The Concentration of Dissolved Solids and River Flow

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A general expression for the spatial and temporal distribution of conservative dissolved solids in freshwater rivers which incorporates the contribution of both the groundwater and surface water components of river flow is presented. The first part of this paper deals with the steady state conditions. With certain simplifying assumptions the correlation between concentration of dissolved solids and flow is developed for both spatially uniform and nonuniform conditions. The analysis includes the effect of both geophysical discontinuities and point sources. Examples from a number of rivers throughout the country are presented to indicate the utility of the analysis. The second part addresses the temporal variation of the dissolved solids concentration for two time scales. One describes the annual variation in concentration due to the time variable components of the river flow, and the second the variation over a semimonthly period due to a time variable point input. Applications to a variety of river conditions are also presented for the time variable analysis.

INTRODUCTION: STEADY STATE ANALYSIS

Many factors affect the concentration of total dissolved solids in natural water systems. These solids are the result of both natural phenomena and man's activity and may enter the stream as either distributed or point sources. In freshwater streams and rivers one of the most significant factors which affects the concentration of dissolved solids is the spatial and/or temporal variation of flow. It is the purpose of this paper to present an analytical framework relating the river flow to the concentration of dissolved solids for both steady state and time variable conditions.

The correlation between flow and concentration of dissolved lids has long been recognized [*Lenz and Sawyer*, 1944; *Hem*, 1959; *Toler*, 1965]. Various forms of inverse relationships have been presented: hyperbolic [*Durum*, 1953] and logarithmic [*Gunnerson*, 1967; *Pionke and Nicks*, 1970]. In some cases, consideration of antecedent flow conditions has improved the correlation [*Ledbetter and Gloyna*, 1964; *Hall*, 1971; *Pionke et al.*, 1972]. The inclusion of interflow, in addition to surface and base flow, has been suggested to provide a more realistic basis of analysis [*Hart et al.*, 1964]. The groundwater and surface water components of the total flow have been analyzed according to the respective concentrations of various constituents [*La Sala*, 1967; *Pinder and Jones*, 1969].

Development of Equations

The basic equation is developed by applying the principle of conservation of mass. A mass balance is taken about an elemental volume of streams ΔV along the longitudinal axis of the channel of cross-sectional area A and length Δx. It is assumed that vertical and lateral uniformity exists and that longitudinal dispersion is small by contrast to the advective component of the flow. The dissolved constituent enters the stream from both surface runoff Q_s and groundwater inflow Q_g with concentrations c_s and c_g, respectively.

The mass balance of the dissolved solids yields

$$\Delta V c = Qc\Delta t + c_g \Delta Q_g \Delta t + c_s \Delta Q_s \Delta t$$

$$- \left(c + \frac{\partial c}{\partial x}\Delta x\right)\left(Q + \frac{\partial Q}{\partial x}\Delta x\right)\Delta t$$

Dividing by Δt and Δx and simplifying yield

$$\frac{\partial}{\partial t}(Ac) = -\frac{\partial}{\partial x}(Qc) + c_g \frac{\partial Q_g}{\partial x} + c_s \frac{\partial Q_s}{\partial x} \qquad (1)$$

in which c, c_g, and c_s are the concentrations of dissolved solids in the river, groundwater inflow, and surface runoff, respectively; Q, Q_g, and Q_s are the flow rates of the river, groundwater inflow, and surface runoff, respectively; and $Q = Q_g + Q_s$.

Equation (1) is the general expression of mass flux. When it is applied to a specific case, the equation takes on a particular form depending on the temporal conditions (steady state or time variable) and the nature of the inputs (distributed or point sources). Distributed sources are commonly associated with natural phenomena, agricultural drainage, and runoff from melting snow containing salt used for deicing purposes. Point sources are usually industrial and municipal waste water discharges or irrigation return flow. This part of the paper considers various examples of steady state conditions describing the spatial distribution of dissolved solids in freshwater streams from both distributed and point sources.

Spatially Uniform Distributions

Spatial uniformity of dissolved solids concentration is considered in this case and is assumed to be due to distributed sources which are derived only from surface runoff and groundwater inflow. The steady state in which the concentrations c_s and c_g are assumed to be constant is considered. It is recognized that the surface water and groundwater concentrations may vary and may be functions of the surface runoff and groundwater flow. In spite of the approximation involved in the assumption that c_g and c_s are constant, it is informative to develop the analysis, which will indicate the general nature of the relationship between total river flow and concentration.

For the steady state, integration of (1) yields the obvious solution
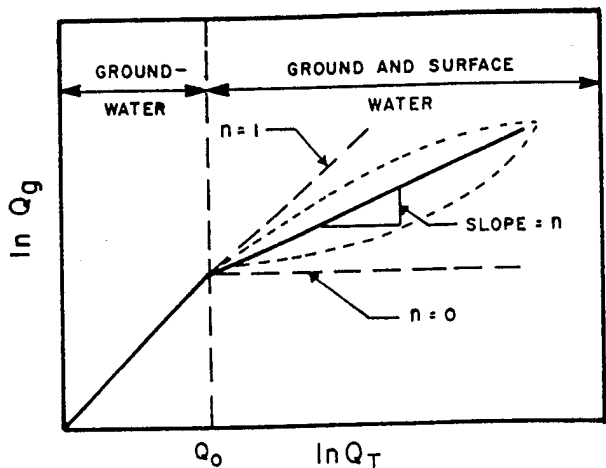
$$0 = -Qc + Q_g c_g + Q_s c_s \qquad (2a)$$

or

$$c = rc_g + (1 - r)c_s \qquad (2b)$$

in which $r = Q_g/Q$.

Equation (2a) is essentially the relationship used by many of the investigators referenced above. It expresses the con-

Fig. 1.   The relationship between river flow and (a) groundwater, (b) the ratio of river flow to groundwater, and (c) the concentration of dissolved solids.

centration of the substance in the river as a function of the groundwater and surface water concentrations and of the ratio of the groundwater flow to the total flow. The limits of the expressions c_g and c_s define the upper and lower concentration values of a conservative substance which may be expected in a freshwater stream. During the dry periods of the year, when the surface flow is zero and the streamflow is composed only of groundwater, the concentration in the river equals that in the groundwater. During the high-flow period the surface component is much greater than the groundwater component, and the concentration in the river approaches that of the surface

ing data or obtained from appropriate analyses of well water and/or soil water.

The crux of the analysis is, of course, the ratios of the groundwater and surface water to the total river flow. These ratios vary with the magnitude of the total flow. During dry periods the surface flow is zero or a relatively small quantity, and the groundwater flow is a large percentage of the total flow. Thus the ratio r equals or approaches unity up to a specified flow value Q_0 which is characteristic of a particular drainage basin. Above this base flow Q_0 the surface component becomes significant. As the total river flow increases, owing to surface runoff, the relative influence of the groundwater component becomes less; i.e., the groundwater component also increases but not as quickly as the surface runoff. The general nature of these relationships is shown diagrammatically in Figures 1a and 1b. The dashed line in Figure 1a represents realistically a range of the groundwater component when both surface runoff and groundwater are contributing to the total flow in the river. For a given flow Q_T the rising limb of the hydrograph may have a small component of groundwater by contrast to the falling limb. If this range is significant, a time variable analysis is required. In many cases, however, the range may be sufficiently compressed so that a reasonable approximation is realized by the solid line, as is shown, and the steady state analysis is adequate. If it is assumed therefore that the groundwater is equal to the total river flow during periods of low runoff and may be expressed as a fractional power of the total flow during periods of high flow, the following relationships hold:

For $Q < Q_0$

$$Q_g = Q_T \quad \text{or} \quad r = Q_g/Q_T = 1 \qquad (3a)$$

for $Q > Q_0$

$$Q_g = \beta Q^n \quad n < 1.0 \quad \text{or} \quad r = Q_g/Q_T = B/Q_T^{1-M} \qquad (3b)$$

at $Q_T = Q_0$, $r = 1$, and $\beta = Q_0^{1-n}$, where Q_0 is the base flow below which the river flow is totally groundwater, n is the logarithmic slope of the river flow–groundwater relation for flows greater than Q_0, and β is the groundwater flow component at unit river flow.

The relationship between river flow Q_T and the ratio of the river flow to the groundwater component, in accordance with (3a) and (3b), is shown diagrammatically in Figure 1b.

Substitution of (3a) and (3b) in (2b) yields, respectively,
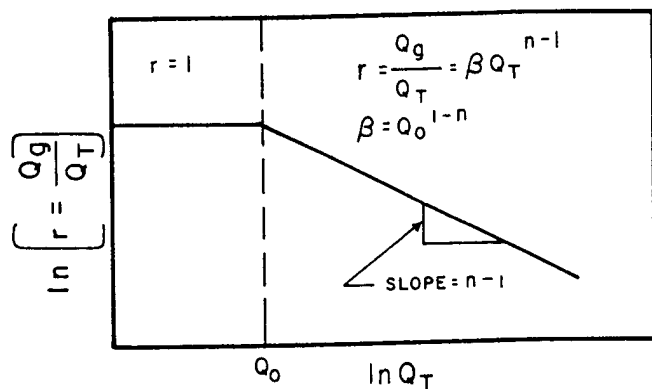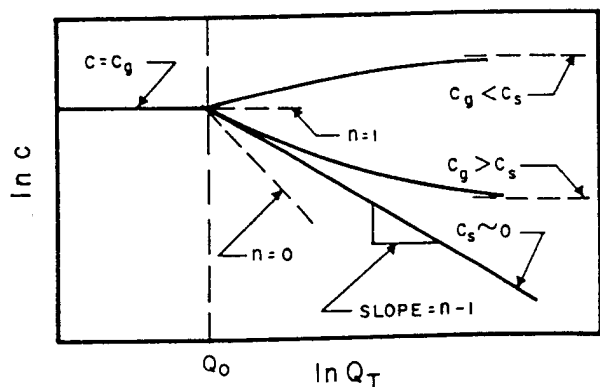
$$c = c_g \quad \text{for} \quad Q < Q_0 \qquad (4a)$$

$$c = c_s + [\beta(c_g - c_s)/Q^{1-n}] \quad \text{for} \quad Q > Q_0 \qquad (4b)$$

Figure 1b presents the relation between the river flow and the ratio of the river flow to the groundwater component in logarithmic coordinates.

On the basis of (3a) and (3b) the flow-concentration relationship follows in accordance with (4a) and (4b). The shape of the flow-concentration relationship varies from one drainage area to another depending on the absolute and relative magnitudes of the surface water and groundwater concentrations and the ratio of the groundwater to the total flow, as is shown in Figure 1c. This figure diagrammatically indicates the flow-concentration relationship for a surface concentration of dissolved solids c_s equal to zero and also for a surface concentration less than and greater than the groundwater concentration c_g.

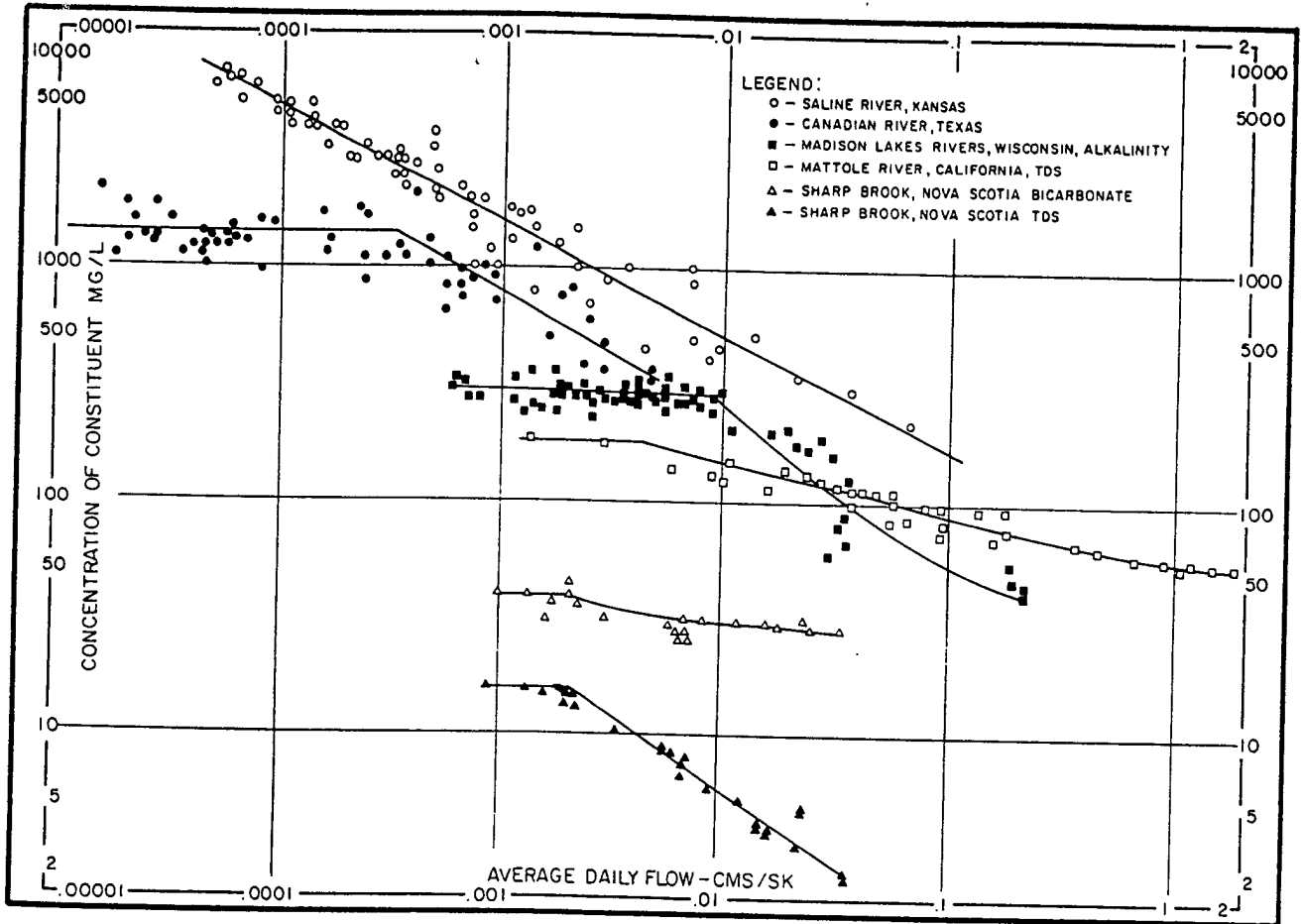Applications of the above equations are shown in Figure 2

Fig. 2. Concentration by constituent versus flow for various rivers throughout the country.

for various rivers throughout the country. The solid lines are the correlations based on (4a) and (4b) using the parameters given in Table 1. Approximate values of these parameters were indicated in some of the references or were estimated from the data given. In some cases where these were not available, they were approximated from the characteristics of the drainage area and then refined to fit the data.

Inspection of Table 1 indicates that in those regions of high groundwater concentrations the assumption of a zero concentration of surface water permits a realistic approximation of the flow-concentration relationship and accordingly simplifies (4b). In spite of the fact that the surface water concentration is probably nonzero, its magnitude is generally such that the correlations are not markedly altered, whether or not this component is included. In general, the rivers in the eastern part of the country may have values of the order of 10–50 mg/l.

The analysis of the Sharpe Brook data [Pinder and Jones, 1969] is very significant in this regard. Constituents, such as sodium and chloride, are present in both ground and surface runoff, while others, such as calcium and bicarbonate, are contributed almost exclusively by groundwater. Thus the particular constituent considered affects the shape of the concentration-flow correlation. This point is evident from the shape of the total dissolved solids (TDS) and bicarbonate correlations for Sharpe Brook shown in Figure 2. As was pointed out by these investigators, the groundwater component may thus be readily identified.

There appears to be an approximate correlation between the exponent n and the ratio Q_m/Q_0, where Q_m is the mean annual flow. Thus the exponent of the flow in (4b) contains the mean flow. This observation is generally in accord with that made by Ledbetter and Gloyna [1964].

Figure 3 presents an annual average relationship on a countrywide basis between flow and concentration [Langbein and Dawdy, 1964]. Each point is an average of between 9 and 17 locations throughout the country. A total of 168 stations were analyzed. All stations with less than 0.004 $m^3/s/km^2$ are west

TABLE 1. Characteristics of the River Systems

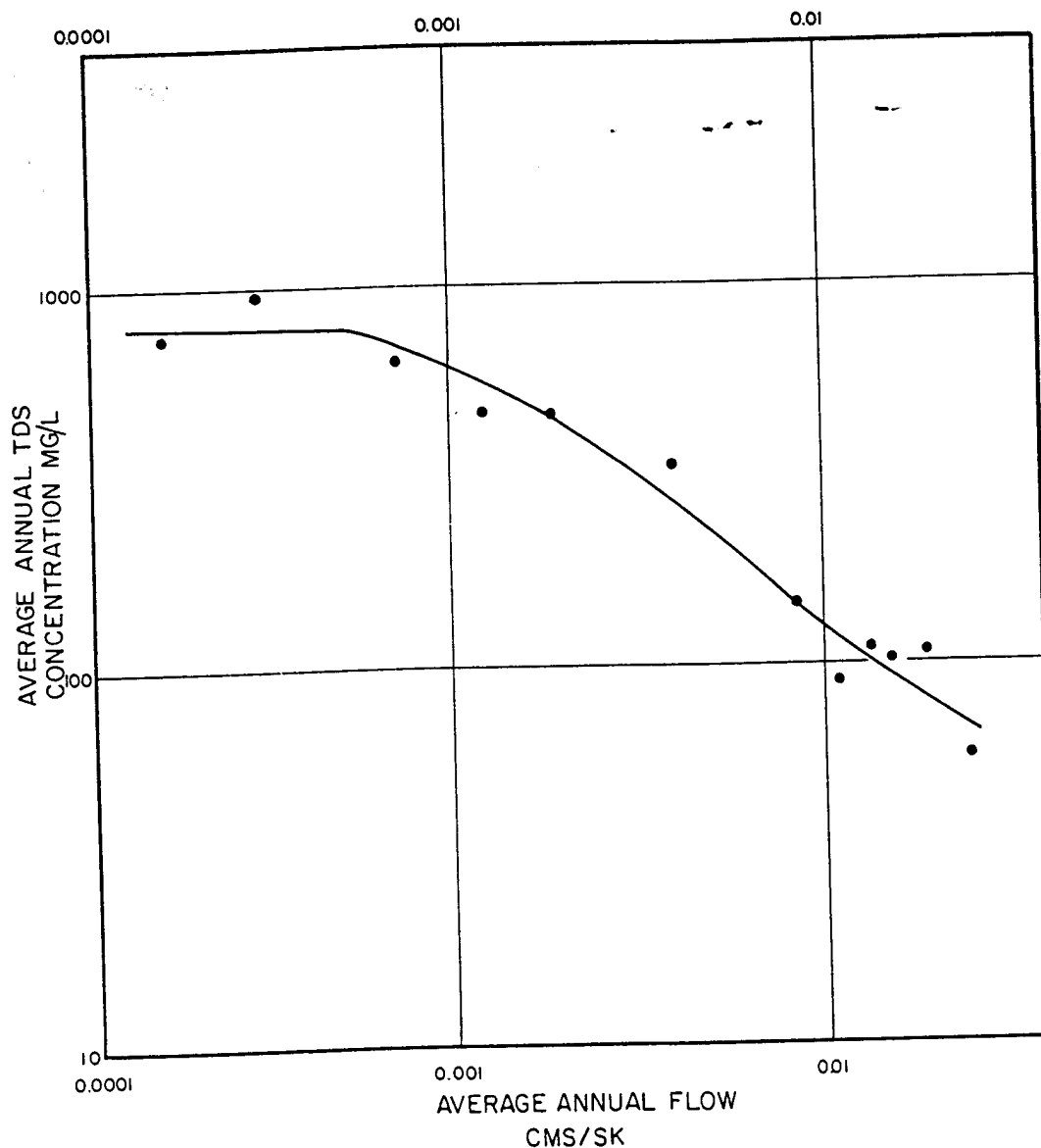| River	Location	Constituent	Drainage Area, km^2	Q_m, $m^3/s/km^2$	Q_0, $m^3/s/km^2$	n	c_g, mg/l	c_s, mg/l
Sharpe Brook	Nova Scotia	bicarbonate TDS	15	0.010	0.0022	0.3	40	25
Madison Lake streams	Wisconsin	alkalinity	80–230	0.055	0.0022	0.3	16	0
					0.0087	0.1	300	30
Mattole	California	conductivity	620	0.060	0.0033	0.7	180	45
Saline	Kansas	TDS	4,000	0.0003	0.000042	0.5	7400	0
Canadian	Texas	TDS	60,400	0.0033	0.00033	0.6	1400	0

Fig. 3. The relationship between average annual flow and average annual TDS concentration on a countrywide basis.

of the Mississippi. It is interesting to note the similar trend of the relationship on the larger temporal and spatial scale.

It is not suggested that the analysis described above is applicable in all cases. Patterns other than those presented in Figure 2 are often evident and may be ascribed to any one or more of the following factors: (1) the nature of the drainage basin, which may be composed of a number of tributaries from areas of different geochemical characteristics and varying hydrological patterns by contrast to the tacit assumption of spatial uniformity, (2) the input of mass associated with the interflow or subsurface flow, in addition to mass from the ground and surface components, and (3) the ratio of the groundwater flow to the surface flow, which may be variable rather than constant, as was assumed above.

The steady state procedure outlined above may be appropriate in the analysis and synthesis of composite drainage areas if the lag effects are minimal. Although the compositing of both flow and solids from various drainage areas introduces the need for additional approximations, the analysis may well be sufficient for water quality purposes, at least for preliminary assessment.

The interflow problem, in addition to the bank storage phenomenon, has been addressed in the hydrological liter-

ature, but little quantitative analysis is presently available. Some investigators [Hart et al., 1964] have included the interflow component in the analysis. Equation (2) becomes

$$Q_c = Q_g c_g + Q_s c_s + Q_i c_i \qquad (5)$$

The inclusion of the interflow factor is particularly appropriate for those substances which are concentrated more in the surface layer of the soil, an example of which is presented in the second part of this paper. In many cases the addition of the interflow yields better correlations but imposes the added difficulty of assigning numerical values to both the flow and the concentration of this component.

The last factor relates essentially to the time variable nature of the problem. The steady state assumption may be appropriate during certain seasons of the year, notably the fall, but it is, at best, an approximation during the high-runoff period.

The variable ratio of groundwater flow to surface or total flow, which has been more fully studied, is primarily attributable to the relative effects of storage in the groundwater reservoir and retention of the surface runoff. Because of these effects, there usually results a lower groundwater component on the rising limb and a higher value on the falling limb for the same total flow, as is shown by the range in Figure 1a. The
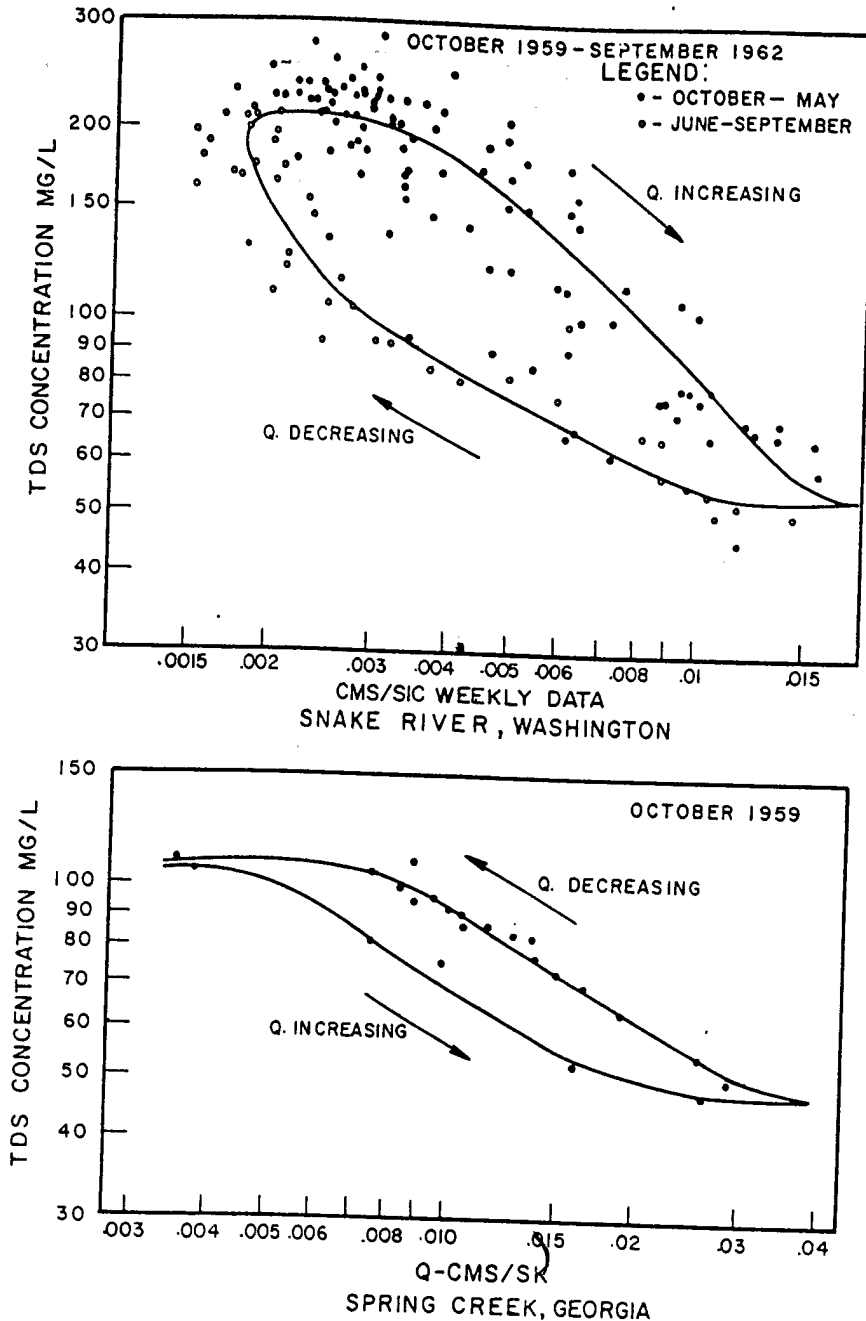
Fig. 4. TDS concentration versus flow for Snake River, Washington, and Spring Creek, Georgia.

effect may be further compounded by bank storage. In a concentration versus flow plot a 'hysteresis' effect is thus produced, the direction of which is dependent on the characteristics of the runoff and drainage basin. This effect is shown in Figure 4 for Snake River in Washington and Spring Creek in Georgia. The solid lines are not calculated but sketched through the data to indicate the trends.
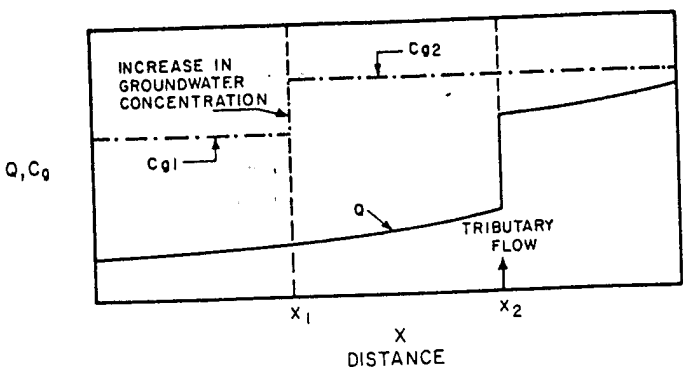
In the case of the Snake River, a large tributary of the Columbia River, the solid circles are the data from October through May, and the open circles the data from June through September. During the former period the flow increases from 0.002 to 0.016 $m^3/s/km^2$, and the concentration decreases from about 250 mg/l to about 50 mg/l. During the latter the w drops rapidly, and the concentration rises but relatively more slowly, two concentrations thus being given for a certain flow, a higher value on the rising limb of the hydrograph and a lower one on the falling limb, a clockwise hysteresis.

Figure 4 also shows the data from a single storm at Spring Creek, Georgia. As the flow increases from about 0.008 to 0.03 $m^3/s/km^2$, the concentration decreases from 110 mg/l to 50

mg/l. The concentration is greater on the rising limb than on the falling limb, a counterclockwise hysteresis thus occurring. These time variable phenomena are discussed in the second part of this paper.

Longitudinal Distributions

Distributed sources. The preceding analysis assumed not only a steady state condition but also a spatial uniformity. The latter condition is undoubtedly realized in those streams whose groundwater component contains a constant concentration along the longitudinal axis of the river. In those drainage areas which are characterized by a nonuniform geology, concentrations in the ground discharge may vary appreciably from headwater to mouth. A common example is an area in which the upland feeder streams are underlaid by igneous rocks such as granites, which are relatively resistant to erosion, while the downstream beds may consist of sedimentary material such as shales, which are more readily susceptible to erosion and solution. In addition, the nature of the soil in the flood valley contributes to the overall composition of the substances
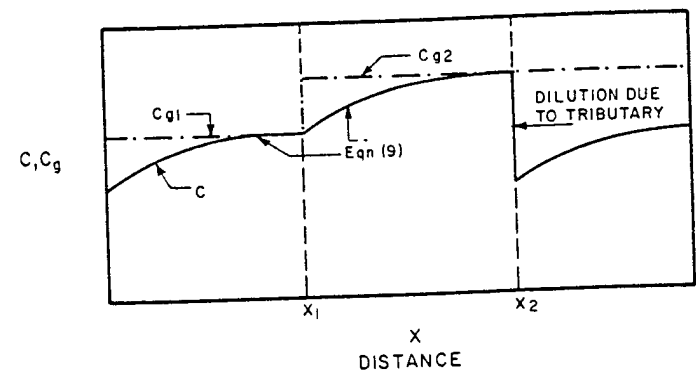
Fig. 5. The spatial variation of flow and groundwater concentration.

dissolved or carried in the water. Thus the ground concentration in the headwater area may be relatively low (~ 100 mg/l or less), while in the downstream area it may be significantly greater (~ 1000 mg/l or greater). This spatial variability may be gradual, or it may be abrupt owing to a geological discontinuity. The effects of an abrupt change are shown diagrammatically in Figure 5. The streamflow is increasing owing to the groundwater inflow. At the location of this discontinuity x_1, the upstream groundwater concentration c_{g1} is less than that downstream c_{g2}, and the upstream concentration is in equilibrium with that of the groundwater. Downstream from this point the groundwater concentration is greater; therefore the stream concentration increases in the direction of flow, approaching the new groundwater value as a limit. At location x_2, a tributary inflow dilutes the main stream. The new concentration is established by a mass balance and, in a similar fashion, increases the downstream direction. Thus the change in concentration in the stream depends on the rates of change in both the concentration and the flow of the groundwater and tributaries.

The analysis for this case is based on the steady state condition of flow, which varies spatially downstream. The steady state further implies that surface runoff is zero, and the flow in the stream therefore is derived from groundwater only. Under these conditions the basic differential equation (1) reduces to

$$0 = -(d/dx)(Q_g c) + c_g(dQ_g/dx) \qquad (6)$$

Since the flow is only groundwater, the subscript 'g' is dropped in the following equations. Expansion of the first term, grouping of similar terms, and integration lead to

$$-\ln (c_g - c) = \int_0^x \frac{1}{Q} \frac{dQ}{dx} dx + K \qquad (7)$$

where K is a constant.

The change of flow with respect to distance has various functional forms, either exponential or linear, depending on the characteristics of the drainage basin. If an exponentially increasing function is assumed,

$$Q = Q_0 e^{qx} \qquad (8)$$

and

$$(dQ/dx) = qQ \qquad (9)$$

in which q has units L^{-1} and is the fractional increase in flow per unit length of the stream. Substitution of (9) into (7) and integration, by applying the boundary condition $c = c_0$ at $x = 0$, evaluate the constant and yield

$$c = c_0 e^{-qx} + c_g(1 - e^{-qx}) \qquad (10)$$

This equation requires specification of the flow parameter q and groundwater concentration c_g. The former is obtained from flow measurements made at different locations along the length of the stream or may be approximated by the change in drainage area expressed as a fraction per unit distance. The latter value may be obtained from analyses, as was described in the previous section, or from field data. The initial condition is either specified by the upstream groundwater concentration or obtained from survey data. Furthermore, for large values of x these equations indicate that equilibrium is reached and the concentration in the stream is constant and equal to c_g.

An example of the application of (10), describing the spatial distribution of total dissolved solids in the Powder River Basin in Wyoming and Montana [Swenson, 1953], is shown in Figure 6. The exponential increase in flow is employed in this case. The data were obtained in the low-flow period of September, during which time steady state flow conditions prevailed. The groundwater concentrations were assigned on the basis of the maximum values recorded in the two areas. Ideally, these values should be obtained from measurements of well waters in their respective areas, more accurate assignment of these parameters as well as a more detailed segmentation of the system thus being permitted. The parameter q was calculated on the assumption that the exponential rate of increase of flow equals that of the increase in drainage area. The locations of tributaries are shown by arrows with their concentrations indicated in parentheses in the legend. A mass balance was made at each junction. Clear Creek drains an area consisting primarily of granite bedrock, while the main branch of the Powder River and its other tributaries flow through regions of limestone, gypsum, and shale. The inflow of Clear Creek thus provides a dilution which reduces the concentration in the main stream by a factor greater than 2.

By contrast to the step increase in groundwater concentration, shown in Figures 5 and 6, a continuously increasing function of concentration may also be representative of a particular drainage area. If an exponential increase in groundwater concentration is assumed, the equation is

$$c_g = c_{g0} e^{gx} \qquad (11)$$

in which c_{g0} is the groundwater concentration at $x = 0$. Expanding (6) and substituting (9) and (11) for the flow and concentration functions, respectively, result in

$$(dc/dx) + qc = qc_{g0} e^{gx} \qquad (12)$$

The solution of (12) with the boundary condition $c = c_0$ at $x = 0$ is

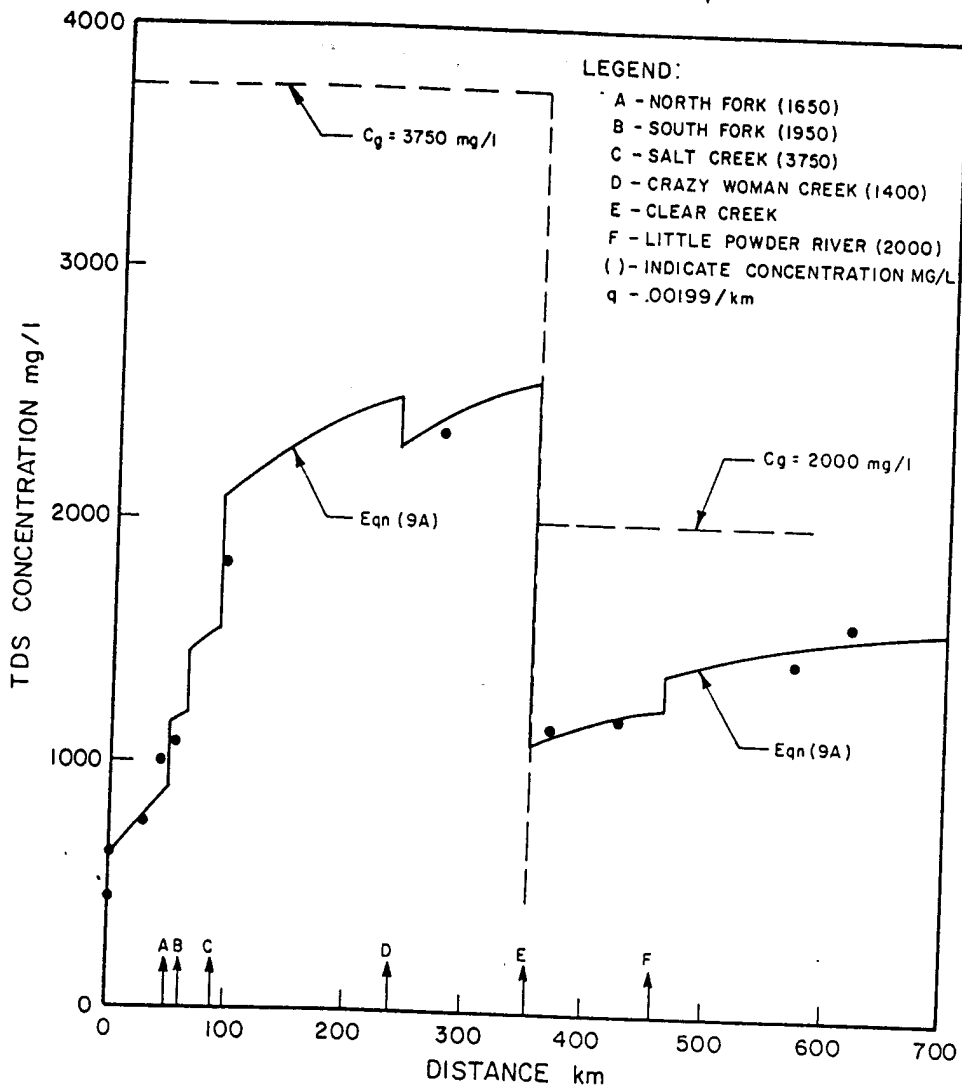$$c = [qc_{g0}/(q + g)](e^{gx} - e^{-qx}) + c_0 e^{-qx} \qquad (13)$$

Fig. 6. The spatial distribution of TDS in the Powder River Basin in Wyoming and Montana.

When $g = 0$, i.e., a constant groundwater concentration, (13) reduces to (10).

An example is presented in Figure 7 for Sharpe Brook in Nova Scotia [*Pinder and Jones*, 1969]. The parameter $q = 0.60/km$ was approximated from the increase in drainage area. The geological structure of the basin consists of porphyritic granite in the upstream area, changing to sandstone and shale in the downstream section. The parameter $g = 0.85/km$ was arbitrarily assigned to reflect the increase in the groundwater concentration. The concentration as a function of flow (4) and as a function of distance (13) for the low-flow period is shown.

Point sources. The discussion presented in the preceding section is directed to distributed sources of dissolved solids in streams. Such sources are primarily of natural origin. The major impact of man's activity is felt in the area of irrigation return waters, which invariably contain higher concentrations of solids after usage. The return flows may enter as either ⁿistributed sources or point discharges. Furthermore, munici- ⁿl and industrial waste effluents, which cause increases in dissolved solids, are usually discharged as point sources. The effect that such inputs have on water quality can be added to the natural background quality.

Consider a point source of used water containing W_0 (mass per unit of time) solids which are discharged to a stream whose total flow is Q_0 at $x = 0$, the outfall location. The spatial

increase in flow is again taken as being exponential (10). The concentration in the river at $x = 0$, the upstream flux plus the mass input from the plant being taken into account, is
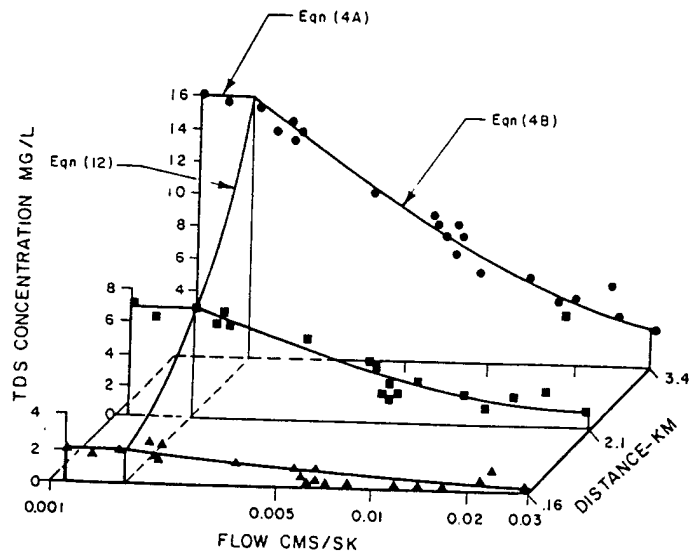
$$c_0 = (W + Q_u C_u)/Q_0 \qquad (14)$$

Fig. 7. TDS concentration as a function of flow and as a function of distance during the low-flow period of Sharpe Brook, Nova Scotia

in which c_u and Q_u are the upstream concentration and flow and Q_0 is the total flow, which is equal to the upstream flux plus effluent.

If the background concentration is at equilibrium, (10) reduces to

$$c = c_0 e^{-qx} + c_s \qquad (15)$$

The application of (15) to the analysis of dissolved solids in the Clarion River illustrates the procedure [*Camp, Dresser, and McKee, Consulting Engineers*, 1949]. A plot of the drainage area of the main channel with its tributaries is shown in Figure 8a. The points, which are measured values of the drainage area, are plotted on a semilogarithmic scale in order to facilitate the reading of the exponent, which is assumed to equal that of the drainage area; i.e., the assumption is made that the flow in the river is directly proportional to the tributary drainage area. Figure 8b presents a similar plot of the logarithm of the ratio of observed concentrations minus the background to the initial observed concentration minus the background. The slope of the line for the total and fixed solids is equal to that of the drainage area plot with the obvious change of sign, the increasing groundwater flow causing a dilution of the concentration produced by the plant discharge. It should be noted that the concentration of volatile dissolved solids decreases more rapidly in the first 15 km, as is shown by the steeper slope. This phenomenon is due to the oxidation of
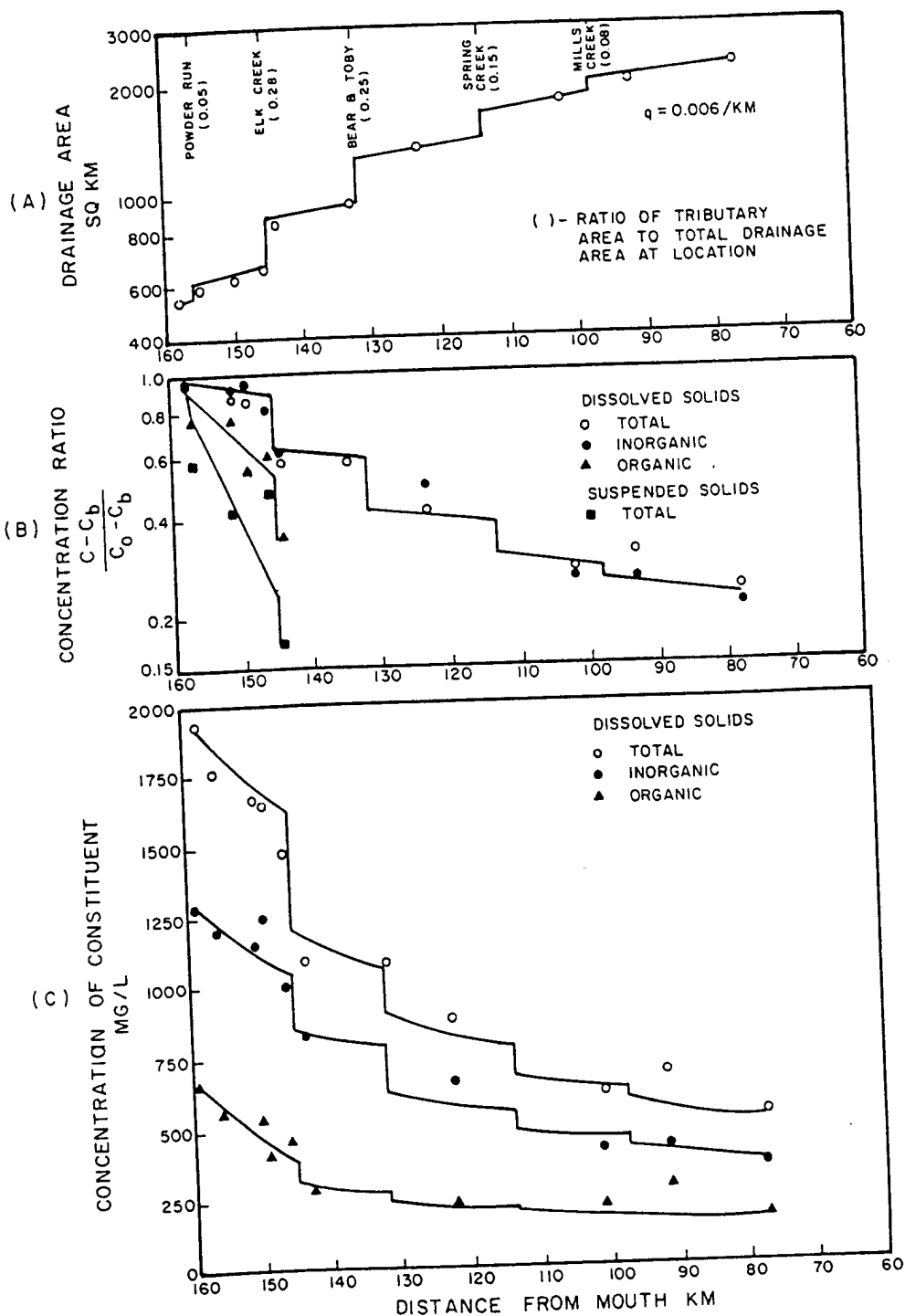

Fig. 8. Tributary area versus total drainage area, the ratio of observed concentrations minus the background to initial observed concentration minus the background, and the spatial distribution of dissolved solids for the Clarion River,

some of the organic dissolved solids, causing a further diminution in concentration in addition to that due to dilution. Furthermore, the drop in suspended solids is even more rapid owing to the settling of this material, which generally proceeds at a more rapid rate than oxidation. Although the data for these constituents are more erratic, the trend is evident. Figure 8c indicates the profiles calculated by (14) for the inorganic and organic solids. The distribution of the total solids, which is the sum of the fixed and volatile, is also shown. The initial concentration is due to the discharge of approximately 136,000 and 680,000 kg/d of inorganic and organic dissolved solids, respectively, in a total flow of approximately 1.3 m³/s.

Conclusions

In spite of the simplifying assumptions involved in the development of the equations, the various relationships between flow and concentration of dissolved solids are adequate for the analysis of certain water quality problems. The importance of the groundwater component and its relation to total flow in the river is emphasized, as it has been by many investigators. One of the most critical assumptions is the steady state condition, which may realistically describe low-flow conditions but at best is an approximation during periods of high flow. Aspects of the time variable nature of the problem are discussed in the next part of this paper.

TIME VARIABLE ANALYSIS

This part of the paper considers various time variable conditions which affect the concentration of dissolved solids in freshwater systems. Following the format of the previous section, two types of sources are considered: first, a distributed spatial source of dissolved solids due to groundwater inflow and surface runoff and, second, a point source of solids due to a waste water input. In the first case the time variable aspect is introduced by virtue of the nonsteady hydrograph of river flow, while spatial uniformity of an unspecified extent is assumed. In the second instance the river flow is at steady state, and the input of dissolved solids from the waste source is the significant time variable factor.

Basic Equations

The basic equations are developed by applying the principle of the conservation of mass to the dissolved solids and also to the fluid flow. The differential equation for the dissolved solids, as it was developed in the first part of the paper (1), is

$$\frac{\partial}{\partial t}(Ac) = -\frac{\partial}{\partial x}(Qc) + c_g \frac{\partial Q_g}{\partial x} + c_s \frac{\partial Q_s}{\partial x}$$

Expanding the left-hand term and the first term on the right-hand side yields

$$A\frac{\partial c}{\partial t} + c\frac{\partial A}{\partial t} = -Q\frac{\partial c}{\partial x} - c\frac{\partial Q}{\partial x} + c_g\frac{\partial Q_g}{\partial x} + c_s\frac{\partial Q_s}{\partial x} \quad (16)$$

In a similar fashion a flow balance is taken about an element of volume ΔV of cross-sectional area A and length Δx:

$$\Delta V = Q\Delta t - (Q + (\partial Q/\partial x)\Delta x)\Delta t + \Delta Q_s \Delta t + \Delta Q_g \Delta t$$

Dividing through by Δx and Δt and transposing yield

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = \frac{\partial Q_g}{\partial x} + \frac{\partial Q_s}{\partial x} \quad (17)$$

Equation (16) is simply an expression of flow continuity and states that the time rate of change of area plus the spatial rate of change of the river flow equals the sum of the spatial differentials of groundwater and surface flow.

Equations (1) and (17) are identical in principle, describing, respectively, the mass balance of the constituent in the fluid and the mass balance of the fluid itself. The general expression is

$$\frac{1}{A}\frac{(A\phi)}{\partial t} + \frac{1}{A}\frac{\partial(Q\phi)}{\partial x} = S$$

in which ϕ refers to the concentration c of the constituent or the density ρ of the fluid and S represents the various sources and sinks of the material.

Time Variable Flow

The problem addressed in this case is the variability of concentration in time at a specific location in the river. It is assumed that the concentration is uniform over a length of river upstream from the location under consideration or if a spatial differential of concentration does exist, it is small by contrast to the other terms in (16). When this condition is applied, after transposing and combining, (16) becomes

$$\frac{dc}{dt} = c_g\frac{\partial Q_g}{A\,\partial x} + c_s\frac{\partial Q_s}{A\,\partial x} - \frac{c}{A}\left(\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x}\right) \quad (18)$$

Substituting (17) in (18) yields

$$\frac{dc}{dt} = c_g\frac{\partial Q_g}{A\,\partial x} + c_s\frac{\partial Q_s}{A\,\partial x} - c\left(\frac{\partial Q_g}{A\,\partial x} + \frac{\partial Q_s}{A\,\partial x}\right) \quad (19)$$

TABLE 2. Parameters of the River Systems

River	Figure	Constituent	c_g, mg/l	c_s, mg/l	c_i, mg/l	f Interval,* day⁻¹					Component
						1	2	3	4	5	
Snake†	9	TDS	300	40	...	0.15	0.05	0.40	0.40	0.15	ground
Saline	10	TDS	7500	1000	...	...	0.80	1.6	...	...	surface
						0.03	0.03	...	...	...	ground
ʼring	11	TDS	140	40	...	0.06	...	...	...	...	surface
						0.085	0.08	0.22	0.07	...	ground
Mattole	12	TDS	168	42	98	1.02	0.17	0.68	...	...	surface
						0.75	0.09	0.09	...	...	ground
		silica	7	8	12	2.5	...	...	...	...	surface
						0.75	0.09	0.09	...	...	ground
						...	1.5	...	...	...	interflow

*See individual figure to identify actual interval.
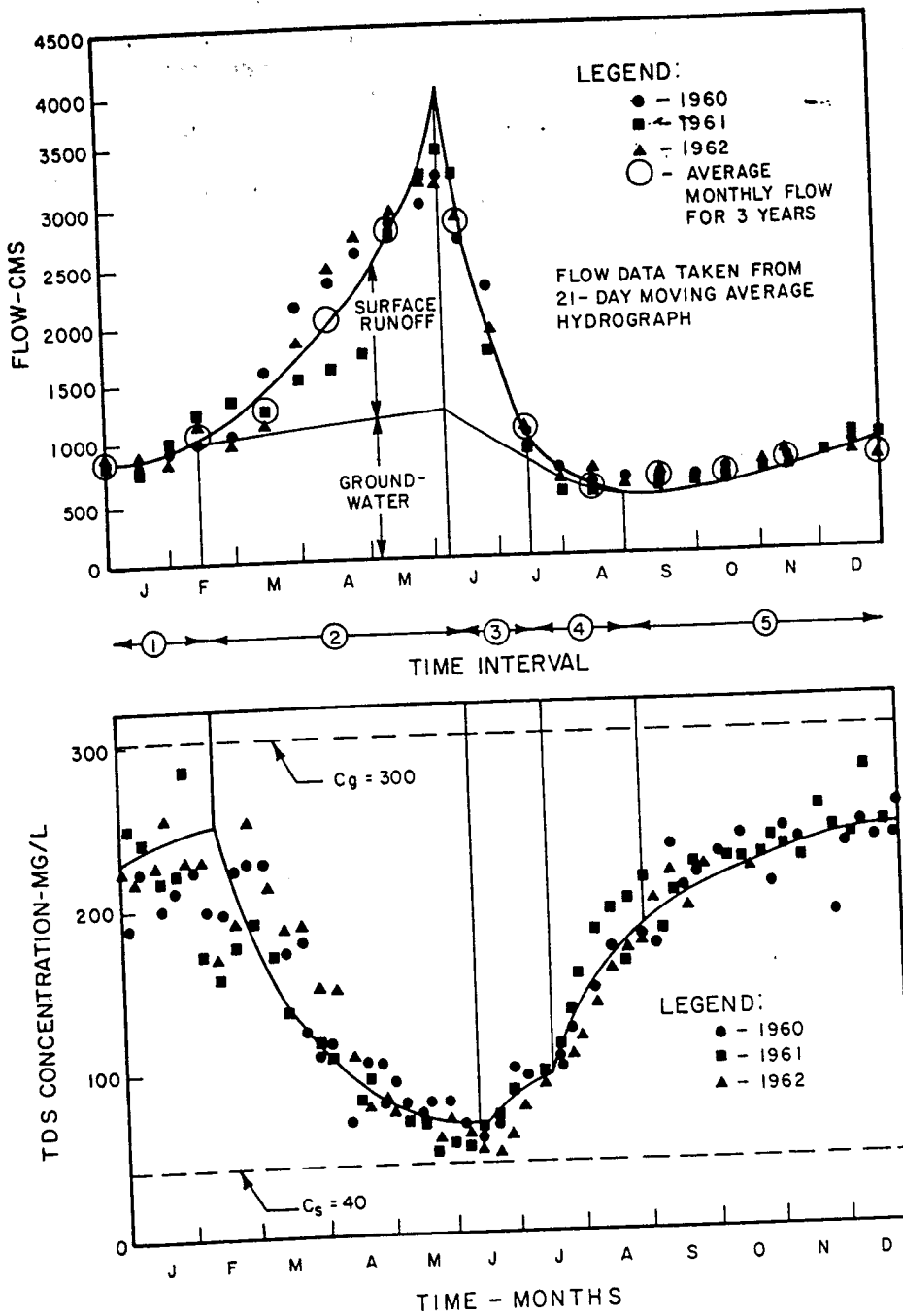†The f interval for the Snake River is in month⁻¹.

Fig. 9. The annual distribution of flow and TDS concentration for the Snake River, Washington.

The factors multiplying c_g and c_s have the units of reciprocal time and may be regarded as measures of times of detention. Although these parameters may themselves be time variable, let them be approximated by the constants f_g and f_s, respectively, over particular and limited intervals of the hydrograph. In general, these intervals are the rising and falling limbs of the hydrograph and the groundwater recession.

Equation (19) may then be written for each interval:

$$(dc/dt) + fc = f_g c_g + f_s c_s \qquad (20)$$

in which $f = f_g + f_s$.

The solution of (20) for the usual initial condition is

$$c = F(1 - e^{-ft}) + c_0 e^{-ft} \qquad (21a)$$

$$F = (f_g c_g + f_s c_s)/(f_g + f_s) \qquad (21b)$$

When the surface flow is zero and the river flow is derived

$$c = c_g(1 - e^{-f_g t}) + c_0 e^{-c_g t} \qquad (21c)$$

The values of the exponents f may be approximated as follows. As was indicated above, the hydrograph may be divided into three intervals: a period of surface runoff increasing to a peak value, one of decreasing runoff, and, finally, a period of groundwater recession. Various empirical procedures have been proposed to separate the surface and ground components of the hydrograph. The common approach is to obtain a groundwater flow curve by a graphical extension of the groundwater recession curve. The difference between the groundwater component thus defined and the total flow is called the surface flow [Linsley et al., 1958]. Semilogarithmic plotting of these flows with time usually yields straight lines whose slopes q_s and q_g satisfy

$$Q_g = Q_{g0} e^{\pm q_g t} \qquad (22a)$$
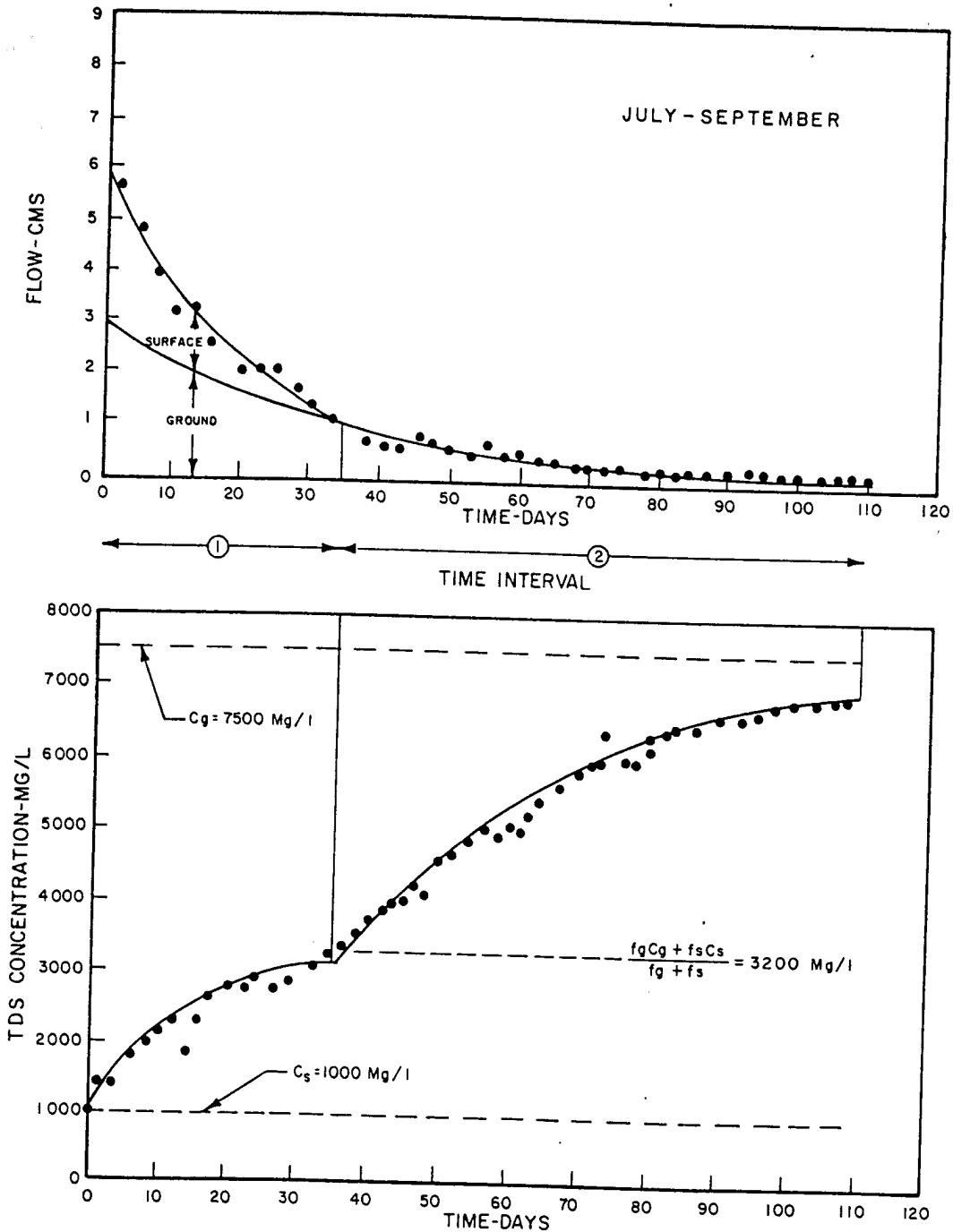
$$Q_s = Q_{s0} e^{\pm q_s t} \qquad (22b)$$

Fig. 10. The distribution of flow and TDS concentration for an intermediate time scale for the Saline River, Kansas.

The plus sign refers to the rising limbs of the hydrograph, and the negative sign to the falling limb and the groundwater recession. The exponents q in $(22a)$ and $(22b)$ are measures of detention times, and it is assumed that they are equal, respectively, to the detention times f in (20) and (21). Specifically, it is assumed that

$$|q_g| = f_g \qquad |q_s| = f_s$$

Although this assumption is admittedly arbitrary, it is generally in accord with physical reasoning and empirical observations, as may be seen from the following examples on the Snake and Saline rivers and Spring and Mattole creeks. The values of the coefficients and parameters for each system are given in Table 2.

The annual distribution of dissolved solids in the Snake River is given in Figure 9. Daily values of total runoff are averaged, as is indicated. The data on concentrations of dis-

solved solids are weekly samples. The June–July period is characterized by a rapid decrease in flow. However, the concentration does not respond as quickly owing to the long detention time of the groundwater component; f_g is equal to 0.40–0.15/month, equivalent to a detention time of 75–200 days. By the end of the annual year the concentration is that of the groundwater ($c_g = 300$ mg/l), which extends into the first few months of the next year. The increase in surface runoff in February causes a dilution of the concentration, which approaches the surface concentration ($c_s = 40$ mg/l) by the middle of June.

An example of the analysis for an intermediate time scale is presented in Figure 10 for the Saline River in Kansas. The flow components are determined as described in the previous paragraph. The distribution for the Saline River is for the decreasing leg of the hydrograph during the dry period in summer and early fall. The groundwater concentration of 7500 mg/l of
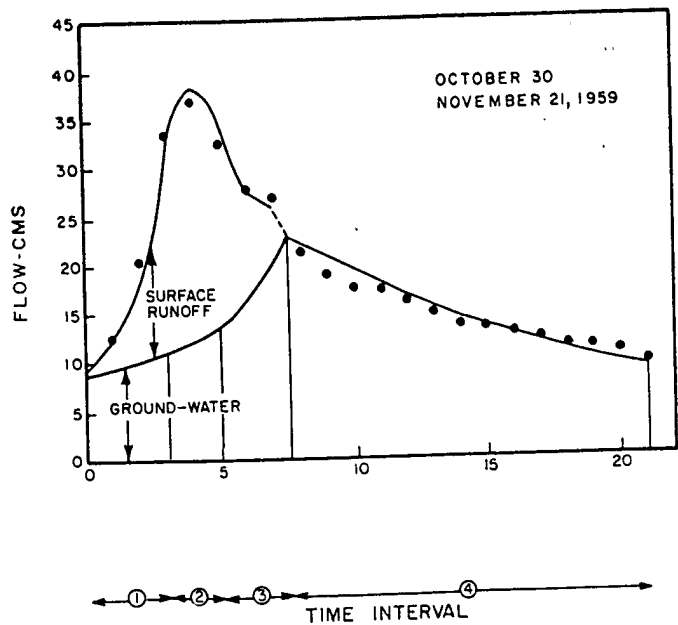
the various components are also indicated. The values for the conductance are consistent with those used in the steady state analysis presented in Figure 2 of the first part of this paper, the concentration in the interflow being assigned arbitrarily between the two limits. The values for the silica, however, follow a different trend, the interflow concentration having the maximum value. These were abstracted from a plot of silica versus flow in the reference noted above.

Inspection of these figures indicates that the agreement between the calculated profiles and the observations is reasonably satisfactory. Furthermore, the determination of the numerical values of the exponents f_g and f_s is based on calculations derived from hydraulic continuity. Although there is a limited range of flows within which the groundwater component could fall, the assignment within this range is rather arbitrary. The fact remains, however, that there is a set of exponents and parameters for each case which are consistent with hydraulic continuity and yield the profiles shown in the figures.
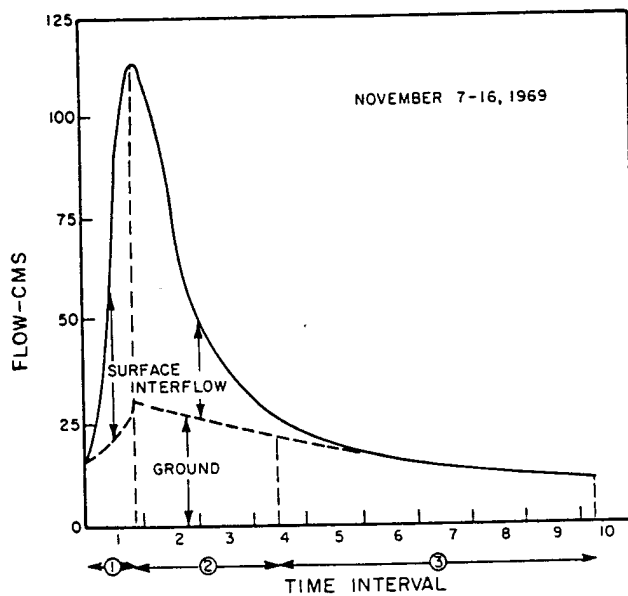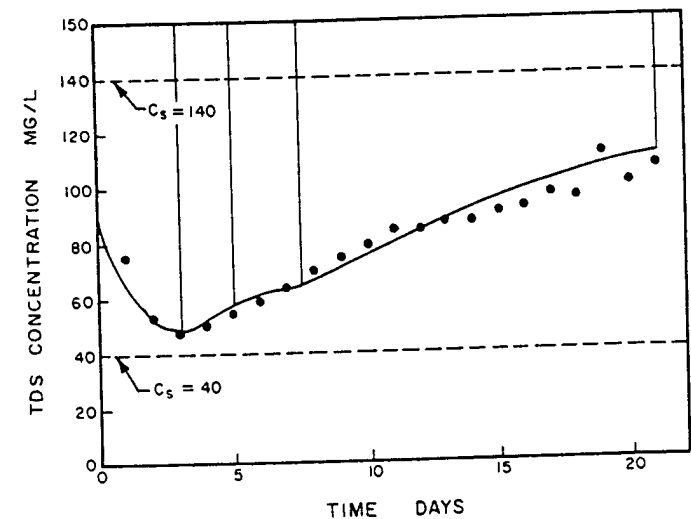

Fig. 11.   The distribution of flow and TDS concentration over a short time interval for Spring Creek, Georgia.

total dissolved solids is consistent with the steady state analysis described in the first part of this paper. The intermediate equilibrium value of 3300 mg/l, calculated by (21b), is also presented.

An example of the analysis applied over a short time interval is given in Figure 11, which shows the flow and solids distribution over a 20-day period for Spring Creek, Georgia [Toler, 1965]. The rising curve of the total hydrograph, caused by surface runoff, is paralleled 3 days later by a similar upturn in the groundwater flow curve.

Inspection of Figures 9 and 11 indicates the reason for the hysteresis effect of the flow-concentration relationships shown in Figure 4 of the first part of the paper, the clockwise pattern for Snake River by contrast to the counterclockwise pattern for Spring Creek.

The analysis of the silica concentration in Mattole Creek, as shown in Figure 12, indicates the importance of the interflow or subsurface component [Kennedy, 1971]. As was indicated previously, it is necessary to include this component if its concentration varies from that of the surface or groundwater. The model is then composed of three components. The detention times, estimated as described above and expressed as the _____ , ___ tabulated in Table 2. The concentrations in
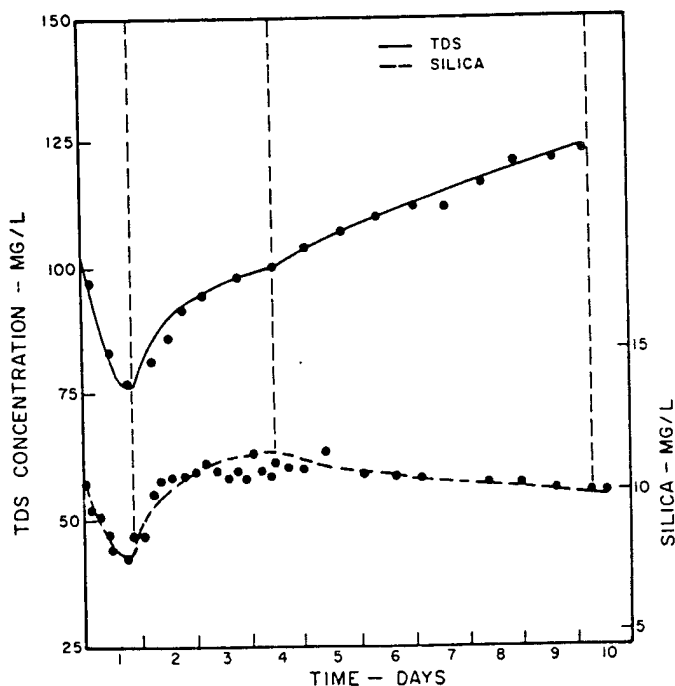

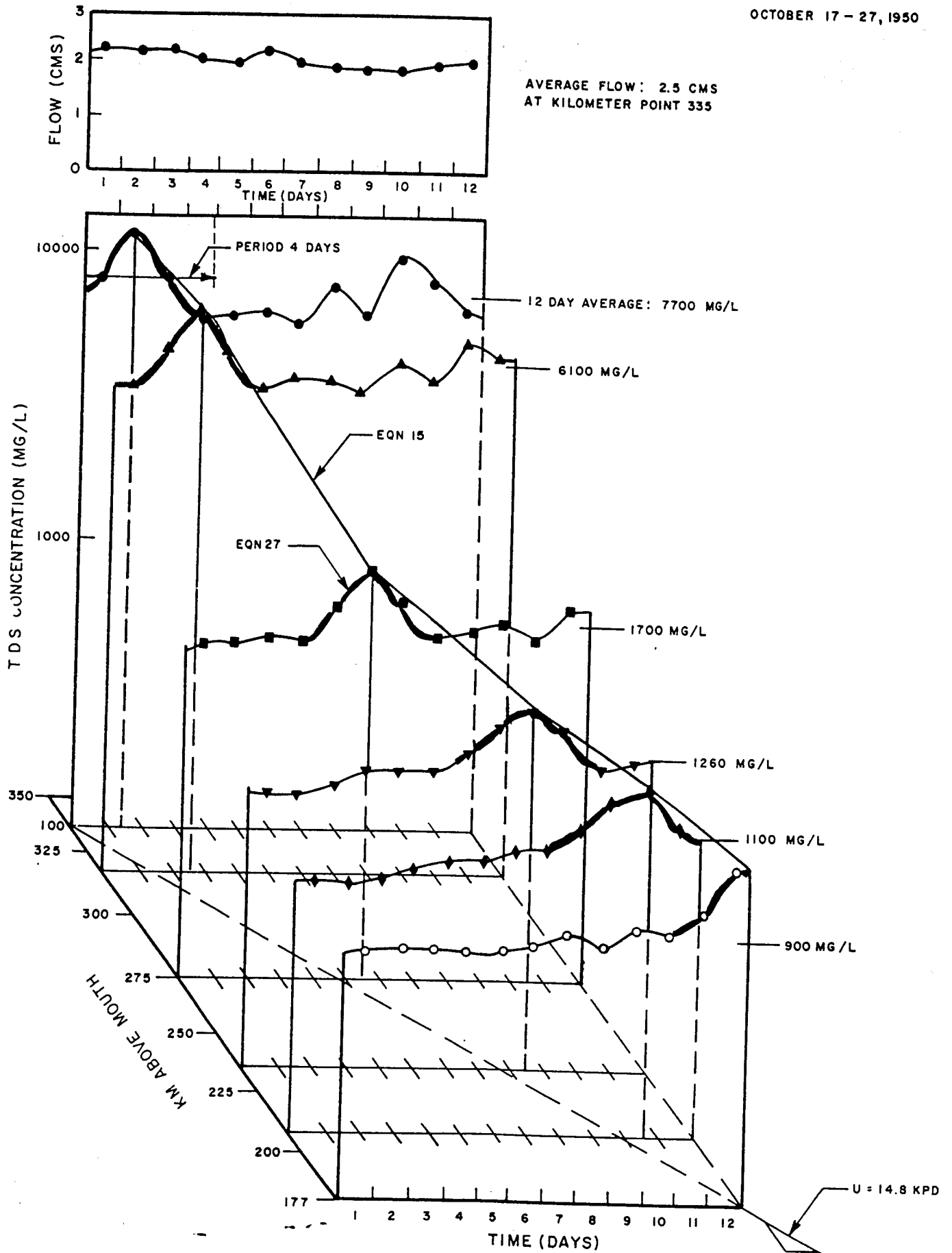Fig. 12.   The distribution of flow and TDS concentration for Mattole Creek, California.

Fig. 13. The chloride distribution in the Muskingum River, Ohio.

Time Variable Input

The nonsteady state condition of dissolved solids in natural streams is due not only to variations in flow, as was discussed in the previous section, but also to time variable inputs. Waste waters from municipal, industrial, or agricultural activities are the common sources of these solids. These variations may be cyclic, consisting of one or more components with hourly, daily, or seasonal periods, or long-term trends over monthly or annual time scales. Furthermore, random fluctuations are frequently superimposed on these phenomena.

Assume a time variable input $W(t)$ discharging to a river at $x = 0$ whose flow is at steady state. This condition usually occurs during the low-flow period of the year, at which time the flow in the stream is due to groundwater ($Q = Q_g$) and the surface runoff is zero ($Q_s = 0$). Since steady state hydraulic conditions are stipulated, $(\partial A / \partial t) = 0$, and (1) reduces to

$$A \frac{\partial c}{\partial t} = -\frac{\partial (Qc)}{\partial x} + c_g \frac{\partial Q}{\partial x} + W(t)|_{x=0} \qquad (23)$$

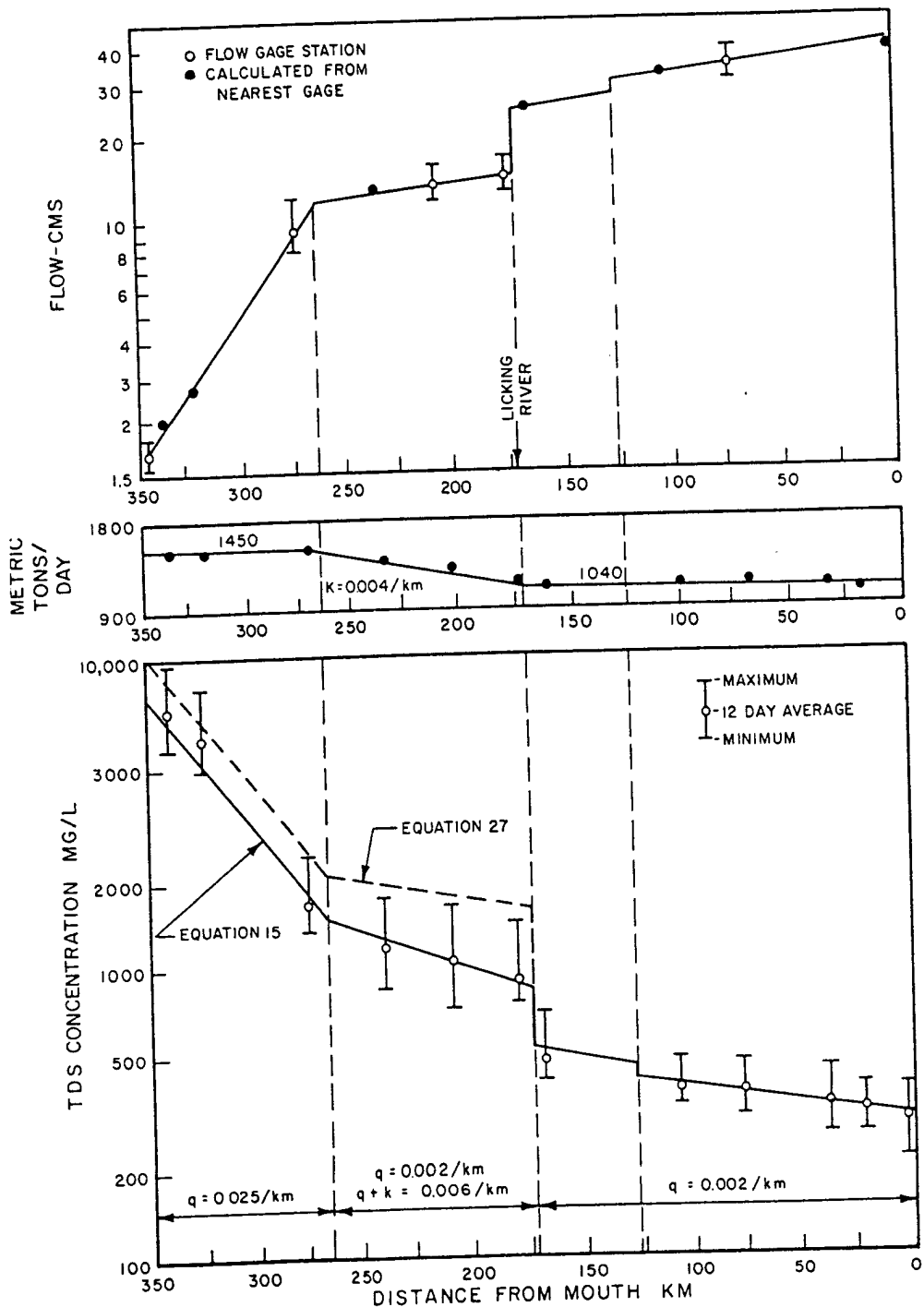When the first term on the right-hand side is expanded and divided by A, (23) becomes

$$\frac{\partial c}{\partial t} = -\frac{Q}{A} \frac{\partial c}{\partial x} - \frac{c}{A} \frac{\partial Q}{\partial x} + \frac{c_g}{A} \frac{\partial Q}{\partial x} + \frac{1}{A} W(t)|_{x=0}$$

which may be further simplified to

$$\frac{\partial c}{\partial t} = U \frac{\partial c}{\partial x} - Uq(c - c_g) + \frac{1}{A} W(t)|_{x=0} \qquad (24)$$

in which

$$U = Q/A \qquad q = (1/Q)(dQ/dx)$$

Fig. 14. The distribution of flow and TDS concentration for the Muskingum River, Ohio.
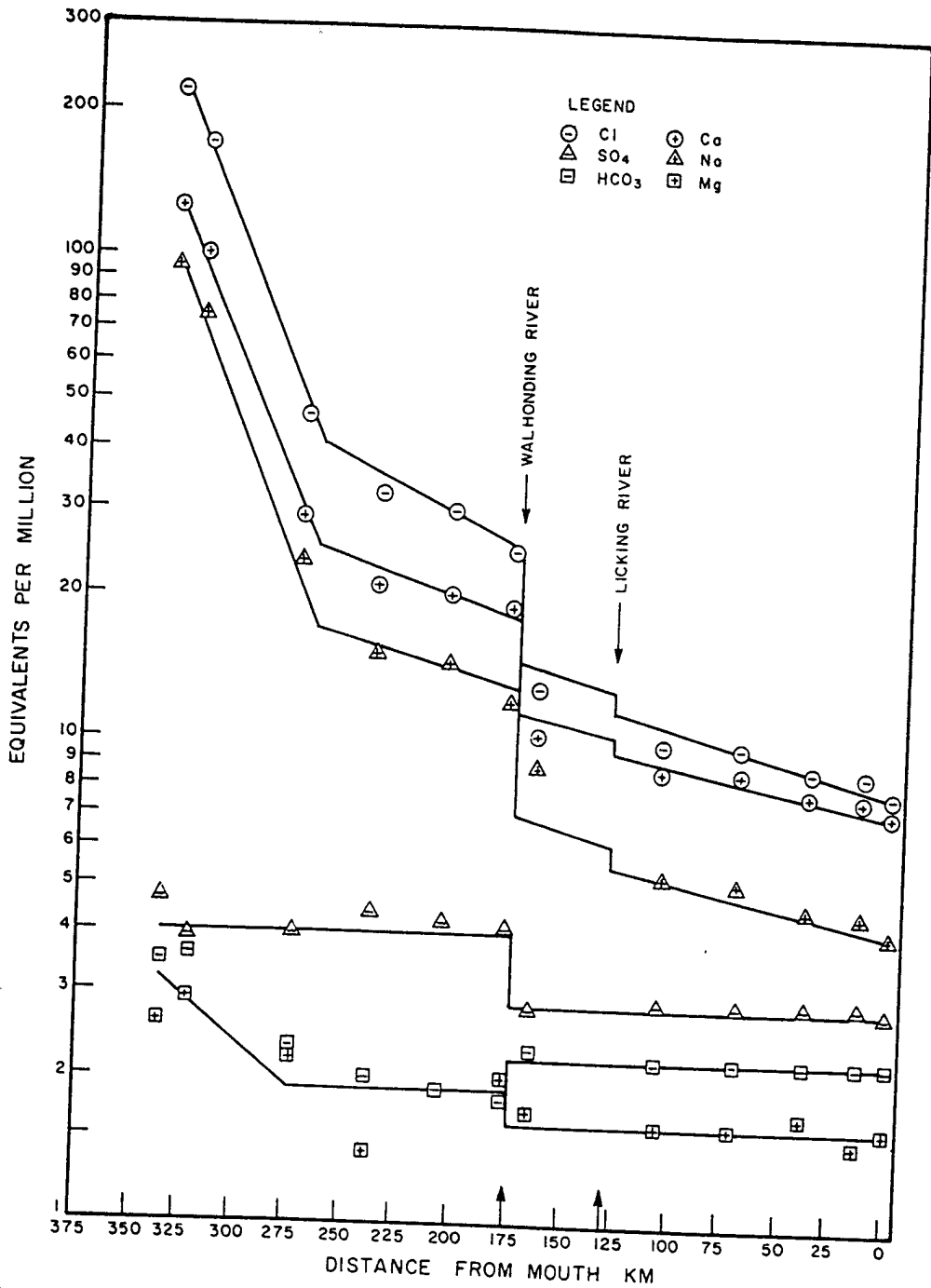
Fig. 15. The spatial distribution of chloride, bicarbonate, sulfate, calcium, sodium, and magnesium for the Muskingum River, Ohio.

The equation defining q assumes an exponential increase in flow with distance ((8) and (9)). If it is assumed that the concentration in the river due to groundwater inflow is in equilibrium, the concentration at $x = 0$ is

$$c(0, t) = [W(t)/Q_0] + c_g \qquad (25)$$

in which $Q_0 = Q$ at $x = 0$, and for any x the concentration is

$$c(x, t) = \left[\frac{W(t - x/U)}{Q_0}\right]e^{-\alpha x} + c_g - t \geq \frac{x}{U} \qquad (26)$$

Solutions (25) and (26) assume that the flow and area functions increase equally such that the velocity is a spatial constant. The solutions apply to any arbitrary function of tem-

poral input. If a simple periodic function is assumed, (26) becomes

$$c(x, t) = \left[\frac{W_m - W_a \cos\left[(t - x/U)2\pi/\tau\right]}{Q_0}\right]$$
$$\cdot e^{-\alpha x} + c_g \qquad t \geq x/U \qquad (27)$$

in which W_m is the mean mass input, W_a is the amplitude about the mean, and τ is the period.

The application of (27) to the chloride distribution in the Muskingum River, a tributary of the Ohio River, is shown in Figure 13. The river is located in the eastern part of the state of Ohio. The upstream section, known as the Tuscarawas River, flows through areas rich in salt deposits. Two companies remove salt from these sources by dissolution

produce sodium chloride, sodium hydroxide, and chlorine. The liquid residues from these processes contain concentrations of chloride, calcium, sodium, and, to a lesser extent, sulfates. The waste waters are stored in lagoons, from which they enter, by seepage and release, the headwaters of the Tuscarawas River. Although exact measurements of the quantity and strength of these wastes were difficult to obtain, it was estimated that the combination was of the order of 1400 metric tons per day of chloride.

A water quality survey of the river was conducted by the *Ohio River Valley Water Sanitation Commission* [1951] in October. Hourly samples were collected at a few selected stations, and daily samples at the other stations for a continuous period of 12 days (October 16–27). The flow hydrograph is presented in Figure 13 at $x = 0$ (kilometer 335), which is downstream from the two sources. The temporal distributions at various stations downstream from this location are also shown. Inspection of the hydrograph indicates that an approximate steady state flow condition prevailed and that the inputs produced significant temporal variations in the concentration in the river. The average concentration over the 12-day period at $x = 0$ is 7700 mg/l, as is indicated, with a minimum and maximum of 5700 mg/l and 12,000 mg/l, respectively. The 12-day average concentrations are also presented for the downstream stations.

Over the first few days of the survey the input, and therefore the boundary concentration, may be reasonably represented by a simple periodic function, as is shown by the heavy line in Figure 13. A mean concentration of 9000 mg/l, with an amplitude of 2400 mg/l over a period of 4 days, adequately describes the distribution at $x = 0$. The velocity was 14.8 km/d. The value of the groundwater exponent q is determined from the type of analysis presented in the first part of this paper ((8) and (9)). The temporal distributions at the various downstream stations are computed in accordance with (27) and compare favorably with the observations at these locations.

The characteristic of the movement of the peak concentration at a velocity of $U = 14.8$ km/d is presented as an example of the time-of-travel concept. This characteristic is identified by the diagonal plane, and the associated concentrations most appropriately represent the spatial distribution. It is interesting to compare this distribution with that determined by an assumed steady state analysis. Figure 14 presents the 12-day average concentrations with the maximum and minimum values. The solid line is in accordance with (15) of the first part of this paper, and the dashed line represents the peak values computed by (27).

Figure 14 also shows the flow distribution from which the values of the exponent q and the mass flow rate of chlorides are determined. It should be noted that in the reach above Licking River (kilometer 177) a loss of salt occurs. A loss rate of 0.009/km is assigned. This is added to the exponent q in (15) to yield the distribution of concentration shown by the dotted line.

A further observation of note is the ionic balance, which is maintained between the anions (chloride, bicarbonate, and sulfate) and the cations (calcium, sodium, and magnesium). Figure 15 presents the spatial distribution of these constituents, whose concentrations are expressed as equivalents per million to facilitate a check of the ionic balance. It should be noted that the bicarbonate, sulfate, and magnesium distributions have flatter slopes than the distributions of the ... of these constituents in the

tain a constant level in the river. Furthermore, the Licking River contribution increases in bicarbonate concentration by contrast to the decrease of the other constituents. Tracking the individual components of the dissolved solids in this fashion leads to a better definition of groundwater during periods of high flow.

Conclusion

This paper presented various methods of analysis relating the concentration of dissolved solids and their components to variations in river flow and waste water inputs. Both steady state and time variable conditions were considered. Although the methods were primarily addressed to water quality considerations, some should be useful in analyzing the groundwater component of the total river flow.

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