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## ESTIMATION OF SPATIAL RECHARGE DISTRIBUTION USING ENVIRONMENTAL ISOTOPES AND HYDROCHEMICAL DATA. I. MATHEMATICAL MODEL AND APPLICATION TO SYNTHETIC DATA

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### ABSTRACT

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A mathematical model is proposed to estimate the spatial distribution of annual recharge rates into an aquifer using environmental isotopes and hydrochemical data. The aquifer is divided into cells within which the isotopes and dissolved constituents are assumed to undergo complete mixing. For each mixing cell mass-balance equations expressing the conservation of water, isotopes and dissolved chemicals are written. These equations are solved simultaneously for unknown rates of recharge into the various cells by quadratic programming. The degree to which individual dissolved constituents may be considered conservative is tested a-priori by means of a chemical equilibrium model such as WATEQF. Constituents which do not pass this test are either disregarded or suitably assigned a small weight in the quadratic program. In Part I, the model is applied to synthetic data corrupted by random noise and its sensitivity to input errors is examined. Part II\* describes an application of the model to real data from the Aravaipa Valley in southern Arizona.

### INTRODUCTION

To properly manage groundwater resources, there is a need for accurate information about the inputs (recharge) and outputs (pumpage and natural discharge) within each groundwater basin. Experience has shown that evaluating pumpage and natural discharge is often technically easier than estimating recharge. In fact, the largest uncertainty in calculating the water budget of a groundwater basin often stems from the hydrologist's inability to reliably estimate the spatial and temporal distribution of recharge rates. In arid and semiarid regions the difficulty is compounded by the intermittent

\* Adar and Neuman (this volume).

nature of recharge which often occurs in pulses of relatively short duration, lasting from several hours to several days (Zimmerman et al., 1966, 1967).

In many studies, surface infiltration and stream losses are equated with recharge. It is important to recognize, however, that the fate of the waters which have infiltrated underground is determined by the saturated/unsaturated flow regime prevailing above the regional water table. Only that water which actually reaches the water table, and in this way becomes part of the saturated zone, should be considered as recharge. Since not all the water infiltrated reaches the water table, the volume and rate of the water table recharge are generally less than those of infiltration. In addition to these numerical differences between water table recharge and infiltration, the former lags in time behind the latter due to travel through the vadose zone. This time lag may be short (hours, days, weeks) if the water table is situated at relatively shallow depths, or long (months or years) if the water table is deep or overlain by low-permeability strata.

#### PREVIOUS WORK

Models that compute recharge by equating it to infiltration at the soil surface, including stream beds, in response to rainfall, irrigation, and stream flow, abound in the literature. Examples can be found in the works of Eakin (1966), Feth et al. (1966), Briggs and Werho (1966), Burkham (1970), Rantz and Eakin (1971), Belan (1972), Mazor et al. (1974), Schick (1977), Ben-Asher (1978), Durbin et al. (1978), Kafri and Ben-Asher (1978), Howard and Lloyd (1979), and others. Of particular interest for recharge from ephemeral stream losses in the arid southern United States are the studies of Matlock (1965), Marsh (1968) and Keith (1981).

Surface and stream infiltration represent gross input of water into the subsurface, initiating the water-table recharge process. For the computation of net input, one needs to transform the infiltration into volumes or rates of deep percolation beneath the root zone, including the root zone of phreatophytes near streams and washes. Methods for effecting such a transformation have been described by numerous authors including Thornwaite and Mather (1957), Mero (1963, 1978), Walker (1970), Olmsted et al. (1973), Bos and Nugteren (1974), Heerman and Kincaid (1974), Wind and Van Doorne (1975), King and Lambert (1976), Hillel (1977), Tanji (1977), Wilmot (1977) and Karmeli et al. (1978). While some of these methods may work well in humid regions, their applicability to arid and semiarid conditions is in question.

Deep percolation may be regarded as net input of water into the vadose zone. Most or all of this water will ultimately reach the water table in the form of groundwater recharge. When the time delay involved in the flow through the vadose zone is significant, its effect on the computation of recharge must be considered. A rigorous approach to the problem of routing water through the vadose zone, starting directly beneath the root zone and ending at the groundwater table, would require the solution of highly nonlinear differential

equations describing unsaturated flow in soils (e.g. Richard's equation). Such an approach, however, is not feasible for basin-wide recharge studies. Simplified models tailored specifically for such studies have been proposed by Mero (1963, 1978), King and Lambert (1976) and Besbes et al. (1978).

Among the most readily available hydrologic data that could be used to estimate groundwater recharge in arid and semiarid regions are streamflow records and hydrographs of nearby wells. Very often, the fluctuation of water levels in wells situated close to streams reflects fluctuation in the rate of recharge as well as the rate of deep percolation beneath the stream. The idea of using groundwater level fluctuation as an indicator of recharge dates back to the early works of Jacob (1943, 1944). Various methods based on this idea have been discussed by Wilson and DeCook (1968), Matlock (1970), Moench and Kisiel (1970) Venetis (1971), Matlock and Davis (1972), Gelhar (1974), Besbes et al. (1978), Duffy et al. (1978) and Flug et al. (1980). When streamflow infiltration is the main source of recharge some of these methods may yield acceptable results. However, none of the techniques mentioned thus far are able to deal with situations where the relative importance of various potential recharge sources is unknown.

In this work we are interested in developing a methodology for the identification and quantification of multiple recharge sources. In other words, we are interested in identifying the major mechanisms of recharge in a given basin, the spatial distribution of recharge sources, and the relative as well as absolute strength of each such source. Under certain conditions this can be accomplished by solving the so-called "inverse problem" of aquifer hydrology, i.e., by treating recharge as an unknown parameter in a numerical aquifer flow model (Carrera and Neuman, 1986a,b,c). However, hydrologic data for such an analysis are not always available. On the other hand, information about groundwater chemistry and environmental isotopes can often be collected rapidly and at relatively small expense. We wish to examine the degree to which such data can be used to estimate recharge.

In the past, hydrologists have used chemical and isotopic data for recharge studies primarily in a qualitative sense. Environmental isotopes played a dominant role in such studies, as exemplified by the works of Verhagen et al. (1970, 1978), Gat and Dansgaard (1972), Blake et al. (1973), Bredenkamp et al. (1974), Mazor et al. (1974), Yurtsever and Payne (1978), Shampine et al. (1979), Levin et al. (1980), Issar and Gat (1981), Issar and Gilad (1982), Mazor (1982) and Issar (1983). In some studies, tritium was used to obtain quantitative estimates of recharge (Zimmerman et al., 1966; Zimmerman et al., 1967; Dincer et al., 1974; Bredenkamp et al., 1974; Vogel et al., 1974). More recent attempts to extract quantitative information about recharge from hydrochemical data often rely on statistical analyses. As an example, Lawrence and Upchurch (1982) use factor analysis to identify the recharge source for certain groups of dissolved chemical species in an aquifer. In all such works, the authors either evaluate the magnitude of a given recharge source, or evaluate the potential of recharge without providing quantitative estimates of recharge rates.

A serious attempt to incorporate hydrological and hydrochemical information into a mathematical groundwater model for the purpose of source identification and quantification was presented by Gorelik et al. (1983). This attempt deals with the question of identifying the location and magnitude of pollution sources that might have contributed to the contamination of an aquifer. For this, they utilize a two-dimensional numerical model of solute transport in the aquifer, coupled with various optimization techniques. The method could, in principle, be used for recharge estimation when enough information about the hydraulic and transport parameters of an aquifer is available.

#### SCOPE OF PRESENT WORK

In this series of papers, we present a mathematical model for the estimation of recharge under conditions where the hydraulic and transport characteristics of the aquifer are unknown or poorly known. In our model, the aquifer is divided into cells within which the isotopes and dissolved constituents are assumed to undergo complete mixing. This idea derives from the mixing cell approach of Simpson and co-workers (Simpson and Duckstein, 1976; Campana and Simpson, 1984). For each mixing cell, mass-balance equations are written expressing the conservation of water, isotopes and dissolved chemicals. These equations are solved simultaneously by quadratic programming for unknown rates of recharge into the various cells. A similar approach was used by Woolhiser et al. (1982) to estimate the inflow rate into a river reach, the latter being analogous to a single cell in our model.

In our approach, the degree to which individual dissolved constituents may be considered conservative is tested a-priori by means of a chemical equilibrium model such as WATEQF. Constituents which do not pass this test are either disregarded or assigned a suitably small weight in the quadratic program. This paper applies the model to synthetic data and examines its sensitivity to random errors superimposed on the data. Adar and Neuman describe an application of the model to real data from the Aravaipa Valley in southern Arizona.

#### THEORY

In a mixing cell approach, the aquifer is divided into  $N$  discrete cells within each of which complete mixing is assumed to take place. Flow into any given cell,  $n$ , can be derived from  $I_n$  different sources. Similarly, discharge from cell  $n$  can occur through  $J_n$  different avenues. Let  $Q_{ni}$  represent the average volumetric flow rate into  $n$  from the  $i$ th source during a discrete time interval,  $\Delta t$ , and let  $Q_{nj}$  be the average volumetric flow rate out of  $n$ , through the  $j$ th discharge avenue, during  $\Delta t$  (Fig. 1). If  $H_n$  is the average change in hydraulic head within cell  $n$  during  $\Delta t$ , then the water balance equation for this cell is:

$$\sum_{i=1}^{I_n} Q_{ni} - \sum_{j=1}^{J_n} Q_{nj} = S_n \frac{\Delta H_n}{\Delta t} \quad (1)$$

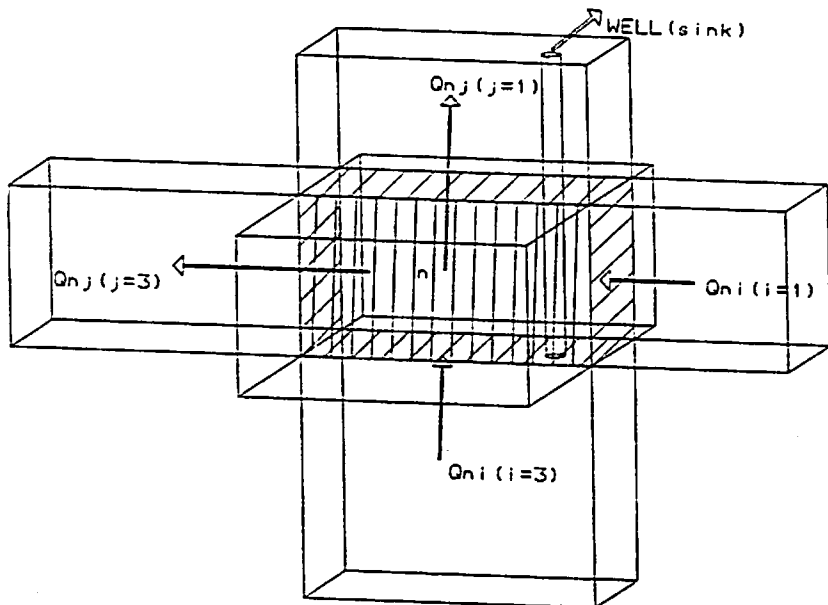


Fig. 1. Schematic configuration of cells showing flow components appearing in eqns. (1)-(4).

where  $S_n$  is the storage capacity of the cell. If the cell does not contain a water table,  $S_n = V_n S_{sn}$  where  $V_n$  is the saturated volume of  $n$  and  $S_{sn}$  is its specific storage. If a water table crosses the cell,  $S_n = A_n S_{yn}$  where  $A$  is the horizontal area of the cell and  $S_{yn}$  is the corresponding specific yield.

Due to the assumption of complete mixing within each cell, the mass balance expressions for the conservative chemical species in the  $n$ th cell are written as:

$$\sum_{i=1}^{I_n} C_{nik} Q_{ni} - C_{nk} \sum_{j=1}^{J_n} Q_{nj} = V_n \phi_n \frac{\Delta C_{nk}}{\Delta t} \quad (2)$$

Here  $C_{nik}$  is the average concentration over  $\Delta t$  of the  $k$ th isotope or chemical constituent in the waters entering into cell  $n$  at the rate  $Q_{ni}$ ,  $C_{nk}$  is the average concentration of the  $k$ th species inside  $n$ ,  $\Delta C_{nk}$  is the change in the concentration of  $k$  in  $n$  during  $\Delta t$ , and  $\phi_n$  is the porosity of  $n$ . If water is flowing from cell  $n$  at the rate  $Q_{nj}$  into cell  $m$  at the rate  $Q_{mi}$ , then clearly:

$$Q_{mi} = Q_{nj}, \quad \text{and} \quad C_{mi} = C_{nk} \quad (3)$$

Hence, in order to include all the flow components in the mass balance equations, it is necessary that the flow pattern into, out of, and within the basin be well defined.

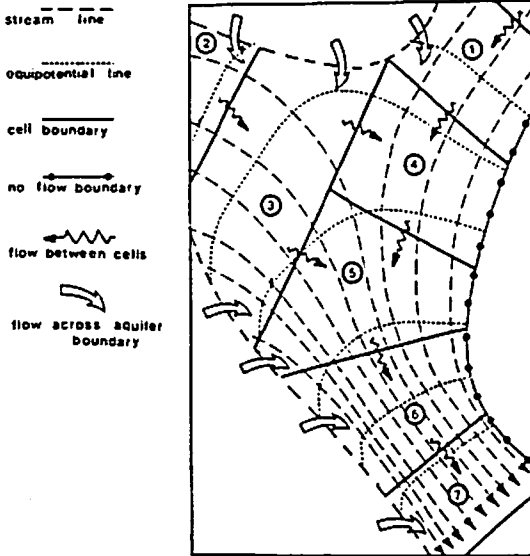


Fig. 2. Schematic flow pattern with cell configuration.

Figure 2 shows a hypothetical example of how a two-dimensional flow region could be divided into a number (in this case 7) of mixing cells and how the cell geometry affects the number of flow components associated with each cell. In this schematic aquifer, outflow from one cell (say 3) may become inflow into two cells (say 4 and 5), and two cells (say 3 and 4) or more may contribute inflows into a single cell (say 5).

When one works with real data, one should not expect the mass balance eqns. (1) and (2) to be closed, as both the model and data are subject to various errors. The water balance expression (1) may not close due to errors in the measurement and/or averaging of  $Q$ ,  $S$  and  $\Delta H$ . The chemical balance eqn. (2) may not close due to sampling and analytical errors in the evaluation of  $C$ , errors in the estimation of  $Q$  and  $\phi$ , and the high probability that at least some of the assumptions behind the model may not hold for several of the dissolved species. These assumptions, we recall, include the conservation of each species and complete mixing within each cell.

To account for such errors, we replace eqns. (1) and (2) by:

$$\sum_{i=1}^{I_n} Q_{ni} - \sum_{j=1}^{J_n} Q_{nj} - S_n \frac{\Delta H_n}{\Delta t} = \epsilon_n \tag{4}$$

and:

$$\sum_{i=1}^{I_n} C_{nik} Q_{ni} - C_{nk} \sum_{j=1}^{J_n} Q_{nj} - V_n \phi_n \frac{\Delta C_{nk}}{\Delta t} = \epsilon_{nk} \tag{5}$$

for every  $n$  and  $k$ , where  $\epsilon_n$  and  $\epsilon_{nk}$  represent the mass balance errors associated with the water and the  $K$  species in the  $n$ th cell, respectively. Since some of the  $Q_{ni}$  and  $Q_{nj}$  values are known while others are unknown, it is convenient to designate the known terms by  $Y_{ni}$ ,  $Y_{nj}$  and the unknown terms by  $X_{ni}$ ,  $X_{nj}$  for inflows and outflows, respectively. We can then write eqns. (4) and (5) in the matrix form as:

$$C_n X_n - D_n = E_n \quad (6)$$

where  $X_n$  is a vector of unknowns including  $X_{ni}$  and  $X_{nj}$ ,  $C_n$  is a matrix having  $K + 1$  rows ( $K$  being the number of species) and as many columns as there are unknown  $X$  terms,  $D_n$  is a vector of known terms of the length  $K + 1$ , and  $E_n$  is an unknown vector of errors having a similar length. The components of  $C_n$  corresponding to  $X_{ni}$  are 1 in the first row (standing for the water-balance equation) and  $C_{nik}$  otherwise. The components of  $C_n$  corresponding to  $X_{nj}$  are  $-1$  in the first row and  $-C_{nk}$  otherwise.  $D_n$  is a vector containing the known terms of inflows, outflows and the flux of each species in each cell. The components of  $D_n$  are:

$$D_{n1} = \sum_i Y_{ni} - \sum_j Y_{nj} - S_n \frac{\Delta H_n}{\Delta t} \quad (7)$$

$$D_{n1+k} = \sum_i C_{nik} Y_{ni} - C_{nk} \sum_j Y_{nj} - V_n \phi_n \frac{\Delta C_{nk}}{\Delta t}, \quad k = 1, 2, 3, \dots, K \quad (8)$$

where the summation over  $i$  and  $j$  involves as many terms as there are known  $Y_{ni}$  and  $Y_{nj}$  values, respectively. The components of  $E_n$  are:

$$E_{n1} = \epsilon_n, \quad E_{n1+k} = \epsilon_{nk}, \quad k = 1, 2, 3, \dots, K \quad (9)$$

The unknown values of  $X_{ni}$ ,  $X_{nj}$  are estimated by minimizing the weighted sum of squared error terms:

$$J = \sum_{n=1}^N (E_n^T W E_n) \quad (10)$$

subject to the cell interface constraints (3), and the nonnegativity constraints:

$$X_{ni} > 0, \quad X_{nj} > 0 \quad (11)$$

for all  $n$ ,  $i$  and  $j$ . In eqn. (10),  $T$  designates transpose and  $W$  is a  $(K + 1) \times (K + 1)$  matrix of weights. The weights account for whatever prior knowledge there is about the relative magnitudes of the errors,  $\epsilon_n$  and  $\epsilon_{nk}$ . Ideally,  $W$  should be the inverse of the covariance matrix of these errors. Since in practice little is known about the correlation between these errors we take  $W$  to be diagonal. The manner in which the non-zero elements of  $W$  are assigned will be discussed later.

Substitution of eqn. (6) into eqn. (10) yields:

$$J = \sum_{n=1}^N (C_n X_n - D_n)^T W (C_n X_n - D_n) \quad (12)$$

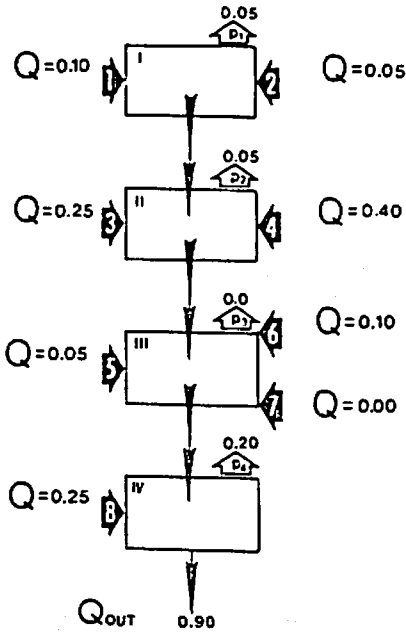


Fig. 3. Schematic compartmental aquifer used for testing the mathematical algorithm.  $Q$  = rate of inflow (cfs);  $P$  = rate of discharge (cfs).

The minimization of eqn. (12), subject to eqns. (3) and (11), is performed by quadratic programming. We use the Wolfe (1959) algorithm as described in Hadley (1970). In what follows, we restrict ourselves to steady-state data. This does not change the form of eqn. (12), but merely eliminates the storage terms  $S_n \Delta H / \Delta t$  and  $V_n \phi_n \Delta C_{n\alpha} / \Delta t$  from  $D_n$ .

#### MODEL TESTING WITH SYNTHETIC DATA

To test the mathematical model, two sets of synthetic data have been generated for a hypothetical aquifer divided into four mixing cells. A schematic representation of the flow regime prevailing during the first test is given in Fig. 3. Recharge into the aquifer derives from eight sources. Discharge occurs at the outlet from cell IV, and via pumpage from each of the four cells. To generate the synthetic data, the corresponding recharge and discharge rates were assigned arbitrary values (consistent with water balance requirements) in cfs, as indicated in the figure. The concentrations of 14 isotopes and chemical constituents were assigned to the various components of the model according to the table in Appendix A. These values, while arbitrarily chosen (so as to maintain isotopic and chemical balance for each species), are nevertheless in



TABLE 1

Comparison between assigned and calculated inflows obtained with exact data in Test 1

Inflow	$Q_1$	$Q_2$	$Q_3$	$Q_4$	$Q_5$	$Q_6$	$Q_7$	$Q_8$	Total
Assigned inflows (cfs)	0.100	0.050	0.250	0.40	0.050	0.100	0.000	0.250	1.200
Calculated inflows (cfs)	0.0988	0.0492	0.2537	0.4001	0.053	0.0977	0.000	0.2470	1.199

accord with actual data from the Aravaipa Valley in southern Arizona to be presented in Part II. With the flow rates in Fig. 3 and the concentrations in Appendix A, the error terms in eqns. (6) and (10) should be zero, and the minimization of  $J$  in eqn. (12) should yield a zero value for the optimum  $J$ .

For the purpose of our exercise, we treated the discharge,  $Q_{out}$  (see Fig. 3), and pumpage rates,  $P_1 - P_4$ , as known terms, and the recharge rates,  $Q_1 - Q_8$ , as unknowns. To facilitate convergence of the quadratic program we followed the approach of Woolhiser et al. (1982) setting the components of the diagonal weight matrix  $W_n$ , corresponding to each cell  $n$  equal to:

$$W_{n11} = Q_{out}^{-2}, \quad W_{n1..k1..k} = C_{ok}^{-2}, \quad k = 1, 2, 3, \dots, K \quad (13)$$

where  $C_{ok}$  is the concentration of the  $k$ th species at the outlet from the aquifer. The effect of this weighting scheme is to normalize the balance equations so they are all expressed on a scale relative to the downstream outflow equations.

TABLE 2

Comparison between assigned and calculated mass flow rates with exact data in Test 1

Ionic and isotopic species	True mass inflow	Estimated mass inflow	Percentage error
EC	352.654	352.020	0.180
Mg	12.260	12.339	-0.640
Ca	40.279	40.251	0.071
Na	27.165	27.161	0.017
K	6.543	6.512	0.477
HCO <sub>3</sub>	182.869	182.276	0.325
Cl	7.240	7.215	0.342
NO <sub>3</sub>	2.082	2.068	0.693
SO <sub>4</sub>	58.938	59.174	-0.400
F	0.601	6.608	-1.184
Li	0.017	0.017	1.246
Si	18.525	18.530	-0.025
<sup>2</sup> H	-81.292	-81.310	-0.022
<sup>18</sup> O	-10.563	-10.568	-0.052
Total lbs d <sup>-1</sup>	3326.1	3331.7	+0.17

\* EC is electrical conductivity in mMHO, ionic species are in mg l<sup>-1</sup>, isotopic species are in %.

TABLE 3

Comparison between assigned and calculated inflows obtained with exact data in Test 2

Inflow	$Q_1$	$Q_2$	$Q_3$	$Q_4$	$Q_5$	$Q_6$	$Q_7$	$Q_8$	$Q_9$	Total
Assigned inflows (cfs)	45.00	7.50	2.50	1.50	4.00	1.50	4.00	6.00	2.00	75.0
Calculated inflows (cfs)	44.30	7.40	2.36	1.44	4.17	1.36	4.37	6.30	2.14	75.6

Inflow	$Q_{11}$	$Q_{12}$	$Q_{13}$	$Q_{14}$	$Q_{15}$	$Q_{16}$	$Q_{17}$	$Q_{18}$	$Q_{19}$	Total
Assigned inflows (cfs)	4.00	4.00	6.00	2.00	2.60	8.00	2.00	1.50	2.00	113.6
Calculated inflows (cfs)	3.97	3.76	6.04	2.01	2.66	8.07	2.06	1.54	2.01	113.59

The results of this preliminary test are listed in Tables 1 and 2. The computed flow rates in Table 1 are seen to be very close to the true (assigned) values, the total water-balance error being only  $-9.5 \times 10^{-3}\%$ .  $Q_7$ , which was assigned a value of zero, is correctly computed.  $Q_5$  and  $Q_8$ , derived from the same source (carry same isotopic and chemical signature) but contributing to two separate cells, are also correctly identified. The total isotopic and chemical mass-balance error in Table 2 is 0.17%. The errors in Tables 1 and 2 stem essentially from rounding off and incomplete convergence of the Wolfe algorithm.

In the second test with exact data, the number of unknown flow rates exceeds the number of isotopic and chemical species by 19 to 14. The test

TABLE 4

Comparison between assigned and calculated mass flow rates obtained with exact data in Test 2

	True mass inflow	Estimated mass inflow	Percentage error
EC*	36,815.94	36,785.62	0.074
Mg	1,019.42	1,019.21	0.021
Ca	4,289.66	4,285.13	0.106
Na	2,211.36	2,211.69	-0.015
K	260.52	260.18	0.130
HCO <sub>3</sub>	17,984.83	17,987.77	-0.016
Cl	756.67	756.13	0.074
NO <sub>3</sub>	406.21	408.85	-0.651
SO <sub>4</sub>	3,570.12	3,562.35	0.218
F	60.55	60.41	0.228
Li	1.61	1.58	1.749
Si	1,894.77	1,894.87	-0.005
<sup>2</sup> H	-7,942.92	-7,943.65	-0.012
<sup>18</sup> O	-1,049.62	-1,049.53	0.009
Total	325,133.7	325,326.6	0.06

\* Electrical conductivity.

setup is similar to that in Fig. 2 except that now there are four inflows into cell 1 and five into each of cells 2, 3 and 4. The assigned inflows are listed in Table 3, and the assigned concentrations appear in Appendix B. Inflows  $Q_3$ ,  $Q_6$ ,  $Q_{13}$  and  $Q_{17}$  have identical isotopes and chemical signatures (they could represent recharge from winter floods), and so have inflows  $Q_4$ ,  $Q_9$ ,  $Q_{14}$  and  $Q_{18}$  (which could represent stream bed infiltration due to summer floods).

Table 3 compares the calculated and assigned inflow rates, and Table 4 juxtaposes the calculated and assigned mass flow rates for the isotopic and chemical species. Again, the results are seen to be very good, the total water balance error being  $7.8 \times 10^{-3}\%$ , and the total isotopic and chemical balance error 0.06%. The two tests show that, as long as the data are precise and the number of mass balance expressions exceeds the number of unknowns, our algorithm is able to estimate correctly a number of flow components which may be less or more than the number of isotopic and chemical species entering into the model.

#### EFFECT OF ERRORS IN THE DATA

In real field situations the input data are not known with precision and the assumptions behind the model are not always satisfied. The model, therefore, should not be expected to provide precise estimates of flow rates. To examine the effect of erroneous input data on the quality of such estimates, we repeated Test 1 after corrupting our synthetic input data with various levels of uncorrelated Gaussian noise.

The rationale for the particular method used to generate our noise stems from the assumption that laboratory errors are a major cause of error in isotopic and hydrochemical analysis. The first step is to generate normal errors of zero mean and unit variance  $N_{(0,1)}$  by means of the formula (Box and Muller, 1958, as cited in Bard, 1974):

$$N_{(0,1)} = (-2 \log_{10} U_1)^{0.5} \cos(2\pi U_2) \quad (14)$$

where  $U_1$  and  $U_2$  are independent random variables drawn from uniform distribution. Next, each "true"  $C_k$  value entering into the model is transformed into a noisy concentration  $C_k^*$  according to:

$$C_k^* = C_k [1 + \beta_k N_{(0,1)}] \quad (15)$$

where  $\beta_k$  is a weighting parameter controlling the magnitude of the corrupted concentration  $C_k^*$  relative to that of the "true" concentration  $C_k$ . This causes the errors to increase linearly with concentration in a manner similar to that assumed by Woolhiser et al. (1982). We believe that this is realistic for laboratory data. When the noise was made independent of concentration, the Wolfe algorithm at times failed to converge. Woolhiser et al. (1982), in the case of a single river reach, found that errors in  $C$  are more important than errors in  $Q$  when the number of flow rate equations in the model is less than the number of chemical balance equations. Since in Test 1 we have a similar situation, we have not superimposed noise on the assigned values of our flow rates.

A preliminary test was conducted with 100 noisy  $C$  data sets for each of four

TABLE 5

Statistics of inflow estimates from 100 realizations of noisy  $C$  data with four uniform  $\beta$  values assigned to the various species

$\beta^*$	$Q_1$	$Q_2$	$Q_3$	$Q_4$	$Q_5$	$Q_6$	$Q_7$	$Q_8$
<i>Assigned (true) inflows (<math>m^3 s^{-1}</math>)</i>								
	0.1	0.05	0.25	0.40	0.05	0.10	0.00	0.25
<i>Average inflow estimates</i>								
0.20	0.062	0.025	0.10	0.14	0.110	0.130	0.100	0.60
0.10	0.082	0.041	0.18	0.29	0.076	0.110	0.050	0.39
0.05	0.093	0.047	0.23	0.37	0.055	0.103	0.029	0.31
0.01	0.0998	0.049	0.252	0.398	0.052	0.0975	0.022	0.253
<i>Percent deviation of estimates from true inflows</i>								
0.20	35.0	50.0	60.0	65.0	120.0	30.0		140.0
0.10	18.0	18.0	28.0	27.5	52.0	10.0		56.0
0.05	7.0	6.0	8.0	7.5	10.0	3.0		24.0
0.01	0.2	2.0	0.8	0.5	4.0	2.5		1.2
<i>Standard deviation of estimates</i>								
0.20	0.0340	0.0175	0.056	0.076	0.070	0.051	0.086	0.430
0.10	0.0395	0.0194	0.048	0.065	0.050	0.060	0.048	0.260
0.05	0.0275	0.0125	0.029	0.028	0.025	0.026	0.025	0.113
0.01	0.0058	0.0029	0.007	0.0075	0.007	0.0055	0.004	0.027
<i>Coefficient of variation of estimates</i>								
0.20	0.55	0.70	0.56	0.54	0.64	0.62	0.86	0.72
0.10	0.48	0.47	0.27	0.22	0.66	0.55	0.96	0.67
0.05	0.30	0.27	0.13	0.08	0.45	0.25	0.86	0.36
0.01	0.06	0.06	0.03	0.02	0.13	0.11	0.18	0.11

different  $\beta$  values 0.20, 0.10, 0.05 and 0.01. The same  $\beta$  was used for every  $k$ . For each of these 400 noisy realizations, the quadratic program was used to obtain an estimate of the unknown  $Q$  values. The weight matrix  $W$  was the same used earlier in connection with the noise free data. The results for all four uniform  $\beta$  values are summarized in Table 5.

It was observed that, regardless of the magnitude of  $\beta$ , the mean  $Q$  values converge to stable values after about 40–50 realizations (Adar, 1984, fig. 50). Table 5 shows that the magnitudes of the average  $Q$  estimates depend heavily on the magnitude of  $\beta$ . When  $\beta = 0.2$ , these averages (with the exception of  $Q_7$  which is zero) differ from the true values by 30–140%. When  $\beta = 0.01$ , this difference is reduced to 0.2–4%. The manner in which the standard deviation of the computed  $Q$  estimates varies with  $\beta$  is shown in Fig. 4. The larger  $\beta$  is, the greater the error of estimation. On the other hand, although the rate at which the estimation error increases with  $\beta$ , it decreases as the amplitude of the noise goes up. A second test was performed in which different  $\beta_k$  values had been assigned to the various isotopic and chemical species  $k$  according to:

$$\beta_k = \frac{\sigma_k}{\mu_k} \quad (16)$$

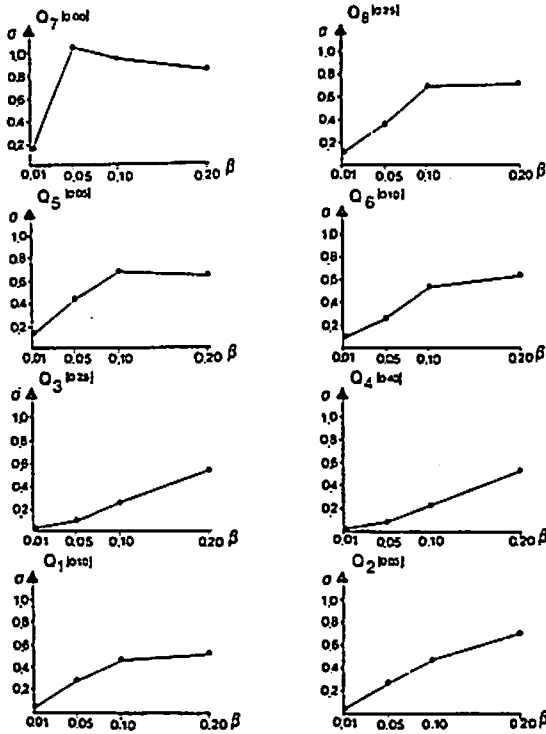


Fig. 4. Standard deviation of computed  $Q$  estimates versus four uniform  $\beta$  values.

TABLE 6

Statistics of inflow estimates from 100 realizations of noisy  $C$  data with different  $\beta_i$  values assigned to each species

$Q_1$	$Q_2$	$Q_3$	$Q_4$	$Q_5$	$Q_6$	$Q_7$	$Q_8$
<i>Assigned (true) (<math>m^3s^{-1}</math>)</i>							
0.1	0.05	0.25	0.4	0.05	0.10	0.00	0.25
<i>Average inflow estimates</i>							
0.0845	0.041	0.210	0.315	0.084	0.112	0.055	0.360
<i>Percent deviation of estimates from true inflows</i>							
15.5	18.0	16.0	21.3	68.0	12.0		44.0
<i>Standard deviation estimates</i>							
0.041	0.0188	0.058	0.069	0.05	0.054	0.055	0.260
<i>Coefficient of variation of estimates</i>							
0.455	0.459	0.276	0.219	0.595	0.446	1.00	0.722

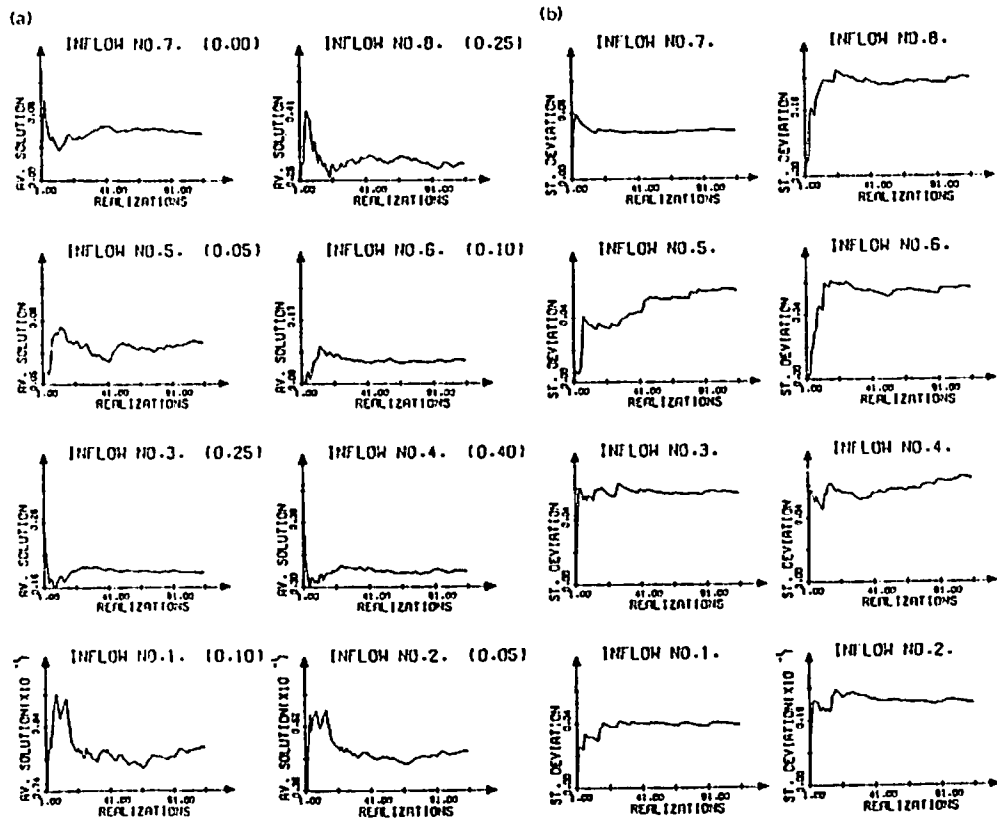


Fig. 5. Results of Monte Carlo simulations with  $\beta_h$  values equal to coefficient of variation from laboratory standards: (a) average  $Q$  versus number of realizations; (b) standard deviation of  $Q$  versus number of realizations.

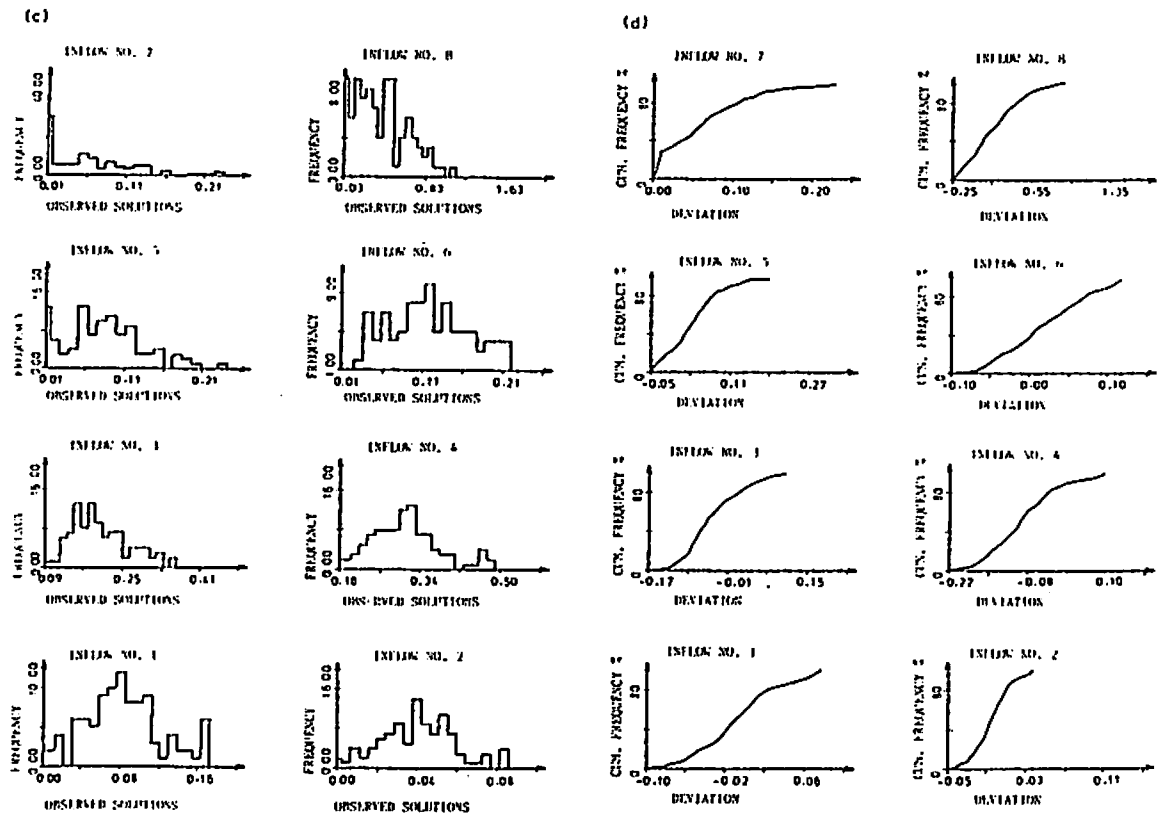


Fig. 5. (c) frequency distribution of computed  $Q$  values; (d) cumulative frequencies of estimated  $Q$  values.

Here  $\mu_k$  is the mean of a large number of concentrations determined by us for laboratory standards of the  $k$  species, and  $\sigma_k$  is the associated standard deviation (see Appendix C). In this manner  $\beta_k$  becomes the coefficient of variation of the error in determining the laboratory standard for the  $k$  species.

The results of this second test are summarized in Table 6. Fig. 5a and b shows the mean computed  $Q$  values and the standard deviation of these values varies with the number of realizations. Figure 5c and d shows the frequency distribution of the computed  $Q$  values and the cumulative frequencies of the estimation errors, respectively. From Table 6 and Figure 5a and b, we see that ultimate stable mean  $Q$  values differ by 22–100% from the true values. Figure 5c and d shows that the estimation errors have a large standard deviation and their distribution is generally far from Gaussian (even though artificial noise in the data is such). These deviations from normality are due in part to the non-negativity constraints imposed on the estimates which affect primarily the smaller  $Q$  values. However, most of the difficulty stems from having neglected to maintain ionic balance between the chemical species and the fixed empirical ratios between D and  $^{18}\text{O}$  in generating the noisy data. Laboratory analyses are customarily rejected if the concentrations of all cations (in meq) do not match those of all anions; if D does not vary linearly with  $^{18}\text{O}$ ; or if electrical conductivity does not vary linearly with the total dissolved ion (TDI). We must do the same with the artificial concentrations obtained when generating our noise. To do so, we performed 250 simulations with the above nonuniform  $\beta_k$  values for each of six different levels of constraints on ionic balance, electrical conductivity to total dissolved ions ratios and D to  $^{18}\text{O}$  ratios. These six sets of constraints are given in the first three columns of Table 7. The last three minimum and maximum sets of constraints correspond to the extremes of values actually obtained at the Aravaipa Valley. To achieve each level of constraints, more than 250 noisy data sets were originally generated, out of which only those 250 which satisfied the given constraints were retained for further analysis. The results are given in Table 7. We see that the stricter the constraints, the closer the average to the true flow rates. Consequently, the standard deviation and coefficient of variations of the estimation errors decrease as the constraints are tightened.

Figure 6 shows the results for the case of the tightened constraints corresponding to the bottom row of each category in Table 7. The ionic balance was maintained within 2%, the ratio between electrical conductivity and TDI ranged from 35 to 55, and the ratio between D and  $^{18}\text{O}$  from 6.5 to 8.5. The estimation errors are seen to be much smaller than those in Fig. 5 and their distributions less skewed and closer to normal, especially for large  $Q$  values.

Table 7 further shows that under severe but nevertheless realistic chemical and isotopic constraints, the average inflow estimates are almost identical to the assigned (true)  $Q$  values. The assigned value of  $Q_7$  is zero; due to the nonnegativity requirement its estimates are heavily skewed toward this number. This notwithstanding, Fig. 6d shows that 42% of the estimates of  $Q_7$  are zero as they should be, 95% of them deviate from zero by not more than 0.07



TABLE 7

Statistics of inflow estimates from 250 realizations satisfying various levels of chemical and isotopic constraints

Constraints			$Q_1$	$Q_2$	$Q_3$	$Q_4$	$Q_5$	$Q_6$	$Q_7$	$Q_8$
Ionic balance (%)	EC/TDI	D/ <sup>18</sup> O								
<i>Assigned true inflows</i>			0.1	0.05	0.25	0.40	0.05	0.10	0.00	0.25
<i>Average inflow estimates</i>										
10.0	30-55	5-11	0.0875	0.0458	0.193	0.315	0.086	0.125	0.068	0.295
10.0	35-55	6-10	0.0882	0.0462	0.185	0.320	0.075	0.120	0.060	0.285
3.0	30-60	6-9	0.080	0.042	0.200	0.320	0.070	0.120	0.060	0.320
3.0	35-60	6-9	0.087	0.044	0.218	0.350	0.063	0.109	0.039	0.320
3.0	35-55	6.5-9	0.093	0.047	0.235	0.376	0.056	0.105	0.028	0.280
2.0	35-55	6.5-8.5	0.095	0.048	0.240	0.383	0.056	0.102	0.016	0.260
<i>Percent deviation of estimates from true inflows</i>										
10.0	30-55	5-11	12.5	8.4	22.8	21.3	70.0	25.0		18.0
10.0	35-55	6-10	12.0	7.6	26.0	20.0	50.0	20.0		9.4
3.0	30-60	6-9	20.0	16.0	20.0	20.0	40.0	20.0		28.0
3.0	35-60	6-9	13.0	12.0	12.8	12.5	27.0	9.0		28.0
3.0	35-55	6.5-9	7.0	6.0	6.0	7.5	12.0	5.0		12.0
2.0	35-55	6.5-8.5	5.5	4.4	4.0	4.25	12.0	2.0		3.2
<i>Standard deviation of estimates</i>										
10.0	30-55	5-11	0.04	0.022	0.058	0.068	0.060	0.058	0.070	0.230
10.0	35-55	6-10	0.04	0.021	0.056	0.070	0.058	0.0575	0.055	0.240
3.0	30-60	6-9	0.0385	0.021	0.0576	0.070	0.058	0.057	0.070	0.260
3.0	35-60	6-9	0.038	0.019	0.042	0.045	0.040	0.041	0.050	0.170
3.0	35-55	6.5-9	0.028	0.016	0.032	0.039	0.032	0.037	0.037	0.130
2.0	35-55	6.5-8.5	0.017	0.009	0.025	0.034	0.024	0.0281	0.0215	0.130
<i>Coefficient of variation of estimates</i>										
10.0	30-55	5-11	0.467	0.480	0.301	0.216	0.698	0.464	1.029	0.780
10.0	35-55	6-10	0.454	0.455	0.303	0.219	0.773	0.460	0.917	0.842
3.0	30-60	6-9	0.481	0.500	0.288	0.219	0.829	0.476	1.167	0.813
3.0	35-60	6-9	0.437	0.443	0.193	0.129	0.630	0.390	1.282	0.513
3.0	35-55	6.5-9	0.308	0.330	0.136	0.105	0.554	0.357	1.339	0.464
2.0	35-55	6.5-8.5	0.185	0.188	0.104	0.089	0.410	0.235	1.295	0.504

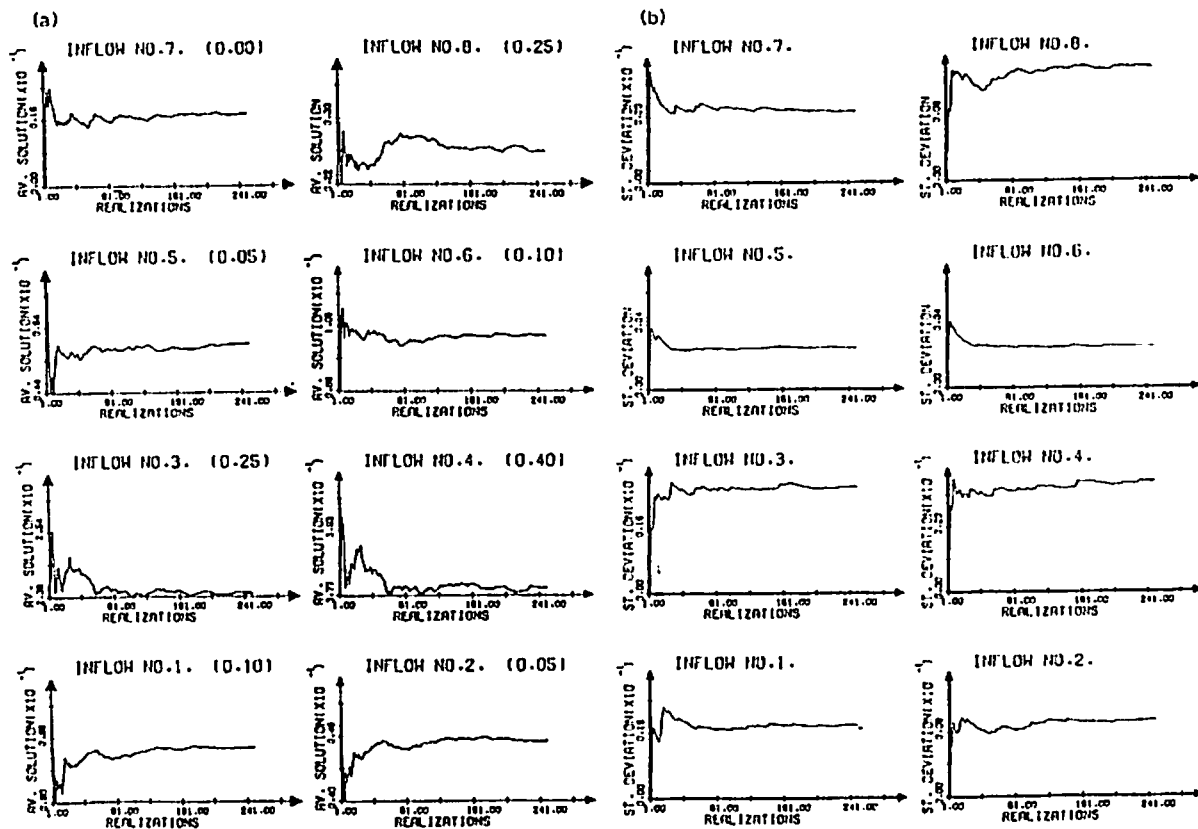


Fig. 6. Results of Monte Carlo simulations with perturbed concentrations restricted to ionic balance of 2%, electrical conductivity to TDI ratios between 35 and 55, and D to  $^{18}\text{O}$  ratios between 6.5 and 8.5. (a) average  $Q$  (in cfm) versus number of realizations; (b) standard deviations of  $Q$  versus number of realizations.

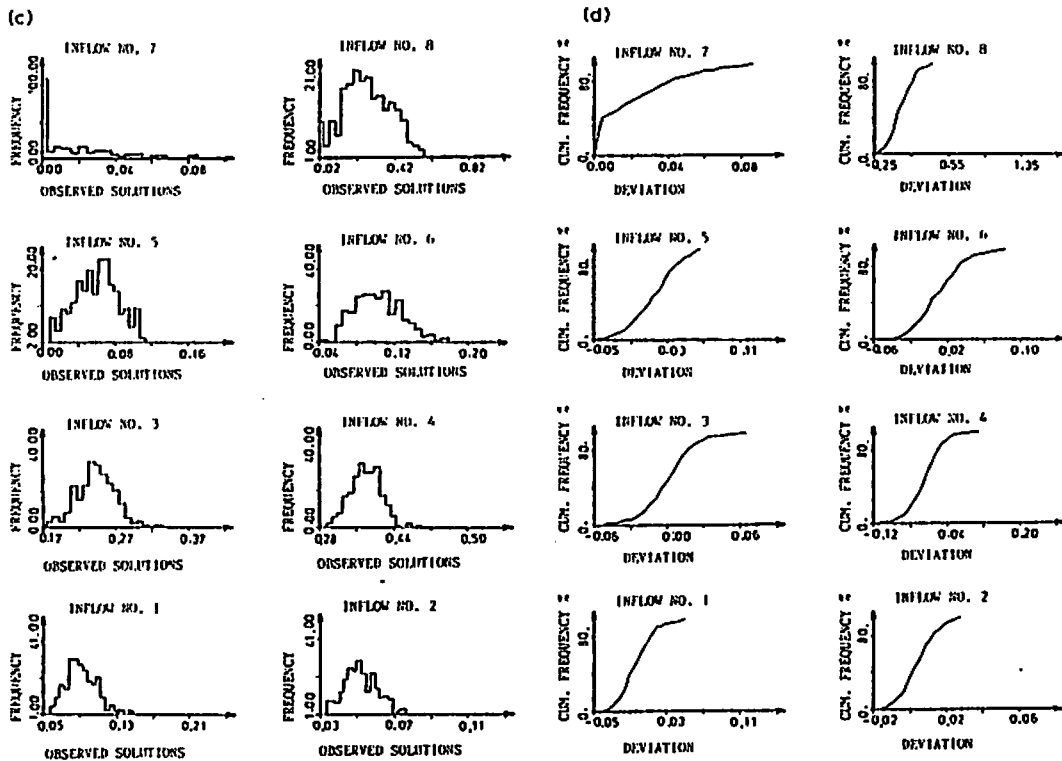


Fig. 6. (c) frequency distributions of computed  $Q$  values; (d) cumulative frequencies of  $Q$  estimation errors.

cfs. Detailed results for other combinations of constraints are given in Adar (1984). The importance of ion balance for a single cell model was demonstrated for laboratory mixtures by Woolhiser et al. (1985).

The fact that the model yields good results when noisy data satisfy constraints similar to those that real data usually satisfy suggests that the model should be applied to real hydrologic conditions in the field. Part II gives an example of such an application.

#### SUMMARY AND CONCLUSIONS

This study leads to a number of important conclusions about the use of isotopic and chemical data in hydrology.

(1) Regional hydrochemistry and environmental isotopic data have traditionally been used by hydrologists as an important qualitative tool to help the postulation, support, or rejection of hypotheses on flow regimes in subsurface environments. However, only on rare occasions have such data been used in a quantitative manner to compute the magnitudes of physical quantities characterizing these flow regimes. It has been demonstrated that by excluding hydrochemical and stable isotope data from the domain of quantitative hydrology, much information may be lost. This is especially true in situations where information about hydraulic gradients and aquifer parameters is limited. For such situations, it is useful to have a mathematical model which can extract information about basin hydrology from the spatial distribution of stable isotopes and chemicals dissolved in surface and subsurface waters.

(2) In this work, a mathematical model has been postulated for the computation of recharge into, and flow through, an aquifer system. The model has been developed specifically for basins in which information about environmental hydrochemistry and the spatial distribution of stable isotopes is more easily accessible than information about groundwater levels and aquifer parameters such as transmissivity and storativity. Its development has been prompted by actual conditions encountered in the semiarid Aravaipa Basin (Adar, 1984).

(3) The proposed model assumes that a groundwater basin or aquifer of mixing cells is arranged in a one, two, or three-dimensional pattern. All waters entering the cell mix instantaneously so that the concentrations of the constituents within each cell are uniform. A system of  $K + 1$  water and chemical balance equations is written for each cell (one water balance equation and  $K$  mass balance equations for each of the dissolved species). The resulting system of coupled equations is solved for the unknown annual flow rates by quadratic programming. The algorithm minimize the sum of squared errors in the mass balance expressions, normalized with respect to the total (known) outflow from the basin and the associated concentrations. These errors may be further weighted so as to account for uncertainties in the results of chemical laboratory analyses, and to minimize the adverse effect of nonconservative constituents on the mass balance calculation (as chemical reactions along the flow paths are ignored in the current version of the model).

(4) The sensitivity of the proposed model to errors in the data was inves-

tigated by means of a Monte Carlo approach. A set of "exact" data was generated synthetically by the mixing cell model and then corrupted by uncorrelated Gaussian noise. The noisy data were fed into the quadratic program to yield corresponding estimates of the "unknown" flow rates. A comparison of these computed flow rates with their known true values showed that the model works reasonably well (leading to estimates characterized by near-Gaussian estimation errors showing a small bias and error variance) as long as ionic balance is maintained between the dissolved constituents (a condition laboratory analyses will generally satisfy), the relation between  $^{18}\text{O}$  and D is linear as expected from real data, and the species are conservative. In Part II, Adar and Neuman (this volume) we will show how chemical equilibrium models, such as *WATEQF*, can be used to determine the degree to which the various species satisfy this latter requirement, and how to handle nonconservative species by proper weighting of the mass-balance expressions. Clearly, for the solution to be meaningful, the number of constituents must be sufficiently large so that the number of mass-balance expressions exceeds the number of unknown flow rates by a substantial margin.

#### ACKNOWLEDGEMENTS

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## APPENDIX A

Synthetic data used in test No. 1 (4 cells; 14 dissolved species and 8 unknown inflows)

Inflow	EC <sup>a</sup>	Mg	Ca	Na	K	HCO <sub>3</sub>	Cl	NO <sub>3</sub>	SO <sub>4</sub>	F	Li	Si	D <sup>b</sup>	<sup>18</sup> O <sup>c</sup>
1	353.8	0.74	1.97	0.97	0.062	3.08	0.205	0.082	0.42	0.023	0.0030	18.01	-73.8	-9.73
2	147.8	0.84	0.41	0.33	0.030	1.97	0.070	0.008	0.98	0.120	0.0010	7.80	-68.9	-9.36
3	303.7	0.08	0.27	2.46	0.034	2.52	0.292	0.019	0.12	0.058	0.0030	14.13	-71.0	-9.12
4	356.0	1.72	3.18	0.73	0.340	3.64	0.140	0.016	1.93	0.015	0.0020	14.80	-67.0	-8.43
5	631.6	1.22	3.66	0.66	0.025	4.02	0.283	0.027	1.37	0.047	0.0030	14.91	-69.0	-9.43
6	184.0	0.35	0.76	0.37	0.040	0.85	0.105	0.001	0.76	0.001	0.0010	17.55	-66.3	-8.66
7	407.5	0.86	2.69	0.87	0.056	2.91	0.240	0.077	1.01	0.031	0.0020	21.07	-71.5	-10.40
8	184.0	0.35	0.76	0.37	0.040	0.85	0.105	0.001	0.76	0.001	0.0010	17.55	-63.3	-8.66
Cell 1	285.1	0.77	1.46	0.76	0.051	2.71	0.160	0.057	0.61	0.055	0.0023	14.61	-72.2	-9.61
Cell 2	329.1	1.05	1.98	1.31	0.199	3.14	0.193	0.038	1.15	0.035	0.0021	14.55	-69.0	-8.82
Cell 3	323.9	0.98	1.94	1.16	0.170	2.92	0.188	0.033	1.12	0.032	0.0023	14.92	-68.7	-8.83
Cell 4	292.1	0.84	1.67	0.88	0.140	2.45	0.169	0.026	1.04	0.025	0.0020	15.52	-67.5	-8.77

Concentrations are in  $\text{meq l}^{-1}$  unless otherwise indicated.<sup>a</sup>Electrical conductivity ( $\mu\text{MHO cm}^{-1}$ ).<sup>b</sup>Deuterium (‰).<sup>c</sup>Oxygen-18 (‰).

## APPENDIX B

Synthetic data used in test No. 2 (4 cells; 14 dissolved species and 19 unknown inflows)

Inflow	EC <sup>a</sup>	Mg	Ca	Na	K	HCO <sub>3</sub>	Cl	NO <sub>3</sub>	SO <sub>4</sub>	F	Li	Si	D <sup>b</sup>	<sup>18</sup> O <sup>c</sup>
1	353.8	0.74	1.97	0.97	0.062	3.08	0.205	0.082	0.42	0.023	0.0026	18.01	-73.8	-9.73
2	187.1	0.56	0.81	0.39	0.035	0.89	0.093	0.001	0.80	0.001	0.0003	18.18	-66.3	-8.56
3	146.0	0.52	1.13	0.51	0.048	1.40	0.080	0.036	0.67	0.007	0.0003	17.70	-60.6	-8.55
4	332.3	0.62	2.31	0.69	0.174	2.97	0.151	0.030	0.38	0.025	0.0013	16.83	-58.7	-7.41
5	301.5	0.10	0.24	2.01	0.048	2.52	0.263	0.022	0.05	0.036	0.0022	14.00	-67.2	-8.70
6	370.3	0.77	1.67	1.70	0.069	3.04	0.690	0.224	0.14	0.008	0.0032	8.80	-63.1	-6.52
7	454.0	1.28	2.52	0.98	0.028	3.71	0.419	0.059	0.64	0.012	0.0016	16.35	-76.3	-10.18
8	242.0	0.39	1.51	0.33	0.063	1.20	0.086	0.044	0.63	0.030	0.0020	17.70	-67.1	-8.98
9	332.3	0.62	2.31	0.69	0.174	2.97	0.151	0.030	0.38	0.025	0.0013	16.83	-58.7	-7.41
10	356.0	1.72	3.18	0.73	0.034	3.64	0.140	0.016	1.93	0.015	0.0016	14.80	-67.0	-8.43
11	147.8	0.84	0.41	0.33	0.030	0.07	0.070	0.008	0.98	0.120	0.002	7.80	-68.9	-9.36
12	362.0	0.66	2.06	0.87	0.050	2.93	0.140	0.080	0.51	0.022	0.0023	17.10	-69.3	-9.66
13	242.0	0.39	1.51	0.33	0.063	1.20	0.086	0.044	0.63	0.030	0.0020	17.70	-67.1	-8.98
14	332.3	0.62	2.31	0.69	0.174	2.97	0.151	0.030	0.38	0.025	0.0013	16.83	-58.7	-7.41
15	355.5	0.70	2.10	0.89	0.050	2.90	0.175	0.142	0.56	0.024	0.0023	18.55	-72.3	-9.68
16	444.2	1.16	3.21	0.76	0.029	3.39	0.275	0.027	1.36	0.052	0.0016	14.58	-68.6	-9.56
17	242.0	0.39	1.51	0.33	0.063	1.20	0.086	0.044	0.63	0.030	0.0020	17.70	-67.1	-8.98
18	332.3	0.62	2.31	0.69	0.174	2.97	0.151	0.030	0.38	0.025	0.0013	16.83	-67.7	-9.70
19	302.8	0.05	0.30	2.89	0.020	2.52	0.320	0.021	0.19	0.080	0.0037	14.25	-74.8	-9.44
Cell 1	321.9	0.6771	0.788	0.865	0.0608	2.712	0.1832	0.0678	0.480	0.0194	0.0022	17.98	-71.82	-9.461
Cell 2	322.9	0.6551	0.733	0.902	0.0671	2.646	0.2019	0.066	0.468	0.0207	0.0021	17.44	-70.89	-9.303
Cell 3	314.4	0.7341	0.807	0.818	0.060	2.538	0.1793	0.0594	0.623	0.0254	0.0020	16.78	-69.885	-9.186
Cell 4	324.20	0.7441	0.895	0.844	0.0583	2.593	0.1871	0.0576	0.667	0.0286	0.0020	16.62	-69.856	-9.235

Concentrations are in meq l<sup>-1</sup> unless otherwise indicated.<sup>a</sup>Electrical conductivity ( $\mu\text{MHO cm}^{-1}$ ).<sup>b</sup>Deuterium (‰).<sup>c</sup>Oxygen-18 (‰).

## APPENDIX C

Statistics for 14 isotopic and ionic species from repeated laboratory standards

Species	Expected value	No. of repeated analyses	Average $\bar{X}$	Standard deviation $\sigma$	Variance <sup>-1</sup> $1/\sigma^2$	Coefficient of variation $\sigma/\bar{X}$
EC**	420.0	150	422.0	13.99	0.0051	0.0316
Mg	56.5	17	57.6	3.13	0.1020	0.0543
Ca	141.0	20	136.3	14.09	0.0050	0.1030
Na	207.0	27	202.7	20.84	0.0023	0.1030
K						0.0540*
HCO <sub>3</sub>	724.0	27	761.5	87.53	$1.31 \times 10^{-4}$	0.1150
Cl	251.0	30	229.9	37.86	0.0007	0.1650
NO <sub>3</sub>	558.0	30	573.3	76.32	0.0002	0.1330
SO <sub>4</sub>	223.0	29	232.2	14.23	0.0049	0.0513
F						0.0500*
Li						0.0600*
Si						0.1500*
<sup>3</sup> H	-58.0	122	-58.1	3.71	0.0727	0.0639
<sup>18</sup> O	-8.6	78	-8.56	0.198	25.6	0.0230

\* Estimated values obtained from UOA Analytical Center, Tucson, Ariz.

\*\* Electrical conductivity.

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