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

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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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List of Symbols

$\bar{A}_{jm}\bar{a}_{jm}$	Auxiliary coefficients
B_1, B_2	Mathematical operators
$\bar{B}_{jm}\bar{b}_{jm}$	Auxiliary coefficients
b_{jm}	Boundary source coefficient
C_0	Dimensional reference solute concentration
$C_j(X, T)$	Dimensional solute concentration of the jth species
$c_j(x, t)$	Dimensionless solute concentration of the jth species
D	Dispersion coefficient
$\bar{f}_{jmi}$	Integral coefficient
$G_j(X)$	Dimensional initial concentration of the jth species
$g_j(x)$	Dimensionless initial concentration of the jth 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 jth 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

Greek Symbols

α_i	Source leaching coefficient
β_i	Eigenvalue
Γ	Mathematical operator
γ_j	Damkohler number
δ_{ik}	Kronecker delta
$\bar{\delta}_{jm}$	Auxiliary coefficient
$\theta_{jm}(x, t)$	Unknown function in purely diffusive equation
$\bar{\theta}_{jmi}(t)$	Integral transform of the function $\theta_j(x, t)$
λ_j	First-order decay constant for the jth species
$\bar{\lambda}_m$	Source decay constant
μ_i	Eigenvalue
ξ	Auxiliary integration variable
σ_m	Auxiliary coefficient
$\Phi_j(T)$	Dimensional transient boundary function
$\phi_j(t)$	Dimensionless transient boundary function

$\varphi_{jm}(x)$ Spatial function related to the filter
$\psi_i(x)$ Eigenfunction
$\tilde{\psi}_i(x)$ Normalized eigenfunction
$\omega_j(x, t)$ Unknown function
$\omega_j(x, t)$ Unknown function
$\Omega_{jm}(x, t)$ Unknown function

1 Introduction

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:

$$R_j \frac{\partial C_j}{\partial T} = D \frac{\partial^2 C_j}{\partial X^2} - U \frac{\partial C_j}{\partial X} - \lambda_j R_j C_j + \lambda_{j-1} R_{j-1} C_{j-1}$$
$$(j = 1, 2, 3, \ldots; \ \lambda_0 = 0) \tag{1a}$$

where the index j signifies the particular solute species, R_j is the retardation factor, λ_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:

$$C_j(X, 0) = G_j(X) \tag{1b}$$

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 ($X = L_0$):

$$-D\frac{\partial C_j(0, T)}{\partial X} + UC_j(0, T) = U\Phi_j(T) \tag{1c}$$

$$\frac{\partial C_j(L_0, T)}{\partial X} = 0 \tag{1d}$$

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

$$\Phi_j(T) = \sum_{m=1}^{j} b_{jm} \exp(-\bar{\lambda}_m T) \tag{2a}$$

$$\bar{\lambda}_m = \lambda_m + \alpha_m \tag{2b}$$

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

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

$$x = \frac{X}{L_0}; \quad t = \frac{T}{(L_0/U)}; \quad c_j = \frac{C_j}{C_0} \tag{3a–c}$$

$$g_j(x) = \frac{G_j}{C_0}; \quad \phi_j(t) = \frac{\Phi_j(T)}{C_0} \tag{3d,e}$$

$$Pe = \frac{UL_0}{D}; \quad \gamma_j = \frac{\lambda_j R_j L_0}{U} \tag{3f,g}$$

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

$$R_j\frac{\partial c_j}{\partial t} = \frac{1}{Pe}\frac{\partial^2 c_j}{\partial x^2} - \frac{\partial c_j}{\partial x} - \gamma_j c_j + \gamma_{j-1} c_{j-1} \quad (j = 1, 2, 3, \ldots; \gamma_0 = 0) \tag{4a}$$

$$c_j(x, 0) = g_j(x) \tag{4b}$$

$$-\frac{\partial c_j(0, t)}{\partial x} + Pe\, c_j(0, t) = Pe\, \phi_j(t) \tag{4c}$$

$$\frac{\partial c_j(1, t)}{\partial x} = 0 \tag{4d}$$

$$\phi_j(t) = \sum_{m=1}^{j} f_{jm}(t) \tag{5a}$$

$$f_{jm}(t) = b_{jm} \exp\left(-\bar{\lambda}_m \frac{L_0}{U} t\right) = b_{jm} \exp(-\sigma_m t) \tag{5b}$$

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

Define the following operators on c_j:

$$\Gamma c_j \equiv R_j \frac{\partial}{\partial t} c_j \tag{6}$$

$$L c_j \equiv \frac{1}{Pe} \frac{\partial^2 c_j}{\partial x^2} - \frac{\partial c_j}{\partial x} - \gamma_j c_j \tag{7}$$

$$B_1 c_j \equiv -\frac{\partial c_j}{\partial x} + Pe \, c_j \tag{8}$$

$$B_2 c_j \equiv \frac{\partial c_j}{\partial x} \tag{9}$$

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

$$\Gamma c_j = L c_j + \gamma_{j-1} c_{j-1} \quad (j = 1, 2, 3, \ldots; \ \gamma_0 = 0) \tag{10a}$$

$$c_j(x, 0) = g_j(x) \tag{10b}$$

$$B_1 c_j(0, t) = Pe \sum_{m=1}^{j} f_{jm}(t) \tag{10c}$$

$$B_2 c_j(1, t) = 0 \tag{10d}$$

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:

$$c_j(x, t) = \omega_j(x, t) + h_j(x, t) \quad (j = 1, 2, 3, \ldots) \tag{11}$$

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:

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

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:

$$\begin{aligned}
\varphi_{jm}(x) = {} & \bar{A}_{jm} \exp\left(x \frac{\bar{a}_{jm}}{2}\right) + \bar{B}_{jm} \exp\left(x \frac{\bar{b}_{jm}}{2}\right) \\
& + \exp\left(x \frac{\bar{a}_{jm}}{2}\right) \frac{\bar{\delta}_{jm}\gamma_{j-1}r_{jm}\sqrt{Pe}}{w_{jm}} \int_{1}^{x} \exp\left[\xi\left(\frac{\bar{b}_{jm}}{2} - Pe\right)\right]\varphi_{j-1m}(\xi)\mathrm{d}\xi \\
& - \exp\left(x \frac{\bar{b}_{jm}}{2}\right) \frac{\bar{\delta}_{jm}\gamma_{j-1}r_{jm}\sqrt{Pe}}{w_{jm}} \int_{1}^{x} \exp\left[\xi\left(\frac{\bar{a}_{jm}}{2} - Pe\right)\right]\varphi_{j-1m}(\xi)\mathrm{d}\xi
\end{aligned} \tag{13a}$$

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

$$w_{jm} = \sqrt{Pe - 4\sigma_m r_j + 4\gamma_j} \tag{13b}$$

$$\bar{a}_{jm} = Pe - w_{jm}\sqrt{Pe} \tag{13c}$$

$$\bar{b}_{jm} = Pe + w_{jm}\sqrt{Pe} \tag{13d}$$

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 $\omega_j(x, t)$:

$$\Gamma\omega_j = L\omega_j + \gamma_{j-1}\omega_{j-1} \quad (j = 1, 2, 3, \ldots; \ \gamma_0 = 0) \tag{14a}$$

$$\omega_j(x, 0) = g_j(x) - h(x, 0) = g_j(x) - \sum_{m=1}^{j} f_{jm}(0)\varphi_{jm}(x) \tag{14b}$$

$$B_1\omega_j(0, t) = 0 \tag{14c}$$

$$B_2\omega_j(1, t) = 0 \tag{14d}$$

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,

$$\omega_j(x, t) = \sum_{m=1}^{j} \Omega_{jm}(x, t) \tag{15}$$

Representing $\omega_j(x,t)$ in terms of $\Omega_{jm}(x,t)$ allows Eq. 14 to be rewritten as

$$\Gamma\Omega_{jm} = L\Omega_{jm} + \gamma_{j-1}\Omega_{j-1m}\bar{\delta}_{jm}$$
$$(j = 1, 2, 3, \ldots; \ m = 1, 2, \ldots, j; \ \gamma_0 = 0) \tag{16a}$$

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

$$B_1\Omega_{jm}(0,t) = 0 \tag{16c}$$

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

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

$$\bar{\delta}_{jm} = \begin{cases} 0 \text{ if } j = m \\ 1 \text{ if } j \neq m \end{cases} \tag{16e}$$

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:

$$\Omega_{jm}(x,t) = \theta_{jm}(x,t)\exp(px + q_jt) \quad (j = 1, 2, 3, \ldots; \ m = 1, 2, \ldots, j) \tag{17}$$

In which the coefficients p and q_j are given by

$$p = \frac{Pe}{2} \tag{18a}$$

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

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

$$R_j\frac{\partial\theta_{jm}}{\partial t} = \frac{1}{Pe}\frac{\partial^2\theta_{jm}}{\partial x^2} + \gamma_{j-1}\theta_{j-1m}(x,t)\exp(-px - q_jt)\bar{\delta}_{jm}$$
$$(j = 1, 2, 3, \ldots; \ m = 1, 2, \ldots, j) \tag{19a}$$

with initial condition and boundary conditions as follows:

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

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

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

3.3 Integral Transform Solution

Equation 19 can be solved using the CITT. In this procedure, the potential θ_{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 $\gamma_{j-1}\theta_{j-1m}(x, t)\exp(-px - q_jt)\bar{\delta}_{jm}$),

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

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

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

where $\psi_i(x)$ is the eigenfunction and β_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 ψ_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 $\int_0^1 \tilde{\psi}_i(x)\mathrm{d}x$ to both sides of Eq. 19 removes the space variable and leads to the following infinite system of ordinary differential equations:

$$R_j \frac{\mathrm{d}\bar{\theta}_{jmi}(t)}{\mathrm{d}t} + \mu_i^2 \bar{\theta}_{jmi}(t) = \bar{S}_{jmi}(t) \tag{28a}$$

$$\bar{\theta}_{jmi}(t=0) = \bar{f}_{jmi} \tag{28b}$$

where

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

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

(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:

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

(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

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

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 1 Parameters values for the radionuclide decay chain problem

Parameter	^{238}Pu ($j=1$)	^{234}U ($j=2$)	^{230}Th ($j=3$)	^{226}Ra ($j=4$)
Retardation coefficient, R_j	10000	14000	50000	500
Decay constant, λ_j [year^{-1}]	0.0079	0.0000028	0.0000087	0.00043
Source decay constant, $\bar{\lambda}_j$ [year^{-1}]	0.0089	0.00100280	0.00100870	0.00143
Pore-water velocity: $U = 100$ m/year		Dispersion coefficient:		
		$D = 10$ m^2/year		

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

Species, j	b_{jm}			
	$m = 1$	$m = 2$	$m = 3$	$m = 4$
$j = 1 \left(^{238}\text{Pu}\right)$	1.25	****	****	****
$j = 2 \left(^{234}\text{U}\right)$	-1.25044	1.25044	****	****
$j = 3 \left(^{230}\text{Th}\right)$	0.443684E-3	0.593431	-0.593874	****
$j = 4 \left(^{226}\text{Ra}\right)$	-0.516740E-6	0.120853E-1	-0.122637E-1	0.178925E-3

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

X (m)	Numbers of terms summed (N)			
	$N = 0$	$N = 150$	$N = 200$	$N = 300$
0	2.812617661E-39	2.812617661E-39	2.812617661E-39	2.812617661E-39
5	4.660944797E-39	4.660944797E-39	4.660944797E-39	4.660944797E-39
10	7.723910258E-39	7.723910258E-39	7.723910258E-39	7.723910258E-39
15	1.279972029E-38	1.279972029E-38	1.279972029E-38	1.279972029E-38
20	2.121112674E-38	2.121112674E-38	2.121112674E-38	2.121112674E-38
25	3.515013512E-38	3.515013512E-38	3.515013512E-38	3.515013512E-38
30	5.824923938E-38	5.824923938E-38	5.824923938E-38	5.824923938E-38
35	9.652804682E-38	9.652804682E-38	9.652804682E-38	9.652804682E-38
40	1.599619827E-37	1.599619827E-37	1.599619827E-37	1.599619827E-37
45	2.650818778E-37	2.650818778E-37	2.650818778E-37	2.650818778E-37
50	4.392818890E-37	4.392818890E-37	4.392818890E-37	4.392818890E-37
55	7.279583939E-37	7.279583939E-37	7.279583939E-37	7.279583939E-37
60	1.206340249E-36	1.206340249E-36	1.206340249E-36	1.206340249E-36
65	1.999093366E-36	1.999093366E-36	1.999093366E-36	1.999093366E-36
70	3.312808546E-36	3.312808545E-36	3.312808545E-36	3.312808545E-36
75	5.489838868E-36	5.489838122E-36	5.489838122E-36	5.489838122E-36
80	9.097516619E-36	9.097255384E-36	9.097255384E-36	9.097255384E-36
85	1.507599961E-35	1.504826035E-35	1.504825228E-35	1.504825228E-35
90	2.498327551E-35	-5.724418127E-31	2.405667399E-35	2.405667399E-35
95	4.140117217E-35	3.054489808E-20	3.094978514E-35	3.094978514E-35
100	6.860817975E-35	-8.958409266E-10	2.234612976E-35	2.234612976E-35
105	1.136944217E-34	-44.76951213	6.612991375E-36	6.612991375E-36
110	1.864865906E-34	1.027415565E13	7.119825525E-37	7.119825525E-37

extended version of the problem studied previously by Higashi and Pigford (1980) in which the concentration field was obtained for the decays chain $^{238}\text{Pu} \rightarrow \ ^{234}\text{U} \rightarrow \ ^{230}\text{Th} \rightarrow \ ^{226}\text{Ra}$. 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}U ($D = 10\,\text{m}^2/\text{year}$)

X (m)	Numbers of terms summed (N)			
	$N = 0$	$N = 250$	$N = 300$	$N = 400$
0	0.00005599763985	0.00005599763985	0.00005599763985	0.00005599763985
5	0.0001139083231	0.0001139083231	0.0001139083231	0.0001139083231
10	0.0002317080881	0.0002317080881	0.0002317080881	0.0002317080881
15	0.0004713320030	0.0004713320030	0.0004713320030	0.0004713320030
20	0.0009587660877	0.0009587660877	0.0009587660877	0.0009587660877
25	0.001950286433	0.001950286433	0.001950286433	0.001950286433
30	0.003967200362	0.003967200362	0.003967200362	0.003967200362
35	0.008069931907	0.008069931907	0.008069931907	0.008069931907
40	0.01641555632	0.01641555632	0.01641555632	0.01641555632
45	0.03339191609	0.03339191609	0.03339191609	0.03339191609
50	0.06792455098	0.06792456385	0.06792456385	0.06792456385
55	0.1381008536	0.1381533789	0.1381533789	0.1381533789
60	0.1800304721	0.2788444392	0.2788444392	0.2788444392
65	-147.6865682	0.4978363297	0.4978363297	0.4978363297
70	-217564.8353	0.5054199873	0.5054199873	0.5054199873
75	$-3.192736368\text{E}8$	0.1692657773	0.1692657773	0.1692657773
80	$-4.685275158\text{E}11$	0.01366328526	0.01366328526	0.01366328526
85	$-6.875545178\text{E}14$	0.0002334133628	0.0002334133628	0.0002334133628
90	$-1.008972150\text{E}18$	8.083817021E-7	8.083817021E-7	8.083817021E-7
95	$-1.480645932\text{E}21$	5.727475188E-10	5.727475188E-10	5.727475188E-10
100	$-2.172817530\text{E}24$	8.920290957E-14	8.920290957E-14	8.920290957E-14
105	$-3.188565151\text{E}27$	-1.753009868E-12	3.736568695E-18	3.736568695E-18
110	$-3.880320834\text{E}30$	0.1236300738	7.792826947E-23	7.792826947E-23

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 $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}Pu concentration required $N = 200$ terms, ^{234}U required $N = 300$ terms, and ^{230}Th and ^{226}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 ($D = 10\,\text{m}^2/\text{year}$)

X (m)	Numbers of terms summed (N)			
	$N = 0$	$N = 500$	$N = 600$	$N = 700$
0	1.557998045E−6	1.557998045E−6	1.557998045E−6	1.557998045E−6
5	0.00001620869188	0.00001620869188	0.00001620869188	0.00001620869188
10	0.0001410791354	0.0001410795680	0.0001410795680	0.0001410795680
15	0.0007747723527	0.0007919552487	0.0007919552487	0.0007919552487
20	93.59969043	0.001298528478	0.001298528478	0.001298528478
25	−6.857605987E12	0.001259505239	0.001259505239	0.001259505239
30	5.002484732E23	0.001268644491	0.001268644491	0.001268644491
35	−3.634030382E34	0.001271527472	0.001271527472	0.001271527472
40	2.629133751E45	0.001269732017	0.001269732017	0.001269732017
45	−1.894414442E56	0.001258502707	0.001258502707	0.001258502707
50	1.359496019E67	0.001228041189	0.001228041189	0.001228041189
55	−9.716494897E77	0.001158416815	0.001158416815	0.001158416815
60	6.915816389E88	0.001009486912	0.001009486912	0.001009486912
65	−4.901592658E99	0.0007163481928	0.0007163481928	0.0007163481928
70	3.458849405E110	0.0003080549531	0.0003080549531	0.0003080549531
75	−2.429675808E121	0.00005314325832	0.00005314325832	0.00005314325832
80	1.698582612E132	2.636721747E−6	2.636721747E−6	2.636721747E−6
85	−1.181462475E143	3.120865554E−8	3.120865554E−8	3.120865554E−8
90	8.173153485E153	7.933489062E−11	8.108033619E−11	8.108033619E−11
95	−5.620800411E164	0.1448010034	4.563235436E−14	4.563235436E−14
100	3.840591902E175	−4.795194372E9	5.930826803E−18	5.930826803E−18
105	−2.605422444E186	−2.882208268E20	2.193954540E−22	2.193954540E−22
110	1.753240837E197	5.211513301E31	4.335249640E−27	4.335249640E−27

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

X (m)	Numbers of terms summed (N)			
	$N = 0$	$N = 500$	$N = 600$	$N = 700$
0	2.397063545E−8	2.397063545E−8	2.397063545E−8	2.397063545E−8
5	1.691266186E−7	1.691266186E−7	1.691266186E−7	1.691266186E−7
10	1.511139130E−6	1.511140077E−6	1.511140077E−6	1.511140077E−6
15	0.00001052414499	0.00001057726603	0.00001057726603	0.00001057726603
20	0.09247382809	0.00003590353701	0.00003590353701	0.00003590353701
25	−6.774597698E9	0.00006313026700	0.00006313026700	0.00006313026700
30	4.941931866E20	0.00009010807819	0.00009010807819	0.00009010807819
35	−3.590042051E31	0.0001169082851	0.0001169082851	0.0001169082851
40	2.597309249E42	0.0001434364490	0.0001434364490	0.0001434364490
45	−1.871483393E53	0.0001695417278	0.0001695417278	0.0001695417278
50	1.343039920E64	0.0001949155053	0.0001949155053	0.0001949155053

Table 6 continued

X (m)	Numbers of terms summed (N)			
	$N = 0$	$N = 500$	$N = 600$	$N = 700$
55	−9.598881022E74	0.0002189277052	0.0002189277052	0.0002189277052
60	6.832103489E85	0.0002402964566	0.0002402964566	0.0002402964566
65	−4.842261046E96	0.0002565305838	0.0002565305838	0.0002565305838
70	3.416981562E107	0.0002643627198	0.0002643627198	0.0002643627198
75	−2.400265656E118	0.0002642455651	0.0002642455651	0.0002642455651
80	1.678022020E129	0.0002610955418	0.0002610955418	0.0002610955418
85	−1.167161394E140	0.0002576059772	0.0002576059772	0.0002576059772
90	8.074221075E150	0.0002541482106	0.0002541482106	0.0002541482106
95	−5.552763107E161	0.0002785185520	0.0002507349829	0.0002507349829
100	3.794103235E172	−919886.1135	0.0002473658487	0.0002473658487
105	−2.573884957E183	−5.531608337E16	0.0002440402537	0.0002440402537
110	1.732018632E194	1.000039572E28	0.0002408228593	0.0002408228593

Table 7 Comparison of calculated dimensionless concentrations ($D = 20\text{m}^2/\text{year}$)

X (m)	^{238}Pu		^{234}U	
	Present solution ($N = 100$)	CHAIN	Present solution ($N = 150$)	CHAIN
0	2.842233909E−39	2.842E−39	5.684118059E−05	5.684E−05
5	4.735141085E−39	4.735E−39	1.168676484E−04	1.169E−04
10	7.888710715E−39	7.889E−39	2.402843694E−04	2.403E−04
15	1.314253486E−38	1.314E−38	4.940338836E−04	4.940E−04
20	2.189536778E−38	2.190E−38	1.015752622E−03	1.016E−03
25	3.647752397E−38	3.648E−38	2.088426366E−03	2.088E−03
30	6.077129045E−38	6.077E−38	4.293884745E−03	4.294E−03
35	1.012445293E−37	1.012E−37	8.828391788E−03	8.828E−03
40	1.686726517E−37	1.687E−37	1.815150838E−02	1.815E−02
45	2.810074148E−37	2.810E−37	3.731952687E−02	3.732E−02
50	4.681563156E−37	4.682E−37	7.667966749E−02	7.668E−02
55	7.799450274E−37	7.799E−37	1.559649552E−01	1.560E−01
60	1.299382752E−36	1.299E−36	2.956393295E−01	2.956E−01
65	2.164761203E−36	2.165E−36	4.425247909E−01	4.425E−01
70	3.606405149E−36	3.606E−36	4.204066087E−01	4.204E−01
75	6.005587956E−36	6.006E−36	2.139721046E−01	2.140E−01
80	9.951251375E−36	9.951E−36	5.284934788E−02	5.285E−02
85	1.597732605E−35	1.598E−35	6.010275612E−03	6.011E−03
90	2.293955203E−35	2.294E−35	3.061362252E−04	3.061E−04
95	2.582403850E−35	2.582E−35	6.885135661E−06	6.885E−06
100	1.999021368E−35	1.999E−35	6.795238168E−08	6.795E−08
105	9.680618782E−36	9.681E−36	2.942584009E−10	2.943E−10
110	2.929004446E−36	2.767E−36	6.811823364E−13	5.625E−13

Table 7 continued

X (m)	^{230}Th		^{226}Ra	
	Present solution ($N = 300$)	CHAIN	Present solution ($N = 300$)	CHAIN
0	1.651367539E−6	1.651E−06	2.486450976E−8	2.486E−08
5	1.922822867E−5	1.923E−05	2.008439226E−7	2.008E−07
10	1.714762193E−4	1.715E−04	1.913007451E−6	1.913E−06
15	7.961635560E−4	7.961E−04	1.208412229E−5	1.208E−05
20	1.268186445E−3	1.268E−03	3.638133476E−5	3.638E−05
25	1.260841900E−3	1.261E−03	6.366748116E−5	6.366E−05
30	1.268188125E−3	1.268E−03	9.062266913E−5	9.062E−05
35	1.270842955E−3	1.271E−03	1.174019006E−4	1.174E−04
40	1.267980669E−3	1.268E−03	1.438914086E−4	1.439E−04
45	1.254346371E−3	1.254E−03	1.699158765E−4	1.699E−04
50	1.218541546E−3	1.219E−03	1.951154845E−4	1.951E−04
55	1.137533012E−3	1.138E−03	2.187512277E−4	2.187E−04
60	9.709188295E−4	9.709E−04	2.393662913E−4	2.394E−04
65	6.855210651E−4	6.855E−04	2.545932531E−4	2.546E−04
70	3.449596549E−4	3.450E−04	2.623426781E−4	2.623E−04
75	1.058832537E−4	1.059E−04	2.633518991E−4	2.633E−04
80	1.754331684E−5	1.754E−05	2.609030583E−4	2.609E−04
85	1.446926314E−6	1.446E−06	2.575425035E−4	2.575E−04
90	5.652603367E−8	5.659E−08	2.540953389E−4	2.541E−04
95	1.015680336E−9	1.016E−09	2.506839621E−4	2.507E−04
100	8.258661987E−12	8.259E−12	2.473163668E−4	2.473E−04
105	3.018191040E−14	3.018E−14	2.439922763E−4	2.440E−04
110	6.031571078E−17	4.966E−17	2.408414731E−4	2.407E−04

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.
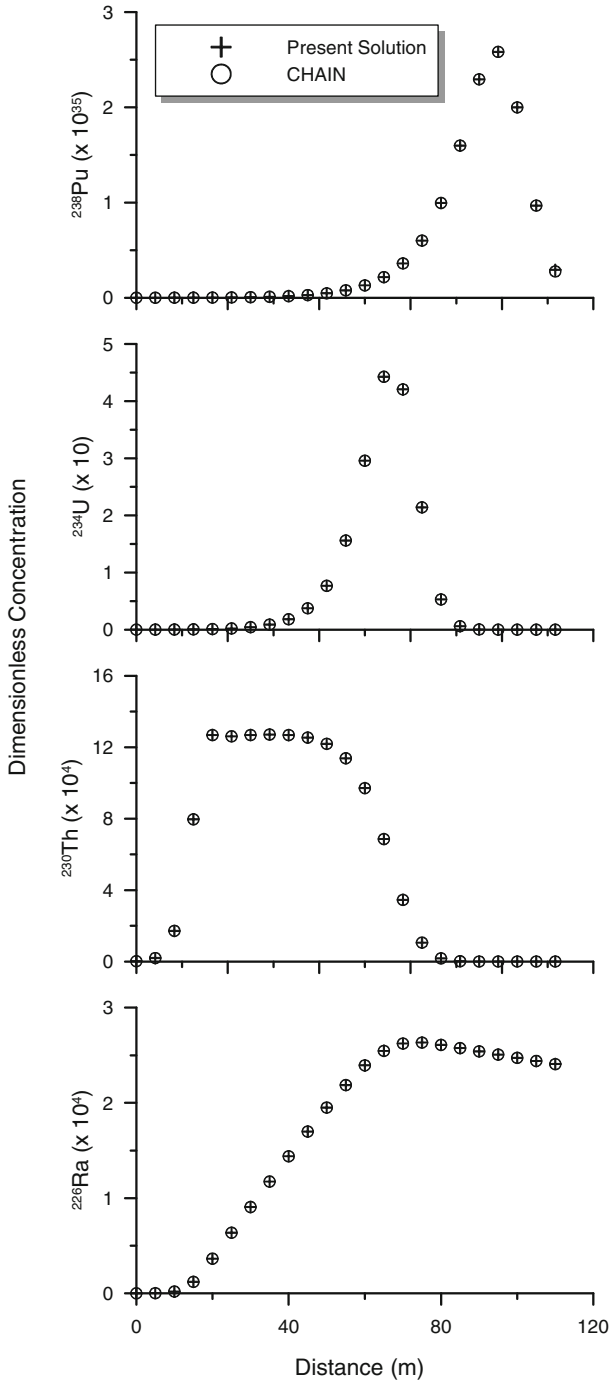
Fig. 1 Computed results for the decay chain $^{238}\text{Pu} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow ^{226}\text{Ra}$, as given in Table 7 ($t = 10000\,\text{year}$, $D = 20\,\text{m}^2/\text{year}$, $U = 100\,\text{m/year}$)

5 Conclusions

Using the CITT in combination with a filter function with separable space and time-dependencies, 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 transport 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 applications, the new solution should be useful for benchmarking numerical solutions involving the finite boundary conditions.

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,

$$\Gamma h_j = L h_j + \gamma_{j-1} h_{j-1} \tag{A1}$$

$$B_1 h_j(0, t) = Pe \sum_{m=1}^{j} f_{jm}(t) \tag{A2}$$

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

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:

$$\sum_{m=1}^{j} R_j \sigma_m f_{jm}(t)\varphi_{jm}(x) + f_{jm}(t)L\varphi_{jm}(x) + \bar{\delta}_{jm}\gamma_{j-1}f_{j-1m}(t)\varphi_{j-1m}(x) = 0 \quad \text{(A6)}$$

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 determinate $\varphi_{jm}(x)$ are given by

$$R_j \sigma_m \varphi_{jm}(x) + L\varphi_{jm}(x) + \bar{\delta}_{jm}\gamma_{j-1}r_{jm}\varphi_{j-1m}(x) = 0$$
$$(j = 1, 2, \ldots; \; m = 1, 2, \ldots, j) \quad \text{(A10)}$$
$$B_1\varphi_{jm}(0) - Pe = 0 \quad \text{(A11)}$$
$$B_2\varphi_{jm}(1) = 0 \quad \text{(A12)}$$

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

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