrations, but the timing of such responses varies greatly. Lead (Fig.6(b iv)), coincidence (Fig.6(b ii)) and lag (Fig.6(b iii)) relationships between chemograph troughs and hydrograph peaks have all been observed and many factors, including rates of mineralization and nitrification, storm hydrograph characteristics and antecedent soil moisture levels, are responsible for this varying behaviour.

As a consequence of the complex storm-period responses of individual ions, a clearer picture of water chemistry changes in tributaries during a storm event is often obtained by considering the evolution of water composition, which takes into account simultaneous variations in concentrations of the main constituents. Trilinear plotting (Piper, 1944) of major cation and anion components, expressed as percentages based on equivalent weight units, provides a convenient means of investigating through-storm changes in water composition, and results in this form are illustrated for a storm at Clyst Honiton on the River Clyst (Fig.7). This event produced a simple dilution

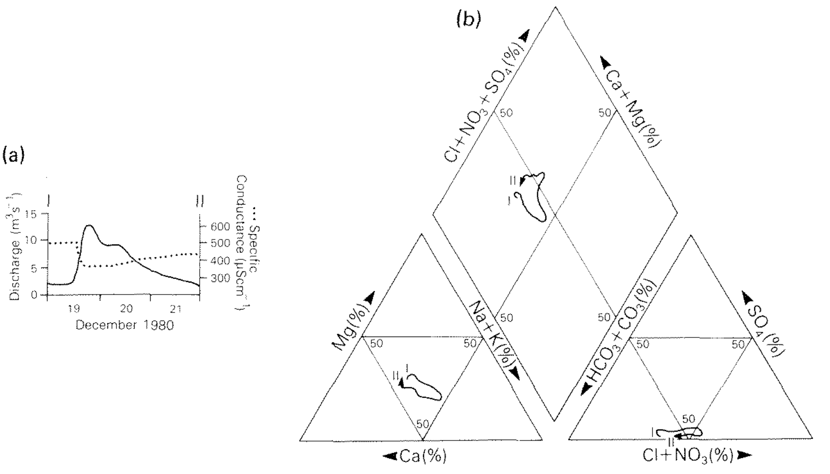

FIG.7 The response of specific conductance (a) and the evolution of water composition (b) during a storm event in the River Clyst at Clyst Honiton.

response in specific conductance levels (Fig.7(a)) but the trilinear diagram also reveals a distinct evolution in water chemistry (Fig.7(b)). Pre-storm baseflows were relatively rich in calcium, magnesium and bicarbonate, but during the early part of the hydrograph rise incoming drainage from road and other surfaces treated with de-icing salt promoted a rapid change to more sodium and chloride rich water types. This effect, however, was short-lived and disappeared by the time of the peak discharge, but water chemistry continued to evolve during the early stages of the flow recession in a direction away from pre-storm composition. This trend was related, in particular, to the strong dilution of bicarbonate compared with other anions and to an increase in nitrate concentrations following the hydrograph peak. It is also apparent from Fig.7(b) that river water had almost regained its pre-storm composition by a period of 60 h after the discharge rise.

Mainstream sites

The difficulties of interpreting stream solute behaviour are compounded at mainstream sites in the Exe basin by the influence of aggregation and transmission processes. The precise nature of

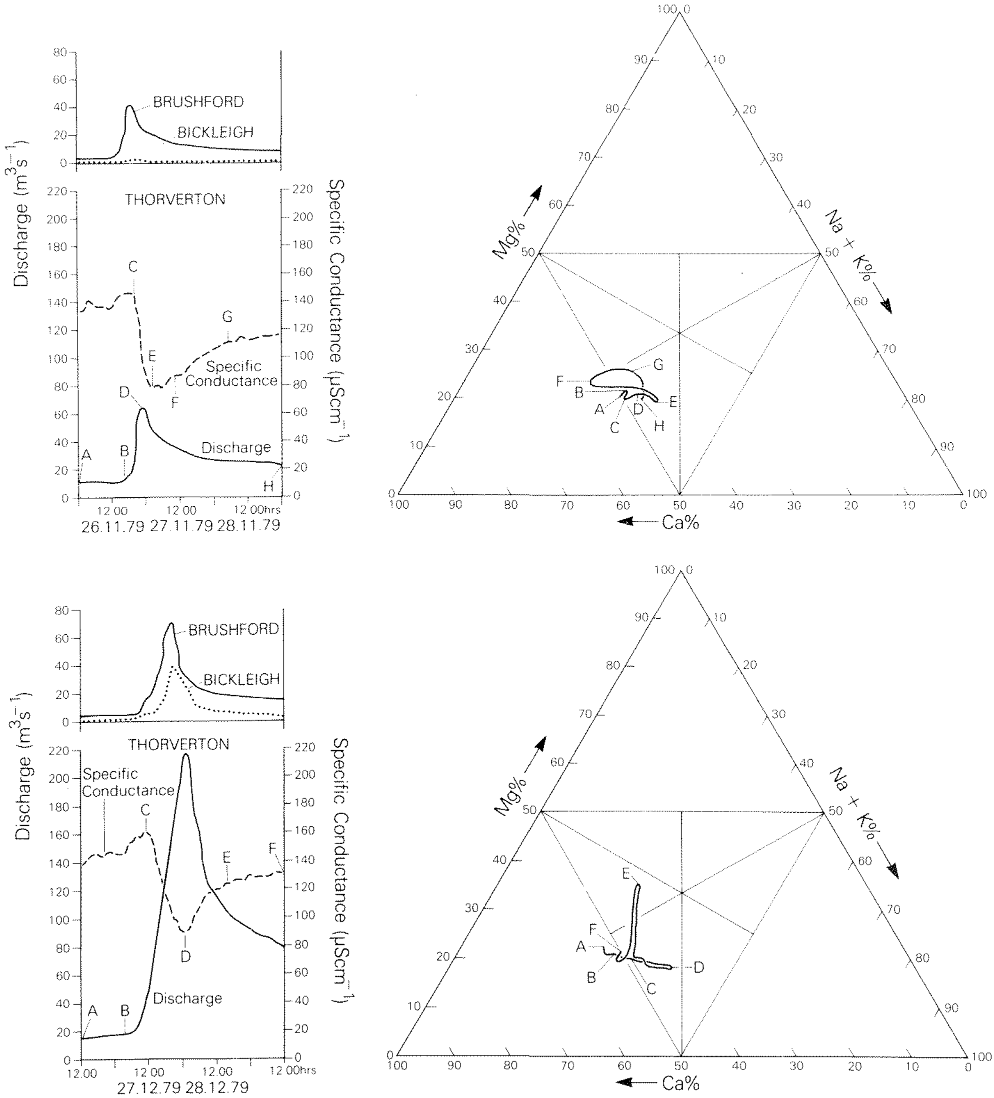

FIG.8 Flow contributions from upstream tributaries, specific conductance response and change in cation composition for two contrasting storm events at the mainstream station of Thorverton.

downstream solute response reflects the timing and distribution of storm events across the sizeable drainage area which, in turn, determines how the varying and often complex hydrological and chemical responses of upstream tributaries are aggregated in the main channel (Walling & Webb, 1980). Flood routing mechanisms and flood plain storage (Glover & Johnson, 1974; Webb & Walling, 1982) involved in the downstream transmission of flows through a river network will also modify solute behaviour and particularly the timing of the chemograph in relation to the hydrograph.

The influence of these additional factors is apparent in the records for two events which occurred late in 1979 (Fig.8). The storm of 26-28 November, which produced a discharge peak of 65 $m^3 s^{-1}$ at the mainstream site of Thorverton, was generated mainly by runoff from Exmoor so that a substantial hydrograph was recorded for the River Barle at Brushford but only a very small rise was monitored in tributaries to the south of Exmoor such as the River Dart at Bickleigh. In contrast, the storm of 26-28 December was a major event in which peak flow at Thorverton approached 220 $m^3 s^{-1}$ and high flows occurred in all upstream tributaries. Minimum specific conductance levels recorded at Thorverton were lower in the November event, despite much smaller peak flows, and this behaviour not only reflects the greater proportion of runoff supplied from less strongly mineralized northern tributaries during the first event, but also would be very difficult to explain without reference to the spatial origins of the downstream discharge hydrograph. Furthermore, the trough in specific conductance values in the November event occurred after the passage of the hydrograph peak and this timing can be attributed to a kinematically induced lag effect which was not present during the different conditions of the December storm.

The sequence of events which generate hydrographs and chemographs at downstream sites in large and heterogeneous drainage areas are so varied that each storm is characterized by unique solute behaviour which is related to the history of the event, although certain general patterns are evident. This individuality of solute behaviour is apparent in the changes of cation composition of river water which occurred at Thorverton during the two storms of November and December 1979, discussed above, and appear as unique "signatures" on a triangular plot derived from the major cation concentrations expressed in equivalent weight units (Fig.8). The detailed interpretation of such signatures in relation to upstream events appears to offer considerable scope for an improved understanding of stream solute behaviour in the study basin.

CONCLUSIONS

A long-term study in the Exe basin has revealed considerable complexity of stream solute behaviour which the authors consider to be typical of many mesoscale drainage systems. Investigations of spatial and temporal behaviour have highlighted contrasts in patterns and controls between individual solute parameters and between particular tributaries of the study area, which are aggregated and transmitted by the river network to determine downstream solute responses. It is suggested that future studies in the study basin and elsewhere would benefit from greater attention to the integration of different ion responses in terms of water composition and from further investigation and modelling of the linkages between upstream and downstream solute behaviour.

ACKNOWLEDGEMENTS The authors gratefully acknowledge the support of the Natural Environment Research Council for solute studies in the Exe basin and also are indebted to South West Water for the provision of discharge data.

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