Generation of Ground-Water Age Distributions

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ABSTRACT

Discrete-state compartment (DSC) models and their associated age distribution functions permit the quantitative interpretation of environmental radioisotope data such as carbon-14 ground-water decay ages. These mixing-cell models offer a means for constructing ground-water flow models that can be used to relate decay ages to ground-water mean ages. In addition, DSC models can also generate the entire distribution of ages in various subregions of a ground-water reservoir. A preexisting DSC model of a portion of the Tucson Basin alluvial aquifer is used as an example. Ground-water mean ages in this aquifer range from 100 to almost 15,000 years old, with the oldest waters about 40,000 years old. Since the ground-water ages are not normally distributed, means and medians are not equivalent. The results indicate that care must be used in interpreting both ground-water radioisotope decay ages as well as mean ground-water ages and that knowledge of the entire age distribution is preferable. Age distributions are especially useful in hydrogeologic studies in which mixing is important and may find use in paleohydrogeologic investigations.

INTRODUCTION

The dating of ground water with carbon-14 (half-life = 5,730 years) is a useful tool for obtaining estimates of ground-water ages and residence times. The ground-water age is the amount of time that has elapsed between the time a given parcel of water enters the system as recharge to the time it is sampled. The residence or transit time is the length of time a given parcel of water resides within the system or subsystem thereof, i.e., the elapsed time between system or subsystem entry and exit. The "age" obtained from carbon-14 (or any other environmental radioisotope) dating is called the decay age of the sample. This number, often called the "raw" age, may have to be adjusted to account for the dilution of carbon-14 activity by "dead" (i.e., nonradioactive) carbon in the aquifer (Wallick, 1973). Once this adjustment is accomplished, the adjusted decay age of the sample is obtained. However, even the adjusted decay age of the sample is not necessarily equal to the age of the ground water from which the sample was taken. This age discrepancy is caused by the mixing of waters of different ages in the aquifer; only in the case of pure piston flow are the two ages identical (Simpson and Duckstein, 1976; Campana and Simpson, 1984).

Since the decay age is known but the ground-water age is not, a flow or mixing model must be selected to obtain the latter from the former. Nir (1964) was one of the first to discuss how mixing could affect ground-water ages. He presented several cases: pure piston flow, complete mixing, and dispersive mixing, with equations for each case. Since the early work of Nir, much effort has been devoted toward relating carbon-14 data and tracer data in general to ground-water ages and residence times via mathematical models. These models generally consist of simple lumped-parameter analytical models describing perfect mixing, piston flow, exponential mixing, or dispersive mixing (Maloszewski and Zuber, 1982; Bitner, 1983; Zuber, 1985). Certain models attempt to combine the features of some of the above; the exponential and piston flow model (EPM) of Maloszewski and Zuber (1982) is such an example.

Despite the usefulness of some of the analytical models, they are unable to account for the distributed-parameter systems typical of ground-water reservoirs. Numerical mixing-cell models called discrete-state compartment (DSC) models (Simpson and Duckstein, 1976) offer a convenient and relatively simple means for simulating distributed-parameter systems and relating carbon-14 decay ages to ground-water ages (Llamas *et al.*, 1982; Campana and Simpson, 1984). These models have also been used to obtain aquifer

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parameters and mean residence times from the transient distribution of tritium in an aquifer (Campana and Mahin, 1985).

Although knowledge of ground-water mean ages is preferable to mere knowledge of decay ages, the ideal situation is knowledge of the entire age distribution of the ground water in an aquifer. Mean ages can be misleading, since one generally does not know the shape of the distribution from which the mean is derived. This paper will demonstrate that DSC models calibrated with carbon-14 decay age data can generate the entire age distribution function for any specified subsystem of an aquifer. Since these distributions are not necessarily normal, the median and mean ages are not always equivalent, and reliance upon the mean age to characterize the age regime of the ground water in an aquifer may be unwise. A DSC model previously developed by Campana and Simpson (1984) will be used as an example.

DISCRETE-STATE COMPARTMENT MODELS

Previous publications (Simpson and Duckstein, 1976; Campana and Simpson, 1984; Campana and Mahin, 1985) presented detailed information on DSC models; some repetition is necessary here since these models are not in wide use. DSC models are essentially sophisticated mixing-cell models; they are conceptually similar to the population-balance models used in chemical engineering (Himmelblau and Bischoff, 1968, Ch. 4). The basic principle behind DSC models consists of subdividing a given hydrogeologic system into mixing cells; the subdivision is based upon hydrogeologic information. The cells can be of any desired size and arranged in a one-, two-, or three-dimensional network. By applying the conservation of mass to each cell and specifying one of two mixing rules, the movement of a tracer can be simulated. The conservation of mass equation is:

$$S(N) = S(N-1) + BRV(N) \cdot BRC(N) - BDV(N) \cdot BDC(N) \pm R(N) \qquad (1)$$

where

S(N) = cell state at iteration N, the mass or amount of tracer in the cell;

BRV(N) = boundary recharge volume at iteration N, the input volume of water to the cell;

BRC(N) = boundary recharge concentration at iteration N, the input concentration of tracer;

BDV(N) = boundary discharge volume at iteration N, the output volume of water from the cell;

BDC(N) = boundary discharge concentration at iteration N, the output concentration of tracer; and

R(N) = source/sink term at iteration N.

Equation (1) is applied sequentially to each cell in the network such that boundary discharge volumes and concentrations from "upstream" cells become boundary recharge volumes and concentrations to "downstream" cells.

In equation (1), the only unknown on the right-hand side is BDC(N). This quantity can be obtained by specifying one of two mixing rules: the simple mixing cell (SMC) rule or the modified mixing cell (MMC) rule. The former rule simulates perfect mixing within a cell; the latter simulates some regime between perfect mixing and pure piston flow. For the SMC, the expression for BDC(N) is:

$$BDC(N) = \frac{[S(N-1) + BRV(N) \cdot BRC(N)]}{[VOL + BRV(N)]} \qquad (2)$$

where VOL = volume of water in the cell. Since the SMC simulates perfect mixing, the tracer concentration in a cell's output equals that within the cell. For the MMC, the expression for BDC(N) is:

$$BDC(N) = S(N-1)/VOL \qquad (3)$$

It should be noted that even though pure piston flow may be specified for the individual cells, this does not imply pure piston flow for the system as a whole, since there is still mixing among the various cells of the model.

DISTRIBUTION FUNCTIONS OF DSC MODELS

Introduction

Ground-water age distributions show the entire range of ground-water ages and the fraction of each age present in an aquifer or portion thereof. In this respect, they are analogous to frequency distributions. Since they show the entire suite of ages, they provide more complete information on the ground-water age regime than a single number such as the mean age. For example, the mean age of the ground water in a portion of an aquifer may be 5,000 years old, yet the age range of the water may be from a few tens of years to 15,000 years. Knowledge of this range, which could be obtained from the age distribution, would be important if one were interested in predicting contaminant travel times. In this section, the conceptual basis for DSC age distribution functions is first presented, followed by a description of the technique actually used to calculate these functions.

Conceptual Considerations

Based on the concepts of fluid elements and modifying the development given in Himmelblau and Bischoff (1968, Ch. 4), Simpson and Duckstein (1976) defined two DSC model distribution functions: a transit number distribution T(N) and an age number distribution A(N), where N is the iteration number. In the context of the population-balance models used in chemical engineering, A(N) can be viewed as the discrete analog of the internal age distribution I(t) of a fluid in a closed vessel; similarly, T(N) can be viewed as the discrete analog of the exit age distribution E(t) of the fluid leaving a closed vessel (Himmelblau and Bischoff, 1968, Ch. 4). The exit age distribution is identical to the distribution of residence times or transit times.

According to Simpson and Duckstein (1976), these two distributions and the concepts embodied in them can be clarified somewhat by assuming that as each fluid element enters the model it automatically displays a positive integer, starting with the number one. This integer increases by one at each iteration and continues to do so as long as the fluid element remains in the model. This integer shall be called the age number of the fluid element. The maximum age number of a given fluid element is that which it has at the interation of its discharge from the DSC model or some subregion thereof. This maximum age number is called the transit number of the fluid element. In other words, each fluid element receives a number, called its age number, which increases by one unit for each iteration of the model, to a maximum value called the transit number, which is the number coinciding with the iteration at which the fluid element is discharged from the model or some subregion. Thus, A(N) describes the distribution of iteration numbers among all fluid elements within a cell or cells at a given iteration, and T(N) describes the distribution of iteration numbers among all fluid elements discharged from the model or some subregion (cell or cells). Both distributions are functions of the iteration number, N.

The previous discussion, while important in providing a conceptual framework for DSC distribution functions, is not very useful for describing how these functions are actually calculated. The actual calculation is accomplished using the impulse-response method (Himmelblau and Bischoff, 1968, Ch. 4), since these distributions can be viewed as the response of a system to an instantaneous input of conservative tracer (Danckwerts, 1953).

Calculation of the Age and Transit Number Distributions

For a continuous-time system, the mean value $\overline{t}$ of the concentration-time curve is given by (Levenspiel, 1972, p. 261):

$$\overline{t} = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt} \qquad (4)$$

The variance can be obtained from:

$$\sigma^2 = \frac{\int_0^\infty (t-\overline{t})^2 C\,dt}{\int_0^\infty C\,dt} = \frac{\int_0^\infty t^2 C\,dt}{\int_0^\infty C\,dt} - \overline{t}^2 \qquad (5)$$

where C = tracer concentration in the system; t = time; and σ^2 = variance of the C vs. t curve.

Since the DSC model operates in discrete time, the discrete analogs of the above equations must be used (Levenspiel, 1972, p. 261):

$$\overline{A} = \frac{\sum_{i=1}^{N} iC(N)_i}{\sum_{i=1}^{N} C(N)_i} \qquad (6)$$

$$\sigma^2 \approx s^2 = \frac{\sum_{i=1}^{N} i^2 C(N)_i}{\sum_{i=1}^{N} C(N)_i} - (\overline{A})^2 \qquad (7)$$

where C(N) = tracer concentration as a function of iteration number N in a cell of a DSC model; $\overline{A}$ = mean of the age number distribution A(N); and s^2 = variance of A(N). Both $\overline{A}$ and s^2 can be converted to real-time units by multiplying them by Δt and $(\Delta t)^2$ respectively, where Δt is the constant time between each iteration.

The actual age number distribution A(N) can be determined by noting that for an instantaneous tracer input at the first iteration, the concentration of tracer in any cell at any subsequent iteration is a measure of the fractional amount of fluid elements of age number N in that particular cell (Simpson and Duckstein, 1976). Thus, C(N) is a measure of A(N).

The transit number distribution T(N) can be determined in a fashion similar to that used to calculate A(N) in the previous section, except that T(N) is computed with respect to the concentration of tracer in the discharging fluid. For a SMC, the BDC at any iteration is identical to the cell concentration at that iteration. Consequently, T(N) is identical to A(N) and $\bar{A} = \bar{T}$.

For a MMC, the BDC at any iteration is equal to the concentration in the cell at the previous iteration. Thus, for a MMC:

$$A(N)_i = T(N)_{i+1} \tag{8}$$

where $A(N)_i$ = value of the age distribution function at iteration i; and $T(N)_{i+1}$ = value of the transit number distribution function at iteration i+1.

For a MMC, as the BRV becomes small relative to VOL, the MMC approaches the perfect mixing of the SMC. Under these conditions, $\bar{A}$ is a good estimate of $\bar{T}$. In a similar manner A(N) will be a good approximation to T(N). Transit number distributions T(N) and $\bar{T}$ are usually calculated only for those cells discharging some or all of their contents outside the model boundaries.

Therefore, to obtain the distribution functions for the cells in a given steady flow DSC model, one must inject an arbitrary nonzero concentration of tracer into the model at the first iteration; tracer concentration is zeroed for all iterations greater than one. Values of $\bar{A}$, A(N), T(N), and $\bar{T}$ can then be calculated from the previous equations. Once A(N) or T(N) is found, it is then easy to determine a cumulative age distribution function F(N). Currently, these distribution functions are defined for steady flow systems only; efforts to define them for transient systems are underway.

APPLICATION OF DSC DISTRIBUTION FUNCTIONS

Tucson Basin DSC Model

The DSC model of a portion of the Tucson Basin alluvial aquifer in Arizona (see Figure 1) will be used as an example of how DSC distribution functions can be generated for an aquifer. The development, construction, calibration, and interpretation of this model were described in detail by Campana and Simpson (1984) and will not be repeated here; a brief summary will be given instead. The model used herein is slightly different from the original one (23 cells versus 26) and was recalibrated, which resulted in slight changes in the mean ages of the water in the cells. The model used the SMC mixing rule, so A(N) and T(N) are equivalent.

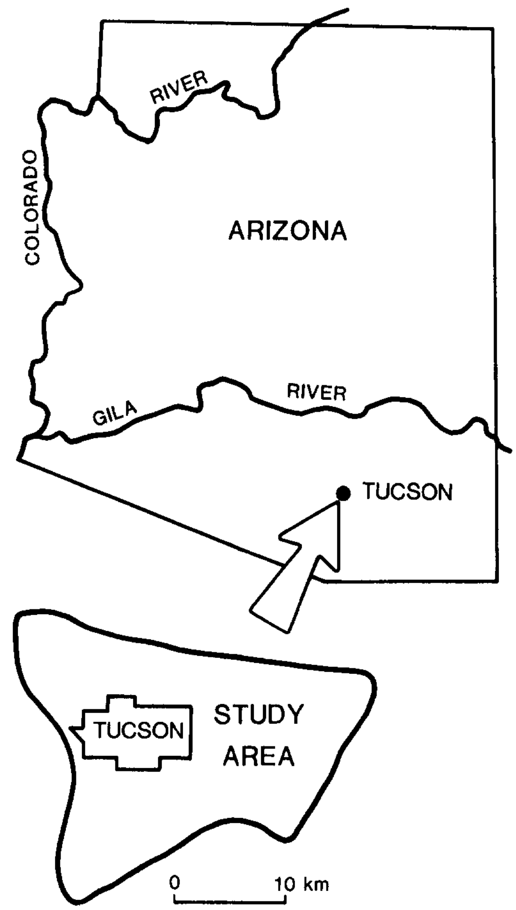

Fig. 1. Location of study area.

The model consisted of a three-dimensional array of cells: a 450-m-thick lower tier of 9 cells (Figure 2) and a 150-m-thick upper tier of 14 cells (Figure 3). The model was calibrated against the observed adjusted carbon-14 decay ages of Wallick (1973); these ages (from the upper tier only) as well as the calculated decay ages and the mean water ages are shown in Tables 1 and 2; note the differences between the mean and decay ages. The mean ages of the ground water in the various cells are also shown in Figures 2 and 3. Table 3 shows the sources, amounts, and carbon-14 concentrations (as percent modern carbon or pmc) of the recharge to the model.

Table 1. Calculated Carbon-14 Decay and Mean Ages for the Lower Tier Cells, Tucson Basin DSC Model

Cell number	*Calculated decay age (yrs)*	*Mean age (yrs)*
1	3,000	3,100
2	3,300	3,400
3	5,800	6,900
4	2,600	2,900
5	2,800	3,200
6	9,700	14,600
11	7,800	8,500
12	10,200	13,300
16	6,000	6,900

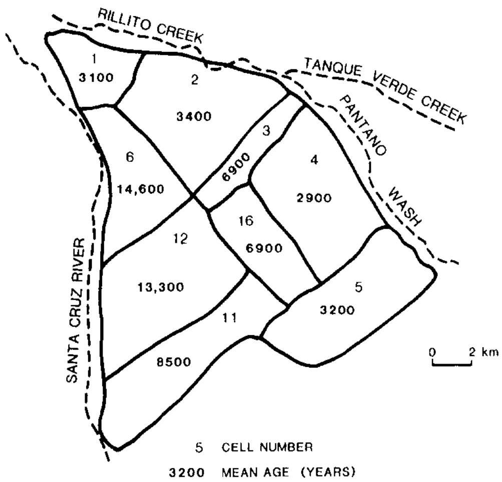

Fig. 2. Lower tier of cells, Tucson Basin DSC model. Mean age of ground water in each cell is also shown.

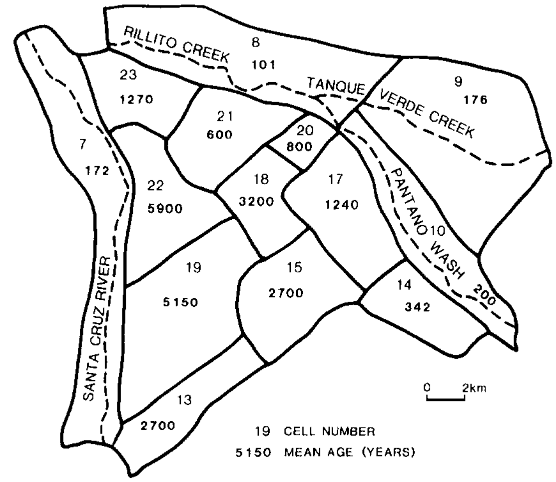

Fig. 3. Upper tier of cells, Tucson Basin DSC model. Mean age of ground water in each cell is also shown.

Table 2. Carbon-14 Decay and Mean Ages for the Upper Tier Cells, Tucson Basin DSC Model

Cell number	*Observed adjusted decay age (yrs)*	*Calculated decay age (yrs)*	*Mean age (yrs)*
7	–	167	172
8	0	100	101
9	–	175	176
10	–	198	200
13	1,902	2,550	2,700
14	166	340	342
15	–	2,300	2,700
17	1,318	1,078	1,240
18	3,106	2,540	3,200
19	3,703; 3,788	3,730	5,150
20	658	660	800
21	0	467	600
22	4,298	4,000	5,900
23	1,895	960	1,270

Ground-Water Age Distributions

Figure 4 shows the age distribution A(N) for cells 7, 8, and 14; Figure 5 shows the cumulative age distribution function F(N) for each of these cells. The age distributions for cells 7 and 8 have the characteristic shapes of those boundary cells that receive "young" recharge water. These kinds of cells have very young waters that have not been well-mixed with other waters. Cell 14, on the other hand, while a boundary cell, receives some water from cell 10, so its percentage of very young water is lower than that in either cells 7 and 8. In addition, cell 14 has a recharge input concentration of 80 pmc instead of 100 pmc as in the cases of the two former cells. Part of the recharge to cell 14 consisted of underflow, which had been in the aquifer for some time and was assigned a nonzero decay age. The cumulative distribution functions

Table 3. Recharge Sources, Average Annual Amounts, and Carbon-14 Concentrations, Tucson Basin DSC Model

Cell number	*Recharge source*	*Average annual recharge (km^3)*	*Carbon-14 concentration (pmc)*
1	Mountain front recharge	0.00062	90
2	Mountain front recharge	0.00111	90
3	Mountain front recharge	0.00003	90
4	Mountain front recharge	0.00012	90
5	Mountain front recharge/underflow	0.00012	90
6	Mountain front recharge	0.00012	90
7	Infiltration from Santa Cruz River/mountain front recharge	0.00863	100
8	Infiltration from Rillito Creek/mountain front recharge	0.01973	100
9	Infiltration from Tanque Verde Creek/mountain front recharge	0.01134	100
10	Infiltration from Pantano Wash/mountain front recharge	0.00617	100
11	Underflow	0.00012	60
12	Mountain front recharge	0.00012	90
13	Underflow/infiltration from Santa Cruz River	0.00006	80
14	Underflow/infiltration from Pantano Wash	0.00003	80
15	Underflow	0.00005	60
	TOTAL	0.04837	

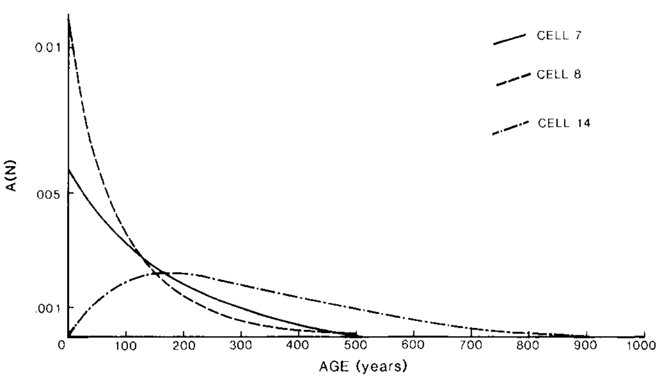

Fig. 4. Age distribution function A(N) for cells 7, 8, and 14.

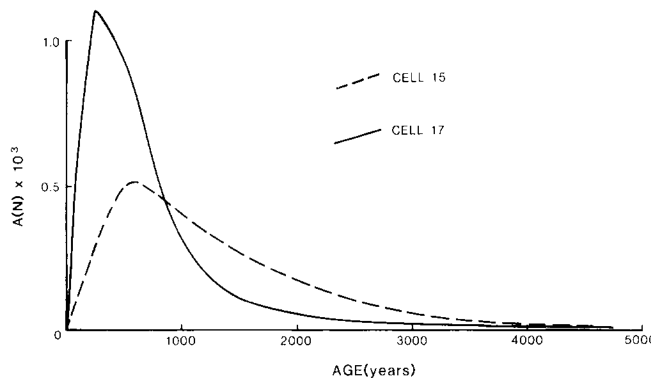

Fig. 6. Age distribution function A(N) for cells 15 and 17.

(Figure 5) illustrate a very important point that must be considered when dating ground waters: the mean age may not be very relevant when it comes to characterizing water ages in a system. Mean ages for these cells were calculated previously and shown in Figure 3 and Table 2. Note that for each cell, the median and mean ages do not coincide, and that the oldest water in each cell is quite a bit older than either the mean or the median age. Since the median age indicates that half the ground water is older and half younger than the median, it is arguably a more representative indicator of age than the mean age. It is also instructive to examine the entire age distribution, A(N) or F(N), since one can immediately see the distribution of ages as well as the discrepancy between the mean and median.

Figure 6 shows A(N) for cells 15 and 17; F(N) for these cells and cell 3 is shown in Figure 7. The comparison of means (see Figure 3 and Table 2) and medians for cells 15 and 17 illustrates even greater disparities than in the aforementioned case. In each of these two cells, the median is approximately half the mean age: 580 versus 1,240 years for cell 17 and 1,350 versus 2,700 years for cell 15. In each case, use of the median to characterize the age of the water in the cell might be better than the mean. As Figure 6 shows, each of these cells has a highly skewed age distribution with the mean falling to the right of the median. The cumulative age distribution for cell 3, a cell from the lower tier of cells, indicates an age distribution without as much skew as those for cells 15 and 17; the median age of 5,500 years is quite close to the mean age of 6,900 years. It is worth noting that each cell in Figure 7 has some water older than 10,000 years. In the cases of cells 15 and 17, only a small percent of the water is this old, while in cell 3, about 25 percent of its water is older than 10,000 years.

The cumulative age distributions for three cells from the lower tier of cells, 2, 12, and 16, are shown in Figure 8. Cell 12, with the second oldest mean age (13,300 years) in the entire system, has a median age (11,500 years) reasonably close to its mean. Note that the oldest water in this portion of the aquifer is about 40,000 years old. Cell 16 has a mean age (6,900 years) in the vicinity of its median age (5,700 years); it also has a small amount of old water on the order of 20,000 years old. In cell 2, the agreement between the mean (3,400 years) and median (2,000 years) ages is not quite as good. The age distribution for cell 2 is similar to those for cells 15 and 17 in that it is highly skewed to the right (positively skewed) with the mean to the right of the median. In the case of cell 2, the mean

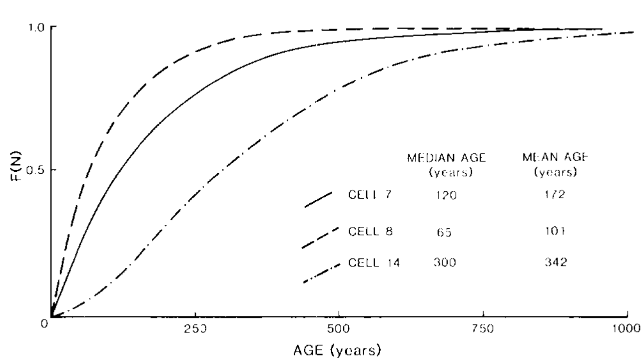

Fig. 5. Cumulative age distribution function F(N) for cells 7, 8, and 14.

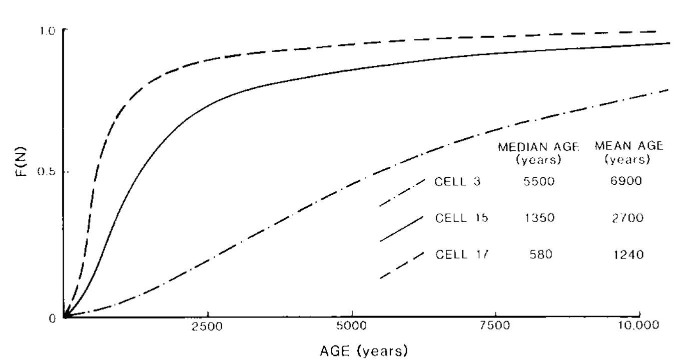

Fig. 7. Cumulative age distribution function F(N) for cells 3, 15, and 17.

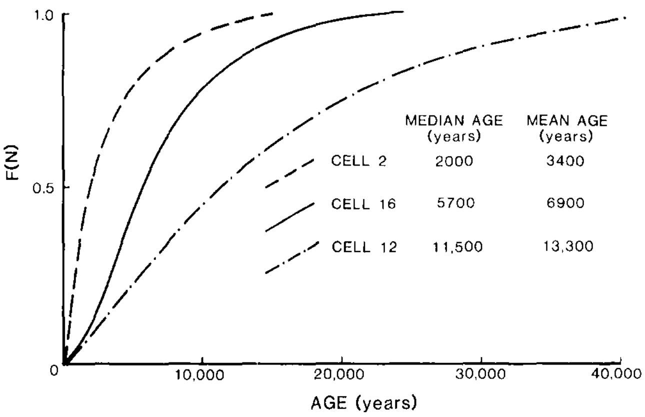

Fig. 8. Cumulative age distribution function F (N) for cells 2, 12, and 16.

age would not be a good parameter by which to characterize the age distribution in this portion of the aquifer.

The reader will have noted by now that each of the nine cells discussed in this section has a component of very young water, i.e., on the order of a few years old. The percentage of this extremely young water varies from cell to cell, but it can be found in each cell of the model. Very young water in a boundary cell with a recharge concentration of 100 pmc (e.g., cells 7 through 10) is not troublesome; however, its presence may be somewhat disturbing in other cells, particularly those with mean or median ages on the order of thousands of years. The physically unrealistic presence of this young water is simply an artifact of the model. When the DSC model is operated, by the end of the second iteration each cell in the model will have some amount of young water and associated tracer in it, albeit small. However, this unrealistic behavior is mitigated somewhat by the fact that it may take many iterations before the tracer reaches physically measurable amounts.

Significance and Applications

Generation of ground-water age distributions is more than an academic exercise; these distributions can be useful in hydrogeologic investigations, especially those in which mixing is an important consideration. Aquifer regions with high degrees of mixing will contain waters of many different ages; this will be reflected in the A(N) function, which will have a relatively large "spread" or variance. In Figure 4, cell 14 illustrates this; the waters of this cell are the best mixed of the three shown. The cumulative age distribution F(N) also shows the differences in mixing (Figure 5). Figures 7 and 8 show the differences in mixing among six cells. In Figure 7, cell 3 is the best mixed; its F(N) rises more gradually than those of the other two, indicating good representation of waters from a variety of ages. Cell 17's cumulative distribution function rises rapidly, and although it has water as old as 10,000 years, about 75% of its water is less than about 1,200 years old. In Figure 8, cell 12 is the best mixed while cell 2 is the worst mixed. These inferences on mixing, albeit semiquantitative at this stage, are not apparent from the mean or median ages; the entire distribution is necessary. The distributions also provide information on the range in ground-water ages in an aquifer.

This information on mixing and age distributions can be important in a number of studies. In keeping with today's concern about ground-water contamination, knowledge of mixing in an aquifer is very important, and age distributions can be useful in this regard. For example, suppose someone wanted to dispose of a hazardous substance that requires 5,000 years of isolation before it is rendered harmless. Further suppose that the cumulative age distribution in a portion of the aquifer downgradient from the disposal site is identical to that of cell 3 in Figure 7 and that the disposal site is in the vicinity of the recharge area for the portion of the aquifer. If the only age information available in this portion of the aquifer were the mean age (6,900 years), it would be tempting to say that there is little danger of contamination in this area, since the water here is older than the amount of time it takes the substance to become innocuous. Should any of the substance leak into the aquifer beneath the disposal site, it will be harmless by the time it reaches the region in question. However, F(N) tells us otherwise: about 15% of the water is less than 2,500 years old, and a little over 40% is less than 5,000 years old! Clearly, the risk of contamination exists here. This example is simple, but it serves to illustrate the usefulness of ground-water age distributions and the danger in relying on mean ages. In a related vein, one could use age distributions to locate aquifer regions in which most of the water is very old. This information could be useful in waste isolation studies.

Aside from contamination studies, age distributions may be of use in recharge studies, particularly those studies aimed at delineating which areas provide the highest percentage of ground-water recharge to a particular aquifer region. Paleohydrologic studies could also be aided, since the distribution functions describe the range in ages and the fractions of each age present. It is obvious that some regions of the Tucson Basin received recharge during the pluvial periods a few tens of thousands of years ago; cells 3 and 12 fall into this category. This information on past recharge regimes may be of use in predicting future ones. The paleohydrologic implications of these functions and DSC models in general are speculative at this point; a great deal more research is required.

CONCLUSIONS

The research results illustrate that carbon-14 decay ages, whether "raw" or adjusted, must be used with caution when attempting to characterize ground-water ages. Unless one can justify the assumption of no mixing, carbon-14 (or any other environmental radioisotope) ground-water decay ages can be related to actual ground-water ages only with a specific flow/mixing model. The model used can be analytical or numerical, simple or complex. The necessity of using an interpretive flow/mixing model is often overlooked in hydrogeologic studies involving environmental radioisotopes.

In addition, even if one can obtain the mean age of the ground water in an aquifer or some subregion thereof, it may not be representative of the age of the water in that area. The mean age of ground water in some portion of an aquifer may be a few hundred years old, yet because of mixing, that same region may have some water that is thousands of years old. Conversely, very old ground water may also have a very young component. In the Tucson Basin aquifer, ground-water mean ages range from about 100 years to almost 15,000 years old, yet in some portions of the aquifer, 40,000 years-old ground waters exist. Thus, the best information is not simply the mean or median age of the ground water but the entire age distribution.

Discrete-state compartment models, in addition to serving as interpretive flow/mixing models that make few restrictive *a priori* mixing assumptions, can generate ground-water age distributions. A major limitation is that the age distribution functions are well-defined for steady flow systems only; extensions to transient systems are under investigation. Despite this limitation, the approach described herein represents an additional step in the quantitative interpretation of environmental radioisotope data. It also is a further step in the direction of integrating ground-water flow modeling and environmental isotope hydrogeology.

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