THE VARIATION OF DISSOLVED CONSTITUENTS WITH DISCHARGE IN SOME NORFOLK RIVERS

A.M.C. EDWARDS *

School of Environmental Sciences, University of East Anglia, Norwich (Great Britain) *

ABSTRACT

Edwards, A.M.C., 1973. The variation of dissolved constituents with discharge in some Norfolk rivers. *J. Hydrol.*, 18: 219–242.

Weekly samples were collected during 1970 from the rivers Yare, Tud, Tas and Wensum in Norfolk and analysed for dissolved sodium, potassium, calcium, magnesium, silicon, chloride, bicarbonate, nitrate, phosphate and sulphate. The relationship between the concentration and discharge was examined by regression analysis. Magnesium, bicarbonate and, for the Yare and Wensum, phosphorus were diluted by increases in discharge. Nitrate and sulphate concentrations were positively correlated with discharge, possibly due to these constituents being derived from the leaching of the upper part of the soil profile. Potassium concentration increased at the beginning of most storm hydrographs but, like sodium, was diluted on other occasions. Large increases in nitrate, sulphate, potassium, sodium, chloride and silicon occurred in November, with accumulated weathered products being flushed from the soil, as the summer moisture deficit was replenished. Silicon was insensitive to changes in discharge during the first months of 1970. During the spring and summer it was depleted by diatoms. Calcium concentration was also uncorrelated with discharge, possibly due to being derived from the solution of calcium carbonates and calcium sulphate. The rivers were supersaturated calcium carbonate, when compared with the solubility product of calcite and showed no signs of equilibrating.

INTRODUCTION

Water discharge is one of the major factors influencing the concentration of dissolved constituents in river water. An inverse relationship is commonly recorded for at-a-station observations of these parameters (Hem, 1970). This relationship has been investigated in a series of studies and attempts made to produce solute rating curves. The potential uses of such relationships are for predicting concentrations of pollutants and quality of potable water, for calibrating curves of dissolved load and discharge in order to estimate the solution output of solute erosion/nutrient budgets. Another possible applica-

* Present address: Yorkshire River Authority, Pollution Prevention Department, Olympia House, Geldred Road, Leeds 12 (Great Britain).

tion is an aid in the segregation of the various discharge components of the flood hydrograph.

This paper describes the results of weekly sampling of the Yare, Tud, Wensum and Tas rivers in Norfolk, England during 1970. The sampling of the Tas and Wensum did not begin until March and that of the Yare was continued until May 1971. The relationship between discharge and concentration was investigated by regression analysis for each river except the Tas. The constituents analysed were potassium, sodium, calcium, magnesium, silicon, chloride, bicarbonate, nitrate, phosphate and sulphate. This data, as well as that from periods of more intensive sampling is used in a discussion of the solution processes operating in these catchments. The companion paper (Edwards, 1973) describes the relationship between the dissolved load (the product of the concentration and discharge) of each constituent and the rivers' discharge and discusses the solute budgets for the Yare and Tud catchments during 1970.

CONCENTRATION–DISCHARGE MODELS

The inverse trend between solute concentration and discharge, which has been described for many rivers, is to be expected at a time of increasing discharge if all the other factors affecting river chemistry are constant. Baseflow, which is usually relatively rich in solutes, is diluted by interflow and surface flow, which have shorter residence times in the catchment and hence a shorter period in which solution reactions can take place. Hembree et al. (1964) have suggested that water velocity might be used as the independent variable instead of discharge. Changes in discharge are accommodated in the channel by changes in the width, depth and velocity of the water. The ratio of surface area of channel in contact with water to volume will decrease in a unit time period if either width or depth is increased.

Hem (1970) has derived a hyperbolic relationship between discharge and concentration from a simple model of the dilution of baseflow by a component of the hydrograph with a lower concentration of a dissolved constituent:

$$C_1 Q_1 + C_2 Q_2 = (Q_1 + Q_2)C_3 \qquad (1)$$

where Q_1 is the discharge before dilution (i.e. baseflow), Q_2 is the discharge of dilutant, C_1 is the initial concentration, C_2 is the dilutant concentration, C_3 is the resultant concentration.

Assuming $Q_1 C_1$ to be a constant (a), and that $C_2 = 0$, then $a/(Q_1 + Q_2) = C_3$ or:

$$\log C_3 = \log a - \log(Q_1 + Q_2) \tag{2}$$

Equation 2 has the form of a straight line with a slope of -1. In reality it is unlikely for C_2 to be 0 (or for $C_1 Q_2$ to be constant). There are some cases, however, when C_2 may be zero; for example the dilution of a pollutant from a sewage outfall, which is absent from the river upstream of that source. $(Q_1 + Q_2)$ is the river's discharge Q. In a situation where C_2 is greater than 0, the form of eq. 2 is:

$$\log C_{ij} = \log a - b \log Q_j \tag{3}$$

or

$$\log C_{ij} = aQ_j{}^b \tag{4}$$

when C_i is the concentration of a constituent (i) of a sample j and Q is the discharge at the time of collecting j.

This is a theoretical derivation of the expression that has been used in a number of studies to relate concentration to discharge (e.g., Ledbetter and Gloyna, 1964; Gunnerson, 1967; Steele, 1968).

Johnson et al. (1969) have derived an expression for the relationship between discharge and concentration from similar mass balance considerations as Hem (1970) (eq. 1). They have, however, derived for Q in eq. 4 the term of $1/(1 + \beta Q)$. β is a constant obtained from the ratio of the residence time of water in the catchment to the volume of water in the system. In practice they used a systematic trial and error calculation to find a value which best fitted the data. Hall (1970, 1971) has produced six mixing models and a number of equations to study dissolved solids — discharge relationships in streams. These include eq. 4 and an expression similar to that of Johnson et al. (1969). He finds, however, that it is often difficult to decide which model is the appropriate one and which equation gives the best fit, and that the straightforward use of eq. 4 was usually adequate.

Steele (1968) and Hart et al. (1964) both predict the concentration of constituents in a river from the discharge and chemical composition of various components of the hydrograph. Steele uses baseflow and surface flow, while Hart includes interflow as well. The problem with these models is that the hydrograph is often not readily segregated into distinct components. Furthermore the chemistry of any one component may not be constant throughout the entire catchment, and may change with time. In fact river chemistry has been used in several studies as an aid to hydrograph segregation (e.g., Pinder and Johns, 1969). Ledbetter and Gloyna (1964), build antecedent flow conditions into their predictive models of concentration. Pionke and Nicks (1970) tested various instantaneous and antecedent measures of discharge

and rainfall to predict the salinity of some ephemeral streams. They found that the highest degree of explanation was obtained by using the daily precipitation at the time of sampling.

In many situations the dilution of dissolved load by increased discharge is a simplification. At the onset of a storm hydrograph concentrations of some elements in solution may increase as the drainage network extends to areas of the catchment, where accumulated weathered and organic deposits are readily flushed out. Steele (1968) eliminated these first storm effects before trying to predict concentration from discharge. Hendricksen and Krieger (1964) have proposed a cyclic model of chemical changes through storm hydrographs. At first there is no significant change in concentration as discharge rises because of increased leaching. This is followed by dilution and then a rise in concentration again on the falling stage. In terms of eq. 1 this is the result of the C_2 value not being zero or constant. Keller (1970) has included a measure of soil moisture deficit along with discharge and water temperature in a stepwise regression analysis of variation of dissolved constituents. In his study only a small proportion of variation was explained by these two additional independent variables. Imeson (1970) used principal components analysis for the same purpose as Keller. The components giving the highest degrees of explanation were measures of catchment wetness, storm intensity and seasonality (temperature). In all multi-variant analyses of river chemistry there is difficulty in selecting variables that are truly independent of each other.

Hall (1971) points out that the concentration discharge relationships over long periods of time may be obscured by non-random diurnal or seasonal fluctuations due to biological or chemical processes. These trends in concentration may be better investigated by time series analysis rather than by regression analysis with discharge as the independent variable. In catchments of variable geology and land use, and especially where man is active, only a small proportion of the variance in concentration may be explained by discharge. Discharge—concentration models may be applied to two different time scales. The first is to specific events in the hydrograph, where some of the models of Hall may be of use. The second is to obtain the amount of variation due to discharge over a long time period covering a number of different hydrological episodes. This paper is concerned with the second application in some agricultural catchments of low relief and with minerals of high solubility.

METHODS

Samples were collected at weekly intervals (usually between 0800 and

1000 h) from the discharge gauging stations that mark the outlet of each catchment. They were obtained midstream, immediately below the gauging structure, where the water was thoroughly mixed. Temperature and initially pH were measured in the field. During the second half of the sampling programme pH was not measured until the samples were returned to the laboratory (usually within 1 h of collection). No differences were found between laboratory and field determinations. The precision was ± 0.1 pH unit. The water was collected in polythene bottles and on return to the laboratory was filtered through Whatman GF/C filter pads. A subsample for silicon analysis was separately filtered using 0.5 μm Oxoid membranes. Where necessary, the samples were stored after filtration in a deep freeze (usually within 1–3 h of collection).

Chloride and bicarbonate ions were determined immediately on return to the laboratory. Chloride was titrated against silver nitrate (Am. Publ. Health Assoc., 1965) and bicarbonate was titrated with 0.05 N hydrochloric acid to pH 4.5 (Mackereth, 1963). The titration alkalinity is taken to be the result of bicarbonate ions as at the pH of these waters (7.7–8.1) inorganic carbon is virtually wholly in this form. The contribution to the alkalinity of other strong bases is thought to be negligible because the borate, silicate and phosphate anions are present in very low concentration. Sodium and potassium were analysed by flame photometry and calcium and magnesium by atomic absorption spectrophotometry. Deep freeze storage proved to be unsuitable for preserving calcium. The rivers were supersaturated with calcium carbonate, which precipitated out on thawing. The bottles were, thus, shaken well and diluted with hydrochloric acid. The precision was approximately ± 5 mg/l Ca^{2+}. Sulphate—sulphur was determined turbidimetrically (Goltermann and Clymo, 1969). Reactive silicon was analysed by the procedure of Strickland and Parsons (1968), as modified by Liss and Spencer (1969). Reactive nitrate-nitrogen was analysed by the method of Strickland and Parsons (ammonium and nitrate concentrations were negligible) and reactive soluble phosphate-phosphorus by that of Murphy and Riley (1962). Only orthophosphate is reactive in this procedure though poly- and organic phosphates may be partly hydrolysed by the acid reagents. The phosphate results may underestimate the total phosphate present in a sample and are not specific to orthophosphate. The precision of the analyses was for phosphorus ± 0.01 mg/l PO_4^{3-} — P, ± 0.1 mg/l for Si, K^+, and Mg^{2+} and NO_3^- — N, ± 0.5 mg/l for Na^+, ± 1.0 mg/l for SO_4^{2-} - S and Cl^- and ± 3.0 mg/l for HCO_3^-.

The discharge data were obtained from the continuous stage records of the East Suffolk and Norfolk River Authority. No estimate of their accuracy is available. Rainfall data were also obtained from the River Authority and
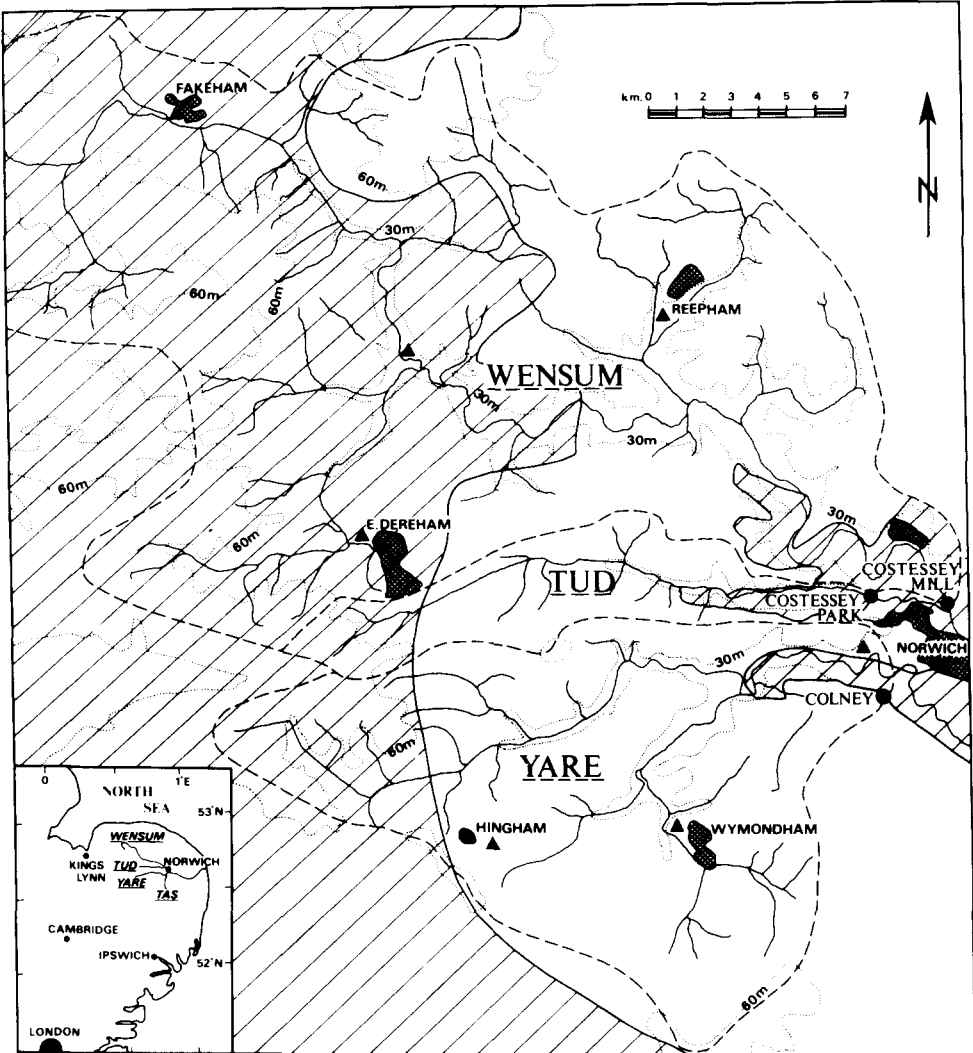
Fig. 1. Location of catchments. ● = sampling station; — — — indicates limit of watershed; ▲ = sewage outfall. Diagonal shading = chalk bedrock; unshaded = Pleistocene Crag.

were weighted by Theissen's polygons (Ward, 1967) to give the mean rainfall over each catchment.

DESCRIPTION OF THE CATCHMENTS

Figure 1 shows the Yare, Tud and Wensum catchments and the solid geology of the region. Table I summarises some relevant aspects of the morpho-

TABLE I

Hydrology of the catchments during 1970

	Yare	Tud	Wensum	Tas
Catchment area (km)	232	73	536	147
Catchment relief (m)	73	82	88	55
Rainfall (mm)	617	641	659	614
Runoff (mm)	203	161	180	—
Summer baseflow discharge (m^3/sec)	0.45	0.15	1.8	0.25
Maximum discharge (m^3/sec)	8.79	2.41	16	—

metry and hydrology of these rivers. The gauging station of the Tas catchment lies 10 km to the south east of the one on the Yare. The continuous water stage recorder of the Tas was out of operation for much of 1970. The mean annual rainfall between 1915 and 1950 was 660 mm and up to two thirds of this may be lost through evapotranspiration (Ministry of Housing and Local Government, 1963). The relief on the catchments is low (80 m) and the rivers are sluggish, except when in flood. This gentle relief leads to an absence of large limestone springs, as are found in areas of karst topography and along the chalk scarps of southern England. The channel networks are much extended by ditches and drains. The hydrographs for 1970 are similar in form for all the rivers. This can be seen from the mean daily discharge graphs of the Yare and Tud (Fig. 2). The concentrations of suspended sediment are mostly low (10–30 mg/l) compared with the dissolved load, though they probably rise to over 100 mg/l during the larger floods.

The geology is described in Larwood and Funnell (1970). The bedrock is chalk, which dips eastward at a rate of 1–2 m/km. It is overlain in the east by the Pleistocene Norwich Crag, which is composed mostly of shelly sands with micaceous silts and clays. The solid geology is exposed only in the river
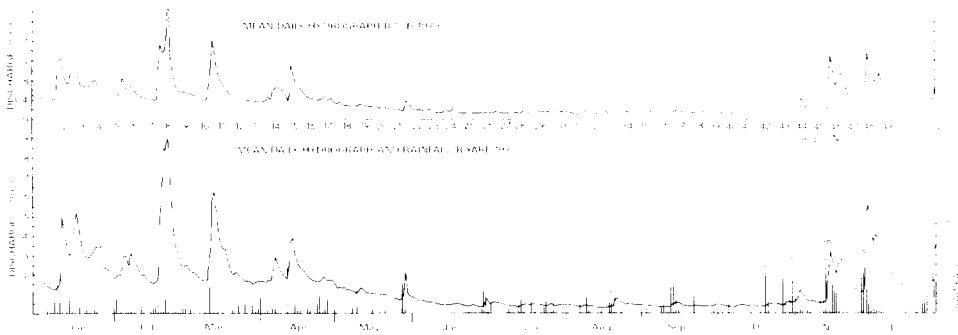

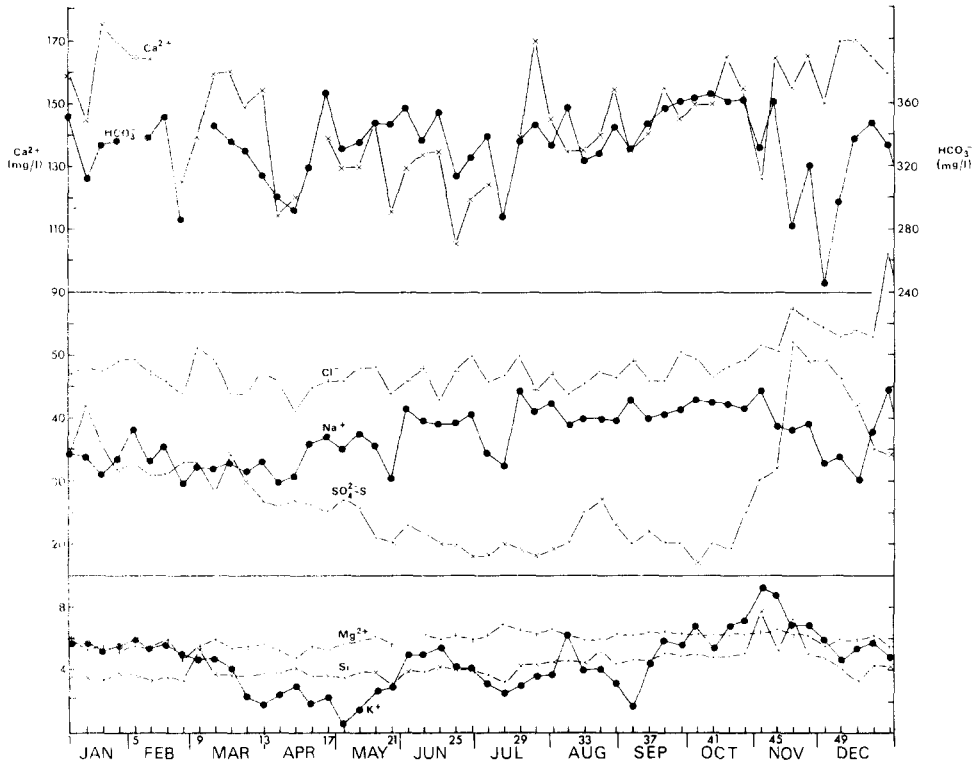Fig. 2. Hydrographs and rainfall of the rivers Yare and Tud, 1970.

Fig. 3. Weekly concentrations of calcium, bicarbonate, chloride, sodium, sulphate-sulphur, magnesium, silicon, and potassium, River Yare, 1970.

valleys and elsewhere is overlain by the chalky boulder clay of the Quaternary glaciation with patches of outwash sands and gravels, and in the north by a thin covering of loess. The lithology over the whole region is thus calcareous though locally there are highly variable proportions of sand and clay. The channel beds are largely covered with flint gravel with silt along the banks. Chalk is exposed in a few places, where scour is sufficiently strong.

The rivers were all sampled above the tidal limit and upstream of the city of Norwich. Their land use is mainly agricultural with much arable land. The settlement is mostly in villages and the three small towns of Fakenham, East Dereham and Wymondham. The population of the Yare catchment is approximately 21,100, the Tud 3,000, the Wensum 38,500 and the Tas 8,000. There are a number of sewage treatment plant outfalls into the rivers (the ones with licensed discharges of over 50 m^3/day are shown in Fig. 1). The rivers are all classified as unpolluted except for a short reach of the Yare near Wymondham (Department of the Environment, 1971).

TABLE II

Regression and correlation coefficients, means and range of concentration, Yare

Constituent	Regression equation	Correlation coefficient	Range	Sampled mean (mg/l)	Discharge (weighted mean)
Na^+	$\log Y = 1.566 - 0.104 \log X$	-0.66 **	29.5–44.5	36.8	36.3
K^+		-0.25	3.1–7.7	4.3	4.3
Ca^{2+}		0.22	110–170	140	150
Mg^{2+}	$\log Y = 0.774 - 0.072 \log X$	-0.77 **	4.7–6.4	5.9	5.9
Si		-0.05	0.5–9.2	4.5	4.8
Cl		0.11	41.0–66.0	48.0	51
HCO_3^-	$\log Y = 2.523 - 0.053 \log X$	0.53 **	245–365	335	340
$NO_3^- - N$	$\log Y = 0.656 + 0.406 \log X$	0.77 **	2.8–14.0	5.1	7.1
$PO_4^{3-} - P$	$\log Y = -0.649 - 0.585 \log X$	-0.67 **	0.03–0.56	0.26	0.2
$SO_4^{2-} - S$	$\log Y = 1.413 + 0.214 \log X$	0.75 **	17–52	28	34

Y = concentration, X = discharge. ** Indicates significance at 0.1% level.

TABLE III

Regression and correlation coefficients, means and ranges of concentration, Tud

Constituent	Regression equation	r	Range	Sampled mean (mg/l)	Discharge (weighted mean)
Na^+	$\log Y = 1.496 + 0.058 \log X$	0.38 *	27.5–44.0	31	30
K^+	$\log Y = 0.636 + 0.149 \log X$	0.55 **	2.8–6.9	3.6	3.7
Ca^{2+}	$\log Y = 2.148 + 0.066 \log X$	0.43 *	110–150	130	125
Mg^{2+}	$\log Y = 0.605 - 0.126 \log X$	−0.66 **	4.1–5.5	4.8	5.1
Si		0.05	0.4–6.7	4.2	4.3
Cl^-	$\log Y = 1.656 + 0.077 \log X$	0.41 *	35.0–62.5	41	43
HCO_3^-		−0.23	275–350	320	310
$NO_3^- - N$	$\log Y = 0.962 + 0.410 \log X$	0.89 **	2.7–10.4	4.9	6.1
$PO_4^{3-} - P$		−0.03	0.01–0.18	0.10	0.10
$SO_4^{2-} - S$	$\log Y = 1.478 + 0.224 \log X$	0.64 **	14–48	23.5	25.5

Y = concentration, X = discharge.   ** Indicates significance at 0.1% level;   * indicates significance at 1%.

TABLE IV

Regression and correlation coefficients, mean and range of concentration, Wensum

Constituent	Regression equation	Correlation coefficient	Range	Sampled mean (mg/l)
Na^+	$\log X = 1.539 - 0.03 \log Y$	-0.36 *	$28.5-36$	32.5
K^+	$\log X = 0.484 + 0.161 \log Y$	0.36 *	$4.2-5.0$	3.8
Ca^{2+}	$\log X = 2.080 + 0.048 \log Y$	0.36 *	$110-140$	130
Mg^{2+}	$\log Y = 0.683 - 0.062 \log X$	-0.58 **	$2.5-6.7$	4.5
Si		0.22	$0.7-6.3$	3.3
Cl^-		0.00	$33-56.5$	42
HCO_3^-	$\log Y = 2.490 - 0.058 \log X$	-0.55 **	$243-320$	290
$NO_3^- - N$	$\log Y = 0.418 + 0.521 \log X$	0.84 **	$2.9-9.7$	4.9
$PO_4^{3-} - P$	$\log Y = -0.717 + 0.410 \log X$	-0.44 *	$0.02-0.21$	0.13
$SO_4^{2-} - S$	$\log Y = 1.040 + 0.307 \log X$	0.71 **	$12-34$	16

Y = concentration, X = discharge, ** indicates significance at 0.1% level; * indicates significant at 1%.

EMPIRICAL RELATIONSHIPS BETWEEN CONCENTRATION AND DISCHARGE

The pattern of the concentrations of eight of the analysed constituents of the Yare of the 52 samples collected during 1970 is shown in Fig. 3. The phosphate and nitrate results are shown for 1970 in Fig. 9 and 10 on pp. 238 and 239. The relationship between the concentration (C) of each constituent (i) and the discharge (Q) at the time of collecting the sample (j) has been tested for all the samples collected during 1970 from the Yare, Tud and Wensum. There are 52 observations for each of the former but only 43 for the Wensum as sampling did not commence until March. The relationship tested was that of the linear equation 3:

$$\log C_{ij} = \log a - b \log Q_{j}$$

This is the most commonly used expression for investigating concentration—discharge relationships. The amount of linear association between C and Q was ascertained by using the product moment correlation coefficient and the regression lines fitted by the method of least squares. The regression equations and correlation coefficients (r) are listed in Table III and IV, along with the range and mean concentrations. For the Yare and Tud the discharge weighted means are also shown. These are obtained from total output (in grams) of each constituent during 1970 divided by the total discharge in cubic metres (obtained from Edwards, 1973).

The only constituent whose concentration is significantly diluted by discharge in all 3 catchments is magnesium, though all the bicarbonate concentrations also had negative slope coefficients. On the other hand there are significant increases of nitrate and sulphate with discharge. The highest amount of explained variance ($r^2 \cdot 100$) is 80% for the Tud's nitrate. These results differ markedly from the findings of Steele (1968) who analysed for a catchment in California for all the constituents described for the Norfolk rivers, except nitrate and phosphate. The regression lines for 72 observations collected over 15 months all had negative slopes and in all but one case (sulphate at low flows) the amount of explained variance was greater than 62%.

The regression lines for the elements in the Yare with a significant concentration—discharge relationship are shown in Fig. 4. The spread of the constituents' concentrations over 5 orders of magnitude makes it difficult to compare the rates of change in concentration. To facilitate this Fig. 5 has been prepared by plotting the change in ($b \log X$) over one decade change in discharge (X), when b is the slope coefficient of eq. 3. It can be seen that bicarbonate has a small relative rate of dilution though, because of its high concentration, it is enough to maintain the charge balance, as nitrate and
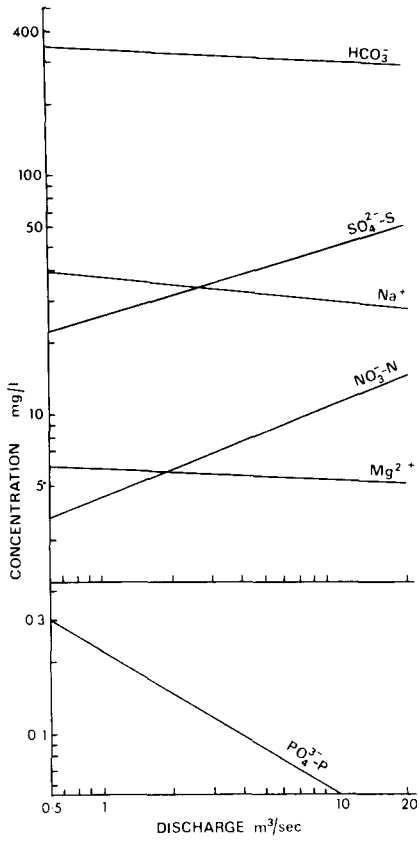
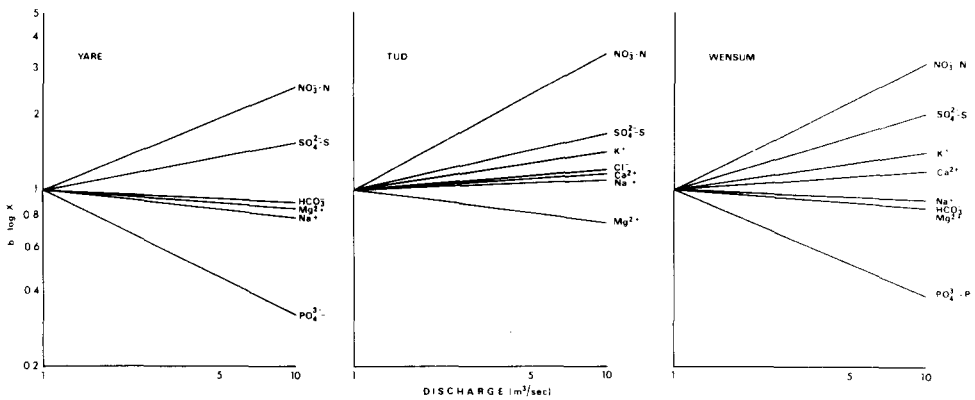Fig. 4. Regression lines of concentration against discharge, River Yare.

Fig. 5. Change in $b \log X$ with discharge, where X is concentration and b is the slope coefficient of the regression of concentration against discharge.

TABLE V

Effectiveness of rainfall during November and December storm hydrographs of the river Yare

Duration of hydrograph event	Rainfall (mm)	Runoff (mm)
2–7 November	37.0	2
15–27 November	76.6	10
29 November–6 December	56.6	40

Summer baseflow runoff = 1.2 mm/week.

sulphate have high relative rates of increase but are less abundant in the water. Phosphorus is strongly diluted in the Yare and Wensum and sodium and potassium have an intermediate position. The variations of chloride, silicon and calcium samples are independent of discharge.

Two other measures of discharge were tested as the independent variable in eq. 3 for the Yare and Tud. These were the mean discharge and the maximum discharge of the week immediately prior to the collection of each sample. The few correlation coefficients that were higher than those given by instantaneous discharge were found to be not a significant improvement in "explanation", when tested by the "Fisher Z" test (Moroney, 1956). The amount of rain falling over the Yare catchment during the week prior to each sample was also used as the independent variable. Again, no significant increases in the correlation coefficients were obtained.

DISCUSSION

The results of the regression analysis are used in a discussion of the processes influencing the concentrations of the dissolved constituents. Results of the more detailed sampling are also considered and of particular interest are the three storm hydrographs of November and early December (see Fig. 2). These were the first high flows after a long, dry summer and autumn and the effectiveness of each rain storm with successive hydrographs as the soil moisture deficit was replenished (Table V).

Sodium, potassium and chloride

The potassium concentration increases at the onset of most storm hydrographs. This can be seen well for the Yare in March (Fig. 6) and also during the storm of the 14th April (sample 15) and very markedly on all rivers during the two storms of November (e.g., the Tud, Fig. 7). Each small in-
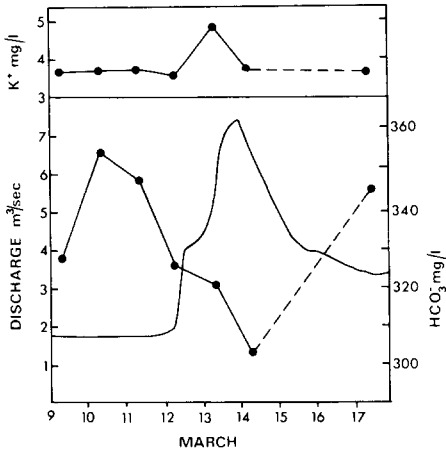
Fig. 6. Fluctuations of potassium and bicarbonate concentrations during a March flood, River Yare.

crease in flow during a period of daily sampling in August and September resulted in a small increase in potassium concentration. In each case the concentration returns rapidly as discharge falls to one before the onset of the rising stage. There is one exception during 1970 and this is for the December episode of high flow, when the concentration was not affected until the falling stage, when in each river it decreased. The potassium concentration
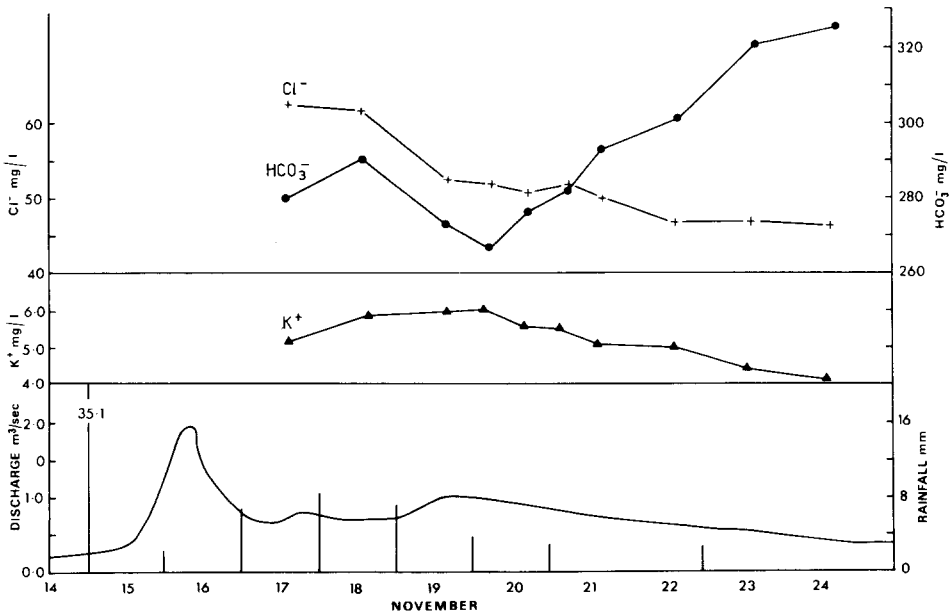
Fig. 7. Fluctuations of potassium, chloride and bicarbonate after a November storm, River Tud.

did not change at the time of the largest sampled flow of the Yare (9.45 m^3/sec, 26th January 1971).

Sodium and chloride concentrations of the Yare were slightly diluted during March and the sodium concentration fell by 4—5 mg/l between 14th and 21st April in all the catchments except the Tud, where it increased by 8.5 mg/l. The trend of sodium fluctuations in the Yare is erratic with a general pattern of higher concentration at times of summer baseflow than in winter. This results in the negative correlation coefficient. The first November hydrograph resulted in increases in sodium in the Yare and Tas. The second showed no change in sodium concentrations in the Yare but a slight increase in the Wensum and a large one of 9 mg/l in the Tud (the Tas was not sampled). There was dilution during the falling stage of the large December storm. It is assumed that sodium and potassium are derived mainly from the solution of their highly soluble chlorides, though some will be supplied from silicate minerals. The chloride concentration reached 62 mg/l (sample 46) in the Tud, when both potassium and sodium were also high. The pattern of response of potassium to discharge is probably a result of both solubility and location in the soil. It is an essential nutrient for plant growth and thus may be concentrated in a mobile form at the top of the soil profile by biological activity. It is readily leached into drains and ditches at the onset of rain. There is no clear evidence of the summer potassium concentrations being depleted by plant storage and uptake of the nutrient. The large amounts carried by the rivers in November coincided with the first large flows of autumn, as well as the end of the growing season. The recalculation of the potassium concentration—discharge correlation for the Yare without samples 44—52 showed that dilution explained a significant amount of the variation in the first 10 months of the year ($r = -0.59$). Sodium is less likely to be so concentrated by plants and hence the less well defined pattern. Potassium is added as a fertilizer in spring and autumn. A small proportion of these constituents is supplied by sewage effluent (12% of the Yare's potassium, the remainder 5% or less — Edwards, 1971, 1973). Much is supplied from the atmosphere as the input in rainwater is concentrated approximately 3 times by evaporation in the catchments. Rainwater was also collected and analysed on a weekly basis and the highest proportion supplied was estimated to be chloride in the Tud (55%) (Edwards, 1971, 1973). Sodium chloride applied to melt snow and ice on the roads can cause large increases in the concentrations of these elements in rivers. Sodium chloride was repeatedly applied to the roads of Norfolk between 26th and 28th December. This led to a maximum sampled concentration of 90.5 mg/l Cl^- in the Tas on 29th December (sample 52). This was an increase of 42.5 mg/l over sample 51, when the discharge was only one sixth of that of week 52. Chloride concentrations were affected in

the other 3 rivers with 66 mg/l in the Yare, 62 mg/l in the Tud and 56.5 mg/l in the Wensum. Sodium was similarly affected. These values were not used in the regression analysis.

Calcium, magnesium and bicarbonate

Calcium and bicarbonate are the most abundant constituents in the Norfolk rivers. The precipitation of calcium carbonate in the bottles after thawing and the inaccuracies in the calcium determinations have been referred to in section 3. This indicates that freezing has either changed the equilibrium or speeded up its attainment by water initially in disequilibrium with respect to calcium carbonate. The equilibrium state of the water in the rivers was investigated to find out which of these two possibilities caused the precipitation. This was examined by comparing the ion activity product of calcium carbonate ($I.A.P._{CaCO_3}$) in the rivers with the solubility product of calcite ($K_{calcite}$) at the in situ temperature of the river water. When the $I.A.P._{CaCO_3}/K_{calcite}$ ratio is 1.0, the water is in equilibrium with respect to calcite. Ratios higher than 1.0 indicate supersaturation and those lower unsaturation. The ion activity product was calculated by the procedures described in Back and Hanshaw (1970). A series of samples drawn from all 4 rivers collected at different temperatures and with varying concentration (including the highest and lowest recorded) of calcium and bicarbonate were tested. The $I.A.P._{CaCO_3}/K_{calcite}$ ranged from 1.7 to 7.4, indicating that all the rivers were supersaturated with respect to calcite.

The soil water probably had a carbon dioxide partial pressure of 10–100 times greater than that in the atmosphere, due to plant respiration and the decay of organic matter. When the soil water seeps into the channels its carbon dioxide partial pressure falls, as it equilibriates with that of the atmosphere, and this results in a rise in pH. If the calcium carbonate was present in equilibrium with the soil water, it will now be supersaturated and can be expected to precipitate out. The East Anglian river waters show no sign of doing this, even when kept in the laboratory for 2 months. There appears to be some factor present inhibiting the nucleation of carbonates that results in a metastable equilibrium and which is overcome by freezing. It is not uncommon for river or lake water to be supersaturated with calcite (e.g., Ruttner, 1963; Barnes, 1965) and this applies also to many surface seawaters (Berner, 1971). A number of processes are thought to be responsible for this phenomena, including the deactivation of calcium carbonate nuclei by organic matter and the competition between Mg^{2+} and Ca^{2+} for crystallographic sites in growing carbonate crystal embryos (Berner, 1971). The latter explanation seems unlikely for the East Anglian river waters owing to the low $Mg^{2+}:Ca^{2+}$
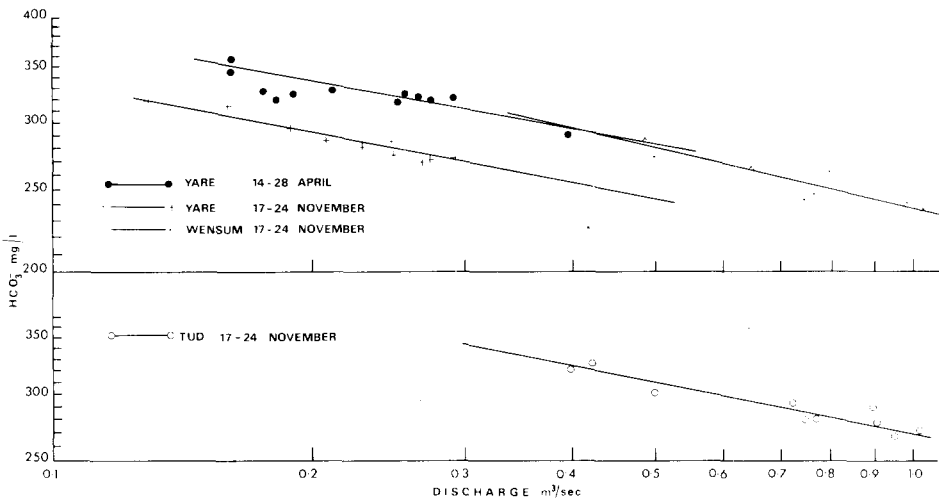
Fig. 8. Variations of bicarbonate concentration through storm hydrographs.

ratio (1:20 compared with 1:0.3 for seawater).

The dilution of the bicarbonate concentration is evident during all the major storm periods. They have been sampled in detail on the Yare from 14th—28th April and on the Yare, Tud and Wensum from the 17th—24th November, when in all cases the correlation coefficients were higher than −0.88 (Fig. 8). It is interesting to note for the 2 Yare sampling periods the slope of the line is similar (−0.175 and −0.196) though the April concentrations are 40 mg/l greater than those in November. The temperature of the April period ranged between 5.5 and 13.5° C and that of November between 4.8 and 9.0° C. There are a number of samples in summer with decreases in bicarbonate concentration, which are not correlated to any discharge changes. These on the Tud are lower than the correlation coefficient for the whole year to −0.23, which is not a significant indication of correlation between discharge and bicarbonate at the 1% level of the "t" test. There is no ready explanation for some of these low concentrations and there is no evidence of diurnal variations in temperature leading to a lowering of bicarbonate concentration. The calcium—discharge correlation coefficients are low. Large storms seem to have little effect on the calcium concentrations. Between the 19th and 26th January, 1971 (the period of the highest discharges sampled), calcium fell by 20 mg/l and bicarbonate by 70 mg/l on the Yare (on the Tud 15 and 70 mg/l). On other occasions the effects of dilution, if present, were of the same order as the analytical precision. The explanation of this apparent lack of relationship between calcium and discharge is thought to be due to there being 2 major sources of calcium in these catchments, calcium

carbonate and calcium sulphate; whereas bicarbonate shows a significant inverse trend with discharge, sulphate displays a significant positive one. Thus one source of calcium increases with discharge as the other decreases.

Magnesium is probably mostly derived from magnesium limestones in the superficial deposits and chalk and seems to respond to discharge in a similar manner to bicarbonate. The high inverse correlations in the three rivers tested and apparent in the Tas as well, appear to be due to concentrations being higher in summer than winter. There is little evidence of pronounced dilution during specific storm hydrographs.

Silicon

In all four rivers the silicon concentrations showed marked depletions, which are probably the result of assimilation of silica by blooms of diatoms. These episodes of low concentration are not correlated with any hydrological event or major change in the other solutes. The largest depletion occurred in an eleven week period in the spring and in the first week of May all the rivers had concentrations of 0.4—0.7 mg/l Si and in the Yare and Tud it was estimated that over 90% of the load had been removed (Edwards, 1971). Two later depletions were observed on the Yare and Tud during the summer and a well defined one on the Tas. The Wensum pattern was more variable with fluctuations in concentration of 3—4 mg/l from week to week. These depletions explain the lack of correlation between silicon and discharge. There is some evidence, however, that in the first weeks of 1970 in the Yare and Tud, when biological removal is unlikely, the silicon concentrations were insensitive to discharge and maintained equilibrium concentrations of between 4.7 and 5.9 mg/l Si. There was, however, observed dilution of silicon due to the flood on the 26th January, 1971. The highest silicon concentrations in all 4 rivers corresponded with the first storm hydrograph of November, with 9 mg/l Si for the Yare, 6—7 mg/l Si for the Wensum and Tud and 7—8 mg/l Si for the Tas. This is presumably a leaching effect, though the solubility of silicate minerals is low and the rates of reaction slow.

Phosphorus

Only part of the phosphorus fraction of the rivers has been analysed (see "Methods" section) and it has been estimated (Edwards, 1971) that much, if not all, of this could have been supplied to the Yare from sewage. Table VI shows the concentrations expected in the rivers, if sewage was the only source of supply. The observed concentrations in the baseflow of the Tud are slightly higher than those predicted but agreement is good for the low flows of the

TABLE VI

Estimated resultant concentrations of the dilution of phosphate phosphorus from sewage effluent by summer baseflow

	Yare	Tud	Wensum
Supply of P (Kg/day)	25.7	1.86	22.7
Baseflow (m^3/sec)	0.45	0.15	1.8
Resultant concentration (mg/l P)	0.64	0.14	0.21
Range of baseflow concentration (mg/l P) [*]	0.5–0.55	0.15–0.2	0.15–0.2

[*] For weeks with no diatom blooms.

other rivers. Attempts to predict winter concentrations were less successful, with the observed values being higher than the predicted ones. Phosphorus is also supplied from land drainage (which includes the leaching of fertilizer phosphates). The low solubility of phosphate minerals, however, usually results in low concentrations (e.g., Owens and Wood (1968) find only 0.03– 0.04 mg/l backgrounds in the Great Ouse catchment). Biological removal depleted phosphorus concentrations. The lowest values (0.05 mg/l P) were observed in all 4 rivers during April and May at the time of the diatom bloom. In the summer the lower values of samples 25–28 and 34–38 are also at the time of silicon depletions.

Figure 9 shows the pattern of phosphorus concentration in the Yare and Tud, which respectively have the highest and the lowest proportion of their discharge supplied from effluent. The high concentrations of the Yare in summer are the result of the low dilution of the effluent by the baseflow discharges and this results in the good inverse relationship between phosphorus and discharge. The Tud's effluent input is a much smaller proportion of its total flow and hence the lack of correlation with discharge. The Wensum and Tas are intermediate between the Yare and Tud.
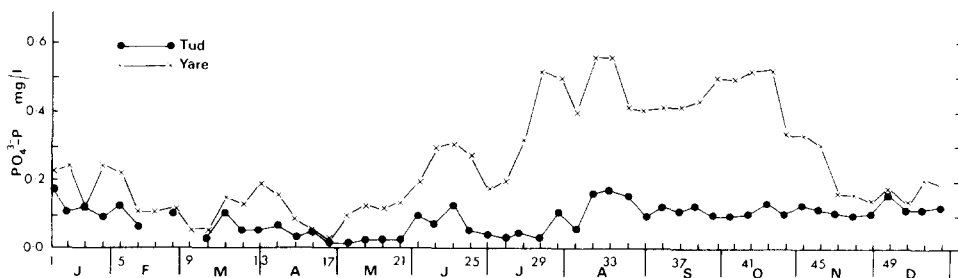

Fig. 9. Weekly phosphate–phosphorus concentrations, Rivers Yare and Tud 1970.
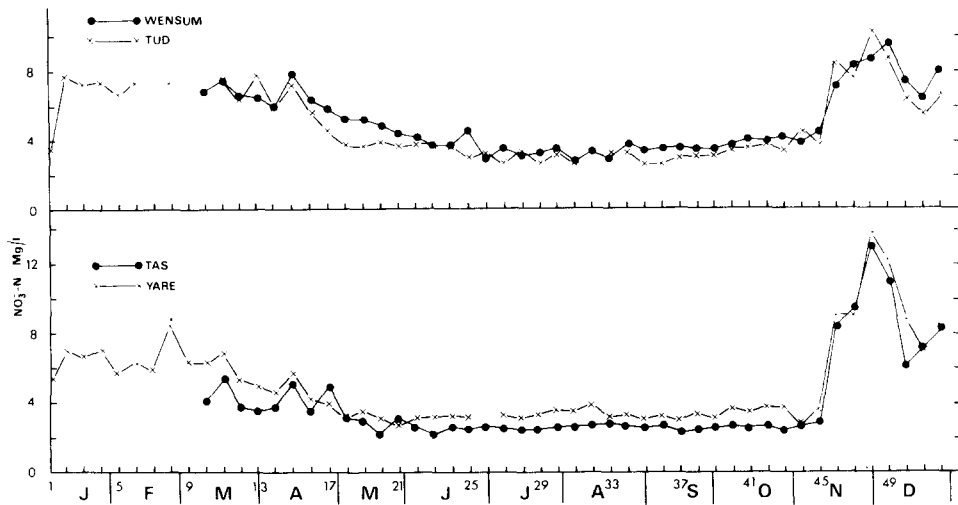
Fig. 10. Weekly nitrate—nitrogen concentrations, 1970.

Nitrate and sulphate

The concentrations of nitrate-nitrogen and sulphate-sulphur have a highly significant positive correlation with discharge in the Yare, Tud and Wensum and a similar pattern of high winter and low summer concentrations are displayed by the Tas (Fig. 10). At times of the Yare's summer baseflow it is estimated by similar methods as used for phosphorus, that over two thirds of the nitrate is supplied from outfall effluents (Edwards, 1971), with little leached from the soil. Periods of high flow result in the addition of much nitrate from the land. The summer concentrations may be reduced by uptake by plants. The close correlation of nitrate concentration with discharge and sulphate (which should not be significantly affected by biological activity), indicates that the pattern is caused by leaching rather than by removal and storage of the nutrient by plants. Each period of high discharge results in an increase of nitrate concentrations and in most cases in sulphate as well. The first storm hydrograph of November (the smallest of the three) resulted in a rise of 1 mg/l on the Tud but had no effect on the others. The second hydrograph resulted in concentration of 7–9 mg/l NO_3^- — N and the third and largest of 9–14 mg/l NO_3^- — N. The pattern of sulphate concentrations is similar to potassium with there being large increases with the first hydrograph (sample 44) and the highest recorded concentration (52 mg/l SO_4^{2-} — S in the Yare) coinciding with sample 46. Concentrations of sulphate were still high at the time of the third event (sample 48). The nitrate and, to a lesser extent, the sulphate (probably calcium sulphate) minerals are fairly soluble and

this series of variations is probably again a result of this and the location of the minerals in the soil profile. The nitrates are concentrated by biological activity in the top horizons and are of only trace concentration in the bedrock. Sulphates are particularly abundant in the drifts of the Lowestoft glaciation which originated to the west of East Anglia and contains much Kimmeridge clay (West and Donner, 1956). These are, thus, only found in the upper layers of the profile through which the water percolates. The drifts of North Norfolk contain less clay than those to the south and this accounts for the lower sulphate concentrations in the Wensum.

Williams (1971) found from the analysis of the drainage effluent at Saxmundham, Suffolk (35 km to the south of Norwich) that nitrates applied as fertilizer are readily leached from the soil after heavy rainfall. Nitrogenous fertilizers are applied in Norfolk in the spring. These may contribute to the nitrate concentration of the April hydrographs though the periods when high loads of nitrogen were transported in the rivers occurred during January, February, March, November and December, 1970.

CONCLUSIONS

The effect of increases in river discharge in the Norfolk rivers on the ten constituents analysed can be divided into four classes:

(1) Nitrate and sulphate which nearly always increase in concentration.

(2) Magnesium, bicarbonate and phosphorus which are usually diluted.

(3) Sodium and potassium, probably mostly derived from chlorides, which fall into an intermediate category, though potassium concentration increases at the beginning of most storm events.

(4) Calcium and silicon which show no significant correlations with discharge. It is hypothesised that calcium is derived from the solution of calcium sulphates and carbonates, the former increasing in concentration with discharge and the latter being diluted. The pattern for silicon is obscured by biological depletions, though there is evidence that concentration was insensitive to discharge changes during the first months of 1970.

These relationships are tentatively explained by a combination of the solubility of minerals dissolved and their location in the vertical profile of the catchments' deposits. The leaching effect of the three hydrographs of November and December may be exaggerated due to the preceeding long period of low flows. The detailed sampling of the rising and falling stages of storm hydrographs at different seasons may, however, provide more information on the solution processes operating.

It is interesting to speculate on why the Norfolk catchments do not display well defined dilution patterns of dissolved load as described by Steele (1968),

Ledbetter and Gloyna (1964), Gunnerson (1967) and Hem (1970). Many of their conclusions are based on work done in the western United States, where seasonal extremes of discharge are much greater. Steele's discharges range over 5 orders of magnitude, while in East Anglia it is over only 2. The Norfolk catchments are composed of highly soluble minerals. Their relief is low and overland flow lacking. The rapid runoff component is mostly by way of ditches and drains in the soil, which is the most favourable zone for chemical reactions to take place.

REFERENCES

American Public Health Association, 1965, *Standard Methods for The Examination of Waters and Wastewater*. Am. Publ. Health Assoc., New York, 769 pp.
Back, W. and Hanshaw, B.B., 1970. Comparison of the chemical hydrology of the carbonate peninsulas of Florida and Yucatan. *J. Hydrol.*, 10: 330–368.
Barnes, I., 1965. Geochemistry of Birch Creek, Ingo County, California, a travertine depositing creek in an arid climate. *Geochim. Cosmochim. Acta*, 29: 85–112.
Berner, R.A., 1971. *Principles of Chemical Sedimentation*. McGraw-Hill, New York, N.Y., 240 pp.
Department of the Environment, 1971. *A River Pollution Survey of England and Wales, Volume 1*. H.M.S.O., London, 39 pp.
Edwards, A.M.C., 1971. *Aspects of the Chemistry of four East Anglian Rivers*. Thesis, University of East Anglia, 292 pp. (unpublished).
Edwards, A.M.C., 1973. Dissolved load and tentative solute budgets for some Norfolk catchments. *J. Hydrol.*, 18
Goltermann, H.L. and Clymo, R.S., 1969. Methods for chemical analysis of freshwater. *Int. Biol. Programme, Handb.*, 8. Blackwells, Oxford, 172 pp.
Gunnerson, C.G., 1967. Streamflow and quality in the Columbia river basin. *J. Sanit. Eng., Proc. Am. Soc. Civ. Eng.*, 93 (S.A. 6): 1–16.
Hall, F.R., 1970. Dissolved solids–discharge relationship, 1: Mixing models. *Water Resour. Res.*, 6: 845–850.
Hall, F.R., 1971. Dissolved solids–discharge relationships, 2: Applications. *Water Resour. Res.*, 7: 591–601.
Hart, F.C., King, P.H. and Tchobanoglous, G., 1964. Discussion on "Predictive techniques for water quality inorganics" by J.O. Ledbetter and E.F. Gloyna. *J. Sanit. Eng., Proc. Am. Soc. Civ. Eng.*, 90 (S.A. 5): 63–64.
Hem, J.D., 1970. Study and interpretation of chemical characteristics of natural waters. *U.S. Geol. Surv. Water Supply Pap.*, 1473: 363 pp.
Hembree, C.H., Krieger, R.A. and Johnson, P.R., 1964. Chemical quality of surface waters and sedimentation in the Grand River drainage basin, North and South Dakota. *U.S. Geol. Surv. Water Supply Pap.*, 1769: 76 pp.

Hendrickson, G.E. and Krieger, R.A., 1964. The geochemistry of natural waters of the Blue Grass Region, Kentucky. *U.S. Geol. Surv. Water Supply Pap.*, 1300: 136 pp.

Imeson, A.C., 1970. Erosion in Three East Yorkshire Catchments and Variations in the Dissolved, Suspended and Bedload. Thesis, Univ. of Hull, 330 pp. (unpublished).

Johnson, N.M., Likens, G.E., Bormann, F.H. and Pierce, R.S., 1969. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. *Water Resour. Res.*, 5: 1353–1363.

Keller, H.M., 1970. Factors affecting water quality of small mountain catchments. *J. Hydrol. (N.Z.)*, 9: 133–141.

Larwood, G.P. and Funnell, B.M., (Editors), 1970. *The Geology of Norfolk*. Geol. Soc. Norfolk, Norwich, reprinted edition, 107 pp.

Ledbetter, J.O. and Gloyna, E.F., 1964. Predictive techniques for water quality inorganics. *J. San. Eng., Proc. Am. Soc. Civ. Eng.*, 89 (S.A. 1): 127–150.

Liss, P.S. and Spencer, C.P., 1969. Investigation of some methods used for the determination of silicate in sea water. *J. Mar. Biol. Assoc. U. K.*, 49: 589–601.

Mackereth, F.J.H., 1963. Some methods of water analysis for limnologists. *Freshwater Biol. Assoc. Sci. Publ.*, 21: 70 pp.

Ministry of Housing and Local Government, 1963. *East Anglian Rivers Hydrometric Survey*. H.M.S.O., London, 93 pp.

Moroney, M.J., 1956. *Facts From Figures*. Penguin, Harmondsworth, 3rd edition, 472 pp.

Murphy, J. and Riley, J.P., 1962. A modified single solution method for the determination of soluble phosphate in sea water. *J. Mar. Biol. Assoc. U. K.*, 37: 9–14.

Owens, M. and Wood, G., 1968. Some aspects of the eutrophication of water. *Water Res.*, 2: 151–159.

Pinder, G.F. and Johns, S.F., 1969. Determination of the groundwater component of peak discharge from chemistry of total runoff. *Water Resour. Res.*, 5: 438–445.

Pionke, H.B. and Nicks, A.D., 1970. The effect of selected hydrologic variables on stream salinity. *Bull. Int. Assoc. Sci. Hydrol.*, 15: 13–21.

Ruttner, F., 1963. *Fundamentals of Limnology*. Univ. of Toronto Press, Toronto, 242 pp.

Steele, T.D., 1968. Digital-computer application in chemical-quality studies of surface water in a small watershed. *Int. Assoc. Sci. Hydrol. Publ.*, 80: 203–214.

Strickland, J.D.H. and Parsons, T.R., 1968. A practical handbook of seawater analysis. *Fish. Res. Board Canada Bull.*, 137: 311 pp.

Ward, R.C., 1967. *Principles of Hydrology*. McGraw-Hill, London, 403 pp.

West, R.G. and Donner, J.J., 1956. The glaciation of East Anglia and the East Midlands: a differentiation on the basis of stone orientation. *Q. J. Geol. Soc. Lond.*, 112: 69–91.

Williams, R.J.B., 1971. The chemical composition of water from land drains at Saxmundham and Woburn, and the influence of rainfall upon nutrient losses. *Rep. Rothamsted Exp. Stn. for 1970*, Pt. 2: 36–67.