

THE EFFECTS OF DISPERSION AND MIXING ON
RADIONUCLIDE DATING OF GROUNDWATER

by

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ABSTRACT

In general, the decay age of a water sample and the average age or transit time of the sample are the same only in the case of zero mixing or piston flow. A unified discussion of the theoretical distributions of ages and transit times in hydrologic systems is presented, focusing on transit time distributions for piston flow, exponential, dispersive and mixing cell models. Distributions of two component systems and the errors caused by not considering a two component mixture in radionuclide dating are also considered.

After outlining the mathematical treatment of multiple tracer data, these concepts are employed along with computer models to examine hydrochemical data from the Bunter aquifer in England. This analysis indicates the importance of model selection to the interpretation of radionuclide data.

CHAPTER 1

INTRODUCTION

1.1 The "Age" of Groundwater

The "age" of groundwater can be defined as the length of time the water has been isolated from the atmosphere. This conceptually simple definition, however, obscures the extremely complex nature of groundwater flow (Davis and Bentley, 1982). In an aquifer, flow takes place through a complex network of interconnected pores or openings; it is virtually impossible to describe in an exact mathematical manner the complicated geometry of the solid surfaces that bound the flowing fluid. Hydrologists are therefore forced to overlook the microscopic flow patterns inside individual pores, and to consider instead some fictitious average velocity in the porous medium--the so-called "continuum approach" (Bear, 1979, p. 28). The spatial variability of these microscopic flow patterns, as well as gross changes in local flow directions caused by non-uniformities in hydraulic conductivities (Smith and Schwarz, 1980) and, to a lesser extent, molecular diffusion due to the thermal-kinetic energy of the solute molecules (Freeze and Cherry, 1979, p. 75) are responsible for large-scale hydrodynamic dispersion or megadispersion.

An obvious consequence of this mixing of water as it flows through porous media is that any finite sample of water from an aquifer will contain molecules of different "ages". Some fluid elements will

have traveled faster than the average velocity and some slower than the average velocity. Rather than being able to associate an "age" with the sample, we are confronted with the problem of identifying a distribution of ages.

Identification of this distribution of ages may be difficult because most groundwater is taken from wells which tap two or more water-bearing zones which may be separated by semipervious layers or aquitards. Even if hydrodynamic dispersion in the aquifers is small or nonexistent (the case of "piston flow"), the sampled water will still be a mixture of waters of different ages (Davis and Bentley, 1982). In addition to mixing of different waters in the sampling well, leakage between two different aquifers separated by an aquitard (Fontes, 1980), or diffusion of solutes through the aquitard (Matthess, Münnich, and Sonntag, 1976) may occur and further complicate the picture. Natural springs, for example, are commonly connected to various water-bearing zones so that samples of spring water may represent mixtures of waters of vastly different ages (Davis and Bentley, 1982).

The cases of dispersion and mixing described above can, in theory, be described by the deterministic partial differential groundwater flow equation and the advection-dispersion equation. For many idealized systems with simple boundary conditions, analytical solutions are available (Carslow and Jaeger, 1959, and Ogata and Banks, 1961). However, when one considers a real aquifer as opposed to a conceptual aquifer, a numerical rather than an analytical method must be used to solve the governing equation (Neuman, 1983). Much literature has been

devoted to the continued evolution of sophisticated numerical techniques of solution. Unfortunately, because the detailed hydrogeologic conditions of an aquifer are difficult to define accurately, purely hydrodynamic methods of age estimation are subject to large uncertainties (Davis and Bentley, 1982).

On the other hand, much can be inferred about an aquifer system from the distribution of environmental tracers, which are mostly naturally occurring solutes, in the system. In 1957, Münnich first proposed a method to obtain and use the corrected age of radioactive carbon-14 (^{14}C) to estimate the residence time of water in an aquifer (Campana, 1975). Since that time, much work has been done using radionuclides of atmospheric origin to estimate groundwater ages and flow rates independently of knowledge of the detailed hydraulics of the system. Radiometric ages can be determined from the well-known radioactive decay equation

$$C = C_0 e^{-\lambda t} \quad (1)$$

where

C = measured activity or concentration

C_0 = initial activity or concentration

λ = decay constant

t = transit time.

The measured activities can be viewed as the weighted averages of the respective contributions of many elementary flows, each with its own isotope content (Fontes, 1980). Interpretation of radionuclide data

must, of course, be based on an assumed model of transport and mixing in the aquifer (Gupta and Lal, 1978). For example, in order to correlate radiometric ages with calendar ages, one frequently assumes that dispersion is restricted to recharge episodes corresponding to short periods of time compared with the transit times of the system (Fontes, 1980), or, more simply, piston flow. Another popular model is the so-called well mixed reservoir, where the system is assumed to be uniformly mixed. This is also known as the exponential model, because the distribution of transit times in such a model is exponential (Geyh, 1970). Clearly, an incorrect choice of assumed transport and mixing model may lead to erroneous interpretations of the data.

1.2 Objectives of the Thesis

This thesis will attempt to address the problem of evaluating the effects of dispersion and mixing on groundwater dating. Much work has been done on the treatment of residence time and transit time distributions in the field of chemical engineering (Danckwerts, 1953, and Himmelblau and Bischoff, 1968, Chapter 4). Nir and Lewis (1975) used similar concepts and the work of Eriksson (1958, 1971), Nir (1964), and Bolin and Rodhe (1973) to present some theoretical discussions of tracer applications to evaluating transit times in hydrologic systems. Making use of this body of literature, this thesis will first present a unified discussion of various theoretical distributions of ages and transit times. Building on this discussion, I will review some previous suggestions of models for interpretation of radiometric information and compare the results of different model selections. Finally, I will outline

the use of multiple environmental tracers and independent age and mixing information in the solution of several simple models; these models will be applied to a "real world" situation.

CHAPTER 2

THEORY OF AGE AND TRANSIT TIME DISTRIBUTION FUNCTIONS

2.1 Transit Time Distribution Functions

As I have said, in general, a quantity of tracer entering an aquifer at a given time will not leave the system simultaneously. The time a fluid element spends in the system, from input to exit, is called the transit time or residence time of that fluid element. One may consider a probability density function, $E(t)$, of the transit times of the out-going flux. We may restrict the discussion to the steady-state case if the volume or mass of fluid elements in the reservoir is constant with time and the rate of inflow and outflow is also constant. If the basic characteristics of the reservoir are constant with time, $E(t)$ is also and we consider the system a stationary state (Eriksson, 1971).

The transit time distribution function may be defined as a normalized probability density function, so that

$$\int_0^{\infty} E(t) dt = 1. \quad (2a)$$

The fraction of fluid leaving the reservoir (or at the sampling point) that is younger than age t is

$$\int_0^t E(t') dt' \quad (2b)$$

This observed spread of transit times may be viewed, from the perspective of the chemical engineer, as the response of a lumped system to an instantaneous (Dirac delta function, δ) input of conservative tracer (Danckwerts, 1953). We can also look at $E(t)$ as a weighting function describing the relative contributions of different inflows at times $(t-\tau)$ to the present outflow at time t . As Nir and Lewis (1975) pointed out, the action of this weighting function can be described by the convolution integral

$$Q(t) = \int_0^t Q_i(t-\tau) E(\tau) d\tau \quad (3)$$

where

$Q(t)$ = flow rate out of the system

$Q_i(t)$ = flow rate into the system

We can define a cumulative distribution function, $F(t)$, describing the distribution of the outgoing flux, Q , with respect to the time spent in the reservoir, t , such that $F(t)$ is the amount of exiting fluid with transit times less than or equal to t . From the definition of $E(t)$ as probability density, this distribution is given by Nir and Lewis (1975) as

$$F(t) = Q \int_0^t E(t') dt' \quad (4a)$$

where

Q = the steady state flux through the system, or in the terms of equation (3), $Q(t) = Q_i(t-\tau) = Q = \text{constant}$.

Alternatively, we may write

$$E(t) = \frac{1}{Q} \frac{dF(t)}{dt} \quad (4b)$$

Note that $\lim_{t \rightarrow \infty} F(t) = Q$. The relationship between $F(t)$ and $E(t)$ is illustrated in Figure 1.

In analogy to $E(t)$ and $F(t)$, which relate to the flow rate, we can define the probability density function, $\phi(t)$, and the corresponding cumulative distribution function, $M(t)$, which relate transit times to the total volume of fluid in the system. Here we assume that each fluid element entering the system has a constant transit time, t , associated with it, even though we may not know its value (Nir and Lewis, 1975). The fraction of material in the system having transit times between t and $t + dt$ is by definition $\phi(t) dt$. Because of how we have defined the distributions, we may write

$$\phi(t) dt = \frac{dM(t)}{V} = \frac{t}{V} \frac{dF(t)}{dt} dt = \frac{tQ}{V} E(t) dt \quad (5a)$$

where

V = total volume of pore space in the system.

As Nir and Lewis (1975) showed, formally integrating the incoming part of the flux with transit time between t and $t + dt$, $dF(t) = Q E(t) dt$, over the whole range of residence in the system (the age range 0 to t) gives

$$dM(t) = \int_0^t dF(t) dT = t dF(t) = tQ E(t) dt \quad (5b)$$

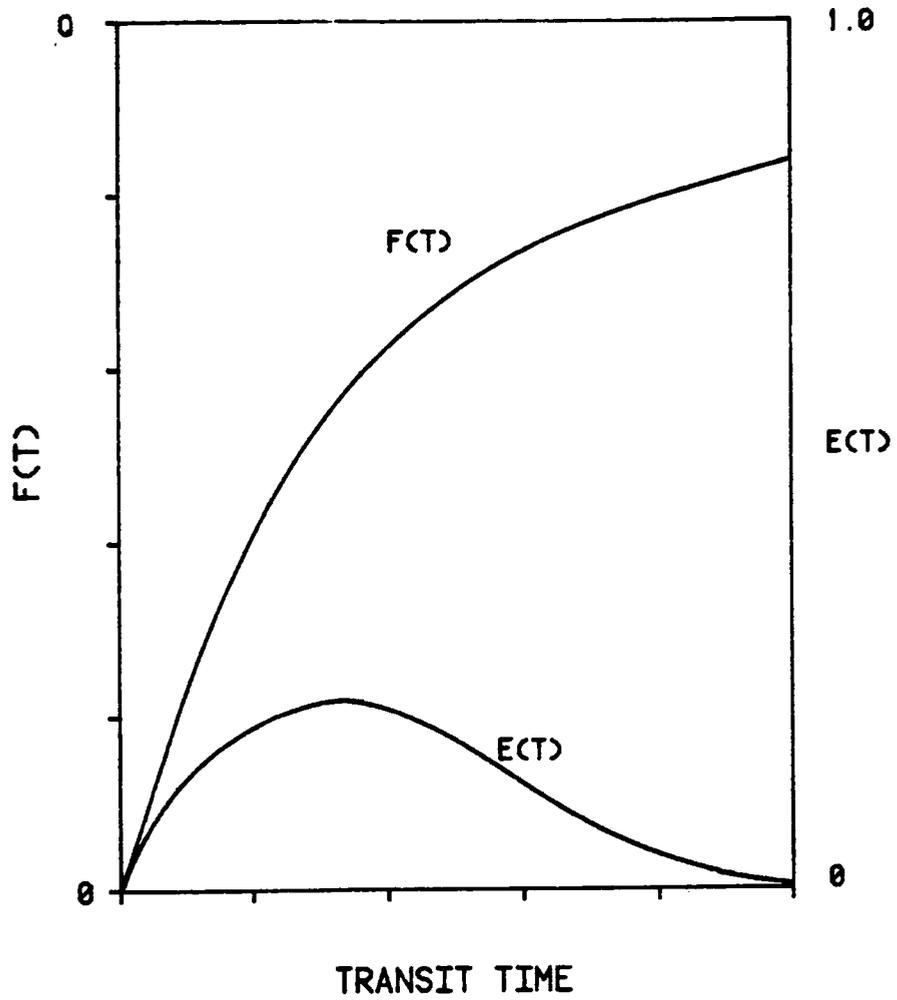


Figure 1. Schematic representation of transit time density, $E(t)$, and cumulative, $F(t)$, functions.

where

T = "age" in the system as opposed to transit time, t , which is the "age" of the exiting fluid elements.

This is equivalent to equation (5a) and indicates that those parts of the flux having longer transit times occupy parts of the system in direct proportion to these times. Integration of equation (5b) gives $M(t)$, the volume of all fluid elements having transit times less than t

$$M(t) = Q \int_0^t t' E(t') dt' \quad (5c)$$

The total volume, V , is given by

$$V = \lim_{t \rightarrow \infty} M(t) = Q \int_0^{\infty} t E(t) dt = Q \bar{t}_E \quad (6a)$$

where

\bar{t}_E = mean transit time of the flux.

The ratio V/Q is defined as the turnover time of the system. Therefore, the mean transit time in steady state systems, without making any specific assumptions about the mixing pattern or time distributions, equals the turnover time (Nir and Lewis, 1975):

$$\bar{t}_E = V/Q \quad (6b)$$

2.2 Age Distribution Functions

We can also define a probability density function, $I(T)$, and a cumulative distribution, $M(T)$, which relate the fluid elements in the system to T , the age of the fluid elements in the system (i.e., the time

that has elapsed since a fluid element entered the system). Danckwerts (1953) originally described $I(T)$ as the internal age distribution.

Because we require that

$$\int_0^{\infty} I(T) dT = 1 \quad (7a)$$

it follows that (Bolin and Rodhe, 1973)

$$I(T) = \frac{1}{V} \frac{dM(T)}{dT} \quad (7b)$$

or equivalently,

$$M(T) = V \int_0^T I(T') dT' \quad (7c)$$

where

$M(T)$ = the volume of fluid elements in the system of age T or younger.

Nir and Lewis (1975) noted that after an elapsed time T , all the molecules in the system having transit times t less than T have left the system. This amount is $F(T)$ according to equation (4a). The amount of material with ages between T and $T + dT$ is therefore $(F(\infty) - F(T)) dT$, and

$$I(T) dT = \frac{1}{V} (F(\infty) - F(T)) dT \quad (7d)$$

Since $F(\infty) = Q$,

$$I(T) = \frac{Q}{V} \left[1 - \int_0^T E(t) dt \right] = \frac{Q}{V} \int_T^{\infty} E(t) dt \quad (7e)$$

2.3 Mean Transit Times and Ages

We have already seen in equation (6b) that the mean flux transit time is given by

$$\bar{t}_E = \int_0^{\infty} t E(t) dt = V/Q \quad (8a)$$

We can calculate (Nir and Lewis, 1975) the average volumetric transit time, \bar{t}_ϕ , using the volumetric transit time density, $\phi(t)$

$$\bar{t}_\phi = \int_0^{\infty} t \phi(t) dt = \int_0^{\infty} t^2 \frac{Q}{V} E(t) dt \quad (8b)$$

The average age of the matter in the system can be found in a similar way. Using the age density, $I(T)$, from equation (7e) we have

$$\bar{T}_I = \frac{Q}{V} \int_0^{\infty} T dT \int_T^{\infty} E(t) dt \quad (9a)$$

Nir and Lewis (1975) have shown that for steady state,

$$\bar{T}_I = \frac{1}{2} \bar{t}_\phi \quad (9b)$$

2.4 Variance of Transit Times

The variance of the transit time of the flux is a parameter of interest. It can be found directly if we know the first and second moments of the transit time distribution

$$(\sigma_E)^2 = m_2^E - (m_1^E)^2 \quad (10)$$

where

$(\sigma_E)^2$ = the variance of transit times

m_2^E = the second moment of the $E(t)$ distribution = $\int_0^{\infty} t^2 E(t) dt$

m_1^E = the first moment of the $E(t)$ distribution = $\int_0^{\infty} t E(t) dt = \bar{t}_E$.

2.5 The Population Analogy

Before attempting to proceed with applications of these concepts, we can illustrate them by considering some similar concepts used in the discussion of biological populations. Similar analogies have appeared in the literature, for example, Eriksson (1971), Nir and Lewis (1975), and Himmelblau and Bischoff (1968, Chapter 4).

The transit time is equivalent to lifespan. Age in the system corresponds with the common usage of the word. $F(t)$ corresponds to the cumulative distribution by age of the dying group. In steady state, Q represents the equal birth and death rates. V is the total population. $E(t)$ represents the frequency distribution of lifetimes. $M(t)$ and $M(T)$ are the cumulative distributions with respect to lifetime, t , and age, T . The average lifetime is equivalent to \bar{t}_ϕ and \bar{T} is the average age of the living population. Note that $M(T)$ has a physical meaning in that it can be measured in a biological population, while $M(t)$ only has meaning in a statistical sense in a stationary system; one cannot determine the lifespan "assigned" to each individual in the population. However, certain geophysical systems have recognizable and definite streamtubes

with assigned transit times and negligible mixing among them (Nir and Lewis, 1975).

2.6 Relationship Between Internal Age Distributions and Transit Times

The flux transit time density, $E(t)$, and the volumetric cumulative distribution, $M(T)$, described above can be related through an unsteady-state macroscopic age population balance expressing the continuity of ages of the fluid elements. A simpler, though less general relationship is derived below, modified from Himmelblau and Bischoff (1968, p. 62).

If we consider again a reservoir with constant volume, V , and constant flow rate, Q , and call all the fluid entering the reservoir at $t > 0$ "new" fluid, M_{new} , we can write

$$M_{\text{new}} = V \int_0^t M(t') dt' \quad (11a)$$

The amount of "old" fluid that has left the aquifer during all times from 0 to t , M_{old} , is

$$M_{\text{old}} = \int_0^t Q dt' \int_{t'}^{\infty} E(t'') dt'' \quad (11b)$$

Equating the amount of "old" fluid which has left with the "new" fluid which replaced it, we have

$$V \int_0^t M(t') dt' = Q \int_0^t dt' \int_{t'}^{\infty} E(t'') dt'' \quad (11c)$$

Noting that $\bar{t} = V/Q$ and differentiating equation (11c) gives

$$\bar{t} M(t) = \int_t^{\infty} E(t') dt' = 1 - \int_0^t E(t') dt' \quad (11d)$$

Differentiating again gives

$$E(t) = -\bar{t} \frac{d}{dt} M(t) \quad (11e)$$

2.7 The Tracer Integral Equation

If we neglect for the moment tracer loss and decay, conservation of matter allows us to modify equation (3) and write (Nir and Lewis, 1975)

$$Q(t)C(t) = \int_0^{\infty} Q_i(t-\tau) C_i(t-\tau) E(\tau) d\tau \quad (12a)$$

where

$C(t)$ = concentration of tracer in outflow

$C_i(t-\tau)$ = concentration of tracer in the inflow at time $(t-\tau)$

τ = transit times.

The steady state assumption allows us to write

$$C(t) = \int_0^{\infty} C_0(t-\tau) E(\tau) d\tau \quad (12b)$$

or in discrete form

$$C(t) = \sum_{\tau=0}^{\infty} C_{t-\tau} E_{\tau}, \quad t, \tau = 0, 1, 2, \dots \quad (12c)$$

This discrete form was applied by Eriksson (1973) and Gat (1970) to river and lake systems. It can be solved with respect to E_{τ} by standard numerical or analytical deconvolution techniques.

By expressing input concentration as an instantaneous impulse function--a Dirac delta function, we obtain from equation (12a) and the properties of a Dirac delta function (Nir and Lewis, 1975)

$$C(t) = \int_0^{\infty} \delta(t-\tau) E(\tau) d\tau = E(t) \quad (12d)$$

which shows that the system response to an impulse function is identical to the weighting function or the transit time density function in steady state systems (Danckwerts, 1953).

2.8 Examples of Transit Time Distributions

2.8.1 The Completely Mixed Model

Perfect mixing assumes that the reservoir contents are perfectly homogeneous and therefore have the same composition as the exit stream. This system has been regarded as a fair description of not too deep surface water bodies (Kaufman and Libby, 1954), but is usually only useful as a limiting case for groundwater aquifers (Nir, 1964) or where the reservoir or "mixing cell" is sufficiently small.

A mass balance equation for a steady state flow rate, Q , into and out of a perfectly mixed reservoir is

$$QC_0 = QC + V \frac{dC}{dt} \quad (13a)$$

where

C_0 = concentration of inflowing tracer

C = concentration of tracer in the reservoir = concentration of tracer in the exit stream

V = volume of the reservoir.

If we recall from equation (8a) that the mean transit time, $\bar{t} = V/Q$, we may write

$$\bar{t} \frac{dC}{dt} + C = C_0 \quad (13b)$$

For the initial condition, $C(t=0) = 0$, the solution of equation (13b) is

$$\frac{C}{C_0} = 1 - \exp(-t/\bar{t}) \quad (13c)$$

We note that for a constant step function input with concentration C_0 equation (12b) simplifies to

$$\frac{C(t)}{C_0} = \int_0^{\infty} E(t') dt' \quad (13d)$$

By substituting equation (4e) into the above, we have

$$F(t) = Q \frac{C(t)}{C_0} = Q(1 - e^{-t/\bar{t}}) \quad (13e)$$

so

$$E(t) = \frac{1}{Q} \frac{dF(t)}{dt} = \frac{1}{\bar{t}} e^{-(t/\bar{t})} \quad (13f)$$

Since the fluid within the perfectly mixed reservoir has the same composition as the exiting fluid, the internal age distribution, $M(T)$ is identical to $E(t)$, and in this case the average age of fluid elements in the system, the average transit time of the fluid elements exiting the reservoir and the turnover rate are identical.

If we are interested in the concentration of a radioactive tracer, we modify the weighting function in the tracer integral equation (12b) from $E(t)$ to $E(t)e^{-\lambda t}$ (Nir and Lewis, 1975), which gives

$$C(t) = \int_0^{\infty} C_0(t-\tau) \frac{1}{\bar{t}} e^{-t/\bar{t}} e^{-\lambda t} dt \quad (13g)$$

For constant C_0 we have

$$\frac{C(t)}{C_0} = \int_0^{\infty} \frac{1}{\bar{t}} e^{-(1/\bar{t}+\lambda)t} dt = \frac{1/\bar{t}}{1/\bar{t}+\lambda} = \frac{1}{1+\lambda\bar{t}} \quad (13h)$$

Eriksson (1958) may have been the first to suggest an exponential distribution of arrival times of salt and water draining through a soil whose hydraulic conductivity decreases with depth (Raats, 1978). The well mixed or exponential model has been used in several theoretical discussions (Eriksson, 1971; Nir, 1964; Bolin and Rodhe, 1973; Nir and Lewis, 1975). This model has also been used in attempts to fit experimental data (Eriksson, 1963; Geyh, 1970; Peck and Hurlé, 1973).

Raats (1978) has pointed out that some systems behave as "apparently well mixed" systems. Consider the saturated porous medium in Figure 2. The flow inside the isotropic homogeneous region, neglecting dispersion, is governed by the Laplace equation. The potential

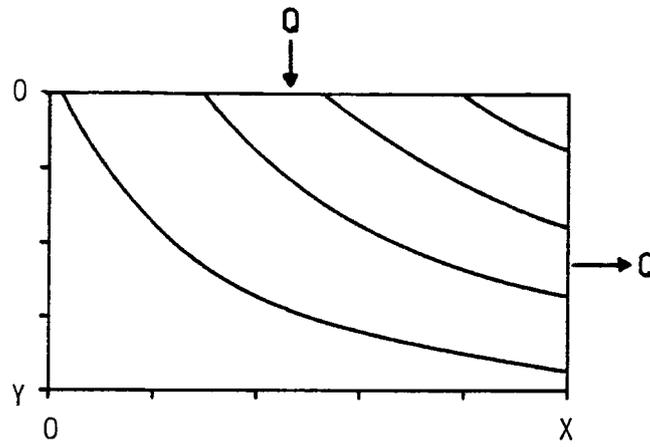


Figure 2. Two dimensional flow with uniform and constant inflow and outflow (After Raats, 1978).

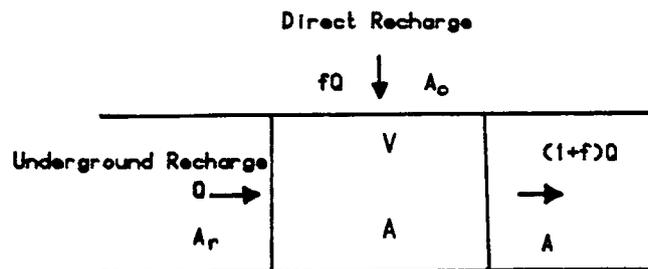


Figure 3. Two components of recharge to a mixing cell (After Gupta and Lal, 1978).

function satisfying the Laplace equation and the boundary conditions is (Raats, 1978)

$$\phi = (2\bar{t})^{-1}[(Y-y)^2 - x^2] \quad (14a)$$

The stream function is

$$\psi = \bar{t}^{-1}x(Y-y) \quad (14b)$$

where

$$\bar{t} = \text{the turnover time} = V/Q.$$

The streamlines are hyperbolas with asymptotes at the y-axis and the line $y = Y$. The components of the velocity field are given by

$$v_x = \left. \frac{\partial x}{\partial t} \right|_x = - \frac{\partial \phi}{\partial x} = - \frac{\partial \psi}{\partial y} = x/\bar{t} \quad (14c)$$

$$v_y = \left. \frac{\partial y}{\partial t} \right|_y = - \frac{\partial \phi}{\partial y} = \frac{\partial \psi}{\partial x} = (Y-y)/\bar{t}$$

Integration of equations (14c) gives

$$x = x_0 \exp[(t-t_0)/\bar{t}] \quad (14d)$$

$$y = Y - (Y-y_0) \exp[-(t-t_0)/\bar{t}]$$

where

(x,y) = coordinates of a particle at time t whose coordinates at time t_0 were (x_0,y_0) .

If we set $t_0 = 0$, and $x = X$, t is the transit time for a parcel introduced into the system at $x = x_0$.

$$t = \bar{t} \ln(X/x_0) \quad (14e)$$

Since parcels introduced near $x = X$ are the first to appear in the output, the cumulative transit time distribution, $F(t)$, is given by (Raats, 1978)

$$F(t) = Q[1 - \exp(-t/\bar{t})] \quad (14f)$$

Differentiation with respect to t gives the transit time density distribution

$$E(t) = \bar{t}^{-1} \exp(-t/\bar{t}) \quad (14g)$$

This is identical to equation (13f), the transit time density of a well mixed system, although based on piston displacement along streamlines.

Gupta and Lal (1978) considered a modified well mixed system in which the mixing cell receives a component of relatively young groundwater by leakage through semiconfining layers in addition to an "old" component. This model is shown in Figure 3. The steady state equation for a well mixed reservoir with mean flushing time, \bar{t} was given by Gupta and Lal (1978) as

$$QA_r + fQA_0 = VA + (1+f)QA \quad (15a)$$

or

$$\frac{A}{A_0} = \frac{f + (A_r/A_0)}{(1+f)(1+\lambda\bar{t})} \quad (15b)$$

where

λ = decay constant of tracer

A_0 = activity of tracer in direct recharge

A_r = activity of tracer in underground flow recharge

Q = underground flow rate

f = fractional amount of direct recharge

A = measured activity of tracer

t = turnover time of mixing cell = $\frac{V}{(1+f)Q}$.

For the extreme case where $A_r \cong A_0$,

$$\frac{A}{A_0} = \frac{1}{1+\lambda t} \quad (15c)$$

In this simplest case, the apparent age, as derived from equation (1), will agree with the true turnover time only when $\lambda t < 1$, because in this case

$$\frac{A}{A_0} = \frac{1}{1+\lambda t} \cong e^{-\lambda t} \quad (15d)$$

However, when $\lambda t > 1$, the apparent age departs from the turnover time, as shown in Figure 4. This departure is greater for shorter lived isotopes since their decay constant is greater than longer-lived isotopes.

For the case where the activity of the "old" component is much less than the direct recharge component, the other extreme, we have

$$\frac{A}{A_0} \cong \frac{f}{(1+f)(1+\lambda t)} \cong \frac{1}{1+\lambda t} \quad (15e)$$

So the system attains a steady state value of tracer concentration which is lower by a factor f than the first case; the apparent ages would be

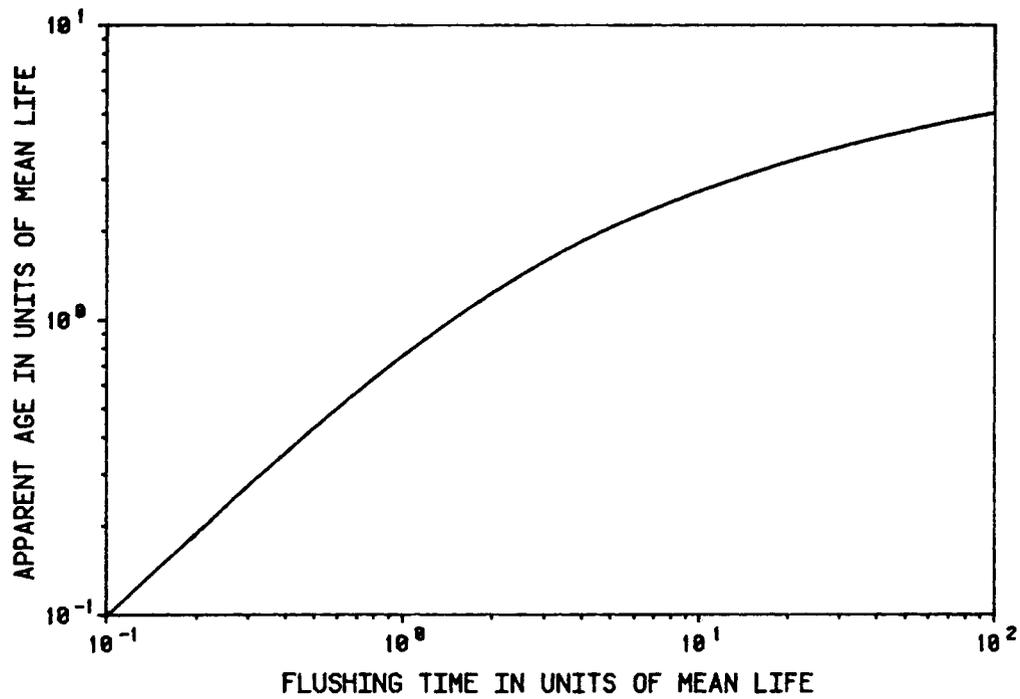


Figure 4. Relationship between true turnover time and apparent radiometric age of a mixing cell where $A_r = A_0$ (After Gupta and Lal, 1978).

larger and in some cases close to the true turnover time (see Figure 5). The authors also pointed out that the uncertain parameter f can be determined if two radionuclides are used. The steady state ratio of the concentrations of two such nuclides, say carbon-14 and silicon-32, would be

$$\frac{A^{14}\text{C}/A_0^{14}\text{C}}{A^{32}\text{Si}/A_0^{32}\text{Si}} = \frac{1 + \lambda^{32}\text{Si}_t}{1 + \lambda^{14}\text{C}_t} \quad (15f)$$

which is independent of f .

2.8.2 The Piston Flow Model

In piston flow, all fluid elements pass through the reservoir without any mixing. The transit time distribution, $E(t)$, can be represented by a Dirac delta function of the form:

$$E(t) = \delta(t-t_0) \quad (16a)$$

where

t_0 = the delay between input and output.

The cumulative transit time distribution, $F(t)$, is given by:

$$F(t) = Q \int_0^t \delta(t'-t_0) dt' = Q u(t-t_0) \quad (16b)$$

where

$$u(t-t_0) = \begin{cases} 0, & t < t_0 \\ 1, & t \geq t_0 \end{cases}$$

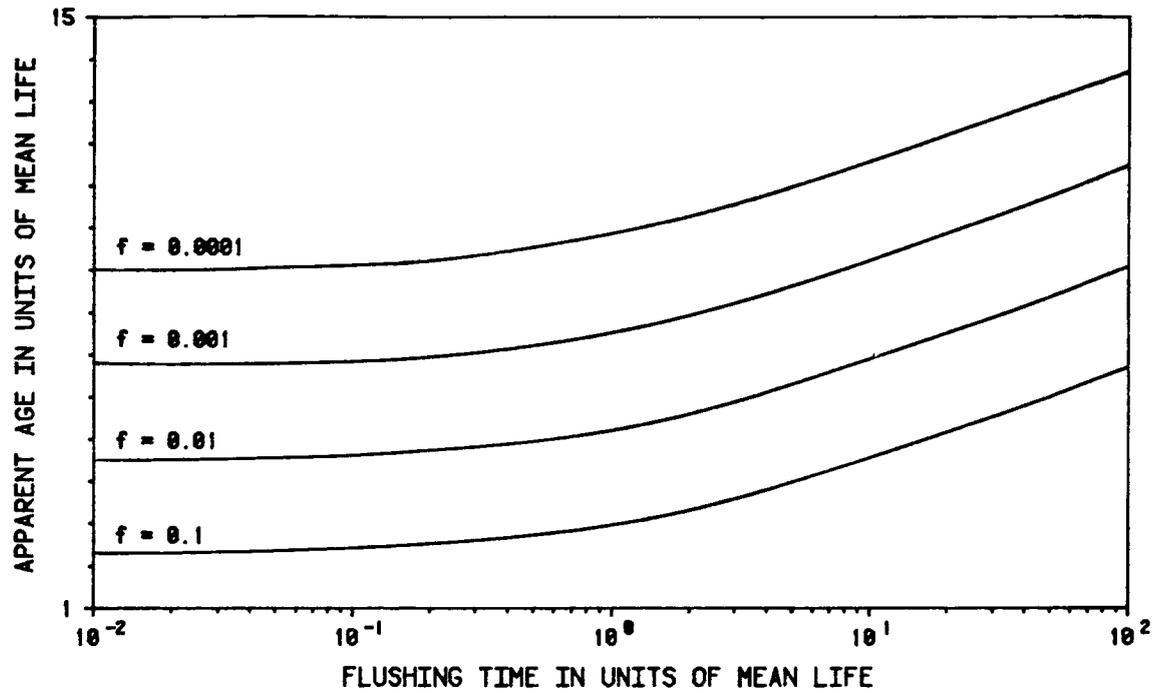


Figure 5. Relationship between true turnover time and apparent radio-metric age of a mixing cell where $A_r \ll A_0$, for various values of the relative quantity of direct recharge, f (After Gupta and Lal, 1978).

The mean transit time is:

$$\bar{t}_E = \int_0^{\infty} t \delta(t-t_0) dt = t_0 = Q/V \quad (16c)$$

And the average age of the fluid elements in the reservoir is:

$$\bar{T}_I = \frac{\int_0^{\infty} t^2 \delta(t-t_0) dt}{2t_0} = \frac{t_0}{2} \quad (16d)$$

This relationship, that the average age in a piston flow system is 1/2 the mean transit time, to return to the population analogy, is similar to the case of populations with low infant mortality and narrow life expectancy distributions; a population with uniform age distributions from 0 to t_0 has an average age of half the maximum value (Bjorkstrom, 1978).

If we consider the radioactive decay of a tracer in a piston flow regime, the tracer integral equation becomes (Nir and Lewis, 1975):

$$\begin{aligned} C(t) &= \int_0^{\infty} C_0(t-\tau) \delta(t-t_0) e^{-\lambda t} dt \\ &= C_0(t-\tau) e^{-\lambda t_0} \end{aligned} \quad (16e)$$

For a constant input, $C_0(t) = C_0$, we have:

$$C(t) = C_0 e^{-\lambda t} \quad (16f)$$

the well-known radioactive decay equation.

As I mentioned previously, a well from which a water sample comes may tap two or more water-bearing zones. The effect of the mixing of waters on the determination of mean ages by radioactive isotope measurements can be large, especially when the "old" water component is very old (Evans et al., 1978).

Consider a simple groundwater system with two separate water components which will be mixed in the sampling well. If a fraction, f , of the water in the system is the "younger" component 1, with $(1-f)$ of component 2, the mean concentration of a given isotope in the mix is given by:

$$\bar{C} = fC_1 + (1-f)C_2 \quad (17a)$$

where

\bar{C} = the mean concentration of the measured isotope.

C_i = the concentration of the tracer in the i^{th} component.

The actual mean age, \bar{t} , is:

$$\bar{t} = ft_1 + (1-f)t_2 \quad (17b)$$

where

t_1 and t_2 = the ages of the first and second components, respectively.

The apparent radiometric age can be expressed as:

$$\bar{t}_i = -\lambda_i^{-1} \ln \frac{\bar{C}}{C_0} = -\lambda_i^{-1} \ln \left[\frac{fC_1 + (1-f)C_2}{C_0} \right] \quad (17c)$$

where

t_i = the apparent radiometric age derived from the i^{th} isotope

λ_i = the decay constant of the i^{th} isotope.

To illustrate the discrepancies that can result, I made some sample calculations for two hypothetical groundwater systems. In Case I, component 1, the younger component, constitutes 0.1% of the system ($f = 0.001$). Calculations were made for the case where component 1 is modern ($t_1 = 0$) and where $t_1 = 1,000$ years for several ages of component 2, using three isotopes with different half-lives. In Case II, I made calculations using the same age combinations, but now the mixing ratio of the young water in the system is 20% ($f = 0.20$). These results are tabulated in Table 1 and summarized in Figure 6. Several trends are readily apparent:

- (1) When the fractional component of young water, f , is small, the results are relatively insensitive to t_1 .
- (2) The errors increase with increasing age of the older component.
- (3) The errors are less for the longer-lived isotopes.
- (4) Increasing the mixing ratio of the younger component accelerates the departure of the apparent age from the actual mean age for all isotopes.

In considering the two-component piston flow system, equation (17a) is basic to a mathematical solution to the problem. The equation contains three unknowns, which suggests that three isotopes are required for its solution. However, the problem is non-linear and an analytical

Table 1. Apparent and actual mean ages (years).

t_1	t_2	\bar{t}	\bar{t}'_{14C}	\bar{t}'_{36Cl}	\bar{t}'_{39Ar}
Case I: $f = 0.001$					
0	1000	999	999	999	995
0	10000	9990	9981	9990	2694
0	100000	99900	57060	99888	2694
0	1000000	999000	57100	996200	2694
1000	1000	1000	1000	1000	1000
1000	10000	9991	9984	9991	3694
1000	100000	99901	58055	99889	3694
1000	1000000	999001	58106	996252	3694
Case II: $f = 0.20$					
0	1000	800	790	800	522
0	10000	8000	6813	7982	627
0	100000	80000	13305	78118	627
0	1000000	800000	13305	558902	627
1000	1000	1000	1000	1000	1000
1000	10000	8200	7253	8185	1625
1000	100000	80200	14305	78357	1625
1000	1000000	800200	14305	559606	1625

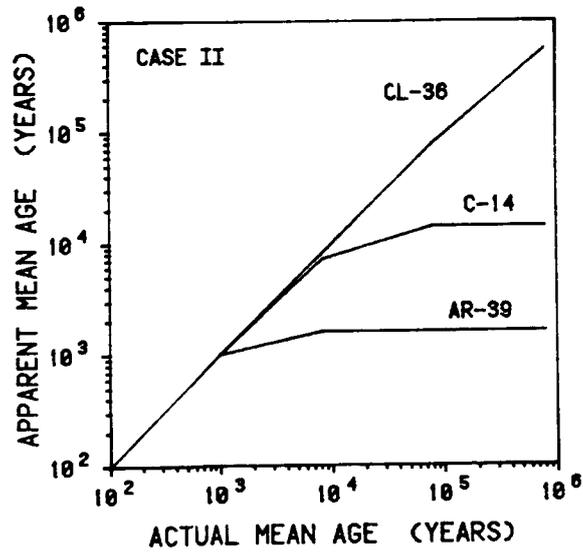
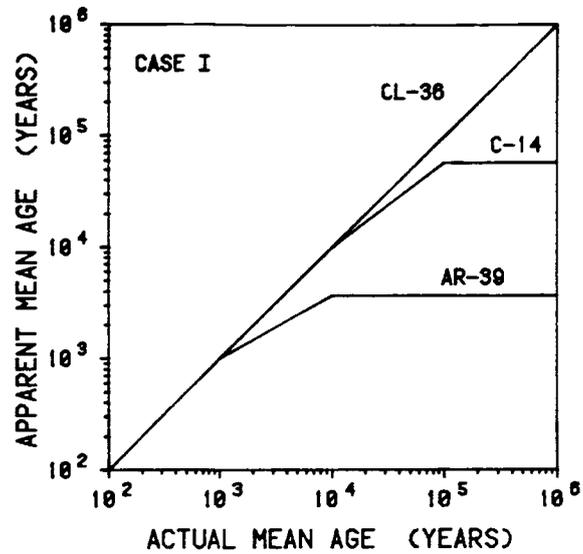


Figure 6. Comparison of actual and mean ages in a two component system where the younger water is 1000 years old. In Case I fractional amount of young component is 0.1%; in Case II young component is 20% of the system.

solution will, in general, not be possible. But, the set of equations can be manipulated to allow solution by a variety of interative numerical techniques.

Noting that the age of a component of the system, t_j , can be expressed as:

$$t_j = \lambda_i^{-1} \ln[C_{oj}^i/C_j^i] \quad (18a)$$

where

C_{oj}^i = the initial concentration of the i^{th} tracer in component j .

C_j^i = the concentration of the i^{th} tracer in component j .

Making use of equations (16f) and (18a), it can easily be shown (see Appendix B) that:

$$\frac{C_j^i}{C_{oj}^i} = \left[\frac{C_j^n}{C_{oj}^n} \right]^{(\lambda_i/\lambda_n)}$$

where the sub- and superscripts i and n denote two different tracers. Making these substitutions into equation (18a) and rearranging gives:

$$\bar{C}^i = f \left[\frac{\bar{C}^n - (1-f)C_2^n}{f} \right]^{(\lambda_i/\lambda_n)} + (1-f) C_2^n^{(\lambda_i/\lambda_n)} \quad (18c)$$

When $i \neq n$, this set of equations can be solved by iteratively determining a value of C_2^n for various values of f , and plotting the results for each equation. The point of intersection which satisfies the constraints of the system will yield values of f and C_2^n , from which

t_1 and t_2 can be calculated. This method is explained in detail in Appendix B.

As pointed out by Jesus Carrera (1983, personal communication), if three different isotopes are available, equations (17a) are a system of three non-linear equations with three unknowns and can be solved by the Newton-Raphson iterative technique. He, in effect, substituted equation (16f) into (17a) and obtained equations of the form:

$$g^i = -\bar{C}^i + fC_{01}^i e^{-\lambda_i t_1} + (1-f)C_{02}^i e^{-\lambda_i t_2} = 0 \quad (19)$$

The Newton-Raphson method could also be applied to the reduced equations of the form of equation (18c). The Newton-Raphson method, also known as Newton's method, is a fairly widely used method of solving non-linear equations. It involves solving a linear Taylor Series approximation of the system. The reader is referred to Gerald (1980) for a discussion of useful numerical techniques.

While these methods, in theory, allow for the solution of simple two-component systems, as Carrera has shown, the resulting age estimates tend to be sensitive to the initial (assumed known) and measured concentrations of the isotopes. But this sensitivity does not appear to be much greater than the sensitivity of a one-component system to the same parameters.

2.8.3 The Dispersive Case

It is well known that the laminar flow patterns prevailing in aquifers differ from these two limiting cases of Sections 2.8.1 and

2.8.2. A more realistic mathematical model may be the convection dispersion equation, which in one-dimension is:

$$D \frac{\partial^2 C}{\partial x^2} + v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (20a)$$

where

D = the coefficient of dispersion

v = constant velocity.

An elementary solution of this partial differential equation (Bear, 1979) is:

$$C(x_0, t) = \frac{C_0 v}{(4\pi Dt)^{1/2}} \exp \left[\frac{-(x_0 - vt)^2}{4Dt} \right] dt \quad (20b)$$

where the initial amount of tracer is $C_0 v dt$, and x_0 is the distance to the sampling point.

For a continuously injected tracer, we have:

$$\frac{C(x_0, t)}{C_0} = \frac{v}{(4\pi Dt)^{1/2}} \int_0^\infty \exp \left[\frac{-(x_0 - vt)^2}{4Dt} \right] dt \quad (20c)$$

As Nir and Lewis (1975) pointed out, by comparing equation (20c) with equation (13d), it will easily be seen that:

$$E(t) = \frac{v}{(4\pi Dt)^{1/2}} \exp \left[\frac{-(x_0 - vt)^2}{4Dt} \right] \quad (20d)$$

For a radioactive tracer, the governing equation is:

$$D \frac{\partial^2 C}{\partial x^2} + v \frac{\partial C}{\partial x} - \lambda C = \frac{\partial C}{\partial t} \quad (20e)$$

For continuous injection at a constant rate, the solution is
(Bear, 1979):

$$\frac{C(x_0, t)}{C_0} = \frac{v}{(4\pi D)^{1/2}} \exp\left\{\frac{v}{2D}\right\} \int_0^{t'=t} t'^{-1/2} \exp\left[\frac{-a}{t'} - bt\right] dt \quad (20f)$$

where

$$a = x_0^2 / 4D$$

$$b = v^2 / 4D + \lambda$$

If we let $x = vt$, the average distance traveled by the waters, we can express the concentration of the tracer as a function of X_0 , the distance from the origin, and X (Nir, 1964). If the sampling point is not too close to the recharge area, we have:

$$\frac{C(x_0, t)}{C_0} = \int_0^{x'=x} \frac{\exp\left[\frac{-(x_0 - x')^2}{4\alpha x'} - \frac{x'\lambda}{v}\right]}{(4\pi\alpha x')^{1/2}} dx' \quad (20g)$$

where

$$\alpha = \text{the dispersivity of the medium} = D/v.$$

Nir (1964) introduced dimensionless variables into equation (20g) and obtained for the steady state solution:

$$\frac{C(x_0)}{C_0} = (4D' + 1)^{-1/2} \exp\left\{\frac{X'}{2}[1 - (4D' + 1)^{1/2}]\right\} \quad (20h)$$

where

$$X' = x_0/\alpha; X' \gg 1 \text{ required}$$

$$D' = \alpha\lambda/v$$

Equation (20f) is represented in Figure 7 for various values of D' . Transit times can be conveniently determined from this figure. The distance from the recharge area, x_0 , and the dispersivity are assumed to be known and C/C_0 is measured experimentally. The value of D' corresponding to x' and C/C_0 can be found from Figure 7. Finally, transit time, t , can be determined from:

$$t = \frac{X'D'}{\lambda}$$

In addition, if two radioactive isotopes are available, we need not assume that the dispersivity is known; it can be determined (Nir and Lewis, 1975).

Equation (20d) can also be expressed as a complimentary error function (Bear, 1979, p. 264):

$$\frac{C(x_0, t)}{C_0} = \frac{1}{2} \operatorname{erfc} \left[\frac{-(x_0 - vt)^2}{2(DT)^{1/2}} \right] \quad (20j)$$

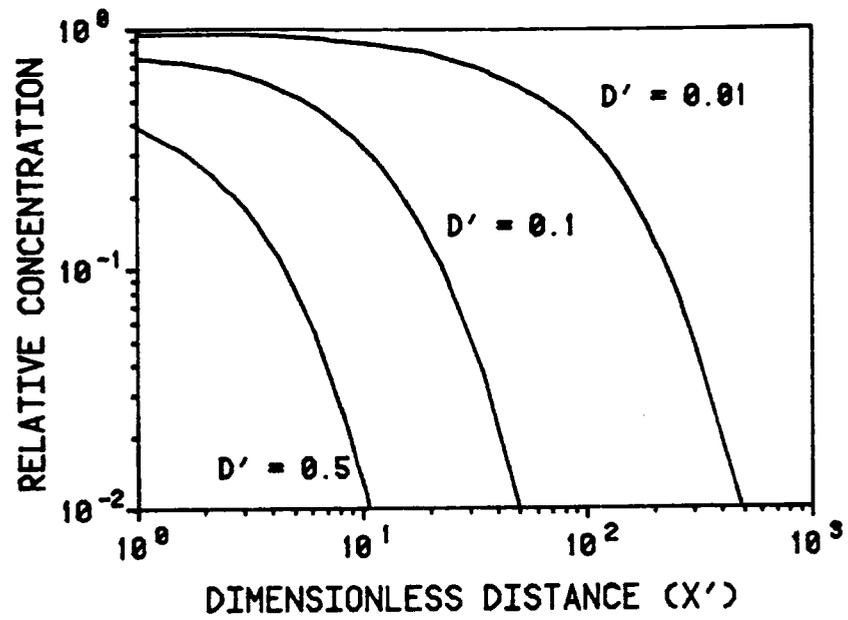


Figure 7. Solutions of equation (20h) for various values of D' (After Nir, 1964).

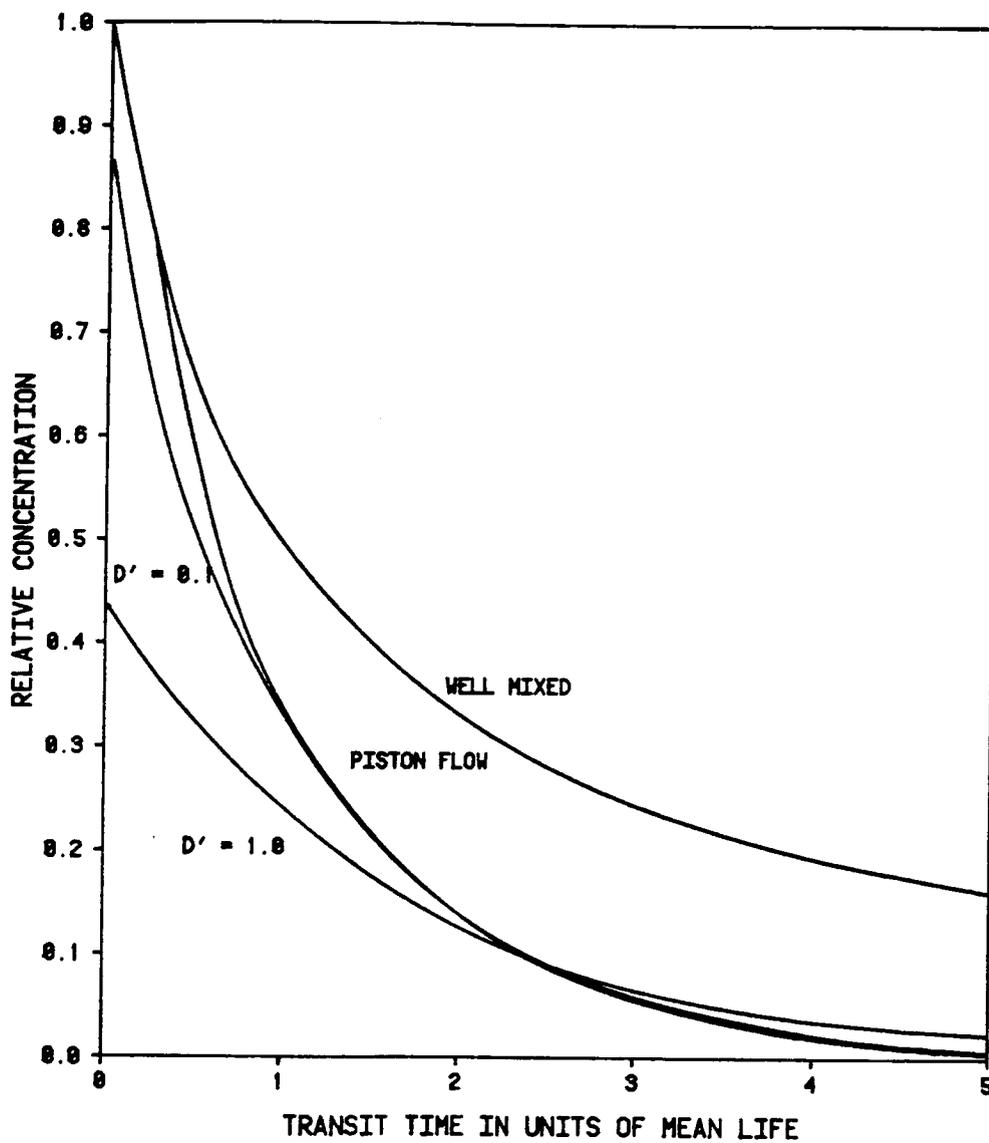


Figure 8. Comparison of well mixed, piston flow and dispersive models (After Nir, 1964).

The variance of this distribution is:

$$\sigma^2 = 2Dt = 2\alpha vt \quad (20k)$$

It is interesting to compare the behavior of the dispersive case with solutions of the piston flow model and the well mixed case. Nir (1964) presented a graphical comparison of these cases (see Figure 8). It can be seen that in the range of C/C_0 values between 0.1 and 0.12, the value of λt , the number of "mean life times", is fairly independent of D' for $D' < 1$. The λt values in this range are $\lambda t = 2.1$ to 2.3 . For tritium (^3H), this corresponds to 38 to 42 years. With ^{14}C , this age range would be 17,000 to 19,000 years; for ^{36}Cl , the range is 900,000 to 1,000,000 years.

As we noted earlier, the well mixed and piston flow solutions are seen to coincide for $\lambda t \ll 1$, but large differences exist for later times.

Let us consider the range of D' values in nature. For the case of a relatively large dispersivity, say $\alpha = 100$ m, a low average velocity, say $v = 10$ m/yr, with tritium ($\lambda = .0565$), we obtain a value of $D' = 0.6$. For less extreme dispersivities or isotopes with longer half-lives, we obtain still smaller values of D' . For example, with $\alpha = 100$ m, $v = 10$ m/yr, and λ for $^{14}\text{C} = 0.00012$, $D' = 0.0012$. Clearly, this range of D' values does not require significant corrections of the transit times obtained from the simple piston flow approximation.

For vanishing D' , both solutions coincide, just as for $\alpha \rightarrow 0$ the dispersion effects disappear (Nir, 1964). For example, a ^{14}C

concentration of five percent modern carbon (pmc) would have a piston flow age of 24,964 years. The average transit time determined from the one-dimensional dispersive case (with exaggerated longitudinal dispersivity of 1,000 m, and $v = 10$ m/yr, $D' = 0.01$) is 25,046 years.

When $D' \ll 1$, we may approximate equation (20h) by (Nir, 1964):

$$\frac{C}{C_0} = e^{-\lambda t(1-D')}/(1+2D') \quad (21a)$$

So the ratio of the above expression to the piston flow solution is:

$$\frac{C/C_0(\text{dispersive})}{C/C_0(\text{piston flow})} = \frac{e^{-\lambda t D'}}{(1+2D')} \approx \frac{1+\lambda t D'}{1+2D'} \quad (21b)$$

for $\lambda t D' \ll 1$.

Thus, the dispersive solution will give lower C/C_0 values for small λt and higher C/C_0 values for large λt , the crossover point being at $\lambda t \approx 2$ as can be seen in Figure 8 (Nir, 1964). This represents transit times of about 35 years for ^3H , 17,000 years for ^{14}C , and 870,000 years for ^{36}Cl .

So, it would appear that the piston flow approximation is a good one for the one-dimensional dispersive case. But, the treatment of an aquifer as a one-dimensional medium is justified only if the boundaries are parallel and transverse mixing is complete. Sedimentary rocks are often of nearly constant height for significant distances, but a major source of error in real world applications may be ignorance of the exact extent and shape of the aquifer (Nir, 1964).

The assumption of complete transverse mixing may be valid on the scale of regional groundwater dating experiments. For example, if we consider an aquifer 100 m thick with a transverse dispersivity, α_t of 2 m, the condition of good lateral mixing being $(2\alpha x)^{1/2} \geq 100$ m, we obtain $x \geq 2500$ m; transverse mixing will be practically complete after 2.5 km of travel through the aquifer (Nir, 1964).

2.8.4 Mixing Cells

Chemical engineers have for some time been interested in simulating dispersive flow processes using mixing cell models which are essentially combinations of the completely mixed reservoir described in Section 2.8.1. A series of completely mixed cells, the so-called tanks in series model, has been popular for this purpose. The general approach is to characterize the mixing with a model whose parameters can be correlated for broad classes of processes (Himmelblau and Bischoff, 1968, Chapter 4). The transit time distribution for a series of j completely mixed tanks of constant volume can be found by solving a series of equations similar to equation (13a) for each tank in the series. Solution by applying Laplace transforms (Himmelblau and Bischoff, 1968) gives:

$$E(t) = \frac{j^j}{(j-1)!} \frac{t^{(j-1)}}{(\bar{t})^j} e^{-(jt/\bar{t})} \quad (21a)$$

and variance is given by:

$$\sigma^2 = \frac{1}{j} \quad (21b)$$

Similarly, for two parallel series, as shown in Figure 9 with a fraction of flow, f , to branch 1, the transit time distribution is given by (Himmelblau and Bischoff, 1968):

$$E(t) = f \frac{n^n}{(n-1)!} \frac{(t)^{n-1}}{(\bar{t}_1)^n} e^{-(nt/\bar{t}_1)} \quad (21c)$$

$$+ (1-f) \frac{m^m}{(m-1)!} \frac{(t)^{m-1}}{(\bar{t}_2)^m} e^{-(mt/\bar{t}_2)}$$

and the average transit time is given by:

$$\bar{t}_E = f\bar{t}_1 + (1+f)\bar{t}_2 = \frac{V_1+V_2}{Q} \quad (21d)$$

We can relate the dispersive model to the series of stirred tanks model by comparing the variances of the corresponding transit time distributions:

$$\sigma^2 = \frac{1}{j} = 2Dt \quad (21e)$$

As Himmelblau and Bischoff observed (1968, Chapter 4), the limiting case where $D = 0$ (piston flow) corresponds to an infinite number of mixing cells in series.

The mixing cell concept can be extended to include complex networks of cells with complicated flow patterns. Using a network of interconnected cells, the transport of solutes can be described by a set of recursive equations based on the equation of continuity. The recursive equations govern the transformation from one state to the next. A

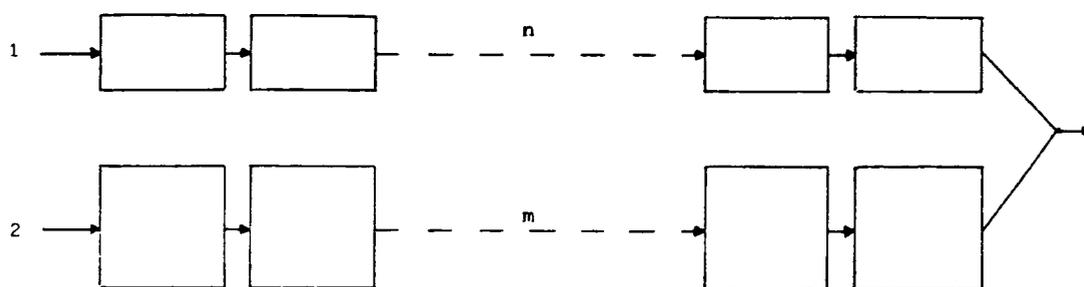


Figure 9. Two parallel series of mixing cells.

FORTTRAN computer model (Campana, 1975) allows for the determination of discrete versions of the transit time distribution, $T(N)$, which corresponds to $E(t)$, and the internal age distribution, $A(N)$, which corresponds to $M(T)$. Note that $T(N)$ and $A(N)$ are defined with respect to iteration number, with each iteration being associated with a time step, Δt . The computer program makes use of the relationship defined in equation (12d), that the system response to an instantaneous input is identical to the age distribution of fluid elements exiting a cell (for constant flow). Hence, for an instantaneous input at the first iteration, at all subsequent iterations, N , the concentration of numerical tracer remaining in any cell is a measure of the fractional amount of fluid elements of age number N (age = $\Delta t \times N$) in that cell (Simpson and Duckstein, 1975). For any cell

$$A(N)_i = \frac{C(N)_i}{C'} * \frac{BRV}{VOL'} = \frac{C(N)_i}{SBRC} \quad (22a)$$

where

$C(N)_i$ = concentration of numerical tracer in a cell at iteration i ($= N$).

C' = "instantaneous" nominal tracer concentration at iteration $i = 1$, entering the boundary cell.

BRV = boundary recharge volume.

VOL' = volume of boundary cell receiving tracer.

$SBRC$ = system boundary recharge concentration.

The mean age number, \bar{A}_N , is given by (Campana, 1975):

$$\bar{A}_N = \frac{\sum_{i=1}^N i \frac{C(N)_i}{SBRC}}{N} \quad (22b)$$

or, in real time units:

$$\bar{A} = \Delta t \frac{\sum_{i=1}^N i C(N)_i}{\sum_{i=1}^N C(N)_i} \quad (22c)$$

The variance is given by:

$$\sigma^2 = (\Delta t)^2 \left[\frac{\sum_{i=1}^N (i^2) C(N)_i}{\sum_{i=1}^N C(N)_i} - (\bar{A})^2 \right] \quad (22d)$$

The transit time distribution, $T(N)$, for a cell discharging from the system, in the case of a "Simple Mixing Cell" model (SMC) where input to each cell is assumed to be completely mixed with the cell's contents before the cell discharges fluid, is identical to $A(N)$ for that cell. For a "Modified Mixing Cell" model (MMC), where the discharge concentration at any iteration is equal to the concentration in the cell at the previous iteration, the equation becomes (Campana, 1975):

$$T(N)_i = \frac{C(N)_{i-1}}{SBRC} \quad (22e)$$

where

$C(N)_{i-1}$ = the concentration of tracer in the cell at iteration $i-1$.

The mean transit time can be determined by the volumetric parameters of the model. Under conditions of steady flow, steady volume, and with a single SBRV that is distributed throughout all the cells and discharged from a single cell, the mean transit time is given by (Campana, 1975):

$$\bar{T} = \frac{\Sigma VOL + SBDV}{SBDV} = \frac{\Sigma VOL + SBRV}{SBRV} = \frac{V}{Q} = \bar{t}_E \quad (22f)$$

where

ΣVOL = total volume of cells in the model.

SBDV = system boundary discharge volume.

SBRV = system boundary recharge volume.

CHAPTER 3

USE OF INDEPENDENT AGE INFORMATION

Given the uncertainties associated with the so-called known parameters--the historic initial concentrations and the measured concentrations of the radionuclides--and the need for several isotopes to solve a multicomponent system, it is clearly advantageous to incorporate independent sources of information into the analysis. This chapter will consider the use of such information and examine the simplification of the mathematics that various scenarios allow.

3.1 Age of One Component Assumed Known

When the age of one water component in a two-component system can be reliably estimated, by hydrodynamic methods or perhaps by the presence of anthropogenic chemicals in the sampled water, the problem simplifies greatly. The two-component system can be solved using only two isotopes. We may solve equation (17a) for f , which gives:

$$f = \frac{\bar{C} - C_2}{C_1 - C_2} \quad (22a)$$

For two different isotopes, denoted A and B, we have:

$$f = \frac{\bar{C}^A - C_2^A}{C_1^A - C_2^A} = \frac{\bar{C}^B - C_2^B}{C_1^B - C_2^B} \quad (22b)$$

For simplicity of notation, let the concentrations in this equation represent fractional values of the modern activities (C/C_0). Substituting equation (18b) into the above and rearranging gives:

$$\frac{\bar{C}^A - C_2^A}{C_1^A - C_2^A} + \frac{(C_2^A)^{\lambda_B/\lambda_A} - \bar{C}^B}{(C_2^A)^{\lambda_B/\lambda_A} - C_1^B} = 0 \quad (22c)$$

Here, since the age of component one is assumed known, the concentrations of isotopes A and B in component one, C_1^A and C_1^B , are known. The only unknown in equation (22c) is C_2^A ; this equation can be solved quite easily by iteration. I have found the interval halving technique to work quite well.

Similarly, we may solve directly for t_2 :

$$g(t_2) = \frac{\bar{C}^A - C_{02}^A e^{-\lambda_A t_2}}{C_1^A - C_{02}^A e^{-\lambda_A t_2}} + \frac{C_{02}^B e^{-\lambda_B t_2} - \bar{C}^B}{C_{02}^B e^{-\lambda_B t_2} - C_1^B} = 0 \quad (22d)$$

Newton's method can be applied to the above equation. For equations with one variable, this iterative method takes the form:

$$t_2^{i+1} = t_2^i + \frac{g(t_2^i)}{\left. \frac{\partial g}{\partial t_2} \right|_{t_2=t_2^i}} \quad (22e)$$

This method converges quadratically, which is faster than the interval halving technique. However, the method may not converge unless the initial estimate is sufficiently close to the true root.

3.2 Dating Very Old Waters

In some situations, a two-component system can be solved exactly, without recourse to numerical iterative techniques. Consider a system in which the age of the older component is great, say over 50,000 years. In this case, the older component should be nearly devoid of isotopes such as tritium, silicon-32, and carbon-14 (if subsurface production of these isotopes can be neglected or accounted for). If analyses of two of these radionuclides are available along with a longer-lived isotope, such as chlorine-36, we may solve the system. The system of equations becomes:

$$\bar{C}^A = f C_{01}^A e^{-\lambda_A t_1} \quad (23a)$$

$$\bar{C}^B = f C_{01}^B e^{-\lambda_B t_1} \quad (23b)$$

$$\bar{C}^C = f C_{01}^C e^{-\lambda_C t_1} + (1-f) C_{02}^C e^{-\lambda_C t_2} \quad (23c)$$

By applying Cramer's rule, after taking natural logarithms of both sides of equations (23a) and (23b), we have:

$$\ln f = \frac{\begin{vmatrix} \ln \bar{C}^A & -\lambda_A \\ \ln \bar{C}^B & -\lambda_B \end{vmatrix}}{\begin{vmatrix} C_{01}^A & -\lambda_A \\ C_{01}^B & -\lambda_B \end{vmatrix}} = \frac{\lambda_A \ln \bar{C}^B - \lambda_B \ln \bar{C}^A}{C_{01}^B \lambda_A - C_{01}^A \lambda_B} \quad (23d)$$

So,

$$f = \exp \frac{\lambda_A \ln \bar{C}^B - \lambda_B \ln \bar{C}^A}{C_{o1}^B \lambda_A - C_{o1}^A \lambda_B} \quad (23e)$$

and

$$t_1 = \frac{\begin{vmatrix} C_{o1}^A & \ln \bar{C}^A \\ C_{o1}^B & \ln \bar{C}^B \end{vmatrix}}{\begin{vmatrix} C_{o1}^A & -\lambda_A \\ C_{o1}^B & -\lambda_B \end{vmatrix}} = \frac{C_{o1}^A \ln \bar{C}^B - C_{o1}^B \ln \bar{C}^A}{C_{o1}^B \lambda_A - C_{o1}^A \lambda_B} \quad (23f)$$

Finally, equation (23c) can be solved for t_2 :

$$t_2 = \ln \left[\frac{\bar{C}^C - f C_{o1}^C e^{-\lambda_C t_1}}{(1-f) C_{o2}^C} \right] \lambda_C^{-1} \quad (23g)$$

3.3 Use of Chlorine-36

Recent work has indicated good potential for the use of chlorine-36, with a half-life of 301,000 years, in the dating of old waters (Bentley, Phillips, and Davis, 1983).

While some subsurface production may occur as a result of the natural neutron flux, it appears that the extent of this production can be quantitatively accounted for. Because of the long half-life, decay of the thermonuclear bomb pulse in modern waters can be neglected and the system of equations simplifies somewhat. We now have:

$$\bar{C}^A = f C_{o1}^A e^{-\lambda_A t_1} \quad (24a)$$

$$\bar{C}^B = f C_{01}^B e^{-\lambda_B t_1} + (1-f) C_{02}^B e^{-\lambda_B t_2} \quad (24b)$$

$$\bar{C}^{C1} = f C_{01}^{C1} + (1-f) C_{02}^{C1} e^{-\lambda_{C1} t_2} \quad (24c)$$

from which we get:

$$f = \frac{\bar{C}^A}{C_{01}^A} e^{\lambda_A t_1} \quad (24d)$$

$$t_2 = -\frac{1}{\lambda_{C1}} \ln \left[\frac{\bar{C}^{C1} - f C_{01}^{C1}}{(1-f)} \right] \quad (24e)$$

and

$$\begin{aligned} & -\bar{C}^B + \frac{\bar{C}^A}{C_{01}^A} C_{01}^B e^{t_1(\lambda_A - \lambda_B)} \\ & + \left[1 - \frac{\bar{C}^A}{C_{01}^A} e^{\lambda_A t_1} \right] C_{02}^B \left[\frac{\bar{C}^{C1} - \left[\frac{\bar{C}^A}{C_{01}^A} e^{\lambda_A t_1} \right] C_{01}^{C1}}{\left[1 - \frac{\bar{C}^A}{C_{01}^A} e^{\lambda_A t_1} \right]} \right]^{\lambda_B / \lambda_{C1}} = 0 \end{aligned} \quad (24f)$$

3.4 Helium-4 Accumulation

Recently, attempts have been made to utilize the buildup of products of radioactive decay in groundwater to estimate water age. This method is advantageous in dating very old water, as the older the water, the greater the concentration and the easier the detection of the products. Helium-4 may be the most useful of the products of

radioactive decay because of its relatively rapid rate of production (Davis and Bentley, 1982). Bath, Edmunds and Andrews (1978) measured levels of excess (above atmospheric levels) helium-4 in the groundwater of the Bunter Sandstone aquifer in England, and demonstrated a correlation with ^{14}C ages, albeit not a one-to-one correlation. A major source of error in the helium-4 dating method is the lack of knowledge of bulk properties of the aquifer, namely intergranular porosity, bulk density, and uranium and thorium contents. The ^4He age calculations are quite sensitive to these parameters, which may account, to some extent, for the general lack of agreement between ^4He ages and ^{14}C dates in the literature. If, however, we can neglect for the moment these practical problems, the linear buildup of helium-4 complements the use of radioactive tracers in solving the two-component system. If, in addition to the helium-4 information, we have two isotopes available, the system of equations becomes:

$$\bar{C}^A = f C_{01}^A e^{-\lambda_A t_1} \quad (25a)$$

$$\bar{C}^B = f C_{01}^B e^{-\lambda_B t_1} + (1-f) C_{02}^B e^{-\lambda_B t_2} \quad (25b)$$

$$\bar{C}^{\text{He}} = (1-f) R t_2 \quad (25c)$$

where

R = a constant depending on the aquifer's radioelement contents and porosity (Andrews and Lee, 1979).

Implicit in this treatment are the assumptions that isotope A is of sufficiently short half-life to be absent from the older component 2, and any excess helium would come only from the older component, as the rate of buildup is very slow--in the case of the Bunter Sandstone about $3 \times 10^{-12} \text{ cm}^3 \text{ } ^4\text{He STP/cm}^3 \text{ H}_2\text{O/year}$ (Andrews and Lee, 1979).

This system of equations (25a-c) can be solved by applying Newton's method. However, some algebraic manipulation will allow us to solve for t_1 by an iterative interval-halving method. Then, the fractional contribution of component 1, f , and the age of component 2, t_2 , can be solved for directly. This derivation is presented in Appendix C. The operational equations are:

$$\frac{\bar{C}^A}{C_{01}^A} C_{01}^B e^{t_1(\lambda_A - \lambda_B)} + \left[1 - \frac{\bar{C}^A}{C_{01}^A} e^{\lambda_A t_1} \right] C_{02}^B \quad (25d)$$

$$\cdot \exp \left[-\lambda_B \frac{\bar{C}^{\text{He}}}{R} \left[1 - \frac{\bar{C}^A}{C_{01}^A} e^{\lambda_A t_1} \right] \right] - \bar{C}^B = 0$$

which gives t_1 , and

$$f = \frac{\bar{C}^A}{C_{01}^A} e^{\lambda_A t_1} \quad (25e)$$

$$t_2 = \frac{\bar{C}^{\text{He}}}{R(1-f)} \quad (25f)$$

This treatment will be applied to the data of Bath et al. (1978) in Chapter 4.

3.5 Constraints on the System

As a preliminary step, it is often possible to place some limits on the possible solutions of the two-component system. We have already noted that relatively short-lived radionuclides of atmospheric origin, such as tritium or silicon-32, should not be present in the older component. We have:

$$f = \frac{\bar{C}^A}{C_{01}^A e^{-\lambda_A t_1}} \quad (26a)$$

Since $C_{01}^A e^{-\lambda_A t_1} \leq C_{01}^A$, we can write:

$$f \geq \frac{\bar{C}^A}{C_{01}^A} \quad (26b)$$

That is, the concentration of isotope A relative to its initial concentration may be taken as a lower limit to the fractional concentration of the younger component; this is the case when the younger component is modern ($t_1 = 0$) and here we may limit the iterative solution process to cases where f is greater than the average concentration of the radioisotope with the shortest half-life. This procedure was applied by Downing, Pearson, and Smith (1979) in an analysis of the flow mechanism in the Chalk aquifer in southeast England. They assumed that the weighted mean of tritium in infiltration derived from rainfall since 1953 (approximately 100 TU) could be used for C_1 . They assumed the tritium content expressed as TU indicated the percentage of post-1953 water. A similar procedure was used by Hobbs, Fisher, Pearson, and

Chemerys (1979) in estimating the proportion of shallow cool waters mixing with an older thermal component of hot springs in the Appalachians.

We can put an upper limit on the proportion of younger water mixing with older water if we assume that the older water is devoid also of a longer-lived isotope such as carbon-14. In this case:

$$f = \frac{\bar{C}^B}{C_1^B} = \frac{\bar{C}^B}{\exp\left[\frac{\lambda_B}{\lambda_A} \ln \left[\frac{\bar{C}^A}{f}\right]\right]} = \frac{\bar{C}^B}{\left[\frac{\bar{C}^A}{f}\right]^{\lambda_B/\lambda_A}} \quad (26c)$$

Solving for f, we have:

$$f = \left[\frac{\bar{C}^B}{\bar{C}^A \lambda_B/\lambda_A} \right]^{1/(1-\lambda_B/\lambda_A)} \quad (26d)$$

This, then is an upper limit to the fractional amount of the younger water in the system.

CHAPTER 4

A CASE STUDY OF THE BUNTER SANDSTONE AQUIFER

In this chapter, I will examine some published hydrochemical data from the Triassic Bunter Sandstone aquifer of Nottinghamshire, England, in the context of some of the models previously mentioned. This area was chosen because it is one of the few areas which have been studied using many environmental tracers and multiple dating techniques. Work by Bath et al. (1978) and Andrews and Lee (1979) includes analyses of tritium, carbon-14, excess helium-4 buildup, as well as stable isotopes and elemental constituents.

4.1 Site Description

The study area is in the English East Midlands area, northwest of London, in the vicinity of the towns of Mansfield, Worksop, Gainsborough, and Newark (see Figure 10). The topography of the area is subdued, varying from about 640 feet above sea level near Mansfield on the west to less than 100 feet above sea level in the Trent valley on the east (Land, 1966).

The Bunter Sandstone is a yellowish to reddish brown, poorly cemented, locally pebbly, quartzose sandstone. It varies in thickness from around 120 m in the south to 300 m in the north. The aquifer dips gently to the east at about 1:50. Two lithological divisions are observed at the western outcrop: the Lower Mottled Sandstone below and

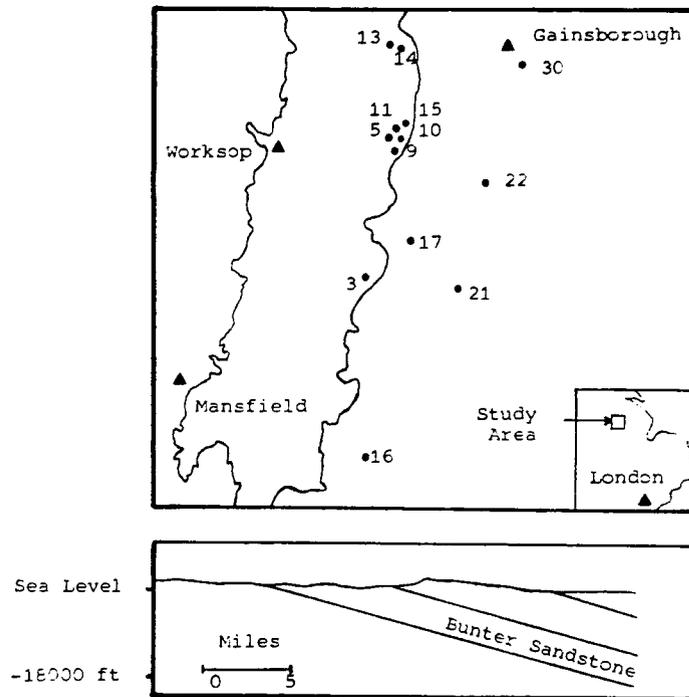


Figure 10. Map of study area and typical cross section of Bunter Sandstone aquifer. Numbers indicate well locations (After Bath et al., 1978).

the Bunter Pebble Beds above. North of Worksop, the boundary between the Pebble Beds and Lower Mottled Sandstone becomes almost unrecognizable. Hydrogeologically, these two divisions of the Bunter Sandstone form a single aquifer (Land, 1966).

The sandstone is confined effectively in the east by a thick (200-300 m) sequence of marls, the Keuper Marl and Waterstones. Locally, however, fine-grained interbedded sandstones near the base of the Keuper act as a transitional minor aquifer. The outcropping Bunter is overlain by Pleistocene and recent alluvium that is generally widespread, thin, and nearly everywhere sandy. It is therefore largely permeable and can be regarded hydrogeologically as part of the Bunter Sandstone (Land, 1966). The Bunter is underlain by a mixed sequence of Permian mudstones and marls. Below these Upper Permian Marls is the Upper Magnesian Limestone. The Permian Marls form an impermeable basal seal, except perhaps where cut by faults (Bath et al., 1978), which mostly trend between west-northwest and west-southwest (Land, 1966).

The intergranular hydraulic conductivity of the sandstone averages 3.4 meters per day. The average porosity is 30 percent (Lovelock, 1977). The hydraulic conductivities determined from pumping tests, however, are typically five times higher than this, reflecting the dominance of fissure flow over intergranular flow in the system (Bath et al., 1978). The natural hydraulic gradients are about 1:250 in the outcrop area and, in the confined part of the aquifer, the piezometric surface is subhorizontal. However, as Bath et al. (1978) pointed out, the natural gradients have been significantly modified by the extensive cones of depression which exist around the major borehole sites.

The whole of the Bunter outcrop area is in the Trent river basin and several of its tributaries flow across the Bunter outcrop en route to the Trent. Precipitation in the study area is fairly evenly distributed throughout the year, averaging 23 to 26 inches per year. Percolation gages indicate an average annual infiltration of about seven inches, with about 80% of the infiltration coming from winter (October-March) rains (Land, 1966).

4.2 A Two-Component System

Table 2 summarizes the tritium, carbon-14, and helium-4 data from the study area and presents the range of corrected carbon-14 concentrations determined by the computer program WATEQF-ISOTOP (Bath et al., 1978). These corrections are needed to account for changes in carbon-14 concentrations caused by carbon isotope behavior in the geochemical evolution of the groundwater. The need for these corrections is examined in some detail by Fontes and Garnier (1979).

In the unconfined portion of the aquifer, many of the wells show significant levels of tritium combined with ^{14}C activities around 50 ± 10 pmc. Bath et al. (1978) pointed out that this could be explained by the rapid equilibration with respect to calcite and by dissolution of a carbonate with $\delta^{13}\text{C}$ around 0 ‰. As the bulk carbonate content of the Bunter is about -7 ‰, this explanation requires the postulation of an isotopically distinct carbonate material within the unsaturated zone or shallow saturated aquifer. Another possible mechanism for this might be the mixing of a young component with older water. Such a mechanism would also be consistent with the observations of

Table 2. Tritium, carbon-14 and helium-4 data from the Bunter aquifer.

Well No. ^a	Location ^a	Tritium ^a (TU)	Carbon-14 ^a (pmc)	Excess Helium-4 ^b (cm ³ STP cm ⁻³ H ₂ O)/ age (years)	Corrected Carbon-14 ^a (pmc)	
					min.	max.
3	Boughton	15.0	55.1	--	84.4	121.1
5	Elkesley, No. 6	8.0	77.6	0.0	112.9	156.5
9	Elkesley, No. 5	25.0	70.8	0.0	99.4	147.3
10	Retford, Clarks No. 2	4.0	52.6	1.8	84.1	114.2
11	Ordsall, No. 1	10.0	42.4	0.0	69.6	99.5
12	Retford, Clarks No. 1	2.0	65.1	2.7	96.4	142.0
13	Everton, No. 1	0.0	42.1	0.0	72.1	102.4
14	Everton, No. 3	0.0	42.0	0.0	60.9	90.8
15	Retford, Whisker Hill	0.0	39.2	0.0	67.1	94.1
16	Haliam, No. 1	0.0	28.6	9.3	59.4	83.4
17	Markham Clinton	0.0	26.7	0.0	43.9	65.5
21	Egmanton, B.P.	0.5	26.3	6.0	41.3	61.6
22	Rampton	0.3	0.7	14.3	1.3	1.8
30	Gainsborough	2.0	1.6	22.3	3.3	4.9

^aData from Bath et al., 1978

^bData from Andrews and Lee, 1979

small amounts of tritium in samples with ^{14}C ages over 20,000 years and the fact that the ^4He accumulation ages are consistently higher than the corresponding ^{14}C ages (Gupta, 1978). An appropriate model for the evaluation of this hypothesis is the two-component system described earlier.

4.2.1 A Well-Mixed Young Component

I will first consider the case of a well-mixed younger component. As it turns out, the average tritium value, expressed as the tritium existing in 1974, for rain entering groundwater in the United Kingdom from 1954 to 1975 is approximately 100 TU. This has been called the "classical value" for the recharge (Smith et al., 1976). Adjusting this value to 1977 and allowing for the lower levels of tritium in precipitation, the concentration of tritium in the younger component would be approximately 80 TU. If we further assume there is no tritium in the older component and that the younger component has a carbon-14 concentration of 150 pmc (Downing, Pearson, and Smith, 1979), the fraction of young water and the age of the older component can be easily determined:

$$f = \frac{^3\text{H}}{\bar{C}} \quad (27a)$$

$$t_2 = -\lambda_{^{14}\text{C}} \ln \left[\frac{\bar{C}^{^{14}\text{C}} - 1.5f}{(1-f)} \right] \quad (27b)$$

The results of these calculations are tabulated in Table 3. Obviously, this correction results in an increased estimate of the age of the older water component. Where the fraction of young water is small and the

Table 3. Results of a well mixed young component model.

Well No.	Fractional Amount of Modern Water (f)	Mixing Corrected Age of Old Water (t_2)*		Age of Water without Mixing Correction*	
		min.	mean	min.	mean
3	0.188	-1140	874	-1600	100
10	0.050	-960	545	-1100	300
11	0.125	663	2501	40	1500
12	0.025	-2886	-1240	-2900	-1300
21	0.006	4080	5753	4000	5650
22	0.004	36300	38300	33000	34550
30	0.025	36700	48570	24900	26550

*years

older component is relatively young, as is the case for wells 10, 12, and 21, this increase is not great, especially when compared with the range of ages. But when the fraction of young water is large (wells 3 and 11) or the age of the old component is great (well 30), the correction is larger, greater, in fact, than the range of ages established by the isotopic correction process.

It should be pointed out, however, that the presence of up to a few tritium units in old water (such as wells 21, 22, and 30) may be due to subsurface production of tritium and not leakage of modern water into the sample (Davis, 1983, personal communication). Although, in the case of significant subsurface production, one would expect to find the tritium in all of the wells sampling the mature water, and in this area, tritium is absent from several samples with carbon-14 ages similar to well 30. On the other hand, limited sensitivity of the tritium analyses may explain this apparent contradiction.

4.2.2 Two Piston Flow Components

The above analysis has not included the helium-4 ages. But if they were corrected for mixing using equation (25c), the corrected ages would still not be consistent with the carbon-14 ages. This discrepancy may be the result of the uncertainties in the helium-4 accumulation dating techniques mentioned in Section 3.4. However, it is interesting to incorporate the helium-4 ages into the analysis of a two component system. A FORTRAN computer program was written to solve equations (25d-f). The program uses Newton's method, an iterative technique for solving non-linear equations. The general algorithm is given in

equation (22e). A finite difference approximation of the time derivative of equation (25d) is used.

Data from the wells which showed positive tritium, excess helium-4 and positive carbon-14 ages were analyzed using this program. Table 4 shows the input parameters and results of these calculations for the cases where feasible solutions were obtained. The piston flow approximation is a simplifying assumption, but as indicated in Section 2.8.3, the average transit times determined by the piston flow model and the dispersive model are similar. A more troubling problem was the variability of recent tritium and carbon-14 inputs caused by atmospheric testing of thermonuclear devices in the 1950's and 1960's. To account for this, the initial concentrations of these isotopes were varied in an attempt to match the average transit time of the young component with the isotopic input corresponding to the year of recharge. For 3 out of the 6 wells which showed positive tritium, excess helium-4 and positive carbon-14 ages, no solution was found (wells 10, 12 and 21). In all three of these cases solution was probably prevented by helium ages which were much greater than the carbon-14 ages. The results from the wells for which feasible solutions were obtained can be compared to the results of the well mixed young component model. Evidently, the inclusion of the helium-4 data results in greater estimates of the age of the old component.

Almost all of the parameters in equations (25d-f) have at least some degree of uncertainty associated with them. A sensitivity analysis was conducted to evaluate the effects of these uncertainties on the

Table 4. Results of a two piston flow components model.

Well No.	Input Parameters			Calculated Values			
	Tritium (TU) Measured	Tritium (TU) Initial ^a	Carbon-14 (pmc) Measured	Carbon-14 (pmc) Initial ^a	f	t ₁ *	t ₂ *
3	15	100	84.4	120	0.30	12	6314
22	0.3	100	1.53	150	0.006	12	42450
30	2.0	110	4.03	110	0.040	12	68500

^aInitial input concentration to young component

* Years

solutions to the two component system. Using the input parameters for well 3 shown in Table 4 as a base, the input concentrations of tritium and carbon-14 to component 1, the measured concentrations of tritium and carbon-14 and the helium-4 ages were varied. The equations were then solved again using the adjusted values. The results are presented graphically in Figures 11 through 15. In general, the two component system does not appear to be much more sensitive to small changes in these parameters than a single component system would be. The age of the young component is more sensitive to changes in the initial and measured tritium concentrations than is the age of the old component. Similarly, the age of the old component is more sensitive to changes in the carbon-14 and helium-4 parameters.

4.3 A Discrete State Compartment Model

In an attempt to account for the "plumbing" of the Bunter aquifer system, the Discrete State Compartment computer program (Campana, 1975) was used to model solute transport through the Bunter aquifer. Water table and piezometric level information (Land, 1966) and radio-nuclide dating results (Bath et al., 1978, and Andrews and Lee, 1979) indicate that flow in the Bunter is essentially down-dip, from west to east. Treating the aquifer as hydrologically homogeneous, a Discrete State Compartment model was constructed along a typical west to east section, 4 miles wide and about 16 miles long, through the Worksop groundwater unit defined by Land (1966). This model, depicted schematically in Figure 16, allows for vertical and horizontal flow in the Bunter outcrop. In the unconfined portions of the aquifer flow is

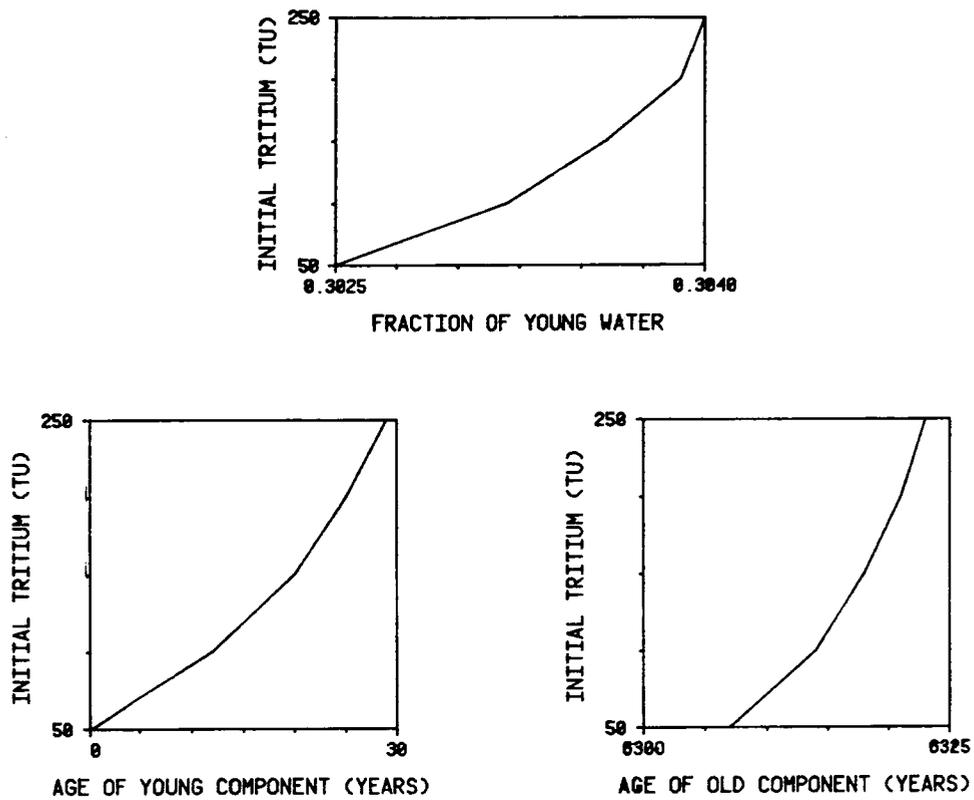


Figure 11. Sensitivity of two component system to initial tritium input to young component.

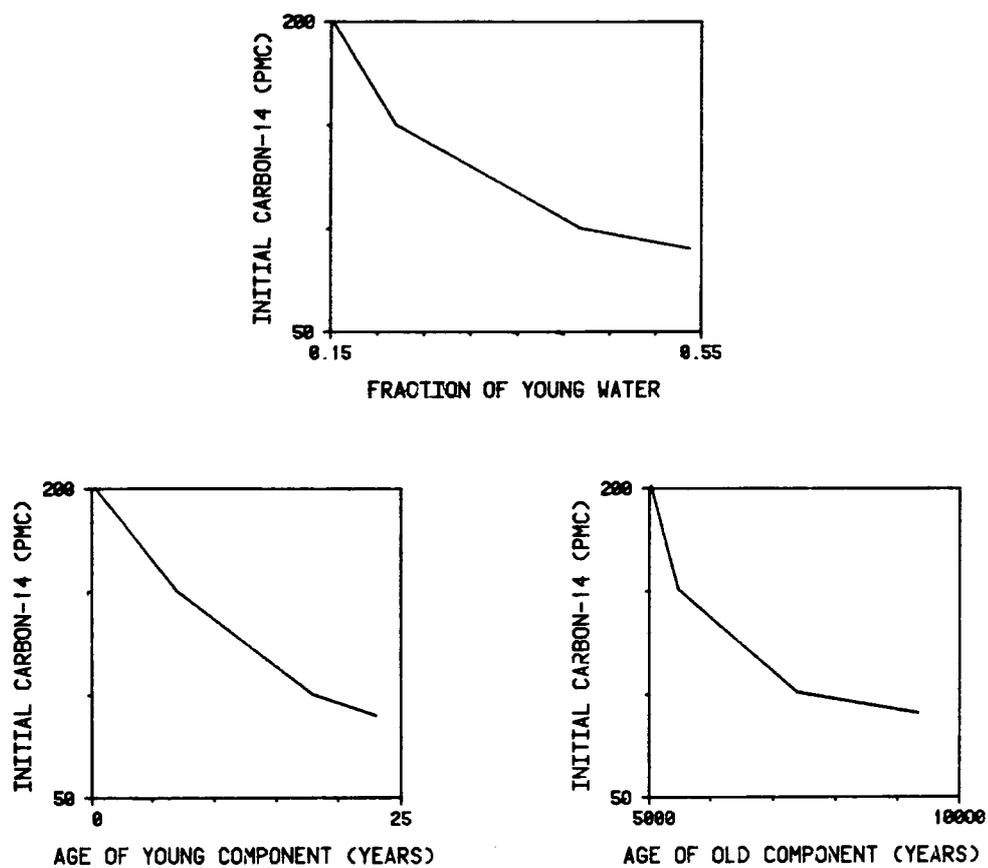


Figure 12. Sensitivity of two component system to initial carbon-14 input to young component.

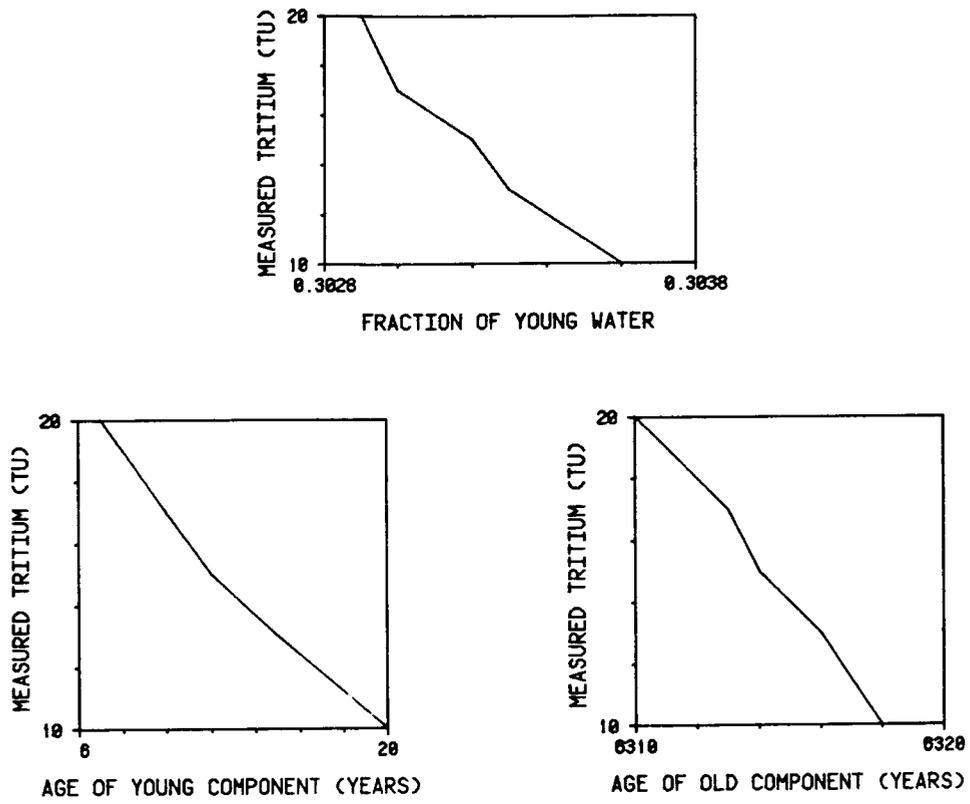


Figure 13. Sensitivity of two component system to measured tritium concentration.

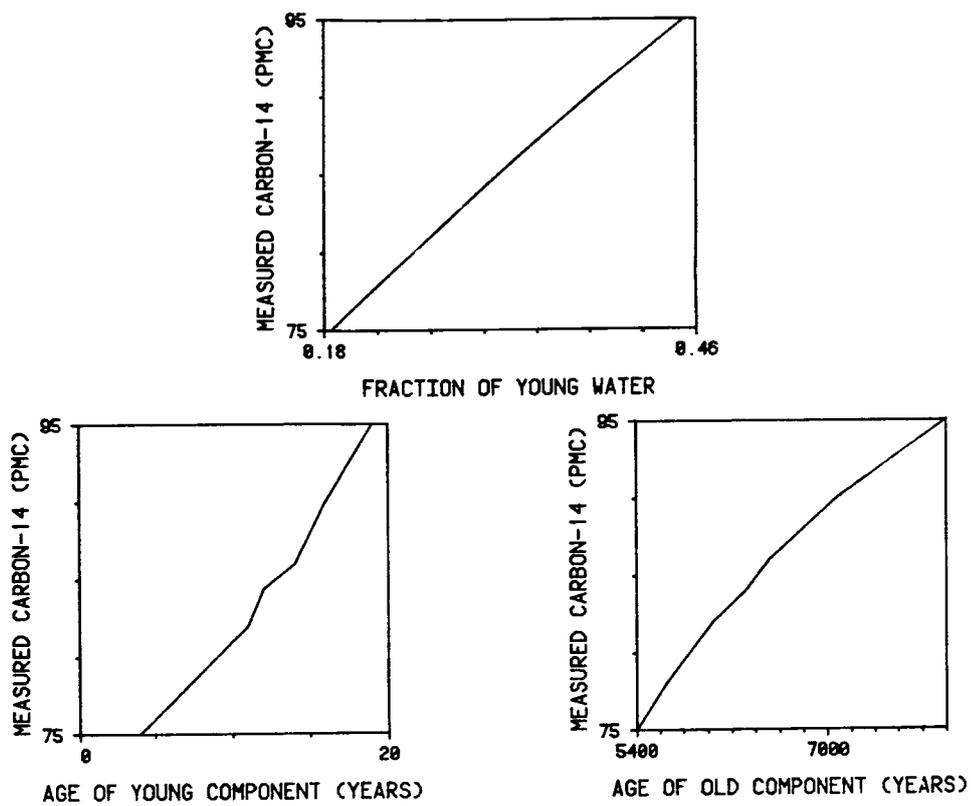


Figure 14. Sensitivity of two component system to measured carbon-14 concentration.

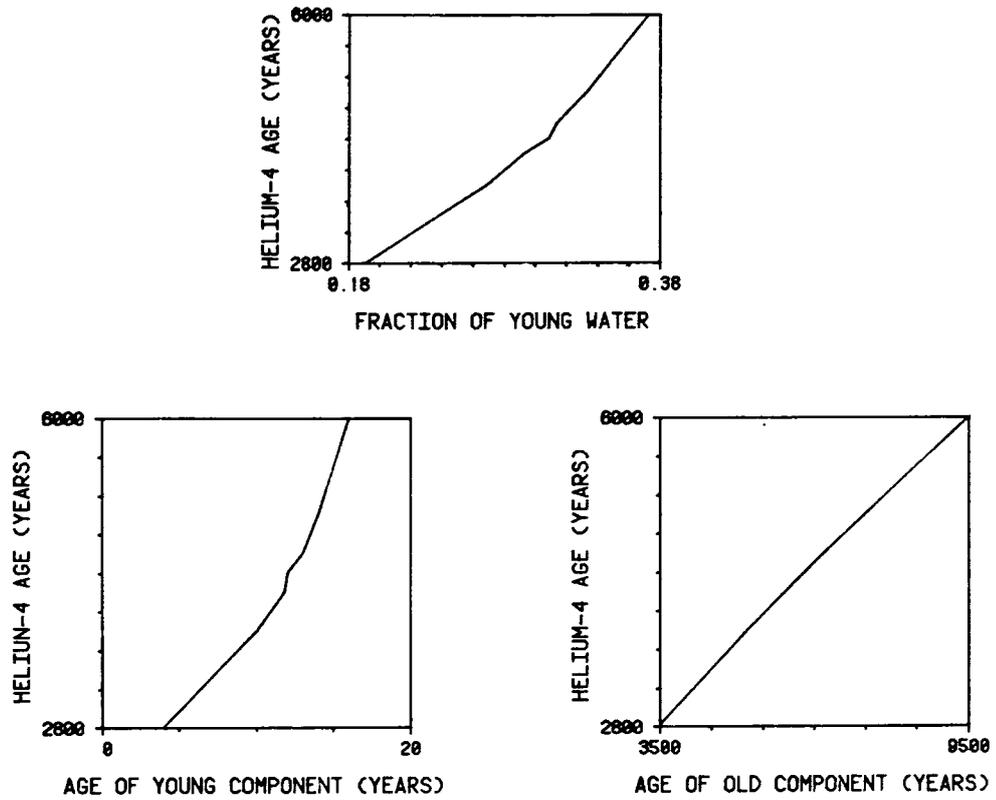


Figure 15. Sensitivity of two component system to helium-4 age estimate.

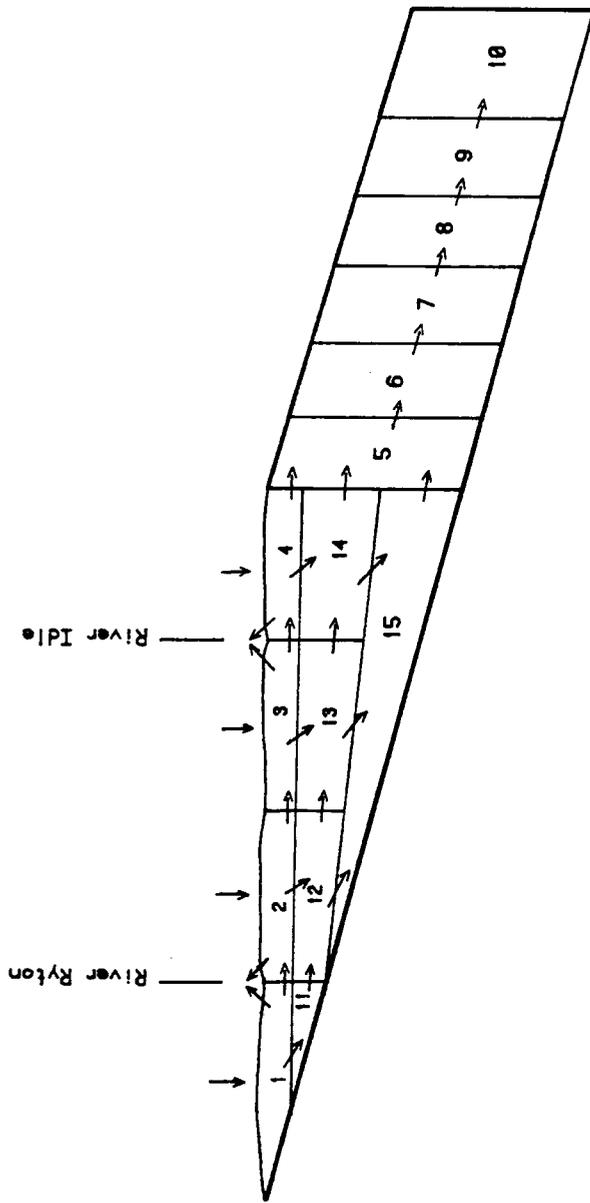


Figure 16. Schematic of Discrete State Compartment model of the Bunter aquifer.

considered to be one dimensional. The effective volumes of the cells are based on an effective porosity of 0.30 (Bath et al., 1978) and a thickness of 600 feet in the confined area.

Inputs are based on Land's (1966) reported estimates of infiltration in the area--about 7 inches per year. The inflows were divided evenly between cells 1 through 4. Outflows to the River Ryton and the River Idle, gaining streams which flow across the Bunter outcrop, were based on Land's estimates: about 85% of the infiltration is lost to these rivers and springs in the outcrop area. The volumes and recharge and discharge values of these cells are shown in Table 5.

The model was calibrated using the corrected carbon-14 concentrations shown in Table 2. Using a time step of 5 years, about 9000 iterations were required for all the cells to reach a steady state concentration (to 5 significant figures) after starting with an initial concentration of 0.0 pmc in all the cells. After reaching steady state, 20 years of thermonuclear bomb contaminated carbon-14 were introduced in 5-year increments averaging 120 pmc. The resulting carbon-14 distribution is shown in Table 6.

The model was validated using the reported tritium concentrations. The natural steady state tritium distribution was obtained using an input concentration of 10 tritium units. Steady state was reached after 1000 iterations with a time step of 1 year. After reaching steady state, 20 years of thermonuclear bomb tritium were introduced. These inputs were based on data from the International Atomic Energy Agency (1969) and Smith et al. (1976) and are tabulated in Table 7. The resulting distribution of tritium in the model is shown in Table 6.

Table 5. System recharge and discharge values for Discrete State Compartment model.

Cell No.	Effective Volume (10^{10} ft ³)	SBRV	BRV	SBDV
1	0.1190	0.0125	0.0125	0.0100
2	0.1190	0.0125	0.0140	0.0126
3	0.1190	0.0125	0.0133	0.0107
4	0.1190	0.0125	0.0141	0.0113
5	3.0290	0.0	0.0027	0.0
6	3.1680	0.0	0.0027	0.0
7	3.1680	0.0	0.0027	0.0
8	3.1680	0.0	0.0027	0.0
9	3.1680	0.0	0.0027	0.0
10	4.5000	0.0	0.0027	0.0027
11	0.3290	0.0	0.0010	0.0
12	0.9000	0.0	0.0011	0.0
13	1.1000	0.0	0.0016	0.0
14	1.1000	0.0	0.0019	0.0
15	2.6000	0.0	0.0023	0.0

Table 6. Tritium and carbon-14 concentrations in the Discrete State Compartment model

Cell No.	Tritium (TU)	Carbon-14 (pmc)
1	26.5	107.1
2	26.5	107.1
3	26.5	107.1
4	26.5	107.1
5	0.03	49.1
6	--	27.7
7	--	15.7
8	--	8.9
9	--	4.9
10	--	2.4
11	0.2	82.0
12	0.04	58.9
13	0.07	59.5
14	0.07	60.6
15	--	43.5

Table 7. Tritium input.

Year	Tritium (TU)
1953	15
1954	135
1955	15
1956	40
1957	25
1958	138
1959	110
1960	146
1961	43
1962	237
1963	917
1964	500
1965	180
1966	140
1967	100
1968	80
1969	80
1970	70
1971	50
1972	50
1973	50
1974	50
1975	40
1976	40

The observed and modeled distributions of tritium and carbon-14 are compared in Table 8. In general, there is fair agreement, within the ranges of the isotopically corrected observed values.

In the recharge area, the general circulation pattern defined by the model is one of relatively rapid circulation in the upper part of the aquifer, with older water in the deeper parts of the unconfined Bunter aquifer. The flow from the recharge area then moves down dip into the confined zone. Table 9 presents the flow distribution of the Discrete State Compartment model of the Bunter aquifer.

The mean ages of the fluid elements in the cells, as defined by the volumetric parameters in equation (22f), are tabulated in Table 10 and compared with the decay ages of the model. Using the impulse method, described in Section 2.8.3, the transit time distributions of the cells in the model were determined. Figures 17, 18 and 19 show these distributions for selected cells.

4.4 Discussion of Results

Three different models have been used to evaluate the transit time distributions of the water in the Bunter aquifer. Each model leads to transit time distributions which differ from the mean transit times determined by the decay age of corrected carbon-14 concentrations. The most significant departure from the carbon-14 decay ages is found in the results of the two piston flow components model. This model generally indicated old component ages much larger than the carbon-14 decay ages. These large differences may be due in part to the inclusion of

Table 8. Comparison of observed and modeled tritium and carbon-14 concentrations.

Well No.	Observed Values		Modeled Values		
	Carbon-14 Range (pmc)	Tritium (TU)	Mixing Cell(s)	carbon-14 (pmc)	Tritium (TU)
3	86.4 - 121	15 ± 2	58% 4, 42% 14	87.5	15.0
5	113 - 157	8 ± 2	38% 4, 62% 14	78.5	10.0
9	99.4 - 147	25 ± 2	4	107.1	26.5
10	84.1 - 114	4 ± 2	23% 4, 77% 14	70.2	6.0
11	69.6 - 99.5	10 ± 2	45% 4, 55% 14	82.0	12.0
12	96.4 - 142	2 ± 2	4	107.1	26.5
13	72.1 - 102	0 ± 2	8% 4, 92% 14	64.8	2.0
14	60.9 - 90.8	0 ± 2	1% 4, 99% 14	61.5	0.3
15	67.1 - 94.1	0 ± 2	8% 4, 92% 14	64.8	2.0
16	59.4 - 83.4	0 ± 2	5	49.1	0.03
17	43.9 - 65.5	0 ± 2	5	49.1	0.03
21	41.3 - 61.5	0.5 ± 2	5	49.1	0.03
22	1.3 - 2.8	0.3 ± 2	10	2.4	0.0
30	3.3 - 4.9	2.0 ± 2	9	4.9	0.0

Table 9. Distribution of flow in Discrete State Compartment model of the Bunter aquifer.

Output Cell	Input Cell	Flow as Fraction of Total BDV of Output Cell
1	2	0.12
1	11	0.08
2	3	0.06
2	12	0.04
3	4	0.12
3	13	0.08
4	5	0.12
4	14	0.08
5	6	1.00
6	7	1.00
7	8	1.00
8	9	1.00
9	10	1.00
11	12	0.50
11	15	0.50
12	13	0.50
12	15	0.50
13	14	0.50
13	15	0.50
14	5	0.50
14	15	0.50
15	5	1.00

Table 10. Comparison of decay ages and volumetrically determined mean transit times of cells in Discrete State Compartment model of Bunter aquifer.

Cell No.	Carbon-14 Decay Age (years)	Mean Transit Time (years)
1	modern	53
2	modern	53
3	modern	53
4	modern	53
5	5874	9040
6	10594	10022
7	15315	15988
8	20040	21953
9	24790	27918
10	30972	36391
11	1636	1697
12	4375	5073
13	4289	5162
14	4147	5025
15	8915	10756

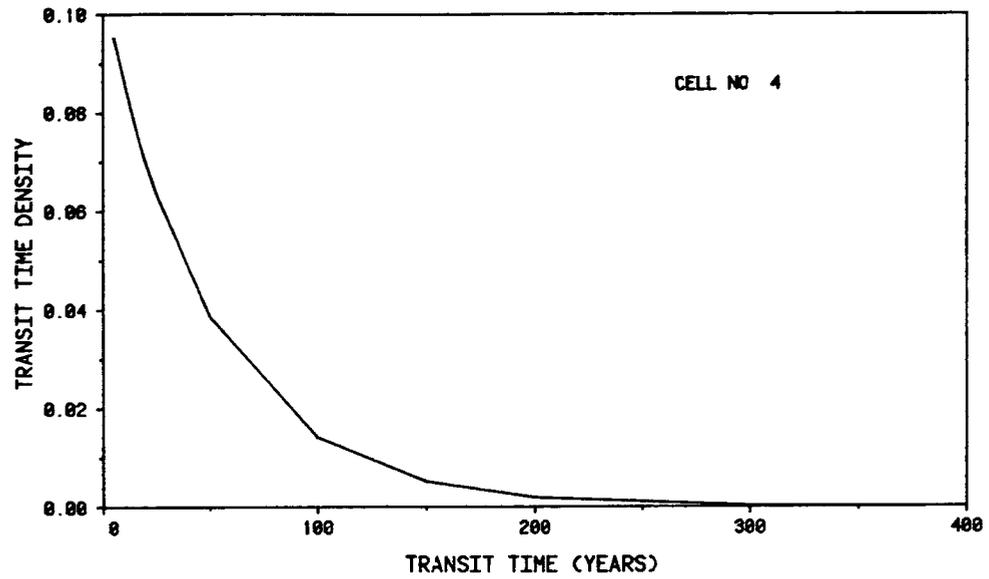


Figure 17. Transit time density function for cell no. 4.

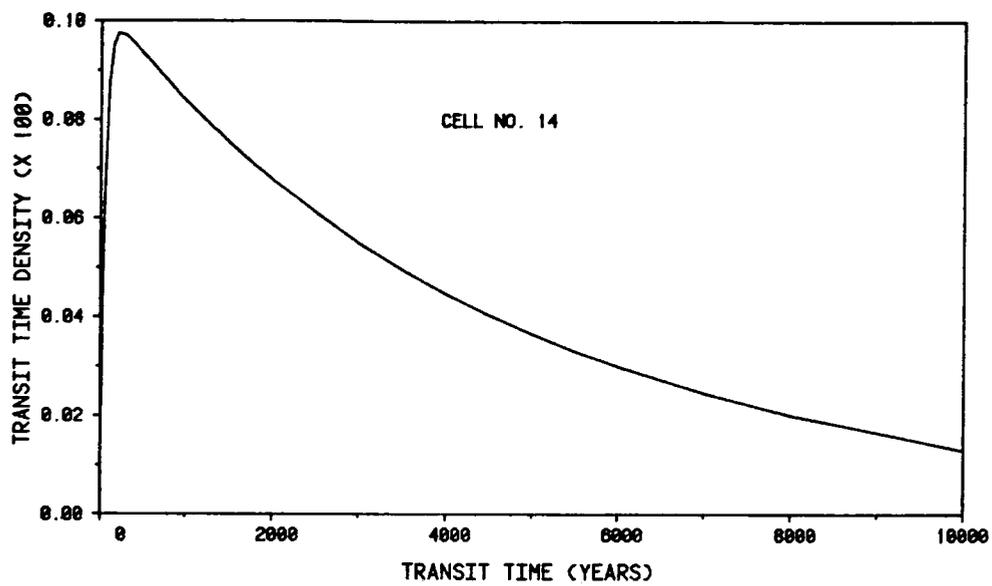


Figure 18. Transit time density function for cell no. 14.

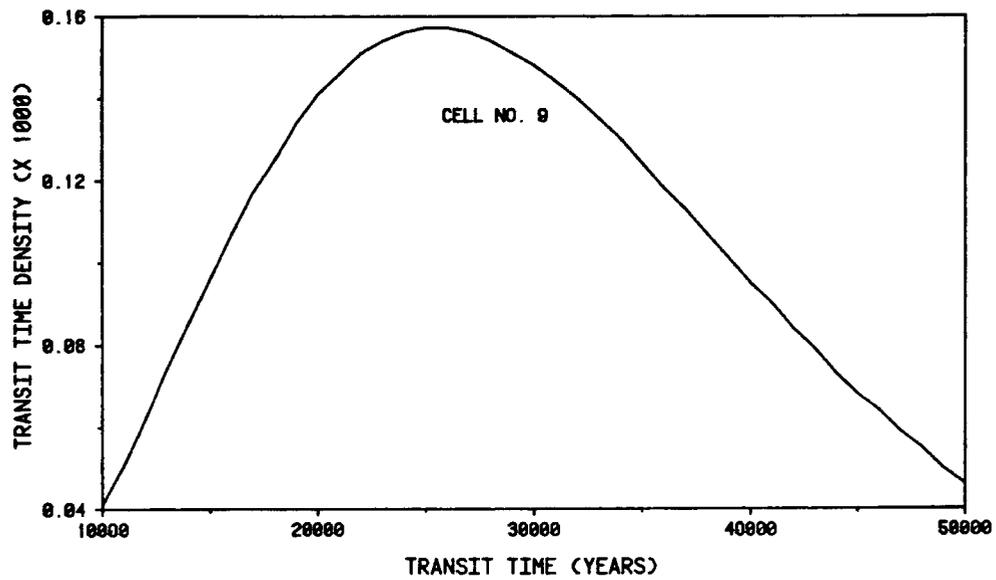


Figure 19. Transit time density function for cell no. 9.

of the helium-4 accumulation data, which indicated ages which were much greater than the carbon-14 ages.

The well mixed young component model also yielded significant corrections to the single component ages of Bath et al. (1978), although these corrections were not as extreme as the two piston flow components model. The true two component situation should probably include a young component somewhere in between these two models.

The Discrete State Compartment model was calibrated using the corrected carbon-14 concentrations, so not surprisingly, the mean transit times are similar to the single piston flow component ages in the unconfined portion of the aquifer. This model differs from the above two in that it does not allow for leakage of modern water into the deeper portions of the confined aquifer. But, as was pointed out earlier, the presence of small amounts of tritium in these waters may be the result of some sub-surface production. The Discrete State Compartment model does, however, support the two component concept in the unconfined portion of the Bunter. Here, measured concentrations of tritium and carbon-14 in samples from wells 3, 5, 10, 11, 13, 14 and 15 can be explained as mixtures of water from cells 4 and 14. In addition, the use of the impulse method in determining transit time distributions allows for a more realistic model of the actual distributions of transit times in the Bunter aquifer.

CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 Summary

In general, the decay age of a water sample and the average age or transit time of the sample are the same only in the special case of zero mixing or piston flow. This thesis has dealt with this problem of assessing the effects of dispersion and mixing on groundwater dating. I have reviewed the literature and attempted to present a unified discussion of the theoretical distributions of ages and transit times of fluid elements in hydrologic systems. Using this framework, transit time distributions for the piston flow, exponential, dispersive and mixing cell models were presented. In addition, distributions of two-component systems were introduced and the errors caused by not considering a two-component mixture in radionuclide dating were discussed.

This theoretical discussion continued as I outlined the potential use of independent age information in analyzing a two-component system. The simplifications in the mathematics that multiple tracer sampling and hydrodynamic age estimates allow were treated briefly.

Turning to a practical, "real world" application of these concepts, I examined some published hydrochemical data from the Bunter aquifer in England. This analysis indicated the importance of the model selected to represent the system to the determination of transit time distributions.

5.2 Conclusions

The data from the Bunter aquifer were used to evaluate the transit time distributions determined by three different models. The well mixed young component model is clearly the simplest to apply. Because it requires only tritium and carbon-14 information, this may be the most generally applicable model. While it does not include the helium-4 ages, owing to the large uncertainty associated with these ages, one might be better off excluding them from attempts to precisely quantify the constituents of a two-component system.

The two piston flow components model has been included in the treatment of the Bunter data mainly as an illustrative example of the potential use of multiple tracer sampling in determining transit time distributions. Results from the application of this model must be interpreted carefully; the variable modern tritium and carbon-14 inputs and also the problems of helium-4 dating certainly complicate the picture. Nevertheless, the judicious use of this model, accounting for the various possible values of the input parameters, will at least alert the hydrologist to alternative interpretations of radionuclide data.

The Discrete State Compartment model, although conceptually simple and easy to use, requires somewhat more effort than the above two models. However, this model is more flexible than the simpler two component models and probably comes closer to representing the actual hydrologic system.

The major limitation of all of the models considered appears to be uncertainties in the dating techniques themselves. In the case of

carbon-14 dating, attempts to correct for the isotopic evolution of the carbon may leave a fairly wide range of "corrected" carbon-14 concentrations. The recent carbon-14 and tritium inputs have been highly variable and in many cases can only be estimated. The calculation of groundwater age from excess helium-4 is very dependent on the porosity and radioelement contents of the aquifer. Because it is difficult to select single values of these parameters, the use of helium-4 to estimate groundwater age leaves considerable margin for error.

As the accuracy of existing dating techniques is improved and new methods are perfected, the procedures outlined in this paper may be used with greater confidence to quantify the mixing phenomena of flow through porous media. Despite shortcomings in current attempts to precisely define these phenomena, it is essential that possible mixing of young water with old water be considered, even if only with a simple model.

APPENDIX A

LIST OF SYMBOLS AND ABBREVIATIONS

A_o	Activity of tracer in direct recharge (disintegrations T^{-1})
A_r	Activity of tracer in underground flow (disintegrations T^{-1})
A	Measured activity (disintegrations T^{-1})
\bar{A}_N	Mean age number
\bar{A}	Mean age (T)
BDV	Boundary discharge volume (L^3)
BRV	Boundary recharge volume (L^3)
C	Concentration (ML^{-3})
C'	Instantaneous numerical tracer concentration (ML^{-3})
$C(N)_i$	Concentration of numerical tracer at iteration i (ML^{-3})
C_o	Constant concentration of inflowing tracer (ML^{-3})
$C()$	Outflow concentration at time () (ML^{-3})
C_n^m	Concentration of tracer "m" in component n (ML^{-3})
\bar{C}^m	Mean measured concentration of tracer "m" (ML^{-3})
C_{on}^m	Initial concentration of tracer "m" in component n (ML^{-3})
$E(t)$	Transit time distribution function
$F(t)$	Cumulative transit time distribution function
f	Fractional amount of younger water in a two component system
$I(T)$	Internal age distribution function
K_m	Inverse of decay constant λ for tracer "m" (T)

$M(t)$	Volumetrically based cumulative transit time distribution function
$M(T)$	Cumulative age distribution function
m_i^E	The i -th moment of the $E(t)$ function
pmc	Percent modern carbon
Q	Constant volumetric flow rate (L^3T^{-1})
$Q(\)$	Volumetric rate of outflow at time () (L^3T^{-1})
$Q_i(\)$	Volumetric rate of inflow at time () (L^3T^{-1})
R	Constant depending on porosity and radioelement contents of aquifer ($L^3M^{-1}T^{-1}$)
SBRC	System boundary recharge concentration (L^3)
t	Transit time (T)
t_0	Delay between input and output (T)
\bar{t}	Turnover time (T)
\bar{t}_ϕ	Mean volumetric transit time (T)
\bar{t}_E	Mean transit time of the flux (T)
T	Age (T)
\bar{T}_I	Mean age of water in the system (T)
\bar{T}	Mean transit time (T)
TU	Tritium units
v	Velocity (LT^{-1})
v_x	Velocity in x direction (LT^{-1})
v_y	Velocity in y direction (LT^{-1})
V	Effective volume (L^3)
VOL'	Volume of a boundary cell receiving a tracer (L^3)
x_0	Distance from recharge area to sampling point (L)

α	Dispersivity (L)
$\delta()$	Dirac delta function
λ	Radioactive decay constant (T^{-1})
σ^2	Variance
τ	Time or transit time where noted (T)
$\phi(t)$	Volumetrically based transit time density function

APPENDIX B

A GRAPHICAL TECHNIQUE FOR SOLUTION OF A TWO COMPONENT SYSTEM

Consider a simple groundwater system composed of 2 components of water of different ages. The 2 components will be mixed to some extent by dispersion and diffusion phenomena in the aquifer. The waters will also be mixed in the well where they are sampled. Analyses of radioactive isotopes in the water will yield an "apparent" age of the water, based on the average concentration of the isotope in the mixed water. The apparent ages derived from radioactive isotopes of different half-lives will, in general, be different. The actual ages of the 2 components will be a function of the average concentration of the radioisotope in the sampled water and the relative contributions to the sampled water of the 2 components. If the mean concentrations of three or more radioisotopes are known, we can solve for the relative contributions of the 2 components and the ages of them. A simple graphical technique has been developed to solve this problem.

The mean concentrations of three radioisotopes, say \bar{C}^A , \bar{C}^B , and \bar{C}^C , may be expressed as

$$\bar{C}^A = f C_1^A + (1-f) C_2^A \quad (1)$$

$$\bar{C}^B = f C_1^B + (1-f) C_2^B \quad (2)$$

$$\bar{C}^C = f C_1^C + (1-f) C_2^C \quad (3)$$

where \bar{C}^A is the mean concentration, C_i^A is the concentration of A in the i-th component, expressed as a fraction of modern concentration, f is the fraction of component 1 in the sampled water and (1-f) is the fraction of component 2 in the sampled water, and similar notation for equations (2) and (3).

The ages of the 2 components may be written as

$$t_1 = -K_A \ln C_1^A \quad (4)$$

$$t_2 = -K_A \ln C_2^A \quad (5)$$

where

t_i = age of water in component i

$$K_A = \frac{\text{half-life of A}}{\ln 2} = \frac{1}{\lambda}$$

Concentration of C_1^B and C_1^C can be expressed in terms of C_1^A :

$$C_1^A = e^{-t_1/K_A} \quad (6)$$

$$C_1^B = e^{-t_1/K_B} \quad (7)$$

$$\frac{C_1^A}{C_1^B} = \exp \left[\frac{t_1 (K_A - K_B)}{K_A K_B} \right] \quad (8)$$

Substituting equation (4) into equation (8) gives

$$\frac{C_1^A}{C_1^B} = \exp \left[\ln C_1^A \left(\frac{K_B - K_A}{K_B} \right) \right] = C_1^A \left[\frac{K_B - K_A}{K_B} \right]$$

So,

$$C_1^B = C_1^A C_1^A \left[\frac{K_A}{K_B} - 1 \right]$$

or

$$C_1^B = C_1^A \left[\frac{K_A}{K_B} \right] \quad (9)$$

Similarly, we may write

$$C_1^C = C_1^A \left[\frac{K_A}{K_C} \right] \quad (10)$$

$$C_2^B = C_2^A \left[\frac{K_A}{K_B} \right] \quad (11)$$

$$C_2^C = C_2^A \left[\frac{K_A}{K_C} \right] \quad (12)$$

Equation (1) may be rewritten as

$$C_1^A = \frac{\bar{C}^A - (1-f) C_2^A}{f} \quad (13)$$

Finally, substituting equations (9) through (13) into equations (2) and (3) gives

$$\bar{C}^B = f \left[\frac{\bar{C}^A - (1-f) C_2^A}{f} \right]^{K_A/K_B} + (1-f) C_2^A^{K_A/K_B} \quad (14)$$

$$\bar{C}^C = f \left[\frac{\bar{C}^A - (1-f) C_2^A}{f} \right]^{K_A/K_C} + (1-f) C_2^A^{K_A/K_C} \quad (15)$$

Equations (14) and (15) are two equations with two unknowns. Unfortunately, neither can be easily solved for the unknowns, f or C_2^A , explicitly. However, each equation can be solved for C_2^A as a function of f by a trial and error technique. These functions can be plotted as f versus C_2^A . The point of intersection which satisfies the constraints of the system will yield the correct values of f and C_2^A , and the ages of the 2 components can be determined.

A Numerical Example

Consider the case where C represents ^{39}Ar whose half-life is 270 years. Let B be ^{14}C , $T_{1/2} = 5730$ years, and A be ^{36}Cl , $T_{1/2} = 301,000$ years.

For the hypothetical case where $\bar{C}^A = 0.97925$, $\bar{C}^B = 0.3571$, and $\bar{C}^C = 0.0077$, equations (14) and (15) were solved for C_2^A for various values of f . The iterative process involved finding a value of C_2^A to satisfy the equations for the desired value of f using a programmable calculator. The results are tabulated below.

<u>f</u>	<u>C_2^A - equation (14)</u>	<u>C_2^A - equation (15)</u>
0.005	.9807	.9791
0.01	.9808	.9790
0.02	.9785	.9788
0.05	.9779	.9782
0.10	.9772	.9772
0.20	.9759	.9748
0.30	.9747	.9718

A plot of these values (Fig. 20) shows intersections at $f = 0.1$, $C_2^A = 0.9772$ and at $f = 0.015$, $C_2^A = .9789$. The second point of intersection, when solving for C_1^A yields $C_1^A = 1.002$ which implies a negative age. Thus, we may conclude that the correct solution is $(1-f) = 0.9$, $f = 0.1$, $C_2^A = 0.9772$. By equation (13), $C_1^A = .9977$. So by equations (4) and (5), $t_1 = 1000$ years, $t_2 = 10,000$ years.

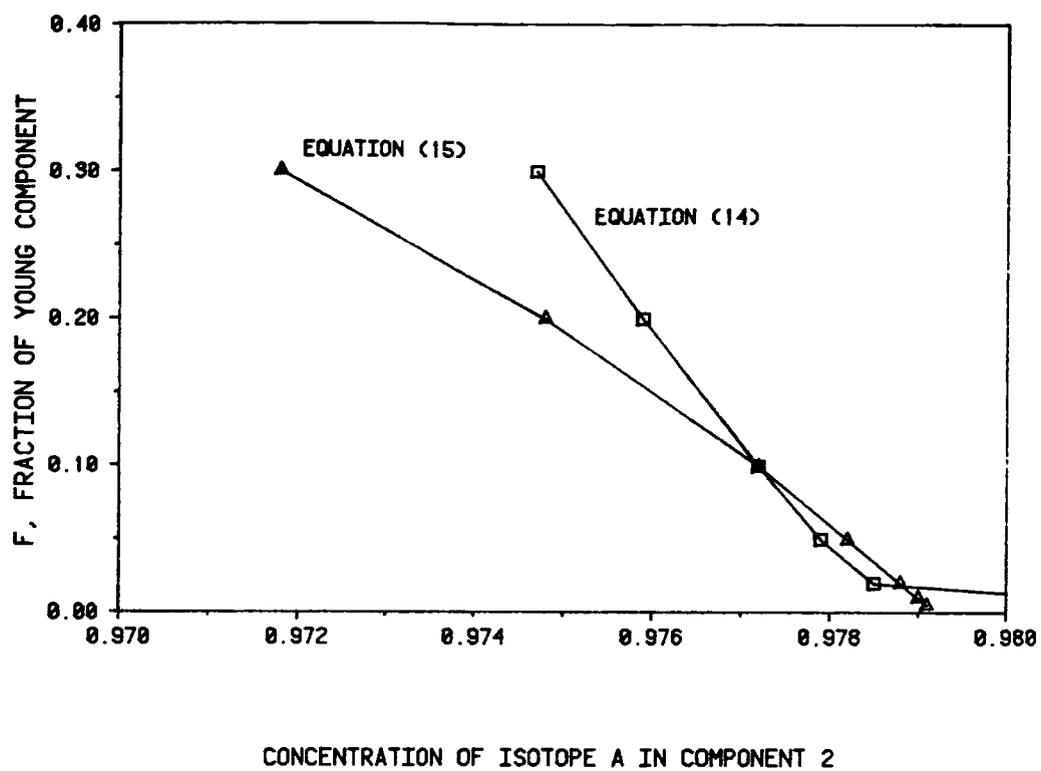


Figure 20. Graphical solution to the two component problem.

APPENDIX C

DERIVATION OF THE HELIUM-4 EQUATIONS

For a two component system with helium-4 and two radioactive isotopes available, if one of the isotopes is short-lived, the system of equations to be solved is:

$$\bar{C}^A = fC_{01}^A e^{-\lambda_A t_1} \quad (a)$$

$$\bar{C}^B = fC_{01}^B e^{-\lambda_B t_1} + (1-f)C_{02}^B e^{-\lambda_B t_2} \quad (b)$$

$$\bar{C}^{\text{He}} = (1-f)Rt_2 \quad (c)$$

Solving for f gives:

$$f = \frac{\bar{C}^A}{C_{01}^A} e^{\lambda_A t_1} \quad (d)$$

Solving for t_2 gives:

$$t_2 = \bar{C}^{\text{He}} (1-f)^{-1} R^{-1} = \frac{\bar{C}^{\text{He}}}{\left(1 - \frac{\bar{C}^A}{C_{01}^A} e^{\lambda_A t_1}\right) R} \quad (e)$$

Substituting (d) and (e) into (b) and rearranging gives:

$$\frac{\bar{C}^A}{C_{o1}^A} C_{o1}^B e^{t_1(\lambda_A - \lambda_B)} + \left[1 - \frac{\bar{C}^A}{C_{o1}^A} e^{\lambda_A t_1} \right] C_{o1}^B .$$

(f)

$$\exp \left[-\lambda_B \frac{\bar{C}^{He}}{R} \left(1 - \frac{\bar{C}^A}{C_{o1}^A} e^{\lambda_A t_1} \right) \right] - \bar{C}^B = 0$$

which is a form suitable for solution by the interval having method or Newton's method.

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