Analytical Solution for Multi-Species Contaminant Transport in Finite Media with Time-Varying Boundary Conditions

Jesús S. Pérez Guerrero · Todd H. Skaggs · M. Th. van Genuchten

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Abstract Most analytical solutions available for the equations governing the advective–dispersive transport of multiple solutes undergoing sequential first-order decay reactions have been developed for infinite or semi-infinite spatial domains and steady-state boundary conditions. In this study, we present an analytical solution for a finite domain and a time-varying boundary condition. The solution was found using the Classic Integral Transform Technique (CITT) in combination with a filter function having separable space and time dependencies, implementation of the superposition principle, and using an algebraic transformation that changes the advection–dispersion equation for each species into a diffusion equation. The analytical solution was evaluated using a test case from the literature involving a four radionuclide decay chain. Results show that convergence is slower for advection-dominated transport problems. In all cases, the converged results were identical to those obtained with the previous solution for a semi-infinite domain, except near the exit boundary where differences were expected. Among other applications, the new solution should be useful for benchmarking numerical solutions because of the adoption of a finite spatial domain.

Keywords Multi-species transport · Finite domain · Analytical solution · Integral transform

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J. S. Pérez Guerrero
Radioactive Waste Division, Brazilian Nuclear Energy Commission (DIREJ/DRS/CNEN), Rio de Janeiro, Brazil
e-mail: jperez@cnen.gov.br

T. H. Skaggs (✉)
U.S. Salinity Laboratory, USDA-ARS, Riverside, CA, USA
e-mail: Todd.Skaggs@ars.usda.gov

M. Th. van Genuchten
Department of Mechanical Engineering, LTTC/COPPE, Federal University of Rio de Janeiro, UFRJ, Rio de Janeiro, Brazil
e-mail: rvangenuchten@yahoo.com
List of Symbols

\( \bar{A}_{jm} \)  Auxiliary coefficients
\( B_1, B_2 \)  Mathematical operators
\( \bar{B}_{jm} \)  Auxiliary coefficients
\( b_{jm} \)  Boundary source coefficient
\( C_0 \)  Dimensional reference solute concentration
\( C_j(X, T) \)  Dimensional solute concentration of the \( j \)th species
\( c_j(x, t) \)  Dimensionless solute concentration of the \( j \)th species
\( D \)  Dispersion coefficient
\( f_{jmi} \)  Integral coefficient
\( G_j(X) \)  Dimensional initial concentration of the \( j \)th species
\( g_j(x) \)  Dimensionless initial concentration of the \( j \)th species
\( H_1, H_2 \)  Coefficients
\( h_j(x, t) \)  Filter function
\( L \)  Mathematical operator
\( L_0 \)  Spatial length domain
\( N_i \)  Norm
\( p \)  Constant used in algebraic substitution
\( Pe \)  Peclet number
\( q_j \)  Constant used in algebraic substitution
\( R_j \)  Retardation coefficient for the \( j \)th species
\( \bar{S}_{jmi}(t) \)  Integral coefficient
\( T \)  Dimensional time
\( t \)  Dimensionless time
\( U \)  Constant pore water velocity
\( w_{jm} \)  Auxiliary coefficient
\( r_{jm} \)  Auxiliary coefficient
\( X \)  Dimensional spatial coordinate
\( x \)  Dimensionless spatial coordinate

\[ \alpha_i \]  Source leaching coefficient
\[ \beta_i \]  Eigenvalue
\( \Gamma \)  Mathematical operator
\( \gamma_j \)  Damkohler number
\( \delta_{ik} \)  Kronecker delta
\( \bar{\delta}_{jm} \)  Auxiliary coefficient
\( \theta_{jm}(x, t) \)  Unknown function in purely diffusive equation
\( \theta_{jmi}(t) \)  Integral transform of the function \( \theta_j(x, t) \)
\( \lambda_j \)  First-order decay constant for the \( j \)th species
\( \bar{\lambda}_m \)  Source decay constant
\[ \mu_i \]  Eigenvalue
\( \xi \)  Auxiliary integration variable
\( \sigma_m \)  Auxiliary coefficient
\( \Phi_j(T) \)  Dimensional transient boundary function
\( \phi_j(t) \)  Dimensionless transient boundary function
Analytical solutions for transport problems involving sequential decay reactions have been developed mostly for steady-state boundary conditions and for infinite or semi-infinite spatial domains. Relatively very little literature is available about analytical solutions for multi-species transport problems for either finite media or time-dependent boundary conditions. Detailed surveys of the literature were given recently by Srinivasan and Clement (2008a,b) and Pérez Guerrero et al. (2009a). Hence, we mention here only a relatively few studies that are most pertinent to our current efforts.

Higashi and Pigford (1980) previously used Laplace transforms to develop an analytic solution for purely advective multi-species transport in finite media. Again using Laplace transforms, van Genuchten (1985) later extended the analytical solution to advective–dispersive multi-species transport in a one-dimensional semi-infinite domain. He obtained solutions for up to four species using either first- (Dirichlet) or third-type (Cauchy) inlet boundary conditions. The solutions for each species additionally featured transient source terms which were related through the Bateman equations (Bateman 1910).

Srinivasan and Clement (2008a,b) recently developed a closed-form analytical solution for the sequential decay problem featuring an arbitrary number of species, spatially varying initial conditions, and a generic, exponentially decaying Bateman-type source boundary. The coupled, one-dimensional system of partial differential equations was solved for both Dirichlet and Cauchy boundary conditions using a combination of Laplace transforms and the matrix diagonalization procedure of Clement (2001) which uncouples the transport equations. The solution was obtained for a semi-infinite domain.

Having a solution for a finite domain and time-varying boundary conditions would be very useful for benchmarking numerical solutions since numerical solutions generally pertain only to finite domains. We recently used the Classic Integral Transform Technique (CITT) to obtain an analytical solution for a first-order sequential decay problem with steady-state boundary conditions and a finite domain (Pérez Guerrero et al. 2009a). The objective of this study is to extend the CITT procedure to obtain an analytical solution for a sequential decay reaction transport problem with time-varying boundary conditions and a finite domain.

2 Problem Formulation

Consider the transport of first-order sequentially decaying species in a homogeneous finite porous media of length $L_0$, subject to linear equilibrium adsorption processes and a constant advective velocity. The governing transport equations are given by the following coupled system of dimensional partial differential equations:

\[ R_j \frac{\partial C_j}{\partial T} = D \frac{\partial^2 C_j}{\partial X^2} - U \frac{\partial C_j}{\partial X} - \lambda_j R_j C_j + \lambda_{j-1} R_{j-1} C_{j-1} \]

\[ (j = 1, 2, 3, \ldots; \lambda_0 = 0) \]
where the index $j$ signifies the particular solute species, $R_j$ is the retardation factor, $\lambda_j$ is the first-order decay coefficient [T$^{-1}$], $D$ is the dispersion coefficient [LT$^{-2}$], $U$ is the pore-water velocity [LT$^{-1}$], $C_j$ is the solute concentration [ML$^{-3}$], $X$ is position [L], and $T$ is time [T].

The initial condition may be a function of position as follows:

$$C_j(X, 0) = G_j(X)$$

(1b)

The boundary conditions are specified as being of the third type for the inlet boundary ($X = 0$) and the second type for the exit boundary ($X = L_0$):

$$-D \frac{\partial C_j(0, T)}{\partial X} + U C_j(0, T) = U \Phi_1(T)$$

(1c)

$$\frac{\partial C_j(L_0, T)}{\partial X} = 0$$

(1d)

The time-varying source functions $\Phi_j(T)$ are the same as those used by van Genuchten (1985) for the generalized Bateman equations:

$$\Phi_j(T) = \sum_{m=1}^{j} b_{jm} \exp(-\bar{\lambda}_m T)$$

(2a)

$$\bar{\lambda}_m = \lambda_m + \alpha_m$$

(2b)

in which the coefficients $b_{jm}$ and $\bar{\lambda}_m$ account for decay reactions ($\lambda_m$) in the waste source and the leaching ($\alpha_m$) of each species from the source.

Equations 1 and 2 can be written in dimensionless form after defining the following variables:

$$x = \frac{X}{L_0}; \quad t = \frac{T}{(L_0/U)}; \quad c_j = \frac{C_j}{C_0}$$

(3a-c)

$$g_j(x) = \frac{G_j}{C_0}; \quad \phi_j(t) = \frac{\Phi_j(T)}{C_0}$$

(3d,e)

$$Pe = \frac{UL_0}{D}; \quad \gamma_j = \frac{\lambda_j R_j L_0}{U}$$

(3f,g)

where $Pe$ is the finite domain Peclet number and $\gamma_j$ the Damkohler number for species $j$. Equations 1 and 2 then become

$$R_j \frac{\partial c_j}{\partial t} = \frac{1}{Pe} \frac{\partial^2 c_j}{\partial x^2} - \frac{\partial c_j}{\partial x} - \gamma_j c_j + \gamma_{j-1} c_{j-1} \quad (j = 1, 2, 3, \ldots; \gamma_0 = 0)$$

(4a)

$$c_j(x, 0) = g_j(x)$$

(4b)

$$-\frac{\partial c_j(0, t)}{\partial x} + Pe c_j(0, t) = Pe \phi_j(t)$$

(4c)

$$\frac{\partial c_j(1, t)}{\partial x} = 0$$

(4d)

$$\phi_j(t) = \sum_{m=1}^{j} f_{jm}(t)$$

(5a)

$$f_{jm}(t) = b_{jm} \exp\left(-\bar{\lambda}_m \frac{L_0}{U} t\right) = b_{jm} \exp(-\sigma_m t)$$

(5b)

with $\sigma_m = \bar{\lambda}_m \frac{L_0}{U}$. 

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Define the following operators on $c_j$:

$$
\Gamma c_j \equiv R_j \frac{\partial}{\partial t} c_j
$$

(6)

$$
L c_j \equiv \frac{1}{P e} \frac{\partial^2 c_j}{\partial x^2} - \frac{\partial c_j}{\partial x} - \gamma_j c_j
$$

(7)

$$
B_1 c_j \equiv -\frac{\partial c_j}{\partial x} + P e c_j
$$

(8)

$$
B_2 c_j \equiv \frac{\partial c_j}{\partial x}
$$

(9)

These operators allow Eq. 4 to be written more compactly as

$$
\Gamma c_j = L c_j + \gamma_{j-1} c_{j-1} \quad (j = 1, 2, 3, \ldots; \gamma_0 = 0)
$$

(10a)

$$
c_j(x, 0) = g_j(x)
$$

(10b)

$$
B_1 c_j(0, t) = P e \sum_{m=1}^{j} f_{jm}(t)
$$

(10c)

$$
B_2 c_j(1, t) = 0
$$

(10d)

### 3 Analytical Solution

The solution to Eq. 10 will be obtained using several steps. First, Eq. 10 will be transformed into a system with homogeneous boundary conditions. Next, according to the procedure reported by Pérez Guerrero et al. (2009a,b), the advection–dispersion system with homogeneous boundary conditions will be transformed into a system of diffusion equations. The final transformed system is subsequently solved analytically using the CITT (e.g., Ozisik 1980; Mikhailov and Ozisik 1984; Cotta 1993).

#### 3.1 Homogenizing the Boundary Conditions

As noted by Ozisik (1980) and Cotta and Mikhailov (1997), solutions of nonhomogeneous problems based on eigenfunction expansions may converge slowly or even exhibit anomalous behavior, especially in the vicinity of the boundaries. The reason is that the source terms are not accounted for in the auxiliary problems. Therefore, we homogenize the boundary conditions by defining a filter function, $h_j(x, t)$, conditioned to reproduce the original boundary conditions given by Eq. 10c, d for each species:

$$
c_j(x, t) = \omega_j(x, t) + h_j(x, t) \quad (j = 1, 2, 3, \ldots)
$$

(11)

where $\omega_j(x, t)$ is an unknown function with homogeneous boundary conditions.

For the case of multi-species transport in a finite medium with non-time-dependent boundary conditions, Pérez Guerrero et al. (2009a) found an appropriate filter function $h_j$ using the procedure presented by Sun et al. (1999a,b) and Sun and Clement (1999c). However, using the procedure for time-dependent boundary conditions is not easy because of the need to define the filter over both the time and spatial domains.

For this reason, i.e., for overcoming the above constraint, we implemented a version of the method suggested by Ozisik (1980) for homogenizing problems with transient boundary conditions. The method involves defining a filter function with temporal and spatial dependencies.
that are separable. As detailed in Appendix A, the procedure leads to the following form for
the filter function when extended to multi-species transport problems:

\[ h_j(x, t) = \sum_{m=1}^{j} f_{jm}(t)\varphi_{jm}(x) \] (12)

The temporally dependent term \( f_{jm}(t) \) in this equation is known and given by Eq. 5b, whereas
Appendix A gives details for developing a mathematical formulation for \( \varphi_{jm}(x) \). A general
analytical expression for \( \varphi_{jm}(x) \), obtained by solving Eqs. A10–A12 with the Mathematica
(2007) software, is:

\[ \varphi_{jm}(x) = \bar{A}_{jm} \exp \left( x \bar{a}_{jm} \right) + \bar{B}_{jm} \exp \left( x \bar{b}_{jm} \right) 
+ \frac{\bar{\delta}_{jm}}{w_{jm}} \sqrt{\gamma_{j-1} \sigma_{jm} \gamma_{j} \gamma_{j-1}} \int_{1}^{x} \exp \left( \frac{x - \bar{b}_{jm}}{2} \right) \varphi_{j-1m}(\xi) d\xi 
- \frac{\bar{\delta}_{jm}}{w_{jm}} \sqrt{\gamma_{j-1} \sigma_{jm} \gamma_{j} \gamma_{j-1}} \int_{1}^{x} \exp \left( \frac{x - \bar{a}_{jm}}{2} \right) \varphi_{j-1m}(\xi) d\xi \] (13a)

where \( w_{jm}, \bar{a}_{jm}, \bar{b}_{jm} \) are respectively:

\[ w_{jm} = \sqrt{\gamma_{j} \sigma_{jm} \gamma_{j-1}} - 4\gamma_{j} \] (13b)
\[ \bar{a}_{jm} = \gamma_{j} \sigma_{jm} \gamma_{j-1} + w_{jm} \sqrt{\gamma_{j}} \] (13c)
\[ \bar{b}_{jm} = \gamma_{j} \sigma_{jm} \gamma_{j-1} + w_{jm} \sqrt{\gamma_{j}} \] (13d)

The coefficients \( \bar{A}_{jm} \) and \( \bar{B}_{jm} \) in Eq. 13a are calculated from the boundary conditions such
as specified in Appendix A. The integrals in Eq. 13a are analytic since the terms \( \varphi_{j-1m}(\xi) \) are
a combination of exponential functions. While it is evident that the above analytical solution
is relatively elaborate for large values of \( j \), strategic grouping of the coefficients and using
the Mathematica software made it possible to generate simplified structures appropriate for
computational purposes.

Substituting Eq. 11 into Eq. 10 yields a problem reformulated in terms of \( \omega_{j}(x, t) \):

\[ \Gamma \omega_{j} = L\omega_{j} + \gamma_{j-1} \omega_{j-1} \quad (j = 1, 2, 3, \ldots; \gamma_{0} = 0) \] (14a)
\[ \omega_{j}(x, 0) = g_{j}(x) - h(x, 0) = g_{j}(x) - \sum_{m=1}^{j} f_{jm}(0)\varphi_{jm}(x) \] (14b)
\[ B_{1}\omega_{j}(0, t) = 0 \] (14c)
\[ B_{2}\omega_{j}(1, t) = 0 \] (14d)

In order to allow the use of a systematized solution procedure as described below, we decouple
the initial condition from the overall solution using the superposition principle. Thus,

\[ \omega_{j}(x, t) = \sum_{m=1}^{j} \Omega_{jm}(x, t) \] (15)
Representing $\omega_j(x,t)$ in terms of $\Omega_{jm}(x,t)$ allows Eq. 14 to be rewritten as

$$\Gamma \Omega_{jm} = L \Omega_{jm} + \gamma_{j-1} \Omega_{j-1m} \delta_{jm}$$  \hspace{1cm} (16a)

$$\Omega_{jm}(x,0) = g_j(x) - f_{jm}(0)\varphi_{jm}(x)$$  \hspace{1cm} (16b)

$$B_1 \Omega_{jm}(0, t) = 0$$  \hspace{1cm} (16c)

$$B_2 \Omega_{jm}(1, t) = 0$$  \hspace{1cm} (16d)

with the coefficient $\tilde{\delta}_{jm}$ defined by

$$\tilde{\delta}_{jm} = \begin{cases} 0 & \text{if } j = m \\ 1 & \text{if } j \neq m \end{cases}$$  \hspace{1cm} (16e)

In summary, the advection–dispersion problem with time-dependent boundary conditions given by Eq. 10 was homogenized using a filter function having separable time and space dependencies. The resulting problem (Eq. 14) with a coupled initial condition (Eq. 14b) was re-written using the superposition principle so that the condition was decoupled (Eq. 16). Once $\Omega_{jm}(x,t)$ is found, $c_j(x, t)$ can be obtained from Eqs. 11, 12, and 15. The analytical solution for $\Omega_{jm}(x,t)$ is obtained below.

3.2 Transforming the Advection–Dispersion Equation into a Diffusion Equation

As detailed in Pérez Guerrero et al. (2009a,b), the following algebraic substitution can be used to transform an advection–dispersion differential system such as Eq. 16 into a purely diffusive system:

$$\Omega_{jm}(x,t) = \theta_{jm}(x,t) \exp(px + q_j t) \hspace{1cm} (j = 1, 2, 3, \ldots; \hspace{0.1cm} m = 1, 2, \ldots, j)$$  \hspace{1cm} (17)

In which the coefficients $p$ and $q_j$ are given by

$$p = \frac{Pe}{2}$$  \hspace{1cm} (18a)

$$q_j = -\frac{1}{R_j} \left( \frac{Pe}{4} + \gamma_j \right)$$  \hspace{1cm} (18b)

Using this substitution in Eq. 16 results in the purely diffusive system

$$R_j \frac{\partial \theta_{jm}}{\partial t} = \frac{1}{Pe} \frac{\partial^2 \theta_{jm}}{\partial x^2} + \gamma_{j-1} \theta_{j-1m}(x,t) \exp(-px - q_j t) \tilde{\delta}_{jm}$$  \hspace{1cm} (19a)

with initial condition and boundary conditions as follows:

$$\theta_{jm}(x,0) = \exp(-px)[g_j(x) - f_{jm}(0)\varphi_j(x)]$$  \hspace{1cm} (19b)

$$-\frac{\partial \theta_{jm}(0,t)}{\partial x} + \frac{Pe}{2} \theta_{jm}(0,t) = 0$$  \hspace{1cm} (19c)

$$\frac{\partial \theta_{jm}(1,t)}{\partial x} + \frac{Pe}{2} \theta_{jm}(1,t) = 0$$  \hspace{1cm} (19d)

3.3 Integral Transform Solution

Equation 19 can be solved using the CITT. In this procedure, the potential $\theta_{jm}$ is expanded in a series of eigenfunctions. An orthogonality property is established and used to specify
a transform and inverse transform rule. The transform is applied to the system of partial differential equations to remove the spatial variable, thus producing a system of ordinary differential equations. The above system is solved, and the inverse transformation is applied. Details of the systematized procedure used here can be found in Ozisik (1980), Mikhailov and Ozisik (1984), and Cotta (1993). Specific steps in the solution procedure are as follows:

(a) The auxiliary eigenvalue problem

A Sturm–Liouville eigenvalue problem is obtained applying a separation-of-variables to the homogeneous version of Eq. 19b (i.e., without the source term \( \gamma_j \theta_{j-1m}(x, t) \exp(-px - q_j t) \delta_{jm} \)).

\[
\frac{d^2 \psi_i(x)}{dx^2} + \beta_i^2 \psi_i(x) = 0; \quad \beta_i^2 = \frac{\mu_i^2}{(1/Pe)} \tag{20a,b}
\]

\[
- \frac{d\psi_i(0)}{dx} + \frac{Pe}{2} \psi_i(0) = 0 \tag{20c}
\]

\[
\frac{d\psi_i(1)}{dx} + \frac{Pe}{2} \psi_i(1) = 0 \tag{20d}
\]

where \( \psi_i(x) \) is the eigenfunction and \( \beta_i \) the eigenvalue. The analytical solution of this problem is (Ozisik 1980):

\[
\psi_i = \beta_i \cos(\beta_i x) + H_1 \sin(\beta_i x) \tag{21}
\]

The eigenvalues and norm can be calculated from the following equations:

\[
\tan(\beta_i) = \frac{\beta_i (H_1 + H_2)}{\beta_i^2 - H_1 H_2} \tag{22}
\]

\[
N_i = \frac{(\beta_i^2 + H_1^2) + H_1 + H_2}{2} \tag{23}
\]

respectively, where \( H_1 = \frac{Pe}{2} \) and \( H_2 = \frac{Pe}{2} \).

The normalized eigenfunction \( \tilde{\psi}_i(x) \) and the orthogonality property are respectively:

\[
\tilde{\psi}_i(x) = \frac{\psi_i(x)}{N_i^{1/2}} \tag{24}
\]

\[
\int_0^1 \tilde{\psi}_i(x) \tilde{\psi}_k(x) dx = \delta_{ik} \tag{25}
\]

where \( \delta_{i,k} \) is the Kronecker delta.

(b) The integral transform pair

A transform pair is established for the potential \( \theta_{jm}(x, t) \). The inverse transform is given by a series expansion of \( \theta_{jm}(x, t) \) in terms of the eigenfunctions \( \psi_i \), whereas the forward transform is found by applying the orthogonality property of Eq. 25. The transform pair is given by

\[
\bar{\theta}_{jmi}(t) = \int_0^1 \tilde{\psi}_i(x) \theta_{jm}(x, t) dx \quad \text{(Transform)} \tag{26}
\]

\[
\theta_{jm}(x, t) = \sum_{i=1}^\infty \tilde{\psi}_i(x) \bar{\theta}_{jmi}(t) \quad \text{(Inverse)} \tag{27}
\]
(c) **Integral transform of the system of partial differential equations**

Application of the operator \( \int_0^1 \tilde{\psi}_i(x) \, dx \) to both sides of Eq. 19 removes the space variable and leads to the following infinite system of ordinary differential equations:

\[
R_j \frac{d\tilde{\theta}_{jmi}(t)}{dr} + \mu_i^2 \tilde{\theta}_{jmi}(t) = \tilde{S}_{jmi}(t) \tag{28a}
\]

\[
\tilde{\theta}_{jmi}(t = 0) = \tilde{f}_{jmi} \tag{28b}
\]

where

\[
\tilde{S}_{jmi}(t) = \gamma_{j-1} \tilde{\theta}_{j-1mi}(t) \exp[(q_{j-1} - q_j)t] \tilde{\delta}_{jm} \tag{28c}
\]

\[
\tilde{f}_{jmi} = \int_0^1 \tilde{\psi}_i(x) \exp(-px)[g_j(x) - f_{jm}(0)\varphi_j(x)] \, dx \tag{28d}
\]

(d) **Solution of the transformed system**

Solving the system of ordinary differential equations given by Eq. 28, subject to the transformed initial condition, results in the transformed potential:

\[
\tilde{\theta}_{jmi}(t) = \exp\left(\frac{-\mu_i^2}{R_j} t\right) \left[ \tilde{f}_{jmi} + \frac{1}{R_j} \int_0^1 \tilde{S}_{jmi}(\tau) \exp\left(\frac{\mu_i^2}{R_j} \tau\right) \, d\tau \right] \tag{29}
\]

(e) **Calculation of the concentration**

The inverse formula (27) can be invoked to obtain the desired solution for the potential \( \theta_{jm}(x, t) \). Once \( \theta_{jm}(x, t) \) is obtained, the desired concentration field for species \( j \) can be computed as

\[
c_j(x, t) = h(x, t) + \sum_{m=1}^j \exp(px + q_mt) \sum_{i=1}^{\infty} \tilde{\psi}_i(x) \tilde{\theta}_{jmi}(t) \quad (j = 1, 2, 3, \ldots) \tag{30}
\]

For computational purposes, the infinite series in Eq. 30 is truncated to a number of terms \( N \) which produces the desired precision.

4 **Test Application**

The classic four species radionuclide decay chain problem solved by van Genuchten (1985) is used here as a test case for the analytic solution procedure developed above. The test case is an

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( ^{238}\text{Pu} ) ((j = 1))</th>
<th>( ^{234}\text{U} ) ((j = 2))</th>
<th>( ^{230}\text{Th} ) ((j = 3))</th>
<th>( ^{226}\text{Ra} ) ((j = 4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retardation coefficient, ( R_j )</td>
<td>10000</td>
<td>14000</td>
<td>50000</td>
<td>500</td>
</tr>
<tr>
<td>Decay constant, ( \lambda_j[\text{year}^{-1}] )</td>
<td>0.0079</td>
<td>0.0000028</td>
<td>0.0000087</td>
<td>0.00043</td>
</tr>
<tr>
<td>Source decay constant, ( \lambda_j[\text{year}^{-1}] )</td>
<td>0.0089</td>
<td>0.00100280</td>
<td>0.00100870</td>
<td>0.00143</td>
</tr>
<tr>
<td>Pore-water velocity: ( U = 100 \text{ m/year} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dispersion coefficient: ( D = 10 \text{ m}^2/\text{year} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the concentration field was obtained for the decays chain $^{238}\text{Pu}$ → $^{234}\text{U}$ → $^{230}\text{Th}$ → $^{226}\text{Ra}$. The governing system of transport equations is given by Eq. 1 with an extended version of the problem studied previously by Higashi and Pigford (1980).

Table 2  Values for the boundary source coefficient $b_{jm}$

<table>
<thead>
<tr>
<th>Species, $j$</th>
<th>$b_{jm}$</th>
<th>$m = 1$</th>
<th>$m = 2$</th>
<th>$m = 3$</th>
<th>$m = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j = 1$ ($^{238}\text{Pu}$)</td>
<td>1.25</td>
<td>****</td>
<td>****</td>
<td>****</td>
<td>****</td>
</tr>
<tr>
<td>$j = 2$ ($^{234}\text{U}$)</td>
<td>-1.25044</td>
<td>1.25044</td>
<td>****</td>
<td>****</td>
<td>****</td>
</tr>
<tr>
<td>$j = 3$ ($^{230}\text{Th}$)</td>
<td>0.443684E−3</td>
<td>0.593431</td>
<td>-0.593874</td>
<td>****</td>
<td>****</td>
</tr>
<tr>
<td>$j = 4$ ($^{226}\text{Ra}$)</td>
<td>-0.516740E−6</td>
<td>0.120853E−1</td>
<td>-0.122637E−1</td>
<td>0.178925E−3</td>
<td>****</td>
</tr>
</tbody>
</table>

Table 3  Convergence of dimensionless concentration for $^{238}\text{Pu}(D = 10\text{ m}^2/\text{year})$

<table>
<thead>
<tr>
<th>$X$ (m)</th>
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<td>110</td>
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An extended version of the problem studied previously by Higashi and Pigford (1980) in which the concentration field was obtained for the decays chain $^{238}\text{Pu}$ → $^{234}\text{U}$ → $^{230}\text{Th}$ → $^{226}\text{Ra}$. The governing system of transport equations is given by Eq. 1 with $C_1 = ^{238}\text{Pu}$, $C_2 = ^{234}\text{U}$, $C_3 = ^{230}\text{Th}$, and $C_4 = ^{226}\text{Ra}$. Model parameter values for the example application are specified in Tables 1 and 2 and are the same as those employed previously by van Genuchten (1985).
Table 4  Convergence of dimensionless concentration for $^{234}\text{U}$ ($D = 10 \text{ m}^2/\text{year}$)

<table>
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<tr>
<th>$X$ (m)</th>
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The analytical solution of this study was implemented using the symbolic-numerical software package Mathematica 6.0 (Wolfram Research, Inc 2007), with the Mathematica system variable $\text{MaxExtraPrecision}$ set to 300. Computations were done on a desktop PC with a 2.0 GHz processor and 1 GB of RAM. The concentration field for each radionuclide was computed at time $t = 10000$ years assuming a domain length $L_0$ of 110 m. Tables 3, 4, 5, and 6 show, with 10 significant figures, the convergence of the dimensionless concentration of the four species for differing numbers of terms $N$ in the truncated infinite summation of Eq. 30. CPU time duration required to compute the results ranged from 5 s (Table 3) to 75 s (Table 6). The case $N = 0$ corresponds the value of the filter function $h_j(x, t)$, as given in Eq. 12.

The results show that the number of terms required to achieve convergence throughout the spatial domain differed depending upon the species. Convergence of the $^{238}\text{Pu}$ concentration required $N = 200$ terms, $^{234}\text{U}$ required $N = 300$ terms, and $^{230}\text{Th}$ and $^{226}\text{Ra}$ both required $N = 600$ terms. The Peclet number for those calculations was relatively large (1100), reflecting advection-dominated transport. The large Peclet number was responsible for the large number of terms required for the summation to converge. The converged dimensionless concentrations reported in Tables 3, 4, 5, and 6 for each radionuclide are in exact agreement.
Table 5  Convergence of dimensionless concentration for $^{230}$Th ($D = 10 \text{ m}^2/\text{year}$)

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Table 6  Convergence of dimensionless concentration for $^{226}$Ra ($D = 10 \text{ m}^2/\text{year}$)

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### Table 6 continued

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### Table 7 Comparison of calculated dimensionless concentrations (D = 20 m²/year)

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<th>CHAIN</th>
<th>$^{234}$U</th>
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with the results reported by van Genuchten (1985) for a semi-infinite domain, except near the boundary at \( X = 110 \) m where, as expected, the results deviated slightly due to the effect of the finite domain. Optimal values of \( N \) for achieving convergence to a desired level of accuracy can be found using an adaptive procedure described by Cotta (1993). In addition, it may be possible to improve the rate of convergence by finding better auxiliary eigenvalue problems and filters (Cotta 1993).

Table 7 gives results for a less advective case. All model parameters are the same as before except that the dispersion parameter was increased to \( D = 20 \text{ m}^2/\text{year} \). The Peclet number in this case was \( Pe = 550 \), which reduced the number of terms required for convergence by half. The required CPU time was 18 s. Also shown in Table 7 are results obtained with the CHAIN program of van Genuchten (1985) that is contained within the STANMOD software package (Simunek et al. 1999). CHAIN implements the original analytical solutions of van Genuchten (1985). The results obtained with the solution of this study were identical to those obtained with CHAIN except near the exit boundary, where again slight differences appear due to the differing spatial domains (finite and infinite). Figure 1 contains plots of the data presented in Table 7.
Fig. 1 Computed results for the decay chain $^{238}\text{Pu} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow ^{226}\text{Ra}$, as given in Table 7 ($t = 10000\ \text{year}, D = 20\ \text{m}^2/\text{year}, U = 100\ \text{m/yr}$)
5 Conclusions

Using the CITT in combination with a filter function with separable space and time-dependen-
cies, the superposition principle, and a classic algebraic substitution, we were able to obtain
an analytical solution for the transport of multiple solutes undergoing sequential first-order
decay reactions for a finite domain and time-varying inlet condition. The analytical solution
is general and permits different values for the retardation coefficients of each species.

The convergence of the solution was investigated by means of a test case in which trans-
port was advection-dominated. Those conditions typically require a large number of terms
for the eigen-expansion series to converge. Another test case with more dispersion required
fewer terms. In all the cases, the converged results were exactly the same as those computed
using analytical solutions published previously by van Genuchten (1985) for a semi-infinite
domain, except near the exit boundary where differences were expected. Among other appli-
cations, the new solution should be useful for benchmarking numerical solutions involving
the finite boundary conditions.

Acknowledgements The first author acknowledges support given by the Brazilian National Research Coun-
cil, the University of California at Riverside (UCR), and the United States Salinity Laboratory of the USDA
Agricultural Research Service. The research was supported also in part by a fellowship from CAPES to M.
Th. van Genuchten.

Appendix A

Obtaining a solution of Eq. 10 requires a filter function, $h_j(x, t)$, capable of homogenizing
the boundary conditions (Eqs. 10c, 10d). Additionally, it is desirable that the filter function
be as similar as possible to $c_j(x, t)$. In order to accomplish these objectives, we consider a
system for $h_j$ with the same structure as Eq. 10,

\[ \Gamma h_j = Lh_j + \gamma_{j-1} h_{j-1} \tag{A1} \]

\[ B_1 h_j(0, t) = P e \sum_{m=1}^{j} f_{jm}(t) \tag{A2} \]

\[ B_2 h_j(1, t) = 0 \tag{A3} \]

but impose the following functional form on the solution:

\[ h_j(x, t) = \sum_{m=1}^{j} f_{jm}(t) \varphi_{jm}(x) \tag{A4} \]

This representation of $h_j$, in which the time and spatial dependences are separated into
different terms in the series, is an extension of the split procedure presented by Ozisik (1980).
In Eq. A4, the function associated with the time domain ($f_{jm}$) is known and given by Eq. 5b,
while $\varphi_{jm}(x)$ is unknown and needs to be found. Substituting Eq. A4 into Eq. A1 gives:

\[ \sum_{m=1}^{j} \Gamma f_{jm}(t) \varphi_{jm}(x) = \sum_{m=1}^{j} f_{jm}(t) L\varphi_{jm}(x) + \gamma_{j-1} \sum_{m=1}^{j-1} f_{j-1m}(t) \varphi_{j-1m}(x) \tag{A5} \]
Rearranging this result gives:

\[ \sum_{m=1}^{j} R_j \sigma_m f_{jm}(t) \varphi_{jm}(x) + f_{jm}(t) L \varphi_{jm}(x) + \delta_{jm} \gamma_{j-1} f_{j-1m}(t) \varphi_{j-1m}(x) = 0 \quad \text{(A6)} \]

For the boundary condition we similarly obtain:

\[ \sum_{m=1}^{j} f_{jm}(t) B_1 \varphi_{jm}(0) - Pe f_{jm}(t) = 0 \quad \text{(A7)} \]

\[ \sum_{m=1}^{j} f_{jm}(t) B_2 \varphi_{jm}(1) = 0 \quad \text{(A8)} \]

\[ r_{jm} = \frac{f_{j-1m}(t)}{f_{jm}(t)} = \frac{b_{j-1m}}{b_{jm}} \quad \text{(A9)} \]

Therefore, the equation and boundary conditions which determine \( \varphi_{jm}(x) \) are given by

\[ R_j \sigma_m \varphi_{jm}(x) + L \varphi_{jm}(x) + \delta_{jm} \gamma_{j-1} r_{jm} \varphi_{j-1m}(x) = 0 \quad \text{(j = 1, 2, \ldots; m = 1, 2, \ldots, j)} \quad \text{(A10)} \]

\[ B_1 \varphi_{jm}(0) - Pe = 0 \quad \text{(A11)} \]

\[ B_2 \varphi_{jm}(1) = 0 \quad \text{(A12)} \]

A solution for \( \varphi_{jm}(x) \) is given in the main text.

References


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