Exact analytical solutions for contaminant transport in rivers
2. Transient storage and decay chain solutions

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Abstract: Contaminant transport processes in streams, rivers, and other surface water bodies can be analyzed or predicted using the advection-dispersion equation and related transport models. In part 1 of this two-part series we presented a large number of one- and multi-dimensional analytical solutions of the standard equilibrium advection-dispersion equation (ADE) with and without terms accounting for zero-order production and first-order decay. The solutions are extended in the current part 2 to advective-dispersive transport with simultaneous first-order mass exchange between the stream or river and zones with dead water (transient storage models), and to problems involving longitudinal advective-dispersive transport with simultaneous diffusion in fluvial sediments or near-stream subsurface regions comprising a hyporheic zone. Part 2 also provides solutions for one-dimensional advective-dispersive transport of contaminants subject to consecutive decay chain reactions.

Keywords: Contaminant transport; Analytical solutions; Surface water; Transient storage models; Solute decay chains.

INTRODUCTION

Contaminant transport processes in streams and rivers have been analyzed and predicted now for several decades using a range of mathematical models (Bencala, 1983; DeSmedt et al., 2007; Fisher et al., 1979; Runkel et al., 2003; Thomann, 1973). Because many complex and often nonlinear physical, chemical and biological processes affect contaminant transport in streams and rivers, transport model formulations now increasingly utilize partial differential equations which must be solved using numerical methods. Exact analytical solutions are generally available only for more simplified formulations based on idealized representations of the transport domain and transport processes. Yet despite the apparent simplifications, analytical solute transport models remain useful for many applications such as providing initial or approximate analyses of a variety of contaminant transport scenarios, especially for longer times, facilitating transport analyses when insufficient data are available to warrant the use of a comprehensive numerical model, and for serving as a benchmark to test the accuracy of numerical models.

In this two-part series, we assembled a large number of analytical solutions for modeling solute transport in streams, rivers and other open surface water bodies. In part 1 (van Genuchten et al., 2013) we summarized solutions for one- and multidimensional equilibrium transport, with and without zero-order production and first-order decay. In the current part 2 we provide solutions for transport with simultaneous first-order exchange between the river and relatively immobile or stagnant water zones (transient storage models) and for situations where exchange with the hyporheic zone is modeled as a diffusion process (further referred to here as hyporheic zone diffusion models). Also presented in this paper are several solutions for transport of solutes subject to consecutive decay chain reactions.

Most of the presented solutions were derived from solutions to mathematically very similar problems in subsurface contaminant transport (Leij and Toride, 1997; Leij et al., 1993; Toride et al., 1993; van Genuchten, 1985a,b; Weerts et al., 1995). Except for those pertaining to diffusion in hyporheic zones, all solutions have been incorporated in the public-domain windows-based STANMOD software package (Šimůnek et al., 2000).

TRANSIENT STORAGE MODELS

All solutions presented in Part 1 (van Genuchten et al., 2013) hold for equilibrium contaminant transport characterized by relatively symmetrical or sigmoidal concentration distributions versus time or distance, unless modified by production and degradation processes, or special initial or boundary conditions. This ideal situation generally does not occur in streams and rivers because of the presence of relatively immobile or stagnant zones of water connected to the mean stream channel. Such stagnant zones include pools and eddies along the river banks, water isolated behind rocks, gravel or vegetation, or relatively inaccessible water along an uneven river bottom. Fluvial sediments and more generally subsurface hyporheic zones may also contribute to the presence of such relatively stagnant water. By providing sinks or sources of solute during transport, stagnant water zones typically cause tailing in observed concentration distributions, which cannot be predicted with the conventional equilibrium ADE formulation.

Several conceptual approaches are possible for modeling solute exchange between the river and stagnant water zones. One popular approach inherent in most transient storage models is to assume first-order mass transfer between the river and stagnant water (Bencala and Walters, 1983; De Smedt, 2006; LeGrand-Marcq and Laudelout, 1985; Runkel et al., 1996; Thackston and Schnelle, 1970, 2000; Włodkowski et al., 2013, and many others). The resulting model assumes that no advective and disper-
sive transport occurs in the transient storage zone, and that an average concentration can be assigned to this zone at any value of time, \( t \), and longitudinal distance, \( x \), along the stream. A more refined approach would be to assume that exchange of contaminant with stagnant zones, or the hyporheic zone in general, occurs by diffusion (De Smedt, 2007; Grant et al., 2012; Jackman et al., 1984; Wörman, 1998). Simulating this situation requires coupling the transport equation for the stream or river with some diffusion model for the near-stream subsurface environment (De Smedt, 2007; Grant et al., 1984). In this paper we first consider the relatively traditional quasi-empirical approach based on first-order mass transfer (transient storage models), while subsequently we consider more elaborate models assuming diffusion-based formulations for exchange between the river and the hyporheic zone (referred to here as hyporheic diffusion models).

Assuming a constant cross-sectional area \( A \) of the river and a constant longitudinal dispersion coefficient \( D_s \), the transient storage model in its most general form is given by (e.g., Benca et al., 1983; Runkel and Chapra, 1993; Wlostowski et al., 2013)

\[
\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} + \frac{Q_l}{A} (C_x - C) - \alpha (C - C_s) - \mu C, \quad (1)
\]

\[
\frac{\partial C}{\partial x} = \alpha \frac{A}{A_s} (C - C_s) - \mu_s C_s, \quad (2)
\]

where \( C \) and \( C_s \) are concentrations of the stream and storage zones, respectively (\( \text{ML}^{-1} \)), \( D_s \) is the longitudinal dispersion coefficient (\( \text{L}^2 \text{T}^{-1} \)), \( u \) is the longitudinal fluid flow velocity (\( \text{L} \text{T}^{-1} \)), \( x \) is the longitudinal coordinate (\( \text{L} \)), \( t \) is time (\( \text{T} \)), \( A_s \) is the cross-sectional area of the storage zone (\( \text{L}^2 \)), \( Q_l \) is the lateral volumetric inflow rate per unit length (\( \text{L}^{-1} \text{T}^{-1} \)), \( C_x \) is the concentration of the lateral inflow (\( \text{ML}^{-1} \)), \( \alpha \) is a dead-zone storage mass transfer coefficient (\( \text{T}^{-1} \)), and \( \mu \) and \( \mu_s \) are first-order decay coefficients for the stream and storage zone, respectively (\( \text{T}^{-1} \)). The terms on the right-hand side denote longitudinal dispersive and advective transport, lateral inflow from groundwater, and solute exchange with the storage zone. Several variations of this model have been applied to river transport; they typically require a numerical solution, particularly when \( A \), \( A_s \), and \( Q_l \) vary with distance. However, as pointed out by van Genuchten et al. (1988) and Huang et al. (2006), analytical solutions are readily available for mathematically very similar problems of nonequilibrium transport in porous media (Coats and Smith, 1964; Leij and Toride, 1997; Toride et al., 1993; van Genuchten and Wagenet, 1989; van Genuchten and Wierenga, 1976).

If the lateral inflow and degradation terms in (1) and (2) are negligible, then the dead zone storage model for constant \( A \), \( A_s \), \( D_s \) and \( \alpha \) reduces to

\[
\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - \alpha (C - C_s), \quad (3)
\]

\[
\frac{\partial C}{\partial x} = \alpha \frac{A}{A_s} (C - C_s). \quad (4)
\]

Many analytical solutions for one-dimensional nonequilibrium transport with or without accounting for zero-order production and first-order degradation are given by Toride et al. (1993). Two solutions are listed here as an example.

**Case E1.** We give here first the solution of Eqs. (3) and (4) for the initial condition

\[
C(x,0) = C_i(x,0) = C_i \quad (5)
\]

the third-type inlet condition

\[
\begin{align*}
C - \frac{D_s}{u} \frac{\partial C}{\partial x} \bigg|_{x=0^+} &= \begin{cases} C_o & 0 < t \leq t_o \\ 0 & t \geq t_o \end{cases} \\
\end{align*}
\]

and a semi-infinite profile

\[
\frac{\partial C}{\partial x} (\infty,t) = 0. \quad (7)
\]

The solutions for the stream and the dead storage zone concentrations are, respectively,

\[
C(x,t) = \begin{cases} C_i + (C_o - C_i) A(x,t) & 0 < t \leq t_o \\ C_i + (C_o - C_i) A(x,t) - C_o A(x,t - t_o) & t > t_o \end{cases} \quad (8)
\]

and

\[
C_s(x,t) = \begin{cases} C_i + (C_o - C_i) B(x,t) & 0 < t \leq t_o \\ C_i + (C_o - C_i) B(x,t) - C_o B(x,t - t_o) & t > t_o \end{cases} \quad (9)
\]

where

\[
A(x,t) = \int_0^t \frac{\tau}{\pi D_s} \exp \left[ -\frac{(x - u \tau)^2}{4 D_s \tau} \right] d\tau,
\]

\[
B(x,t) = \int_0^t \left[ 1 - J(b,a) \right] \frac{\tau}{\pi D_s} \exp \left[ -\frac{(x - u \tau)^2}{4 D_s \tau} \right] d\tau,
\]

\[
a = \alpha t, \quad b = \alpha (t - \tau) \frac{A}{A_s}. \quad (12)
\]

These expressions contain Goldstein's function which is defined as (Goldstein, 1953):

\[
\begin{align*}
J(a,b) &= \int_0^\infty \frac{\tau}{\sqrt{\pi D_s}} \exp \left[ -\frac{(x - u \tau)^2}{4 D_s \tau} \right] d\tau, \\
\end{align*}
\]

in which \( I_0 \) is the zero-order modified Bessel function.
The above solutions are for a third-type inlet boundary condition. For a first-type inlet condition, (10) and (11) must be replaced by, respectively,

\begin{align}
A(x,t) &= \frac{1}{\alpha} \int_0^\infty J(a,h) \left\{ \frac{\sqrt{\pi}}{4 \pi D} \exp \left[ -\frac{(x-a)^2}{4D \tau} \right] \right\} d\tau, \\
B(x,t) &= \frac{1}{\beta} \left[ 1 - \int J(b,a) \left\{ \frac{\sqrt{\pi}}{4 \pi D} \exp \left[ -\frac{(x-a)^2}{4D \tau} \right] \right\} d\tau \right].
\end{align}

(14)

(15)

Fig. 1 shows an application of the above solution for a third-type boundary condition (Eq. (6)). Like for several examples presented in part 1 (van Genuchten et al., 2013), the problem draws upon calculations and parameter values used by De Smedt et al. (2005). The example involves the injection of 1 kg of a solute in the main channel of a river having a cross-sectional area (A) of 10 m², a connected storage zone (A,τ) of 2 m³, an average flow velocity of 1 m/s in the river, and a dispersion coefficient of 5 m²/s. Fig. 1 shows for three values of the dead-storage zone mass transfer coefficient (α) calculated solute concentrations at a distance 1000 m downstream from the injection point. The curves were obtained assuming that 1 kg of solute was injected during a time period of only 10 seconds (t = 10 in Eq. (6)). De Smedt et al. (2005) used for this purpose a Dirac function, similarly as we selected in part 1 (Fig. 1). The resulting curves however are essentially identical, i.e., our Fig. 1 here and Fig. 1 of De Smedt et al. (2005). The curve for α = 0 assumes no exchange of solute with the storage zone, and hence could be calculated also immediately with the equilibrium transport model.

Calculations for Fig. 1 were obtained with the CXTFIT code of Toride et al. (1999) as incorporated in the STANMOD software of Šimůnek et al. (2000). Even though CXTFIT was derived for porous media transport problems, the code is applicable immediately to most or all models listed in this paper, as well as in part 1, by assuming a volumetric water content of 1.0 in the code. However, some care is needed when the transient storage model is simulated using the deterministic nonequilibrium ADE option in CXTFIT. In that case the average pore-water velocity v, the dispersion coefficient D, and the dimensionless parameters β and ω in CXTFIT must be defined in terms of transient storage model parameters as follows

\[ v = \beta u, \quad D = \beta D_s, \quad \beta = \frac{A}{A + A_s}, \quad \omega = \frac{\alpha B L}{u}, \]

where L is some characteristic length used to place the transport model in dimensionless form (L = 1000 m in the current example). For the calculations of Fig. 1 we hence used in CXTFIT the parameter values \( v = 0.83333 \) m/s, \( D = 4.16667 \) m²/s, \( \beta = 0.83333 \), and \( \omega = 0, 0.83333 \) and 8.333 1/s).

We also used the above transient storage model to analyze the experimental data (exp. I–3) of Brevis et al. (2001) and De Smedt et al. (2005) that were examined earlier in part 1 using the equilibrium transport model. The data are for a tracer experiment conducted in the Chillán River in Chile in which 157.1 g of a 20% Rhodamine WT tracer was injected at location \( x = 0 \), with measurements made at \( x = 4604 \) m downstream of the injection point. Fig. 2 shows the data along with fitted curves obtained with both the transient storage model (solid line) and the standard ADE equilibrium transport model discussed in part 1 (dashed line). Parameters were estimated using the nonlinear least-squares optimization features of CXTFIT, which provided estimates of the four parameters given by Eq. (16), as well as the concentration \( C_o \) of the applied tracer solution for a given value of the injection or pulse time \( t_o \) in Eq. (8).

![Fig. 1. Calculated concentration distributions obtained with Eq. (8) for near-instantaneous injection (\( t_o = 10 \) s) of 1 kg of solute (\( C_o = 10 \) g/m³) in the main channel of a stream having a cross-sectional area of 10 m², an average flow velocity of 1 m/s, a dispersion coefficient of 5 m²/d, and a connected transient storage zone of 2 m³, assuming three values of the mass transfer coefficient, \( \alpha \).](image1)

![Fig. 2. Observed (solid squares) and fitted (continuous and dashed lines) concentrations for tracer experiment I-3 of Brevis et al. (2001) and De Smedt et al. (2005). Assuming a very short injection time of only 10 s, similarly as in part 1 for the equilibrium analysis, we obtained the following parameter values (with their 95% confidence intervals): \( v = 0.414 \pm 0.002 \) m/s, \( D = 2.66 \pm 1.40 \) m²/s, \( \beta = 0.8647 \pm 0.0304 \), \( \omega = 2.934 \pm 0.936 \), and \( C_o = 1808 \pm 33 \) mg/m³. The coefficient of determination (R²) of the fit was 0.997, and the root mean square error (RMSE) 0.299 mg/m³. Using Eq. (16), the CXTFIT estimates translate to the following parameters in the transient storage model: \( u = 0.478 \) m/s, \( D_s = 3.07 \) m²/s, \( A_s/A \approx 0.156 \), and \( \alpha = 3.52 \times 10^{-4} \) s⁻¹. The total amount of solute mass (m) injected per m³ cross-sectional can now be calculated using \( m = u C_o t_o \), or 8.642 g/m³. Given that a total amount of 157.1 g of tracer was applied to the river, this translates to an effective cross-sectional area of 157.1 (g)/(8.642 (g/m³)) or 18.2 g/(8.642 (g/m³)).](image2)
Exact analytical solutions for contaminant transport in rivers: 2. Transient storage and decay chain solutions

\[ E(x, \tau) = \frac{u^2}{\pi D_s \tau} \exp \left[ -\frac{(x - ut)^2}{4D_s \tau} \right] \]

\[ F(x, t) = \frac{1}{2} \frac{u^2 \exp \left[ -\frac{(x - ut)^2}{4D_s \tau} \right]}{D_s} \]

\[ a = \frac{\alpha^2 \tau}{\alpha + \mu_s} \]

\[ b = \frac{(\alpha + \mu_s)(t - \tau)A_i}{A_i} \]

Additional one-dimensional analytical solutions for the transient storage model are readily derived from the solutions given by Toride et al. (1993a) for transport in porous media. They are all incorporated in the CXTFIT code (Toride et al., 1999) as part of STANMOD.

Multidimensional versions of the transient storage nonequilibrium model can be obtained by adding terms for the transverse dispersive flux similar as for the equilibrium case (see Eq. (41) of van Genuchten et al., 2012). Because the nonequilibrium effects generally manifest themselves only in the longitudinal flow direction, solutions for multidimensional transient storage models can often be deduced from available one-dimensional nonequilibrium solutions. We refer to Leij et al. (1993) for a complete set of analytical solutions for three-dimensional nonequilibrium transport, again for porous media transport. Green’s functions have proved to be particularly convenient for constructing solutions for nonequilibrium transport in multiple dimensions and for different mathematical conditions (cf. Leij and van Genuchten, 2000). Many or most of the multi-dimensional solutions are included in the 3DADE (Leij and Bradford, 1994) and N3DADE (Leij and Toride, 1997) computer programs for equilibrium and nonequilibrium transport, respectively. Like CXTFIT for one-dimensional transport, 3DADE (but not N3DADE) includes parameter estimation capabilities to estimate selected transport parameters from observed contaminant concentration distributions versus distance and/or time.
HYPORHEIC ZONE DIFFUSION MODELS

The transient storage models in the previous section use a first-order mass transfer equation to account for solute exchange between the river and relatively stagnant zones along the river banks or bottom. This conceptual picture can be refined by using Fick’s law to describe solute diffusion from the stream into the stagnant water zones, the fluvial sediment or more generally the entire hyporheic zone (Jackman et al., 1985; Runkel et al., 2003; Wörman, 1998). Similar problems have been described and solved analytically for contaminant transport in fractured or macroporous media (Sudicky and Frind, 1982; Tang et al., 1981; van Genuchten, 1985a; van Genuchten et al., 1984). Typically, the porous media solutions account for advective-dispersive transport through well-defined fractures or soil macropores with simultaneous diffusion from the fractures into the surrounding soil matrix. Many of these solutions are again readily applied to river systems. Here we consider two cases, one for vertical diffusion from the river into its sediments at the bottom (Case F1), and one for radial diffusion from a semi-circular stream into the surrounding subsurface (Case F2).

Fig. 3. Schematic of river system with a rectangular hyporheic zone.

Case F1. Assuming a rectangular geometry of the river and hyporheic zone (Fig. 3), the transport/diffusion model may be written as (see also Sudicky and Frind, 1982)

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - \frac{J_x}{d}, \quad (28)$$

$$J_x = -\theta_x D_x \left. \frac{\partial C}{\partial z} \right|_{z=0}, \quad (29)$$

$$R_x \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial z^2} \quad (0 < z \leq z_o), \quad (30)$$

$$C_s(x,0,t) = C(x,t), \quad (31)$$

$$\frac{\partial C_s(x,z_o,t)}{\partial z} = 0, \quad (32)$$

where $C$ and $C_s$ are solute concentrations in the stream and sediment, respectively, $d$ is the depth of the river, $z$ is vertical distance below the river, $J_x$ is the vertical solute diffusive flux into the hyporheic zone (ML$^{-2}$T$^{-1}$), $z_o$ is the effective depth of the sediment, $\theta_x$ is the volumetric water content of the sediments, $D_x$ is the apparent solute diffusion coefficient in the sediment (L$^2$T$^{-1}$), and $R_x$ is a solute retardation factor accounting for linear sorption/exchange in the sediment ($\cdot$). Note that, as before, the stream solute concentration, $C(x,t)$, is a function of longitudinal distance, $x$, and time, $t$, but that the solute concentration in the sediment, $C_s(x,z,t)$, is now also a function of the vertical distance $z$ below the river bottom. Advective transport as well as longitudinal diffusive transport in the hyporheic zone are ignored.

We present here solutions of the above hyporheic zone transport/diffusion model subject to the initial and boundary conditions

$$C(x,0) = C_s(x,z,0) = C_i, \quad (33)$$

$$\left\{ \begin{array}{ll}
C - \frac{D_x}{u} \frac{\partial C}{\partial x} |_{x=x_0^+} = C_o & 0 < t \leq t_o \\
0 & t > t_o,
\end{array} \right. \quad (34)$$

$$\frac{\partial C}{\partial x} (\infty, t) = 0. \quad (35)$$

The analytical solution for the stream concentration is (van Genuchten, 1985a)

$$C(x,t) = \left\{ \begin{array}{ll}
C_i + (C_o - C_i)A(x,t) & 0 < t \leq t_o \\
C_i + (C_o - C_i)A(x,t) - C_o A(x,t-t_o) & t > t_o,
\end{array} \right. \quad (36)$$

where

$$A(x,t) = \frac{1}{2} + \frac{2u}{\pi D_x} \int_0^\infty \frac{\exp \left( \frac{ux - \eta_p z}{2D_x} \right)}{(u/2D_x + \eta_p)^2 + \eta_m^2} \left[ \frac{u}{2D_x + \eta_p} \sin \left( \gamma_k^2 t - \eta_m z \right) \right. \left. - \eta_m \cos \left( \gamma_k^2 t - \eta_m z \right) \right] \frac{d\lambda}{\lambda} \quad (37)$$

in which

$$\eta_m = \sqrt{\frac{\Omega_o - \Omega_i}{2}}, \quad \eta_p = \sqrt{\frac{\Omega_o + \Omega_i}{2}}, \quad (38a,b)$$

$$\Omega_o = \sqrt{\Omega_1^2 + \Omega_2^2}, \quad (39)$$

$$\gamma = \frac{D_x}{2d^2 R_x}, \quad (40)$$

$$\Omega_1 = \frac{u^2}{4D_x} + \frac{\theta_x D_x^2}{d^2 D_x} H_1, \quad (41a)$$

$$\Omega_2 = \frac{D_x \lambda^2}{2d^2 R_x D_x} + \frac{\theta_x D_x \lambda^2}{d^2 D_x} H_2, \quad (41b)$$

$$H_1(\lambda) = \frac{\sinh(\lambda z_o / d) - \sin(\lambda z_o / d)}{\cosh(\lambda z_o / d) + \cos(\lambda z_o / d)}, \quad (42a)$$

$$H_2(\lambda) = \frac{\sin(\lambda z_o / d)}{\cosh(\lambda z_o / d)}.$$
Eqs. (28) through (32) must be replaced by

\[ H_2(\lambda) = \frac{\sinh(\lambda z_o/d) + \sin(\lambda z_o/d)}{\cos(\lambda z_o/d) + \cos(\lambda z_o/d)}. \]  

(42b)

The above solution holds for a third-type inlet boundary condition. The solution for a first-type boundary condition is exactly the same, except that (37) must be replaced by

\[ A(x,t) = \frac{1}{2 \pi} \int_0^\infty \exp\left( \frac{-ux}{2D_s} - \eta \right) \sin\left( \lambda x - \eta u\right) \, d\lambda. \]

(43)

The same solutions also hold for the slightly simpler situation where diffusion in the sediments occurs over a semi-infinite region, i.e., \( z_o \to \infty \). Eqs. (42a,b) then reduce to unity, and Eqs. (41a,b) become

\[ \Omega_1 = \frac{u^2}{4D_x} + \frac{\theta D \lambda}{d^2 D_s}, \]  

(44a)

\[ \Omega_2 = \frac{D \lambda^2}{2d^2 R_s D_x} + \frac{\theta D \lambda}{d^2 D_s}. \]  

(44b)

If dispersion in the river system is neglected \((D_s \to 0)\), \( A(x,t) \) for the first- and third-type boundary conditions both reduce to (see also Skopp and Warrick, 1974)

\[ A(x,t) = \frac{1}{2} \frac{2 \pi}{\int_0^\infty \exp\left( -\frac{\theta D x \lambda}{2d^2 u} H_1 \right) \cdot \sin\left[ \frac{D \lambda^2 (x-t) H_1}{2d^2 u R_s} - \frac{\theta D x \lambda H_2}{2d^2 u} \right] \, d\lambda}{\int_0^\infty \exp\left( -\frac{\theta D x \lambda}{2d^2 u} H_1 \right) \, d\lambda} \]  

(45)

which holds for \( t > x/u \). Eq. (45) and similar expressions for \( A(x,t) \) pertaining to transport problems which neglect dispersion in the river system are understood to be zero for \( t < x/u \). Eq. (45) for \( z_o \to \infty \) may be expressed in a much simpler alternative form (Grisak and Pickens, 1981; Tang et al., 1981).

\[ A(x,t) = \text{erfc} \left[ \frac{\theta x D R_s}{2d^2 u^2 t - ux} \right] (x < ut). \]

(46)

Alternative expressions for the solution of the above transport/diffusion problem for a first-type inlet boundary condition were given by Sudicky and Frind (1982) assuming a finite \( z_o \), and Tang et al. (1981) for the case where \( z_o \to \infty \). These two studies also presented solutions for the sediment concentration.

**Case F2.** This example is the same as F1, except that the stream has a semi-circular cross-sections as shown in Fig. 4. Diffusion now takes place in a radial direction. For this case, Eqs. (28) through (32) must be replaced by

\[ \frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - \frac{J_r}{\pi a^2}, \]

(47)

\[ J_r = -2\pi a \theta_D D_a \left. \frac{\partial C}{\partial r} \right|_{r=a}, \]

(48)

\[ R_s \frac{\partial C_s}{\partial r} = \frac{D_s}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_s}{\partial r} \right) (a < r \leq r_s), \]

(49)

\[ C_s(x,a,t) = C(x,t), \]

(50)

\[ \frac{\partial C_s(x,r_o,t)}{\partial r} = 0, \]

(51)

where \( a \) and \( r_o \) are as shown in Fig. 2, and \( r \) is the radial coordinate.

![Fig. 4. Schematic of river system with cylindrical hyporheic zone.](image)

The solutions for this case is the same as for Case F1, except for the following expressions (van Genuchten et al., 1984)

\[ \gamma = \frac{D_s}{a^2 R_s}, \]

(52)

\[ \Omega_1 = \frac{u^2}{4D_x} + \sqrt{\frac{\pi}{2}} \frac{D \lambda}{a^2 D_s} H_1, \]

(53a)

\[ \Omega_2 = \frac{2D \lambda^2}{r_o^2 R_s D_x} + \frac{\sqrt{\pi}}{a^2 D_s} H_2, \]

(53b)

where

\[ H_1 = \frac{N_1(M_1 - M_2) + N_2(M_1 + M_2)}{N_1^2 + N_2^2}, \]

(54a)

\[ H_2 = \frac{N_1(M_1 + M_2) - N_2(M_1 - M_2)}{N_1^2 + N_2^2}, \]

(54b)

\[ M_1(\lambda) = \text{Ber}_1(\xi_1) \text{Kei}_1(\lambda) - \text{Bei}_1(\xi_1) \text{Kei}_1(\lambda), \]

(55a)

\[ M_2(\lambda) = \text{Ber}_1(\xi_1) \text{Kei}_1(\lambda) + \text{Bei}_1(\xi_1) \text{Kei}_1(\lambda), \]

(55b)

\[ N_1(\lambda) = \text{Bei}_1(\xi_1) \text{Kei}_1(\lambda) + \text{Ber}_1(\xi_1) \text{Kei}_1(\lambda), \]

(56a)

\[ N_1(\lambda) = \text{Bei}_1(\xi_1) \text{Kei}_1(\lambda) + \text{Bei}_1(\xi_1) \text{Kei}_1(\lambda), \]

(56b)
involved in the consecutive decay chain. We consider here the transport of acid mine drainage or other anthropogenic or natural sources. Chlorinated hydrocarbons, organic phosphates, pharmaceuticals, and nitrogen species, pesticides in the movement of solutes involved in sequential first-order decay chains (1984) for efficient procedures to evaluate the transport equations for this problem are

\[
\frac{\partial C_i}{\partial t} = D_x \frac{\partial^2 C_i}{\partial x^2} - u \frac{\partial C_i}{\partial x} - \mu_i C_i, \quad (i = 2, 3, 4).
\]

where \( C_i \) represents the concentration of the \( i \)-th species, and \( \mu_i \) is the \( i \)-th first-order degradation coefficient. Eqs. (62a,b) are solved for the initial and boundary conditions

\[
C_i(x, 0) = 0 \quad (i = 1, 4), \quad C_i(\infty, t) = 0, \quad t > t_0,
\]

in which \( g_i(t) \) are the prescribed input concentration functions. We give here the solution for the very general situation where the input concentrations are given by

\[
g_1(t) = B_1 e^{-\lambda_1 t}, \quad g_2(t) = B_2 e^{-\lambda_2 t} + B_3 e^{-\lambda_3 t}, \quad g_3(t) = B_4 e^{-\lambda_4 t} + B_5 e^{-\lambda_5 t} + B_6 e^{-\lambda_6 t}, \quad g_4(t) = B_7 e^{-\lambda_7 t} + B_8 e^{-\lambda_8 t} + B_9 e^{-\lambda_9 t} + B_{10} e^{-\lambda_{10} t},
\]

where \( B_i \) and \( \lambda_i \) are constants. The multiple terms in Eqs. (66) may describe possible decay processes in the contaminant source, and/or account for finite release rates from the source into the river system. For one particular release mechanism, the constants \( B_i \) are related to each other through the Bateman equations (Bateman, 1910). A detailed description of this situation is given by van Genuchten (1985b). The analytical solution of the above transport problem is

\[
C_i(x, t) = \begin{cases} C_i^*(x, t) & 0 < t \leq t_0, \\ C_i^*(x, t) - e^{-\lambda_i t_0} C_i^*(x, t-t_0) & t > t_0, \end{cases}
\]

where

\[
C_i^* = B_i F_{10},
\]
The solution for a first-type inlet boundary condition is the same as the above third-type inlet solution, except for the term $F_{ij}$ (Eqs. (73) and (74)), which should be replaced by

$$F_{ij} = \exp(-a_{ijk} t) \left\{ \begin{array}{ll}
\frac{1}{2} \erfc \left[ \frac{x - \xi t}{\sqrt{4D_j t}} \right] & \text{for } \mu_i \neq a_{ijk}, \\
\frac{1}{2} \erfc \left[ \frac{x + ut}{\sqrt{4D_j t}} \right] + \frac{u^2 t}{\pi D_j} \exp \left[ \frac{-(x - ut)^2}{4D_j t} \right] & \text{for } \mu_i = a_{ijk},
\end{array} \right.$$  

(74)

$$a_{ijk} = \left\{ \begin{array}{ll}
\lambda_j & \text{for } k = 0 \\
\mu_i - \mu_j & \text{for } k > 0
\end{array} \right.$$  

(75)

$$\xi = \sqrt{u^2 + 4D_j} (\mu_i - a_{ijk}).$$  

(76)

The solution for a first-type inlet boundary condition is the same as the above third-type inlet solution, except for the term $F_{ij}$ (Eqs. (73) and (74)), which should be replaced by

$$F_{ij} = \exp(-a_{ijk} t) \left\{ \begin{array}{ll}
\frac{1}{2} \erfc \left[ \frac{x - \xi t}{\sqrt{4D_j t}} \right] & \text{for } \mu_i \neq a_{ijk}, \\
\frac{1}{2} \erfc \left[ \frac{x + ut}{\sqrt{4D_j t}} \right] + \frac{u^2 t}{\pi D_j} \exp \left[ \frac{-(x - ut)^2}{4D_j t} \right] & \text{for } \mu_i = a_{ijk},
\end{array} \right.$$  

(77)

Here we give one illustrative hypothetical application of the consecutive decay chain solution given by Eqs. (67)-(76). Fig. 5 shows calculated distributions versus distance for a three-member decay chain ($E_1 \rightarrow E_2 \rightarrow E_3$) assuming a finite pulse type injection ($t_p = 500$ s) of solute $E_1$ with concentration $C_o = 1$ g/m$^3$, using mostly the same parameters as before for Fig. 1 (i.e., $u = 1$ m/s and $D_i = 5$ m$^2$/s), and with values of 0.004, 0.001 and 0.002 s$^{-1}$ for the degradation coefficients of solutes $E_1$, $E_2$ and $E_3$, respectively.

A useful computer program for evaluating the above consecutive chain transport solutions is the CHAIN code of van Genuchten (1985b), also incorporated into STANMOD. We note that the decay chain solutions in this section assume no sorption of all species involved. The CHAIN code is for the more realistic case where sorption can occur, and where the retardation factors ($R_s$) of the individual species can be different. Finally, we note similar decay chain solutions for multi-dimensional transport with unequal retardation factors, but for first-type boundary conditions and without the Bateman source equations, are discussed in a recent paper by Quezada et al. (2004).

CONCLUDING REMARKS

In this two-part paper we collected a large number of analytical solutions for contaminant transport in rivers and surface water bodies. The solutions in part 1 pertain to one-dimensional longitudinal transport in streams and rivers, and longitudinal transport and lateral dispersion in rivers and larger surface water bodies. The current part 2 focused on nonequilibrium transport caused by the presence of stagnant water zones (transient zone models), and simultaneous longitudinal advective-dispersive transport in a river and diffusion into and out of the hyporheic zone. We also provided several solutions for the transport of solutes involved in consecutive decay chains. Most of the solutions were derived from solutions to mathematically very similar problems in subsurface contaminant transport. Except for solutions pertaining to diffusion in hyporheic zones, all solutions have been incorporated in the public-domain windows-based STANMOD software package (Šimánek et al., 2000). This software package also includes parameter estimation capabilities, and hence may be a convenient tool for analyzing observed contaminant concentration.
distributions versus distance and/or time. While inherently less flexible than more comprehensive numerical models for contaminant transport in streams and rivers, we believe that the analytical solution can be very useful for simplified analyses of alternative contaminant transport scenarios, as well as for testing of numerical models.

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