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Variation in solute concentration within the River Almond and its effect on the estimated dissolved load

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ABSTRACT Solute concentrations monitored over one complete year in the River Almond, Scotland, ranged between 47 and 88 mg l^{-1}. The responses to water level and seasonal variations were evaluated and separate summer and winter solution load rating curves established. Generally summer concentrations were higher than those of winter and a simple dilution model holds for the River Almond, with anticlockwise loop patterns of covariation of concentration with discharge.

Variations dans la concentration en matières dissoutes dans la rivière Almond et leur effet sur la charge en matières dissoutes estimée
RESUME Les concentrations en matières en solution observées pendant plus d'une année dans la rivière Almond, Ecosse, sont comprises entre 47 et 88 mg l^{-1}. Les réponses aux variations du niveau de l'eau et aux variations saisonnières ont été évaluées et on a mis au point des courbes s'étalonnage séparées de la charge en matières dissoutes pour l'été et l'hiver. Généralement les concentrations en été sont plus élevées que celles en hiver et un modèle simple de dilution pour la rivière Almond avec un schéma en boucle en sens inverse des aiguilles d'une montre de la covariation de la concentration avec le débit.

INTRODUCTION

During the last 20 years, much attention has been devoted to the movement of solid particles in streams but less research has been undertaken on the dissolved load. In most rivers, the dissolved load is an important part of the material carried and so there is a substantial need to study solute production and transportation. Such studies will improve our understanding of the geomorphological significance of the movement of materials in solution, the mechanisms controlling solute production, the significance of solute removal in denudation and the assessment of fertilizer loss from agricultural land.

The dissolved load passing gauging stations on the principal rivers of the Tay basin has been estimated over the three successive water years 1972/1973 (dry), 1973/1974 and 1974/1975 (average wet years) (Al-Jabbari *et al.*, 1980). The aim of this study was to examine the interrelationship of solute concentrations and flow, and their responses to the seasonal changes in the River Almond catchment.

GEOLOGICAL SETTING

The River Almond is a minor right bank tributary of the River Tay, whose 6500 km^2 basin dominates the central Grampian Highlands of Scotland. The drainage basin of the Almond is 176 km^2 in area, rises to approximately 900 m a.m.s.l. and joins the Tay at the limit of the tidal intrusion of the Tay Estuary. The basin is aligned east to west, and crosses the Highland Boundary Fault, which separates Dalradian metamorphic rocks in the northwest from mixed assemblages of sedimentary and volcanic rocks of the Devonian Lower Old Red Sandstone to the southeast (Fig.1). The former are largely impervious and of low porosity, whereas the latter are both pervious and porous. Bedrock is exposed in many of the higher parts of the basin, but most of the area is mantled with drift deposited during repeated glaciations of the Pleistocene period. Tills principally occur in the uplands, but many lower areas, especially the valley floors, are blanketed by outwash sands and gravels deposited during deglaciation. In the lowermost reaches the valley is underlain by varied laminated "Arctic" silts which accumulated in the headwater sectors of a largely land-locked marine inlet formed during ice retreat and before the effects of crustal downwarping had been removed at the end of the Pleistocene (McManus, 1967).

Most of the upland, which comprises 71% of the total basin, is used for rough grazing, mainly for sheep and deer. The tills, silts, sands and gravels of the lower ground yield soils valuable for a variety of agricultural purposes. Cultivated grasslands occupy 14.8% of the basin, with grain production accounting for a further 10.2% of the land. Woodlands are of minor importance (1.2%) and root crops are grown in only 2.8% of the area

HYDROLOGY

Records of flow of the River Almond based on staff gauge readings were taken for over 20 years before the installation of an autographic water level recorder, in October 1972, at the present Almondbank gauging station (National Grid Reference: NO 067 258) which lies 20 m above Ordnance Datum and some 3 km above the confluence with the Tay. The rainfall data provided by three monthly and four daily raingauges (HM Meteorological Office, Edinburgh) for the relatively dry water year 1972/1973 show that the average rainfall was 673 mm, but in the following "wet" years 1973/1974 and 1974/1975 the rainfall input was more than doubled to reach 1453 mm. The rainfall is at its minimum in the summer months of May, June and July. During the dry year 1972/1973 no less than 40% of the annual precipitation fell in this period, whereas during the wetter years 1973/1974 and 1974/1975, summer

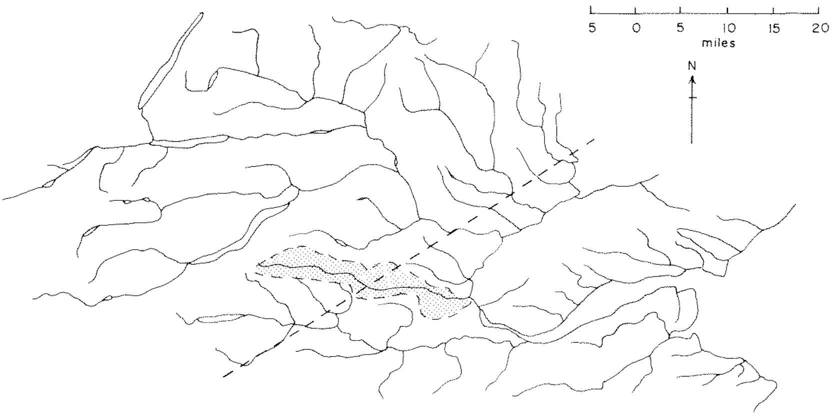

FIG.1 The drainage area of the River Almond (stippled) in relation to the Tay basin (dashed line represents the Highland Boundary Fault).

rainfall accounted for only 15% of the annual total.

The greatest instantaneous flow on record occurred in January 1974 (138.4 m^3s^{-1}) and the least was measured in July 1975 (0.49 m^3s^{-1}), whereas the mean daily maximum discharge was 82.6 m^3s^{-1} (January 1974) and the minimum was 0.49 m^3s^{-1} (July 1975). The records reveal that the River Almond is very flashy, and the discharge may increase by as much as 30 m^3s^{-1} in less than one hour. The total loss in the water budget over the catchment ranged between 29% (dry year) and 34% (average wet year) of the total annual precipitation.

FIELD WORK

In order to examine the fluctuation in the dissolved matter concentration, a series of water samples were collected from a mid-stream position, by means of a suspended bottle sampler operated by hand from a bridge near the Almondbank gauging station during a wide range of flow discharges. Sampling at weekly intervals throughout one complete year ensured that the water was examined during a range of discharges, as suggested by Hem (1959). The water samples were kept in airtight 250 ml polythene bottles which were completely filled with river water so that no air remained within the bottle. Polythene bottles were used because they produce minimal chemical contamination of the water. Information on water discharge at the time of sampling was determined from the water level records of the nearby gauging station. Preliminary site surveys revealed that, unlike some rivers, there were no differences in solute concentrations across the river nor through the water column. This is a result of well mixed turbulent flow in the river.

LABORATORY ANALYSIS

Of the many methods in use for evaluating the dissolved solids concentration in river water, gravimetric methods were used throughout this investigation for reasons of simplicity and convenience in handling large numbers of samples. The method recommended by Guy (1970), and used by Imeson (1970), involves the withdrawal of a 100 ml sub-sample from the water by pipette followed by oven drying in two stages. The first phase of drying took place at 60°C and the second phase (the last few millilitres) at about 90°C to prevent loss of the water due to boiling. After drying, the beakers were removed to a desiccator, cooled to room temperature and weighed on a balance reading to four decimal places. Prior preparation involved filtration through 0.45 μm pore filter paper to eliminate suspended sediments and organic matter. For some samples separation of colloidal matter was acheived by centrifuging at 5000 r.p.m. Distilled water was used to check that no material was taken into solution from the filter papers themselves. A series of sub-samples revealed that this method gave a good degree of reproducibility.

RESULTS AND DISCUSSION

The plot of solute concentration against flow discharge for the study period (Fig.2) reveals that the concentration values varied within a narrow range from 47 to 88 mg l^{-1}. The dissolved solids level in the River Almond during low flows was about double that during floods. However, these values are similar to the concentrations of about 50 mg l^{-1} reported from rivers in humid temperate regions of North America (Langbein & Dawdy, 1964).

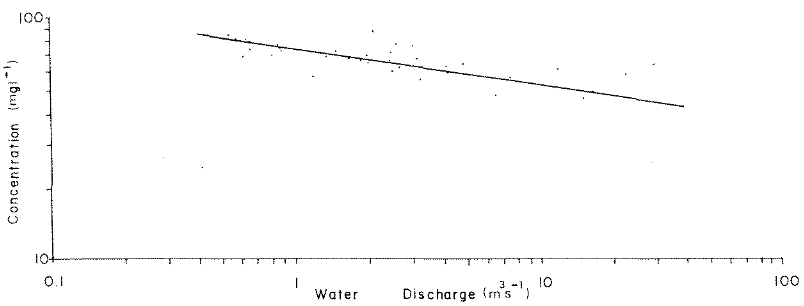

FIG.2 Dissolved matter concentration-water discharge relationship at the Almondbank gauging station.

Investigations of temporal variation in solute response to flow changes provide an insight into the processes operating. The solute concentration-streamflow relationship is often used to provide a general representation of this temporal behaviour (Walling, 1978). There is an inverse relationship between the solute concentration and water discharge at Almondbank. During high discharge, the salts have no time to become concentrated, so that the solute strength is less than that during low discharge due to dilution. This relationship has been widely recognized (Durum *et al.*, 1960; Livingstone, 1963; Gibbs, 1970; Meybeck, 1976; Walling, 1978), and is particularly evident in arid areas. The data points are scattered within a

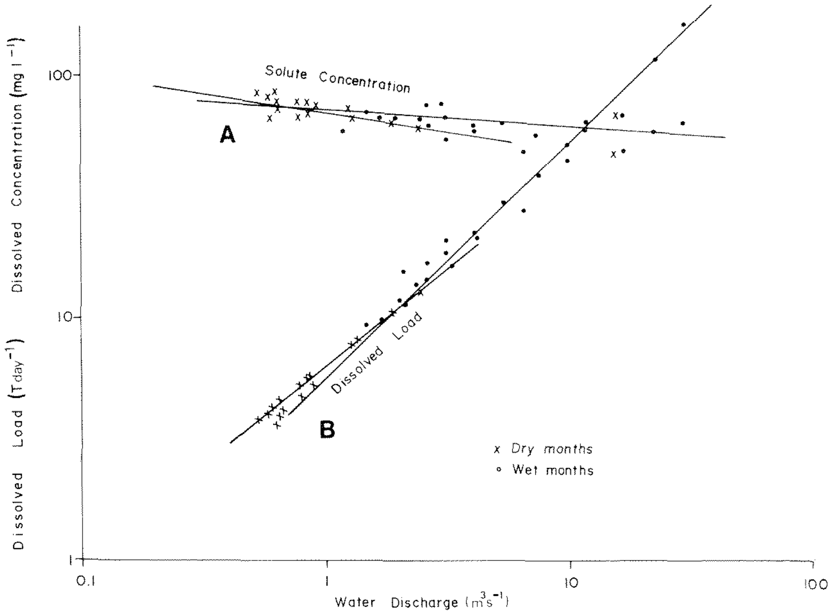

FIG.3 Seasonal variation in (a) dissolved matter concentration-water discharge and (b) dissolved load-water discharge rating relationships.

narrow field around the best fit curve and a linear relationship is well defined. In this way solutes are seen to behave very differently from suspended sediment at the same station, for which the covariation plot with discharge reveals data points scattered over a wide field around the best fit line (Al-Ansari *et al.*, 1977). This basic contrast is due to the differences in the response time of the various loads and to the nature of the factors controlling their concentration. The general solute levels associated with this site reflect solute availability and controls. The slope of the relationship is partly conditioned by the range of flows experienced within the catchment and the contrast between runoff with long and short residence times. This, in turn relates to the buffering capacity of soil and bedrock as well as solute availability (Walling, 1978).

The data collected from Almondbank have been separated into two sets, one representing the dry period of the year and the other the wet period. Plotting the solute concentration for each period against water discharge (Fig.3) reveals that the dry summer period is characterized by higher values, less scattering and a much stronger correlation with flow levels than the winter period. In winter the concentrations are lower and the points more scattered through the irregularities of higher discharges. Both summer and winter data sets exhibit similar inverse linear relationships with discharge. The seasonal variation in solute concentration results from the greatly increased intensity of the rainfall during the winter period when there is little opportunity for material to be taken into solution. The summer and winter period relationships intersect at a very low discharge (1 m^3s^{-1}), and the solute concentration for any specific discharge greater than this value is higher on the winter curve than the summer curve.

A similar seasonal pattern emerges when dissolved load rating curves are established for the same data (Fig.3), and the rating relationship used in the estimation of the dissolved load should therefore be that for the appropriate season. The total dissolved solids load passing the Almondbank gauging station during the average wet water year 1974/1975, estimated from the general dissolved load rating curve (the best fit line through the data points), was 7326 tons. Using the summer and winter curves, in separate calculations, the total annual dissolved load is computed at 6749 and 8424 tons respectively, which represents 8% less and 15% more than the estimate based on the general curve. The difference between the load estimated at this site using the summer relationship and the winter curve was 20%. Thus, when estimating the solute load at any site it is important to use the best fit rating curve for the appropriate range of conditions at that station, and, in order to obtain the closest approximation to the dissolved load actually transported, it is recommended that rating relationships should be established on a seasonal basis or for even shorter periods. Both the solute and suspended sediment rating curves show direct linear relationships with water discharge. However, the data points for the suspended sediment relationship are more widely scattered around the fitted line. Minimal suspended sediment concentrations occur at low discharges. The association of high solute concentration with low flow discharge increases the importance of dissolved solids transport during the summer period, and in some years up to 44% of the total annual solute load is carried in the summer months.

Analysis of the variation in annual loads in the study period (Table 1) reveals that about double the dissolved load was transported during each of the wetter water years than during the dry year. A greater dissolved load was carried during the water year 1974/1975 than during the wet year 1973/1974, and this clearly reflects the influence of annual runoff totals on dissolved load transport. Examination of the dissolved and suspended loads carried to the River Tay during the study period shows that the dissolved load was higher than the suspended load during the dry water year 1972/1973, while the situation was reversed in the wet water years of 1973/1974 and 1974/1975. This variation is mainly attributed to the flow conditions in the dry year which are characterized by a high concentration of salts and low suspended sediment concentration in the river water. It is apparent from monthly and seasonal load data that a major part of the transport of dissolved material takes place in the wet season of the year, while it is almost constant during the dry season. Even so, a high percentage of the dissolved load was transported during the dry season reflecting the importance of this part of the year. The data show that the percentage of total dissolved load transported during the dry period of the dry year is much higher than that in the dry period of the wet year (Table 1). The results also indicate that the dissolved load discharge is higher than the suspended sediment discharge during the summer period, while the situation is reversed in winter. Dissolved material is continuously transported throughout the year, but the suspended sediment is transported in significant amounts only during winter.

TABLE 1 Annual suspended, dissolved and bed loads discharge passing Almondbank gauging station (all values in tons, W.P. = wet period and D.P. = dry period, the bed load in this investigation was estimated as 10% of the suspended load)

Water year	*Suspended load*		*Dissolved load*		*Bed load*
1972/1973 (dry)	*2754*	*91% (W.P.)* *9% (D.P.)*	*5125*	*56% (W.P.)* *44% (D.P.)*	*275*
1973/1974 (wet)	*8397*	*84% (W.P.)* *16% (D.P.)*	*7183*	*74% (W.P.)* *26% (D.P.)*	*839*
1974/1975 (wet)	*10325*	*86% (W.P.)* *14% (D.P.)*	*7326*	*78% (W.P.)* *22% (D.P.)*	*1032*

A plot of solute concentration and water discharge through time (Fig.4(a)) reveals a seasonal variation in solute levels of the River Almond. Between April and September the solute concentrations were not only greater but also more stable than the levels during the rest of the year. The response of the total solute concentration to individual storm events lends itself to interpretation in terms of a simple dilution model. This pattern is suggested by the weekly analyses, in which the interrelationships of discharge peaks and solute concentration is clearly seen (Fig.4(a) peaks A to I).

Goto (1961) investigated the interrelationship between water discharge and solute levels for individual storms and identified a

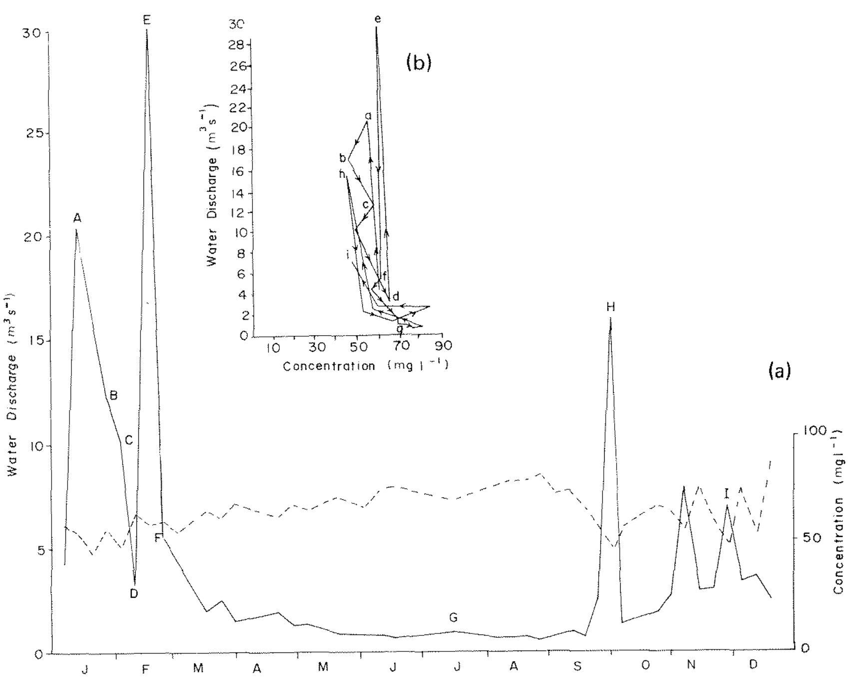

FIG.4 Variation of dissolved matter concentration with time at the Almondbank gauging station.

cyclic loop-like behaviour. He stressed that solute concentrations fall rapidly as discharge increases and they rise again as the discharge decreases, and at any discharge the solute concentration on the rising stage of a hydrograph differs from that of the falling stage. The nature of this hysteresis varies with catchment area and characteristics, and Toler (1965) has described anticlockwise rating loops for streams in Georgia, USA, whereas Hendrickson & Krieger (1960) reported clockwise rating loops for streams in Kentucky, USA. No attempt has been made in the present study to separate solute levels which characterize the rising and falling stages of the hydrograph because no hourly or daily analysis was undertaken, and the weekly interval of sampling serves to smooth out all the instantaneous fluctuations in concentration. Nevertheless, the long term interrelationship for the River Almond (Fig.4(b)) reveals a dilution effect associated with an anticlockwise pattern. The lower part of the curve indicates that the range of concentrations in summer, associated with relatively stable and lower baseflow, is minimal. The middle and upper parts of the diagram relate to higher rainfall and runoff in the winter season, when the loops are more open and spread over a wider field. This pattern also confirms that summer solute concentrations were higher than those of the winter period.

CONCLUSIONS

The dissolved solids concentration and load passing a gauged point on the River Almond into the River Tay was estimated from flow duration and dissolved load rating curves for three successive water years in order to determine long period variation and responses to different water conditions. The concentration of dissolved matter exhibits an inverse relationship with water discharge, and ranged between 47 and 88 mg l^{-1}. Over the summer season the concentration was higher, more stable, less scattered with much stronger correlation to flow level than in the winter season. Of the controls which might affect dissolved solids production and concentration in the Almond catchment, the rainfall-runoff factor seems to be the most important. A long term interrelationship between water discharge and dissolved solids concentration in the River Almond indicates that the response of total solute concentration to the individual storm events lends itself to interpretation in terms of a simple dilution model. The dissolved load has a direct relationship with water discharge. The dissolved load passing the Almondbank gauging station in the study period ranged between 5125 tons in the 1972/1973 (dry water year) and 7326 tons in 1974/1975 (average wet water year). During the summer season an appreciable amount of dissolved loads were transported (up to 44%) and a seasonal variation in the dissolved load and concentration curves was also recognized. Estimates of annual dissolved load transport based on seasonal rating curves applied to the whole year differ by up to 20%, and it is, therefore, recommended that estimation of dissolved loads should be undertaken by deriving and applying rating relationships for seasonal or even shorter periods.

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