A GENERAL MATHEMATICAL MODEL FOR THE INTERPRETATION OF TRACER DATA AND CALCULATION OF TRANSIT TIMES IN HYDROLOGIC SYSTEMS

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Hydrology and Hydrogeology

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A general mathematical model for the interpretation of tracer data and calculation of the mean transit time of steady and nonsteady hydrologic systems is developed. The model takes the form of the 3-parameter gamma distribution, and accounts for seven mixing possibilities: perfect or complete mixing, piston flow or no mixing, the mixing type in between perfect and piston flow (partial mixing) and their combinations: exponential-piston flow or perfect-piston flow, perfect-partial, partial-piston flow, and perfect-partial-piston flow. Partial mixing is defined in terms of the mixing efficiency \( \mu \), which varies from zero for piston flow to unity for perfect mixing. The combination of perfect-partial-piston flow gives the general model from which all the other remaining six mixing possibilities are obtained as special cases. In other words, the proposed model represents a unified modeling approach as far as modeling of the mixing types and their combinations is concerned since all mixing types and their combinations can be modeled with one set of parameters.

The applicabilities of the proposed models are demonstrated by examples which resulted in good fitting, thus indicating reasonable estimates of the mean transit time and the other fitting parameters. In these examples, data obtained from two groundwater systems, site 45 and site 2, on Cheju Island, Republic of Korea, and one surface-water system, the Ottawa River Basin, Canada, are reinterpreted. Interpretations of site 45, site 2, and the Ottawa River Basin are made by the models of partial mixing, partial-piston flow, and perfect-partial mixing, respectively; mean transit times obtained for these systems are 2.4, 21.0, and 3.0 years, respectively. In addition, information other than the mean transit time about the systems is obtained from the fitting parameters.
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1.1 General

The current technique of using tracer data to estimate the mean transit or turnover time of water in groundwater systems is based on solutions provided by mathematical models. The models describe the tracer input-output relations for the system by means of the transit time distribution function. In general, the model is understood to be the distribution function that links the input and output. In groundwater systems, mixing due to hydrodynamic dispersion and molecular diffusion takes place and influences the tracer concentration. This effect is accounted for by assuming specific mixing fashion(s) in the development of the models.

The most commonly assumed mixing forms are the two extremes of "perfect mixing" and "piston flow". Perfect mixing refers to the situation in which tracer concentration in the system is homogeneous and the output concentration is identical to that within the system. On the other hand, piston flow occurs when fluid velocity is uniform over the entire system and each element of fluid that enters the system "marches" without intermingling with other fluid elements that entered earlier or later (Himmelblau and Bischoff, 1968). Stated differently, piston flow refers to the exceptional case of little or no dispersion in the system, i.e., no mixing. Perfect mixing, in general, is a characteristic of not-too-deep surface water systems (Kaufman and Libby, 1954), but is useful only as a limiting case for groundwater systems (Nir, 1964). Both perfect mixing and piston flow represent limiting cases that seldom occur in groundwater systems. It is most
probable that the type of mixing encountered in groundwater systems, or natural systems in general, lies somewhere between these two extremes. In this study, this type of mixing is called partial mixing.

1.2 Objective

The overall objective of this study is to develop a general mathematical model which accounts for all possible types of mixing (piston flow, partial and perfect mixing) and their combinations, which represents the simultaneous existence of the three or any two of the mixing types in the system, for the interpretation of transit times in steady and nonsteady groundwater systems.

The importance of this objective is explained in the following:

1. The proposed model accounts for seven mixing possibilities. These are the three basic mixing types and the combinations of perfect-partial-piston flow, perfect-partial, perfect-piston flow, and partial-piston flow. The first combination gives the general model from which all the six remaining possibilities are obtained as special cases. It is obvious that these combinations are more likely to occur in natural systems than piston flow, perfect mixing, or the combination of perfect-piston flow, which is the only combination modeled at the present time. Currently, there are no models to account for the first three combinations.

2. At the present time, partial mixing is modeled by the dispersive models (Nir, 1964; Maloszewski and Zuber, 1982) or discrete state compartment models (Przewlocki and Yurtsever, 1974; Campana, 1975; Simpson and Duckstein, 1976). As will be shown in section 1.4, these models have certain limitations. Accordingly, modeling of partial mixing, free from these limitations, the case in the proposed model, is desired.
3. Currently, there is no model available to account for the three mixing types and their combinations by one formula, i.e., one model from which the three mixing types and their combinations can be obtained as special cases. Clearly, a model with this ability, such as the proposed model, is required.

The stated objective is achieved by a lumped parameter model which will be successfully applied to real world situations. The model takes the form of the 3-parameter gamma distribution.

1.3 Lumped Parameter Models

The most common approach used in the interpretation of tracer data in hydrologic systems is the lumped parameter or "black box" approach (Zuber, 1986a).

As indicated earlier, the use of tracers to estimate hydrologic systems parameters is based on mathematical models which describe the tracer input-output relations for the system. Accurate modeling requires a very detailed knowledge of the system internal structure and the physical processes relating the input and output. Because of data limitations, it is often necessary to simplify the representation of these processes and the system structure. The most common simplification made is that of lumping or spatially averaging the input, output (system response) and the system parameters. In other words, the lumped parameter approach considers the overall way in which the system converts the input to an output, and does not concern itself with details, which, in any case, may not be known.

The mean transit time is the main parameter to be obtained in the lumped parameter approach. The approach is particularly useful in interpreting tracer data variable in time; however it does not give an unequivocal answer for systems
with constant tracer input unless some physical knowledge of the system is available (Zuber, 1985).

A review of the existing lumped parameter models that are used in the interpretation of tracer data in groundwater systems was given by Maloszewski and Zuber (1982). The models are: piston flow, exponential or perfect mixing, linear, exponential-piston flow, linear-piston flow, dispersive models, and discrete-state compartment models, the latter which can be considered as distributed parameter models with lumping if prior knowledge of the system exits. The piston flow model assumes that dispersion is negligible and flow velocity is uniform over the entire system. Thus, the tracer moves in the system with the mean velocity of water. In the exponential model, it is assumed that the exponential distribution of transit times corresponds to a probable situation of decreasing permeability with the aquifer depth (Eriksson, 1958). The exponential model is applicable to groundwater systems and it is mathematically equivalent to the perfect mixing model, which is applicable to surface water systems, as mentioned in section 1.1. The linear model assumes that the aquifer has a linearly increasing thickness and a uniform velocity. As a result of these restrictive assumptions, no practical application of this model is known (Zuber, 1986a). The models of exponential-piston flow and linear-piston flow combine the piston flow model with the exponential model and the linear model, respectively. As the case with the linear model, the linear-piston flow model has not been applied so far (Zuber, 1986a). The dispersive models are obtained from the solution of the unidimensional form of the dispersion equation. Four analytical solutions are possible depending on the boundary conditions which describe the injection-detection mode of the tracer, i.e., whether the tracer concentration is measured as a flux or resident concentration (see section 2.1 for the definition of these concentrations). Discrete state compartment models are mixing cell models. In these models, the
The system is divided into mixing cells which can be of any size, and may be arranged in one-, two-, or three-dimensional networks. Determination of tracer output concentration is made by specifying the mixing type and applying the conservation of mass to each cell.

1.4 Current Modeling of Partial Mixing

Currently, partial mixing is modeled by the dispersive models (Nir, 1964; Maloszewski and Zuber, 1982) and discrete-state compartment models (Przewlocki and Yurtsever, 1974; Campana, 1975; Simpson and Duckstein, 1976). However, these models have certain limitations. The dispersive model employs the unidimensional form of the dispersion equation; hence, it is limited to one-dimensional flow systems. Also, it is well known that reliable estimation of the scale-dependent dispersivity is very difficult. Furthermore, Zuber (1986a) reported that, in general, the use of the dispersive model in its lumped parameter form is not theoretically justified for systems other than packed beds (e.g., soil columns) or pipelines with turbulent or laminar flow including rivers and karstic conduits. This is true because the boundary conditions are easier to describe mathematically in such systems than in natural systems. In groundwater systems it is assumed that injection to the system takes place at a point, whereas it extends over the recharge area. Therefore, the dispersivity observed in the lumped parameter approach as applied to environmental tracers is an apparent one and has nothing to do with the real dispersion processes (Zuber, 1985).

Discrete-state compartment models, on the other hand, are convenient for modeling spatial variations of the parameters (i.e., they should be treated as distributed parameter models), but they are unsuitable for solving the inverse problem because of their large number of fitting parameters (Zuber, 1986a).
1.5 Tracer Interpretation in Nonsteady Flow Systems

In general, the interpretation of groundwater systems by the tracer method is usually made under the assumption of steady flow. Studies dealing with transient systems have recently started; the theoretical aspects of the subject are discussed by Lewis and Nir (1978). Nir (1973) has considered tracer relations in well (perfectly) mixed lakes in the nonsteady state. Niemi (1977) has approached the problem of interpreting tracer data in variable flow systems with the assumption of a constant volume system. Obviously, this approach is not applicable to nonsteady hydrologic systems because their volumes vary with time. In another attempt, Yurtsever and Payne (1978) applied a discrete-state compartment model to a system in which the cells are assumed to be perfectly mixed, and the turnover time constant; however the applicability of this approach is limited by these assumptions. Recently, Zuber (1986b) has developed a general approach for the interpretation of tracer data in variable flow systems. His approach avoided the limitations of Niemi (1977) and Yurtsever and Payne (1978). In general it can be stated that tracer theory for variable flow systems is in its infancy.

\[ C(t) = \frac{\Delta m(t)}{AV} \]

\[ \frac{\partial C}{\partial t} = \frac{Q}{AV} C + \frac{\Delta m}{AV} \]
CHAPTER 2

THEORETICAL BACKGROUND

The principles and concepts presented in this chapter are based mainly on the studies of Maloszewski and Zuber (1982) and Zuber (1985; 1986a; 1986b). For more details the reader is referred to these studies.

2.1 The Flux and Resident Concentrations

The common definition of the concentration is suitable only for immobile fluids. For mobile fluids or dynamic flow systems, such as groundwater systems, two concentration types can be defined: the resident concentration ($C_R$) and the flux concentration ($C_F$).

The resident concentration expresses the mass of solute ($\Delta m$) per unit volume of the fluid ($\Delta V$) contained in a given element of the system at a given instant, $t$:

$$C_R(t) = \frac{\Delta m(t)}{\Delta V} \quad (2-1)$$

$C_R$ is a mean concentration obtained by weighting over a given cross-section of the system.

The flux concentration expresses the ratio of the solute mass flux ($\Delta m/\Delta t$) to the volumetric fluid flux ($Q = \Delta V/\Delta t$) passing through a given cross-section:

$$C_F(t) = \frac{\Delta m(t)/\Delta t}{\Delta V/\Delta t} = \frac{\Delta m(t)}{Q \Delta t} \quad (2-2)$$
\( C_F \) is the mean concentration obtained by weighting volumetric flow rates through a given cross-section of the system.

Differences in the observed concentrations, whether \( C_F \) or \( C_R \), are due to the detection mode and the injection mode, or how the tracer is injected into the system. Two injection modes are possible: the tracer may enter the system either proportionally to the cross-sectional area or to the volumetric flow rates. The injection-detection modes are identified by two subscripts, the first of which refers to the injection mode and the second to the detection mode e.g., \( C_{FF} \) means the tracer is injected and detected in the flux, and \( C_{FR} \) denotes injection in the flux and detection in the resident concentration mode (\( C_R \)).

### 2.2 Steady State Systems

For systems in steady state, the mean transit time of water in the system or the turnover time, \( T \), is defined as:

\[
T = \frac{V_T}{Q}
\]  

(2-3)

where \( Q \) is the volumetric flow rate through the system, and \( V_T \) is the total volume of mobile water (accessible to the tracer) in the system.

Because the turnover time does not describe the system behavior sufficiently, it is necessary to define the transit time distribution or the exit-age distribution function, \( E(t) \), which describes the exit time distribution of fluid elements (water) of the system which entered the system at a given time, \( t = 0 \). The function is normalized in such a way that:
The mean transit time of water leaving the system is given by:

\[ \int_{0}^{\infty} t \, E(t) \, dt = T \quad (2-5) \]

Equations (2-4) and (2-5) pertain to the water; tracer behavior is treated below.

The mean transit time of a tracer (\( \bar{t}_t \)) is defined as:

\[ \bar{t}_t = \frac{\int_{0}^{\infty} t \, C_I(t) \, dt}{\int_{0}^{\infty} C_I(t) \, dt} \quad (2-6) \]

where \( C_I(t) \) is the tracer concentration observed at the measuring point as a result of an instantaneous injection at the entrance to the system at time \( t = 0 \); the subscript I stands for instantaneous. Equation (2-6) is applicable to any injection-detection mode. However, \( \bar{t}_t \) is equal to \( T \) only if an ideal tracer, a substance that behaves in the system exactly as the traced material, is both injected and measured in the flux, i.e., when \( C_{IF}(t) \) for an ideal tracer appears instead of the unspecified \( C_I(t) \) in equation (2-6). When \( \bar{t}_t \) differs from \( T \), then the tracer distribution does not follow that of the traced mass. Therefore, it will be necessary to define the tracer distribution, \( g(t) \).
The transit time distribution function or the exit age distribution function of a conservative tracer describes the exit time distribution of the particles of tracer which entered the system at time $t = 0$. The function is also called the system response function or the weighting function and is defined as:

$$g(t) = \frac{C_i(t)}{\int_0^\infty C_f(t') \, dt'}$$  \hspace{1cm} (2-7)

The above discussion shows that if $C_f(t)$ is represented by $C_{ff}$ for an ideal tracer, then the $g(t)$ function is identical with the $E(t)$ function. Accordingly, an ideal tracer can be defined as a substance that when injected and measured in the flux, has the same response function as the traced material (Zuber, 1986a).

When molecular diffusion exists in the system, the $g(t)$ function does not equal the $E(t)$ function and $\bar{t}_i$ differs from $T$. In this case, due to the exchange of tracer between flow lines of different velocities, both the $g(t)$ and $E(t)$ functions are not related to the velocity distribution of flow lines (Zuber, 1986a).

In hydrologic systems during recharge events tracer injection is usually continuous; therefore the entire past history of the input concentration should be taken into account. The convolution integral is used for this purpose. For systems in steady state, the convolution integral reads:

$$C_{out}(t) = \int_0^\infty C_{in}(t - t') \exp(-\lambda t') \, g(t') \, dt'$$  \hspace{1cm} (2-8a)

or:

$$C_{out}(t) = \int_0^\infty C_{in}(t - t') \exp(-\lambda t') \, g(t') \, dt'$$  \hspace{1cm} (2-8b)
\[ C_{\text{out}}(t) = \int_{-\infty}^{t} C_{\text{in}}(t') \exp \left\{ -\lambda(t - t') \right\} g(t - t') \, dt' \] (2-8b)

where

\[ C_{\text{out}}(t) = \text{output concentration}; \]
\[ C_{\text{in}}(t) = \text{input concentration}; \]
\[ \exp (-\lambda t') = \text{factor to correct for decay if a radiotracer is used}; \]
\[ \lambda = \text{radioactive decay constant}; \] and
\[ g(t') = \text{weighting function}. \]

In equation (2-8a) \( t \) is the calendar time and \( t' \) is the integration variable which represents the transit time or exit age of water. In equation (2-8b), \( t' \) is the time of entry, \( t \) is the time of exit and \( (t - t') \) is the transit time.

Equations (2-8a) and (2-8b) are applicable only to cases in which an instantaneous injection occurs in the flux (Zuber, 1986a). In groundwater systems, tracers entering the system with precipitation/infiltration are injected proportionally to the volumetric flow rates: the higher the infiltration rate, the higher the tracer amount that enters the system and the tracer concentration is weighted over the flow rates by nature itself (Zuber, 1986a). The situation may be different most noticeably in the case of \(^{14}\text{C}\), namely if \(^{14}\text{C}\) which enters the groundwater system via biogenic material is accompanied by dissolution of inorganic carbon. In this case, the amount of total dissolved carbon may differ from site to site and the injection of \(^{14}\text{C}\) may not be proportional to the volumetric flow rates (Maloszewski and Zuber, 1982; Zuber, 1986a).
2.3 Variable Flow Systems

In the nonsteady state, the transport of tracer is no longer represented by the tracer concentration alone but by the tracer mass flux. Therefore, the weighting function in this case, \( g_P(t,\tau) \), is defined as the transit time distribution of the tracer mass flux which entered the system at time \( \tau \), i.e., it depends on the time of entry and the time of leaving, \( t \). It is given by (Zuber, 1986b):

\[
g_P(t,\tau) = \frac{\Phi_I(t,\tau)}{\int_{\tau}^{\infty} \Phi_I(t,\tau) \, dt} = \frac{C_I(t,\tau) \, Q(t)}{\int_{\tau}^{\infty} C_I(t,\tau) \, Q(t) \, dt} \quad (2-9)
\]

where \( C_I(t,\tau) \) is the concentration, \( Q(t) \) is the volumetric outflow rate, and \( \Phi_I(t,\tau) \) is the output tracer flux resulting from an instantaneous injection of tracer. Note that equation (2-7) is a special case of equation (2-9) when \( Q(t) \) is constant.

The convolution integral in the case of nonsteady flow relates tracer mass fluxes rather than concentrations and is (Zuber, 1986b):

\[
c(t) = \frac{1}{V_T(t)} \int_{-\infty}^{t} \left[ \frac{C_{in}(\tau) \, Q_{in}(\tau)}{\lambda(t - \tau)} \right] C_I(z) \exp[-\lambda(t - \tau)] \, d\tau \quad (2-10)
\]

where

\[
Q_{in}(\tau) = \text{inflow volumetric flow rate};
\]

\[
C_I(z) = C_I(t,\tau) \frac{Q_T(t)}{M}; \text{ and}
\]

\[
z = \int_{\tau}^{t} \frac{Q(t')}{V_T(t')} \, dt'. \quad (2-11)
\]
$C_f(z)$ is the dimensionless concentration expressed in the dimensionless time variable, $z$, the actual time divided by the mean transit time. Physically, equation (2-12) gives the fraction of water which passed through the variable volume system in the time interval $t - \tau$. The normalized response function $C_f(z)$ is given by analytical expressions identical to those of steady state models; for the proposed model, these will be shown in section 4.4.2.

3.1 Introduction

The mean transit time is the main parameter determined from tracer data by the proposed parameter approach. The mean transit time is of great practical interest because it allows estimation of other important parameters, such as the total volume of mobile water and the average effective porosity of the groundwater system. Knowing $Q$ and $T$ allows the volume of mobile water to be determined from equation (3-12), and given the system volume, the effective porosity can be estimated by the ratio of the mobile water volume to the system volume.

Quantitative interpretation of tracer data is particularly useful in investigating systems which lack detailed hydrologic data and systems where the traditional hydrologic methods do not give satisfactory results, such as small karstic or fractured systems (Zuber, 1958). Considering the fickian flow groundwater systems in most of the developing countries characterized by subtle hydrologic observations, the use of tracers can be promising for the evaluation of groundwater.
CHAPTER 3

DETERMINATION OF THE MEAN TRANSIT TIME
BY THE LUMPED PARAMETER APPROACH

This chapter discusses the use of tracer data in estimating the mean transit time or turnover time by the lumped parameter approach. This approach is followed in this study, since it is the most common and most applicable for quantitative interpretation of tracer data in groundwater systems. Procedures introduced in this chapter are used in chapter 5, where the proposed model is applied to evaluate the mean transit time.

3.1 Introduction

The mean transit time is the main parameter determined from tracer data by the lumped parameter approach. The mean transit time is of great practical interest because it allows evaluation of other important parameters such as the total volume of mobile water and the average effective porosity of the groundwater system. Knowing Q and T allows the volume of mobile water to be determined from equation (2-3), and given the system volume, the effective porosity can be estimated by the ratio of the mobile water volume to the system volume.

Quantitative interpretation of tracer data is particularly useful in investigating systems which lack detailed hydrologic data and systems where the traditional hydrologic methods do not give satisfactory results, such as karst formations or fractured systems (Zuber, 1986a). Considering the fact that groundwater systems in most of the developing countries are characterized by little hydrologic observations, the use of tracers can be promising for the evaluation of groundwater
resources in these countries, especially those affected by the recent drought in Africa.

3.2 Mean Transit Time and Mean Age

Groundwater dating is the estimation of the groundwater age, the elapsed time since the groundwater was recharged. In this regard it is important to distinguish between two different concepts, namely the age and the transit or residence time. The age of a water molecule in the system is the time elapsed since the molecule entered the system up to the instant of observation; the transit time is the time a molecule spends in the system from the time it enters the system until it leaves it (Nir and Lewis, 1975). Clearly, the age is less than the transit time except at the system exit where they are equal. The only other case where the mean age and mean transit time are equal is that of perfectly mixed systems (Bolin and Rodhe, 1973). Nir and Kirk (1982) indicated that the failure to realize that the mean age and mean transit time are different has been the cause of repeated confusion in tracer literature.

3.3 Determination of the Mean Transit Time

The mean transit time can be obtained from tracer data by finding the proper mathematical model, or weighting function, which relates the input and output concentrations. Determination of the mean transit time is made graphically by fitting curves of experimental and calculated output concentrations in the case of variable input and analytically when the input is constant and flow is steady. In either case, the appropriate weighting function that best suits the investigated system should be selected on the basis of all available information. The procedure in both cases is based on calculation of the output concentration...
by the convolution integral (equation 2-8 for steady and 2-10 for nonsteady flow) using the known inputs and the selected weighting functions.

In the case of transient inputs, the mean transit time is obtained from the best fit of the calculated and observed output concentrations time records, graphs of calculated and observed output concentrations as a function of time. In this case, the appropriate model should be selected before fitting is attempted. If the selection is not possible prior to the fitting, and if more than one model give equally good fits but with different parameter values, then the selection has to be made after the fitting (Zuber, 1986a).

Analytical evaluation of the mean transit time in the case of constant input and steady flow requires no additional information if the selected model is a one-parameter model, such as a piston flow or perfect mixing model. For two- or more parameter models, on the other hand, prior knowledge of the parameters other than the mean transit time, the unknown, is necessary. In practice, however, knowledge of these parameters a priori is very difficult. In contrast, the case of variable inputs provides these parameters and the mean transit time as a result of the fitting. Therefore, it can be seen that tracers with variable inputs are more flexible and offer better opportunities to determine the mean transit time than those with constant inputs (Maloszewski and Zuber, 1982). It is important to mention here that the case of constant input in the pre-thermonuclear era is a common assumption for the environmental radioisotopes tritium (\(^{3}\)H), \(^{14}\)C, \(^{39}\)Ar, \(^{85}\)Kr and \(^{32}\)Si (Nir and Lewis, 1975; Maloszewski and Zuber, 1982).

The previous discussion shows that whether the input is variable or constant, selection of the appropriate model should be physically justified. However, the piston flow model is commonly used in the determination of the mean transit time without any justification other than its mathematical simplicity. Furthermore,
the piston flow model can be applied to systems with little dispersion and constant input or monotonically changing input, but for variable inputs it does not even approximate systems with little dispersion (Zuber, 1986a).

3.4 The Combined Interpretation

In systems lacking long records of tracer output concentrations, the mean transit time can be evaluated by the combined use of several tracers, the so-called combined interpretation (Grabczak et al., 1982; Zuber, 1986a).

In the combined interpretation, several models are fitted to the output of one tracer whose input is known. These models are then used to calculate the output concentrations of several other tracers based on their known inputs. The model which results in the best agreement of calculated and observed output concentrations of these tracers is selected as the appropriate model, and the mean transit time is the one provided by this selected model. As mentioned above, all the tracers employed in the combined interpretation have short record of output concentrations which do not allow any of them to be interpreted alone by the procedure indicated in section 3.3.

Examples for the combined interpretation can be found in Grabczak et al. (1982). In one of these examples, two exponential models and two dispersive models with different parameters were fitted to $^{85}$Kr data and then used to calculate the output concentration of tritium and $^{14}$C. In this example, the proper model was found to be one of the exponential models since it produced a good agreement between $^{14}$C and tritium observed and calculated output concentrations.
3.5 Environmental Radioisotopes of Hydrologic Interest

The term environmental isotopes is used to indicate globally-distributed isotopes which are of natural or man-made production (e.g., tritium and $^{14}$C from thermonuclear testing).

Environmental radioisotopes commonly used or of potential use in groundwater studies are shown in Table 3-1. Of these, tritium and $^{14}$C are the most widely used at present. Due to analytical problems or the necessity for large sample size the other radioisotopes are not used routinely. Among these, $^{36}$Cl will probably be used routinely in another decade after the present analytical problems are solved (Davis et al., 1985).

The following discussion is restricted to the advantages, limitations, and the general modeling aspects of using these radioisotopes to estimate the mean transit time by the lumped parameter approach.

The major problem with the tritium method is the determination of the tritium input function, the tritium concentration in the recharge water, which has been variable since 1952, the beginning of large-scale atmospheric thermonuclear testing. Calculation of the input function requires knowledge of the seasonal variations of tritium concentration in precipitation, and the contributions of summer and winter infiltration to groundwater (Dincer and Davis, 1967; Davis et al., 1967; Martinec et al., 1974; Maloszewski and Zuber, 1982; Zuber, 1986a). Details of constructing the input function are given in the next section.

Another limitation in the tritium method is that tritium has a short half-life (12.26 years) which makes it useful for dating only relatively young waters no older than about 50 years old.

Because tritium concentrations in many groundwater systems are equilibrating with time, thus making quantitative interpretations very difficult, it has been
### Table 3-1

Environmental radioisotopes of hydrologic interest

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>Half-life (years)(^d)</th>
<th>Useful Age Range (years)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{85})Kr</td>
<td>10.76</td>
<td>3-30</td>
</tr>
<tr>
<td>(^{3})H</td>
<td>12.26</td>
<td>5-50</td>
</tr>
<tr>
<td>(^{32})Si</td>
<td>103(^a,)(^b)</td>
<td>50-100</td>
</tr>
<tr>
<td>(^{39})Ar</td>
<td>269</td>
<td>100-1000</td>
</tr>
<tr>
<td>(^{14})C</td>
<td>5730</td>
<td>500-3000</td>
</tr>
<tr>
<td>(^{81})Kr</td>
<td>210,000</td>
<td>50,000-800,000(^c)</td>
</tr>
<tr>
<td>(^{36})Cl</td>
<td>301,000</td>
<td>50,000-2X10(^6)</td>
</tr>
</tbody>
</table>

\(^a\) Source = Davis et al. (1985).

\(^b\) See text for \(^{32}\)Si half-life.

\(^c\) Source = Oeschger (1978).

\(^d\) Source = Davis and Bentley (1982).
suggested (Maloszewski and Zuber, 1983) to couple the tritium method with the parent-daughter method of $^3$H-$^3$He in which the peak concentration of the daughter $^3$He is delayed relative to that of tritium.

Another radioisotope widely used in groundwater dating is $^{14}$C. Its long half-life (5730 years) allows dating of waters 500 to at least 30,000 years old (Davis et al., 1985).

The major input of $^{14}$C to the groundwater system is from the soil zone carbon dioxide, because the input of carbon dioxide dissolved in precipitation is very small owing to the low partial pressure of atmospheric carbon dioxide (Payne, 1972). Due to the fact that carbonate minerals, which are very old and consequently contains no $^{14}$C, dissolve readily in the infiltrating water containing carbon dioxide from the soil zone, water reaching the groundwater system will contain a mixture of modern and dead carbon (carbon without $^{14}$C). Therefore, in order to date water with $^{14}$C, one must correct for the dead carbon. Models used for this purpose can be found in Wigley et al. (1978), Reardon and Fritz (1978), Fontes and Garnier (1979), and Mook (1980). In all these studies, the piston flow model is used to determine the age or transit time and the correction is applied to the calculated output concentrations of carbon in order to obtain a value which would be expected as a result of all processes except radioactive decay. In this case, the input concentrations are multiplied by the correcting factor. To allow the use of more realistic models other than the piston flow model, Grabezak et al. (1982) proposed correction of the experimental (observed) output concentrations rather than the calculated outputs to obtain the values which would be observed if there were no changes caused by hydrochemical processes. In this approach, the experimental output concentrations are divided by the correction factor and then fitted to the uncorrected calculated outputs.
Because the half-life of $^{32}$Si is intermediate between those of tritium and $^{14}$C, it has been suggested (Gaspar and Oncescu, 1972; Payne, 1972) to date water which is between 50 and 1000 years old, water that cannot be dated with tritium or $^{14}$C. At the present time, however, the $^{32}$Si method of dating is suspect because the geochemistry and the half-life of this radioisotope are not well known (Maloszewski and Zuber, 1982). Published values of the half-life vary from 101 to 710 years (Davis and Bentley, 1982).

The major advantages of dating groundwater with $^{36}$Cl are: the lack of chemical interactions in the aquifer; the ability to date groundwater older than 50,000 years; and the recent advances in analytical techniques which require a small sample size about 10 mg of chloride (Bentley et al., 1986). Problems with $^{36}$Cl dating, on the other hand, include: possible isotope fractionation due to membrane effects of groundwater passing through silt and clay beds; cross-formational flow of groundwater in aquifers which appear to be isolated by non-permeable beds but actually are not; possible diffusion of dead (non-radioactive) chloride from fluid inclusions in minerals within crystalline rocks; and subsurface production of $^{36}$Cl (Davis and Bentley, 1982).

The advantages of using $^{85}$Kr and $^{81}$Kr in groundwater dating derive from their chemical inertness with aquifer materials and well-known atmospheric activities (Florkowski and Rozanski, 1986). Unfortunately, the natural concentrations of these radioisotopes are very small, thus large water sample sizes of 120 to 360 liters and about $10^6$ liters are required for $^{85}$Kr (Rozanski and Florkowski, 1979) and $^{81}$Kr (Oeschger, 1978), respectively. In addition, sophisticated analytical techniques are needed for the radioactivity detection of these isotopes (Florkowski and Rozanski, 1986).
Attempts to date groundwater by $^{85}\text{Kr}$ include those of Rozanski and Florkowski (1979), and Grabczak et al. (1982). As a noble gas, $^{85}\text{Kr}$ should be an ideal tracer for confined aquifers provided no deep production of $^{85}\text{Kr}$ occurs (Zuber, 1986a). However, application of $^{85}\text{Kr}$ to phreatic aquifers may result in underestimation of the mean transit time of water in these aquifers due to direct diffusion of atmospheric $^{85}\text{Kr}$ in the gaseous phase through the unsaturated zone to the water table (Grabczak et al., 1982; Florkowski and Rozanski, 1986). The use of $^{85}\text{Kr}$ to date groundwater may provide better results than the tritium method, where the input function is complicated (Rozanski and Florkowski, 1979). On the other hand, the $^{81}\text{Kr}$ method of dating, if it proves feasible, would be comparable to that of $^{36}\text{Cl}$ since their half-lives are somewhat close (Florkowski and Rozanski, 1986).

$^{39}\text{Ar}$, similar to $^{85}\text{Kr}$ and $^{81}\text{Kr}$, has no chemical interaction with the aquifer material (Oeschger et al., 1974), and has a regular input function and roughly constant atmospheric concentration (Florkowski and Rozanski, 1986). In addition, its half-life of 269 years makes it useful for dating water ranging in age from 50 to 1000 years (Oeschger et al., 1974).

The major difficulty with the application of $^{39}\text{Ar}$ method is the possible underground production of this radioisotope (Loosli and Oeschger, 1979), that can be as high as four times the present atmospheric level, which causes the estimated ages to be younger than they actually are. Other difficulties with the method include the need for large water samples, about 15,000 liters, and sophisticated analytical techniques (Florkowski and Rozanski, 1986).
3.6 Tritium Input Function

Following the period of large-scale atmospheric thermonuclear testing (1952 - 1963), tritium concentrations in precipitation have declined after peaking in 1963 although seasonal variations are still pronounced. In order to account for these seasonal variations, it was proposed (Dincer and Davis, 1967; Davis et al., 1967) to calculate tritium input concentrations or mean yearly concentrations weighted by the monthly amounts of precipitation and monthly values of infiltration coefficients. The input concentration ($C_{in}$) for each year can be expressed as:

$$C_{in} = \frac{\sum_{i=1}^{12} \alpha_i P_i C_i}{\sum_{i=1}^{12} \alpha_i P_i}$$  \hspace{1cm} (3-1)$$

where $\alpha_i$ is the monthly value of the infiltration coefficient, $P_i$ is the precipitation in the $i$th month, and $C_i$ is the tritium concentration in the precipitation of the $i$th month.

Because the infiltration coefficients are usually unknown, equation (3-1) is simplified by assuming two infiltration coefficients, each of which is constant, representing the summer ($\alpha_s$) and winter ($\alpha_w$) months. Introducing $\alpha_s$ and $\alpha_w$ into equation (3-1) gives:

$$C_{in} = \frac{\alpha_s \sum(P_i C_i)_s + \alpha_w \sum(P_i C_i)_w}{\alpha_s \sum(P_i)_s + \alpha_w \sum(P_i)_w}$$  \hspace{1cm} (3-2)$$

Assuming the summer infiltration coefficient to be a given fraction ($\alpha$) of the
winter coefficient equation (3-2) simplifies to:

\[ C_{in} = \frac{\alpha \sum(P_i C_i)_s + \sum(P_i C_i)_w}{\alpha \sum(P_i)_s + \sum(P_i)_w} \] (3-3)

Construction of the input function is made by equation (3-3) for the known \( C_i \) and \( P_i \) data of each year, and for an assumed \( \alpha \) value.

For example, Dincer and Davis (1967) used \( \alpha = 1 \) (equal infiltration coefficients throughout the year), and Dincer et al. (1970) used \( \alpha = 0 \) (no infiltration in the summer months).

Recently, Grabczak et al. (1984) have proposed a method for estimating \( \alpha \) based on the seasonal variations of the stable isotopes \( ^{18}O \) or \( D \) in precipitation. In this method, \( ^{18}O \) or \( D \) is used in equation (3-3) instead of \( C_{in} \) and \( C_i \) to give:

\[ \alpha = \frac{(\delta P_w - \delta G) \sum(P_i)_w}{(\delta G - \delta P_s) \sum(P_i)_s} \] (3-4)

where \( \delta G \) is the mean value of \( ^{18}O \) or \( D \) of the groundwater at the outlet of the system and \( \delta P_w \) and \( \delta P_s \) are the long term weighted mean values of \( ^{18}O \) or \( D \) for winter and summer precipitation, respectively:

\[ \delta P_w = \frac{\sum(P_i \delta P_i)_w}{\sum(P_i)_w} \] (3-5)
In areas lacking surface runoff, equation (3-1) can be used and the $\alpha_i$ coefficients can be found from the actual evapotranspiration and precipitation data (Zuber, 1986a). The study of Andersen and Sevel (1974) is an example of this approach.

\[
\delta P_s = \frac{\sum (P_i \delta P_i)_s}{\sum (P_i)_s}
\]  

(3-6)
CHAPTER 4

THE MODEL

4.1 Necessary Conditions for Application

From chapter 2, it is clear that when an ideal tracer is injected and measured in the flux and if tracer diffusion between flow lines of different velocities is negligible, then the transit time distribution functions of the tracer and water are identical and both are related to the distribution of flow velocities.

Of the currently-used lumped parameter models, only the dispersive model is capable of accounting for the effects of molecular diffusion. All the other models assume that the transit time distribution functions of tracer and water are related to the velocity distribution of flow lines, i.e., molecular diffusion is negligible. In addition, these models require an ideal tracer to be injected and measured in the flux, i.e., the $C_{FF}$ case. The proposed model is no exception. The two conditions mentioned above, have to be met before the model can be applied. However, it can be stated that these conditions are not that restrictive since molecular diffusion is negligible compared to hydrodynamic dispersion for most field situations (Bredehoeft and Pinder, 1973), especially in large scale systems, and samples of the type $C_R$ are difficult to collect in environmental systems whereas those of the type $C_F$ are easier to obtain from outflows (springs) or abstraction wells.

Specific situations in which the model is not applicable are porous fractured aquifers with stagnant water in the micropores and groundwater systems with stagnant water zones accessible to the tracer. Such systems should be interpreted by models which account for the tracer diffusion into these zones (Zuber, 1986b). Stagnant water zones which are not accessible to the tracer, on the other hand,
are not included in $V_T$, the total volume of mobile water in the system, and have no influence on the tracer data. Therefore the model is applicable in this case. However in actual field situations, the existence or nonexistence of stagnant zones is usually not known.

4.2 Partial Mixing

As indicated in section 1.1, partial mixing describes the type of mixing in between piston flow and perfect mixing. Partial mixing can range from near perfect mixing (as an upper limit) to near piston flow (lower limit), but never reaches these extremes. In order to specify the exact location of partial mixing in the range between piston flow and perfect mixing, the concept of mixing efficiency is introduced. In hydrologic systems, mixing is due to hydrodynamic dispersion and molecular diffusion. As indicated earlier, the proposed model is applicable to systems in which molecular diffusion is negligible. Accordingly, it is proposed to define mixing efficiency, $\mu$, as a lumped parameter that describes mixing due to hydrodynamic dispersion. In other words, it is a parameter that assigns the extent or degree of mixing an average value. Hence, mixing efficiency is like any other parameter used in a lumped parameter model, which is the case in this study. Based on the above definition, it can be stated that:

$$\mu = \begin{cases} 
1 & \text{for perfect mixing} \\
0 & \text{for piston flow} 
\end{cases}$$

and partial mixing is defined as the mixing type which is characterized by a mixing efficiency value somewhere between 0 and 1 ($0 < \mu < 1$).
4.3 Model Development

4.3.1 The 3-parameter gamma distribution. It was observed that the exponential-piston flow model (EPM) is a special case of the 3-parameter gamma distribution when \( \alpha = 1 \), where \( \alpha \) is the shape parameter of the 3-parameter gamma distribution (\( \alpha \) is the parameter that determines the shape of the distribution).

The 3-parameter gamma distribution is defined as (Yevjevich, 1972):

\[
g(t) = \frac{1}{\beta^\alpha \Gamma(\alpha)} (t - \gamma)^{\alpha - 1} e^{-\frac{(t - \gamma)}{\beta}} ; \quad t \geq \gamma, \gamma \neq 0 \tag{4-1}
\]

where \( \beta \) and \( \gamma \) are the scale and location parameters, respectively, and \( \Gamma(\alpha) \) is the gamma function. The value of \( \beta \) determines the vertical and horizontal extent of the distribution, and \( \gamma \) locates the point from which the distribution starts on the abscissa (see Figure 4-1).

The mean, \( E(t) \), and variance, \( \text{Var}(t) \), for the 3-parameter gamma distribution are given by (Yevjevich, 1972):

\[
E(t) = \gamma + \alpha \beta \tag{4-2}
\]
\[
\text{Var}(t) = \alpha \beta^2 \tag{4-3}
\]

For \( \alpha = 1 \), equation (4-1) reduces to:

\[
g(t) = \frac{1}{\beta} e^{-\frac{(t - \gamma)}{\beta}} , \quad t \geq \gamma \tag{4-4}
\]
Figure 4-1. Parameter $\gamma$ for the 3-parameter gamma distribution.
since $\Gamma(\alpha) = 1$ for $\alpha = 1$.

The exponential-piston flow model assumes the system total volume ($V_T$) is composed of a perfectly mixed volume ($V_m$) and a volume in which water moves in piston flow ($V$). The exponential-piston flow model is defined as (Maloszewski and Zuber, 1982):

$$g(t) = \frac{1}{(T/\eta)} e^{-\frac{t - T(1 - \frac{1}{\eta})}{T/\eta}}, \quad t \geq T(1 - \frac{1}{\eta})$$

$$= 0, \quad t < T(1 - \frac{1}{\eta})$$

where $\eta = V_T/V_m$.

Comparing equations (4-4) and (4-5) shows that:

$$\beta = T/\eta$$

and

$$\gamma = T(1 - \frac{1}{\eta})$$

Therefore, the exponential-piston flow model is a special case of the 3-parameter gamma distribution when $\beta$ and $\gamma$ are defined by equations (4-6) and (4-7), respectively, and $\alpha = 1$.

The above fact is also supported by the mean and variance of the 3-parameter gamma distribution. Substituting equations (4-6), (4-7), and $\alpha = 1$ in
equations (4-2) and (4-3) gives $E(t) = T$ and $\text{Var}(t) = (T/\eta)^2$, which are the mean and variance of the exponential-piston flow model (Maloszewski and Zuber, 1982).

As indicated in section 1.3, the exponential-piston flow model combines the piston flow model with the exponential or perfect mixing model. For $\eta = 1$, the exponential-piston flow model gives the perfect mixing model, and for $\eta \rightarrow \infty$, it reduces to the piston flow model. Substituting $\eta = 1$ and $\eta \rightarrow \infty$ in equations (4-6) and (4-7) yields $\beta = T$ and $\gamma = 0$ (see Figure 4-2) for the perfect mixing model, and $\beta = 0$, $\gamma = T$ (see Figure 4-3) for the piston flow model. In both perfect mixing and piston flow, the mean is $T$; and the variance is $T^2$ for perfect mixing, and 0 for piston flow (Maloszewski and Zuber, 1982). These values can also be obtained from the mean and variance of the 3-parameter gamma distribution by substituting $\alpha = 1$, $\beta = T$, and $\gamma = 0$ in the case of perfect mixing; and $\alpha = 1$, $\beta = 0$, and $\gamma = T$ in the case of piston flow. In other words, perfect mixing, piston flow, and the combination of perfect mixing-piston flow are all simulated by the 3-parameter gamma distribution. In fact, all the types of mixing and their combinations are accounted for by the 3-parameter gamma distribution, as will be shown in the next section. For this reason, the 3-parameter gamma distribution is proposed as the general model for the determination of the mean transit time in hydrologic systems.

Definitions of the model parameters ($\alpha$, $\beta$, and $\gamma$) for the general case in which piston flow, partial, and perfect mixing exist in the system, i.e., $V_T = V_m + V_{pm} + V$, where $V_{pm}$ is the volume occupied by partial mixing, are given in the following discussion.

To determine the proportions of each of $V_m$, $V_{pm}$, and $V$, the parameters $\theta$ and $\eta$ are defined as follows:
Figure 4-2. Parameter $\gamma$ for the perfect mixing model.

(for perfect mixing, $g(t) = \frac{1}{T} e^{-t/T}$)
Figure 4-3. Parameter $\gamma$ for the piston flow model. (for piston flow, $g(t) = \delta(t - T)$)
Note that equation (4-9) gives $\eta$ in the case of perfect-piston flow model when $\theta = 1$. The parameter $\theta$ gives the proportions of $V_{pm}$ and $(V_m + V)$, and $\eta$ separates $V_m$ and $V$.

### 4.3.2 The parameter $\gamma$

As mentioned previously, the values of $\gamma$ for perfect mixing and piston flow are 0 and $V/Q$, respectively. Both values represent the minimum transit time that can possibly exist in the system (see Figures 4-2 and 4-3). Therefore, it can be stated that physically, $\gamma$ is the minimum transit time in the system. This explains the physical meaning for $t \geq \gamma$ in the proposed model (equation 4-1) as shown in Figure 4-1.

As indicated earlier, the values of $\gamma$ for perfect mixing ($\mu = 1$) and piston flow ($\mu = 0$) are 0 and $V/Q$, respectively. In other words, $\gamma$ decreases with increasing $\mu$. Based on this information, $\gamma$ in the case of partial mixing is given by:

\[
\gamma = T(1 - \mu)
\]  

(4-10)

where $T = \frac{V_{pm}}{Q}$

Equation (4-10) gives $\gamma = 0$ in the case of perfect mixing ($\mu = 1$) and $\gamma = T = \frac{V_{pm}}{Q}$ in the case of partial mixing ($\mu = 0$).
\( V/Q \) for piston flow \((\mu = 0 \text{ and } V_{pm} = V)\), as required.

The above discussion shows that whenever piston flow and partial mixing occur in the system, then their combined effect on \( \gamma \) should be considered. Therefore, in the general case in which \( V_T = V_m + V_{pm} + V \), \( \gamma \) is given by:

\[
\gamma = \frac{V}{Q} + \frac{V_{pm}}{Q}(1 - \mu)
\]  

(4-11)

using the definitions of \( \theta \) and \( \eta \), and \( V_T = V_m + V_{pm} + V \), equation (4-11) can be written as:

\[
\gamma = T \left(1 - \frac{1}{\eta \theta} - \mu + \frac{\mu}{\theta}\right)
\]

(4-12)

Note that \( \gamma \) values in the case of perfect-piston flow, piston flow, perfect mixing, and partial mixing can be obtained from equation (4-12) for the following set of conditions:

\[
V_T = V_m + V, \ V_{pm} = 0, \ \theta = 1.
\]

\[
V_T = V, \ V_m = 0, \ V_{pm} = 0, \ \theta = 1, \ \eta \to \infty.
\]

\[
V_T = V_m, \ V = 0, \ V_{pm} = 0, \ \theta = 1, \ \eta = 1.
\]

\[
V_T = V_{pm}, \ V = 0, \ V_m = 0, \ \theta \to \infty, \ \eta \to \infty.
\]

For example, in the case of perfect mixing, substituting \( \theta = 1 \) and \( \eta = 1 \) gives \( \gamma = 0 \).
4.3.3 The parameter $\alpha$. As indicated earlier, the perfect-piston flow model follows the 3-parameter gamma distribution with $\alpha = 1$. In other words, the condition $V_T = V_m + V$ is obtained from the 3-parameter gamma distribution when $\alpha = 1$. This condition is also obtained when $\theta = 1$ (equation 4-8). Therefore, in the case of perfect-piston flow model

$$\alpha = \theta = \frac{V_T}{V_m + V}$$

(4-13)

Since perfect mixing and piston flow have constant $\mu$ values ($\mu = 1$ for perfect mixing, and $\mu = 0$ for piston flow), $\alpha$ in the case of perfect-piston flow model does not depend on $\mu$, it depends only on $V_m$ and $V$, as shown by equation (4-13). However, when partial mixing occurs in combination with perfect mixing and/or piston flow, $\alpha$ will depend on both $V_{pm}$ and $\mu$, since $\mu$ can assume any value in the range $0 < \mu < 1$.

In the above discussion, it was indicated that perfect-piston flow model follows the 3-parameter gamma distribution, and that it gives the models of perfect mixing and piston flow for $\eta = 1$ and $\eta \rightarrow \infty$, respectively. Therefore, in the case of partial mixing ($V_T = V_{pm}$) $\alpha = 1$ and $\alpha \rightarrow \infty$ should yield the perfect mixing and piston flow models, respectively, since $\alpha$ is a function of $\mu$ only when $V_T = V_{pm}$, and $\mu$ is the parameter that controls when partial mixing approaches perfect mixing or piston flow. Based on this information and knowing $\mu$ and $V_{pm}$ are independent of each other, equation (4-13) can be extended to give $\alpha$ in the general case ($V_T = V_m + V + V_{pm}$) by:

$$\alpha = \frac{V_T}{V_m + V + \mu V_{pm}}$$

(4-14)
in the general case, the expression for $\gamma$ in the general case (equation 4-12) and $E(t) = T$ are substituted in equation (4-2) to give

$$\beta = \frac{T}{\alpha} \left( \frac{1}{\eta\theta} + \mu - \frac{\mu}{\theta} \right)$$  \hspace{1cm} (4-16)$$

where $\alpha$ is defined by equation (4-15).

Equation (4-1), with the parameters $\alpha$, $\beta$, and $\gamma$ defined by equations (4-15), (4-16), and (4-12); respectively gives the proposed model for systems in the steady state. The case of transient systems will be given in the next section.

4.4 The Proposed Model

4.4.1 Steady state case. In this case, the model is given by substituting the expressions for $\gamma$ (equation 4-12) and $\beta$ (equation 4-16) in equation (4-1) and is:

$$g(t) = \frac{[t - T(1- \frac{1}{\eta\theta} - \mu + \frac{\mu}{\theta})]^{\alpha - 1}}{\left[ \frac{T}{\alpha} \left( \frac{1}{\eta\theta} + \mu - \frac{\mu}{\theta} \right) \right]^\alpha \Gamma(\alpha)}$$

$$- \frac{[t - T(1- \frac{1}{\eta\theta} - \mu + \frac{\mu}{\theta})]}{\left[ \frac{T}{\alpha} \left( \frac{1}{\eta\theta} + \mu - \frac{\mu}{\theta} \right) \right]}$$

$$e$$

$$\begin{cases} 0, & t \geq T(1- \frac{1}{\eta\theta} - \mu + \frac{\mu}{\theta}) \\ 0, & t < T(1- \frac{1}{\eta\theta} - \mu + \frac{\mu}{\theta}) \end{cases}$$  \hspace{1cm} (4-17)$$

where $\alpha$ is defined by equation (4-15). The variance in this case is obtained by substituting the expression for $\beta$ (equation 4-16) in equation (4-3) and is given by:

$$Var(t) = \frac{1}{\alpha} \left( \frac{1}{\eta\theta} + \mu - \frac{\mu}{\theta} \right)^2 T^2$$  \hspace{1cm} (4-18)$$
As indicated in the last section, the proposed model (equation 4-17) accounts for perfect mixing \( (V_m) \), partial mixing \( (V_{pm}) \), and piston flow \( (V) \), i.e., equation 4-17 corresponds to the general case in which \( V_T = V_m + V_{pm} + V \).

In addition, equation (4-17) also accounts for six other possibilities which can be obtained as special cases from the general case (equation 4-17). These are:

1. perfect-piston flow:
   \[
   V_T = V_m + V ; \quad V_{pm} = 0
   \]

2. perfect mixing:
   \[
   V_T = V_m ; \quad V = V_{pm} = 0
   \]

3. piston flow:
   \[
   V_T = V ; \quad V_m = V_{pm} = 0
   \]

4. partial-piston flow:
   \[
   V_T = V_{pm} + V ; \quad V_m = 0
   \]

5. perfect-partial mixing:
   \[
   V_T = V_m + V_{pm} ; \quad V = 0
   \]

6. partial mixing:
   \[
   V_T = V_{pm} ; \quad V = V_m = 0
   \]

The first three cases correspond to the existing models of exponential-piston flow, perfect mixing, and piston flow; respectively. At the present time, there are no models to account for cases 4 and 5 which are more likely to occur in natural systems than piston flow, perfect mixing, or the combination of perfect-piston
flow; and case 6 is currently modeled differently by discrete-state compartment models or the dispersive model, as indicated earlier.

It can be shown these six cases can be obtained from the general model for the following conditions:

<table>
<thead>
<tr>
<th>Case</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( V_T = V_m + V ); ( \alpha = 1, \theta = 1 )</td>
</tr>
<tr>
<td>2.</td>
<td>( V_T = V_m ); ( \alpha = 1, \theta = 1, \eta = 1 ).</td>
</tr>
<tr>
<td>3.</td>
<td>( V_T = V ); ( \alpha = 1, \theta = 1, \eta \to \infty ).</td>
</tr>
<tr>
<td>4.</td>
<td>( V_T = V_{pm} + V ); ( \eta \to \infty ).</td>
</tr>
<tr>
<td>5.</td>
<td>( V_T = V_m + V_{pm} ); ( \eta = 1 ).</td>
</tr>
<tr>
<td>6.</td>
<td>( V_T = V_{pm} ); ( \alpha = \frac{1}{\mu}, \theta \to \infty, \eta \to \infty ).</td>
</tr>
</tbody>
</table>

The resulting \( g(t) \) functions for cases 1, 2, and 3 are given in Table 4-1, and those for the other cases are listed below:

4. \( V_T = V_{pm} + V \); \( \eta \to \infty \):

\[
\begin{align*}
\text{Case 4:} \\
g(t) = & \frac{[t - T(1 - \mu + \frac{\mu}{\theta})]^{\alpha-1}}{[\frac{T}{\alpha}(\mu - \frac{\mu}{\theta})]^\alpha \Gamma(\alpha)} e^{-\frac{t - T(1 - \mu + \frac{\mu}{\theta})}{\frac{T}{\alpha}(\mu - \frac{\mu}{\theta})}} \\
& \quad \text{for } t \geq T(1 - \mu + \frac{\mu}{\theta}) \\
& \quad \text{for } t < T(1 - \mu + \frac{\mu}{\theta}) \\
& \quad = 0
\end{align*}
\]
Table 4-1
Weighting functions and variances for the steady state models of perfect mixing, piston flow, and perfect-piston flow.

<table>
<thead>
<tr>
<th>Model</th>
<th>Weighting Function</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect Mixing</td>
<td>$\frac{1}{T} e^{-t/T}$</td>
<td>$T^2$</td>
</tr>
<tr>
<td>Piston Flow</td>
<td>$\delta(t-T)$</td>
<td>0</td>
</tr>
<tr>
<td>Perfect-Piston Flow</td>
<td>$\frac{1}{T/\eta} e^{-t\eta/T} + \eta - 1$</td>
<td>$\left(\frac{T}{\eta}\right)^2$</td>
</tr>
</tbody>
</table>
In this study the models corresponding to cases 4, 5, and 6 will be designated the partial-piston flow model (PPFM), perfect-partial model (PPM), and partial mixing model (PM), respectively.

As indicated in the last section, the partial mixing model gives the perfect mixing model and the piston flow model as special cases when $\alpha = 1$, and $\alpha \to \infty$, respectively. Substituting $\alpha = 1$ in equation (4-21) gives directly the perfect mixing model. It is well-known that the 3-parameter gamma distribution
approaches the normal distribution when \( \alpha \) is large. According to Yevjevich (1972) this condition is obtained for \( \alpha > 30 \). Therefore, for \( \mu < 0.03 \), the 3-parameter gamma distribution approaches the normal distribution, since \( \alpha = 1/\mu \). It is also known that the normal distribution approaches the delta function, which describes piston flow, as the standard deviation (the square root of the variance) goes to zero (Gupta, 1966). The standard deviation in the case of the partial mixing model is \( T\mu^{3/2} \), as will be shown below. Therefore, it can be seen that, as \( \mu \to 0 \), the standard deviation \( \to 0 \) and the partial mixing model approaches the piston flow model.

Equation (4-21) shows that \( \beta \) in the case of the partial mixing model is \( T/\alpha^2 \). Substituting this value in equation (4-3) gives the variance of the partial mixing model to be \( T^2/\alpha^3 \), or \( T^2\mu^3 \). For \( \alpha = 1 \) and \( \alpha \to \infty \), the variance gives \( T^2 \) and 0, which are the required values for the perfect mixing model and the piston flow model, respectively. The variance of the partial mixing model shows that the standard deviation in this case is \( T/\alpha^{3/2} \), or \( T\mu^{3/2} \), as mentioned above.

**4.4.2 Nonsteady state case.** Following the approach of Zuber (1986b) who assumes constant parameters, the parameters in this case can be defined as:

\[
\alpha = \frac{V_T(t)}{V(t) + V_m(t) + \mu V_{pm}(t)} = \frac{1}{\theta + \mu(1 - \frac{1}{\theta})} = \text{constant} \quad (4-22)
\]

where:

\[
\theta = \frac{V_T(t)}{V(t) + V_m(t)} = \text{constant} ,
\]

\[
\eta = \frac{V_T(t)}{\theta V_m(t)} = \text{constant} ,
\]
\[ \mu = \text{constant}, \]

and the weighting function, expressed as the normalized concentration response function \( C_I(z) \), is given by:

\[ C_1(z) = \frac{[z - (1 - \frac{1}{\eta^\theta} - \mu + \frac{\mu}{\theta})]^\alpha - 1}{[\frac{1}{\alpha} (\frac{1}{\eta^\theta} + \mu - \frac{\mu}{\theta})]^\alpha} \Gamma(\alpha) e^{-\frac{[z - (1 - \frac{1}{\eta^\theta} - \mu + \frac{\mu}{\theta})]}{\frac{1}{\alpha} (\frac{1}{\eta^\theta} + \mu - \frac{\mu}{\theta})}} \]  

Equation (4-23) gives the \( C_I(z) \) for the general case: \( V_T(t) = V_m(t) + V_{pm}(t) + V(t) \). The six possibilities discussed in the steady state section are similarly accounted for by the general \( C_I(z) \) expression (equation 4-23) as special cases. They can be obtained from the general \( C_I(z) \) function for the same set of conditions given in the steady state section. For example, in the case of the perfect mixing model \( \alpha = 1, \theta = 1, \eta = 1 \), and the resulting \( C_I(z) \) is:
$C_I(z) = e^{-z}$

which is the same as that obtained by Niemi (1977) and Zuber (1986b).

The $C_I(z)$ functions for the six possibilities are:

1. perfect mixing:

   $C_I(z) = e^{-z}$  \hspace{1cm} (4-26)

2. piston flow:

   $C_I(z) = \delta(1 - z)$  \hspace{1cm} (4-27)

3. perfect-piston flow:

   \begin{align*}
   C_I(z) &= \eta e^{-\eta z + \eta - 1} & \forall z \geq (1 - \frac{1}{\eta}) \\
   &= 0 & \forall z < (1 - \frac{1}{\eta})
   \end{align*}
   \hspace{1cm} (4-28)

4. partial-piston flow:

   \begin{align*}
   C_I(z) &= \frac{[z - (1 - \mu + \frac{\mu}{\theta})]^{\alpha - 1}}{[\frac{1}{\alpha} (\mu - \frac{\mu}{\theta})]^{\alpha}} \Gamma(\alpha) e^{-\frac{[z - (1 - \mu + \frac{\mu}{\theta})]}{[\frac{1}{\alpha} (\mu - \frac{\mu}{\theta})]}} \hspace{1cm} \forall z \geq (1 - \mu + \frac{\mu}{\theta}) \\
   &= 0 & \forall z < (1 - \mu + \frac{\mu}{\theta})
   \end{align*}
   \hspace{1cm} (4-29)
5. perfect-partial mixing:

\[
C_I(z) = \frac{\left[ z - (1 - \frac{1}{\theta} - \mu + \frac{\mu}{\theta}) \right]^{\alpha-1}}{\left[ \frac{1}{\alpha} \left( \frac{1}{\theta} + \mu - \frac{\mu}{\theta} \right) \right]^\alpha \Gamma(\alpha)}
\]

\[
e^{- \left( \frac{z - (1 - \frac{1}{\theta} - \mu + \frac{\mu}{\theta})}{\left[ \frac{1}{\alpha} \left( \frac{1}{\theta} + \mu - \frac{\mu}{\theta} \right) \right]^\alpha \Gamma(\alpha)} \right)}
\]

(4-30)

\[z \geq (1 - \frac{1}{\theta} - \mu + \frac{\mu}{\theta})\]

, \(z < (1 - \frac{1}{\theta} - \mu + \frac{\mu}{\theta})\)

= 0

6. partial mixing :

\[
C_I(z) = \frac{\left[ z - (1 - \frac{1}{\alpha}) \right]^{\alpha-1}}{\left[ \frac{1}{\alpha} \right]^\alpha \Gamma(\alpha)}
\]

\[
e^{- \left( \frac{z - (1 - \frac{1}{\alpha})}{\left[ \frac{1}{\alpha} \right]^\alpha \Gamma(\alpha)} \right)}
\]

(4-31)

\[z \geq (1 - \frac{1}{\alpha})\]

\[z < (1 - \frac{1}{\alpha})\]

= 0

4.5 Discussion

The models developed in this study allow partial mixing to be modeled in combination with piston flow (PPFM) or with perfect mixing (PPM), whereas the current models that deal with partial mixing (discrete-state compartment models or dispersive models) are incapable of handling these combinations which physically represent natural systems better than the simple models of piston flow,
perfect mixing, and perfect-piston flow. In fact, there are currently no models to account for such combinations, or from which the perfect-piston model (EPM) can be obtained as a special case. It is shown in this study that the perfect-piston, perfect-partial, partial-piston, and partial mixing are all special cases of the proposed general model. Therefore, the general model has led to the development of three new models or four new models, including the general model, are introduced in this study.

For systems in the steady state, the minimum number of fitting parameters required to model the mentioned combinations (perfect-partial or partial-piston) is three, which is the case in the perfect-partial and partial-piston. These are: the turnover time \( T \), mixing efficiency \( \mu \), and the parameter \( \theta \) which shows the proportions of \( V_{pm} \) and \( V \) or \( V_m \) in the system. Therefore, it is not possible to account for such combinations with fewer than three parameters. At the same time, the use of more than three parameters is unnecessary since these combinations can be completely described by three parameters. On the other hand, the minimum number of parameters required to model the general case is four. These are: \( T \), \( \mu \), and two other parameters, \( \theta \) and \( \eta \), which specify the proportions of the three volumes involved: \( V_m \), \( V_{pm} \), and \( V \).

Grabczak et al. (1984) reported that in practice, whenever the number of fitting parameters is larger than two, the inverse problem cannot be solved unambiguously. In other words, a number of models can be equally well-fitted. Obviously, such a statement cannot be generalized to include the mentioned combinations as explained above. The statement is certainly true for cases in which the minimum number of parameters required is less than or equal to two, which is the case for the currently known lumped parameter models with the exception of discrete-state compartment models. However, one parameter models are too
simplistic to describe the complex behavior of natural systems. Maloszewski and Zuber (1982), Grabczak et al. (1982), and Zuber (1986a) reported that sometimes it is impossible to obtain a good fit without introducing an additional fitting parameter under the assumption that there are at least two water components, one with the radioisotope (tracer) of interest, and another, older, component in which this radioisotope has decayed to a level beneath detection limits.

Two comments are necessary here. First, a poor fit is not necessarily due to the presence of two water components; it could as well be due to the fact that the selected model simply does not adequately describe the modeled system. Therefore, if the presence of two water components is not physically justified then the additional fitting parameter will have no physical meaning and its use will be merely to obtain a good fit even if the selected model is a one parameter model, in which case the number of fitting parameters will be two. In other words, even if the appropriate model is a one parameter model but the presence of two water components is not physically justified, then the obtained results will be meaningless. In contrast, all the fitting parameters in the proposed model have a clear and precise physical meaning. Second, if the appropriate model to be used is a two parameter model then the number of fitting parameters will exceed two. Therefore, it can be seen that the use of more than two fitting parameters is needed even with the currently known lumped parameter models. The literature also shows that such a need is realized. Eriksson (1985) reported that some unpublished data on river water tritium in Scandinavia indicates that at most, only a three parameter model of the transit time distribution can be used with any confidence. The above discussion also applies to systems in the nonsteady state, in which case the number of parameters will increase because instead of the constant $T$ (in the steady state), there are two fitting parameters, $Q(t)$ and $V_T(t)$. It is interesting to note that the fitting parameters other than $T$ ($\theta, \eta,$ and $\mu$)
provide additional information about the nature of the system (types of mixing and the volumes occupied by them), and thus more information about the system behavior will be gained.

An important feature of the weighting functions obtained in this study deserves some attention. The weighting functions can assume any shape, depending on the value of \( \alpha \), the shape factor. In this regard, the models developed in this study are comparable to the dispersive model and superior to any other currently known lumped parameter model. It is obvious that the flexibility of the weighting functions is very important if a realistic model is desired to describe the complex behavior of natural systems.

Figures 4-4 to 4-7 are graphs for weighting functions of different shapes constructed for the four models developed in this study. Some of these graphs also show how one model approaches another as the value of the parameters change. For example, from Figure 4-4 it can be seen that the graph corresponding to \( V_m + V = 0.95V_T \) is very close to that of the perfect-piston flow model for the same values of \( \eta \) and \( T \) since it approximates a system consisting mainly (95%) of a perfectly mixed volume \( (V_m) \) and a piston flow volume \( (V) \). Also shown in the figure is the case of \( V_{pm} = 0.95V_T \) and \( \mu = 0.05 \) which represents a system approaching piston flow (95% of the system is partially mixed with a low mixing efficiency of 0.05). The figure illustrates this tendency to approach piston flow since the graph has a small variance coupled with a high peak, characteristics of piston flow. This situation is also shown in Figure 4-5 by the graph with a mixing efficiency = 0.10. This figure also shows that the graph corresponding to the mixing efficiency of 0.95 closely approximates that of the perfect mixing model. The same situation can also be seen in Figure 4-6 where it is given by the graph with \( V_m = 0.9V_T \) (90% of the system is perfectly mixed), and \( \mu = 0.50 \).
Figure 4-4. Plot of the weighting function versus time for the general model.

1: $V_m + V = 0.95V_T, V_{pm} = 0.05V_T, V_m = 0.35V_T, V = 0.60V_T, \mu = 0.50$; 2: perfect-piston flow model; 3: $V_{pm} = 0.05V_T, \mu = 0.95, V_m = 0.01V_T, V = 0.04V_T$; 4: $V_{pm} = 0.95V_T, \mu = 0.05, V_m = 0.04V_T, V = 0.01V_T$. 
Figure 4-5. Plot of the weighting function versus time for the partial mixing model.

1: $\mu = 0.95$, 2: perfect mixing model, 3: $\mu = 0.50$, 4: $\mu = 0.10$. 
Figure 4-6. Plot of the weighting function versus time for the perfect-partial mixing model.

$\mu = 0.50$ for cases 2, 3, and 4; 1: perfect mixing model; 2: $V_m = 0.90 V_T$, $V_{pm} = 0.10 V_T$; 3: $V_m = 0.50 V_T$, $V_{pm} = 0.50 V_T$; 4: $V_m = 0.25 V_T$, $V_{pm} = 0.75 V_T$. 
Figure 4-7. Plot of the weighting function versus time for the partial-piston flow model.

$\mu = 0.50$ for all cases; 
1: $V = 0.90V_T$, $V_{pm} = 0.10V_T$; 
2: $V = 0.75V_T$, $V_{pm} = 0.25V_T$; 
3: $V = 0.50V_T$, $V_{pm} = 0.50V_T$; 
4: $V = 0.25V_T$, $V_{pm} = 0.75V_T$. 
Inspection of Figure 4-7 shows that as the piston flow volume increases, the variances of the graphs decrease and their peaks increase, i.e., the graphs approach piston flow since increasing V and decreasing μ imply piston flow.

The most important finding of this study is the development of one model (the general model), with one set of parameters to account for the three mixing types (perfect, partial, and piston) and their combinations. In the current practice of tracer hydrology, the models used to describe the three mixing types and the combination of perfect-piston, which is the only modeled combination at the present time, cannot be obtained as special cases from one general model. For example, the dispersive model, the Poisson distribution which describes a cascade of perfectly mixed cells used in discrete-state compartment models, and the perfect-piston flow model employ parameters of different physical meaning, and as such cannot be obtained as special cases from one general model. Therefore, it can be stated that the proposed model has allowed modeling of the three mixing types and their combinations to be unified by one general formula. In other words, the proposed model represents a unified modeling approach for all possible mixing types and their combinations.
5.1 Introduction

In this chapter three examples are given to illustrate the application of the proposed models for the case of variable tracer input. The examples are limited to systems in the steady state since no data can be found for time variable (non-steady) flow systems. The interpretation of time variable systems by the tracer method requires knowledge of tracer input concentration (given by $C_{\text{in}}(\tau)$ in equation 2-10), observed tracer output concentration, and the time record of the inflow rate to the system or recharge rate (given by $Q_{\text{in}}(\tau)$ in equation 2-10). Such data is very hard to obtain since estimation of the recharge rate is very difficult. Furthermore, there are certain useful approximations recommended for the interpretation of time variable flow systems (Zuber, 1986b); if such approximations are to be used, then in addition to the mentioned data the time record of the outflow rate ($Q_{\text{out}}(t))$ is also needed. Zuber (1985) reported that the approach followed in this study (which is the only one available for the interpretation of lumped parameter systems) for the interpretation of time variable systems has not been applied in practice so far. This is not surprising since the required data is difficult to obtain, as explained above. Also discussed in this chapter is the analytical evaluation of the mean transit time by the proposed models in the case of constant tracer input and steady flow.
5.2 Model Applicability and Data Requirements

5.2.1 Model Applicability. The current literature shows a few guidelines in some clear-cut cases for the interpretation of tracer concentrations in hydrologic systems. These are:

1. Samples collected from springs generally represent good (perfect) mixing, because flowlines tend to converge toward springs. This is especially true for karst springs, and generally holds true for unconfined aquifers as well (Dincer and Davis, 1984).

2. The perfect mixing model is a fair description of not-too-deep surface water bodies (Kaufman and Libby, 1954).

3. Confined aquifers with a narrow recharge area far from the sampling points (width of the recharge zone is negligible in comparison with the distance to the sampling points) can be interpreted by the piston flow model or the dispersive model (Zuber, 1986a).

Based on the above guidelines, and realizing that no two hydrologic systems are alike, the following generalizations can be made for the applicability of the proposed models. Systems that tend to be highly mixed such as those of categories 1 and 2 listed above can be modeled with the partial mixing model with a high mixing efficiency (i.e., the modeler has to specify a high value for $\mu$), or the perfect-partial mixing model with high $\mu$ and/or high $V_m$, or the general model with high $\mu$ and/or high $V_m$. On the other hand, systems characterized by a low degree of mixing, e.g., those of category 3 mentioned above, can be simulated by the partial mixing model with a low $\mu$, or the partial-piston flow model with low $\mu$ and/or high $V$, or the general model with low $\mu$ and/or high $V$. 
5.2.2 Data Requirements. For systems in the steady state, whether the tracer input concentration is variable or constant, the only required field data is the input concentration \( C_{in} \) and the "observed" or "measured" output concentration \( C_{out} \). The model has to be selected based on all available information. If the input concentration is variable with time, the interpretation is made by fitting curves of the "calculated" and "observed" output concentrations with time. For example, if the partial-piston flow model (which assumes \( V_T = V_{pm} + V \), and \( V_m = 0 \)) is selected, then the parameters \( T, \mu, \) and \( \theta \) have to be fitted. In order to fit \( \theta \), the proportions of \( V_{pm} \) and \( V \) should be specified, e.g., if \( V \) is set equal to 0.2 \( V_T \), then \( V_{pm} \) will be 0.8 \( V_T \) and \( \theta \) can be calculated by equation (4-8) which gives \( \theta = 5 \) in this particular example. Once the model (weighting function) parameters \( T, \mu, \) and \( \theta \) in the given example) are specified and knowing \( C_{in} \) from the field data, equation (2-8a) or (2-8b) can be used to determine the "calculated" output concentration, and search for the best fit is made by comparing curves of the calculated and observed output concentrations versus time.

In the case of steady flow and constant tracer input, the proper model also has to be selected from the available information. In this case, \( T \) is determined analytically. For example, if the same model used in the case of steady flow and variable input as an example (the partial-piston flow model) is selected, then equation (2-8a) or (2-8b) gives (see derivation in appendix B):

\[
\frac{C_{out}}{C_{in}} = \frac{1}{\left[ \frac{\lambda T}{\alpha} \frac{1}{(\mu - \frac{\mu}{\theta})} + 1 \right]^\alpha} e^{-\lambda T(1 - \mu + \frac{\mu}{\theta})} \quad (5-1)
\]

Knowing \( \lambda \) and given the input and observed output concentrations from the field data, \( T \) can be solved for analytically if the parameters \( \theta \) and \( \mu \) are known. In
other words, if the selected model is a two- or more parameter model, then $T$ can be obtained only if the other parameters are known. Note that in the case of variable tracer input these parameters are obtained together with $T$ as a result of the fitting process. In the case of one-parameter models, $T$ can be solved for directly since there are no other parameters involved. For example, in the case of perfect mixing model, equation (2-8a) or (2-8b) gives:

$$\frac{C_{out}}{C_{in}} = \frac{1}{1+\lambda T}$$  \hfill (5-2)

where the only unknown is $T$.

In the nonsteady state case, field data required for the interpretation are $C_{in}$, $C_{out}$ (observed output concentration), $Q_{in}$ and $Q_{out}$, as indicated in section 5.1. Assuming no stagnant water in the system, a useful approximation in this case (Zuber, 1986a) is:

$$Q(t) = t_d^{-1} V_T(t)$$  \hfill (5-3)

where $Q(t)$ is the volumetric outflow rate and $t_d$ is the turnover time of the system (if the system consists of stagnant water, then $t_d$ will be the turnover time of the dynamic part of the system). The mass balance of water is:

$$\frac{dV_T(t)}{dt} = Q_{in}(t) - Q(t)$$  \hfill (5-4)

Putting equation (5-3) into (5-4) gives:

$$t_d = \frac{Q_{in}(t) - Q(t)}{\frac{dQ(t)}{dt}}$$  \hfill (5-5)

Knowing the time records of $Q_{in}(t)$ and $Q(t)$, $t_d$ can be calculated from equation
(5-5), and using the value of $t_d$ in equation (5-3) allows the determination of $V_T(t)$. The parameter $z$ can be obtained by substituting equation (5-3) into (2-12) to give:

$$z = \frac{t - \tau}{t_d} \tag{5-6}$$

Now the calculated output concentrations can be determined from equation (2-10) by fitting the parameters of the selected model ($C_I(z)$). For example, if the selected model is the partial mixing model (equation 4-31), then the parameter $\mu$ has to be fitted. Search for the best fit is then made by comparing curves of the calculated and observed output concentrations with time.

### 5.3 Examples of Variable Tracer Input

In the first two examples, data obtained by Davis et al. (1970) from two springs (site 45 and site 2) in Cheju Island, Republic of Korea, are reinterpreted.

In the two investigated systems, groundwater flow takes place in lava tunnels and fractured volcanic rocks of which basalt is predominant. The interest in transit times was for the purpose of evaluating the availability of groundwater resources. All the waters sampled contained more than 50 tritium units (TU), thus indicating modern or post-bomb recharge. Accordingly, tritium was used for estimating the mean transit times.

To select the proper models for interpreting the mean transit times, use is made of the tritium content of the output (observations) as well as the nature of flow in the two systems. Observations at site 2 are characterized by relatively low tritium content, generally less than 100 TU, which is indicative of relatively long transit times and a high degree of mixing, whereas those at site 45 are characterized by relatively high tritium content (140-265 TU) which is indicative of
relatively shorter transit times and a lower degree of mixing than those of site 2. On the other hand, the fact that flow is taking place in lava tunnels and fractures is suggestive of mixing that can assume any degree or efficiency depending on the interconnection of fractures.

Based on the above information, the partial mixing model with relatively short $T$ and moderate $\mu$ is selected for the interpretation of site 45. Using this model, the best fit is obtained for $T = 2.4$ years (standard deviation = 0.8 years), $\mu = 0.5$, and it is good at the 0.01 significance level as indicated by the chi-square goodness of fit test. The predicted and observed output concentrations are given in Figure 5.1. In the case of site 2, the partial-piston flow model with relatively long $T$ and high $\mu$ is chosen as the proper model. The best fit, significant at the 0.1 significance level, is obtained for $T = 21$ years (standard deviation = 19.3 years), $\mu = 0.98$, $\theta = 18.9$; and it is also given in figure 5.1. Note that the value of $\theta$ which corresponds to $V_{pm} = 0.95 V_T$, and $V = 0.05 V_T$ and the high mixing efficiency show the tendency of the system to be highly mixed. Davis et al. (1970) used the binomial model, which is a simplified form of the dispersive model, and determined $T = 3$ years for site 45, and $T = 8.5$ years for site 2. Later, Maloszewski and Zuber (1982) reinterpreted the data from both sites with the exponential-piston flow model which resulted in $T = 2.5$ years for site 45, comparable to the value of $T = 2.4$ years obtained in this study, and $T = 21$ years for site 2, the same value estimated in this study.

The third example shows the applicability of the proposed models to river basin studies. The example is a reinterpretation of tritium data collected by Eriksson (1963) for the Ottawa River Basin in Canada. The length of the river above the sampling point is 400 miles, the drainage area is 24,000 square miles, and the bedrock geology of the basin consists of Precambrian granites and
Figure 5-1. Interpretation of site 45 and site 2, Cheju Island, Republic of Korea.
gneisses (Brown, 1961). Monitoring of tritium in the Ottawa River (output) and in the precipitation of the Ottawa River Basin (input) began in 1953 following the inception of large-scale atmospheric thermonuclear testing in 1952. This makes it the only river system with a fairly complete record of tritium (Eriksson, 1985). The availability of this data allowed Brown (1961) to estimate the mean transit time of water in the basin. Later, Eriksson (1963) derived the transit time distribution by analyzing the data with a different approach, the so-called identification approach in system analysis terminology.

In this study, determination of the mean transit time of water in the system is made with the perfect-partial mixing model due to the general tendency of such systems to be highly mixed. Figure 5-2 shows the best fit obtained for $T = 3$ years (standard deviation = 2.6 years), $\mu = 0.2$, and $\theta = 1.1$ (indicating $V_m = 0.9 V_T$ i.e., 90% of the system is perfectly mixed). In this case, the obtained fit is found to be good at the 0.5 significance level. The $T$ values obtained by Brown (1961) and Eriksson (1963) compare very well to the one found in this study. Brown’s interpretation resulted in $T = 3.3$ years, and that of Eriksson yielded $T = 3.0$ years.

It should be noted that, in addition to the value of the mean transit time ($T$), the other fitting parameters ($\mu$ and $\theta$) have also provided more information about the structure or mixing nature of the investigated systems in all three examples.

5.4 The Case of Constant Tracer Input

The determination of the mean transit time, $T$, in the case of constant tracer input was discussed in section 3.3 where it is indicated that $T$ can be determined analytically for steady flow systems with constant tracer input, if the selected
Figure 5-2. Interpretation of the Ottawa River Basin, Canada.
model is a one parameter model or, in the case of two or more parameter models, if the other parameters are known a priori.

Using the \( g(t) \) function of the general model (equation 4-17) in equation (2-8), the following relationship (see derivation in appendix B) is obtained for the general model \( (V_T = V_m + V_{pm} + V) \):

\[
\frac{C_{out}}{C_{in}} = \frac{1}{\left[ \frac{\lambda T}{\alpha} \left( \frac{1}{\eta \theta} + \mu \right) \right]^\alpha e^{-\lambda T(1 - \frac{1}{\eta \theta} - \mu + \frac{\mu}{\theta})}}
\]

Knowing \( C_{out}, C_{in} \) and the other parameters in equation (5-7), the dimensionless quantity \( \lambda T \) can be obtained and \( T \) can be obtained by multiplying \( \lambda T \) by the \( 1/\lambda \) value of the radiotracer used in the interpretation \( (\lambda = \ln 2/t_{1/2}, \text{where} t_{1/2} = \text{radiotracer half-life}) \). The values of \( 1/\lambda \) for tritium \( (t_{1/2} = 12.26 \text{ years}) \) and \( \text{C} \) \( (t_{1/2} = 5730 \text{ years}) \), the most commonly used radiotracers, are 17.7 years and 8270 years, respectively.

Similarly, relationships for the six special cases accounted for by the model can be obtained as special cases from equation (5-7) for the same set of conditions given in section 4.4.1. For example, in the case of the perfect mixing model, \( \alpha = 1, \theta = 1, \eta = 1, \) and

\[
\frac{C_{out}}{C_{in}} = \frac{1}{1 + \lambda T}
\]

The relationships for the six special cases are:
1. perfect mixing: $\alpha = 1, \theta = 1, \eta = 1$

\[
\frac{C_{out}}{C_{in}} = \frac{1}{1+\lambda T} \tag{5-8}
\]

2. piston flow: $\alpha = 1, \theta = 1, \eta \to \infty$

Note that for $\alpha = 1$ (or $\eta = 0$), equation (5-13) reduces to equations (5-6) and (5-8), respectively. In other words, the relationship obtained by the partial mixing model is similar to the perfect mixing model (equation 4-8) and the piston flow model (equation 6-2), as indicated in section 4.3.

\[
\frac{C_{out}}{C_{in}} = e^{-\lambda T} \tag{5-9}
\]

3. perfect-piston flow: $\alpha = 1, \theta = 1$

\[
\frac{C_{out}}{C_{in}} = \frac{1}{\left[\frac{\lambda T}{\eta} + 1\right]} e^{-\lambda T\left(1 - \frac{1}{\eta}\right)} \tag{5-10}
\]

4. partial-piston flow: $\eta \to \infty$

\[
\frac{C_{out}}{C_{in}} = \frac{1}{\left[\frac{\lambda T}{\alpha} (\mu - \frac{\mu}{\theta}) + 1\right]} e^{-\lambda T(1 - \mu + \frac{\mu}{\theta})} \tag{5-11}
\]

5. perfect-partial mixing: $\eta = 1$

\[
\frac{C_{out}}{C_{in}} = \frac{1}{\left[\frac{\lambda T}{\alpha} \left(\frac{1}{\theta} + \mu - \frac{\mu}{\theta}\right) + 1\right]} e^{-\lambda T\left(1 - \frac{1}{\theta} - \mu + \frac{\mu}{\theta}\right)} \tag{5-12}
\]
6. partial mixing: $\theta \to \infty$, $\eta \to \infty$

$$\frac{C_{\text{out}}}{C_{\text{in}}} = \frac{1}{[\frac{\lambda T}{\alpha} \mu + 1]} e^{-\lambda T(1 - \mu)} \quad (5-13)$$

Note that for $\alpha = 1$ ($\mu = 1$) and $\alpha \to \infty$ ($\mu = 0$), equation (5-13) reduces to equations (5-8) and (5-9), respectively. In other words, the relationship obtained by the partial mixing model gives those obtained by the perfect mixing model (equation 5-8) and the piston flow model (equation 5-9), as indicated in section 4.3.

All the six relationships indicated above can also be obtained by using their respective $g(t)$ functions in equation (2-8).

As indicated earlier, the first three cases (perfect mixing, piston flow, and EPM) are currently known. Their $C_{\text{out}}/C_{\text{in}}$ relationships are given in Table 5-1. It can be seen that the relationships obtained (as special cases from that of the general model) for these three cases are identical to those of Table 5-1.

In summary, in the case of constant tracer input and steady flow the relationships developed for the general model (equation 5-7) and the other six models (or special cases) can be expressed as:

$$\frac{C_{\text{out}}}{C_{\text{in}}} = \frac{1}{[\lambda \beta + 1]^{\alpha}} e^{-\lambda \gamma} \quad (5-14)$$

In the case of the general model, the parameters $\alpha$, $\beta$, and $\gamma$ are given by equations (4-4), (4-5), and (4-6), respectively. For the other six models, the values of
Table 5-1
Constant tracer input relationships for the perfect mixing, piston flow, and perfect-piston flow models.

<table>
<thead>
<tr>
<th>Model</th>
<th>( \frac{C_{out}}{C_{in}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect Mixing</td>
<td>( \frac{1}{1+\lambda T} )</td>
</tr>
<tr>
<td>Piston Flow</td>
<td>( e^{-\lambda T} )</td>
</tr>
<tr>
<td>Perfect-Piston Flow</td>
<td>( \frac{\lambda T}{\left( \frac{\lambda T}{\eta} + 1 \right) \left( 1 - \frac{1}{\eta} \right)} e^{-\lambda T(1 - \frac{1}{\eta})} )</td>
</tr>
</tbody>
</table>
\( \alpha, \beta, \) and \( \gamma \) are found by using the set of conditions indicated in section 4.3. For example, in the case of the perfect-piston flow model \( \alpha = 1, \beta = 1 \) indicating \( \gamma = T/\eta, \) and \( \gamma = T(1 - \frac{1}{\eta}) \). Using these values in equation (5-14) gives:

\[
\frac{C_{\text{out}}}{C_{\text{in}}} = \frac{1}{\frac{\lambda T}{\eta} + 1} \quad \text{e}^{-\lambda T(1 - \frac{1}{\eta})} \quad (5-15)
\]

which is identical to that of the perfect-piston flow model indicated in the third relationship.
CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

The findings of this study can be summarized as follows:

1. A general model that accounts for all possible types of mixing (perfect, partial, piston flow, and their combinations) in steady and nonsteady flow is developed.

2. The proposed general model represents a unified approach for modeling all mixing types and their combinations and it is the only model to present such a unified approach.

3. The existing models of piston flow, perfect mixing, and the perfect-piston flow model or exponential-piston flow model can be obtained from the general model as special cases.

4. The model has allowed partial mixing to be modeled either separately with the partial mixing model or in combination with the other mixing types of piston flow and perfect mixing with the partial-piston flow model and the perfect-partial mixing model, respectively. Currently, there are no models available for these latter two combinations. The partial mixing, partial-piston flow, and perfect-partial mixing models are special cases of the general model.

5. The shape flexibility of the weighting functions developed in this study is comparable to that of the dispersive model, and superior to those of any other currently known lumped parameter model.

6. Modeling of partial mixing separately or in combination with other mixing types will avoid the limitations currently encountered in the dispersive model.
measurement of the dispersivity; applicability to one-dimensional flow systems (in the lumped parameter approach, the dispersive model is applicable to one-dimensional flow systems only), and determination of the boundary conditions.

7. In all cases attempted, testing the applicability of the proposed models has resulted in good fitting, thus providing reliable estimates of the mean transit times and more information (inferred from the fitting parameters other than T) about the structure of the investigated systems.

To extend the applicability of models developed in this study to distributed parameter systems, it is recommended to apply the proposed models in the mixing cells of discrete state compartment (DSC) models. DSC models offer a convenient and relatively simple means for simulating distributed parameter systems (Campana, 1987).
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APPENDIX A

DERIVATION OF EQUATION (4-23)

In the steady state case, equation (2-12) gives the parameter $z$ to be:

$$z = \frac{t - \tau}{T} = \frac{t}{T} \quad \text{(A-1)}$$

when setting $\tau = 0$. Accordingly, nonsteady state models can be obtained from those of steady state if the latter are expressed as a function of $t/T$ (Niemi, 1977; Zuber, 1986b).

Equation (4-17), the general model in the steady state case, reads:

$$g(t) = \frac{[t - T(1 - \frac{1}{\eta \theta} - \mu + \frac{\mu}{\theta})]^\alpha - 1}{\Gamma(\alpha)} \frac{e^{-[t - T(1 - \frac{1}{\eta \theta} - \mu + \frac{\mu}{\theta})]}}{[\frac{1}{\alpha(1 - \frac{1}{\eta \theta} + \mu - \frac{\mu}{\theta})}]^\alpha} \quad \text{(A-2)}$$

$$, \quad t \geq T(1 - \frac{1}{\eta \theta} - \mu + \frac{\mu}{\theta})$$

$$, \quad t < T(1 - \frac{1}{\eta \theta} - \mu + \frac{\mu}{\theta})$$

$$= 0$$

Defining

$$a = (1 - \frac{1}{\eta \theta} - \mu + \frac{\mu}{\theta}) \quad \text{(A-3)}$$

and

$$b = (\frac{1}{\eta \theta} + \mu - \frac{\mu}{\theta}) \quad \text{(A-4)}$$
equation (A-2) can be written as:

\[
g(t) = \frac{(t-Ta)^{\alpha-1}}{\Gamma(\alpha)} e^{-\frac{(t-Ta)}{(\frac{T}{a})}} (\frac{T}{b}) \quad (A-5)
\]

when expressed as a function of \(t/T\), equation (A-5) reads:

\[
g(t) = \frac{1}{T} \frac{1}{(\frac{b}{a})^\alpha \Gamma(\alpha)} \frac{(t/T-a)^{\alpha-1}}{\Gamma(\alpha)} e^{-\frac{(t/T-a)}{(\frac{b}{a})}} = C(t)
\]

or:

\[
g(t) = \frac{1}{T} g(t/T)
\]

where

\[
g(t/T) = \frac{1}{(\frac{b}{a})^\alpha \Gamma(\alpha)} \frac{(z-a)^{\alpha-1}}{\Gamma(\alpha)} e^{-\frac{(z-a)}{(\frac{b}{a})}} = C(z)
\]

since \(z = t/T\) as shown by equation (A-1). Substituting equations (A-3) and (A-4) for \(a\) and \(b\), respectively, into equation (A-8) gives:

\[
C(z) = \frac{[z - (1 - \frac{1}{\eta^2} - \mu + \frac{\mu}{\theta})]^{\alpha-1}}{[\frac{1}{\alpha}(\frac{1}{\eta^2} + \mu - \frac{\mu}{\theta})]^\alpha \Gamma(\alpha)} e^{-\frac{[z - (1 - \frac{1}{\eta^2} - \mu + \frac{\mu}{\theta})]}{[\frac{1}{\alpha}(\frac{1}{\eta^2} + \mu - \frac{\mu}{\theta})]}}
\]

\[
, \quad z \geq (1 - \frac{1}{\eta^2} - \mu + \frac{\mu}{\theta})
\]

\[
= 0
\]

\[
, \quad z < (1 - \frac{1}{\eta^2} - \mu + \frac{\mu}{\theta})
\]
which is equation (4-23). As indicated in section 4.4.2, the $C_i(z)$ functions for the six mixing possibilities can be obtained from equation (A-9) as special cases by using the set of conditions, which describes the parameter values, indicated in section 4.4.1.

In the case of constant source input, substitution of equation (4-1) into (5-2a) gives

\[
\frac{C_{in}}{C_{in}^{\infty}} = \frac{1}{\rho_f} \int_0^t (t - \tau)^{m-1} e^{-t_{eq} \tau} d\tau
\]  

(B-1)

Defining $\omega = 1 - \gamma$, equation (B-1) can be written as

\[
\frac{C_{in}}{C_{in}^{\infty}} = \frac{e^{-t_{eq}}}{\rho_f} \int_0^t \tau^{m-1} e^{\omega \tau} d\tau
\]  

(B-2)

The value of the integral (i) in equation (B-3) is given by

\[
i = \frac{e^\frac{\omega 0}{\omega + 1}}{\frac{1}{\gamma} + 1}
\]  

(B-3)

and when substituted in equation (B-2), it gives

\[
\frac{C_{in}}{C_{in}^{\infty}} = \frac{1}{(\omega + 1)^{m}} e^{-t_{eq}}
\]  

(B-4)
APPENDIX B

DERIVATION OF EQUATION (5-7)

In the case of constant tracer input, substitution of equation (4-1) in (2-8a) gives:

\[
\frac{C_{\text{out}}}{C_{\text{in}}} = \frac{1}{\beta^\alpha \Gamma(\alpha)} \int_0^{\infty} (t - \gamma)^{\alpha - 1} e^{\frac{-(t - \gamma)}{\beta}} e^{-\lambda t} \, dt \quad (B-1)
\]

Defining \( u = t - \gamma \), equation (B-1) can be written as:

\[
\frac{C_{\text{out}}}{C_{\text{in}}} = \frac{e^{-\lambda \gamma}}{\beta^\alpha \Gamma(\alpha)} \int_0^{\infty} u^{\alpha - 1} e^{-\frac{u}{\beta} + \lambda} \, du \quad (B-2)
\]

The value of the integral (I) in equation (B-2) is given by:

\[
I = \frac{\Gamma(\alpha)}{\left(\frac{1}{\beta} + \lambda\right)^\alpha} \quad (B-3)
\]

and when substituted in equation (B-2), it gives:

\[
\frac{C_{\text{out}}}{C_{\text{in}}} = \frac{1}{[\lambda \beta + 1]^\alpha} e^{-\lambda \gamma} \quad (B-4)
\]
Substituting equations (4-16) and (4-12) for $\beta$ and $\gamma$, respectively, in equation (B-4) gives:

$$\frac{C_{\text{out}}}{C_{\text{in}}} = \frac{1}{\left[ \frac{\chi T \left( \frac{1}{\eta^2} + \mu - \frac{\mu}{\theta} \right)}{\alpha} + 1 \right]^\alpha} e^{-\lambda T \left( 1 - \frac{1}{\eta^2} - \mu + \frac{\mu}{\theta} \right)} \quad (B-5)$$

which is equation (5-7). As indicated in section 5.4, $C_{\text{out}} / C_{\text{in}}$ relationships for the six mixing possibilities can be obtained as special cases from equation (B-5) by using the set of conditions given in section 4.4.1.