

CHEMICAL AND GRAPHICAL METHODS COMPARED

by

S. Woo and N.H. Berg^{1/}INTRODUCTION

As snow precipitation becomes stream water, it contacts rock and soil. Contact time influences stream water chemistry in a linearly positive manner (Pilgrim *et al.*, 1979). Water from precipitation can follow many paths before it emerges in the stream channel. All characteristics of the basin--geologic, pedologic, meteorologic, and biologic--interact to determine water flow paths. These flow paths have various terms; for example, overland flow, subsurface flow, macropore or macrochannel flow, and baseflow. A snowmelt hydrograph, representing the change in stream discharge over a melt cycle (usually 24 hours), is a composite representation of water from all flow paths.

Water moving along different flow paths contacts soil or rock for varying lengths of time. Therefore, each component of the hydrograph should have different associated concentrations of total dissolved solids. Water moving as overland flow, subsurface flow, or macrochannel flow, is generally quicker than baseflow, and has lower concentrations of dissolved solutes. Our term for this quick flow is "direct runoff."

Differences in flow paths figure importantly in chemical transport. In acidic deposition to forested basins, for example, it is argued that soils help buffer acidic inputs (Heidelberg, 1985). However, effective buffering happens only if acidic precipitation is in contact with the soil for an adequate duration. If macropore and macrochannel flow transports a major fraction of water to the channel, then the water is unlikely to be significantly buffered and acidic precipitation may reach streams unaltered. Similar considerations are relevant to the movement of pesticides, herbicides, fertilizers, toxic chemicals, and heavy metals through soil and into streams.

This study identified the baseflow component of the total snowmelt hydrograph by two methods--chemical and graphical. The chemical method is based on the assumption that chemical concentrations increase as contact time between water and the lithosphere increases. The graphical method separates hydrograph components by plotting recession curves. Although the results presented here are germane to our study watershed alone and involve only one melt season, the methodology could easily be extrapolated to other watersheds.

METHODS

Baseflow discharge was calculated by solving a system of two mass balance equations with two unknowns:

$$\begin{aligned} Q_t C_t &= Q_b C_b + Q_d C_d && \text{Solute mass balance} && (1) \\ Q_t &= Q_b + Q_d && \text{Water mass balance} && (2) \end{aligned}$$

where Q_t is total stream discharge, C_t , C_b , C_d are concentrations of total dissolved solids for total, baseflow, and direct runoff, respectively; and Q_b and Q_d are the unknowns, baseflow and direct runoff discharges, respectively.

Direct measurement of Q_t , C_t , and C_b is generally straightforward. C_b is assumed equal to the concentration of stream surface water during the summer low flow period. C_d is assumed equal to the concentration of total runoff at the highest elevation point on the watershed at peak flow. After Pinder and Jones (1969), it is assumed that springs are not a significant water source; and that, high on the watersheds any water in the stream channel that is from baseflow has not travelled through a very long flow path through the soil. Waiting until peak melt also ensures that stream water is mostly direct runoff, with baseflow accounting for a small portion of total runoff.

The graphical approach to baseflow separation followed Barnes (1940). After plotting recession discharge, the "shallow" portion of the recession slope represents the baseflow contribution. The area under the extrapolated baseflow curve is the baseflow discharge.

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Stream chemistry and discharge data were collected from a tributary of Onion Creek, on the Onion Creek Experimental Forest, in the central Sierra Nevada, California, 20 km northwest of Lake Tahoe. The Experimental Forest is administered by the Pacific Southwest Forest and Range Experiment Station, Forest Service, U.S. Department of Agriculture, Berkeley, California. The tributary ranges in elevation from 1830 m to 2135 m and drains a 45-ha catchment. A V-notch weir and stage height recorder located at the mouth of the tributary allow calculation of Q_t at 15 min intervals. C_t and C_b were also measured at the weir during the summer 1984 low-flow period.

Water samples were collected before, during, and after significant spring snowmelt in water year 1985. Hourly samples were collected during two experimental runs, each lasting at least 24 hours. In addition, weekly conductivity data were available for a four month period (May to August 1985) for the same tributary. Conductivity values were adjusted to 25°C and total dissolved solids (TDS) were determined from conductivity measurements via the following regression equation (intercept suppressed):

$$\text{TDS [mg/l, as CaCO}_3\text{]} = 0.336 * \text{conductivity} \quad (n=324) \quad (3)$$

Equation (3) is based on stream water, precipitation, and basal snowpack outflow samples collected at several different sites over a 2 year period.

RESULTS

Chemical Method, Based on Hourly Data

The pre-melt study was conducted on March 13-14, 1985. As anticipated, measured stream discharge remained essentially constant, at $6.5 \times 10^{-3} \text{ m}^3/\text{s}$. TDS varied little, ranging from 7.4 to 8.6 mg/l as CaCO_3 , and did not appear to change systematically through time. Q_b and Q_d were not computed, since there was no change in total discharge, Q_t .

The melt period study was conducted on April 23-25, 1985. While weather conditions were favorable to melt, melting was not intense. Stream discharge ranged from 1.8×10^{-2} to $3.4 \times 10^{-2} \text{ m}^3/\text{s}$, an appreciable increase over $6.5 \times 10^{-3} \text{ m}^3/\text{s}$ of the pre-melt study. Discharge also showed a diurnal change, with peaks at 1830 PST on April 23 and 1730 PST on April 24, and low flows at 1030 PST, April 23 and 1330 PST, April 24. The magnitude of TDS change in April was greater than that in March; the range for April was 5.7 to 7.6 mg/l as CaCO_3 . Both TDS maxima and minima occurred at approximately the same time each day--at 1200³PST and 1730 PST, respectively.

Values for C_b and C_d were 11.0 and 6.2 mg/l, respectively as CaCO_3 . Quantities of baseflow and direct flow were calculated from the two mass balance equations. A plot of total discharge and calculated baseflow, using hourly data, allows an estimation of the percentage of baseflow discharge as a function of total discharge (Figure 1). Baseflow discharge was estimated to be 8% of the total; direct runoff discharge, 92%.

Graphical Method, Based on Weekly Data

Graphical methods require large differences between maximum and minimum discharge, so that changes in slope are easily discerned on plots of recession curves (Barnes, 1940; Garstka *et al.*, 1958). Unfortunately, the maximum change in discharge over the hourly intervals used for the chemical method was very small. Therefore, direct comparison between chemical and graphical hydrograph separation was not possible for the data collected in this study.

Weekly discharge data, calculated as the mean of seven daily discharge totals, were available, and the straight line extrapolated from the "shallow" slope represents baseflow discharge on the recession curve (Figure 2). Baseflow discharge was determined from the area under the curve as 12% of total discharge.

Chemical Method, Based on Weekly Data

Direct comparison between chemical and graphical methods is possible only if the same data set is used for both. Weekly TDS data and stream discharge values could be used in the mass balance equations. Baseflow concentration and direct flow concentration values were the same as before (11 and 6.2 ppm respectively, as CaCO_3). Solving for Q_b and Q_d and plotting discharge versus time, led to a baseflow estimation of 32% of total discharge (Figure 2).

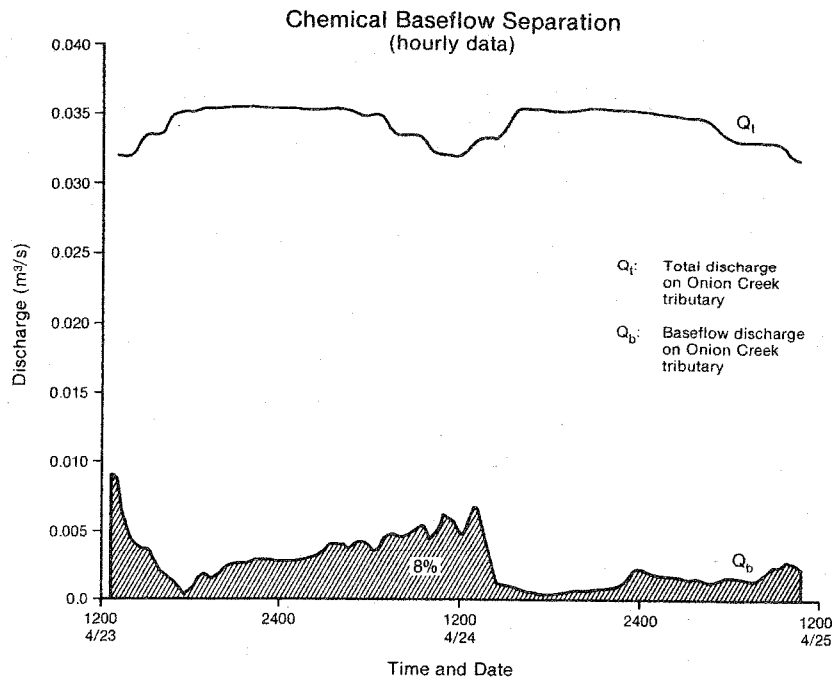


Figure 1. Total and baseflow discharge at Onion Creek 1 (April 1985) calculated by water chemistry method using hourly data.

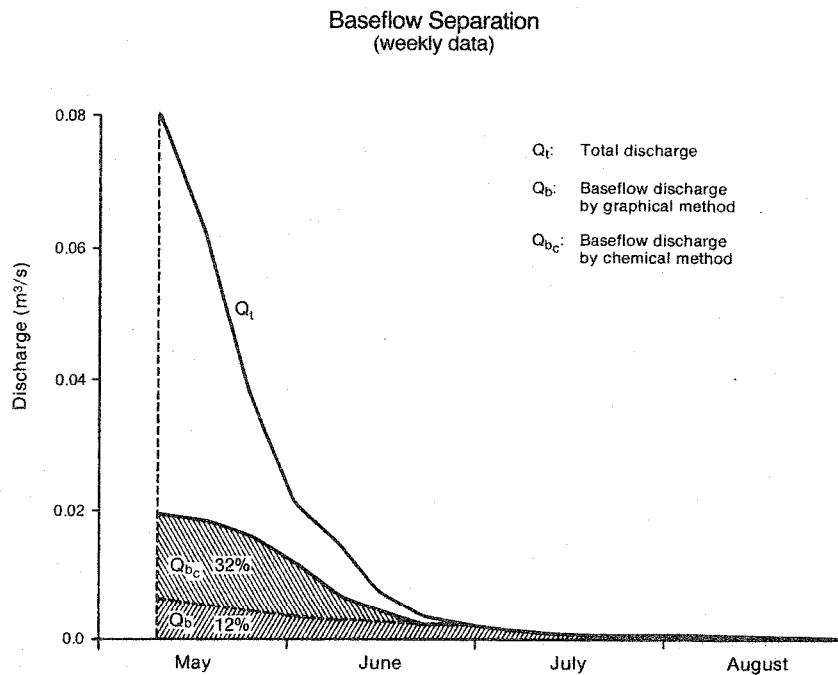


Figure 2. Seasonal (1985) total and baseflow discharge at Onion Creek 1 calculated by water chemistry and graphical methods.

DISCUSSION

Baseflow estimations from the chemical method (hourly data) and the graphical method (weekly data) were similar (8% and 12%, respectively). However, different data sets representing different temporal scales were used. A direct comparison could not be made. Baseflow estimations for the chemical and graphical methods using weekly data do not agree well (32% chemical method, 12% graphical).

Baseflow estimates from the graphical method are sensitive to minor changes in low levels of discharge. The estimates are also sensitive to the selection point for the

baseflow separation extrapolation. These factors contribute an unknown amount of variability to baseflow estimates.

Use of the chemical method assumes that C_b and C_d are constant. For a short period, say a few days, this is probably a good assumption. However, over a long period, the assumption may not hold because baseflow and direct runoff velocities are not constant. Concentration is a function of contact time; hence a difference in velocity would result in a difference in concentration. Given the shallow soils and exposed rocks characteristic of this study watershed, the baseflow estimation of 32% of the total seems high. The weekly data covered a period of four months, and C_b and C_d were probably not constant.

Algebraic manipulation of equations (1) and (2) gives

$$Q_b/Q_t = (C_t - C_d)/(C_b - C_d) \quad (4)$$

where $C_b > C_t > C_d$. The equation, hence the determination of Q_b , is sensitive to the two properties most difficult to evaluate, C_b and C_d . Minor variations in the estimates for C_b and C_d , particularly when their values are similar, are critical in the Q_b calculation.

The absolute values of discharge and chemical loading characteristics of this watershed are very small; and from an environmental impact point of view, the differences are not very significant. However, the methods to estimate baseflow are comparable if applied to certain hydrologic situations. Chemical and graphical methods are comparable if

- The hydrograph represents a large change in total discharge in a short period of time, say from snowmelt in a large watershed or from a rain-on-snow event. Over a short period of time, C_b and C_d could still be constant and the large discharge change would permit graphical separation.
- Concentrations of baseflow and direct runoff could be measured over time. Concentrations of baseflow and direct runoff would not be constant in the mass balance equations in the chemical method.

CONCLUSIONS

Using hourly data over a daily time period, the chemical method of baseflow separation estimated baseflow to be 8% of total discharge for a small mountain watershed in the central Sierra Nevada. Using weekly data over four months, the chemical method estimated baseflow to be 32% of total discharge. The 32% value is likely an overestimate, considering the characteristics of the watershed. Also, the assumption that baseflow and direct runoff concentrations are constant does not hold. The graphical method can be used only if differences in maximum and minimum discharge are large, so it was not appropriate for a daily snowmelt hydrograph on this watershed. Using weekly data over four months, the graphical method estimated baseflow to be 12% of total discharge.

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