

PURCHASED BY USDA
SCIENCE & EDUCATION ADMINISTRATION
FEDERAL RESEARCH
FOR OFFICIAL USE

PAPER NO. 79-2522

EVALUATING WATER QUALITY EFFECTS OF SURFACE MINING

by

D. A. Woolhiser, H. R. Gardner and S. R. Olsen
Research Hydraulic Engineer and Soil Scientists
USDA-SEA-AR
Fort Collins, CO

For presentation at the 1979 Winter Meeting
AMERICAN SOCIETY OF AGRICULTURAL ENGINEERS

Hyatt Regency Hotel
New Orleans, LA
December 11 - 14, 1979

SUMMARY:

A quadratic programming algorithm can be used to estimate several surface and subsurface inflows to a reach of stream if the chemical characteristics of these waters are known. This method may be useful in estimating the salt loading of streams due to surface mining.



American Society of Agricultural Engineers

St. Joseph, Michigan 49085

Papers presented before ASAE meetings are considered to be the property of the Society. In general, the Society reserves the right of first publication of such papers, in complete form. However, it has no objection to publication, in condensed form, with credit to the Society and the author. Permission to publish a paper in full may be requested from ASAE, P.O. Box 410, St. Joseph, Michigan 49085.

The Society is not responsible for statements or opinions advanced in papers or discussions at its meetings. Papers have not been subjected to the review process by ASAE editorial committees; therefore, are not to be considered as refereed.

EVALUATING WATER QUALITY EFFECTS OF SURFACE MINING^{1/}

by D. A. Woolhiser, H. R. Gardner and S. R. Olsen^{2/}

ABSTRACT

To estimate the increased stream loading of inorganic salts caused by surface mining, it is necessary to estimate the quantity and quality of surface runoff and groundwater runoff contributed by the mined and unmined areas tributary to a particular stream reach. Because of the diffuse nature of these inflows conventional techniques often fail.

Assuming that the concentrations of up to eight 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 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 inflow 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 two sets of data from a surface-mined area in western Colorado. The results appear reasonable.

^{1/} Contribution from the U.S. Department of Agriculture, Science and Education Administration, Agricultural Research, Fort Collins, CO, in cooperation with the Colorado Experiment Station. Work supported in part by Environmental Protection Agency Agreement Funds EPA-1AG-D5-3763.

^{2/} Research Hydraulic Engineer and Soil Scientists, USDA-SEA-AR, Fort Collins, CO

INTRODUCTION

Fracturing of overburden by surface mining and subsequent topsoiling and reclamation activities change the relative amounts of water that move as surface runoff, shallow groundwater flow, and deep groundwater flow and may also change the total amount of runoff by reducing evapotranspiration. Fracturing of the overburden also increases the contact area between water and soluble minerals. As a consequence, one would expect an increase in the dissolved inorganic salts of streams draining surface-mined areas. An estimate of the dissolved inorganic salts contributed by surface mining activities is particularly important within the Colorado River watershed because of the adverse effects of salinity on irrigated agriculture. (Rowe and McWhorter, 1978)

To estimate the increased stream loading of inorganic salts caused by a surface mine, it is necessary to estimate the quantity and quality of surface runoff and groundwater runoff contributed by the mined and unmined areas tributary to a particular stream reach. Estimating surface and subsurface runoff from a mined area is difficult because of the transient nature of the postmining hydrological regime. Immediately after mining the overburden is graded to approximately the premining configuration, topsoil is spread, and the area is seeded. Until the new vegetation has established a canopy and rooting pattern similar to the original vegetation, evapotranspiration is reduced and total runoff is greater. Because the physical properties of the soil are adversely affected by the topsoil removal and replacement operation, surface runoff is usually increased. The porosity and hydraulic conductivity of the fractured overburden may be quite different from the unmined formation, so flow velocities as well as quantities of groundwater may be affected.

The purpose of this paper is to describe a method that can be used to estimate the quantities of inflow from several sources to a reach of stream if the chemical characteristics of the inflows are known. These estimates of flow from mined and unmined portions of the watershed can then be used to estimate the water balance and the water quality effects of surface mining.

PREVIOUS INVESTIGATIONS

Differences between the total dissolved solids (TDS) content of surface runoff and groundwater runoff (base flow) have been used 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.

Few published studies have documented the dissolved inorganic salts contributed by surface mines in the Western United States, and only one study has developed a predictive technique (Rowe and McWhorter, 1978, McWhorter et. al. 1979)

In that study a predictive equation was developed from a combined material balance for water and total dissolved solids inputs to and outputs from a watershed. Thus the total dissolved solids budget is:

$$V_t P_t = V_m P_m + V_n P_n \quad (1)$$

where:

P_t = average total dissolved solids (TDS) concentration in V_t ,
the total runoff from the watershed.

P_m = average TDS concentration in the drainage Volume, V_m , from
the disturbed area;

P_n = average TDS concentration in drainage Volume, V_n , from the natural portion.

If K is defined as the ratio of total runoff per unit area on the natural portion of the watershed to the total runoff per unit area on the disturbed portion then:

$$K = \frac{V_n}{V_m} \frac{A_m}{A_n} \quad (2)$$

where A_m and A_n are the mined and unmined areas of the watershed. Further let R equal the ratio of the natural area to the mined area.

$$R = \frac{A_n}{A_m} \quad (3)$$

If these expressions are substituted into equation (1) the following equation can be obtained:

$$P_t = \frac{KRP_n + P_m}{1 + KR} \quad (4)$$

Rowe and McWhorter (1978) used annual data of P_t and R from four watersheds in western Colorado to estimate the parameters P_n , P_m and K by a trial and error least squares technique.

This equation can be used to estimate P_t if P_m , P_n and K are known. However, under many circumstances it is difficult to measure or estimate these quantities and their temporal variation makes determination of averages difficult. Multiple land uses within a mined watershed increase the difficulty of parameter estimation.

USING WATER QUALITY ANALYSES TO ESTIMATE INFLOWS TO A REACH OF STREAM

The chemical quality of water in any stream is influenced by the physical and chemical composition of the geologic material that it has

come into contact with as it moved through the watershed. The ionic composition of streamflow results from solution of minerals contacted as water flows over the surface or as groundwater and depends upon the distribution of soluble minerals and the physical characteristics of the geologic materials that govern contact between the water and the minerals. Therefore water that moves through a unique environment would be expected to have a characteristic relative abundance of the principal anions and cations. This can be demonstrated graphically by plotting the ionic composition according to the method devised by Korzhinskii (1959) and described by Hounslow et. al. (1978). According to this method the concentrations in milliequivalents per liter (meq/L) are converted to percentages. The plotting technique is shown in the upper right hand corner of Fig. 1. Only the major ions are considered: cations Na^+ , Mg^{++} and Ca^{++} , and anions $\text{SO}_4^{=}$ and HCO_3^- . As the diagram shows, the endpoint A of line AB indicates the relative content of HCO_3^- and $\text{SO}_4^{=}$. If these are the only anions present, all points A will fall on the line $x + y = 50$. The slope of AB indicates the Ca/Mg ratio. The horizontal distance from point B to the line $x + y = 100$ represents primarily the Na^+ content plus such cations as K^+ if A falls on the line $x + y = 50$. The compositions plotted on Fig. 1 are from samples obtained at a mined area in Routt County, CO. The TDS concentration in mg/L is shown on each "vector." The figure shows that $\text{SO}_4^{=}$ was much more abundant in mine seepage than in runoff from either range or wheat fields, which had relatively more HCO_3^- . (On the other hand Na^+ is relatively more abundant in wheat field runoff.) The analysis for the range runoff may contain an error because the point A is not close to the line $x + y = 50$. From Fig. 1 it is evident that the

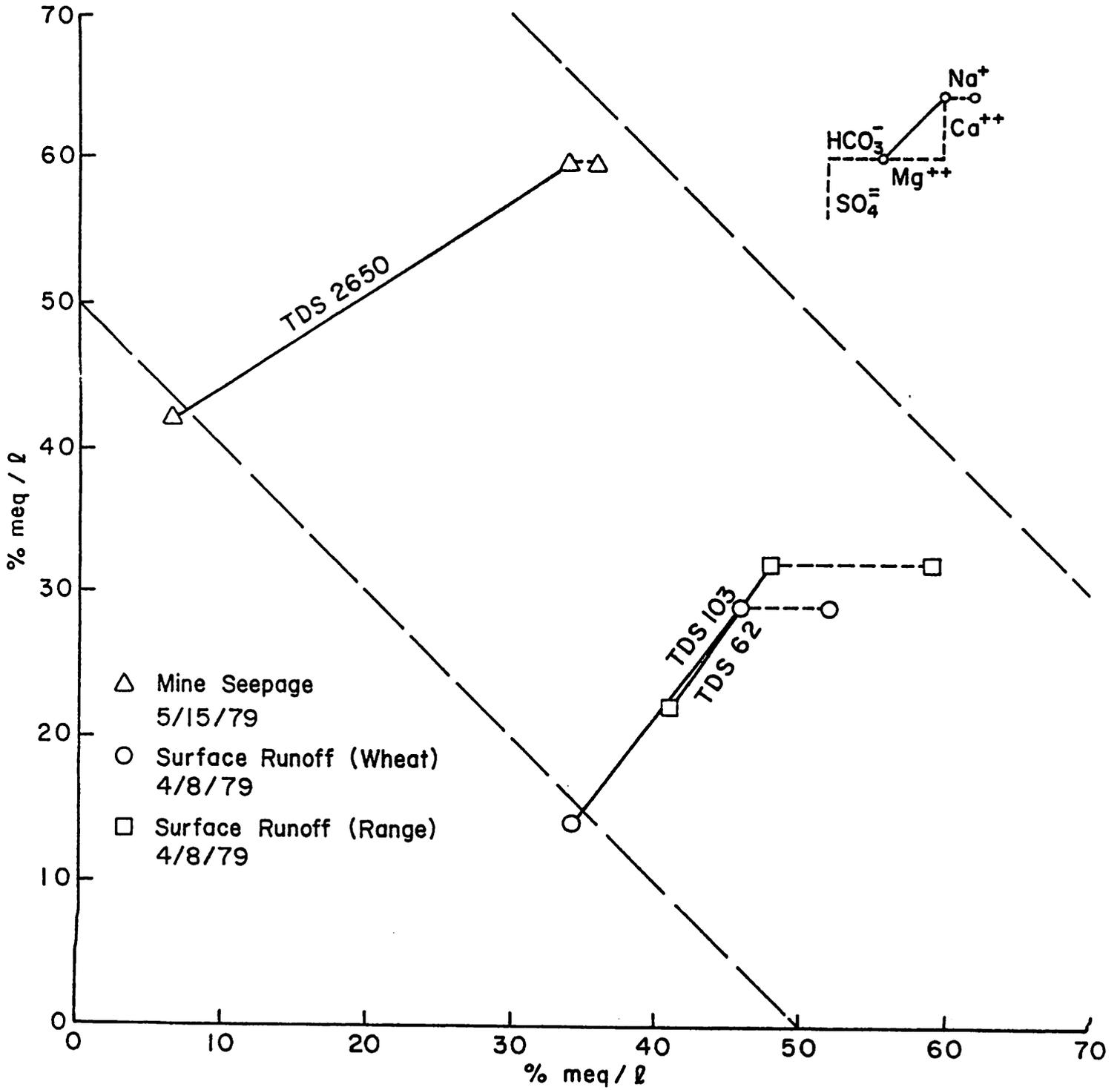


Fig. 1. "Vector Diagram" of Water Composition.

relative abundance of individual ions provides much information that is not used if only the TDS concentration is considered.

To demonstrate how this information may be used let us consider the reach of stream shown schematically in Fig. 2.

Let Q_i represent the measured surface inflow for a time interval Δt , and let Q_o represent the measured surface outflow for the same time period. The area contributing runoff to the reach is designated as A . Of this, an area A_m is surface mined. For a given time interval there may be several distinct (but unknown) inflows to the reach, X_1 , $X_2 \cdot \cdot \cdot X_j \cdot \cdot \cdot X_n$. These might represent surface water runoff from the undisturbed area and the disturbed area and groundwater runoff from the undisturbed area and from the disturbed area. Let S represent the volumetric storage of water within the stream channel at any instant and let ΔS represent the change in storage over some time interval Δt .

Thus the mass balance equation for water can be written:

$$Q_i + \sum_{j=1}^n X_j = Q_o + \Delta S \quad (5)$$

if subsurface inflow and outflow to 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 (5) becomes

$$\sum_{j=1}^n X_j = Q_o - Q_i \quad (6)$$

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 species.

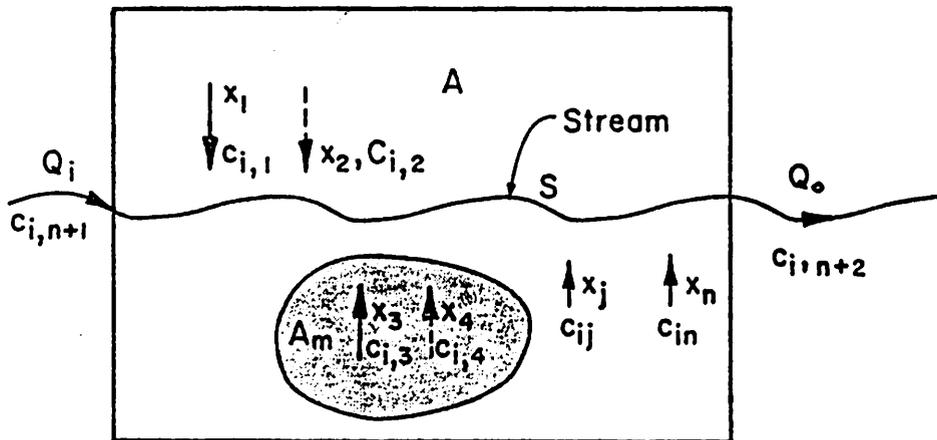


Fig. 2. Schematic diagram of stream reach and contributing watershed area.

$$\begin{aligned}
C_{11} X_1 + C_{12} X_2 + \dots + C_{1n} X_n - C_{1,n+2} Q_o + C_{1,n+1} Q_i &= 0 \\
\vdots & \\
C_{i1} X_1 + C_{i2} X_2 + \dots + C_{in} X_n - C_{i,n+2} Q_o + C_{i,n+1} Q_i &= 0 \\
\vdots & \\
C_{m1} X_1 + C_{m2} X_2 + \dots + C_{mn} X_n - C_{m,n+2} Q_o + C_{m,n+1} Q_i &= 0
\end{aligned} \tag{7}$$

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 equations (7) 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 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 added an error term ϵ_i to the right hand side of each equation and tried to find the set of inflows X_1, X_2, \dots, X_n that minimize the sum of the squared error terms.

With the added error terms, equation (7) can be written in matrix notation as

$$[C] \{X\} + \{B\} = \{\epsilon\} \quad (8)$$

where

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

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

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

From equation (6) we can eliminate one of the X_j resulting in a set of m equations in $n-1$ unknowns. Equation (8) is still appropriate but now the $[C]$ matrix is $(n-1) \times m$ and

$$C_{ij} = (C_{ij} - C_{in}) \quad \begin{matrix} i=1, \dots, m \\ j=1, \dots, n-1 \end{matrix} \quad (9)$$

$$\text{and } B_i = (C_{in} - C_{i,n+2}) Q_o + (C_{i,n+1} - C_{i,n}) Q_i \quad (10)$$

Consider the following objective function

$$E = \sum_{k=1}^m \epsilon_k^2 \quad (11)$$

By substituting equation (8) into equation (11) we obtain the quadratic form:

$$\text{Min } E = \sum_{k=1}^m \epsilon_k^2 = \{x_1, x_2, \dots, x_{n-1}, 1\} \underline{Q} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_{n-1} \\ 1 \end{pmatrix} \quad (12)$$

$$\text{where: } \underline{Q} = \sum_{i=1}^m \underline{D}_i \underline{A}_i \quad (13)$$

$$\underline{D}_i = \begin{bmatrix} (C_{i1} - C_{in}) & & & & 0 \\ & (C_{i2} - C_{in}) & & & \\ & & \ddots & & \\ & & & \ddots & \\ & & & & (C_{i,n-1} - C_{in}) \\ 0 & & & & & B_i \end{bmatrix} \quad (14)$$

$$\text{and } \underline{A}_i = \begin{bmatrix} (C_{i1} - C_{in}) & (C_{i2} - C_{in}) & \dots & (C_{i,n-1} - C_{in}) & B_i \\ \vdots & & & & \\ (C_{i1} - C_{in}) & (C_{i2} - C_{in}) & \dots & (C_{i,n-1} - C_{in}) & B_i \end{bmatrix} \quad (15)$$

The objective function, equation (12), can be separated into its linear and quadratic terms

$$E = \sum_{j=1}^m a_j x_j + H [x_i, x_j] \quad (16)$$

This expression is to be minimized subject to the constraints:

$$x_j \geq 0 \quad (17)$$

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 (17).

The quadratic programming problem specified by equations (16) and (17) was solved by the Wolfe algorithm (Wolfe, 1959).

SENSITIVITY ANALYSIS

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

1. Errors in the chemical analyses.
2. Errors in determining the discharge rates Q_o and Q_i .
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} .

$$C'_{ij} = C_{ij} + C_{ij} V_i U \quad (18)$$

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 zero and standard deviation of 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_0 is set equal to one and Q_i 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:

$$C_{i0} = 0.2 C_{i1} + 0.4 C_{i2} + 0.4 C_{i3} \quad (19)$$

Therefore the theoretical proportions were

$$X_1 = 0.2, X_2 = 0.4, X_3 = 0.4 \quad (20)$$

The concentration of eight ions, Na^+ , Ca^{++} , Mg^{++} , K^+ , Cl^- , NO_3^- , HCO_3^- and SO_4^{--} were used in the calculations. These data are shown in Table 1.

TABLE 1. CHEMICAL COMPOSITION OF TEST MIXTURE NO. 1
ION CONCENTRATION

Water Sample	HCO_3^-	Cl^-	NO_3^-	SO_4^{--}	Ca^{++}	Mg^{++}	Na^+	K^+
	meq/L							
1	4.80	.09	.03	3.27	4.19	2.88	.49	.06
2	3.98	.21	.53	19.70	10.68	7.90	3.26	.12
3	2.50	.14	1.05	42.2	22.70	19.74	1.19	.14
Mixture	3.55	.16	.64	25.41	14.19	11.63	1.88	.12

Because each concentration, C_{ij} , $i = 1,8$; $j = 1,4$ was perturbed according to equation (18), the unknowns solved for by the quadratic programming algorithm reflected these errors. The perturbed unknowns \hat{X}_1 , \hat{X}_2 and \hat{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 mean, standard deviation and coefficient of variation of \hat{X}_1 , \hat{X}_2 and \hat{X}_3 for each V are shown in Table 2.

Table 2. Sample Statistics for Sensitivity Test, Mixture No. 1.

Coefficient of variation, V , of errors in concentration		
	.03	.05
\bar{X}_1	.187	.171
S_{x1}	.093	.119
V_{x1}	.497	.696
\bar{X}_2	.398	.408
S_{x2}	.146	.189
V_{x2}	.367	.463
\bar{X}_3	.413	.421
S_{x3}	.055	.076
V_{x3}	.134	.181

Table 2 shows that the coefficient of variations 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 9 and 10 we can write the equation for ϵ_i^2 as

$$\epsilon_i^2 = [(C_{i1} - C_{in}) X_1 + (C_{i2} - C_{in}) X_2 + \dots + (C_{i,n-1} - C_{in}) X_{n-1} + (C_{in} - C_{i,n+2}) Q_0 + (C_{i,n+1} - C_{in}) Q_i]^2 \quad (21)$$

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

$$\frac{\partial E}{\partial C_{ij}} = \frac{\partial \epsilon_i^2}{\partial C_{ij}} = 2 \epsilon_i \frac{\partial \epsilon_i}{\partial C_{ij}} \quad (22)$$

The greatest sensitivity is then where ϵ_i and $\frac{\partial \epsilon_i}{\partial C_{ij}}$ are large.

The value of ϵ_i is highest for the most abundant ion, and the maximum $\frac{\partial \epsilon_i}{\partial C_{ij}}$ is Q_0 . Thus to obtain approximately equal sensitivities for each ion balance equation we wish

$$\epsilon_1 \approx \epsilon_2 \approx \epsilon_3 \cdot \cdot \cdot \approx \epsilon_n \quad (23)$$

One method of obtaining the approximate equality in equation (23) 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 I).

$$C_{ij}'' = C_{ij}' / C_{i, n+2}' \quad i = 1, 8; j = 1, n \quad (24)$$

where C_{ij}'' is the normalized concentration. The sample mean, standard deviation and coefficient 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 improved the procedure. The coefficient of variation for X_1 was reduced by a factor of five where the V of the error terms is .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.

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

	Coefficient of variation, V, of concentration errors		
	0.01	0.03	0.05
\bar{X}_1	.191	.187	.190
S_{x1}	.00525	.016	.026
V_{x1}	.0275	.086	.137
\bar{X}_2	.405	.401	.389
S_{x2}	.00945	.031	.043
V_{x2}	.0233	.077	.111
\bar{X}_3	.404	.412	.422
S_{x3}	.00638	.021	.030
V_{x3}	.0158	.051	.071

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 can be accounted for by weighting 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.

Samples 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 shows 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 coefficient of variation for each ion based upon a sample of 25 is shown in Table 4.

TABLE 4. COEFFICIENT OF VARIATION OF ION CONCENTRATION

	HCO_3^-	Cl^-	NO_3^-	SO_4^{ION}	Ca^{++}	Mg^{++}	Na^+	K
V	0.031	0.49	2.09	0.068	0.041	0.052	.085	.0536

The high coefficient of variation for NO_3^- reflects inaccuracies at the very low concentrations present in these samples (≈ 0.9 mg/L). The reasons for the large CV for Cl^- are both the low concentrations (≈ 0.9 mg/L) and, possibly, contamination. Because of the trend present the V's for the other ions have been 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 the outflow.

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

TABLE 5
Ionic Concentrations, Test Case No. 2

Water Source	Concentration								Theoretical Discharge cms
	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	.71
X ₂ Mine Surface Runoff	158.	1.06	5.40	157.	68.6	21.1	5.77	4.05	.28
X ₃ Mine Groundwater No. 7	366	7.59	9.05	1070.	91.0	197.	83.0	8.20	.14
X ₄ Groundwater No. 18	159.	20.5	5.30	27.0	44.0	10.0	17.0	2.50	.05
X ₅ Groundwater No. 28	281.	9.72	4.68	171.	54.0	35.0	27.0	2.30	.14
X ₆ Wheat Surface Runoff	48.8	1.06	21.5	15.9	7.0	3.25	3.50	2.30	1.70
X ₇ Agricultural Seep 1101	366.	95.2	36.1	3950.	256.	399.	879.	9.50	.05
Inflow 1001	195.	12.7	4.54	82.0	45.0	21.0	13.5	2.70	2.97
Outflow 1003	141.	8.22	9.46	120.	33.8	21.6	19.2	2.78	6.06

The output statistics obtained from a sample of ten are shown in

Table 6.

Table 6. Sample Statistics - Test Case No. 2
Sensitivity to Variation in Q_i and Q_o ($V=.10$)

	Inflow						
	X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	X ₇
\bar{X}_i	22.74	7.85	5.18	3.45	4.14	59.60	1.93
$S\bar{X}_i$	6.37	4.70	0.76	4.62	4.42	5.93	0.21
V_{xi}	0.28	0.60	0.15	1.34	1.07	0.10	0.11

Tables 5 and 6 show that the large inflows and the highly concentrated inflows were estimated quite closely but the small flows and

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

$$\theta_j = \frac{[\sum_{i=1}^m C_{ij}^*] X_j}{\sum_{j=1}^m \sum_{i=1}^m C_{ij}^* X_j} \quad (25)$$

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

The coefficient of variation $V(X_j)$ is plotted versus θ_j on Fig. 3 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 seemed 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 ($V = .05$) lie very close to those with Q_i and Q_o perturbed ($V = .10$). 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.

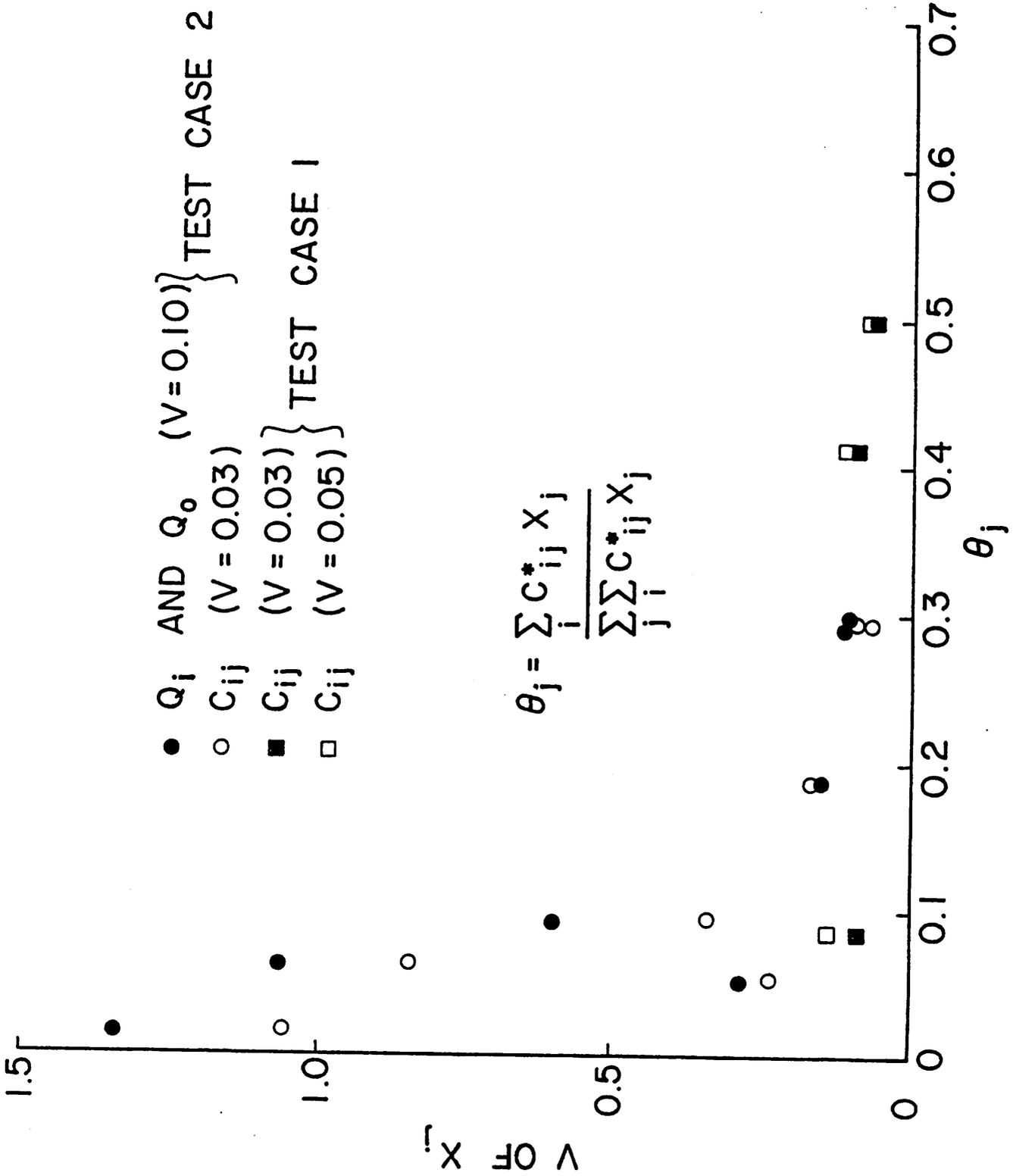


Fig. 3. Coefficient of Variation of unknown inflows versus flow-weighted concentration.

TABLE 7. EFFECTS OF OMITTING A SIGNIFICANT INFLOW

Omitted Inflow	Calculated Inflows, cms						
	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	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	-	0.06
X ₇	0.52	0	0.35	0.29	0.23	1.69	-
Theoretical Mixture	0.71	0.28	0.14	0.06	0.14	1.70	0.06

An examination of Table 7 and the simple correlations between the concentrations of the eight ions at different sites reveals 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 X₆ is omitted from the calculations, most of the error is transferred to X₁. The ionic concentrations, C_{i 6}, have a higher simple correlation with C_{i 1} than with any of the remaining unknown inflows.

EXAMPLES

Data for the following two examples were obtained from a field study in western Colorado. One of the objectives of this study was to determine the effects of surface mining for coal on water quality. A map of the study area is shown in Fig. 4.

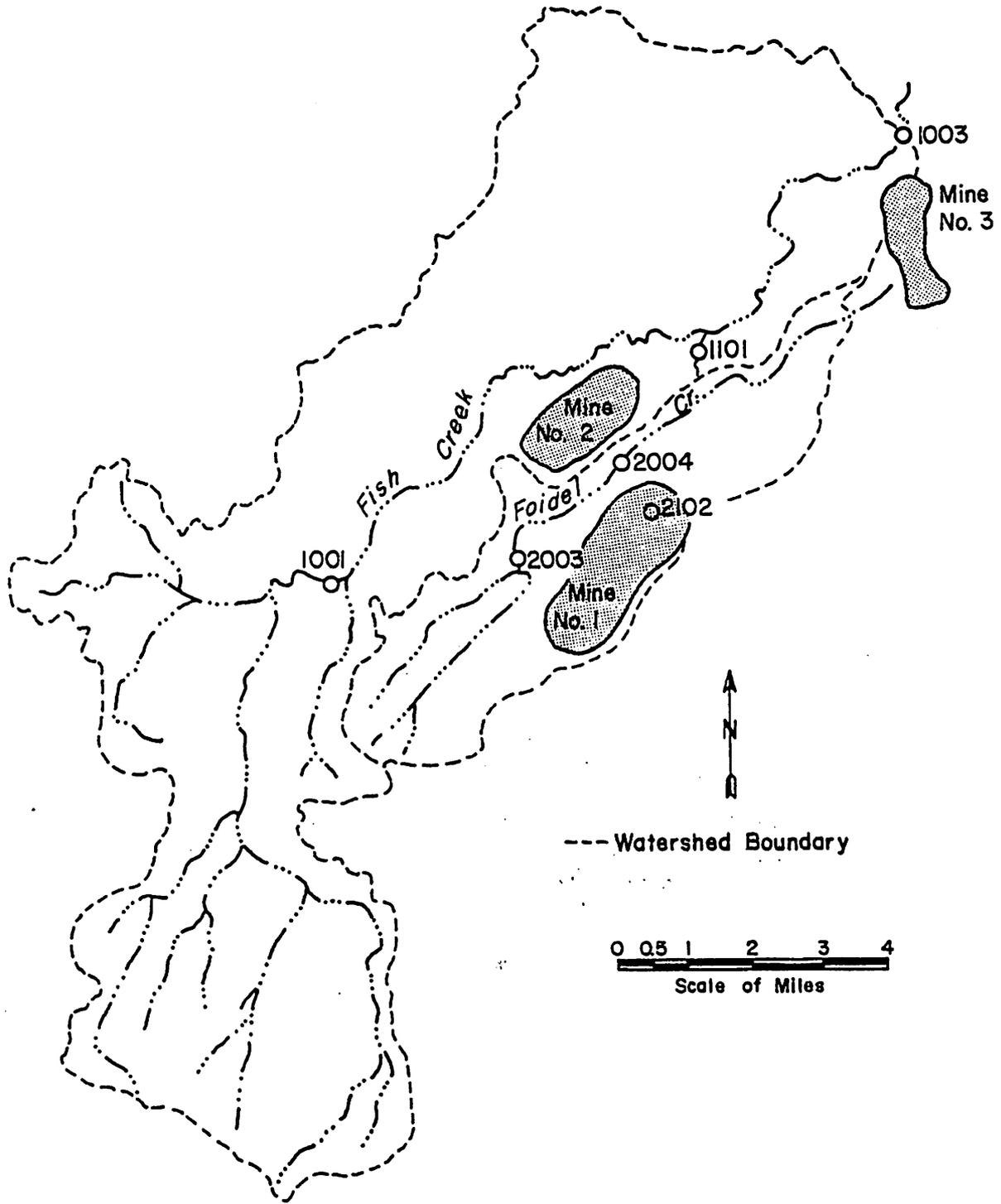


Fig. 4. Map of Field Study Site.

Example 1

The first example uses data for the reach of Fish Creek between station 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 area was observed. The inflow at 1001 was 2.97 cms and the outflow at 1003 was 6.06 cms. 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 ground water 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. The Lewis shale underlies the Fish Creek watershed on the northwest side of Fish Creek and also extends to the southeast side of the stream in the vicinity of station 1002 and south of the county road crossing between station 1001 and 1002.

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. "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. 5. These vectors were plotted according to the method devised by Korzhinskii (1959) and described by Hounslow et al. (1978).

The ionic compositions of these water samples are presented in Table 8. Sample 28 was taken from an intermittent stream entering Fish

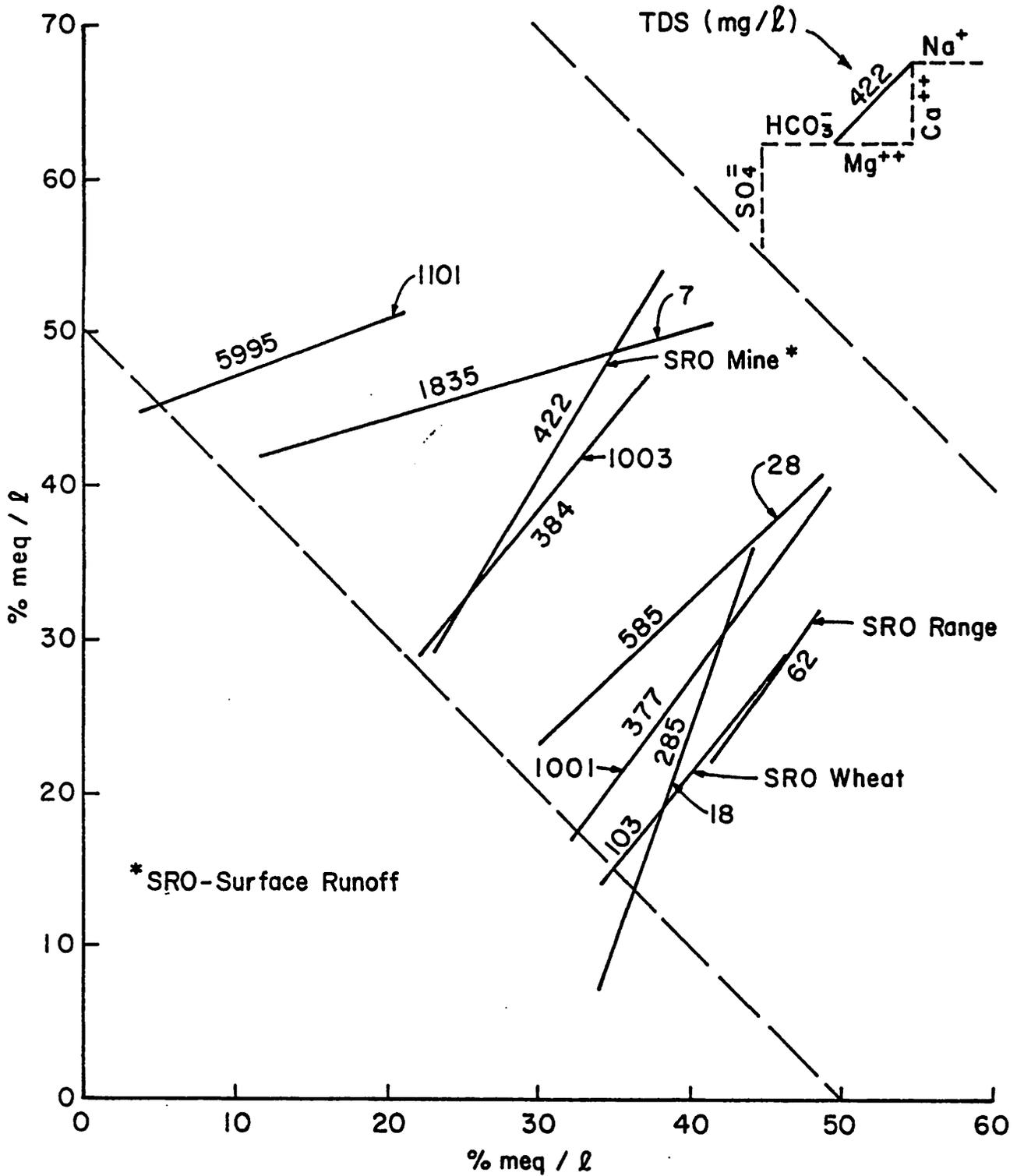


Fig. 5. Vector Diagram of Water Compositions Fish Creek Between 1001 and 1003.

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 number 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 from saline seepage from an agricultural area south of 1002 taken on 26 April 1978. This seepage flows into a series of ponds. During the spring snowmelt these ponds overflow into Fish Creek. The distinguishing feature 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 mg/L							
	HCO ₃ ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ⁼	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺
1001	195	12.8	4.54	82.0	45.0	21.0	13.5	2.70
1003	134	4.79	19.0	142	37.0	18.0	26.2	2.90
1101	366	95.2	36.1	3950	256	399	879	9.50
No 7	366	7.59	9.05	1070	91	197	83	8.20
No 28	281	9.72	4.68	171	54	35	27	2.30
No 18	159	20.5	5.30	27.0	44	10	17	2.50
SRO Range	34.2	.89	2.09	15.1	2.75	1.25	3.50	2.20
SRO Wheat	48.8	1.06	21.5	16.0	7.0	3.25	3.50	2.30
SRO Mine	159	1.06	5.40	158	68.6	21.1	5.77	4.05

The inflows computed by the Wolfe quadratic programming algorithm are shown in Table 9.

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

Station or Sample No.	Discharge cms	Sample Represents
1101	0.06	Agricultural seep
SRO Mine	0.28	Surface Runoff-mine
No. 7	0.12	Mine seepage
No. 18	0	Williams Fork seepage
No. 28	0	Lewis shale seepage
SRO Wheat	2.63	Surface runoff, wheat
1001	2.97	Inflow to reach (measured)
1003	6.06	Outflow from reach (measured)

These values show that the major inflow to this reach of stream was surface runoff from wheat land. This could also include surface runoff from range land 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 hour or longer period. The reach inflow and outflow rates are also subject to errors on the order of ± 10 percent.

Example 2

For the second example we used data from Foidel Creek between stations 2003 and 2004 which is just below Mine No. 1. The ionic compositions of these waters are shown in Table 10. Because we have no flow measurements at station 2003, the rate of flow there was considered as one of the unknown inflows. Data for stations 2003 and 2004 were obtained on 12 April 1978. Possible inflows to the reach include surface runoff from the mined area and the unmined area and shallow groundwater flow from the mined area and the unmined area. Shallow natural groundwater would originate in the Williams Fork Formation. Sample No. 4 was obtained from a pond fed by seepage north of station 2003 and was assumed to represent natural groundwater inflow. Samples taken at station 2102 when no surface runoff was occurring are assumed to represent shallow groundwater that had moved through the mine spoils. Surface runoff samples from the reclaimed watershed on Mine No. 1 were obtained on 25 March 1977. The undisturbed area contributing to Foidel Creek in this reach was quite small; surface runoff probably contributed little. The surface runoff from this source was assumed to have the same quality as the range runoff from the Fish Creek watershed.

"Vector" diagrams of water composition for these samples are shown in Fig. 6.

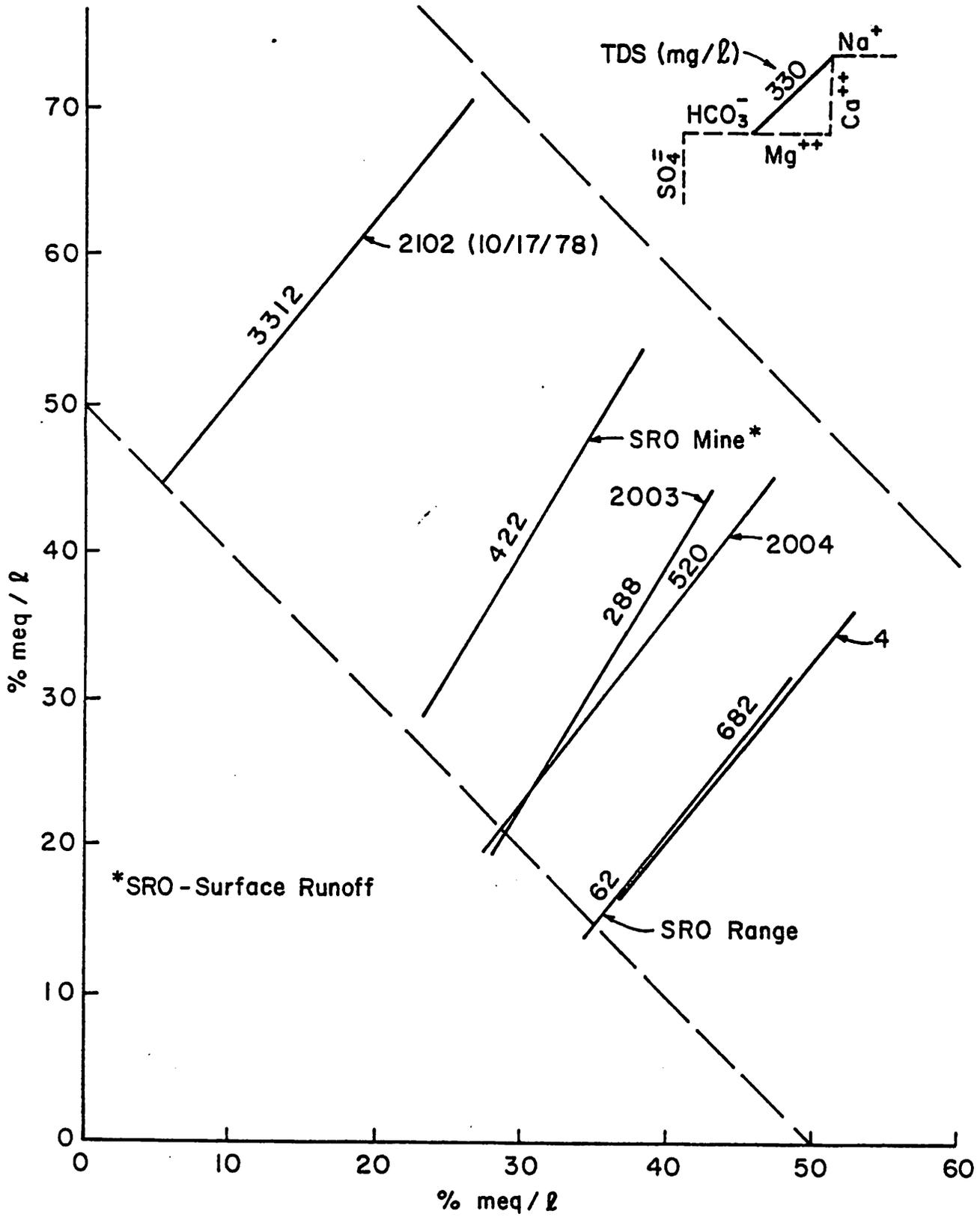


Fig. 6. Vector Diagram of Water Composition Foidel Creek Between 2003 and 2004.

TABLE 10. COMPOSITION OF WATERS ENTERING
FOIDEL CREEK BETWEEN STATIONS 2003 AND 2004 (APRIL 12, 1978)

Station or sample no.	Concentration in mg/L							
	HCO ₃ ⁻	CL ⁻	NO ₃ ⁻	SO ₄ ⁼	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺
2102	311	6.03	62.0	2140	520	250	18.4	5.1
SRO Mine	159	1.06	5.40	158	68.6	21.1	5.77	4.05
2003	134	3.12	1.66	75.9	38.4	14.2	16.6	4.00
2004	244	10.3	1.95	140	71.8	34.1	14.1	3.61
SRO Range	34.2	.89	2.09	15.1	2.75	1.25	3.50	2.30
No 4	391	4.54	5.52	135	70	32	42	2.30

The inflows computed by the Wolfe quadratic programming algorithm are shown in Table 11.

TABLE 11. COMPUTED INFLOWS AT FOIDEL CREEK BETWEEN
STATIONS 2003 AND 2004 ON 12 APRIL 1978

Station or Sample No.	Proportion of Discharge	Discharge cms	Sample Represents
2102	0.0127	0.003	Mine seepage
SRO Mine	0.0	0.0	Surface runoff, mine
Range SRO	0.0	0.0	Surface runoff, undisturbed area
No. 4	0.0377	0.009	Undisturbed ground- water
2003	.9496	0.222	Inflow to reach (calculated)
2004	1.0	0.234	Outflow from reach (measured)

These calculations show that on 12 April 1978, there was no direct surface runoff between 2003 and 2004. The U.S. Geological Survey (USGS) streamflow data at a station downstream from 2003 and the U.S. Depart-

ment of Agriculture data for station 2005 show that the peak runoff in 1978 occurred on April 7 and 8 respectively. Peak runoff at the USGS station is normally caused by rapid melt of the snowpack at the lower elevations. The snowpack in the undisturbed area between 2003 and 2004 normally melts earlier because of its southern aspect and most of the surface runoff from the mine was caught in sedimentation ponds or in the mine pit; it is thus possible that there was no direct surface runoff from the area between 2003 and 2004 on 12 April.

The relative amounts of groundwater contributions are not unreasonable. The technique looks promising, but no definite conclusions should be drawn from the results obtained for the two sample cases until several more cases are studied.

SUMMARY AND CONCLUSIONS

In order to estimate the effects of surface mining on water quality one must identify the amounts of water contributed to a reach of stream from surface and subsurface mine runoff. This is difficult to do by conventional methods because these sources are often diffuse. 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 inflows that minimize the sum of squared error terms for eight 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 inflow estimates are related to the product of the inflow and the dissolved inorganic salt concentration. If a significant inflow is omitted from the calculation the error is transferred to the inflows that have similar chemical characteristics.

Inflows to a reach of stream were calculated for two sample sets of 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.

ACKNOWLEDGEMENTS

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 Wolfe's algorithm. We also wish to thank Energy Fuels Corporation for their cooperation in our field research program.

References

- 1 Hall, F. R. 1970. Dissolved Solids - Discharge Relationships, I, Mixing Models. Water Resour. Res. 6(3):345-850.
- 2 Hounslow, Arthur, Joan Fitzpatrick, Lawrence Cerrillo and Michael Freeland. 1978. Overburden Mineralogy as Related to Ground-Water Chemical Changes in Coal Strip Mining. EPA-600/778156, U. S. Environmental Protection Agency. 298 pp.
- 3 Korzhinskii, D. S. 1959. Physicochemical Basis of the Analysis of the Paragenesis of Minerals. Consultants Bureau, Inc. New York.
- 4 McWhorter, D. B., J. W. Rowe, M. W. VanLiew, R. L. Chandler, R. K. Skogerboe, D. K. Sunada, and G. V. Skogerboe. 1979. Surface and Subsurface Water Quality Hydrology in Surface Mined Watersheds. Part I. Text. EPA-6007-79-193a. 192 pp.
- 5 Pinder, George F. and John F. Jones. 1969. Determination of the Ground-Water Component of Peak Discharge from the Chemistry of Total Runoff. Water Resour. Res. Vol. 5, No. 2. pp. 438-445.
- 6 Rowe, Jerry W. and David B. McWhorter. 1978. Salt Loading in Disturbed Watershed - Field Study. J. Environ. Eng. Div. ASCE pp. 32-38.
- 7 Visocky, A. P. 1970. Estimating the Groundwater Component of Storm Runoff by the Electrical Conductivity Method. Ground Water 8(2): 5-10.
- 8 Wolfe, P. 1959. The Simplex Method for Quadratic Programming. Econometrica 27:382-98.