

Estimation of Multiple Inflows to a Stream Reach Using Water Chemistry Data

D. A. Woolhiser, H. R. Gardner, S. R. Olsen

MEMBER
ASAE

ABSTRACT

IN many hydrological investigations, it is necessary to estimate the quantity of inflow to a stream reach that comes from each of several source areas. Because of the diffuse nature of these inflows, conventional techniques often fail.

Assuming that the concentrations of m conservative ionic species in the influent waters are known, the unknown inflow rates can be estimated by minimizing the sum of squared percentage errors in m ion mass balance equations by using quadratic programming. The inflows are constrained to be positive, and the mass balance of water is maintained.

A sensitivity analysis showed that the method is less sensitive to errors in flow measurements than to errors in chemical concentration. If a significant flow is omitted from the calculation, the error is transferred to the other inflows with similar chemical characteristics. Errors in the estimated inflows are related to the product of the inflow and the dissolved inorganic salt concentrations. As an example, inflows to a reach of stream were calculated for a data set from a surface-mined area in western Colorado. The results appear reasonable.

INTRODUCTION

In many hydrological investigations, it is desirable to estimate the quantity of inflow to a stream reach that comes from each of several source areas. For example, during a surface runoff event, inflow to a reach may include surface runoff from several areas with different land use, runoff from rainfall on saturated areas near the stream, and groundwater inflows from several different geological formations. In special circumstances, small, but chemically significant, inflows may reach the stream from waste disposal ponds or municipal or industrial waste outfalls. Because of the diffuse nature of some of these inflows, it is difficult to measure them directly.

The chemical quality of water in a stream is influenced by four factors: (1) the physical and chemical composition of the geologic material that it has come in contact with as it moved through the watershed, (2) chemicals

Article has been reviewed and approved for publication by the Soil and Water Division of ASAE.

The authors are: D. A. WOOLHISER, Research Hydraulic Engineer, USDA-ARS, Southwest Rangeland Watershed Research Center, Tucson, AZ; H. R. GARDNER and S. R. OLSEN, Soil Scientists, USDA-ARS, Fort Collins, CO.

Acknowledgments: Terri Butkovich did the chemical analyses of the water samples, and JoAnn Ahrens assisted with the computer programming. We thank Dr. John Labadie, Department of Civil Engineering, Colorado State University, for providing the computer program of the Wolfe algorithm. We also wish to thank Energy Fuels Corporation for their cooperation in our field research program. This research was partially supported by the Environment Protection Agency through Interagency Agreement EPA-IAG-DO-E763.

added to the watershed by man's activities, (3) biological and chemical activity within the stream, and (4) environmental factors that influence stream temperature and gaseous exchange between water and air. The ionic composition of streamflow results from the solution of minerals contacted as water flows over the surface or as groundwater, and depends upon the distribution of soluble minerals, the physical characteristics of the soil or geologic materials that govern contact between the water and the minerals and the contact time. Therefore, water that moves through a unique environment would be expected to have a characteristic absolute and relative abundance of the principal anions and cations, and water in the stream would consist of a mixture of water from several different sources, each representing a unique environment.

Previous investigators have used the observed differences between the total dissolved solids content (or electrical conductivity) of surface runoff and groundwater runoff (base flow) to estimate the proportion of stream discharge contributed from each source (Pinder and Jones 1969; Visocky 1970; Hall 1970). This approach is adequate when only two sources of water are considered but cannot be used if there are more than two sources of inflow to a reach of stream.

The purpose of this paper is to present a method that can be used to estimate the quantities of inflow from several sources to a stream reach if the chemical characteristics of the inflows are known.

MATHEMATICAL MODEL

To formulate the model, let us consider the stream reach shown schematically in Fig. 1. Let Q_u represent the measured surface inflow for a time interval Δt , and let Q_o represent the measured surface outflow for the same time period. For a given time interval, there may be several distinct (but unknown) inflows to the reach $X_1, X_2, \dots, X_j, \dots, X_n$. Let S represent the volumetric storage of water within the stream channel at any instant, and let ΔS

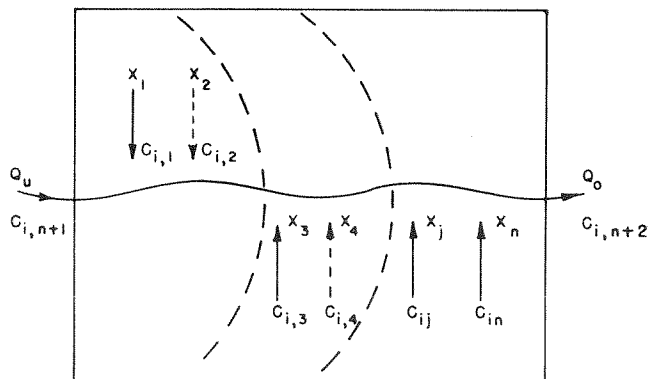


FIG. 1 Schematic diagram of stream reach and contributing watershed area.

represent the change in storage over some time interval, Δt . Thus, the mass balance equation for water can be written:

$$Q_u + \sum_{j=1}^n X_j = Q_o + \Delta S \dots \dots \dots [1]$$

if subsurface inflow to and outflow from the watershed is assumed negligible.

Let us assume that, over the Δt in question, the change in storage is negligible; thus, $\Delta S = 0$, and equation [1] becomes

$$\sum_{j=1}^n X_j = Q_o - Q_u \dots \dots \dots [2]$$

Now, if we let C_{ij} represent the concentration of the i^{th} ionic species in the j^{th} inflow, we can write a mass balance equation for each of the m ionic species.

$$\begin{aligned} C_{i1} X_1 + C_{i2} X_2 + \dots + C_{in} X_n - C_{i,n+2} Q_o + C_{i,n+1} Q_u &= 0 \\ \vdots & \\ C_{i1} X_1 + C_{i2} X_2 + \dots + C_{in} X_n - C_{i,n+2} Q_o + C_{i,n+1} Q_u &= 0 \\ \vdots & \\ C_{m1} X_1 + C_{m2} X_2 + \dots + C_{mn} X_n - C_{m,n+2} Q_o + C_{m,n+1} Q_u &= 0 \end{aligned} \dots \dots \dots [3]$$

where the inflow concentration of the i^{th} ionic species is designated as $C_{i,n+1}$ and the concentration in the outflow is $C_{i,n+2}$.

The most important assumption inherent in equation [3] is that each ionic species is conservative within the reach. There must be no chemical exchange, deposition or gaseous transport, and no uptake by living organisms. These requirements will affect the choice of the ionic species to be used. For example, NO_3^- would be a poor tracer during periods of algal growth or decay, and temperature, or pH changes that affect the solubility of CO_2 may invalidate the use of HCO_3^- , Ca^{++} , and Mg^{++} as tracers.

Additional assumptions include:

- 1 There must be complete mixing within the reach.
- 2 The chemical composition of the influent water must not change from the time of sampling to the time the inflow and outflow samples are taken. Thus the method is best suited to locations where the concentrations of major chemicals are at equilibrium rather than kinetically controlled.
- 3 Water composition must not change between the sampling point and the stream. For example, if groundwater from a mined area must pass through undisturbed formations before reaching the stream, the accompanying chemical transformation, precipitation, exchange, or dissolution must be negligible.

Because of errors in the chemical analysis, and because the concentration of each ionic species in each inflow is not known exactly (some inflows may not be identified at all), these equations will not all be satisfied if $m > n$. Therefore, we add an error term ϵ_i to the right-hand side of each equation and try to find the set of inflows X_1, X_2, \dots, X_n that minimize the sums of the squared error terms.

With the added error terms, equation [3] can be written in matrix notation as

$$[C] \{X\} + \{B\} = \{\epsilon\} \dots \dots \dots [4]$$

where

$$\{B\} = \begin{Bmatrix} -C_{1,n+2} Q_o + C_{1,n+1} Q_u \\ \vdots \\ -C_{m,n+2} Q_o + C_{m,n+1} Q_u \end{Bmatrix}$$

[C] is a $n \times m$ matrix and

$$\{X\} = \begin{Bmatrix} X_1 \\ \vdots \\ X_j \\ \vdots \\ X_n \end{Bmatrix}$$

We can eliminate one of the X_j from equation [2] resulting in a set of m equations in $n-1$ unknowns. Equation [4] is still appropriate, but now the [C] matrix is $(n-1) \times m$ and

$$C_{ij} = (C_{ij} - C_{in}) \begin{matrix} i=1, \dots, m \\ j=1, \dots, n-1 \end{matrix} \dots \dots \dots [5]$$

and

$$B_i = (C_{in} - C_{i,n+2}) Q_o + (C_{i,n+1} - C_{i,n}) Q_u \dots \dots \dots [6]$$

Consider the following objective function:

$$E = \sum_{k=1}^m \epsilon_k^2 \dots \dots \dots [7]$$

By substituting equation [4] into equation [7], we obtain the quadratic form which we wish to minimize, thus:

$$\text{Min } E = \sum_{k=1}^m \epsilon_k^2 = \begin{matrix} X_1 \\ X_2 \\ \vdots \\ X_{n-1} \\ 1 \end{matrix} \underline{Q} \dots \dots \dots [8]$$

where:

$$\underline{Q} = \sum_{i=1}^m \underline{D}_i \underline{A}_i \dots \dots \dots [9]$$

$$\underline{D}_i = \begin{bmatrix} (C_{i1} - C_{in}) & & & 0 \\ (C_{i2} - C_{in}) & & & \\ \vdots & & & \\ 0 & & (C_{i,n-1} - C_{in}) & \\ & & & B_i \end{bmatrix} \dots \dots \dots [10]$$

$$\underline{A}_i = \begin{bmatrix} (C_{i1} - C_{in}) & (C_{i2} - C_{in}) & \dots & (C_{i,n-1} - C_{in}) & B_i \\ \vdots & \vdots & & \vdots & \vdots \\ (C_{i1} - C_{in}) & (C_{i2} - C_{in}) & \dots & (C_{i,n-1} - C_{in}) & B_i \end{bmatrix} \dots \dots \dots [11]$$

TABLE 1. CHEMICAL COMPOSITION OF TEST MIXTURE NO. 1

Water Sample	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ⁼	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺
	meq/L							
1	4.80	0.09	0.03	3.27	4.19	2.88	0.49	0.06
2	3.98	0.21	0.53	19.70	10.68	7.90	3.26	0.12
3	2.50	0.14	1.05	42.20	22.70	19.74	1.19	0.14
Mixture	3.55	0.16	0.64	25.41	14.19	11.63	1.88	0.12

The objective function, equation [8], can be separated into its linear and quadratic terms

$$E = \sum_{j=1}^m a_j X_j + H [X_1, X_2] \dots \dots \dots [12]$$

This expression is to be minimized subject to the constraints:

$$X_j \geq 0 \dots \dots \dots [13]$$

The only situation in which we may wish to relax this constraint is where there is significant evaporative loss or diversion of water from the reach in question. Care must be taken in selecting the X_j to be eliminated, because it is no longer subject to the non-negativity constraint equation [13].

The quadratic programming problem specified by equations [12] and [13] can be solved by several existing techniques such as the Wolfe algorithm (Wolfe 1959).

SENSITIVITY ANALYSIS

The following types of errors can affect the accuracy of the calculated inflows $X_1 \dots X_n$.

- 1 Errors in the chemical analyses.
- 2 Errors in determining the discharge rates Q_o and Q_u .
- 3 Nonrepresentative samples of the inflow water quality.
- 4 Omission of a significant inflow.

Furthermore, if the chemical characteristics of two or more inflow sources are very nearly identical, distinguishing between them should be very difficult.

To assess the sensitivity of the optimum inflow estimates to errors in the chemical analysis, we did an empirical sensitivity study. We wrote a simulation program that added a normally distributed error term to each concentration C_{ij} .

$$C'_{ij} = C_{ij} + C_{ij} V_i U \dots \dots \dots [14]$$

where C'_{ij} is the perturbed concentration, C_{ij} is the concentration of the i^{th} ion in the j^{th} input water, V_i is the coefficient of variation of the error term, and U is an independent, normally distributed random variable with mean of zero and standard deviation of \pm one.

The data set used was a theoretical mixture of three waters found near a surface coal mine in western Colorado. In dealing with a mixture, Q_o is set equal to one, and Q_u is zero. The unknowns, X_j , are then proportions of the mixture. The theoretical mixture concentrations for the i^{th} ion were calculated by the following equation:

$$C_{i5} = 0.2 C_{i1} + 0.4 C_{i2} + 0.4 C_{i3} \dots \dots \dots [15]$$

Therefore, the theoretical proportions were

$$X_1 = 0.2, X_2 = 0.4, X_3 = 0.4 \dots \dots \dots [16]$$

The concentration of eight ions, Na⁺, Ca⁺⁺, Mg⁺⁺, K⁺, Cl⁻, NO₃⁻, HCO₃⁻ and SO₄⁼ were used in the calculations. These data are shown in Table 1. It should be noted that these particular ions are used only as an example. Other ions, including some of the environmental isotopes, may be more effective tracers in many circumstances.

Because each concentration, C_{ij} , $i = 1,8; j = 1,4$ was perturbed according to equation [14], the unknowns solved for by the quadratic programming algorithm reflected these errors. The perturbed unknowns X_1, X_2 , and X_3 were obtained for nine randomly generated samples for coefficients of variation, $V = 0.03$ and 0.05 . The same coefficient of variation was used for all ions.

The sample means, standard deviations, and coefficients of variation of X_1, X_2 , and X_3 for each V are shown in Table 2. Table 2 shows that the coefficients of variation of the unknown inflows X_1, X_2 , and X_3 may be as much as an order of magnitude greater than the coefficient of variation of the concentration errors, although the mean values are quite close to the theoretical values. Because this large variability was unacceptable, we examined methods of reducing it.

From equations [5] and [6], we can write the equation for ϵ_i^2 as

$$\epsilon_i^2 = [(C_{i1} - C_{in}) X_1 + (C_{i2} - C_{in}) X_2 + \dots + (C_{i,n-1} - C_{in}) X_{n-1} + (C_{in} - C_{i,n+2}) Q_o + (C_{i,n+1} - C_{in}) Q_u]^2 \dots \dots [17]$$

The partial derivative of the objective function, E , with respect to the ionic concentration is a measure of the sensitivity to errors in determining the concentration. Thus,

$$\frac{\partial E}{\partial C_{ij}} = \frac{\partial \epsilon_i^2}{\partial C_{ij}} = 2 \epsilon_i \frac{\partial \epsilon_i}{\partial C_{ij}} \dots \dots \dots [18]$$

The greatest sensitivity occurs when ϵ_i and $\partial \epsilon_i / \partial C_{ij}$ are large. The value of ϵ_i is highest for the most abundant ion, and the maximum $\partial \epsilon_i / \partial C_{ij}$ is Q_o . Thus, to obtain approximately equal sensitivities for each ion balance equation we wish,

$$\epsilon_1 \approx \epsilon_2 \approx \epsilon_3 \dots \dots \approx \epsilon_n \dots \dots \dots [19]$$

TABLE 2. SAMPLE STATISTICS FOR SENSITIVITY TEST, MIXTURE NO. 1

Statistic	Coefficient of variation, V, of errors in concentration	
	0.03	0.05
\bar{X}_1	0.187	0.171
S_{X1}	0.093	0.119
V_{X1}	0.497	0.696
\bar{X}_2	0.398	0.408
S_{X2}	0.146	0.189
V_{X2}	0.367	0.463
\bar{X}_3	0.413	0.421
S_{X3}	0.055	0.076
V_{X3}	0.134	0.181

TABLE 3. SAMPLE STATISTICS FOR SENSITIVITY TEST-NORMALIZED DATA MIXTURE NO. 1

Statistic	Coefficient of variation, V, of concentration errors		
	0.01	0.03	0.05
\bar{X}_1	0.091	0.187	0.190
S_{X1}	0.00525	0.016	0.026
V_{X1}	0.0275	0.086	0.137
\bar{X}_2	0.405	0.401	0.389
S_{X2}	0.00945	0.031	0.043
V_{X2}	0.0233	0.077	0.111
\bar{X}_3	0.404	0.412	0.422
S_{X3}	0.00638	0.021	0.030
V_{X3}	0.0158	0.051	0.071

One method of obtaining the approximate equality in equation [19] is to normalize the concentrations C_{ij} in each ion balance equation by dividing them by a characteristic concentration. The outflow, or "mixture" concentration, $C_{i,n+2}$, is an appropriate normalizing quantity.

The following normalizing procedure was used on the perturbed input data for Mixture No. 1 (see Table 1).

$$C'_{ij} = C_{ij}/C'_{i,n+2} \quad i = 1, 8; j = 1, n \dots \dots \dots [20]$$

where C'_{ij} is the normalized concentration. The sample means, standard deviations, and coefficients of variation of the unknown inflows X_1 , X_2 , and X_3 , obtained using this normalizing scheme, are shown in Table 3. A comparison of the coefficients of variation, V, in Table 3 with those in Table 2 shows that normalization significantly reduced the errors in estimating X_1 , X_2 , and X_3 . The coefficient of variation of X_1 was reduced by a factor of five where the V of the error terms is 0.05. For X_3 , the ratio is 2.5. This normalizing technique results in more accurate determinations of the unknown discharges by compensating for the difference in the relative abundance of the ions. A closer examination of the normalizing procedure reveals that it is equivalent to changing the objective function to the sum of squared percentage errors.

Errors in the chemical analyses could be accounted for by weighing each equation by the inverse of the coefficient of variation S_c/\bar{C} where S_c is the standard deviation of concentrations obtained by replicate analysis of a single water sample and \bar{C} is the mean concentration.

To obtain an estimate of the variability of concentrations in replicate samples, we analyzed samples that were taken at hourly intervals with an automatic sampler at two sites on a stream in western Colorado on 14 June, 1978. Although the water quality at these sites showed very little diurnal variation at this time of the year, a flow recession was occurring, so these samples are not true replicates. The variability in the laboratory-determined concentrations represents errors due to sampling, storage of samples, laboratory technique, instrument error, and trends in the water quality. The coefficients of variation for each ion, based upon a sample of 25, are shown in Table 4.

The high coefficient of variation for NO_3^- reflects inaccuracies at the very low concentrations present in these samples ($\cong 0.9$ mg/L). The reasons for the large V for Cl- are both the low concentrations ($\cong 0.9$ mg/L) and, possibly, contamination. Because of the trend present, the V's for the other ions are larger than those due only to sampling technique, laboratory technique, and instrument error. Therefore, the use of a maximum V of 0.05 in the simulations seems appropriate. The V's of the unknown inflows are approximately what one might expect in field applications. Furthermore, except for Cl- and NO_3^- , it appears that the weights should be equal.

The sensitivity of the method to errors in the inflow and outflow was estimated by adding a normally distributed random error term ($V = 0.10$) to the inflow and outflow.

The test case was a theoretical mixture of seven waters, as shown in Table 5.

Tables 5 and 6 show that the large inflows X_1 and X_6 and the small, but highly concentrated, inflows X_3 and X_7 were estimated quite closely, but the small flows with

TABLE 4. COEFFICIENTS OF VARIATION OF ION CONCENTRATIONS

V	ION							
	HCO ₃ -	Cl -	NO ₃ -	SO ₄ =	CA ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺
	0.031	0.49	2.09	0.068	0.041	0.052	.085	.0536

TABLE 5. IONIC CONCENTRATIONS, TEST CASE NO. 2

Water Source	Concentration								Theoretical Discharge m ³ /s
	HCO ₃ -	Cl -	NO ₃ -	SO ₄ =	CA ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	
	mg/L								
X_1 Range Surface runoff	34.2	.89	2.09	15.1	2.75	1.25	3.50	2.20	0.71
X_2 Mine surface runoff	158.0	1.06	5.40	157.0	68.60	21.10	5.77	4.05	0.28
X_3 Mine ground - water No. 7	366.0	7.59	9.05	1070.0	91.00	197.00	83.00	8.20	0.14
X_4 Groundwater No. 18	159.0	20.50	5.30	27.0	44.00	10.00	17.00	2.50	0.05
X_5 Groundwater No. 28	281.0	9.72	4.68	171.0	54.00	35.00	27.00	2.30	0.14
X_6 Wheat surface runoff	48.8	1.06	21.50	15.9	7.00	3.25	3.50	2.30	1.70
X_7 Agricultural seep 1101	366.0	95.20	36.10	3950.0	256.00	399.00	879.00	9.50	0.05
Inflow 1001	195.0	12.70	4.54	82.0	45.00	21.00	13.50	2.70	2.97
Outflow 1003	141.0	8.22	9.46	120.0	33.80	21.60	19.20	2.78	6.06

TABLE 6. SAMPLE STATISTICS—TEST CASE NO. 2;
SENSITIVITY TO VARIATION IN Q_u AND Q_o ($V = 0.10$)

	Inflow						
	X_1	X_2	X_3	X_4	X_5	X_6	X_7
\bar{X}_i (m^3/S)	0.644	0.222	0.147	0.098	0.117	1.690	0.055
S_{xi} (m^3/S)	0.180	0.133	0.021	0.131	0.125	0.168	0.005
V_{xi}	0.280	0.600	0.150	1.340	1.070	0.100	0.110

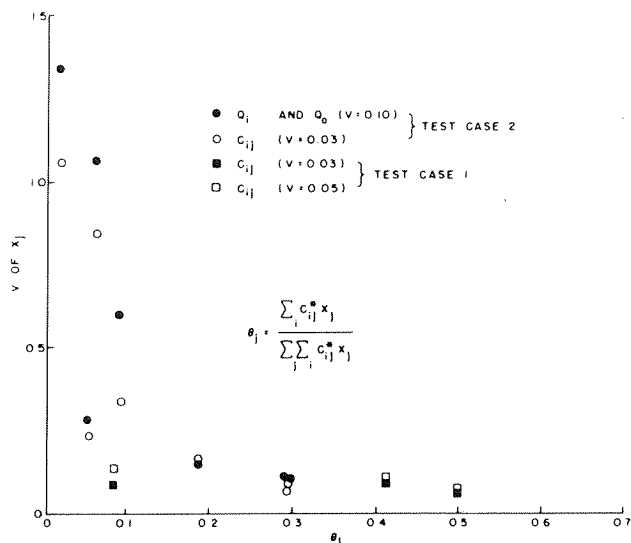


FIG. 2 Coefficient of variation of unknown inflows vs. flow-weighted concentration.

intermediate concentrations were estimated poorly (large variance). This suggested that a flow-weighted concentration might be a useful index related to the coefficient of variation of the estimated inflows. The following index was calculated for each inflow source, X_j .

$$\theta_j = \frac{\sum_{i=1}^{i=m} C_{ij}^* X_j}{\sum_{j=1}^n \sum_{i=1}^m C_{ij}^* X_j} \dots \dots \dots [21]$$

where $C_{ij}^* = C_{ij}/C_{i,n+2}$.

The coefficient of variation $V(X_j)$ is plotted vs. θ_j on Fig. 2 for the data shown in Table 6 and for the cases involving errors in the concentrations. Although only two cases are shown here, in general the coefficient of variation seems to be inversely proportional to θ . The inflow estimates appear to be more sensitive to concentration errors than they are to inflow and outflow errors, because the points for Test Case No. 2, with C_{ij} perturbed ($V = 0.05$), lie very close to those with Q_u and Q_o perturbed (V

$= 0.10$). Although other factors certainly have an influence, the index θ_j can give an idea of the relative error present.

To examine the effect of omitting a significant inflow, seven runs were made with Test Case No. 2, omitting a different inflow each time. Thus, for each case there were six unknown inflows, although the theoretical mixture included seven. The results are shown in Table 7.

An examination of Table 1 and the simple correlations between the concentrations of the eight ions at different sites reveal that the greatest relative errors due to omission were usually in the calculated inflow with chemical characteristics that are the most highly correlated with the source that is omitted. For example, when X_6 is omitted from the calculations, most of the error is transferred to X_1 . The ionic concentrations, C_{i6} , have a higher simple correlation with C_{i1} than with any of the remaining unknown inflows.

EXAMPLE

Data for the following example were obtained from a field study in western Colorado. A map of the study area is shown in Fig. 3. One of the objectives of this study was to determine the effects of surface mining for coal on water quality. Therefore, it would be useful to know the rates at which waters affected by the mine (surface and subsurface runoff) were entering the streams draining the area.

For this example, we used data for the reach of Fish Creek, between stations 1001 and 1003, on 18 April, 1979. The lower elevation snow pack was melting at the time, and considerable surface runoff from the range, agricultural, and surface-mined areas was observed. The inflow at 1001 was $2.97 m^3/s$. Inflows to the reach of stream between the two stations could include surface runoff from winter wheat areas, range areas, and the mined area as well as shallow groundwater flow from the undisturbed area and the mined area. From an examination of the geologic map of the watershed, we concluded that there could be at least two different natural groundwaters contributing: water that had moved through the Lewis shale and water that had moved through the Williams Fork Formation.

TABLE 7. EFFECTS OF OMITTING A SIGNIFICANT INFLOW

Omitted Inflow	Calculated Inflows, m^3/S						
	X_1	X_2	X_3	X_4	X_5	X_6	X_7
X_1	--	0.54	0.09	0.11	0.26	2.03	0.05
X_2	0.78	--	0.17	0.04	0.32	1.73	0.05
X_3	0.54	0.55	--	0.00	0.26	1.67	0.07
X_4	0.71	0.28	0.13	--	0.21	1.70	0.06
X_5	0.72	0.34	0.15	0.13	--	1.69	0.06
X_6	2.02	0.67	0.12	0.22	0.00	--	0.06
X_7	0.52	0.00	0.35	0.29	0.23	1.69	--
Theoretical Mixture m^3/S	0.71	0.28	0.14	0.06	0.14	1.70	0.06

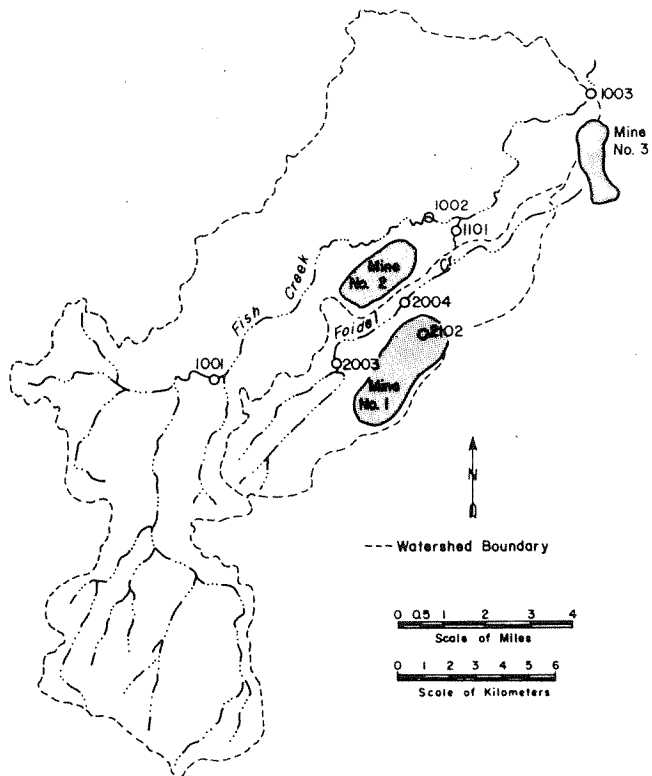


FIG. 3 Map of field study site.

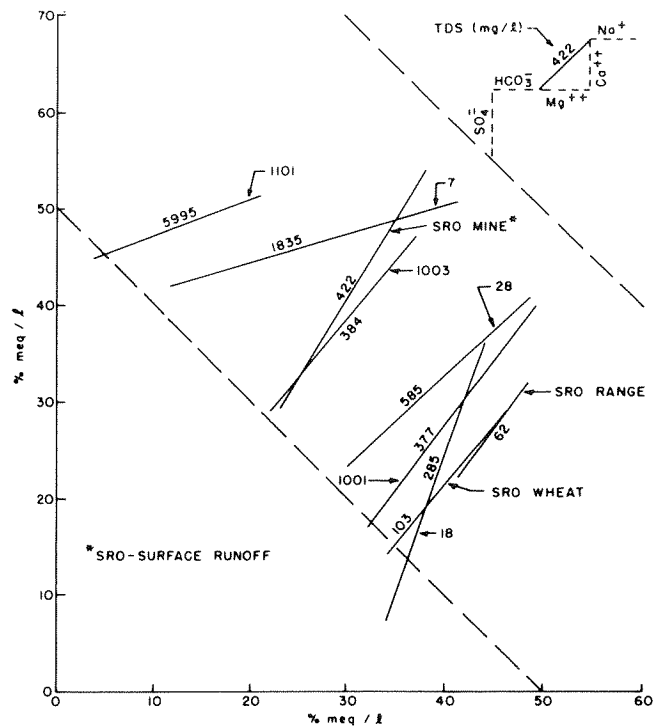


FIG. 4 Vector diagram of water compositions; Fish Creek between 1001 and 1003.

We obtained grab samples of seepage entering Fish Creek on 15 and 16 May, 1979 to characterize the water quality of various inflows. At this time of year, there was no snowmelt from the lower elevations, so inflow was from shallow, saturated flow. It seems safe to assume that the chemical characteristics of these shallow groundwaters do not change significantly with time. "Vector" diagrams of the chemical composition of these samples and of surface runoff (SRO) samples from range and winter wheat land, as well as the water at 1001 and 1003, are plotted in Fig. 4. These vectors were plotted according to the method devised by Korzhinski (1959) and described by Hounslow et al. (1978), and provide a quick graphical method of portraying the relative concentration of the major ions.

The ionic compositions of these water samples are presented in Table 8. Sample 28 was taken from an intermittent stream entering Fish Creek from the north and was assumed to represent natural shallow groundwater from the Lewis shale. Sample 18 was taken from a seep entering Fish Creek from the southwest, between 1002

and 1003, and was assumed to represent natural shallow groundwater draining from the Williams Fork Formation.

Sample 7 was obtained from a seepage zone below the reclaimed spoils of Mine No. 2 and was assumed to represent shallow groundwater that had drained through the mine spoils. Samples of surface runoff from the surface-mined area at Mines No. 2 and 3 were not available, so a snowmelt surface runoff sample, obtained at Mine No. 1 on 25 March, 1977, was used. The vector for this water is labeled "SRO Mine" in Fig. 5.

Samples labeled "SRO Wheat" and "SRO Range" were obtained from snowmelt surface runoff from a winter wheat field and a range watershed along the road leading to 1001. The sample labeled 1101 was saline seepage from an agricultural area south of 1002 taken on 26 April, 1978. This seepage flows into a series of ponds which overflow into Fish Creek during the spring snowmelt. The distinguishing features of water from this source was its high sodium content and high TDS (5995 mg/L).

TABLE 8. IONIC COMPOSITION OF WATERS ENTERING FISH CREEK BETWEEN 1001 AND 1003

Station or Sample No.	Concentration in meq/L							
	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ⁼	Ca ⁺⁺	Mg ⁺	Na ⁺	K ⁺
1001 (inflow)	195.0	12.80	4.54	82.0	45.00	21.00	13.50	2.70
1003 (outflow)	134.0	4.79	19.00	142.0	37.00	18.00	26.20	2.90
1101 (saline seep)	366.0	95.20	36.10	3950.0	256.00	399.00	879.00	9.50
No. 7 (mine seepage)	366.0	7.59	9.05	1070.0	91.00	197.00	83.00	8.20
No. 28 (G.W. Lewis shale)	281.0	9.72	4.68	171.0	54.00	35.00	27.00	2.30
No. 18 (G.W. Williams Fork)	159.0	20.50	5.30	27.0	44.00	10.00	17.00	2.50
SRO Range	34.2	0.89	2.09	15.1	2.75	1.25	3.50	2.20
SRO Wheat	48.8	1.06	21.50	16.0	7.00	3.25	3.50	2.30
SRO Mine	159.0	1.06	5.40	158.0	68.60	21.10	5.77	4.05

TABLE 9. COMPUTED INFLOWS AT FISH CREEK BETWEEN STATIONS 1001 AND 1003 ON APRIL 18, 1979

Station or Sample No.	Discharge m ³ /S	Sample Represents:
1101	0.06	Agricultural Seep
SRO Mine	0.28	Surface runoff-mine
No. 7	0.12	Mine seepage
No. 18	0.00	Williams Fork seepage
No. 28	0.00	Lewis shale seepage
SRO Wheat	2.63	Surface runoff, wheat
1001	2.97	Inflow to reach (measured)
1003	6.06	Outflow from reach (measured)

The inflows computed by the Wolfe quadratic programming algorithm are shown in Table 9. These values show that the major lateral inflow to this reach of stream on April 18, 1979 was surface runoff from wheat land. This could also include surface runoff from rangeland because the program could not distinguish between the two. From hydrologic conditions on the day of sampling, this is quite reasonable. The other amounts predicted seem reasonable, but the relative error present cannot be assessed until several more cases are computed. The input data are subject to significant errors because the water quality data for surface inflows and reach outflow are from single grab samples rather than integrated quantities over a 24-h, or longer, period. The reach inflow and outflow rates are also subject to errors on the order of ± 10 percent.

SUMMARY AND CONCLUSIONS

A technique to identify several unknown inflows to a reach of stream has been developed. It requires that the inflow sources be identified and that the concentrations of the principal anions and cations be measured. A quadratic programming algorithm is used to find the in-

flows that minimize the sum of squared error terms for ion balance equations. We found that the method is less sensitive to errors in the chemical analyses if the concentration of each ion is divided by the concentration of that ion in the mixture. This is equivalent to minimizing the sum of squared percentage errors.

Errors in estimates of a particular inflow are related to the proportion of the total ionic load contributed by that inflow relative to the total ionic load contributed to the reach of stream. If a significant inflow is omitted from the calculation, the error is transferred to the inflows that have similar chemical characteristics.

As an example, inflows to a reach of stream were calculated using data from a surface-mined area in western Colorado. The results seem reasonable.

The procedure described appears to be promising as a method of estimating surface and groundwater inflows to a reach of stream from several sources if the required assumptions are met. Further testing is required to determine the limitations.

References

- Hall, F. R. 1970. Dissolved solids — discharge relationships, I, mixing models. *Water Resour. Res.* 6(3):345-850.
- Hounslow, A., J. Fitzpatric, L. Cerrillo and M. Freeland. 1978. Overburden mineralogy as related to groundwater chemical changes in coal strip mining. EPA-600/778156, U.S. Environmental Protection Agency. 298 pp.
- Korzinski, D. S. 1959. Physicochemical basis of the analysis of the paragenesis of minerals. Consultants Bureau, Inc., New York.
- Pinder, G. F. and J. F. Jones. 1969. Determination of the groundwater component of peak discharge from the chemistry of total runoff. *Water Resour. Res.* Vol. 5, No. 2. pp. 438-445.
- Visocky, A. P. 1970. Estimating the groundwater component of storm runoff by the electrical conductivity method. *Ground Water* 8(2):5-10.
- Wolfe, P. 1959. The simplex method for quadratic programming. *Econometrica* 27:382-398.