Journal of Hydrology, 66 (1983) 305—318
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

[4]

BUILDUP OF DISCHARGE ALONG THE COURSE OF A MOUNTAIN STREAM DEDUCED FROM WATER-QUALITY ROUTINGS (EC ROUTINGS)

C.A.J. APPELO, R. BECHT, A.A. VAN DE GRIEND and T.C.M. SPIERINGS

Instituut voor Aardwetenschappen, Vrije Universiteit, 1081 HV Amsterdam (The Netherlands)

(Received November 4, 1982; accepted for publication November 17, 1982)

ABSTRACT

Appelo, C.A.J., Becht, R., Van de Griend, A.A. and Spierings, T.C.M., 1983. Buildup of discharge along the course of a mountain stream deduced from water-quality routings (EC routings). J. Hydrol., 66: 305—318.

A high-mountain stream in the northern Italian Alps has been surveyed for changes in electrical conductivity (EC) along the stream course. The EC of water contributing to the stream varies with the lithology drained, permitting a chemical gauging of contributing areas. EC routing of the stream allows recognition of small changes in discharge and gives a rapid semi-quantitative insight into the buildup of runoff production from various parts of the catchment under different hydrological conditions.

The method is considered a valuable tool for the recognition of different contributing areas. Under favourable circumstances it can show the response of sub-areas to changing hydrological conditions. The method may therefore contribute to a practical realisation of the partial contributing area concept in hydrology.

INTRODUCTION

Water-quality parameters are useful tools for the detection and hydrological interpretation of source areas, and for tracing flowpaths of water through catchment areas. Chemical gauging by means of existing (natural) quality variations is often attractive, especially at the confluence of streams with different chemical characteristics, or to calculate groundwater inflow with a different composition from the stream (Bonnin, 1958; Kunkle, 1965). The interpretation of water-quality changes with variations in discharge is used in the same way to provide a means for separating flow components. Equations have been formulated, both for variations of electrical conductivity (EC) (Hall, 1970; Hem, 1970; Korn and Walther, 1980), and for individual solutes (Steele, 1968; Johnson et al., 1969; Edwards, 1973; Haubert, 1976).

Even more popular is hydrograph separation based on a time-series analysis of single discharge events (Kunkle, 1965; Toler, 1965; Pinder and Jones,

0022-1694/83/$03.00

1969; Miller and Drever, 1977; Sklash and Farvolden, 1979; Herrmann and Stichler, 1980).The analyses of single events generally show a hysteresis effect in the plot of quality vs. quantity when both vary with time (Gregory and Walling, 1973).

Walling and Webb (1980) have shown that the hysteresis can be the result of spatial heterogeneities in the catchment area and/or routing effects within the stream channels. Another complication is that the water quality of the rapid runoff component may vary, depending on the contact time (or transit time) (Johnson et al., 1969; Nakamura, 1971; Pilgrim et al., 1978). These factors introduce an ambiguity in the physical interpretation of the chemograph in terms of spatial contributions to flow, or of the changing catchment response during the runoff-producing event. Although recording of chemical variations is considered as a field technique for flow separation, there is indeed little connection between this and the "partial (or variable) contributing areas" as the most important concept in field hydrology today (Chorley, 1978; Beven and Kirkby, 1979). The problem is that the interpretation of single station data for the whole catchment area has to be supplemented and supported by knowledge of the actual spatial variations of water quality in the whole upstream reach, as has been shown by Walling and Webb (1980).

EC *routing*

In several fieldwork areas of our hydrology group at the Vrije Universiteit, EC routings were found to be very instructive in showing the buildup of stream discharge. EC routing in a catchment area comprises the measurement of EC in the main stream at a number of points, and in all visible seepage zones, springs and contributing streams.

When chemical variations are sufficiently great, changes in EC along the longitudinal profile permit calculation of groundwater contributions (lateral inflow in general), as has been demonstrated already by O'Connor (1976) for a few large rivers in the U.S.A. that were heavily polluted in their headwater region. The EC profiles obtained in a mountainous catchment discussed here closely resemble O'Connor's (1976) figures, and are similar in appearance to the fence-like diagrams given by Webb (1976) for the River Exe, England. The scale of these figures varies from 4 km to several hundred kilometers, which suggests a fairly general applicability for chemical gauging by quality routings.

It is our purpose to show that EC routings represent a powerful tool in reconnaissance studies, and under favourable circumstances can be used for the estimation of partial area contributions to total flow. The errors associated with a quantitative interpretation of quality routings are discussed and results are presented for a catchment in the northern Italian Alps as an application of the method.

METHODS AND ASSOCIATED ERRORS

Stream reaches that receive inflow with a different quality can be "gauged" by application of the simple chemical gauging formula (Kunkle, 1965; Hem, 1970). Subsequent reaches can be linked continuously (Fig. 1), as long as chemical variations and different errors permit the method to be applied with the required (or available) accuracy. Three types of error principally influence the accuracy obtained: (1) errors associated with measuring the quality parameter; (2) use of EC as a quality parameter; and (3) general physical conditions encountered in a stream-reach.

Measuring errors

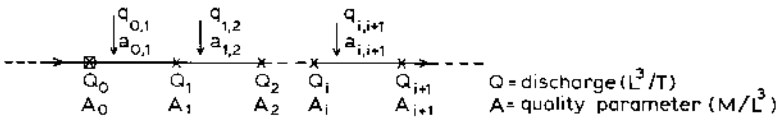

Fig. 1. Stream reaches that receive inflow of different quality can be coupled in a routing procedure.

Errors associated with chemical routing are discussed with Fig. 1 as a basis. The equations of continuity state:

$$Q_i \cdot A_i + q_{i,i+1} \cdot a_{i,i+1} = Q_{i+1} \cdot A_{i+1} \tag{1}$$

and

$$Q_{i+1} = Q_i + q_{i,i+1} \tag{2}$$

When solving for channel discharge in a downstream direction, eqs. 1 and 2 are combined to give:

$$Q_{i+1} = Q_i \cdot [(A_i - a_{i,i+1})/(A_{i+1} - a_{i,i+1})] = Q_i \cdot R_{i+1} \tag{3}$$

and for the inflow one obtains:

$$q_{i,i+1} = Q_i \cdot [(A_{i+1} - A_i)/(a_{i,i+1} - A_{i+1})] = Q_i, S_{i,i+1} \tag{4}$$

If a quality parameter is routed along the stream, and discharge is measured at Q_0 only, the following error is associated with a quantitative estimate of stream discharge:

$$(\Delta Q_{i+1}/Q_{i+1})^2 = (\Delta Q_0/Q_0)^2 + \sum_{j=1}^{i+1} (\Delta R_j/R_j)^2 \tag{5}$$

The fractional error in Q_{i+1} can be approximated as:

$$\Delta Q_{i+1}/Q_{i+1} \leqslant \{(\Delta Q_0/Q_0)^2 + \max\,(\Delta R_j/R_j)^2 \cdot (i+1)\}^{1/2} \tag{6}$$

but a more precise estimate is obtained from a consideration of the individual reaches. The error in R_{i+1} is:

$$\left(\frac{\Delta R_{i+1}}{R_{i+1}}\right)^2 = \frac{(\Delta A_i)^2}{(A_i - a_{i,i+1})^2} + \frac{(A_i - A_{i+1})^2 \cdot (\Delta a_{i,i+1})^2}{(A_{i+1} - a_{i,i+1})^2 \cdot (A_i - a_{i,i+1})^2} + \frac{(\Delta A_{i+1})^2}{(A_{i+1} - a_{i,i+1})^2} \tag{7}$$

The equation shows that the error in estimating main stream discharge is almost entirely dependent on contrasts in water quality of the main stream and the lateral contribution. For the field situation of the Grossklausenbach discussed later, the error was caused mainly by different water qualities of springs and seepage zones within the same reach. Nevertheless, the maximum error in $(\Delta R_j/R_j)$ for the Grossklausenbach is only ~ 3%, so that more than 20 reaches could be linked in the calculation procedure for estimating stream discharge (eq. 3) without surpassing the probable error of ±15% in discharge measurements with a current meter.

More serious is the error in estimating discharge from a contributing reach. The measurements introduce an error in eq. 4.:

$$\left(\frac{\Delta S_{i,i+1}}{S_{i,i+1}}\right)^2 = \frac{(\Delta A_i)^2}{(A_{i+1} - A_i)^2} + \frac{(\Delta a_{i,i+1})^2}{(a_{i,i+1} - A_{i+1})^2} + \frac{(a_{i,i+1} - A_i)^2 \cdot (\Delta A_{i+1})^2}{(a_{i,i+1} - A_{i+1})^2 \cdot (A_{i+1} - A_i)^2} \tag{8}$$

It follows from eq. 8 that small differences in main stream quality always cause large errors in determining the inflow $q_{i,i+1}$. The error depends on the relative contribution to main stream discharge and the contrast in water quality, and increases by the error in main stream discharge estimation. The final error in eq. 4 may, therefore, become very high for smaller areas which contribute less than 5% of total flow.

EC *as a quality parameter*

Electrical conductivity (EC) is a popular and easily measurable quality parameter in hydrology; its use has been discussed recently by Korn and Walther (1980) and by Foster et al. (1981). It is noteworthy, in the present context, that EC is not a $(\mathrm{M\,L^{-3}})$-parameter, but is related to ion content (epm) by:

$$\mathrm{EC} = K \cdot \Sigma(\mathrm{epm})$$

with Σ(epm) being the sum of cations or anions in equivalents per million (milliequivalents per liter). The value of the equivalent conductance K depends on the ion and the ion concentration, as shown in Fig. 2. For most natural watertypes $K \simeq 100\,\mu\mathrm{S\,cm^{-1}\,epm^{-1}}$ at 25°C, representing $\mathrm{Ca(HCO_3)_2}$-water with some chlorides and sulfates.

Rather conspicuous in Fig. 2 is the high concentration dependence of the

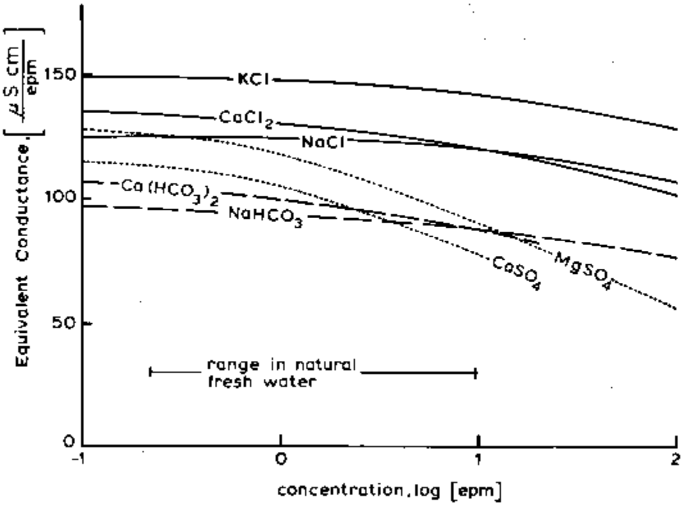

Fig. 2. Equivalent conductance of ion pairs in relation to concentration (data from Landolt and Börnstein, 1960).

equivalent conductance for SO_4-bearing waters. The equivalent conductances of a 5 and 1 epm $CaSO_4$ solution are respectively 86 and 104 $\mu S\,cm^{-1}\,epm^{-1}$; a five-fold dilution of 5 epm $CaSO_4$ would therefore decrease the EC of the solution from 430 to 104 $\mu S\,cm^{-1}$, i.e. suggesting a 4.1-fold dilution only. It may thus be concluded that a straightforward application of the EC-gauging formula results in systematically high estimates for the contribution with the higher EC. This error becomes especially high for sulfate-bearing waters. In such cases it is advantageous to determine the dilution factor empirically, by measuring an appropriate mixture of the water types.

General conditions of the stream reach

Apart from measuring errors in the routing procedure, the method requires some physical conditions to be met. Division of the stream into a number of individual reaches may follow reconnaissance routings in which the homogeneity of transverse profiles with respect to the measured water quality is assured.

The homogeneity depends on the spacing and type of contributing sources and side-branches, and on the mixing characteristics of the stream course. The mixing length can be estimated by empirical formulas (Day, 1977) and can often be reduced in smaller streams by building simple constructions with stones, etc. It is very important to be aware of diffuse sources and seepage zones, since these may influence the representative sampling of stream water quality. The existence of these zones may be observed in reconnaissance routings in even the largest rivers.

Springs and seepage zones which contribute water with different quality in the same reach increase the error in quantitative estimates of flow contributions, since the error of the average quality parameter ($\Delta a_{i,i+1}$ in eqs. 7 and 8) has to be based upon field evidence of relative proportions for the different contributions. Much of this error depends on the degree of terrain homogeneity: this in fact represents the main source of errors for the Grossklausenbach routings discussed below.

EC ROUTINGS IN THE GROSSKLAUSENBACH

Characteristics of the area

The Grossklausenbach is a tributary of the upper Ahr (Aurino) in the northern Italian province of Bozen (Bolzano). The stream flows in a glaciated U-shaped valley ~5 km long and 1.6 km wide. The highest point of the catchment is at 3135 m, the outlet in the Ahr at 1048 m. Fig. 3 gives an impression of the valley, and shows the morphological features of an alpine environment; a steep relief, moraine deposits, slumps, avalanches, and other high-alpine variations of mass transport and deposition. The area is wooded to 2000 m, and partly cultivated with meadows that are used for hay in the more accessible lower parts. Higher up, in the cirque area, grazing occurs during summer.

The catchment is snow-covered during the winter, and a very small glacier

Fig. 3. Photograph of the Grossklausenbach area.

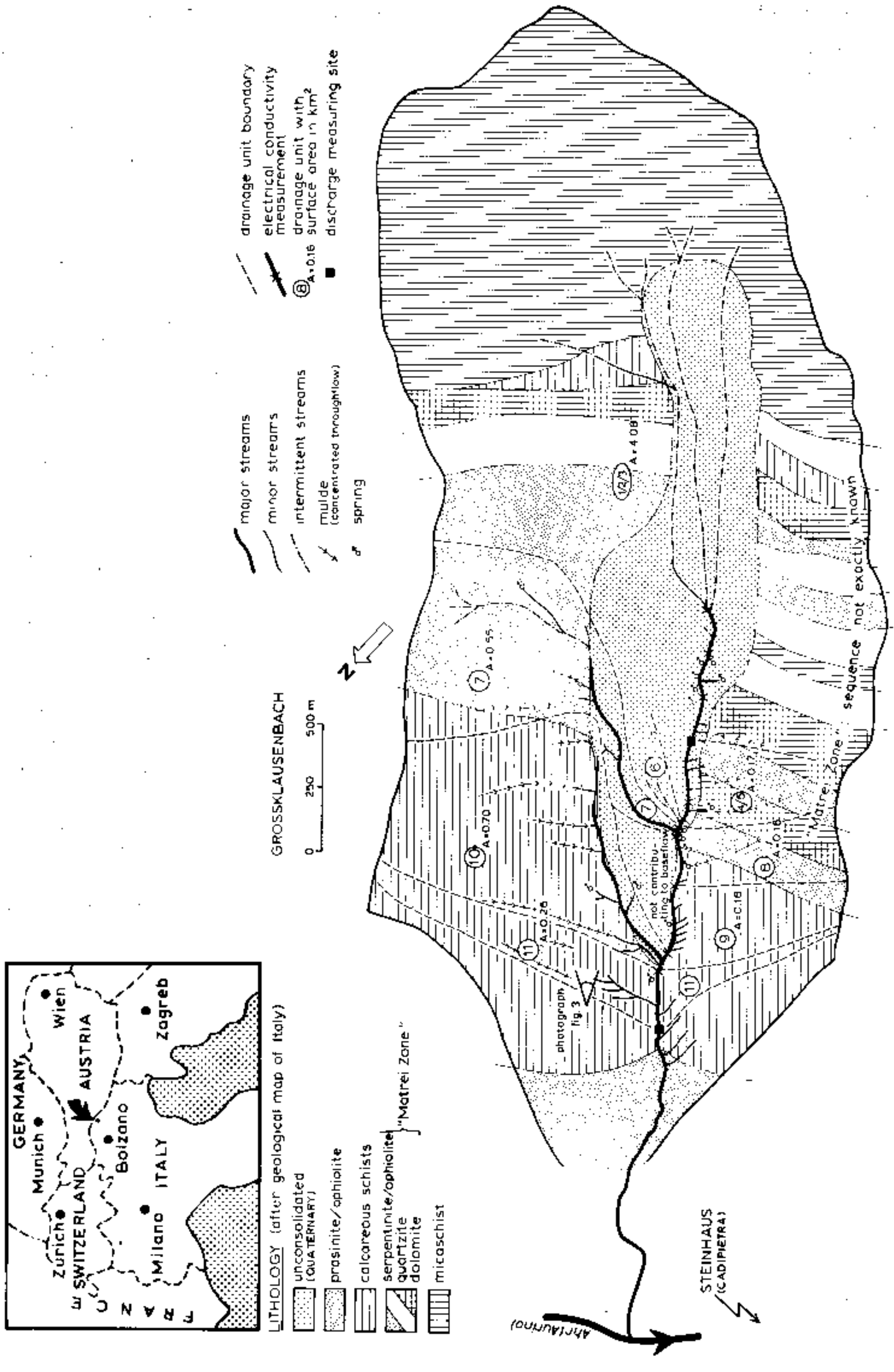

Fig. 4. Map of the Grossklausenbach, showing lithology and drainage pattern.

remnant (±4 ha) still exists in the upper part. The hydrological regime is characterised by low but continuous baseflow in winter, followed by an increase in runoff from snowmelt in spring. Peak flows occur with the summer maximum in precipitation (Van de Griend, 1981).

The lithology of the area shows great variation (Fig. 4). The stream crosses three alpine nappes which strike E—W with vertical to sub-vertical dips.

Hydrochemical characteristics

The sequence of the different geological units is only approximately known, but there is clear evidence that the hydrochemical properties of springs and seepage zones are related to the lithological unit that is drained. Ca, Mg, HCO_3 and SO_4 are the main ions which contribute to EC variations as a result of calcium carbonate, dolomite, serpentinite and gypsum dissolution. Values of Na, K and Cl remain relatively constant and represent the atmospheric input that is changed only by evapotranspiration and biomass uptake (Appelo, 1975). Typical ranges for the electrical conductivity are given in Table I.

Fig. 5 shows the variation of anion concentration with EC, with Cl remaining at a constant level, HCO_3 increasing up to 700 $\mu S\,cm^{-1}$, and SO_4 becoming dominant at still higher EC-values. This can be understood from a general reaction scheme, with low conductivities in water that has been in contact with silicate minerals; EC-values increase as dolomite and/or calcite dissolves, and the highest conductivities are found with high SO_4 values resulting from the dissolution of gypsum. HCO_3 then decreases, since $CaCO_3$ precipitates as a result of the common-ion effect when gypsum ($CaSO_4 \cdot 2H_2O$) dissolves.

TABLE I

Electrical conductivity of water associated with different lithological units

Lithological unit	EC, 25°C ($\mu S\,cm^{-1}$)
Micaschist	10— 70
Serpentinite/ophiolite (with gypsum)	150— 700
Dolomites (with gypsum)	200—1,500
Calcareous schists	300— 500

Drainage characteristics

The Grossklausenbach originates high in a cirque, but most of the water subsequently infiltrates in moraines and debris on the cirque floor. This water feeds large springs in the headwall of the trough-valley. Further downstream, local drainage follows the valley sides, giving rise to a large number

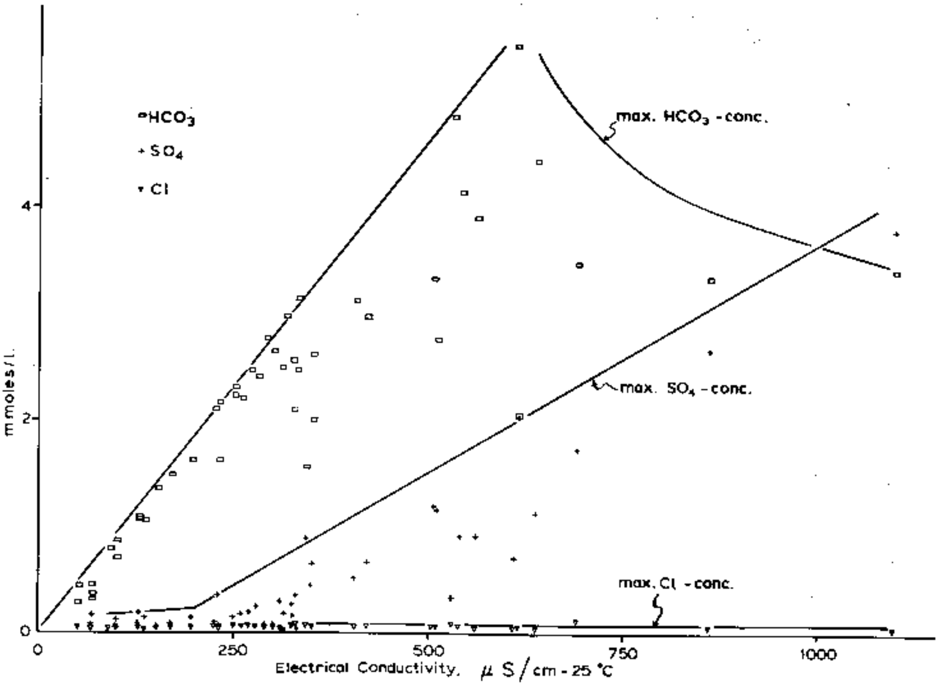

Fig. 5. Variation of anion concentrations with electrical conductivity for spring waters sampled in the Grossklausenbach area.

of closely spaced springs and seepage zones at the base of the slope along the main stream channel. Waters from these springs have a higher EC than water in the stream which originates from the chemically more inert micaschists. The result is a continuous increase of EC in Grossklausenbach water along the stream course.

EC *routings*

In the summer periods of 1979 and 1980 a number of EC routings were performed along the course of the Grossklausenbach. The routing comprised the EC measurement of all visible seepage zones, springs and contributing streams, and of Grossklausenbach water at a number of points. The Grossklausenbach was measured going downhill, at an approximate pace with mean water velocity, and the springs, etc., were measured going uphill. The measurements were completed with synchronous discharge measurements at two sites in the Grossklausenbach, midstream and at a downstream point (Fig. 6).

From the EC profiles and from EC's of the inflow, the partial contributions to the Grossklausenbach were calculated. The calculations were made in an upward and a downward sense, using either of the two current

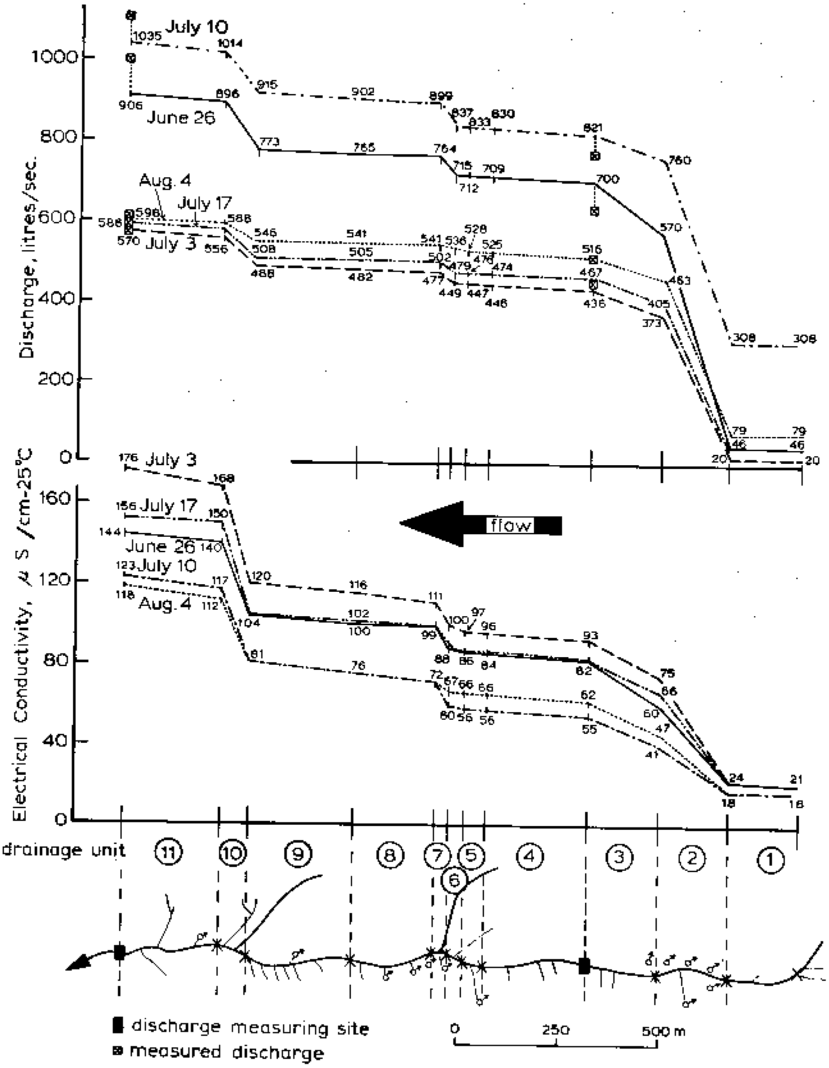

Fig. 6. EC routings and calculated flow profiles in the Grossklausenbach, summer 1980.

meter discharges as the starting point for the calculation procedure according to eq. 3. Results of the two calculations were averaged to obtain flow profiles presented in Fig. 6, for five times in 1980. Differences between discharges estimated from the calculation procedure and those actually measured (given by a crossed square in Fig. 6) differ by 10% at most. This difference can result from the EC-calculated contributions of reaches *4* to *11*, but it is also within the error which may be expected from current meter gauging.

It is of interest that it is possible to detect small increases of less than

1% in total flow, so that a very detailed picture of the buildup of stream discharge may be obtained. Comparable sensitivity in accounting for partial contributions is not easily obtained by other techniques, especially if diffuse sources and seepage zones are involved.

Partial-area responses

It also is possible to give an account of sub-area response to changing hydrological conditions. Fig. 7 shows the percentage contribution from different drainage units of the Grossklausenbach during the measurement period. The change in response results from varying reactions to snowmelt and to a very intense rainfall on July 9.

Snow was present in the lower reaches (*4—11*) during the first two routings, whereas in the cirque area (reaches *1—3*) snow- and glacier meltwater contributed during the whole period. The overall result is a decreasing con-

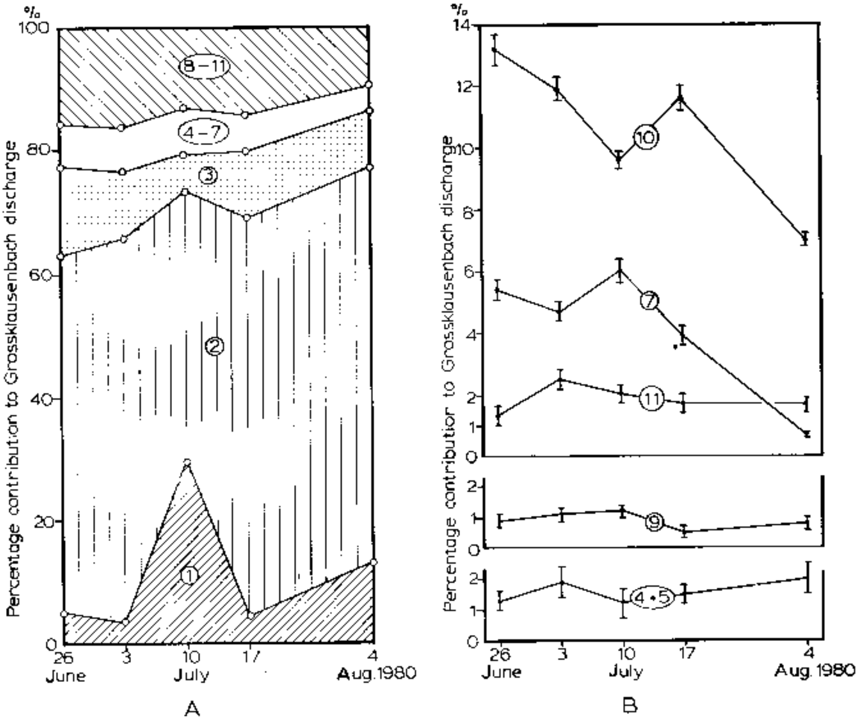

Fig. 7. Partial area contributions to Grossklausenbach discharge under different hydrological conditions. Numbers indicate drainage units as given in Figs. 4 and 6.

tribution from lower reaches during the measurement period, especially from small storage units *7* and *10*. The difference in flow between June 26 and July 3 is caused by decreasing temperature. The routing on June 26 marked the end of a warm period with ample snowmelt, and that on July 3 occurred in a colder period in which units with larger storage took over (i.e. reaches *2*—*5* and *11*).

A rainfall of 60 mm on July 9 led to flood conditions. An EC routing was carried out next day, during the recession, at a discharge estimated to be ~20% of peak flow. Direct runoff from the cirque area showed the most pronounced reaction with an increase in contribution from 5% before the storm to 30% of total runoff after the storm (unit *1* in Fig. 7A). On July 17 the recession of this peak flow had reached its approximate base level, but springs at the headwall of the trough-valley showed an increase in relative contribution (reaches *2* and *3*). These springs are fed from the cirque area and thus show a delayed reaction to the intense rainfall.

In the last week of July and the first week of August, the weather was warm and dry, giving meltwater runoff from the cirque with an increase in the relative contribution of direct runoff. This is a typical cirque-area response under conditions when infiltration in the coarse deposits cannot keep pace with rainfall input or large amounts of meltwater.

Error bars in Fig. 7B indicate the error in the partial contributions estimated using eq. 8. The precision is rather high for drainage units *7* and *10*, which enter the Grossklausenbach via single branches. Unit *7* is developed in ophiolitic rock that weathers to a fine-grained impermeable serpentinite clay. The unit reacted rapidly to the rainfall of July 9 and its contribution to overall flow became very small as soon as the snow melted away. Area *10* lies in calcareous schists and shows a delayed reaction to intense rainfall. The relative contribution shows the opposite trend to unit *7* (Fig. 7B), demonstrating the differences in storage capacity and rainfall response between the two sub-areas. The precision in estimated flow contribution is less for areas which contribute only 1—2% of total flow, and do so via diffuse sources (Fig. 7B). The change in relative contribution is in fact less than the estimated error in a number of cases, prohibiting a detailed interpretation of reactions to rainfall or snowmelt when only limited data are available. There are differences in specific discharge for the areas, however, and it may be expected that more pronounced dissimilarities will be measured on a year-round basis.

OTHER APPLICABILITY CONSIDERATIONS AND CONCLUSIONS

The applicability of the EC-routing method depends totally on the chemical variations given to water in the source areas. The variation may result from different lithologies, as in the Grossklausenbach, from areal characteristics that vary in vegetation or rainfall—runoff response, or from man-induced differences in land use or pollution.

As a reconnaissance technique, the method gives an easily measurable indication of changing conditions along the stream channel. As such, it can improve the interpretation of single point-discharge and quality measurements, since these are influenced by physical and chemical processes upstream (Walling and Webb, 1980). We have shown that under favourable conditions it is possible to obtain discharge estimates from contributing areas (reaches along the main stream channel), and an indication of sub-area response to hydrological events. Although there are restrictions to such quantitative interpretations, it is virtually the only easily applicable way to estimate discharge from diffuse springs and seepage zones.

Developments in field hydrology have shown the importance of partial contributing areas for runoff production (e.g., Beven and Kirkby, 1979). However, delineation of partial areas involves rather time-consuming techniques, and in-field measurements of state parameters on representative plots. This hampers application of the concept in practical hydrology. One is therefore forced to look for easy methods to gain rapid insight into the buildup of discharge from a catchment under different hydrological conditions, as for example with remote sensing techniques (Ishaq and Huff, 1979), or perhaps with EC routings — as we have tried to show.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the help of Prof. Ian Simmers in correcting the English text.

REFERENCES

Appelo, C.A.J., 1975. The hydrochemical cycle in a small Alpine watershed. Vrije Univ., Amsterdam, Aqua VU, 5: 17—40.

Beven, K.J. and Kirkby, M.J., 1979. A physically based, variable contributing area model of basin hydrology. Hydrol. Sci. Bull., 24: 43—69.

Bonnin, J., 1958. Quelques applications de la conductivité à l'hydrologie. Int. Assoc. Sci. Hydrol. Publ., 80: 426—436.

Chorley, R.J., 1978. The hillslope hydrological cycle. In: M.J. Kirkby (Editor), Hillslope Hydrology, Ch. 1, Wiley, New York, N.Y.

Day, T.J., 1977. Observed mixing lengths in mountain streams. J. Hydrol., 35: 125—136.

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

Foster, I.D.L., Grieve, I.C. and Christmas, A.D., 1981. The use of specific conductance in studies of natural waters and soil solutions. Hydrol. Sci. Bull., 26: 257—269.

Gregory, K.J. and Walling, D.E., 1973. Drainage Basin Form and Processes — A Geomorphological Approach. Edward Arnold, London.

Hall, F.R., 1970. Dissolved solids—discharge relationships, I. Mixing models. Water Resour. Res., 6: 845—850.

Haubert, M., 1976. Bilan hydrochimique d'un bassin versant de moyenne montagne: la Drause de Bellevaux (Brévon), Haute-Savoie. Bull. Bur. Rech. Géol. Min., Sect. 3, Hydrogéol. 1976, pp. 5—30.

Hem, J.D., 1970. Study and interpretation of the chemical characteristics of natural water. U.S. Geol. Surv., Water-Supply Pap. 1473, 363 pp., 2nd ed.

Herrmann, A. and Stichler, W. 1980. Groundwater—runoff relationships. Catena, 7: 251—263.

Ishaq, A.M. and Huff, D.D., 1979. Hydrologic source areas, a technique for identification. In: Modelling Hydrologic Process. Proc. Int. Hydrol. Symp., Colorado State Univ., Fort Collins, Colo., 1977, pp. 495—510.

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.

Korn, K. and Walther, W., 1980. Informationsgehalt und Nutzung der elektrolytischen Leitfähigkeit zur Berechnung von Stoff-konzentrationen in Fliessgewässer. Vom Wasser, 55: 77—93.

Kunkle, G.R., 1965. Computation of groundwater discharge to streams during floods, or to individual reaches during base flow, by use of specific conductance. U.S. Geol. Surv., Prof. Pap., 525-D: 207—210.

Landolt, H.H. and Börnstein, R., 1960. Zahlenwerte und Funktionen, 7te Teil. Elektrische Eigenschaften, II. Springer, Berlin.

Miller, W.R. and Drever, J.I., 1977. Water chemistry of a stream following a storm, Absaroka Mountains, Wyoming. Geol. Soc. Am. Bull., 88: 286—290.

Nakamura, J., 1971. Runoff analysis by electrical conductance. J. Hydrol., 14: 197—212.

O'Connor, D.J., 1976. The concentration of dissolved solids and river flow. Water Resour. Res., 12: 279—294.

Pilgrim, D.H., Huff, D.D. and Steele, T.D., 1978. A field evaluation of sub-surface and surface runoff, II. Runoff processes. J. Hydrol., 38: 319—341.

Pinder, G.F. and Jones, J.F., 1969. Determination of the groundwater component of peak discharge from the chemistry of total runoff. Water Resour. Res., 5: 438—445.

Sklash, M.G. and Farvolden, R.N., 1979. The role of groundwater in storm runoff. J. Hydrol., 43: 45—65.

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.

Toler, L.G., 1965. Relation between chemical quality and water discharge in Spring Creek, Southwestern Georgia. U.S. Geol. Surv., Prof. Pap., 525-C: 209—213.

Van de Griend, A.A., 1981. A weather-type hydrologic approach to runoff phenomena. Ph.D. Thesis, Vrije Universiteit, Amsterdam.

Walling, D.E. and Webb, B.W., 1980. The spatial dimension in the interpretation of stream solute behaviour. J. Hydrol., 47: 129—149.

Webb, B.W., 1976. Solute concentrations in the baseflow of some Devon streams. Rep. Trans. Devon Assoc. Adv. Sci., 108: 127—145.