5

Mathematical Modelling of Experimental Data

Tracers are applied in groundwater systems mainly: (i) for the quantitative determination of rock and/or flow properties (e.g. water velocity, hydraulic conductivity, dispersivities, porosities, transit time, volume of water); and (ii) for the calibration or validation of numerical flow and transport models. The estimation of parameter values from tracer experiments is only possible if an adequate mathematical model is used: the selected model must reflect the tracer transport and tracer behaviour in the system being studied. Some of problems related to model selection are discussed by, for instance, Maloszewski and Zuber (1992b, 1993). The definitions used here for tracer modelling are summarized in Chapter 2. The present chapter gives the mathematical description of artificial tracer transport in homogeneous and heterogeneous groundwater systems, in surface water (rivers and streams), as well as in double-porous media, such a fissured rocks, the unsaturated zone and rivers (streams) with stagnant water zones. Furthermore, the lumped-parameter approaches used for quantitative interpretation of environmental tracer data are discussed. Additionally, some examples of using those models are presented.

5.1 Artificial tracer (Ideal) under saturated flow conditions

5.1.1 Transport equations

5.1.1.1 3D equations

In an aquifer containing only mobile water, the transport of nonreactive and nondecaying solutes in groundwater is described by a three-dimensional (3D) dispersion equation in which the dispersion has a tensor form and the water flow velocity a vector

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form (Bear, 1961; Scheidegger, 1961). For an ideal tracer, this transport equation – here referred to as the general 3D transport equation – has the following form:

$$\frac{\partial}{\partial x}\left(D_{xx}\frac{\partial C}{\partial x} + D_{xy}\frac{\partial C}{\partial y} + D_{xz}\frac{\partial C}{\partial z} - v_x C\right)$$

$$+ \frac{\partial}{\partial y}\left(D_{yx}\frac{\partial C}{\partial x} + D_{yy}\frac{\partial C}{\partial y} + D_{yz}\frac{\partial C}{\partial z} - v_y C\right) \tag{5.1}$$

$$+ \frac{\partial}{\partial z}\left(D_{zx}\frac{\partial C}{\partial x} + D_{zy}\frac{\partial C}{\partial y} + D_{zz}\frac{\partial C}{\partial z} - v_z C\right) = \frac{\partial C}{\partial t}$$

where (x, y, z) is an arbitrarily chosen coordinate system; C is the concentration of solute in the water $[ML^{-3}]$; x, y, z are the flow distances [L], in the directions (x, y, z), respectively; t is time [T]; v_x, v_y, v_z $[LT^{-1}]$ are the x-, y-, z- components of the velocity vector $(\overline{v})$, and D_{ij} $[L^2T^{-1}]$ (with i, j = x, y, z) are the components of the dispersion tensor $(\overline{D})$:

$$D_{xx} = D_L\left(\frac{v_x^2}{v^2}\right) + D_T\left(\frac{v_y^2}{v^2}\right) + D_T\left(\frac{v_z^2}{v^2}\right) + \frac{D_m}{\tau} \tag{5.2}$$

$$D_{yy} = D_T\left(\frac{v_x^2}{v^2}\right) + D_L\left(\frac{v_y^2}{v^2}\right) + D_T\left(\frac{v_z^2}{v^2}\right) + \frac{D_m}{\tau} \tag{5.3}$$

$$D_{zz} = D_T\left(\frac{v_x^2}{v^2}\right) + D_T\left(\frac{v_y^2}{v^2}\right) + D_L\left(\frac{v_z^2}{v^2}\right) + \frac{D_m}{\tau} \tag{5.4}$$

$$D_{xy} = D_{yx} = (D_L - D_T)\left(\frac{v_x v_y}{v^2}\right) \tag{5.5}$$

$$D_{xz} = D_{zx} = (D_L - D_T)\left(\frac{v_x v_z}{v^2}\right) \tag{5.6}$$

$$D_{zy} = D_{yz} = (D_L - D_T)\left(\frac{v_z v_y}{v^2}\right) \tag{5.7}$$

where D_m is the molecular diffusion coefficient of tracer in free water $[L^2T^{-1}]$; τ is the tortuosity factor of the porosity matrix $[-]$; and D_L and D_T are the longitudinal and transverse dispersion coefficients $[L^2T^{-1}]$. D_L and D_T are equal to (Scheidegger, 1961):

$$D_L = \alpha_L \ v \tag{5.8}$$

$$D_T = \alpha_T \ v \tag{5.9}$$

where α_L and α_T are, respectively, the longitudinal and transverse dispersivities [L] of the hydrodynamic dispersion, which characterize the heterogeneity of the porous
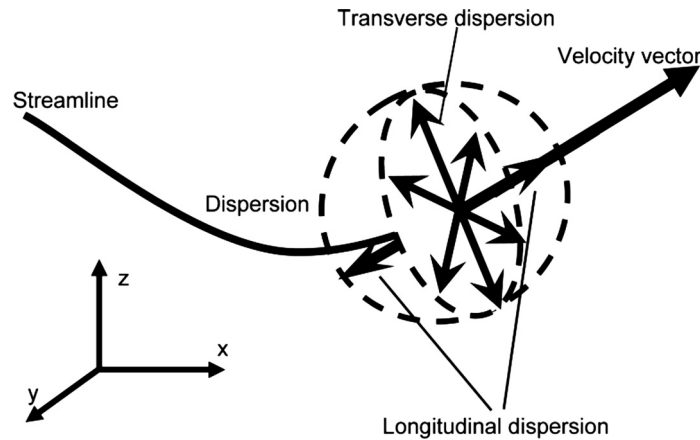
Figure 5.1 Schematic presentation of the two transport processes – convection and dispersion – in the 3D case. The dashed line shows the concentration distribution of an ideal tracer injected instantaneously into the groundwater at beginning of the stream line.

medium. The mean water velocity (v) is equal to:

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \tag{5.10}$$

A schematic presentation of both possible transport processes – convection and dispersion, both longitudinal and transverse – is shown in Figure 5.1.

The solution to the general transport Equation (5.1) can only be found by applying numerical techniques. The solution obtained using finite difference methods (FDM) is used in the computer software MODFLOW, whereas that obtained using finite element methods (FEM) is used in, for instance, FEFLOW.

In a granular porous medium that is assumed to be homogeneous, the flow lines are parallel; the x-axis is then taken to be permanently parallel to the flow lines (Figure 5.2). In this situation the components of the velocity vector reduce to $v = v_x$, $v_y = v_z = 0$, and the dispersion tensor (5.2–5.57) is considerably simplified (5.12–5.14). The 3D transport Equation (5.1) then has following form for steady-state flow – this is here termed the specific 3D transport equation:

$$D_{xx}\frac{\partial^2 C}{\partial x^2} + D_{yy}\frac{\partial^2 C}{\partial y^2} + D_{zz}\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \tag{5.11}$$

Figure 5.2 Schematic presentation of the coordinate system (x, y, z), with the x-axis parallel to the flow direction.

where D_{xx}, D_{yy} and D_{zz} are now given by:

$$D_{xx} = D_L + \frac{D_m}{\tau} \tag{5.12}$$

$$D_{yy} = D_T + \frac{D_m}{\tau} \tag{5.13}$$

$$D_{zz} = D_T + \frac{D_m}{\tau} \tag{5.14}$$

If the water flow velocity is greater then approx. 0.1 m/day, the molecular diffusion is negligibly small in comparison to the hydrodynamic dispersion; then (5.6) reduces to $D_{xx} = D_L$ and $D_{yy} = D_{zz} = D_T$.

5.1.1.2 2D equations

If a tracer is injected through the whole thickness of a homogeneous aquifer, for example into a fully penetrating well (Figure 5.3), then the tracer already vertically well mixed in the injection well (x = 0, y = 0) and the vertical concentration gradient is equal to zero, that is

$$\frac{\partial C}{\partial z} = 0 \tag{5.15}$$

Taking (5.15) into account and assuming (a) that the x-axis is parallel to the flow direction and (b) that the molecular diffusion is negligibly small, the transport Eq. (5.5) can be reduced to the following specific two dimensional (2D) one:

$$D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial y^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \tag{5.16}$$
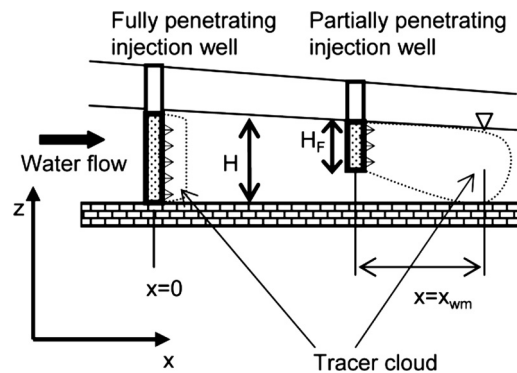

Figure 5.3 Schematic presentation of tracer injection performed into fully or partially penetrating wells.

Equation (5.16) describes tracer transport in the horizontal plane along the flow direction (x-axis) when the tracer is already completely mixed in the injection well through the vertical profile of the aquifer.

The situation is different when the tracer is injected into a partially penetrated well (Figure 5.3). Then it is necessary to estimate x_{wm}, the flow distance from the well within which the tracer will become vertically well mixed as the result of transverse dispersion. x_{wm} is given by following formula:

$$x_{wm} = \frac{(H - H_F)^2}{2\alpha_T} \tag{5.17}$$

where H [L] is the mean thickness of the aquifer and H_F is the length of the filter in the injection well. For flow distances larger then x_{wm} ($x > x_{wm}$), the 2D Equation (5.16) can be applied for parameter estimation.

5.1.1.3 1D equations

In some experiments, transverse dispersion can be neglected in both the y and z directions; an example is when the tracer is injected into the water flowing into a column throughout the whole cross-section of the column perpendicular to the flow direction. If the x-axis is taken along the column axis (flow direction), then the concentration gradients in the y and z directions both equal zero:

$$\frac{\partial C}{\partial y} = \frac{\partial C}{\partial z} = 0 \tag{5.18}$$

The same situation can be assumed for transport in streams or rivers, when the tracer is injected throughout the whole cross-section of the stream. When the x-axis is then taken parallel to the flow direction, Equation (5.16) is reduced to the 1D transport equation:

$$D_L \frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \tag{5.19}$$

Maloszewski and Zuber (1990) note that this equation can also be applied in radial-convergent flow (for instance, in a combined pumping and tracer experiment), provided that the dispersion parameter, $P_D = D_L/(vx) = \alpha_L/x$, is sufficiently small ($P_D < 0.1$).

5.1.2 Solutions to the transport equations

In most practical experiments, the injection of the tracer mass M into the water flux entering the system is performed instantaneously ($t_{inj} \approx 0$), which is mathematically described by the Dirac function $\delta(t)$. The 3D transport equation is in practice hardly ever applicable; for its theoretical solution, see Zuber (1970).

5.1.2.1 2D solution

The initial and boundary conditions for 2D transport in the horizontal (x, y) plane
are as follows (Lenda and Zuber, 1970), assuming instantaneous injection in a fully
penetrating well:

$$C(x = 0, y = 0, t) = \frac{M}{nH} \delta(t) \, \delta(x) \, \delta(y) \tag{5.20}$$

$$C(x, y, t = 0) = 0 \tag{5.21}$$

$$\lim_{(x, y) \to \infty} C(x, y, t) = 0 \tag{5.22}$$

where n is the effective water porosity [−] and $\delta(x)$ and $\delta(y)$ are Dirac space functions
[1/L] in the x and y directions respectively.

The solution to Equation (5.16) with boundary and initial conditions (5.20–5.22) is
(Lenda and Zuber, 1970):

$$C(x, y, t) = \frac{M}{nH} \frac{x}{4\pi v t^2 \sqrt{D_L D_T}} \exp\left[-\frac{(x - vt)^2}{4D_L t} - \frac{y^2}{4D_T t}\right] \tag{5.23}$$

This solution describes the horizontal transport of a tracer mass M that was injected
instantaneously into a fully penetrating well situated at the origin $(0, 0)$ of the coordinate
system (x, y). Equation (5.23) has three parameters (v, D_L, D_T), the values of which
need to be estimated. These parameters can only be found when the tracer experiment
is performed in a test field which has observation wells situated perpendicular to the
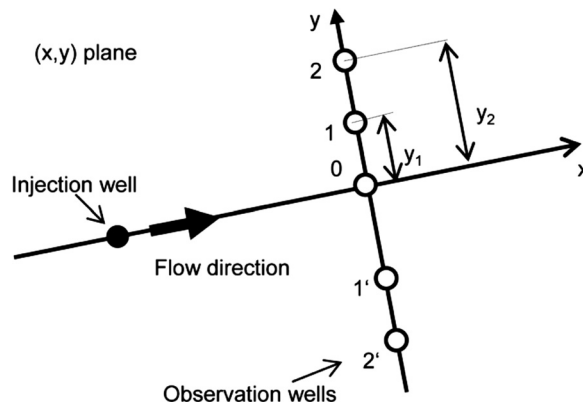flow direction (Figure 5.4).

Figure 5.4 Test field in the horizontal plane (x, y), with injection and observation wells situated
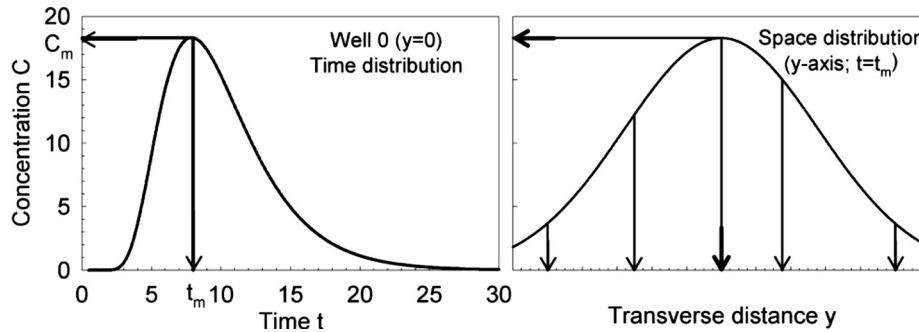perpendicular to the flow direction.

Figure 5.5   Left: Time distribution of tracer concentration C(t), instantaneously injected, observed in well 0 (Figure 5.4). Right: Space (transverse) distribution of tracer concentration C(y) observed in the wells: 2′, 1′, 0, 1, 2 (Figure 5.4) sited perpendicular to the flow direction (y-axis) measured at time t = t$_m$ after injection.

Consider first the tracer concentrations measured in the observation well 0 (x = 0, y = 0) as a function of t, the time after injection (Figure 5.4). The so-called time distribution of the tracer concentration (5.23) then simplifies to:

$$C(t) = C_m \left(\frac{t_m}{t}\right)^2 \exp\left[-\frac{(x - vt)^2}{4D_L\,t} + \frac{(x - vt_m)^2}{4D_L\,t_m}\right] \tag{5.24}$$

where C$_m$ and t$_m$ are the peak concentration and the time of the appearance of that concentration, taken from the tracer concentrations measured in the well 0 (Figure 5.5).

Equation (5.24) has two parameters (v, D$_L$), the values of which can easily be calculated from experimental data obtained in well 0 (see Section 5.1.3). To calculate the transverse dispersion coefficient D$_T$, the tracer concentrations measured in the wells perpendicular to the flow direction (wells 2, 1, 0, 1′, 2′ in Figure 5.4) have to be measured at time t = t$_m$. Then the transverse distribution, the so-called space distribution, of the tracer concentration can be constructed as shown in Figure 5.5 (right). The transverse distribution of the tracer concentration C(y) observed at the flow distance (x) at time t = t$_m$ after injection is described by following equation:

$$C(y) = C_m \exp\left[-\frac{y^2}{4D_T t_m}\right] \tag{5.25}$$

with the transverse dispersion coefficient (D$_T$) now being the only parameter that needs to be obtained.

The application of equations (5.24) and (5.25) to the tracer concentrations measured in the observation wells shown in Figure 5.4 enables the three required parameters (v, D$_L$, D$_T$) to be determined under natural flow conditions.

5.1.2.2 1D solution

For tracer experiments performed in a column, or for combined pumping-tracer experiments (radial flow; Figure 5.6), the 1D transport Equation (5.9) is applicable. When the tracer is injected instantaneously, the initial and boundary conditions are as follows:

$$C(x = 0, t) = \frac{M}{Q}\delta(t) \tag{5.26}$$

$$C(x, t = 0) = 0 \tag{5.27}$$

$$\lim_{x \to \infty} C(x, t) = 0 \tag{5.28}$$

where M [M] is the mass of tracer injected and Q [L^3/T] is the volumetric flow rate through the column (or the pumping rate in a combined pumping-tracer experiment).

With these conditions, the solution to (5.9) is as follows (Lenda and Zuber, 1970; Kreft and Zuber, 1978):

$$C(x, t) = \frac{M}{Q} \frac{x}{\sqrt{4\pi D_L t^3}} \exp\left[-\frac{(x - vt)^2}{4D_L t} \right] \tag{5.29}$$

Here it is assumed that in a column experiment the tracer is injected at x = 0 into the water flowing into the column and measured in the water flowing out of the column (flux–flux mode, see Kreft and Zuber, 1978), and that in a combined pumping-tracer experiment the tracer is injected throughout the whole thickness of the aquifer (H) on the potential (vertical) line $0 \leq z \leq H$ and measured in the pumped water. Equation (5.29) has two parameters (v, D_L), the values of which can be calculated from experimental data obtained from the outflow (see Section 5.1.3).

One measure often used in tracer hydrology is the so-called mean transit time of water (t_0). This is defined as follows:

$$t_0 = \frac{x}{v} \tag{5.30}$$

which for 1D (closed) systems is equivalent to:

$$t_0 = \frac{V}{Q} \tag{5.31}$$

where V [L^3] is the volume of mobile water in the system.

By applying the mean transit time (5.30) and the dispersion parameter P_D:

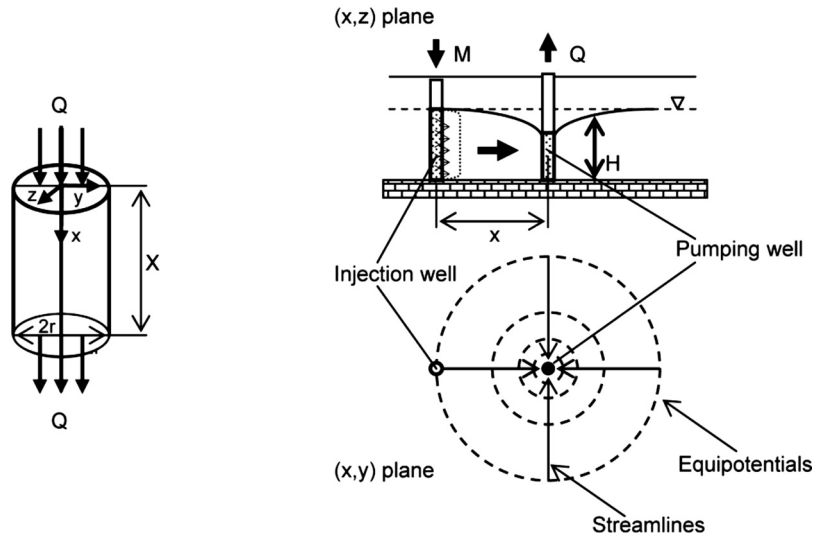$$P_D = \frac{D_L}{vx} = \frac{\alpha_L}{x} \tag{5.32}$$

Figure 5.6 Practical applications of the 1D solution to the transport equation: column experiment (left); and combined pumping-tracer experiment (right). Q stands for the flow rate through the column (left), and for the pumping rate (right).

the solution (5.29) can be reformulated as the so-called normalized solution (Lenda and Zuber, 1970):

$$C(t) = \frac{M}{Q\,t_0} \frac{1}{\sqrt{4\pi P_D(t/t_0)^3}} \; \exp\left[-\frac{(1 - t/t_0)^2}{4P_D\,t/t_0}\right] \qquad (5.33)$$

where C(t) is the theoretical tracer concentration in the outflow from the closed system (a column or a pumping well). Equation (5.33) has two parameters P_D and t_0, the second of which can be used to calculate the effective porosity (n) of the system. For the column experiment:

$$n = \frac{Q\,t_0}{\pi r^2 x} \qquad (5.34)$$

and for a combined pumping-tracer (radial flow) experiment (Zuber, 1974; Kreft and Zuber, 1979):

$$n = \frac{Q\,t_0}{\pi x^2 H} \qquad (5.35)$$

where x is the column length in (5.34) and the distance between the injection and pumping wells in (5.35), r is the column radius, and H is the mean aquifer thickness.

The value of t_0 obtained from a column experiment can be validated by comparing the value of the porosity calculated from (5.34) with the value otherwise obtained,

r instance by weighing the dry (m_d) and water saturated (m_s) column:

$$n = \frac{m_s - m_d}{\pi r^2 x} \tag{5.36}$$

For a combined pumping-tracer experiment, Equation (5.35) is the only way of determining the effective porosity.

Equation (5.33) written in dimensionless form – termed this can be with the $E(t/t_0)$ function – was given by Lenda and Zuber (1970):

$$E(t/t_0) = \frac{C(t)Qt_0}{M} = \frac{1}{\sqrt{4\pi P_D(t/t_0)^3}} \ \exp\left[-\frac{(1 - t/t_0)^2}{4P_D t/t_0}\right] \tag{5.37}$$

The form of the $E(t/t_0)$ function is shown in Figure 5.7, for various values of the dispersion parameter P_D. In this figure can be seen the influence of the system's heterogeneity on the shape of the tracer concentration curve: the time to reach the peak concentration (t_m/t_0) decreases with increasing of P_D values (increasing system heterogeneity). The position of the peak concentration on the time-axis (t_m/t_0) is related to the dispersion parameter P_D as follows:

$$\left(\frac{t_m}{t_0}\right) = \sqrt{1 + (3P_D)^2} - (3P_D) \tag{5.38}$$

(It is worth noting here that the time of appearance of the peak concentration in the 2D case (5.24) at the well situated on the x-axis (y = 0) is described by (5.23) with '$4P_D$' replacing '$3P_D$'.)
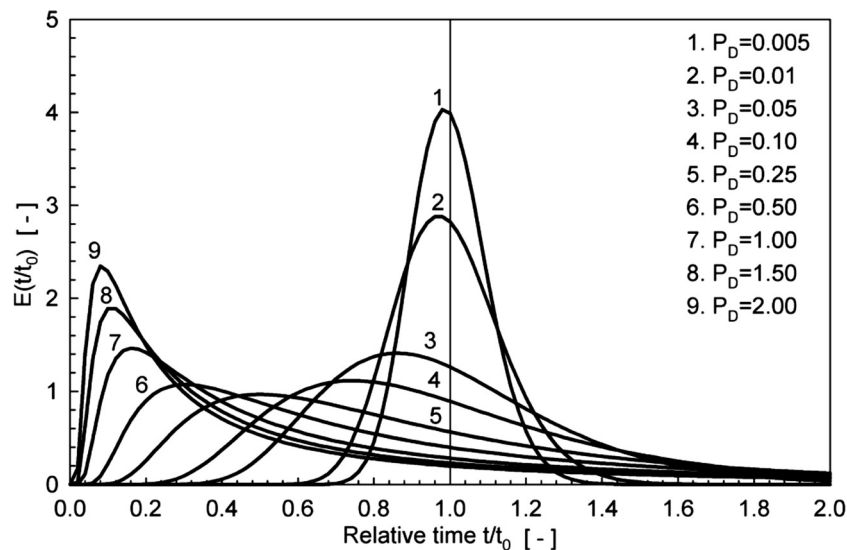

Figure 5.7 Graphical presentation of the solution to the 1D transport equation, function (5.37), given for the normalized time (t/t_0), for various values of the dispersion parameter P_D.

If the volume of water in the system ($V_W = Q \cdot t_0$) is known, and if the range of values of P_D can be estimated, then Figure 5.7 together with Equation (5.37) can be used to plan a tracer sampling campaign and to estimate the mass of tracer that needs to be injected. For the estimate of the mass it is also necessary to estimate the necessary peak tracer concentration $C_m = C(t_m)$. Generally, it is sufficient for C_m to be 10–20 times larger than the background concentration (C_B) measured in the groundwater in the area under investigation. In the worst case (the lowest $E(t)$ curve), this rule results in:

$$M = ca.(10 \ to \ 20)C_B \times V_W \tag{5.39}$$

It was shown by Maloszewski and Zuber (1990) that in tracer experiments performed in closed systems (1D cases) the relative mass recovery RR can readily be calculated as a function of time (t):

$$RR(t) = Q \int\limits_0^t C(t)dt/M \tag{5.40}$$

For the solution (5.33) found for the 1D case, RR(t) is equal to the function $F(t/t_0)$ defined by Lenda and Zuber (1970) as:

$$RR(t) = F(t/t_0) = \frac{1}{2}\left[erfc\left(\frac{1 - t/t_0}{\sqrt{4P_D t/t_0}}\right) + \exp\left(\frac{1}{P_D}\right) erfc\left(\frac{1 + t/t_0}{\sqrt{4P_D t/t_0}}\right)\right] \tag{5.41}$$

with erfc $(\omega) = 1 - erf(\omega)$, where $erf(\omega)$ is the error function defined as:

$$erf(\omega) = \frac{2}{\sqrt{\pi}} \int\limits_0^\omega e^{-\varepsilon^2} d\varepsilon \tag{5.42}$$

The form of the $F(t/t_0)$ function (5.40) is shown in Figure 5.8.

5.1.3 Estimation of the transport parameters

5.1.3.1 Combined least squares method (LSQM)

The solution of the inverse problem (i.e. the estimation of the transport parameters) can be obtained by fitting the appropriate theoretical solutions to experimental concentrations using a trial-and-error procedure. For 1D experiments the solution (5.33) is used; for 2D experiments the procedure starts by fitting (5.24) in the observation well on the x-axis (y = 0) and ends by fitting (5.25) to the transverse distribution of tracer concentrations.

Equations (5.24) and (5.33) can also be used in an automatic fitting procedure that combines the least squares method with Taylor series approximation of both solutions (Maloszewski, 1981). In both the 1D and 2D cases (in 2D, for y = 0), the solutions to
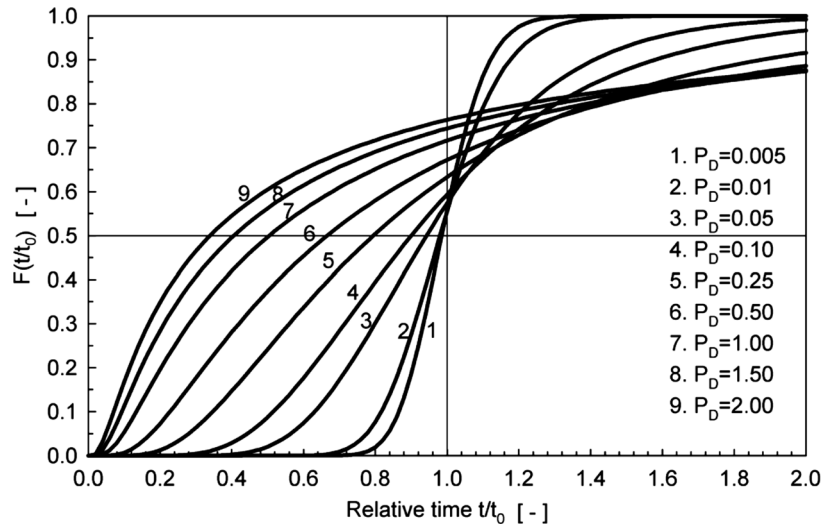
Figure 5.8 Graphical presentation of the solution of Eq. (5.41), the relative recovery curve for the 1D case (this is also the solution C/C_0 of the 1D transport equation for continuous injection of tracer C_0), given for the normalized time (t/t_0), for various values of the dispersion parameter P_D.

the transport equations can be written using one common function $G(a, b, t)$, which has the following form:

$$G(a, b, t) = C_m \left(\frac{t_m}{t} \right)^k \exp \left[-\frac{(1 - t/b)^2}{4at/b} + \frac{(1 - t_m/b)^2}{4at_m/b} \right] \qquad (5.43)$$

where $a = P_D$ and $b = t_0$ are the parameters to be estimated. In the 2D case (for $y = 0$), $k = 2$; in the 1D case, $k = 1.5$.

Assume that N values of the concentration C_i have been measured in an experiment for the times $t = t_i$ ($i = 1, N$). The fitting procedure assumes that the solution to the inverse problem ('best fit') is obtained when the values of parameters (a, b) yield the minimum value of the sum of the squared differences between the theoretical and observed concentrations:

$$\Phi = \sum_{i=1}^{N} [C_i - G(t_i, a, b)]^2 \qquad (5.44)$$

Substitution of (5.43) into (5.44) yields a quadratic equation, which cannot be directly solved. To remedy this difficulty, (5.43) is first written as a Taylor series. Neglecting higher derivatives, this is:

$$G(a, b, t) \approx G(a_0, b_0, t) + \frac{\partial G}{\partial a} \Delta a + \frac{\partial G}{\partial b} \Delta b \qquad (5.45)$$

Substitution of (5.45) into (5.44) now gives the following linear function:

$$\Phi = \sum_{i=1}^{N} [\varepsilon_i - (\beta_i \Delta a + \gamma_i \Delta b)]^2 \tag{5.46}$$

where:

$$\beta_i = \frac{\partial G}{\partial a} = -C_m \left(\frac{t_m}{t_i}\right)^k \left(b - \frac{t_m t_i}{b}\right) \left(\frac{1 - t_m/t_i}{4a^2 t_m}\right) \exp\left[\frac{1 - t_m/t_i}{4a t_m} \left(b - \frac{t_m t_i}{b}\right)\right] \tag{5.47}$$

$$\gamma_i = \frac{\partial G}{\partial b} = C_m \left(\frac{t_m}{t_i}\right)^k \left(1 + \frac{t_m t_i}{b^2}\right) \left(\frac{1 - t_m/t_i}{4a t_m}\right) \exp\left[\frac{1 - t_m/t_i}{4a t_m} \left(b - \frac{t_m t_i}{b}\right)\right] \tag{5.48}$$

$$\varepsilon_i = C_i - G(a, b, t_i) \tag{5.49}$$

Equation (5.46) has its minimum when:

$$\frac{\partial \Phi}{\partial(\Delta a)} = 0 \tag{5.50}$$

$$\frac{\partial \Phi}{\partial(\Delta b)} = 0 \tag{5.51}$$

Solving the above equations leads finally to:

$$\Delta a = \frac{-\left(\sum_{i=1}^{N} \gamma_i^2\right)\left(\sum_{i=1}^{N} \beta_i \varepsilon_i\right) + \left(\sum_{i=1}^{N} \beta_i \gamma_i\right)\left(\sum_{i=1}^{N} \gamma_i \varepsilon_i\right)}{\left(\sum_{i=1}^{N} \beta_i \gamma_i\right)^2 - \left(\sum_{i=1}^{N} \beta_i^2\right)\left(\sum_{i=1}^{N} \gamma_i^2\right)} \tag{5.52}$$

$$\Delta b = \frac{-\left(\sum_{i=1}^{N} \beta_i^2\right)\left(\sum_{i=1}^{N} \gamma_i \varepsilon_i\right) + \left(\sum_{i=1}^{N} \beta_i \gamma_i\right)\left(\sum_{i=1}^{N} \beta_i \varepsilon_i\right)}{\left(\sum_{i=1}^{N} \beta_i \gamma_i\right)^2 - \left(\sum_{i=1}^{N} \beta_i^2\right)\left(\sum_{i=1}^{N} \gamma_i^2\right)} \tag{5.53}$$

The solving of the inverse problem now requires only that the values of Δa and Δb be obtained. This is done iteratively, starting with calculation of all the N values of the functions (5.43) and (5.47–5.49) for the arbitrary initial values $a = a_0$ and $b = b_0$. After calculating Δa and Δb from (5.52) and (5.53), new values of a and b are calculated:

$$a = a_0 + \Delta a \tag{5.54}$$

and

$$b = b_0 + \Delta b \tag{5.55}$$

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The following stopping condition is used for the iteration:

$$\left| \frac{\Delta a}{a} \right| \leq 0.005 \quad and \quad \left| \frac{\Delta b}{b} \right| \leq 0.005 \tag{5.56}$$

If condition (5.56) is not fulfilled, the iteration procedure continues with the values of (5.54) and (5.55) taken now as a_0 and b_0. If condition (5.56) is fulfilled, the iteration procedure ends with last values of a, and b. This procedure allows the transport parameters P_D and t_0 to be estimated for any given set of data (t_i, C_i, for i = 1, ... N), with the best possible mathematical accuracy.

The estimation of parameters for the 1D or 2D (y = 0) cases using the combined least square method (*LSQM*) can be performed on a PC using the user-friendly software FIELD, which is available from one of the authors (Maloszewski).

5.1.3.2 Method of moments (MM)

Parameter estimation is often carried out using the well-known method of moments (Kreft and Zuber, 1978; Maloszewski and Zuber, 1985, 1992b; Maloszewski, 1994). Generally, the lth moment M_l of the tracer curve C(t) is defined as:

$$M_l = \int_0^\infty t^l C(t)\, dt \tag{5.57}$$

which, by applying the numerical (trapezoidal) method of integration (with $C_{i=0} = 0$), yields:

$$M_l = \frac{1}{2} \sum_{i=1}^{N+1} \left(C_{i-1} t_{i-1}^l + C_i t_i^l \right) (t_i - t_{i-1}) \tag{5.58}$$

In using the method of moments in tracer hydrology, two mathematical descriptors are always calculated: the centre of gravity $\bar{t}$, that is the mean tracer transit time (t_t):

$$\bar{t} = t_t = \frac{\int_0^\infty t C(t)\, dt}{\int_0^\infty C(t)\, dt} = \frac{M_1}{M_0} \tag{5.59}$$

and the variance of the tracer concentration curve:

$$\delta_t^2 = \frac{\int\limits_0^\infty (t - \bar{t})^2 C(t)\,dt}{\int\limits_0^\infty C(t)\,dt} = \frac{M_2 M_0 - M_1^2}{M_0^2} \tag{5.60}$$

The calculation of the integrals in (5.59) and (5.60) requires that the tracer concentration curve be obtained for a sufficiently long period – the upper limit of the integrals is $t \to \infty$. In practice this means that the tracer concentration has to be measured until its value tails off and reaches the background concentration in the water. Only in this situation can the values of the descriptors (5.59) and (5.60) be properly calculated. Even then there is a problem in deriving the transport parameters (t_0 and P_D or v and α_L) from these descriptors. Only in the 1D case –, that is only if equations (5.29) or (5.33) are satisfied – are the following well-known relationships between the mathematical descriptors (5.59 and 5.60) and the transport parameters valid:

$$t_0 = \bar{t} \quad or \quad v = \frac{x}{\bar{t}} \tag{5.61}$$

$$P_D = \frac{1}{2}\left(\frac{\delta_t}{\bar{t}}\right)^2 \quad or \quad \alpha_L = \frac{x}{2}\left(\frac{\delta_t}{\bar{t}}\right)^2 \tag{5.62}$$

Unfortunately, (5.61) and (5.62) are often misused and wrongly applied in the 2D case. It must be remembered that, although the mathematical descriptors (5.59) and (5.60) can always be calculated when a tracer curve has been measured over a sufficiently long period, the equations (5.61) and (5.62) are only applicable in 1D cases.

5.1.3.3 The cumulative curve method (CCM)

The cumulative curve method was developed by Fried and Combarnous (1971), and has become very popular in German-speaking countries (Käss, 2004). However, the applicability of this method in practice is strongly limited. Fried and Combarnous (1971) developed the cumulative curve method for the 1D case, using the relative tracer recovery curve, defined here by Equation (5.41). Generally, the experimental relative recovery $RR(t)$, called here the cumulative curve $S(t)$, is constructed using the following equation:

$$S(t) = RR(t) = \frac{\int\limits_0^t C(t)\,dt}{\int\limits_0^\infty C(t)\,dt} \tag{5.63}$$

where $\int\limits_0^\infty C(t)\,dt$ is the area under the experimental curve (A).
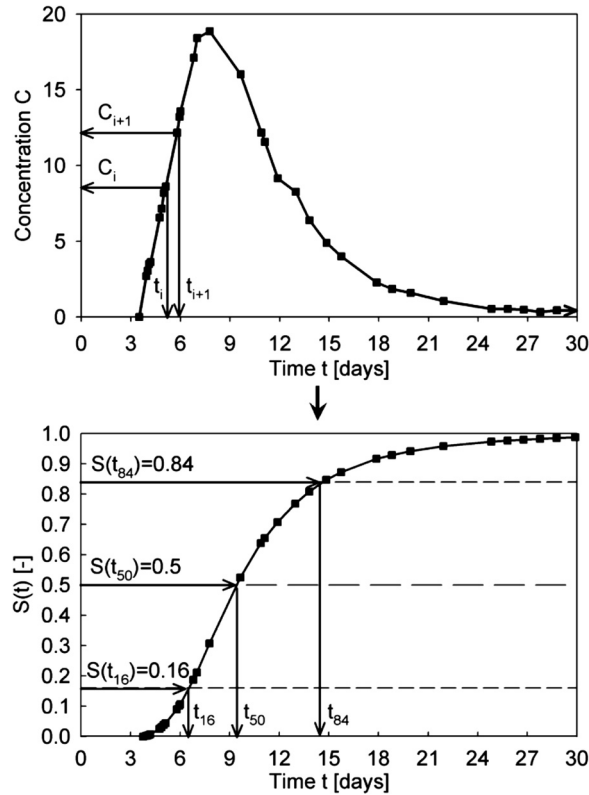
Figure 5.9 Presentation of the experimental tracer concentration curve C (top) and the constructed cumulative curve S(t) (bottom), with the estimated times, t_{16}, t_{50} and t_{84}, needed for applying the method of the cumulative curve.

From that curve (5.63), the times $t = t_{16}$, $t = t_{50}$ and $t = t_{84}$ are read; these are the times for which S(t) obtains the values 0.16, 0.50 and 0.84 (Figure 5.9). These times are then used to calculate the transport parameters using equations (5.71) and (5.72). Unfortunately, these latter equations are very commonly misused (see Käss, 2004), simply because the ideas behind the development used by Fried and Combarnous (1971) have been forgotten.

Fried and Combarnous (1971) considered 1D cases (closed systems), and only in situations in which the second term in Equation (5.41) could be neglected:

$$\exp\left(\frac{1}{P_D}\right) erfc\left(\frac{1 + t/t_0}{\sqrt{4P_D t/t_0}}\right) \cong 0 \qquad (5.64)$$

The above condition is satisfied with sufficient accuracy if

$$P_D \leq 0.005 \qquad (5.65)$$

and only then can (5.41) and (5.63) be simplified to the following form:

$$S(t) = \frac{1}{2} erfc \left(\frac{1 - t/t_0}{\sqrt{4P_D t/t_0}} \right) = \frac{1}{2} erfc \left(\varepsilon(t) \right) \tag{5.66}$$

where $\varepsilon(t)$ is the argument of the erfc function:

$$\varepsilon(t) = \frac{1 - t/t_0}{\sqrt{4P_D t/t_0}} \tag{5.67}$$

To finally find the relationships between the parameters t_{16}, t_{84} and t_{50} of the S(t) and the required transport parameters, the following properties of the erfc(ε) function have to be used. Function (5.66) obtains the values 0.16, 0.84 and 0.50 when the following equations are satisfied:

a) $S\left[\varepsilon(t_{16}) \right] = 0.16$ for:

$$\varepsilon(t_{16}) = \frac{1 - t_{16}/t_0}{\sqrt{4P_D t_{16}/t_0}} = -\frac{1}{\sqrt{2}} \tag{5.68}$$

b) $S\left[\varepsilon(t_{84}) \right] = 0.84$ for:

$$\varepsilon(t_{84}) = \frac{1 - t_{84}/t_0}{\sqrt{4P_D t_{84}/t_0}} = \frac{1}{\sqrt{2}} \tag{5.69}$$

c) $S\left[\varepsilon(t_{50}) \right] = 0.5$ for:

$$\varepsilon(t_{50}) = \frac{1 - t_{50}/t_0}{\sqrt{4P_D t_{50}/t_0}} = 0 \tag{5.70}$$

Solving the above system of equations yields finally:

$$t_0 = t_{50} \tag{5.71}$$

and

$$P_D = \frac{1}{8 t_{50}} \left(\frac{t_{50} - t_{84}}{\sqrt{t_{84}}} - \frac{t_{50} - t_{16}}{\sqrt{t_{16}}} \right)^2 \tag{5.72}$$

When $\sqrt{t_{50}} \approx \sqrt{t_{84}} \approx \sqrt{t_{16}}$ the above equation can be additionally simplified to:

$$P_D = \frac{1}{8} \left(\frac{t_{16} - t_{84}}{t_{50}} \right)^2 \tag{5.73}$$

The applicability of equations (5.71) and (5.72) is limited to 1D cases characterized by very low values of the P_D parameter, which corresponds to very homogeneous systems. That condition is easy to detect from Figure 5.8, which shows the exact $S(t)$-function. This figure demonstrates for different P_D values the difference between time t_{50}, which corresponds to the line $F = 0.5$ and the real mean transit time of water t_0. For extremely heterogeneous media ($P_D = 2.0$), the cumulative curve method yields values of t_{50} about three times smaller than the real value of t_0; for less heterogeneous medium ($P_D = 0.25$), it yields values of t_{50} about 1.33 times smaller than the real value of t_0.

5.1.4 Artificial tracer experiments in multi-flow systems

It is sometimes seen that there are multiple peaks in the tracer concentration curve in the water flowing out of a system (Figure 5.10). This happens: (1) in karst aquifers, when the tracer is injected into a sinkhole and observed in the springs and (2) in heterogeneous multi-layered porous media, when the tracer is injected through the whole thickness of the aquifer and observed in a pumping well or spring. In aquifers such as these, the multiple peaks in the concentration curve result from tracer transport along several flow paths that have different water flow velocities (and therefore different transit times) and different dispersivities. The streamlines finally come together in the outflow from the system (Figure 5.11). Figure 5.12 presents a conceptual model of flow in those situations, which has been used to describe tracer transport in the multi-layered porous media of an artificial wetland (Maloszewski *et al.*, 2006b) and to describe tracer transport between a sinkhole and a spring in a karst aquifer (Maloszewski *et al.*, 1992b). The model assumes that the tracer transport through the system can be approximated by a combination of 1D dispersion-convection equations. Each flow path is characterized
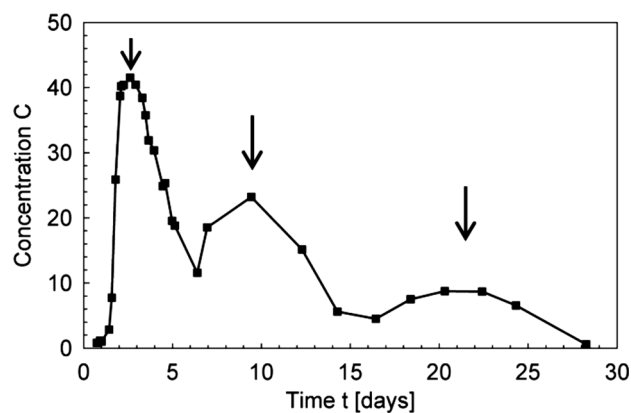

Figure 5.10   A multi-peak experimental concentration curve C(t) resulting from tracer transport on different 'parallel' flow paths.
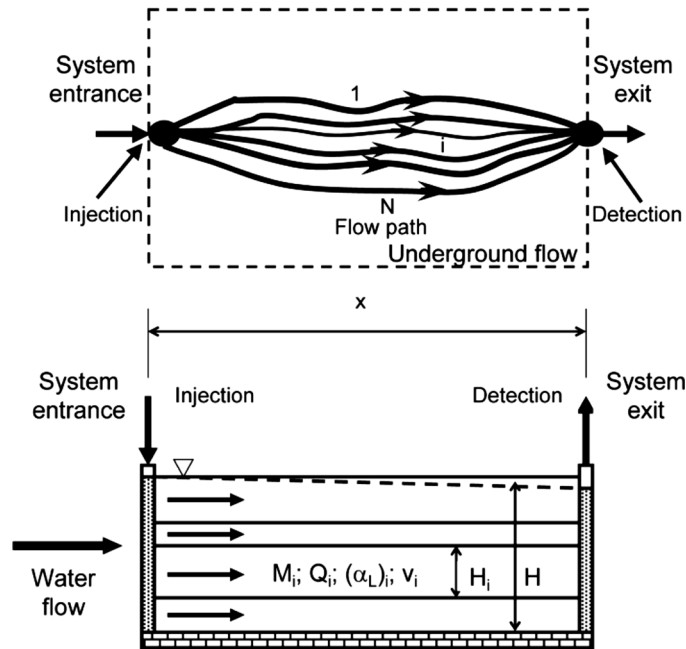
Figure 5.11 Schematic presentation of tracer transport in a multi-flow system, for a karst aquifer (top) and for a multi-layered porous medium (bottom).

by a specific volumetric flow rate, mean transit time of water and dispersivity (or dispersion parameter). It is assumed (a) that the mass of tracer injected is divided into several flow paths proportional to the volumetric flow rates along those paths and (b) that there are no interactions between the flow paths.
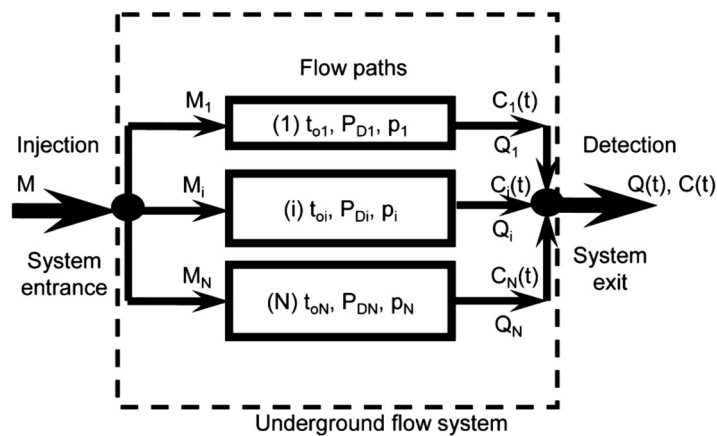

Figure 5.12 Conceptual model of tracer transport in multi-flow systems (multi-layered aquifer or karst aquifer).

The transport of an ideal tracer along the ith flow path is described by the 1D dispersion equation:

$$\alpha_{Li} v_i \frac{\partial^2 C_i}{\partial x^2} - v_i \frac{\partial C_i}{\partial x} = \frac{\partial C_i}{\partial t} \tag{5.74}$$

where $C_i(t)$ is the concentration of tracer in the outflow from the ith flow path (see Figure 5.12), and α_{Li} and v_i are, respectively, the longitudinal dispersivity and the mean water velocity for the ith flow path. x is the length of the flow path and t is the time after injection.

For instantaneous injection of tracer, the solution to (5.74) reads as follows (Kreft and Zuber, 1978):

$$C_i(t) = \frac{M_i}{Q_i t_{oi} \sqrt{4\pi (P_D)_i (t/t_{oi})^3}} \exp\left[-\frac{(1 - t/t_{oi})^2}{4(P_D)_i (t/t_{oi})} \right] \tag{5.75}$$

where Q_i and M_i are the volumetric flow rate and the mass of tracer transported along the ith flow path, respectively and

$$(P_D)_i = \alpha_{Li}/x_i \tag{5.76}$$

is the dispersion parameter, where x_i is the length of the ith flow path.

$$t_{o_i} = \frac{x_i}{v_i} = \frac{(V_m)_i}{Q_i} \tag{5.77}$$

is the mean transit time of water and $(V_m)_i$ is the mean volume of mobile water, in the ith flow path. The model assumes that the whole injected tracer mass, M, is divided into N portions, which enter the N flow paths proportional to the volumetric flow rates Q_i:

$$M_i/Q_i = M/Q \tag{5.78}$$

where Q is the total flow rate through the system, that is the sum of the partial flow rates:

$$Q = \sum_{i=1}^{N} Q_i \tag{5.79}$$

The outflow tracer concentration $C(t)$ is the flux-weighted mean concentration for all flow paths observed in the outflow:

$$C(t) = \sum_{i=1}^{N} p_i C_i(t) \tag{5.80}$$

and

$$p_i = Q_i/Q = M_i/M = R_i/R = \frac{\int\limits_0^\infty C_i(t)\,dt}{\int\limits_0^\infty C(t)\,dt} \tag{5.81}$$

where p_i is the fraction of water flux in the i-th flow path, R_i is the partial tracer recovery observed in the outflow of the ith flow path and R is the total recovery measured in the outflow.

The solution (5.80), combined with (5.75) and (5.81), is called here the Multi Flow Dispersion Model (MFDM). The parameters in the MFDM are: (1) the mean transit time t_{oi}, (2) the dispersion parameter $(P_D)_i$, (3) the fraction of water flux (p_i) for each flow path (i) and (4) the total number of flow paths N. It must be noted here that, due to the high number of unknowns, the calibration of the model to experimental data cannot be done in a straightforward way. The calibration is performed stepwise by fitting one-by-one the partial tracer concentration curves, each time subtracting the fitted (partial) curve from the total tracer concentration curve, beginning with the earliest peak (Maloszewski *et al.*, 1992b, 1998, 2006a). The number of flow paths N is then found automatically. After determining all the parameters, the partial volumetric flow rates (Q_i) and the volume of water in each flow path ($V_m)_i$ can be easily calculated from (5.81) and (5.77) as: $Q_i = p_i \cdot Q$ and $(V_m)_i = Q_i \cdot t_{oi}$, assuming that all the water is mobile. Then the total volume of water in the system is given by:

$$V_m = \sum_{i=1}^{N} (V_m)_i \tag{5.82}$$

and the mean transit time of water through the system is given by:

$$t_0 = \frac{V_m}{Q} = \sum_{i=1}^{N} p_i\, t_{0i} \tag{5.83}$$

For the karst aquifer, the parameter estimation is limited to determining for each flow path the mean transport parameters (transit time and flow velocity, dispersion parameter and dispersivity, portion of tracer transported) and deriving from these the flow rate and volume of water for each flow path and the total volume of water in the system (between the injection and detection sites). The values obtained for the transit times, dispersion parameters, flow rates and volumes of water are real ones, whereas the values of water velocity and dispersivity calculated for each flow path using (5.77) and (5.76) are only approximations made assuming that the flow distance between injection and detection points is for each flow path (x_i) equal to the straight line distance (x) (Figure 5.11).

For the multi-layered porous medium, assuming that the porosities in each layer are similar and equal to n, one can simply calculate the hydraulic conductivity for each layer (k_i) and the weighted mean ($\bar{k}$), by applying Darcy's law:

$$\bar{k} = \frac{x^2 n}{(\Delta H) t_0} \tag{5.84}$$

$$k_i = \frac{x^2 n}{(\Delta H) t_{0i}} \tag{5.85}$$

where $\Delta H/x$ is the hydraulic gradient between the injection and detection wells.

Finally, knowing the hydraulic conductivity for each layer (k_i), one can estimate the mean thickness of the layer (H_i) by combining (5.81) with (5.85):

$$H_i = \frac{p_i H \bar{k}}{k_i} = p_i H \frac{t_{oi}}{t_0} \tag{5.86}$$

Summarizing, in the multi-layered porous aquifer, the tracer experiment enables the estimation of the transport parameters and hydraulic properties of the individual layers. However, the relative position of the layers in the system is unknown.

5.1.5 Experiments in double-porosity aquifers

Mathematical models used to estimate transport and rock parameters in fissured aquifers are well described in Maloszewski (1994). Those models assume that the aquifer can be approximated by a system of parallel, identical fissures, equally distributed in a microporous matrix (Sudicky and Frind, 1982). The fissures have aperture (2b) and include mobile water; in the matrix, which has the porosity (n_{im}), there is only stagnant (immobile) water. The ratio of fissure aperture (2b) to fissure spacing (L) is defined as fissure (effective and/or mobile) porosity (n_f). Tracer with mass (M) is injected into the water entering the aquifer, simultaneously into all the fissures, with flux Q. The tracer is transported in the fissures by convection (v) and dispersion (D) and there is, at the same time, a loss (sink term) due to diffusion through the fissure walls into the immobile water in the matrix. Figure 5.13 shows schematically an aquifer approximated with a system of parallel fissures, and also an aquifer consisting of a single fracture situated in an infinitely large matrix. Maloszewski and Zuber (1985) and Maloszewski *et al.* (2004) have shown that when a tracer experiment is performed over small distances, that is when the mean transit time of water through the fissures is sufficiently short, the tracer transport can be approximated using the single fissure approach. In practice, that assumption is realized when (Maloszewski, 1994):

$$t_o \leq \frac{L^2}{64 D_p} \quad \text{or} \quad t_o \leq \frac{(2b)^2}{64 n_f^2 D_p} \tag{5.87}$$
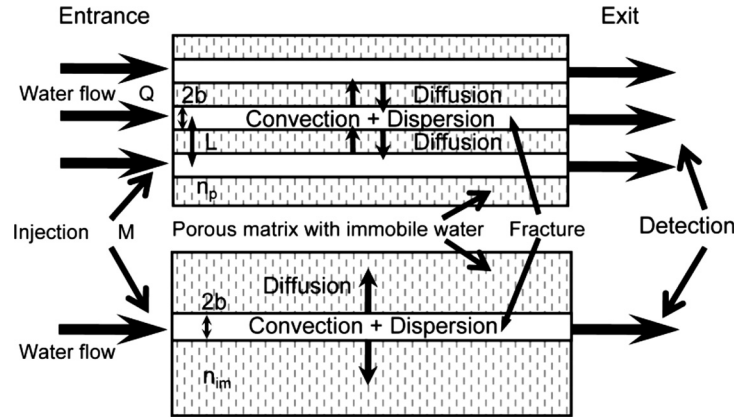
Figure 5.13 Conceptual model of tracer transport in a fissured aquifer consisting of parallel fractures (top), or a single fracture (bottom), with in each case a porous matrix with immobile water.

where D_p is the effective diffusion coefficient in the immobile water in the porous matrix and the fissure (mobile) porosity (n_f) is much smaller than 1.

If this is true, then the following equations describe the transport of an ideal tracer (Maloszewski and Zuber, 1985, 1990):

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} - D\frac{\partial^2 C}{\partial x^2} - \frac{n_{im}D_p}{2b}\frac{\partial C_{im}}{\partial y}\Big|_{y=b} = 0 \quad \text{for} \quad 0 \leq y < b \quad (5.88)$$

$$\frac{\partial C_{im}}{\partial t} - D_p\frac{\partial^2 C_{im}}{\partial y^2} = 0 \quad \text{for} \quad b \leq y < \infty \quad (5.89)$$

where $C(t)$ and $C_{im}(t)$ are the tracer concentrations in mobile and immobile water, respectively, D is the dispersion coefficient in the fissure, D_p is the effective diffusion coefficient of tracer in the immobile water, the x-axis of the coordinate system is parallel to the flow direction (fissure axis), y is the distance perpendicular to the flow axis, *2b* and *v* are the fissure aperture and the mean water velocity in the fissure, respectively.

The solution to (5.87) and (5.88) for instantaneous tracer injection is given by Maloszewski and Zuber (1985, 1990):

$$C(t) = \frac{aM\sqrt{t_o}}{2\pi Q\sqrt{P_D}} \int_0^t \exp\left[-\frac{(t_o - \xi)^2}{4\xi\, t_o P_D} - \frac{a^2\xi^2}{t-\xi}\right] \frac{d\xi}{\sqrt{\xi(t-\xi)^3}} \quad (5.90)$$

where ξ is the integration variable and *a* is a so-called diffusion parameter equal to:

$$a = \frac{n_{im}\sqrt{D_p}}{2b} \quad (5.91)$$

and t_0 is the mean transit time of water through the fissures

$$t_0 = \frac{V_m}{Q} \tag{5.92}$$

where V_m is the volume of mobile water in the whole system.

The solution (5.90) is termed by Maloszewski and Zuber (1985) the Single Fissure Dispersion Model (SFDM). It has three parameters: (1) the mean transit time of water (t_0), (2) the dispersion parameter (P_D) and (3) the diffusion parameter (a). Solution (5.90) is applicable when the tracer experiment is performed over small distances (5.87) in a fissured aquifer under natural flow conditions (e.g. detection in a spring or observation well), and also when it is performed in a radial-convergent (monopole) test (combined tracer and pumping experiment). The SFDM model can be applied for the interpretation of tracer experiments performed in aquifers that consist either of a fracture system or of a single fracture. Figure 5.14 shows the normalized (CQt_0/M) solution (5.90) calculated for constant values of the mean transit time of water (12 h) and the dispersion parameter (0.01), for different values of the diffusion parameter (a). The influence of tracer diffusion into the immobile water in the microporous matrix is easily seen there. Increases in the matrix diffusion (larger values of a) result in the concentration peak being delayed, in a stronger tailing effect and in a decrease of the relative tracer mass recovery.

Generally, the model parameters (t_0, P_D, a) can be estimated relatively easily by fitting (5.90) to the experimental data using a trial-and-error procedure. After the values of those parameters have been found, it is possible to calculate values for other system properties, but this is done in different ways depending on the experimental conditions.

In combined tracer and pumping experiments (Figure 5.6), when the thickness of the aquifer (H) and the hydraulic conductivity (k) are known independently, the following properties can be given approximate values:

– mobile (effective, fissure) porosity (n_f);

$$n_f = \frac{Q t_0}{\pi x^2 H} \tag{5.93}$$

– mean fissure aperture (2b) for the fracture system (Maloszewski, 1994);

$$2b = 4.29\tau_f \sqrt{\frac{k}{n_f}} \tag{5.94}$$

where (2b) in the above expression is expressed in [μm] and (k) in [m/d], and τ_f is the tortuosity factor – equal to about 1.5 for a network of tortuous fissures (Maloszewski and Zuber, 1985).
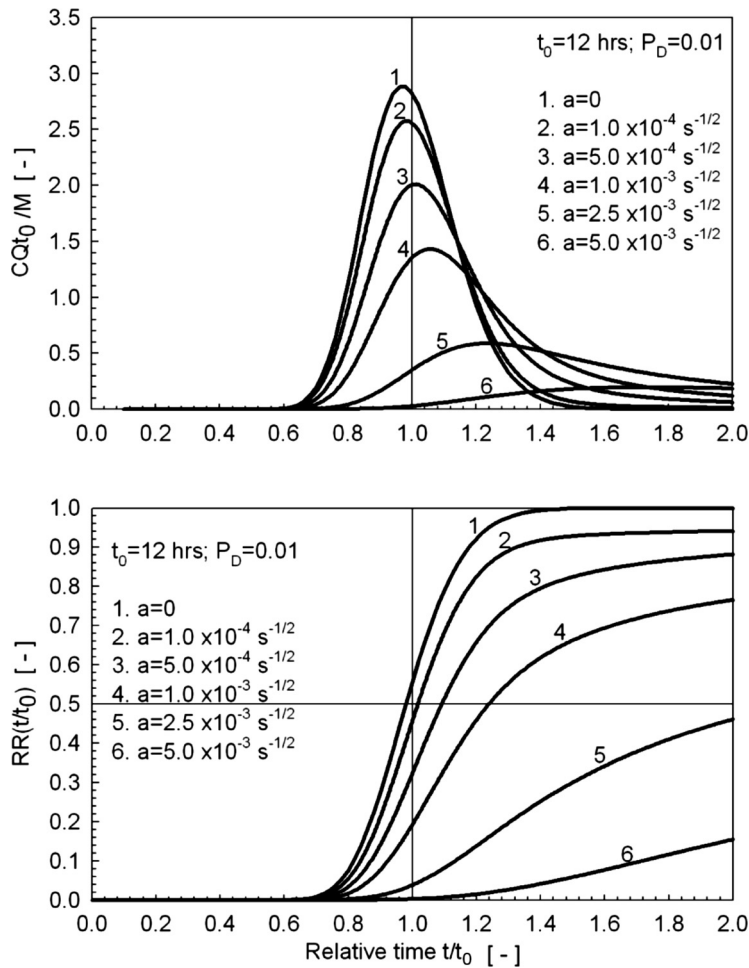
Figure 5.14 Theoretical normalized tracer concentration (top) and relative recovery (bottom) curves calculated for the mean transit time of water $t_0 = 12\,h$ and dispersion parameter $P_D = 0.01$, for different values of the diffusion parameter (a). This set of curves demonstrates the influence of matrix diffusion. Curves labelled '1' correspond to the situation of no diffusion of tracer into the immobile water (a = 0).

When the effective diffusion coefficient of tracer in the immobile water in the microporous matrix (D_p) is known or can be estimated (Neretnieks, 1980; Maloszewski, 1994), then, for a known fissure aperture (2b), the matrix porosity can be calculated from the formula:

$$n_{im} = \frac{(2b)a}{\sqrt{D_p}} \qquad (5.95)$$

5.1.6 Examples

5.1.6.1 Column experiment

In a column (L = 25 cm, 2r = 5 cm) filled with Quaternary gravels and a small pro-
portion of clay, the volumetric flow rate was Q = 6 cm^3/min (for the experimental
setting see Figure 5.6). The tracer experiment was performed using Uranine (injected
mass M = 8.5 mg), which was instantaneously injected through the whole column
cross-section (Dirac impulse). The experimental tracer concentrations (in μg/mL)
measured in the outflow from the column over nearly 40 min are shown in Figure 5.15
(top). The form of the tracer injection in this experiment allows the transport to be
treated as one-dimensional, using equations (5.29) or (5.33). The model has two pa-
rameters (t_0 and P_D), the values of which have to be found from the tracer curve.
As mentioned in Section 5.1.3, the correct way to find these parameters is to use the
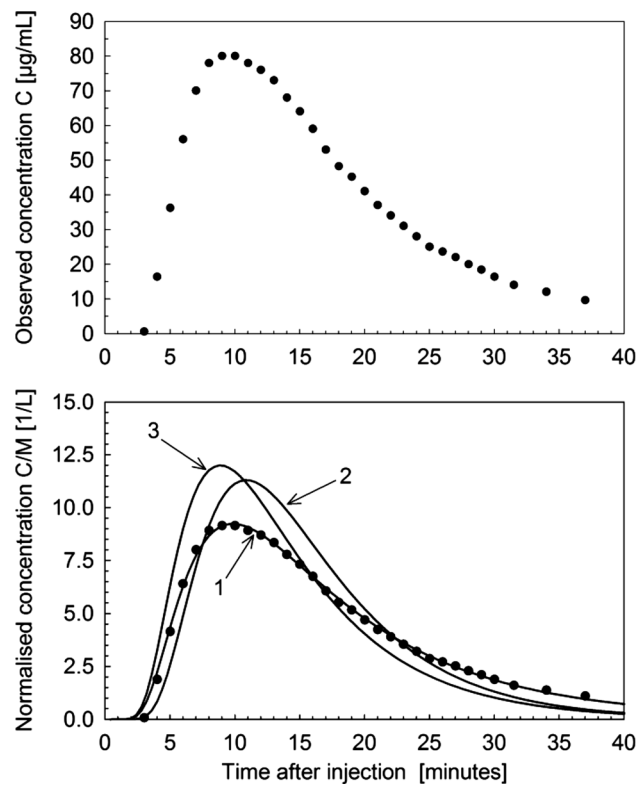

Figure 5.15   Tracer concentration observed in column experiment (top), and normalized C/M con-
centration curves observed (circles, bottom) and calculated (solid lines, bottom) using parameter
values (t_0 and P_D) estimated from (1) least-squares fitting procedure (LSQM), (2) method of mo-
ments (MM) and (3) cumulative curve method (CCM). For parameter values see Table 5.1.

Table 5.1 Estimates of parameters (t_0 and P_D) and system properties (v, α_L, n) found from column experiment by different methods (LSQM, MM, CCM)

Parameters	Symbol	LSQM	MM	CCM
Mean transit time of water (5.18)	t_0 [min]	17.6	15.6	14.0
Dispersion parameter (5.19)	P_D [−]	0.205	0.123	0.157
Goodness-of-fit (5.93)	E [%]	99.7	81.3	73.9
System properties				
Mean water velocity (5.18.1)	v [m/d]	20.5	23.1	25.7
Longitudinal dispersivity (5.19)	α_L [m]	0.051	0.031	0.039
Mean porosity (5.21.1)	n [%]	21.5	19.1	17.1

proposed method of combined least squares (LSQM). Inspection of the tracer concentration curve (Figure 5.15, top) clearly demonstrates that the approximate methods (method of moments and cumulative curve method) cannot be used because the conditions for their application, discussed in Section 5.1.3, are not fulfilled (tracer recovery RR << 100%). Despite this, the values of the parameters were also calculated using MM and CCM in this case, in order to appreciate better the disadvantages of these methods. The calculated parameter values (t_0 and P_D) and the values calculated from these for several system properties (mean water velocity, longitudinal dispersivity and porosity) are summarized in Table 5.1. The goodness-of-fit values are also shown there.

The theoretical concentration curves calculated using the parameter values summarized in Table 5.1 are shown in Figure 5.15 (bottom). The concentration curves are normalized to the mass of tracer injected – this is generally standard in the presentation of tracer data.

(C/M) are expressed in units [1/volume], and, especially in multi-tracer experiments, directly shows the tracer behaviour in the system. From the goodness-of-fit values and from inspection of the curves shown in Figure 5.15 (bottom), it is clear that the approximate methods (MM and CCM) yield completely unsatisfactory results in this case. The worst results are yielded by the cumulative curve method (CCM).

5.1.6.2 Combined pumping-tracer test

A combined pumping and tracer test was performed for a flow distance of x = 100 m in an aquifer of Quaternary gravels, with an average thickness of H = 8 m (for experimental setting, see Figure 5.6, bottom). The aquifer was under steady-state flow conditions, with a constant pumping rate of Q = 50 m³/h. The mass of tracer (Uranine) instantaneously injected into the fully penetrating well was M = 340 g. The experimental tracer concentration (in mg/m³), shown in Figure 5.16 (top), was measured in the pumping well (used for drinking water production) over a period of 150 days. The flow is steady-state radial-convergent flow, therefore the tracer transport can be considered as
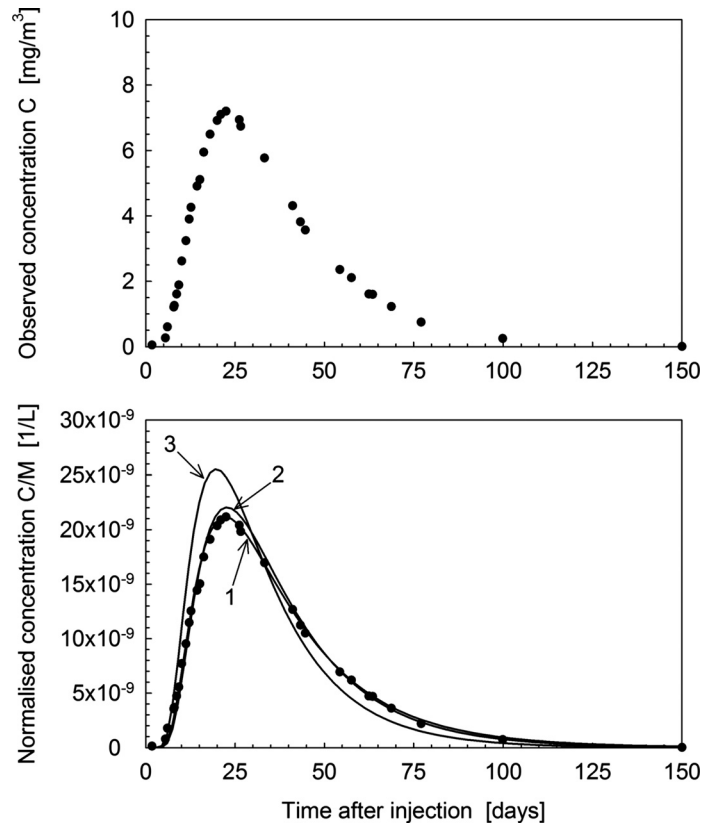
Figure 5.16 Tracer concentration observed in combined pumping-tracer experiment (top), and normalized C/M concentration curves observed (circles, bottom) and calculated (solid lines, bottom) using parameter values (t_0 and P_D) obtained from (1) least-squares fitting procedure (LSQM), (2) method of moments (MM) and (3) cumulative curve method (CCM). For parameter values see Table 5.2.

one-dimensional (5.19); the appropriate mathematical model is that given in Equation (5.15). The model has two unknown parameters (t_0 and P_D), the values of which have to be found. Because the mass recovery of tracer after 150 days was about RR $= 99\%$, it theoretically is possible to apply the approximate parameter estimation methods (see Section 5.1.3). The parameter values found using the least-squares procedure (LSQM) and the approximate methods (MM and CCM) are summarized in Table 5.2.

The sets of parameter values found with LSQM and MM are similar, as are the goodness-of-fitting values (99.5 and 98.5%, for LSQM and MM, respectively). The CCM yields again the worst results (E = 75.4%), but it should be noted that the P_D value found in the experiment (0.173) is much larger than 0.005, which should exclude the application of CCM (see 5.65). The theoretical tracer concentration curves calculated using the t_0 and P_D values found by LSQM, MM and CCM (Table 5.2) are shown in Figure 5.16 (bottom).

Table 5.2 Estimates of parameters (t_0 and P_D) and system properties (v, α_L, n) found from combined pumping-tracer experiment by different methods (LSQM, MM, CCM)

Parameters	Symbol	LSQM	MM	CCM
Mean transit time of water (5.18)	t_0 [days]	38.6	37.5	32.4
Dispersion parameter (5.19)	P_D [−]	0.193	0.174	0.173
Goodness-of-fit (5.93)	E [%]	99.5	98.5	75.4
System properties				
Mean water velocity (5.18.1)	v [m/d]	2.59	2.67	3.09
Longitudinal dispersivity (5.19)	α_L [m]	19.3	17.4	17.3
Mean porosity (5.21.2)	n [%]	18.4	17.9	15.5

5.1.6.3 Experiment in multi-flow system

A tracer experiment was performed in one of the cells in the artificial wetland Nowa Slupia (Maloszewski *et al.*, 2006b). The tracer concentration curve (in [g/l], see Figure 5.17, top) showed three peaks. This is due to the way the wetland was constructed: it consists of parallel porous layers with different hydraulic properties, similar to the system shown in Figure 5.11. The water flux through the wetland cell was relatively stable (Q = 0.77 l/s), and the hydraulic conditions could be assumed to be in a steady-state. Bromide (M = 16.7 kg) was injected through the whole cross-section perpendicular to the flow direction, and was measured in the outflow from the cell (which collected all of the water that flowed through that cell). The average flow distance was equal to x = 25.1 m. The experiment was analysed using the Multi-Flow Dispersion Model (MFDM) presented in Section 5.1.4. The parameters obtained for three single flow-paths found in the system are summarized in Table 5.3.

It must be stressed that estimation of transport parameters in multi-flow systems cannot be done using the approximate methods (MM, CCM); these are applicable only under the conditions mentioned earlier, in 1D and mono-flow systems. The parameter values found by applying the MM and CCM methods in this present experiment are shown here (Table 5.3) only to demonstrate how far those values are from reality. The corresponding theoretical concentration curves are additionally shown in Figure 5.17 (bottom). It is clear that the curves 2 and 3 (calculated with MM and CCM, respectively) do not follow the multi-peak concentration curve observed. The goodness-of-fit (E) of these two concentration curves is 47 and 50% (for MM and CCM, respectively). This contrasts with the value of E = 99.5% for MFDM. It should be noted that, when the relative recovery is close to RR = 100%, the tracer mean transit time calculated by the method of moments (MM) in a multi-flow system can be used to estimate the total volume of water in the system ($V_m = Q \times \bar{t}$). The small difference between the volumes of water calculated here with MFDM and MM results from the fact that the tracer recovery was lower then 100% (RR = 94.5%).
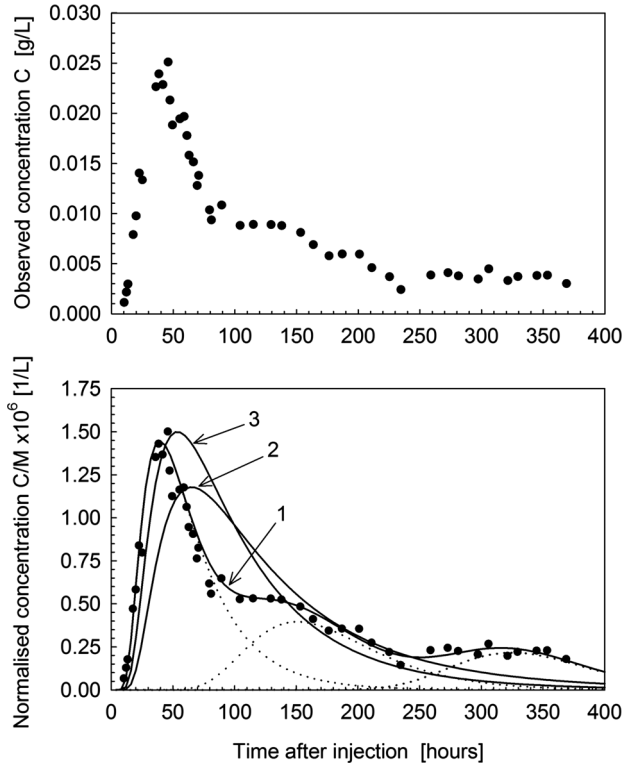
Figure 5.17   Tracer concentration observed in multi-layered porous medium experiment (top), and normalized C/M concentration curves observed (circles, bottom) and calculated (solid lines, bottom) using parameter values obtained from (1) multi-flow dispersion model (MFDM; dashed lines represent partial curves for the three flow-paths), (2) method of moments (MM) and (3) cumulative curve method (CCM). For parameter values see Table 5.3.

Table 5.3   Estimates of parameters and system properties found from multi-layered porous medium experiment (Maloszewski *et al.*, 2006b) by different methods (MFDM, MM, CCM)

Parameters	Symbol	MFDM			MM	CCM
Partial transit times (5.52)	t_{0i} [h]	66	179	346	133.4	104.8
Partial dispersion parameter (5.51)	P_{Di} [−]	0.18	0.06	0.01	0.26	0.24
Portion of flow (5.56)	p_i	0.53	0.29	0.18	1.0	1.0
Goodness-of-fit (5.93)	E [%]		99.5		47	50
System properties						
Mean transit time (5.58)	t_0 [h]		149.2		133.4	104.8
Volume of water (5.57)	V_m [m^3]		400		370	290
Mean porosity (V_m/V_{CELL})	n [%]		17.8		16.5	12.9

5.1.6.4 Experiment in double-porosity (fissured) medium

The tracer experiment described by Einsiedl and Maloszewski (2005) is used here as an example of parameter estimation in a double-porosity medium. The experiment was performed in the Lindau Rock Laboratory (Germany) in a highly permeable ore dike, with the flow distance between the B8 (injection) and BL10 (pumping) wells being x = 11.2 m. The pumping rate was Q = 0.23 l/s. The thickness of the ore dike was approximately equal to H = 2 m, and the hydraulic conductivity approximately equal to k = 2.07 m/d. The test site is described in detail by Himmelsbach, Hötzl and Maloszewski (1998). A new fluorescent dye (pyrene-1, 3, 6, 8-tetra sulfonic acid, PTS) was used. The experiment was performed under radial-convergent flow conditions (Figure 5.6), and the SFDM model (5.63) was used for data interpretation. The best-fit curves are shown in Figure 5.18 (top). The estimated parameter values, found by simultaneous fitting of the tracer concentration and recovery curves, as recommended by Maloszewski and Zuber (1990), were $t_0 = 2.4$ h, $P_D = 0.05$ and $a = 8.5 \times 10^{-3}$ s$^{-1/2}$; a is the diffusion parameter. The goodness-of-fit (E) was 98%. When combined with the known hydraulic properties of the system and the diffusion properties of the tracer, these estimates yield a fissure (mobile) porosity of 0.24%, a matrix (immobile) porosity of 5.0% and a mean fissure aperture of 188 μm. The parameter values found using the SDFM model are summarized in Table 5.4, together with values found using the approximate methods (MM and CCM). Once again, these approximate methods cannot be applied to estimate transport parameters in double-porosity media, as is evident from the values of t_0 and P_D shown in Table 5.4. When these values are used to calculate the tracer concentration curves, the curves obtained are as shown in Figure 5.18 (bottom, curves 2 and 3). The goodness-of-fit (E) values for these curves are 13.9 and 1.5%, for MM and CCM respectively.

Table 5.4 Estimates of parameters and system properties found from fissured-aquifer experiment, using both the SFDM model and, wrongly, the approximate methods (MM, CCM)

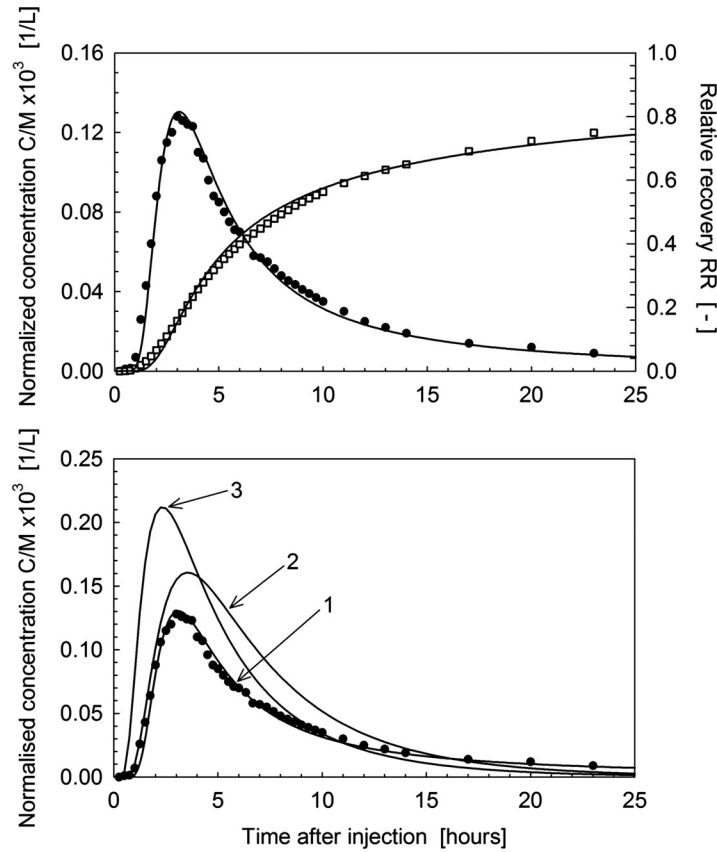| Parameters	Symbol	SFDM	MM	CCM
Mean transit time of water (5.65)	t_0 [h]	2.4	7.3	5.6
Dispersion parameter (5.19)	P_D [−]	0.05	0.26	0.33
Diffusion parameter (5.64)	a [s$^{-1/2}$]	8.5×10^{-3}	—	—
Goodness-of-fit (5.93)	E [%]	97.5	13.9	1.5
System properties				
Dispersivity	α_L [m]	0.56	2.94	3.70
Mean fissure porosity (5.66.1)	n_m [%]	0.24	—	—
Mean fissure aperture (5.66.2)	$2b$ [μm]	188	—	—
Mean matrix porosity (5.66.3)	n_{im} [%]	5.00	—	—

Figure 5.18   Normalized tracer concentration C/M (circles, top) and relative recovery (squares, top) observed in combined pumping and tracer test performed in fissured rock aquifer (Einsiedl and Maloszewski, 2005). Concentration and recovery curves (top) are those obtained by parameter estimation using SFDM (5.63). Bottom: observed concentration (C/M) compared with theoretical concentration curves (solid lines) calculated using parameter values obtained from (1) SFDM, (2) method of moments (MM) and (3) cumulative curve method (CCM). For parameter values see Table 5.4.

5.2 Tracer experiments under unsaturated flow conditions

Mathematical modelling of tracer (pollutant) transport in the unsaturated zone requires as a first step the determination of water flow through the soil, which is a function of time and space. The water flow is described by the Richards equation (Richards, 1931; Feddes *et al.*, 1988; Zaradny, 1993), which is a combination of the Darcy-Buckingham equation and the equation of continuity:

$$\frac{\partial \theta}{\partial t} = -\frac{\partial q}{\partial z} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} - K(h)\right] \tag{5.96}$$

where z is the vertical coordinate, q is the water flux, t is the time, $K(h)$ is the soil hydraulic conductivity function, which depends on the pressure head h and the volumetric water content θ.

The solving of the above equation requires knowledge of the main hydraulic characteristics of the unsaturated soil, such as the relationship between the pressure head h and the hydraulic conductivity K, both of which depend on the soil water content θ. The relationship between $h(\theta)$ and $K(\theta)$ can be described using known laboratory and field methods, and also by many mathematical equations. For practical purposes, the hydraulic functions are defined by a number of closed-form analytical expressions, for example those due to Brooks and Corey (1964), Rijtema (1969), Mualem (1976) and Van Genuchten (1980). Forms for the water retention characteristic $\theta(h)$ and the conductivity function $K(h)$, for the unimodal case without a hysteresis effect, are given by Van Genuchten (1980), based on the Mualem approach (Mualem, 1979):

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha \cdot h)^n]^m} \quad \text{for} \quad h < 0$$
$$\theta(h) = \theta_S \quad \text{for} \quad h \geq 0 \tag{5.97}$$

$$K_r(h) = \frac{[1 - (\alpha \cdot h)^{n-1} \cdot [1 + (\alpha \cdot h)^n]^m]^2}{[1 + (\alpha \cdot h)^n]^{\frac{m}{2}}} \tag{5.98}$$

where θ_s and θ_r are the saturated and residual water content, respectively. α, n and m are empirical parameters describing the shape of the retention curves, where $m = 1 - 1/n$. $K_r(h)$ is the relative hydraulic conductivity function; this is the hydraulic conductivity function $K(h)$ divided by the saturated hydraulic conductivity K_s.

Traditionally, these highly nonlinear functions have been obtained in small-scale laboratory experiments using direct steady-state methods (e.g. Haws, Das and Rao, 2004; Kern, 1995; Vereecken, Maes and Feyen, 1990). Recently, however, experimental lysimeter methods have become more attractive (e.g. Kool and Parker, 1988; Kool, Parker and van Genuchten, 1985, 1987; Maciejewski *et al.*, 2006; Nützmann *et al.*, 1998); these methods are applied under transient-flow conditions, and are coupled with inverse modelling techniques. These methods require a special kind of experiment. During the experiments some auxiliary variables are measured, for example cumulative outflow, pressure head, water content or infiltration rate. Then the a priori unknown soil hydraulic parameters are determined by minimizing an objective function containing the deviations between observed and predicted quantities. An example of the characteristic found for sandy lysimeters by Maciejewski *et al.* (2006) is shown in Figure 5.19. Equations (5.96), with known soil characteristics, and (5.97), can be solved by finite-difference techniques using, for example, the computer programs SWATRE (Feddes *et al.*, 1978; Belmans, Wesseling and Feddes, 1983; Maciejewski, Zaradny and Klotz, 1992) or HYDRUS-1D (Simunek *et al.*, 2008).

Many investigators (e.g. Coats and Smith, 1964; Van Genuchten and Wierenga, 1977; Gaudet *et al.*, 1977; De Smedt and Wierenga, 1979) have shown that under unsaturated flow conditions only a part of the water in a REV (representative elementary
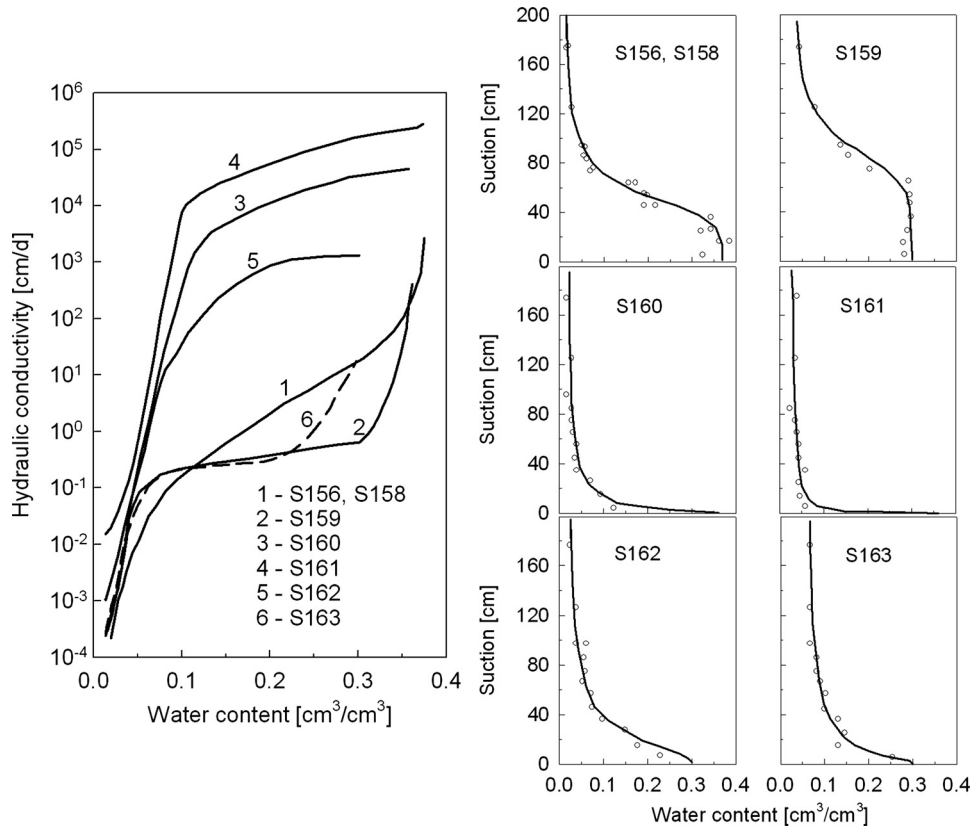
Figure 5.19   An example of soil characteristics: (left) $K(\theta)$; (right) water suction h as a function of water content after free drainage for typical Bavarian sands (after Maciejewski *et al.*, 2006) – circles show observed values, and solid line shows values obtained using van Genuchten Model.

volume; see Bear, 1972) takes part in motion; this is the so-called mobile water. As this the case, the unsaturated zone can be considered as a double-porosity medium with mobile and immobile water components. The transport of an ideal tracer in the mobile phase can be described by the dispersion-convection equation with a source/sink term that describes the tracer transfer between mobile and immobile water using in most cases the approximation introduced by Coats and Smith (1964). The tracer transfer is proportional to the difference between the tracer concentrations in the mobile and immobile water. The existence of immobile water in unsaturated soil is usually very difficult to document experimentally. But, given that there theoretically are two water phases, the mass balance equation for the double-porosity model is as follows (De Smedt, Wauters and Sevilla, 1986):

$$\frac{\partial(\theta_m C)}{\partial t} + \frac{\partial(\theta_{im} C_{im})}{\partial t} = \frac{\partial}{\partial z}\left(D\theta_m \frac{\partial C}{\partial z}\right) - \frac{\partial}{\partial z}(qC) \qquad (5.99)$$

and

$$\frac{\partial}{\partial t}(\theta_{im}C_{im}) = \omega \cdot \theta_m \cdot (C - C_{im}) \tag{5.100}$$

where C and C_{im} are the tracer concentrations in the mobile and immobile water, respectively; θ_m and θ_{im} are the mobile and immobile water contents, respectively; ω is the transfer coefficient of the tracer exchange between the mobile and immobile water components; z and t are space and time variables, respectively.

In practice, it can be assumed that the ratio of immobile to total water content $f = \theta_{im}/\theta$ is constant, which reduces Equations (5.99–5.100) to:

$$(1 - f)\frac{\partial(\theta C)}{\partial t} + f\frac{\partial(\theta C_{im})}{\partial t} = (1 - f)\frac{\partial}{\partial z}\left(D\theta\frac{\partial C}{\partial z}\right) - \frac{\partial(qC)}{\partial z} \tag{5.101}$$

$$f\frac{\partial(\theta C_{im})}{\partial t} = \omega(1 - f)\,\theta\,(C - C_{im}) \tag{5.102}$$

where D is the dispersion coefficient given by:

$$D = \alpha_L\frac{q}{(1 - f)\theta} + D_d \tag{5.103}$$

α_L is the longitudinal dispersivity, D_d is the diffusion coefficient of tracer in the soil, given by $D_d = D_m/\tau$, where D_m is the molecular diffusion coefficient of tracer in free water and τ is the tortuosity.

Because θ and q depend on depth z and time t, Equations (5.99–5.100) or (5.101–5.102) are non-linear. They can only be solved numerically, for example using the method of moving coordinates (Maciejewski, 1993). This approach allows the convection term to be eliminated from the transport equation, which in the numerical solution strongly reduces the effect of numerical dispersion. The following variables are taken as known: the water flux $q(z, t)$, and the total water content $\theta(z, t)$, calculated with (5.96) and (5.97–5.98). The model of the tracer transport through the unsaturated zone (5.101–5.102) has three parameters: the longitudinal dispersivity (α_L), the tracer transfer coefficient between the mobile and immobile water (ω), and the ratio of immobile water to the total water content ($f = \theta_{im}/\theta$).

When all water takes is mobile, Equations (5.99–5.100) reduces to:

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D\frac{\partial C}{\partial z}\right) - \frac{\partial(qC)}{\partial z} \tag{5.104}$$

When this equation is applied to a tracer concentration curve measured in the unsaturated zone there is only one parameter to be estimated, the longitudinal dispersivity (α_L).

The modelling of tracer transport using the equations given above can be performed using software such as HYDRUS-1D (Simunek *et al.*, 2008), which includes different double-porosity models.

5.3 Tracer experiments in streams and rivers

The selection of a model to describe tracer transport in streams or rivers depends on the situation in which the tracer experiment is performed (Figure 5.20). Generally, one has to consider if there exist significant zones with immobile water between the injection and detection sites (e.g. Bencala and Walters, 1983; Choi, Harvey and Conklin, 2000; Kazezyılmaz-Alhan, 2008). When there are no such zones (or when those zones are of negligible importance), the tracer transport can be described by the 1D Equation (5.19) (see Section 5.1.1). This is especially true when the injection of the tracer is performed throughout the whole cross-section of the river; this is done by using several pipes situated at different points across the flow. The solution to (5.19), for the instantaneous injection (5.29 or 5.33), is given in Section 5.1.2. In most practical applications, hydrologists focus their attention on the estimation of the flow rate (Q) of the river. When the tracer concentration curve, $C(t)$, is fully measured at the observation site (see Figure 5.20, top), then the river flow rate, Q, can be easily calculated using Equation (5.40). After rearrangement, this reads as follows:

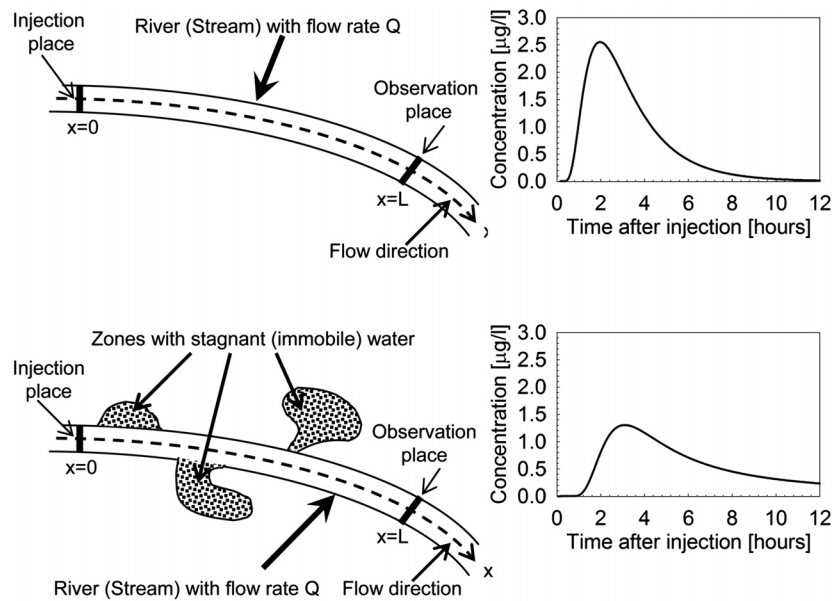$$Q = \frac{M}{\int\limits_0^\infty C(t)\,dt} = \frac{M}{F} \qquad (5.105)$$

Figure 5.20 Schematic presentation of tracer experiments in rivers or streams where (top) there are no zones of immobile water and (bottom) zones of immobile water exist and the tracer transport is modelled using the concept of a double-porosity medium. The tracer concentration curves measured at the observation place in the former case (top) show no tailing effect; in the latter case (bottom), there is a strong tailing effect resulting from tracer diffusion into the immobile water.

where M is the mass of tracer injected (at $x = 0$) and F is the area under the tracer concentration curve, which can be calculated using the trapezoidal method of integration:

$$F = \frac{1}{2} \sum_{i=1}^{N} (C_{i-1} + C_i) \cdot (t_i - t_{i-1}) \tag{5.106}$$

where N is the number of points measured. For C_i and t_i, see Figure 5.9 (top).

Some flow fluorometers perform the above calculation automatically during tracer detection in a river. Then one only has to give the mass of tracer injected (M) in order to obtain the flow rate (Q). To obtain the water flow velocity (v), the mean water transit time (t_o) or the longitudinal dispersivity (α_L), it is necessary to model the observed tracer concentration curve using (5.29) or (5.33). To find those parameters, one can use the LSQ method described in Section 5.1.3. Knowing the flow rate (Q) and the mean water transit time (t_o), the volume of water between the injection and detection sites can be estimated. This is also the volume of the mobile water, $V = V_m = Q \cdot t_o$. For a known flow length (L), the mean cross-sectional area of the river (S) is given by the ratio V_m / L.

When zones of stagnant water exist between the injection and detection sites (Figure 5.20, bottom), the exchange process (diffusion) of tracer between the mobile and immobile phases has to be included in the 1D transport equation. In most practical cases, the model of Coats and Smith (1964) is used, as mentioned in Section 5.2. The solution to (5.101–5.102) for a constant flow rate in the river ($q = Q$) and for instantaneous injection of tracer at $x = 0$ is (e.g. Herrmann, Maloszewski and Stichler, 1987):

$$C(t) = \frac{M}{Q\sqrt{4\pi P_D t^3/t_o}} \left\{ \exp\left[-\frac{(1 - t/t_o)^2}{4P_D t/t_o} - \omega t \right] + \omega t \sqrt{\beta} \exp(-\omega\beta t) \right.$$

$$\left. \times \int_0^1 I_1\left(2\omega t\sqrt{\beta(1-\xi)\xi} \right) \times \exp\left[-\frac{(1 - \xi t/t_o)^2}{4P_D \xi t/t_o} - \omega(1-\beta)t\xi \right] \frac{d\xi}{\xi\sqrt{1-\xi}} \right\}$$

$$\tag{5.107}$$

where:

$$\beta = V_m / V_{im} \tag{5.108}$$

and $I_1(\eta)$ is the modified Bessel function of the first kind and first order of argument η, and ξ is the integration variable $[0, 1]$.

This model (5.107) has four parameters (t_o, P_D, ω, β), which are difficult to estimate because of their possible nonindependence. An alternative approach is to use the SFDM model (5.90), which was developed to describe convective-dispersive transport within mobile water with simultaneous diffusion into the zone with immobile water (see Section 5.1.5). This model has three parameters: t_o, P_D and the diffusion parameter a (5.91). Note that in this case, the fissure aperture (2b) is replaced by the mean river

width (W), and the diffusion parameter (a) reads as follows:

$$a = \frac{\sqrt{D_m}}{W(1 + \beta)} \tag{5.109}$$

where D_m is the molecular diffusion coefficient of tracer in free water.

If the discharge (Q) of the river is known (or can be estimated), then the volume of mobile water (V_m) can be easily calculated from the mean transit time parameter (t_0) of the SFDM model: $V = V_m = Q \cdot t_o$. Furthermore, if the mean width of the river (W) and the diffusion coefficient of tracer in free water (D_m) are known, the parameter β can be calculated from (5.109):

$$\beta = \frac{\sqrt{D_m}}{aW} - 1 \tag{5.110}$$

Finally, by using (5.108), the volume of immobile water is given by:

$$V_{im} = Q t_o / \beta \tag{5.111}$$

5.4 Environmental tracer data

5.4.1 Introduction

The environmental isotopes, for example tritium and the stable isotopes ^{18}O or ^{2}H, are suitable for tracing the behaviour of water at different stages of the hydrological cycle because, among their other characteristics, they are constituents of the water molecule. When used as a supplement to conventional hydrological methods, these tracers may provide additional insight into problems such as the origin of water, the storage properties of catchments, water dynamics in groundwater systems and the interaction between surface and groundwater. The quantitative evaluation of the tracer data in these cases is most often based on the application of lumped-parameter models. The main advantage of these models is the fact that they require only the knowledge of the tracer concentration in the recharge area (input function) together with some records of tracer data at the observation site (output). In spite of their simplicity, lumped-parameter models yield useful information on zonal or regional values of some hydrologic parameters. Their applicability has been confirmed in a number of case studies, for example DeWalle *et al.* (1997), Kendall and McDonell (1998), Maloszewski and Zuber (1993, 1996), Maloszewski *et al.* (1983, 2002), McDonell, Rowe and Stewart (1999), McGuire, DeWalle and Gburek (2002), Stichler, Maloszewski and Moser (1986), Turner, Macpherson and Stokes (1987), Vitvar and Balderer (1997).
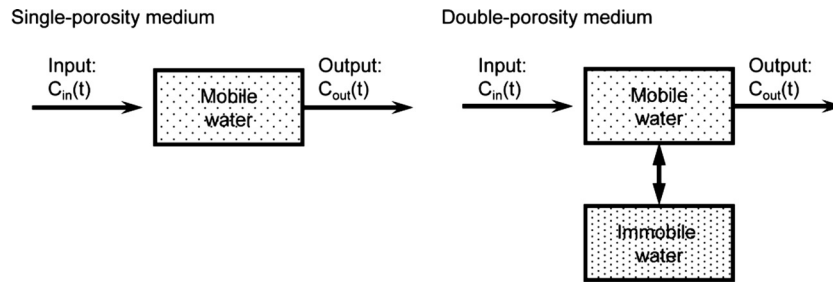
Figure 5.21 Conceptual models of the lumped-parameter approach in groundwater systems.

5.4.2 The basic concept of lumped-parameter models

The basic principles of lumped-parameter models (also called black-box models), together with details of their applicability, have been well described (e.g. Maloszewski and Zuber, 1982, 1996; Zuber and Maloszewski, 2001). Generally, it is presumed that the groundwater system can be considered as a closed system that (1) is sufficiently homogeneous, (2) is in a steady state, (3) has a defined input (recharge or infiltration area) and (4) has a defined output in the form of pumping wells, springs or streams draining the system. The groundwater system can be considered as a single-porosity or double-porosity medium (Figure 5.21). For the single-porosity medium, it is assumed that all the water in the system is mobile, or that the volume of immobile water can be neglected.

Every lumped-parameter model is characterized by its own transit time distribution function. That function has either to be known, or to be assumed on the basis of hydrological information about the system being considered. In most cases, transit time distribution functions have one or two parameters, the values of which can be estimated by calibrating the model to the experimental data observed in the outflow from the system. The input concentration of the environmental tracer is either measured directly, or is calculated from known hydrological and isotope data (e.g. Maloszewski and Zuber, 1982, 1996; Grabczak *et al.*, 1984; McGuire, DeWalle and Gburek, 2002; Stichler *et al.*, 1986). The main parameter of all models for single-porosity media is the mean transit time of water (T) through the system, which is related to the mobile water volume (V_m) in the system and the volumetric flow rate (Q):

$$V_m = Q T \qquad (5.112)$$

This mean transit time represents the average of flow times along all of the individual streamlines in the aquifer, each weighted by the amount of flowing water. To determine the mean transit time of water (T), the temporal variation of the measured tracer input concentration, $C_{in}(t)$, is used to calculate the tracer output concentration, $C_{out}(t)$, which is then compared with the concentrations measured in the output from the system. The relationship between the input and output concentrations is given by the

convolution integral:

$$C_{out}(t) = \int\limits_{0}^{\infty} C_{in}(t-\tau)\,g(\tau)\,\exp(-\lambda\tau)\,d\tau \tag{5.113}$$

where λ is the decay constant of the radioactive tracers and $g(\tau)$ is the transit time distribution function.

It should be remembered that the integral over the $g(\tau)$ for all possible transit times (τ), that is from zero to infinity, has to be equal to unity. For most of the models used for interpreting isotope data in single-porosity media, the mean value ($\bar{\tau}$) of the transit time distribution function $g(\tau)$ has to be equal to the mean transit time of water (T). The most common kinds of transit time distribution functions, $g(\tau)$, used for single-porosity media are:

Piston Flow Model (PFM)

$$g(\tau) = \delta(\tau - T) \tag{5.114}$$

Exponential Model (EM)

$$g(\tau) = \frac{1}{T}\,\exp\left(-\frac{\tau}{T}\right) \tag{5.115}$$

Combined Exponential Piston Flow Model (EPM)

$$g(\tau) = \frac{\eta}{T}\,\exp(-\frac{\eta\tau}{T} + \eta - 1) \quad \text{for } \tau > (\eta-1)T/\eta \tag{5.116}$$
$$g(\tau) = 0 \quad \text{for } \tau = (\eta-1)T/\eta$$

Dispersion-Model (DM)

$$g(\tau) = \frac{1}{\tau\sqrt{4\pi P_D \tau/T}}\,\exp\left[-\frac{(1-\tau/T)^2}{4P_D\tau/T}\right] \tag{5.117}$$

where P_D is the dispersion parameter and η is the ratio of the total water volume in the system to volume of that part of the water characterized by the exponential transit time distribution (V/V_{EM}).

The EPM model is a combination of the PFM and EM models in series; the order in which these models are applied is not important. A schematic representation of lumped-parameter models and their parameters is given in (5.114) and Figure 5.22, and examples of the transit time distribution functions (5.114)–(5.117) are shown in Figure 5.23. The use of the EPM yields the parameters (T) and (η), which are then used to determine the transit times (T_{PFM}) and (T_{EM}):

$$T_{EM} = \frac{T}{\eta} \tag{5.118}$$

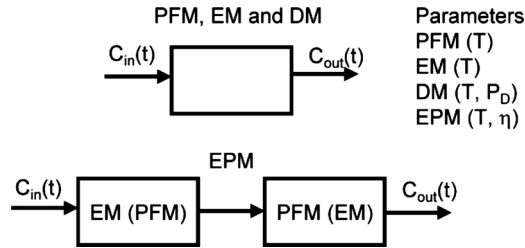$$T_{PFM} = \frac{1-\eta}{\eta}T \tag{5.119}$$

Figure 5.22   Schematic presentation of lumped-parameter models and their parameters.
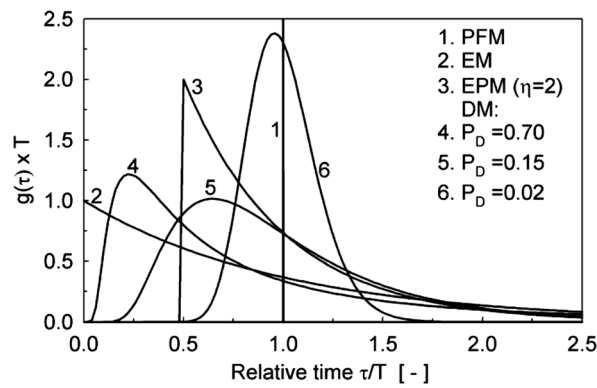

Figure 5.23   Examples of the transit time distribution function of tracer particles through a groundwater system calculated for different lumped-parameter models: PFM is the piston flow model, EM is the exponential model, EPM is the combined exponential-piston flow model and DM is the dispersion model.

and the volumes of water (V_{PFM}) and (V_{EM}):

$$V_{EM} = Q \; T_{EM} \qquad (5.120)$$

$$V_{PFM} = Q \; T_{PFM} \qquad (5.121)$$

in the parts of the system characterized by the piston-flow and the exponential transit time distributions, respectively. The sum of the water volumes in the parts with exponential and piston transit time distributions yields the volume of water in the whole system:

$$V = V_{EM} + V_{PFM} = QT \qquad (5.122)$$

Different lumped-parameter models are required for double-porosity media characterized by systems of fractures (Figure 5.13, top) where there is both mobile water in the fractures and immobile water in the microporous matrix (e.g. Figure 5.13 top and 5.21 right). The transport of tracers within the mobile water (by convection and dispersion), with simultaneous diffusion into the immobile water, was described by

Maloszewski (1994) for a system of parallel fissures having the same aperture and spacing (Figure 5.13); this is referred to by Maloszewski and Zuber (1985) and Maloszewski (1994) as the Parallel Fissure Dispersion Model (PFDM). That model could also be used for the interpretation of environmental tracer data, but its transit time distribution function has four parameters that need to be estimated, which makes it inapplicable in practice in isotope hydrology. This difficulty can be avoided by noting, as did Maloszewski (1994), that after a sufficiently long time in a double-porosity system the transit time distribution function obtained from the PFDM model has the same shape as that obtained from the ordinary dispersion model (5.117). What happens physically is that after a sufficiently long time the tracer diffuses fully into the porous matrix holding the immobile water. Once that state is reached, the tracer observed in the output from the double-porosity system behaves as it would in a single-porosity system with a larger volume of water (porosity). It has been found possible in practice to use the ordinary dispersion model (5.117) to interpret tritium (^{3}H) or stable isotope (^{18}O and ^{2}H) data in double-porosity systems when the transit time of water (T) through the system is greater than 2–3 years (Maloszewski, 1994; Maloszewski, Stichler and Zuber, 2004); this applies to most applications of environmental tracers in fractured rocks. In applying the ordinary dispersion model (5.117) to a double-porosity medium, it must be noted that instead of the mean transit time of water (T) the apparent parameter T^*, referred to as the mean transit time of the tracer is yielded T^* is given by:

$$T^* = \left(\frac{n_m + n_{im}}{n_m} \right) \times T = RT \tag{5.123}$$

where n_m is the mobile porosity defined as $2b/L$ (Figure 5.13) and R is the retardation factor resulting from the diffusion of tracer into the immobile water:

$$R = \left(\frac{n_m + n_{im}}{n_m} \right) = \frac{n_{total}}{n_m} \tag{5.124}$$

where n_{total} is the total water content in the fissured rock ($n_{im} + n_m$).

In practice, the apparent parameter T^* can be used to calculate the total volume of water in the system (V), that is the sum of the mobile (V_m) and immobile (V_{im}) components:

$$QT^* = \left(\frac{n_m + n_{im}}{n_m} \right) \times TQ = RTQ = V_m + V_{im} = V \tag{5.125}$$

Accordingly, the total volume of water (V) in the groundwater system in a heterogeneous fissured aquifer is R times greater than the volume of mobile water (V_m), the volume that mostly is of interest. This fact has to be taken into account in interpreting environmental tracer data in fissured rocks, otherwise the volume of available water resources will be R-times overestimated.
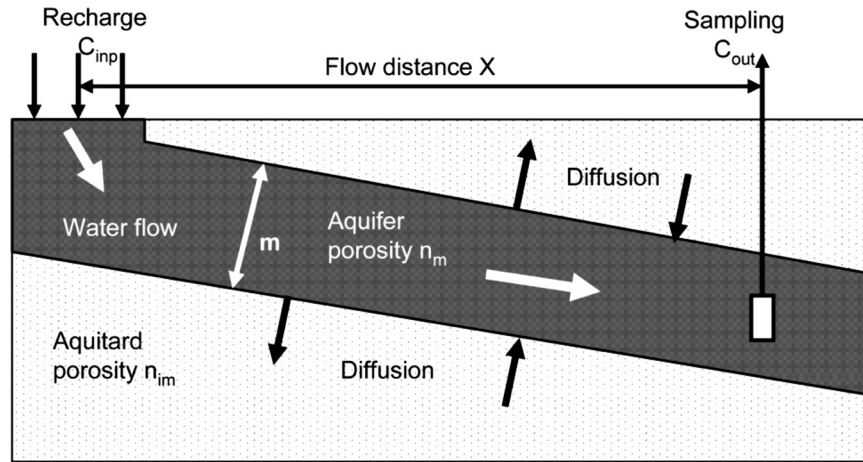
Figure 5.24 Schematic presentation of double-porosity system comprising an aquifer (with mobile water) and an aquitard with immobile water: m is the thickness of the aquifer, x is the distance from the recharge zone measured along the flow path.

The retardation factor R can be calculated when both the porosities n_m and n_{im}, are known. These two porosities can be found only when a combined pumping test and tracer experiment is performed in the area under investigation (Maloszewski and Zuber, 1990, 1991).

There are also tracer losses due to diffusion into regions with immobile water when aquifers are surrounded by large aquitards with immobile water (Figure 5.24). In this situation the tracer transport can be described by the SFDM (5.90) developed for artificial tracer experiments (Section 5.1.5). However, when the flow distance (x) is large and the thickness of the aquifer (H or m) is low, then for simplicity one can assume only convective flow in the aquifer. The analytical solution given by Maloszewski (1994), adapted to the lumped-parameter approach, yields the transit time distribution function given by (5.126) and referred to as the Combined Piston Flow Diffusion Model (SPFM) (see Nolte *et al.*, 1991).

5.4.2.1 Combined piston-flow diffusion model (SPFM)

$$g(\tau) = \frac{n_{im}\sqrt{D_p}}{n_m m\sqrt{\pi T(\tau/T - 1)^3}} \exp\left(-\frac{n_{im}^2 D_p T}{n_m^2 m^2(\tau/T - 1)}\right) \quad \text{for } \tau > T \quad (5.126)$$

$$g(\tau) = 0 \quad \text{for } \tau = T$$

This model can be used for the interpretation of environmental tracer data obtained from wells that are situated long distances away from the recharge area in comparison to the thickness of the aquifer ($x \gg m$). The transit time distribution functions calculated
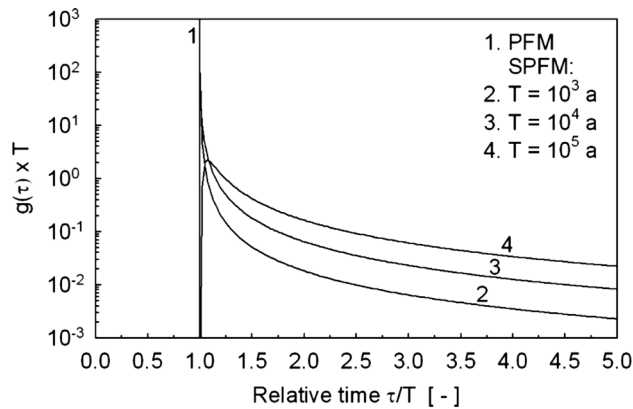
Figure 5.25 Examples of the transit time distribution function of tracer particles calculated for different lumped-parameter models: PFM is piston-flow model; SPFM is combined piston-flow and diffusion model.

using (5.126) are shown in Figure 5.25. It can be seen there that for transit times of water greater than 1000a, the diffusion of the environmental tracer into the aquitard already plays a very important role. In such situations, the interpretation of environmental tracer data using the traditional PFM-model (radioactive water age) expressed by (5.114) will result in greatly underestimated values for the water transit time.

5.4.3 Selection of the model

Which model is selected for use in the groundwater system being considered depends on the hydrological conditions there. Generally, the dispersion and piston flow models are applicable for confined or partially confined aquifers; the exponential model can only be used for unconfined aquifers when the unsaturated zone is negligibly small. The hydrological situations in which different models can be applied are shown in Figure 5.26. The first example illustrated there (Figure 5.26, top) shows a confined aquifer with a narrow recharge zone and a sampling site far away from the recharge (similar to that shown in Figure 5.24). If the confined part of the aquifer has impermeable boundaries and there is negligible immobile water, then the Dispersion Model (5.117) can be applied. If the flow distance is very long (allowing the assumption that $P_D \approx$ 0), then the PFM (5.114) can be applied; this is possible because if P_D has a very small value close to zero, then the dispersive transit time distribution becomes equivalent to the piston-flow distribution. However, that consideration and the application of the PFM model is no more generally valid. It is very well known that the confined part includes always stagnant water. Considering, for example measurements of ^{14}C ($D_p = 2.1 \cdot 10^{-2}$ m^2/a) in typical aquifer with a thickness of $m = 30$ m and an effective (mobile) porosity $n_m = 25\%$ located within an aquitard having a low porosity (stagnant) of about $n_{im} = 5\%$, the SPFM (5.126) has to be used for transit time of water (T $\geq$ 1000
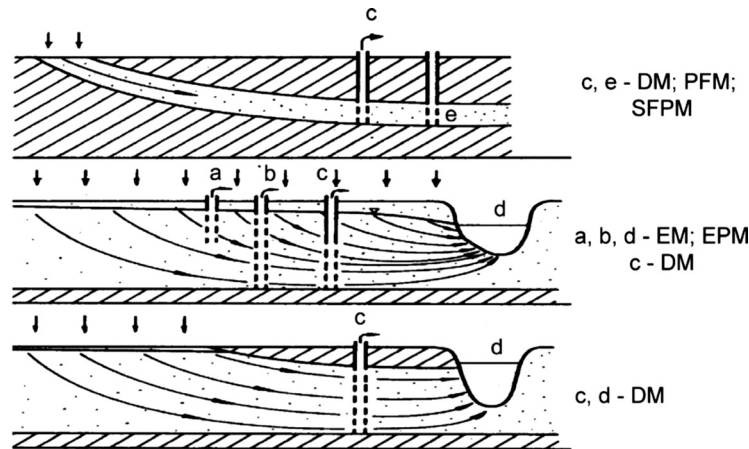
Figure 5.26 Presentation of hydrological situations in which particular models are applicable. Cases a, b, c and d correspond to sampling in out-flowing or abstracted water (in that form of sampling the water samples are automatically averaged by volumetric flow rates). Case e corresponds to samples taken separately at different depths (e.g. during drilling) (after Maloszewski and Zuber, 1982).

years). For tritium or stable isotopes ^{18}O and D the influence of diffusion into aquitard is observed even for smaller transit times.

The second example illustrated in Figure 5.26 (centre) is an unconfined aquifer. If the unsaturated zone in that aquifer is negligibly small, then for sampling points a, b and d the Exponential Model (5.115) is applicable. If the unsaturated zone has to be taken into account, the combined Exponential-Piston Flow Model (5.116) can be used. In this situation, the piston-flow transit time distribution corresponds to tracer transport through the unsaturated zone, the exponential transit time distribution to tracer transport through the saturated zone. Modelling the tracer data with the EPM yields values of T and η. The application of Equations (5.118–5.119) yields $T_{unsat} = T_{PFM}$ and $T_{sat} = T_{EM}$. This enables the volume of water in the unsaturated $V_{unsat}(V_{PFM})$ and the saturated $V_{sat}(V_{EM})$ zones to be estimated using (5.120–5.121). If the water is sampled in a well that is screened in its lower part, the Dispersion Model (5.117) has to be used.

The third example illustrated in Figure 5.26 (bottom) shows a partially confined aquifer. In this case, the streamlines with transit times $\tau = 0$ do not exist, and only the Dispersion Model (5.117) can be applied.

As has been mentioned, each lumped-parameter model has one or two unknown parameters that can be found by solving Equation (5.113) with one of the transit time distribution functions (5.114–5.117) or (5.126). To find these model parameters, the user-friendly software FLOWPC can be used. This has been described in detail by Maloszewski (IAEA, 2002). This software is available free of charge from the Isotope Hydrology Section of the International Atomic Energy Agency (IAEA) in Vienna, or directly from the author (Maloszewski).

5.4.4 Examples

5.4.4.1 *Application of stable isotopes to bank filtration*

The example is taken from Stichler, Maloszewski and Moser (1986) and shows the typical application of stable isotope (^{18}O) measurements in a bank filtration problem. This project was performed (1) to determine the proportion of Danube River water in two pumping wells and (2) to estimate the mean flow times between the river and the wells. Both wells are situated at a distance of about 150 m from the river bank. They produce drinking water for the city of Passau (Southeast Germany), with nearly constant pumping rates of about 105 l/s in total.

It is possible to use stable isotope data to determine the proportion of river water in a production well when (1) the mean δ^{18}O content in the river water is distinctly different from that in the local groundwater and (2) when the data are collected over a sufficiently long time. To determine the flow time between the river and the well also requires that there be strong δ^{18}O variations in the river water (i.e. in the input function). The measurements in the Passau project, shown in Figure 5.27, were performed
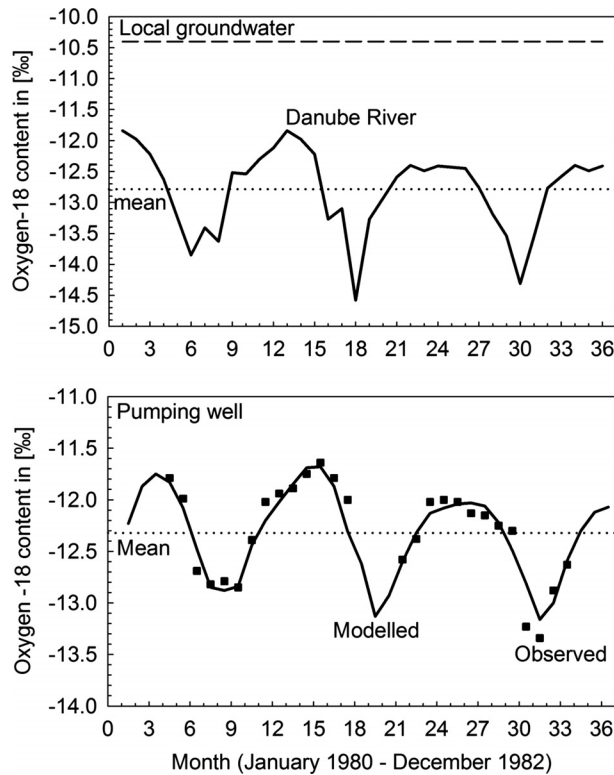

Figure 5.27   Stable isotope (δ^{18}O) contents measured in the Danube River, in the local groundwater (top), and in the pumping well PSI (squares in lower figure) that produces drinking water for the city of Passau (after Stichler, Maloszewski and Moser, 1986).

twice-monthly over a period of three years. The measurements show that the mean $\delta^{18}O$ contents in both water components – the local groundwater and the Danube river water – are strongly different (-10.4 and $-12.9‰$, respectively). Additionally, the $\delta^{18}O$ variations in the river water have an amplitude of more than $2.5‰$, whereas the local groundwater has practically no variation in $\delta^{18}O$ (Figure 5.27, top). In this situation, it is possible to use a very simple conceptual model of the water flow in the area under investigation (Figure 5.28).

The mean proportion (p) of the Danube river water in the production well can be calculated using the following equation (Stichler, Maloszewski and Moser, 1986):

$$p = \frac{\overline{C}_{PW} - \overline{C}_{LG}}{\overline{C}_{DR} - \overline{C}_{LG}} \qquad (5.127)$$

where $\overline{C}_{PW}$, $\overline{C}_{DR}$ and $\overline{C}_{LG}$ are mean $\delta^{18}O$ contents in the pumping well, the Danube River, and local groundwater, respectively.

The time-dependent concentration in the pumping well, that is the output concentration (Figure 5.28), $C(t)$, is given as follows:

$$C(t) = p \int_0^t C_{DR}(\tau)\, g(t - \tau)\, d\tau + (1 - p)\overline{C}_{LG} \qquad (5.128)$$

where the dispersive transit time distribution function $g(t - \tau)$ is taken according to the hydrological situation (Figure 5.26) as:

$$g(t - \tau) = \frac{1}{(t - \tau)\sqrt{4\pi P_D (t - \tau)/T}} \exp\left[-\frac{\left(1 - \frac{t-\tau}{T}\right)^2}{4P_D \frac{t-\tau}{T}} \right] \qquad (5.129)$$

where T and P_D are, respectively, the mean flow time and the dispersion parameter for the flow path between the Danube River and the production well.

The proportion of Danube river water (p) found for both production wells (PSI and PSII) was equal to 0.8. The best fit of Equation (5.128) to the $\delta^{18}O$ contents observed
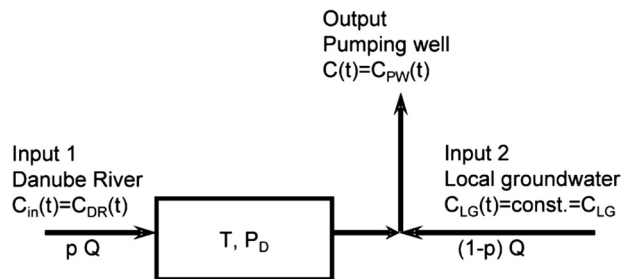

Figure 5.28 Conceptual model of water flow through the river bank to the drinking water supply of the city of Passau.

in the pumping well PSI was given when the mean transit time was 60 days and P_D was equal to 0.12 (see Stichler, Maloszewski and Moser, 1986). The modelled $\delta^{18}O$ curve is shown for the well PSI in Figure 5.27 (heavy line in lower part of figure).

The method presented for using isotope data in bank filtration can be applied in that form whenever the requirements for the isotope signals (mentioned above) are fulfilled. The tracer input function can be measured directly in the water infiltrating into the ground, that is in the river water, and therefore does not need to be calculated. The use of another input function obtained directly (in this case, measured in precipitation) is shown by Maloszewski *et al.* (2006a); this was used for modelling deuterium (δ^2H) transport through the unsaturated zone of unvegetated sandy soils, in lysimeter experiments.

5.4.4.2 *Application of tritium measurements in catchment areas*

Tritium (^3H) concentrations in atmospheric waters were constant and very low (5–10 TU) before the first hydrogen-bomb tests in the atmosphere, in 1954. After that, they increased until the years 1962–1963, when the highest concentrations (up to about 6000 TU) during the summer months in the northern hemisphere were reached. Since then, the atmospheric concentrations of tritium have decreased exponentially, reaching 15–20 TU in the late 1990s. The high tritium concentrations in precipitation during the early 1960s offer a unique opportunity for dating young groundwater systems having a relatively wide range of ages (up to approximately 250 years).

Seasonal variations in the tritium concentration in precipitation, coupled with variations in precipitation and infiltration rates, cause difficulties in the estimation of the input function, $C_{in}(t)$. For each calendar year the value of the input (C_{in}) can be expressed as:

$$C_{in} = \frac{\sum_{i=1}^{12}(C_i\, I_i)}{\sum_{i=1}^{12} I_i} = \frac{\sum_{i=1}^{12}(\alpha_i C_i P_i)}{\sum_{i=1}^{12}(\alpha_i P_i)} \tag{5.130}$$

where C_i, P_i and I_i are the tritium concentration in precipitation, the precipitation rate and the infiltration rate for the ith month, respectively.

The infiltration coefficient ($\alpha_I = I_i/P_i$) for each of the 12 months represents the fraction of precipitation which enters the groundwater system in the ith month; it is generally assumed to be the same each year. The record of C_{in} values, calculated for each year prior to the latest sampling date, represents the input function. For the interpretation of old tritium data, the record of C_{in} should include the constant C_{in} values prior to the beginning of the rise in 1954. In other cases, the calculation of the input function can be started in 1954. In most applications, it is assumed that the infiltration coefficient (α_i) in the summer months (α_s) of each year bears a constant

relationship to the infiltration coefficient in the winter months (α_w); this relationship is given by the infiltration constant ($\alpha = \alpha_s/\alpha_w$). Introducing α into Equation (5.130) results in (Grabczak *et al.*, 1984):

$$C_{in} = \frac{\alpha \sum_{i=4}^{9} (C_i P_i)_s + \sum_{i=10}^{3} (C_i P_i)_w}{\alpha \sum_{i=4}^{9} (P_i)_s + \sum_{i=10}^{3} (P_i)_w} \qquad (5.131)$$

In the northern hemisphere, the summer months are from April to September (the fourth to the ninth month) and the winter months are from October to March (the tenth to the third month of the next calendar year). The monthly precipitation should be taken from the meteorological station and the tritium data should be taken from the nearest station of the IAEA network. However, for moderate and humid tropical climates, the α coefficient is usually within the range of 0.4–0.8, and experience shows that within this range the accuracy of modelling depends only slightly on the assumed α value, provided that the system is more than 10–20 years old.

In general, if the input function is not found independently, the α coefficient is either chosen arbitrarily by the modeller or is taken to be another parameter to be estimated. It is a common mistake to calculate the input function (5.131) assuming $\alpha = 0$ on the basis of conventional hydrological observations, which indicate the lack of net recharge in some areas during summer months, because it does not mean the lack of the summer tritium in recharging water.

Figure 5.29 (left) shows the tritium input function calculated for the Schneealpe karst catchment. The Schneealpe karst massif (Maloszewski *et al.*, 2002), of Triassic limestone and dolomites and with altitudes of up to 1800 m a.s.l., is located 100 km south-west of Vienna, in the northern Calcareous Alps. The aquifer there, underlain by impermeable strata, has a thickness of up to 900 m and is the main drinking water resource for Vienna. The mean precipitation is 1058 mm per year; the mean
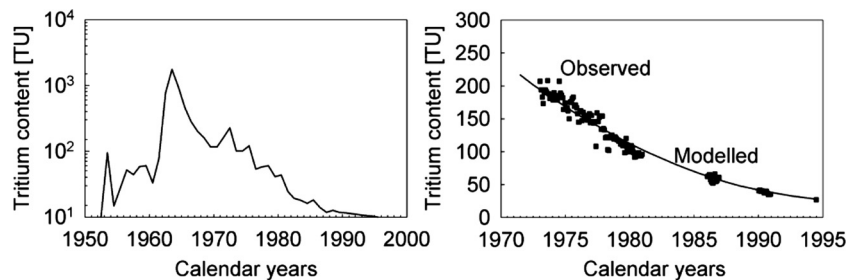

Figure 5.29 Tritium input function (left) calculated for the karst catchment of the Schneealpe Massif (100 km SW of Vienna) and (right) the modelled tritium content (output function) for the spring at Wasseralm (Q = 200 l/s), calculated using the DM (T = 26a, P_D = 0.8, α = 0.4) (after Maloszewski *et al.*, 2002).

evaporation is about 374 mm per year. The catchment area, about 23 km^2 in size (=F), is drained by two springs, the Wasseralmquelle and the Siebenquellen, situated on the northeastern and southwestern sides of the massif, respectively. The springs have mean discharge rates of about 200 and 310 l/s, respectively. The tritium concentrations during the base-flow were measured for nearly 25 years (1970–1995). The modelling of those data using the dispersion lumped-parameter model (5.113, together with 5.117) yielded mean transit times T = 26 years and T = 14 years for Wasseralm and Siebenquellen springs, respectively. The best fit of the DM to the experimental data for the Wasseralm spring is shown in Figure 5.29 (right). The transit times combined with the corresponding discharge rates give the volume of water (5.112) in the whole porous-fissured karst massif system as V = 255 × 10^6 m^3. Taking into account the surface of the catchment area, this volume corresponds to the water equivalent of about h_{eq} = V/F = 11 m.

5.4.5 Multi-cell approach and concluding remarks

Some other modelling approaches are also used for the interpretation of isotope data, for instance, the compartmental (multi-cell or mixing cell) model. That approach was introduced by Campana (1975), Przewłocki and Yurtsever (1974), Simpson and Duckstein (1976) and has been further developed by combining it with a lumped-parameter approach (Amin and Campana, 1996). The mixing-cell approach is well described in Campana, Harrington and Tezcan (2001). The compartmental model represents the groundwater system as a network of interconnected cells or compartments through which water and one or more dissolved constituents (tracers) are transported. Within a given cell, perfect (complete) mixing of the tracer is assumed to occur. Some models however, relax this constraint. The rates of flow of water and tracer between cells can be calculated by:

1) the use of a flow model that solves the partial differential equations of groundwater flow,

2) calibration with observed tracer data,

3) a flow algorithm based on linear or nonlinear reservoir theory, or

4) some combination of these preceding possibilities.

Each cell in the model represents a region of the hydrogeological system. These regions are distinguished from each other on the basis of their hydrogeological uniformity, the availability of data, the degree of resolution desired and constraints imposed by numerical solutions. Compartment (mixing-cell) models have been applied to groundwater flow systems by a number of investigators. They have been used to estimate aquifer properties and recharge boundary conditions (e.g. Adar and Neuman 1988; Adar *et al.*,

1988; Adar and Sorek, 1989; Fontes *et al.*, 1991), to determine groundwater ages and residence times (Campana, 1987; Campana and Simpson, 1984; Campana and Mahin, 1985; Kirk and Campana, 1990; Love *et al.*, 1994) and to analyse tracer data and delineate groundwater dynamics (Yurtsever and Payne, 1985). Other investigators have used them as transport models (Van Ommen, 1985; Rao and Hathaway, 1989). One pioneering approach has used a compartmental model to constrain a finite-difference regional groundwater flow model (Harrington *et al.*, 1999).

When there is an unidimensional arrangement of the cells, the method can be regarded as a less versatile version of the lumped-parameter approach. For a single cell, the method is equivalent to the EM; for a very large number of cells, it approaches the DM or even the PFM. When more complicated configurations are used (e.g. different cell volumes, two- and three-dimensional cell arrangements), the number of parameters to be fitted increases and unique solutions are not attainable. Therefore, multi-cell models can be regarded as a distributed-parameter approach with lumping. When interrelated tracer data distributed in time and space are available, multi-cell modelling is definitely advantageous over the lumped-parameter approach. Unfortunately, there are many cases in which a single ^3H determination, or the mean value of several samples taken over a short period of time, have been interpreted either with the aid of the EM or with the aid of the multi-cell approach. These are examples of incorrect interpretation.

As mentioned above, lumped-parameter models are particularly useful when insufficient data exist to justify the use of multi-cell models, multi-tracer multi-cell models (Adar, 1996), or numerical solutions of the transport equation. They are also very useful in preliminary investigations of little-known systems. In the case when only separate sampling sites exists (e.g. a spring, or a withdrawal well), then the use of the lumped parameter models is sufficiently justified. Some investigators express the opinion that in the era of numerical models, the use of a lumped-parameter approach is out of date. However, as mentioned by Zuber and Maloszewski (2001) it is like trying to kill a fly with a cannon, which is neither effective nor economic. Experience shows that a number of representative hydrologic parameters can be obtained from the lumped-parameter approach to the interpretation of environmental tracer data in a cheap and effective way.

In conclusion, when estimating the parameters of a system, it should always be remembered that the lower the number of parameters to be estimated, the more reliable the result of the modelling usually is (Himmelblau and Bischoff, 1968). A better fit obtained with a larger number of parameters does not necessarily mean that a better model has been found. A modelling exercise should always start with the simplest available model. More sophisticated models with additional parameters should be introduced only if it is not possible to obtain a good fit with a simple model, or if other information excludes a simpler model. It should also be remembered that if a single-parameter model yields a good fit, an infinite number of two-parameter models also yield equally good fits. Therefore, in such situations, other available information should be used for final selection of the most appropriate model.

5.5 The goodness-of-fit of a model

Generally, the goodness of a calculation (model calibration/fitting procedure) can be calculated using the model efficiency (E) defined by Hornberger, Mills and Herman (1992):

$$E = \left\{ 1 - \frac{\sum\limits_{i=1}^{N} (C_f^i - C_{obs}^i)^2}{\sum\limits_{i=1}^{N} (C_f^i - C_{mean})^2} \right\} \times 100\% \tag{5.132}$$

where

$$C_{mean} = \sum_{i=1}^{N} C_{obs}^i / N \tag{5.133}$$

C_f^i and C_{obs}^i are, respectively, the fitted and observed concentrations at the time t_i and N is the number of observations.

A model efficiency E = 100% indicates an ideal fit of the model to the concentrations observed, while E = 0 indicates that the model fits the data no better than a horizontal line through the mean concentration observed. Equation (5.132) is mainly useful for testing breakthrough curves in artificial tracer tests and the periodic output functions as it is, for example in the case of stable isotopes.