DETERMINING THE TURNOVER TIME OF GROUNDWATER SYSTEMS WITH THE AID OF ENVIRONMENTAL TRACERS
1. Models and Their Applicability

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ABSTRACT


Three new lumped-parameter models have been developed for the interpretation of environmental radioisotope data in groundwater systems. Two of these models combine other simpler models, i.e. the piston flow model is combined either with the exponential model (exponential distribution of transit times) or with the linear model (linear distribution of transit times). The third model is based on a new solution to the dispersion equation which more adequately represents the real systems than the conventional solution generally applied so far.

The applicability of models was tested by the reinterpretation of several known case studies (Modry Dul, Cheju Island, Rasche Spring and Grafendorf). It has been shown that two of these models, i.e. the exponential–piston flow model and the dispersive model give better fitting than other simpler models. Thus, the obtained values of turnover times are more reliable, whereas the additional fitting parameter gives some information about the structure of the system. In the examples considered, in spite of a lower number of fitting parameters, the new models gave practically the same fitting as the multiparameter finite state mixing-cell models.

It has been shown that in the case of a constant tracer input a priori physical knowledge of the groundwater system is indispensable for determining the turnover time. The piston flow model commonly used for age determinations by the \(^{14}\)C method is an approximation applicable only in the cases of low dispersion.

In some cases the stable-isotope method aids in the interpretation of systems containing mixed waters of different ages. However, when \(^{14}\)C method is used for mixed-water systems a serious mistake may arise by neglecting the different bicarbonate contents in particular water components.

INTRODUCTION

A number of authors have discussed the advantages and limitations of the environmental radioisotope methods. The reader is referred to Nir (1972) who states that though the radioisotope methods do not supply the informa-
tion which is most needed by the hydrologist, they may be useful in confirming or eliminating various assumed hydrological models. Usually, a qualitative interpretation is sufficient to reach conclusions concerning the origin of water, interconnections of various systems, stratification and mixing patterns. A quantitative interpretation, which involves the application of a mathematical model, gives the turnover time (mean transit time) of water in the system as additional information. Such information may be useful particularly in karstic systems.

Several mathematical models have been applied in the interpretation of environmental radioisotope data. The piston flow and well-mixed models were introduced in hydrology by Kaufman and Libby (1954), von Buttlar and Libby (1955) and Begemann and Libby (1957). Eriksson (1958) introduced the linear and exponential models, the latter being mathematically equivalent to the well-mixed model. This property resulted in misunderstandings which, in turn, led to an unjustified rejection of the exponential model. Nir (1964) considered the dispersion model based on a solution to the dispersion equation. This model was simplified by Davis et al. (1967), and Dinçer and Davis (1967) who applied a symmetrical binomial distribution. Martinec et al. (1974) presented an example of the application of another dispersive model proposed by Siegenthaler. According to Przewłocki and Yurtsever (1974) and Przewłocki (1975), E.S. Simpson introduced in hydrology the finite state mixing-cell models.

All these models differ by the assumed shape of the transit-time distribution of flow in the system. In this work new models are proposed, which combine simple transit-time distributions given by the exponential, linear and piston flow models into more realistic distributions. The dispersion model is improved by the use of a new solution to the dispersion equation, obtained for the initial and boundary conditions, which more adequately describe natural flow systems. The applicability of these models is demonstrated by the reinterpretation of known case studies and by comparison of the results obtained with those obtained by the use of earlier models.

BASIC CONCEPTS

The basic concepts of flow models for the interpretation of tracer experiments were developed mainly in chemical engineering. However, much misunderstanding has resulted from the lack of distinction between considerations related to the mass flux, or volumetric flow rate, through a system, and the considerations related to the tracer movement. Thus, a short review of the basic concepts is appropriate here.

It appears that in flow systems an ordinary concentration term is not sufficient. Instead of that it is necessary to use 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 fluid \( \Delta V \) contained in a given volume of the system at a given instant as (see also the Notation for symbols used in this paper):
NOTATION

List of symbols used

\[ A, B \] auxiliary terms defined underneath Table I
\[ C_1(t) \] unspecified output concentration resulting from an impulse injection
\[ C_F(t) \] flux concentration defined by eq. 2
\[ C_R(t) \] resident concentration defined by eq. 1
\[ C_{IRR} \] concentration observed for both injection and detection performed uniformly at the aquifer cross-section
\[ C_{IRF} \] concentration observed for injection as above and detection in outflowing water (averaged by flow rates)
\[ C_{IFF} \] concentration observed for both injection and detection averaged by flow rates
\[ C_{IFR} \] concentration observed for injection averaged by flow rates and detection averaged by the cross-section area (uniform detection)
\[ C_{in}(t) \] input concentration, specified by the type of the weighting function, \( g(t) \)
\[ C_{out}(t) \] output concentration, specified as above
\[ C_0 \] constant input concentration, specified as above
\[ D \] dispersion coefficient \((m^2 \text{s}^{-1})\)
\[ D/v \] dispersion constant \((m)\)
\[ D/vx \] dispersion parameter, dimensionless
\[ g(t) \] weighting function equal to the system response for a given injection detection mode
\[ H \] aquifer height expressed in metres of water
\[ P \] precipitation \((m^3 \text{s}^{-1})\)
\[ Q \] volumetric flow rate through a system
\[ S \] cross-section area of the system, or area of a basin
\[ T = V/Q \] turnover time = mean transit time of water
\[ \bar{t}_t \] mean transit time of a tracer as defined by eq. 4
\[ V \] volume of water in a system
\[ v \] mean transit velocity, \( v = x/T \)
\[ x \] distance from the recharge area to the measuring point
\[ \alpha_i \] infiltration coefficient for the \( i \)th month
\[ \alpha \] ratio of summer to winter infiltration coefficients
\[ \beta \] ratio of nonradioactive water component to the total flow
\[ \delta \] concentration of \(^{18}\text{O}\) or \( D \) in delta notation \((\%)\)
\[ \eta \] ratio of the total volume of the system to the volume with an exponential or linear flow
\[ \lambda \] radioactive decay constant

\[ C_R(t) = \Delta m(t)/\Delta V \] (1)

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

\[ C_F(t) = [\Delta m(t)/\Delta t] / (\Delta V/\Delta t) = \Delta m(t)/Q\Delta t \] (2)

These two definitions are taken from Kreft and Zuber (1978), but the definitions of Safonov et al. (1979) are also very convenient for a better understanding. Namely, \( C_R \) is a mean concentration obtained by area weighting.
over a given cross-section of the system, whereas $C_F$ is a mean concentration obtained by weighting by volumetric flow rates through a given cross-section of the system. Similar concepts are well known in two-phase flow in pipelines, in laminar flow through capillaries (e.g., Gardner et al., 1973), and in some other systems (Levenspiel and Turner, 1970; Levenspiel et al., 1970). Brigham (1974) introduced them into the dead-end pore model, whereas Kreft and Zuber (1978, 1979) discussed in detail their meaning for the dispersion model. Some examples of differences between these two concentrations will be considered further in the paper. Here it will be stated that $C_R \neq C_F$ whenever flow lines of different velocities have different solute contents, or when there is a gradient of concentration along the flow lines (Kreft and Zuber, 1979).

The mean age of water leaving the system, or the mean transit time, called also the turnover time ($T$), is defined as:

$$T = \frac{V}{Q}$$

(3)

where $Q$ is the volumetric flow rate, and $V$ is the volume of mobile water in the system.

The mean transit time of tracer is defined as:

$$\bar{t}_t = \int_{0}^{\infty} t C_1(t) \, dt / \int_{0}^{\infty} C_1(t) \, dt$$

(4)

where $C_1(t)$ is the tracer concentration observed at the measuring point as the result of an instantaneous injection at the entrance to the system at $t = 0$. Eq. 4 is applicable to any injection—detection mode of the tracer. Kreft and Zuber (1978) pointed out that $\bar{t}_t = T$ only if an ideal conservative tracer is both injected and measured in flux, i.e. when in eq. 4 $C_{IFF}(t)$ appears instead of the unspecified $C_1(t)$. $C_{IFF}(t)$ is the tracer concentration measured in the flux as the result of an instantaneous injection in the flux (i.e. for an infinitesimally short time in which the water containing the tracer enters the system). Similarly, $C_{IFR}(t)$ is the resident concentration resulting from an instantaneous injection in the flux, whereas $C_{IRR}(t)$ and $C_{IRF}(t)$ are the resident and flux concentrations, respectively, resulting from an injection in the form of a resident concentration (i.e. an infinitesimally thin slab of water containing homogeneously distributed tracer appears at a given cross-section of the system). The literature on the tracer method applied in chemical engineering and hydrology contains numerous misconceptions resulting from the lack of distinction between $C_R$ and $C_F$. By confusion of concepts related both to $C_R$ and $C_F$ terms, some investigators arrived at the conclusion that the tracer moves with a different velocity than the traced material.

If $C_{IF}(t)$ is normalized to be independent of the quantity of the injected tracer, it is called the weighting function, $g(t)$.
where $M$ is the mass or activity of the injected tracer.

The weighting function is also called the system response function or the exit age distribution function of a tracer as it describes the exit time distribution of tracer particles which entered the system at a given $t = 0$. The exit age-distribution function of a tracer is equal to the exit age-distribution of the system [well known as the $E(t)$ function] only if an ideal tracer for mass tracing is injected and measured in the flux. Detailed discussion of these functions and basic principles of the tracer method in hydrology will be given elsewhere (Zuber, in press).

Eq. 5 serves for finding $g(t)$ both experimentally and theoretically. Theoretically $g(t)$ is determined if $C_i(t)$ is found by solving the mass balance or transport equation for properly chosen initial and boundary conditions. In environmental groundwater systems the $C_i(t)$ function cannot be found experimentally because of technical difficulties in performing a proper experiment. Thus, it is necessary to rely on theoretical solutions and on the experimental evidence gained in other fields.

The weighting function allows one to find the output concentration for any tracer input variable in time. For a system being in a steady state (i.e. $Q$ and $V$ are constant) the well-known convolution integral applies:

$$C_{\text{out}}(t) = \int_{0}^{\infty} C_{\text{in}}(t-t') \exp(-\lambda t') g(t') \, dt'$$

or

$$C_{\text{out}}(t) = \int_{-\infty}^{t} C_{\text{in}}(t') \exp[-\lambda(t-t')] g(t-t') \, dt'$$

where $C_{\text{out}}(t)$ and $C_{\text{in}}(t)$ are the output and input concentrations, respectively, and $t'$ is the integration variable which physically represents the exit age of the tracer. Kreft and Zuber (1978) showed that eq. 6 is applicable only to the weighting functions given by the $C_{\text{IFF}}$ and $C_{\text{IFR}}$ solutions. In other words, the tracer has to enter the system in the form of flux concentration. Fortunately, the environmental tracers which enter groundwater bodies with precipitation are, in principle, injected proportionally to the volumetric flow rates by nature itself. Doubts may arise in the case of $^{14}$C which enters the groundwater system via biogenic material with accompanying dissolution of inorganic carbonates. In heterogeneous recharge areas it may happen that the total dissolved carbon differs from site to site and thus the injection of $^{14}$C is not necessarily proportional to volumetric flow rates.
<table>
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<th>Model</th>
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<th>Parameters</th>
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<td>$T$</td>
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<td>(2) Exponential (EM) or good mixing</td>
<td>$T^{-1} \exp(-t/T)$</td>
<td>$T$</td>
<td>$T$</td>
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<td>(3) Combined exponential and piston flow (EPM) or real system</td>
<td>$(T/\eta)^{-1} \exp(-\eta t/T + \eta - 1)$, $0$ for $t &lt; T(1 - \eta^{-1})$</td>
<td>$T, \eta$</td>
<td>$T$</td>
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<td>$\begin{cases} 1/2T \text{ for } t \leq 2T \ 0 \text{ for } t &gt; 2T \end{cases}$</td>
<td>$T$</td>
<td>$T$</td>
<td>$0.833 T^2$</td>
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<td>$\eta/2T \text{ for } T - T\eta \leq t \leq T + T\eta \text{ and } 0 \text{ for other } t$</td>
<td>$T, \eta$</td>
<td>$T$</td>
<td>$0.833(T/\eta)^2$</td>
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<td>$-$</td>
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<td>(a) CFF case</td>
<td>$A t^{-1}$</td>
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<td>$T$</td>
<td>$T^2(2D/ux)$</td>
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<td>$(2A - B)T^{-1}$</td>
<td>$T, D/ux$</td>
<td>$T(1 + D/ux)$</td>
<td>$T^2[2D/ux + 3(D/ux)^2]$</td>
</tr>
<tr>
<td>(c) CFR case</td>
<td>$0.5 A t^{-1}(1 + t/T)$</td>
<td>$T, D/ux$</td>
<td>$T(1 + D/ux)$</td>
<td>$T^2[2D/ux + 5(D/ux)^2]$</td>
</tr>
<tr>
<td>(d) CRR case</td>
<td>$AT^{-1}$</td>
<td>$T, D/ux$</td>
<td>$T(1 + 2D/ux)$</td>
<td>$T^2[2D/ux + 8(D/ux)^2]$</td>
</tr>
</tbody>
</table>

$A = (4\pi D/uxT)^{1/2} \exp[-T(1 - t/T)^2 ux/4Dt]$.  
$B = (ux/2D) \exp(ux/D) \text{erfc}[(1 + t/T)(4tD/uxT)^{-1/2}]$. 
MODELS AND THEIR HYDROGEOLOGICAL SIGNIFICANCE

Particular models are defined by formulae describing the weighting functions. In general meaning, the type of the weighting function is understood as the model. In considering a given system the type of the weighting function together with the values of its parameters is called the model of that system. The model is found by looking for the weighting function which satisfies eq. 6.

In the so-called lumped parameter model, or black-box model approach, the spatial variations are ignored. The considerations of this paper are limited to such cases though some attention is given to the finite state mixing-cell models which may be treated rather as distributed parameter models with lumping.

The weighting functions of the models considered here are given in Table I; Fig. 1 shows schematically some hydrogeological situations to which they are applicable. From Table I it is clear that the turnover time \( T \) is the main parameter of all the models. Thus, by finding the \( g(t) \) function which relates the input and output concentrations in eq. 6, the turnover time is determined and in some cases another parameter \( \eta \) or \( D/\nu x \), which supplies some information about the structure of the system. However, it has to be remembered that in hydrology a whole system rarely is observable. Usually, only some outflows from the system are measurable (springs, abstraction wells). In such cases the output concentration represents only a part of the system, and consequently the turnover time and other parameters, if any, also represent that part of the system only.

Consider now some characteristics of the models. The piston flow model (PFM) assumes that the concentration of a tracer changes only due to the radioactive decay. Thus, it applies strictly only to cases where the water has been separated and stagnant since the recharge time. Then, the age of water is defined by the equation:

\[
C(t) = C(0) \exp(-\lambda t)
\]

where \( t \) here is the age of water, and \( C(0) \) is the initial concentration of a radiotracer. As will be shown further, if both the dispersion is low and \( C_{in}(t) \) is constant, or slowly variable, the piston flow model may be applicable to dynamic systems, and the age of water is approximately equal to the turnover time, \( T \). In all other cases "the age of water" defined by eq. 7 differs considerably from the turnover time.

The exponential model (EM) was introduced by Eriksson (1958), under an assumption that the exponential distribution of transit times corresponds to a probable situation of decreasing permeability with the aquifer depth. Later Bredenkamp and Vogel (1970), in their consideration of an aquifer having the permeability and porosity exponentially decreasing with depth, found a formula (their equation 4) equivalent to the exponential model for the case of a constant input (eq. 11 here). Similarly, Vogel (1970) found the
Fig. 1. Schematic situations showing examples of possible applicability of particular models.

1 = a confined aquifer with a narrow recharge area far from the sampling wells. Sampling either in the pumped-out water (case c) or by taking samples at different depths when drilling (case e). Piston flow model (PFM) is applicable if no dispersion is assumed, whereas the dispersion model (DM) requires different weighting functions (C_FF or C_FR type) depending on the sampling mode (see text for details).

2 = an unconfined aquifer with the exponential distribution of transit times. The exponential model (EM) is applicable in cases a, b and d. When the sampling does not include the flow lines with infinitesimally short transit times, either the combined exponential and piston flow model (EPM), or the dispersion model (DM) has to be applied. The weighting function for DM has to be of C_FF type because sampling is performed in pumped-out water (concentration is weighted by flow rates).

3 = an aquifer partly confined. Situation similar to case c described under No. 2.

4 = an unconfined aquifer with increasing thickness. The linear model (LM) is applicable.

5 = an aquifer with increasing thickness, partly confined. Either the combined linear and
same formula (his equation 4) for an aquifer with uniform permeability and porosity. In both cases the hydraulic gradient was proportional to the distance from the water divide. The output concentration was measured in the outflow or in the water pumped from a fully penetrating well, or from partly penetrating well (from the water table to a given depth).

The combined exponential—piston flow model (EPM) introduced here corresponds to two of the situations (Nos. 2c and 3) shown in Fig. 1. This model is mathematically equivalent to the real system model of Wolf and Resnick (1963), or a well-mixed reservoir in series with a piston flow reservoir (Levenspiel, 1972). The additional parameter, \( \eta \), is equal to the total volume divided by the mixed (exponential flow) volume. For \( \eta = 1 \), this model is equal to the exponential model, whereas for \( \eta \to \infty \) it approaches the piston flow.

The linear model (LM) is simple and needs no special discussion here. However, it must be noted that this model describes an aquifer with linearly increasing thickness and a constant hydraulic gradient. No example of a practical applicability of this model has been known so far. When combined with the piston flow model it gives the linear—piston flow model (LPM).

The finite state mixing-cell models (briefly called finite state models or FSM) consist of a number of well-mixed cells. They can be very useful for finding the input—output relationships, but the number of fitting (non-disposable) parameters may increase arbitrarily. In Table I the number of parameters of the FSM is given for the case of cells in series with possibility of individual recharge. Such a case was considered by Przewłocki and Yurtsever (1974). A more complex case of two- or three-dimensional arrays of interconnected cells is also possible. However, as Himmelblau and Bischoff (1968, p.69) point out:

"the engineer can always put enough parameters into a model to fit any data, but the physical significance of the parameters is then in doubt".

In other words the turnover time found by applying these models is doubtful. In Table I the mean transit time of a tracer for the FSM is given as equal to the turnover time, whereas Przewłocki and Yurtsever (1974) claim that in some cases \( \ell_t \neq T \) (their figs. 7–9). However, these authors in their calculation tried to realize the impulse injection by considering cells filled in by the tracer at \( t = 0 \). It is obvious that such a numerical procedure in some cases does not correspond to the impulse injection proportional to volumetric flow rates and distorts the results.

As mentioned earlier, the dispersion model (DM) was introduced by Nir (1964) who used the most commonly known solution to the dispersion equation (in its normalized form this solution is given in Table I under 7d). However, recalling the earlier discussion on the weighting function, neither this solution nor the solution given under 7c are applicable to eq. 6.

The solutions which are applicable to eq. 6, and which more adequately describe the initial and boundary conditions met in nature are given under 7a and 7b. The model given under 7a corresponds to the case when the piston flow model (LPM), or the dispersion model (DM) is applicable. The weighting function in DM is either of \( C_{FF} \) or \( C_{FR} \) type, depending on the sampling mode as described under No. 1.
concentration is measured in the outflow (averaged by flow rates). This model is based on the solution to the dispersion equation found by Lenda and Zuber (1970). This solution created some doubts in the past, which, however, have been clarified by Kreft and Zuber (1978).

The model given as 7b corresponds to the case in which the concentration is measured in the system (i.e. averaged by depth), e.g., samples are collected from different depths when drilling a well. In this case the concentration is not averaged by flow rates and thus the mean transit time of a tracer is not equal to the mean transit time of water. As mentioned earlier, the credit for developing this model goes, according to Martinec et al. (1974), to U. Siegenthaler. However, according to Safonov et al. (1979) this solution was found earlier by C.R. Strang and coworkers. Unfortunately in the work of Martinec et al. (1974) this model was not appropriately used for the situation experimentally corresponding to the $C_{FF}$ case.

The binomial model (not shown in Table I) was introduced as an approximation of the dispersion model easy for slide rule calculations. Dinçer and Davis (1967) described in detail its use as a two-parameter model. Davis et al. (1970) and Martinec et al. (1974) applied that model in a simpler, one-parameter form. In that model a symmetrical weighting function is assumed, which for the cases of a high dispersion is in disagreement with 7a and 7b models. Thus it may be expected that the cases of high dispersion will not be properly treated by the binomial model.

THE DISPERSION CONSTANT AND THE DISPERSION PARAMETER

Nir (1964) considered $D/v$-values known at that time from artificial tracer tests performed on the large scale. Later experiments and pollution studies showed similar orders of magnitude. However, in applying the convolution integral to the dispersion model one must remember that no integration is performed over the recharge area. Thus, the apparent values of $D/v$ will result from the space extended injection, and they may be several orders of magnitude larger than those known from other types of studies. At this stage one may doubt if the use of the dispersion model is justified at all for such studies. However, as Himmelblau and Bischoff (1968) note

"the only justification for the use of dispersion models is their success in representing the real process".

In homogeneous media the dispersion constant, $D/v$, is approximately proportional to the pore length (De Jong, 1958; Saffman, 1959). In heterogeneous media the dispersion constant may be thought of as a measure of the extension of zones having different permeabilities (Zuber, 1974). Following what was said above, it may be expected that the apparent values of $D/v$ in environmental radioisotope studies will be roughly equal to the length of the recharge zone measured along the streamlines. In the case of an unconfined aquifer the mean distance can be one half of the $D/v$-value, thus the expected maximum value of the dispersion parameter, $D/vx$, will be $\sim 2$. 
INPUT FUNCTIONS

It is well known that the tritium concentration in precipitation has been variable since 1952. To overcome this difficulty Davis et al. (1967), and Dinçer and Davis (1967) introduced concentrations weighted by the amount of precipitation, combined with a simple model of infiltration. In general the following relationship holds for each year:

$$C_{in} = \sum_{i=1}^{12} \alpha_i P_i C_i / \sum_{i=1}^{12} \alpha_i P_i$$

(8)

where $P_i$ is the precipitation in the $i$th month, $\alpha_i$ is the infiltration coefficient, and $C_i$ is the tritium concentration in the precipitation of the $i$th month. If the $\alpha_i$ coefficients are unknown the number of nondisposable parameters increases enormously. Assuming that the ratio of summer to winter infiltration coefficients is the same each year the number of additional parameters reduces to one parameter, $\alpha = \frac{\alpha_{4,5,6,7,8,9}}{\alpha_{10,11,12,1,2,3}}$ for the northern hemisphere. For instance, $\alpha = 0$ means that there is no infiltration during the summer months, but it does not necessarily mean that all the winter precipitation infiltrates. The $C_{in}(t)$ function is constructed by performing such calculations for each year.

In some cases, if there is no surface runoff, the $\alpha_i$ are treated as disposable parameters by correcting the precipitation for the evapotranspiration losses (e.g., Andersen and Sevel, 1974; Przewfocki, 1975).

The concentrations of other radioisotopes do not vary during the year and need not be weighted by the amount of precipitation. However, here again it is necessary to assume that the yearly recharge is constant. Time dependence of $^{85}$Kr and $^{14}$C will be discussed in Part 2 and by Zuber et al. (in press). Input concentrations of other radioisotopes are less known. Lal et al. (1970) discussed $^{32}$Si, Oeschger et al. (1974), and Loosli and Oeschger (1979) considered $^{32}$Ar, whereas Zuber et al. (in press) will be dealing with another promising tracer method, namely the tritium—$^3$He method. Freon®-11 (CCl$_3$F) and Freon®-12 (CCl$_2$F$_2$), chemically inert substances, released to the atmosphere by man, are also promising as environmental tracers due to their increasing input concentrations. In the case of $^{14}$C the input concentration has to be corrected for the dilution of the organic carbon by inorganic carbon and for the other effects. The reader is referred in this respect to a recent paper of Fontes and Garnier (1979).

MIXING OF WATERS HAVING DIFFERENT TURNOVER TIMES

In some cases it is impossible to obtain a fitting without assuming a presence of a dead-water component (i.e. water without the measured radioisotope). In such a case there are at least two inflows to the system: non-radioactive and radioactive. If the fraction of nonradioactive component is
denoted as $\beta$, then $(1 - \beta)C_\text{in}(t)$ should appear in eq. 6 instead of $C_\text{in}(t)$. It may happen that this non-radioactive component was recharged under different climatic conditions than the radioactive one. Then, if the stable-isotope compositions of both components are known the $\beta$ parameter can be treated as disposable because

$$
\beta = \frac{(\delta^m - \delta^r)}{(\delta^{nr} - \delta^r)}
$$

where $\delta$ is either $^{18}$O or D concentration expressed in delta notation, and $m$ denotes here the mixed water, whereas $r$ and $nr$ relate to the radioactive and non-radioactive water respectively.

The above considerations were directly related to tritium and $^{32}$Si, whose concentrations are measured in water. In a rough approximation the same approach can be used for $^{85}$Kr and $^{39}$Ar. However, in the case of $^{14}$C the problem is more complex as the concentration of carbon compounds (bicarbonate, carbonate, and CO$_2$) in mixing waters may differ appreciably. Usually a possibility of mixing is either tacitly omitted or the radiocarbon concentration is assumed to be proportional to the mixing components of water. However, it is self-evident that the radiocarbon concentration is weighted both by the volumetric flow rates and by the total dissolved carbon contents (TDC), i.e.

$$
^{14}C_m = \sum_i Q_i(TDC)^i^{14}C^i / [Q \cdot (TDC)]^m
$$

where subscript $i$ relates to the $i$th water component and subscript $m$ relates to the mixed water. This effect, together with the problem of the initial radiocarbon content, makes the interpretation of $^{14}$C very difficult.

CASES OF CONSTANT INPUT

The constant input concerns tritium and $^{14}$C recharged before the atomic bomb era, as well as $^{32}$Si and $^{39}$Ar. In Fig. 2 graphs of relative concentrations are given as a function of dimensionless turnover time. Transition to real time is obtained for any radioisotope tracer by applying the adequate $\lambda$-value. The graphs of this figure were calculated applying eq. 6 for a constant $C_\text{in} = C_0$. The graphs for the dispersion model were calculated with the aid of a computer program described in the following. According to what was said earlier in the paper, the maximum value of $D/vx = 2.5$ used is only slightly larger than the value of the maximum dispersion parameter expected in environmental tracer investigations.

Applying the exponential model to eq. 6 one arrives at a well-known formula:

$$
C(T)/C_0 = 1/(1 + \lambda T)
$$
Fig. 2. Relative radiotracer concentrations as a function of the relative turnover time for a constant input concentration ($C_0$) and for different models (EM = exponential model; LM = linear model; PFM = piston flow model; $D/vx$ = dispersion parameter for the dispersion model).

whereas in the case of the linear model (Eriksson, 1958):

$$\frac{C(T)}{C_0} = \left(\frac{0.5}{\lambda T}\right)[1 - \exp(-2\lambda T)]$$

(12)

From Fig. 2 it is clear that the "age of water" defined by eq. 7 has little to do with the real age (turnover time), which often remains unknown because the experimenter does not know which model is applicable, if any. The concept of age is, however, very convenient because it may be related to the geologic age, and to the climatological past. It is suggested here that the following terms be used: the piston flow age (equal to the age used so far), the exponential age and so on. For instance for $C/C_0 = 0.01$ the piston flow age is $T = 4.65/\lambda$ whereas the exponential age is $T = 100/\lambda$. The real age lies somewhere between the extreme values of Fig. 2. Its better estimate depends on the choice of an adequate model. However, the overwhelming majority of investigators use the piston flow model for interpreting radiocarbon ages, whereas the only justification of this model lies in its mathematical simplicity.

Inspection of Fig. 2 may create doubts at first glance as the dispersion model gives larger dispersion effects than the exponential model, mathematically equivalent to an ideal mixing reservoir. However, it should be remembered that a high dispersion is not necessarily equivalent to a good mixing. On the contrary, in permeable media, it means that flow lines of
extremely different velocities reach the measuring point without a transverse mixing. In an approximate use of the dispersion model to situations with an extended recharge area, a high dispersion may also mean that particular flow lines have different lengths.

It should be noted here that the exponential model, contrary to the equivalent model of good mixing, is also applicable to a semi-infinite medium, and thus is comparable with the dispersion models 7a and 7b obtained for such a medium. However, another doubt may arise here. Namely, is the dispersion model \((C_{\text{FF}} \text{ case})\) derived for a semi-infinite medium applicable to finite systems or not? Evidence from column experiments shows that whenever the flow rate is sufficiently high for the dispersion to be purely hydrodynamical, the existence or non-existence of the medium beyond the measuring point has no influence on the obtained results. In other words, if the interstitial velocity at the outlet boundary is sufficiently high, the existence of a river, or a source, or an abstraction well should not disturb the dispersion effects in the system.

It is generally accepted that radiocarbon measurements at two points along a given flow line allow one to determine the age difference (without knowing \(C_0\)), and consequently the flow velocity. The formula obtained from eq. 6 is:

\[
T_2 - T_1 = \frac{1}{\lambda}\ln \left(\frac{C_1}{C_2}\right)
\]

(13)

It is clear from Fig. 2 that this formula is an approximation valid only in the cases of low dispersion, say for \(D/vx < 0.05\). Other models do not yield such simple relations and require a minimum of three measurement points on a given streamline.

Consider now an imaginary example. Change of \(C/C_0\) from 0.1 to 0.05 gives \(\Delta T = 0.7/\lambda\) for the piston flow, 9.9/\(\lambda\) for the exponential, and 8.6/\(\lambda\) for the dispersive models with \(D/vx = 2.5\) in the \(C_{\text{FF}}\) case, and 5.5/\(\lambda\) for the linear model. Of course, for a confined aquifer the exponential and linear models have to be rejected but their combined versions may be applicable (see Fig. 1). However, still in the cases of a high dispersion the application of eq. 13 leads to the underestimation of the age difference, and consequently to the overestimation of the flow velocity.

In many cases this effect may be overshadowed by another stronger, opposite effect. Namely, radiocarbon ages are commonly interpreted assuming a steady state. Such an assumption may even be questionable for the Holocene. However, when ages older than \(10^4\) a are observed, it becomes much more questionable. Of course, as long as the age of water defined by eq. 7 is concerned, the error cannot be serious. However, if this age is to be related to the turnover time, the obtained result will represent the past history of the aquifer. In most cases the present turnover time will be much shorter than the ancient one as \(^{14}\)C determinations are usually performed in aquifers exploited extensively. However, the period of the extensive exploitation is in most cases very short in comparison with the turnover time. In
such a case, applying the PFM, it can be easily shown that the age differences (eq. 13) are related to the past and do not represent the present turnover time, or velocity, in the aquifer. Such an effect was pointed out by Fontes and Garnier (1979) who found that the velocities calculated by applying eq. 13 were about two orders of magnitude lower than velocities estimated from the hydraulic parameters (known transmissivity, thickness, hydraulic gradient, and assumed porosity). This high discrepancy was explained in the original paper as resulting from the fact that the circulation was only caused by withdrawal. It means that under natural conditions the system was practically stagnant.

In general, it can be stated that the radiocarbon ages calculated with the aid of eq. 7 supply very important information on the origin of water but cannot be used for determining the actual velocities in systems whose hydraulic conditions have changed. This remark concerns waters recharged before the Holocene, and younger systems if recent exploitation has increased the hydraulic gradient.

The $1/\lambda$-values (expressed in years) to be used in Fig. 2 are: 17.7 a for tritium, 8270 a for $^{14}$C, 390 a for $^{39}$Ar, and 426 a for $^{32}$Si (Oeschger et al., 1972). This last value is doubtful as the half-life of $^{32}$Si is not well known. It should be noted here that the $^{39}$Ar method is doubtful because of possible underground production of this radioisotope (Loosli and Oeschger, 1979), whereas the $^{32}$Si method is suspicious because of the unknown geochemistry of this radioisotope. Both methods have little promise because of large sample volumes needed for the analysis ($\sim 20$ m$^3$ of water).

**EXAMPLES OF VARIABLE INPUT**

General discussion on variable inputs will be given in Part 2 and by Zuber et al. (in press). Here, examples of the reinterpretation of the known case studies are given as an illustration of the applicability of the models to complex systems.

The fitting procedure in this work, similarly to all the cited works, is performed by guess-work, i.e. no objective criteria are applied. A low number of experimental data as well as a limited significance of the turnover time of the investigated systems did not justify a great effort needed for a more rigorous reinterpretation. However, it has to be remembered that whenever the fitting is performed by guess-work the term "quantitative" is rather an arbitrary one. The examples given below are not presented chronologically but rather in the order of an increasing complexity.

(a) Przewłocki and Yurtsever (1974) and Przewłocki (1975) interpreted the tritium data of a small spring, $Q = 0.5-5$ dm$^3$ s$^{-1}$, situated at the slope of the Massenberg, near Grafendorf in Styria, Austria. The input function was known (Przewłocki, 1975) thus the fitting could be limited to the main parameters (Fig. 3). The differences in the values of the turnover time
Fig. 3. The interpretation of the turnover time of the St-29 spring near Grafendorf, Austria. FSM = finite state mixing-cell model; EPM = exponential model; DM-C_{FF} = dispersion model with the weighting function characteristic for sampling in the outflow (C_{FF} type); T = turnover time in years; \( \eta \) = ratio of the total volume to the volume with the exponential distribution of transit times; \( D/vx \) = dispersion parameter.

obtained from different models do not seem to be significant. The relatively large scatter of the experimental points is probably caused by the variable flow rate. The low value of the dispersion parameter is in agreement with the shape of the aquifer which is recharged at the top of the Massenberg with a consequent flow along the mountain slope with no recharge. Similarly the value of \( \eta = V_{\text{total}}/V_{\text{mix}} = 2.1 \) agrees reasonably with the values obtained from FSM. Namely, in FSM the ratio of the total volume to that in which the initial mixing takes place as adopted by Przewlo\v{c}ki and Yurtsever (1974) is \( 6.0/2.5 = 2.4 \), whereas in Przewlo\v{c}ki (1975) it is \( 6.5/2.5 = 2.6 \).

From the above example it is clear that both two-parameter models gave as good a fit as FSM with six parameters. Thus EPM and DM have to be considered as more reliable in that case. In addition they supply additional physical information on the aquifer (\( D/vx \) or \( \eta \)), whereas for FSM such information is necessary prior to the interpretation, at the stage of the model selection. The lumped parameter models (or black-box models) do not require any physical knowledge prior to the interpretation, but the obtained weighting function supplies physical information. If a given type of the \( g(t) \) function is unacceptable, the model can be rejected and another model sought. FSM requires a prior physical knowledge which is seldom available.

(b) The second example is related to an important karstic spring (\( Q = 4 \, \text{m}^3 \, \text{s}^{-1} \)) at Rasche, Yugoslavia. Kirkov et al. (1974) used FSM whose
parameters were not unambiguously stated. The dispersive model used here was fitted for two extreme values of $\alpha$ (Fig. 4). As the monthly precipitation was not given in the original paper, the input function for $\alpha = 0$ was calculated from the curve for $\alpha = 1$ by making use of the empirical relationship between the input functions for $\alpha = 0$ and $\alpha = 1$ in southern Poland. Typical differences between the input functions for $\alpha = 0$ and $\alpha = 1$ are shown below (see Fig. 7). None of the models gave a good fit but the dispersive model for $\alpha = 0$ seems to be the most probable. This model gives a reasonable value of the $D/vx$ parameter. Both versions of the dispersive model show a presence of a component without tritium, which is in agreement with the findings of Kirkov et al. (1974) and with the geologic situation of the area.

The reason for the relatively high discrepancy between the experimental and theoretical curves is not known. It may be caused either by incorrect estimation of the input function or by variations of $\beta$, or most probably by a presence of a third input component with variable tritium content. In other words the spring water appears to represent a mixture of three components, one much older without tritium, and two others with different turnover times measurable by the tritium method. Such a possibility is geologically justified as described by Kirkov et al. (1974). However, more data would be necessary to interpret properly the turnover times of these two components containing tritium. The present interpretation gives an approximation of the mean turnover time of the components containing tritium.

Fig. 4. The interpretation of the Rasche spring, Yugoslavia. FSM = the finite state mixing-cell model; DM-$C_{FF}$ = dispersion model with the weighting function characteristic for sampling in the outflow; $T =$ turnover time in years; $D/vx =$ dispersion parameter; $\alpha =$ ratio of the summer to winter infiltration coefficients; $\beta =$ ratio of the nonradioactive flow rate to total rate.
tritium. The component without tritium does not contribute to the mean turnover time given in Fig. 4.

(c) Davis et al. (1970) presented a very interesting study of a volcanic island, Cheju, Republic of Korea. The residence times there were of interest in estimating the potential source of groundwater. Many sites were sampled for tritium and $^{18}$O measurements. The stable-isotope measurements were helpful in determining the altitude of recharge, whereas tritium served for estimating the transit time. Two extreme cases were chosen for the reinterpretation here.

Site 45 is a medium altitude spring with relatively low variations of $^{18}$O content. Davis et al. (1970) used a binomial model with a single fitting parameter. These authors estimated $T = 3 \, \text{a}$ whereas from Fig. 5 it is clear that $T = 2 \, \text{a}$ would be a more appropriate value. However, EPM gave a much better fit for $T = 2.5 \, \text{a}$ and $\eta = 1.7$.

Site 2 is a large coastal spring. Its isotopic composition shows low variations and reveals that the recharge area is in the centre of the island at high altitudes. These isotope characteristics together with a low value of $\eta$ indicate that the main part of the groundwater body is in the recharge area. Water is led from the recharge area to the spring by a system of a low volume. The exponential model ($\eta = 1.0$) has to be rejected because the isotopic composition suggests that this source is recharged only at high altitudes.

![Graph](image-url)

Fig. 5. The interpretation of two springs on Cheju Island, Republic of Korea. The combined exponential and piston flow model (EPM, $\eta > 1$) is compared with the binomial model (dashed lines) and with the exponential model ($\eta = 1.0$).
However, it is evident from Fig. 5 that were measurements started a year earlier there would be no doubt in the fitting procedure. It is also clear that in this case the mean transit time found from the reinterpretation is much more reliable and differs distinctly from that given in the original paper.

In general the reinterpretation of the Cheju Island data confirms the findings of Davis et al. (1970), though the use of more refined models gives more confidence and additional details concerning the physical parameters of the investigated systems.

(d) Dinçer et al. (1970a, b) gave a nice example of the applicability of the environmental tracers to investigations of the snowmelt runoff from a small mountain basin (Modry Dul basin, northern Bohemia, Czechoslovakia).

The baseflow is 0.02–0.03 m³ s⁻¹ whereas the highest discharges in ten years exceeded 3 m³ s⁻¹ and were caused mostly by snowmelt water. It is thus evident that the system cannot be treated as being in a steady state. Dinçer et al. (1970a) ingeniously solved this problem by taking tritium concentrations only in the baseflow for the interpretation of the turnover time.

Neither Dinçer et al. (1970a), nor Martinec in the discussion of Przewołocki and Yurtsever (1974), clearly described their calculations of the input function. However undoubtedly Dinçer et al. (1970a) assumed no contribution from the summer precipitation, whereas it is difficult to imagine that in high mountains the whole summer precipitation (April–September) goes to evapotranspiration. In a study of a similar mountain basin in the Alps, Martinec et al. (1974) assumed that ¼ of the summer precipitation infiltrates. This assumption was more or less in agreement with the average runoff coefficient, which can be calculated from the data of Martinec et al. (1974) as being equal to 0.83 or 0.85.

Przewołocki and Yurtsever (1974) reinterpreted the Modry Dul data using FSM (with seven fitting parameters) for α = 1. Their interpretation yields $T = 5.25 \text{a}$ as compared to 2.5 a of Dinçer et al. (1970a). However, as it can be seen from Fig. 6, the experimental points of Przewołocki and Yurtsever (1974) differ from those of Dinçer et al. (1970a, b) although both papers contain data produced in the same laboratory. The differences are larger than possible errors due to drawing and redrawing. Further considerations of this paper are limited to the experimental points taken from the later work.

Of the models developed in this work DM gave the best fitting. Calculations were performed for α = 1, taking the input function from Przewołocki and Yurtsever (1974), and for α = 0 estimating the input function similarly as in the case of the Rasche spring. In Fig. 6 the final results of fitting are summarized. It can be seen that the differences in $T$ values resulting from the use of different models are lower than the difference resulting from the uncertain input function. However, there is no doubt that the assumed α-values can be treated as extreme cases. Thus the $T$-value should be $\sim 4.5 \text{a}$ with an uncertainty of ±1 a. Of the two extreme values of the dispersion parameter (see Fig. 6) the higher value is more probable for the type of
groundwater system under consideration. Thus it is possible that the value of $T$ taken as the mean of the extreme cases is slightly underestimated.

Taking the mean value of $T$, the volume of the groundwater system contributing to the baseflow is:

$$V = T \cdot Q = 4.5 \text{ (a)} \cdot 0.79 \cdot 10^6 \text{ (m}^3/\text{a}) = (3.6 \pm 0.8) \cdot 10^6 \text{ (m}^3)$$

where $Q$ is here the early average flow rate of the baseflow. For the known area of the basin it gives the average depth of water as:

$$H = \frac{V}{S} = 3.6 \cdot 10^6 / 2.6 \cdot 10^6 = 1.4 \pm 0.3 \text{ (m)}$$

and assuming the porosity of unconsolidated glacial deposits as equal to 0.3 their average thickness is:

$$H_{\text{deposit}} = \frac{H}{(\text{porosity})} = \frac{1.4}{0.3} \approx 4.6 \pm 1.0 \text{ (m)}$$

The large volume obtained may be perhaps astonishing. Dincer et al. (1970a) considered even the water depth of 1 m as an astonishingly high value for such a small basin. However, the average discharge from the basin is, according to Dincer et al. (1970b), 0.152 m$^3$ s$^{-1}$ = 4.8 $\cdot$ 10$^6$ m$^3$ a$^{-1}$, which is 20% more than the total precipitation there. Namely:

$$P \cdot S = 1.5 \text{ (m a}^{-1}) \cdot 2.6 \cdot 10^6 \text{ (m}^2) = 4 \cdot 10^6 \text{ (m}^3 \text{ a}^{-1})$$
A similar conclusion can be drawn from fig. 3 in Dinçer et al. (1970b) where the runoff depth for three consequent years is 33% higher than the precipitation. In other words the Modry Dul Creek discharges much more water than the amount of precipitation on the watershed. There are three possible reasons for this discrepancy. The first, as pointed out by Dinçer et al. (1970b), results from difficulties in properly measuring the precipitation in a mountain basin. The second may result from an underground inflow to the basin, which is of low probability for the known geomorphology of the area. The third may result from a systematic error in the measurement of discharge. In the second case the large volume would be justified, whereas in the third case the volume would be overestimated due to the overestimation of the baseflow.

In Fig. 7 a comparison of the dispersive models with FSM for a wider time span than in Fig. 6 is given. From that figure it is clear that were the investigations started a year earlier, or continued for a year longer, the choice of the best model would be much easier. It should be noted that the concentration scale in Fig. 7 is logarithmic, thus somewhat hiding the differences between the models.

(e) The first use of the binomial model was reported by Davis et al. (1967) and Dinçer and Davis (1967) in an interesting study of the Vienna Basin, an
important groundwater system. These authors rejected this model however from a consideration of the upper part of the aquifer in which there was tritium from direct infiltration. Deeper parts showed relatively homogeneous concentrations along the profile suggesting that this part of water originated in a distant recharge area. This part was interpreted quantitatively as if the aquifer were confined (see Fig. 1, case 5e). The low number of experimental data does not allow any better reinterpretation than the original one. The problem is discussed here for three reasons. The first one was already mentioned above and relates to the interesting approach. The second reason concerns the binomial model applied by these authors. As the main recharge area was probably at a large distance, the apparent dispersion should not be very high and the use of this model acceptable. Finally, the problem is interesting because it is a typical example in which theoretically the $C_{\text{IFR}}$ solution should be used as the weighting function. In other words the injection of tracer is natural, i.e. averaged by flow rates, whereas the detected concentration is averaged by the thickness of the aquifer.

Execution of the calculation described above was carried out by a program written in FORTRAN IV for the Cyber® 72 computer. Each example considered within this work required ~100 trials before a good fit was obtained. For instance for site 2, Cheju Island, 50 unsuccessful trials of dispersive models were performed and 70 trials of the combined model. In that case in the final stages of the fitting process the turnover time steps were equal to 1 a whereas $\eta$ steps were equal to 0.05. Calculations for the dispersive model were the most time-consuming. For that model a run of eight curves takes ~14 s.

CONCLUSIONS

Lumped-parameter models are generally used for the interpretation of environmental radioisotope tracers in groundwaters. In this work, several known models have been discussed and three new models developed. The limitations of the lumped-parameter models are self-evident from the assumptions used for their derivations and from the type of parameters which they supply. As mentioned earlier, they do not supply the information which is most needed by the hydrologist. Under favourable conditions, the age difference may, however, serve for determining one of the basic parameters, i.e. the velocity of water. In spite of all the limitations, whenever environmental radioisotopes are measured, the quantitative interpretation, based on the use of lumped-parameter models, should be attempted. Such an interpretation is particularly useful for karstic or fractured systems, where the applicability of conventional methods is limited.

Two of the three models developed within this work, i.e. the dispersion model (DM) based on a new solution to the dispersion equation, and the
combined exponential and piston flow model (EPM) seem to be more appropriate to real situations than other known models. Their higher reliability results from much better fitting, which is not astonishing because of an additional fitting parameter. However, two-parameter models used for solving the inverse problem are generally physically reliable. In addition to the main fitting parameter, i.e. the turnover time, they supply additional physical information as both $D/vx$ and $\eta$ parameters have a clear physical meaning. In two examples considered, the two-parameter models of this work gave as good a fit as the multiparameter models (FSM) used by other authors. In general, the physical meaning of the parameters obtained from models with a lower number of fitting parameters is more reliable than in the case of a multi-parameter model. Thus it may be surprising that the FSM yielded nearly the same turnover times as the two-parameter models. Perhaps a prior physical knowledge of the systems and the experience of the investigators were decisive.

In general the finite state mixing-cell models (FSM) should be treated as distributed parameter models. Their use with a large number of fitting parameters is not recommended because the physical meaning of the obtained values of the parameters becomes then doubtful. In more general terms it may be stated that the environmental radioisotope distributions offer little hope for obtaining the inverse solutions from the distributed parameter models. However, it does not mean that the environmental radioisotope tracers cannot be used for the confirmation or rejection of assumptions related to the distributed parameter models of the hydrodynamic field.

The binomial model served its purpose when simple approximations were needed. Now that a more rigorous dispersive model and computers are available it seems that there is little need for any further use of this model.

Usually the input function of tritium is not well known. In such a case it is recommended that the interpretation be performed not only for the input function selected by the interpreter as the most probable, but also for the extreme cases. The reinterpretation of the Modry Dul basin and the Rasche spring cases may serve here as examples of differences which may result from extreme values of the infiltration coefficient. Changes in infiltration from year to year may also cause an error but it can be expected to be smaller than the error caused by an inappropriate selection of average values.

Radioisotopes with a constant input offer less interpretational possibilities than those with variable inputs. The use of the piston flow model is generally unacceptable. In each case, an appropriate model should be selected on the basis of a prior physical knowledge. If such knowledge is not available, the uncertainty of the age determination can be estimated by the use of models giving extreme values of the age.

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