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Analytical Solution for Multi-Species Contaminant Transport Subject to Sequential First-Order Decay Reactions in Finite Media

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Abstract Transport equations governing the movement of multiple solutes undergoing sequential first-order decay reactions have relevance in analyzing a variety of subsurface contaminant transport problems. In this study, a one-dimensional analytical solution for multi-species transport is obtained for finite porous media and constant boundary conditions. The solution permits different retardation factors for the various species. The solution procedure involves a classic algebraic substitution that transforms the advection-dispersion partial differential equation for each species into an equation that is purely diffusive. The new system of partial differential equations is solved analytically using the Classic Integral Transform Technique (CITT). Results for a classic test case involving a three-species nitrification chain are shown to agree with previously reported literature values. Because the new solution was obtained for a finite domain, it should be especially useful for testing numerical solution procedures.

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

List of Symbols

b_{0j}, b_{1j}	Auxiliary coefficients
C_0	Dimensional reference solute concentration

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C_j	Dimensional solute concentration of the jth species
C_{0j}	Dimensional inlet boundary concentration of the jth species
$c_j(x,t)$	Dimensionless solute concentration of the jth species
c_{0j}	Dimensionless inlet boundary concentration of the jth species
C_{1j}, C_{2j}	Auxiliary coefficients
D	Dispersion coefficient
F_j	Filter function
$\bar{f}_{ji}$	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
i, j, k	Indices
L	Domain length
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
$\bar{S}_{ji}(t)$	Integral coefficient
T	Dimensional time
t	Dimensionless time
$T_j(x,t)$	Unknown function
U	Constant pore water velocity
w_j	Auxiliary coefficient
X	Dimensional spatial coordinate
x	Dimensionless spatial coordinate

Greek Symbols

β_i	Eigenvalue
γ_j	Damkholer number
δ_{ik}	Kronecker delta
$\theta_j(x,t)$	Unknown function in purely diffusive equation
$\bar{\theta}_{ji}(t)$	Integral transform of the function $\theta_j(x,t)$
λ_j	First-order decay constant for the jth species
Λ_j	Coefficient
μ_i	Eigenvalue
τ	Eigenvalue
$\phi_j(x)$	Auxiliary function
$\psi_i(x)$	Eigenfunction
$\tilde{\psi}_i(x)$	Normalized eigenfunction
$\Omega_j(x)$	Auxiliary function

1 Introduction

Transport equations governing the movement of multiple solutes undergoing sequential first-order decay reactions have been studied extensively for several decades because of their

relevance in modeling the subsurface transport of a variety of contaminants, including radionuclide decay chains, pesticides and their degradation products, petroleum hydrocarbons, and nitrogen species. Early studies such as those by McLaren (1969) and Cho (1971) focused on obtaining analytical solutions for the transport equations, whereas more recently numerical solutions have become increasingly popular using widely available computer software (e.g., Šůimunek 2006). Still, considerable interest remains in analytical solution because they may be used as relatively simple screening models in regulatory decision making (e.g., Aziz et al. 2000; Skaggs et al. 2007), and because analytical solutions may serve as benchmarks for testing numerical solutions.

A variety of analytical methods have been used to solve sequential decay transport problems. Cho (1971) used Laplace transforms to obtain an analytical solution for convective-dispersive nitrogen transport involving a three-species nitrification chain. van Genuchten (1985) similarly used Laplace transforms to obtain the solution for a four-species decay chain, and implemented the solution in a computer program called CHAIN containing example problems dealing with nitrification–denitrification and radionuclide decay chains. In more recent work, Lunn et al. (1996) presented analytical solutions obtained with Fourier sine transforms using a methodology that enabled greater flexibility with respect to initial conditions. These authors were able to produce results identical to those of Cho (1971), while also developing new solutions for constant and exponential initial contaminant profiles.

A somewhat different approach was followed by Sun et al. (1999a,b) and Sun and Clement (1999) who used an ingenious substitution to transform the multidimensional first-order sequential decay problem with any number of species into a decoupled set of transport equations for single species. They then solved the decoupled equations using existing analytical solutions for single-species transport and first-order decay. Unfortunately, the substitution can be used only when the retardation coefficients are the same for all species.

Bauer et al. (2001) subsequently presented a method for solving one-, two-, and three-dimensional sequentially coupled reactive transport problems with distinct retardation coefficients. Their solution was expressed in terms of a linear combination of fundamental solutions in the Laplace domain, with coefficients defined by a recursive formula. In some cases it was possible to transform the solution back to the time domain analytically. However, most transport problems required a numerical approach to obtain the inverse transform. Sun et al. (2001) avoided numerical inversion of the Laplace transforms by applying the solution scheme of Bauer et al. (2000) directly in the time domain instead of the Laplace domain. The approach relied heavily on the use of fundamental analytical solutions for single-species transport subject to first-order decay.

Clement (2001) wrote the equations for coupled species transport using matrix notation and then used a matrix diagonalization procedure to decouple the equations. Their solution method initially required that different species have identical retardation coefficients. Quezada et al. (2004) later extended the procedure of Clement (2001) and presented a general method for solving coupled multidimensional, multi-species reactive transport equations with different retardation factors. The method employs a three-step transformation that involves Laplace transforms and matrix diagonalization in the Laplace domain. Quezada et al. (2004) presented an analytical solution for two-species transport; more general cases could be solved only semi-analytically as they require numerical inversion of the Laplace transform. In related work, Lu and Sun (2008) developed a model that accounted for equilibrium and kinetic reactions. They decoupled the transport equations using the matrix diagonalization approach, and then obtained closed-form analytical solutions.

Most recently, Srinivasan and Clement (2008a,b) developed closed-form analytical solutions for sequential decay problems involving an arbitrary number of species and subject

to spatially varying initial conditions and a generic exponentially decaying Bateman-type source boundary condition as was also used previously by van Genuchten (1985). The coupled one-dimensional system of equations was solved for both Dirichlet and Cauchy boundary conditions using a combination of Laplace transform and the matrix diagonalization technique of Clement (2001).

Several things are apparent from the above literature survey. First and foremost, the review shows that for over three decades there has been steady interest in analytical methods for solving contaminant transport problems with sequential decay reactions, and that interest continues up to the present. Also, many different analytical methods have been used, with Laplace transforms, various decoupling strategies, and matrix diagonalization techniques being the most prevalent. However, one commonality among all methods thus far is that they have produced analytical solutions only for infinite or semi-infinite spatial domains. Given that a primary use of analytical solutions is to test numerical models that compute solutions on finite domains, it would be very useful to also have analytical solutions for finite domains.

Pontedeiro et al. (2007) previously obtained solutions on a finite domain using a semi-analytical approach to perform sensitivity analyses and risk assessments of technologically enhanced, naturally occurring radioactive material (TENORM) disposed in an industrial landfill. They solved the decay chain problem using a semi-analytic approach known as Generalized Integral Transform Technique (GITT), which is a generalization of the Classic Integral Transform Technique, or CITT (Cotta 1993). Very recently, Cassol et al. (2009) combined GITT and CITT techniques with Laplace transforms and matrix diagonalization methods to develop an analytical solution for transient two-dimensional atmospheric pollutant dispersion on a semi-infinite spatial domain.

Using appropriate substitutions, many transport problems can be transformed into a form that is amenable to analytical solution via the CITT. Pérez Guerrero et al. (2009) recently demonstrated the latter approach by obtaining the solution of a general linear advection-dispersion equation for single-species transport. The objective of the present study was to develop the analytical solution for a multi-species advection-dispersion transport equation comprising sequential first-order decay reactions, distinct retardation coefficients for each species, a finite spatial domain, and steady-state boundary conditions.

2 Problem Formulation

Consider a one-dimensional, homogeneous porous medium having a constant saturated or unsaturated water content. For multiple reactive solute species that are subject to linear equilibrium sorption and are involved in a sequential first-order decay chain, the governing system of transport equations is given by:

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

where C_j is the concentration of the jth species, R_j is the retardation coefficient for the jth species, D is the dispersion coefficient, U is the constant pore water velocity, λ_j is the first-order decay constant for the jth species, X is the spatial coordinate, and T is time. The problem definition is completed by specifying for each species the initial and boundary conditions on a finite domain of length L as follows:

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

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

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

We define the following non-dimensional variables:

$$x = \frac{X}{L}; \quad t = \frac{T}{(L/U)}; \quad c_j = \frac{C_j}{C_0}; \quad c_{0j} = \frac{C_{0j}}{C_0} \tag{2a–d}$$

$$Pe = \frac{UL}{D}; \quad \gamma_j = \frac{\lambda_j R_j L}{U}; \quad g_j(x) = \frac{G_j}{C_0} \tag{2e–g}$$

where C_0 is a reference concentration, Pe is termed the Peclet number, and γ_j is the ratio of the reaction and advection time scales, often referred to as the Damkholer number. With these non-dimensional variables, Eq. 1 may be rewritten as:

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

$$c_j(x,0) = g_j(x) \tag{3b}$$

$$-\frac{\partial c_j(0,t)}{\partial x} + Pe\, c_j(0,t) = Pe\, c_{0j} \tag{3c}$$

$$\frac{\partial c_j(1,t)}{\partial x} = 0 \tag{3d}$$

3 Solution Methodology

In this study, a solution of Eq. 3 was developed using the CITT (Ozisik 1980; Mikhailov and Ozisik 1984; Cotta 1993) in combination with a classical algebraic transformation that transforms the governing advection-dispersion equations into purely diffusive equations. The CITT can be applied to Eq. 3 as follows:

(a) define and solve an auxiliary eigenvalue problem related to the original problem;
(b) develop an appropriate integral and inverse transform pair;
(c) transform each of the partial differential equations such that the space variable is eliminated and an infinite system of decoupled ordinary differential equations is obtained;
(d) solve the resulting ordinary differential equation system subject to the transformed initial condition; and
(e) use the inverse transform to obtain the desired solution.

The CITT can be applied to transport problems with homogeneous or non-homogeneous boundary conditions. When the problem has homogeneous boundary conditions, the eigenfunctions resulting from the auxiliary eigenvalue problem in step (a) automatically include boundary information. For the case of non-homogeneous boundary conditions, it is necessary to use the Green's theorem to incorporate the boundary information, as indicated by Ozisik (1980). However, while the application of the Green's theorem is formally correct, its use leads to very slow convergence near the boundary, as illustrated by Cotta (1993). An alternative is to homogenize the boundary conditions using a "filter" function. The idea is to define a new problem with the non-homogeneous boundary conditions of the original problem in

order to obtain a "filter" function capable of homogenizing the boundary conditions of the original problem. We homogenize the boundary conditions using a filter function obtained from a steady-state version of the transport equation. Additionally, we utilize an algebraic substitution to transform the advection-dispersion transport equations into exclusively diffusive equations that are easier to solve analytically.

3.1 The Steady-State Regime and the Filter Function

A filter function capable of homogenizing the boundary condition can be obtained in different ways. Here, we obtain a filter function from the steady-state version of Eq. 3. We define for this purpose the following problem:

$$\frac{1}{Pe}\frac{d^2F_j}{\mathrm{d}x^2} - \frac{\mathrm{d}F_j}{\mathrm{d}x} - \gamma_j F_j + \gamma_{j-1}F_{j-1} = 0; \quad j = 1, 2, 3, \ldots \tag{4a}$$

$$-\frac{\mathrm{d}F_j(0)}{\mathrm{d}x} + Pe\ F_j(0) = Pe\ c_{0j}; \tag{4b}$$

$$\frac{\mathrm{d}F_j(1)}{\mathrm{d}x} = 0 \tag{4c}$$

This is an ordinary differential equation for the function F_j which has an analytical solution that depends upon F_{j-1}. That dependence makes obtaining the analytical solution elaborate for large values of j.

An interesting strategy for solving Eq. 4 is to use the procedure presented by Sun et al. (1999a,b) and Sun and Clement (1999). As noted in the Introduction, their procedure applies only when the retardation factors are the same for each species. In this study, we consider the more general case in which each species has its own retardation factor as indicated by Eqs. 1 and 3. However, we can use the procedure of Sun et al. (1999a,b) and Sun and Clement (1999) to solve the filter problem as Eq. 4 is independent of the retardation factors.

Following the procedure of Sun et al. (1999a,b) and Sun and Clement (1999), we define the following functions:

$$F_j(x) = \phi_j(x) - \Omega_j(x) \tag{5}$$

$$\Omega_j(x) = \sum_{k=1}^{j-1} F_k(x) \left(\prod_{m=k}^{j-1} \frac{\gamma_m}{\gamma_m - \gamma_j} \right) \tag{6}$$

Substitution of Eqs. 5 and 6 into Eq. 4 leads to new equations involving $\phi_j(x)$ that do not have recursive source terms.

$$\frac{1}{Pe}\frac{d^2\phi_j}{\mathrm{d}x^2} - \frac{\mathrm{d}\phi_j}{\mathrm{d}x^2} - \gamma_j\phi_j = 0 \tag{7a}$$

$$-\frac{\mathrm{d}\phi_j(0)}{\mathrm{d}x} + Pe\ \phi_j(0) = b_{0j} = Pe\ c_{0j} - \frac{\mathrm{d}\Omega_j(0)}{\mathrm{d}x} + Pe\ \Omega_j(0\ ) \tag{7b}$$

$$\frac{\mathrm{d}\phi_j(1)}{\mathrm{d}x} = b_{1j} = \frac{\mathrm{d}\Omega_j(1)}{\mathrm{d}x} \tag{7c}$$

The general analytical general solution for $\phi_j(x)$ is:

$$\phi_j(x) = C_{1j}\exp[x(Pe - \sqrt{Pe}\, w_j)/2] + C_{2j}\exp[x(Pe + \sqrt{Pe}\, w_j)/2] \tag{8a}$$

$$w_j = \sqrt{Pe + 4\gamma_j} \tag{8b}$$

$$C_{1j} = \frac{2\exp[(w_j\sqrt{Pe} - Pe)/2]}{\Lambda_j}\{b_{1j}(w_j - \sqrt{Pe}) + \exp[(w_j\sqrt{Pe} + Pe)/2)]b_{0j}(w_j + \sqrt{Pe})\} \tag{8c}$$

$$C_{2j} = \frac{2\exp(-Pe/2)}{\Lambda_j}[\exp(Pe/2)b_{0j}(w_j - \sqrt{Pe}) + \exp(w_j\sqrt{Pe}/2)b_{1j}(w_j + \sqrt{Pe})] \tag{8d}$$

$$\Lambda_j = \sqrt{Pe}\{[\exp(w_j\sqrt{Pe}) - 1]Pe + 2[\exp(w_j\sqrt{Pe}) + 1]w_j\sqrt{Pe} + [\exp(w_j\sqrt{Pe}) - 1]w_j^2\} \tag{8e}$$

The filter function $F_j(x)$ can now be obtained immediately using Eqs. 5, 6, and 8.

3.2 Homogenization of the Boundary Condition and Use of Algebraic Substitution

Equation 3 can be re-written as a homogeneous boundary condition problem by expressing the dimensionless concentration $c_j(x,t)$ as a linear combination of the filter function and a new unknown function $T_j(x,t)$ as follows:

$$c_j(x,t) = T_j(x,t) + F_j(x) \tag{9}$$

Substituting Eq. 9 into Eq. 3 gives the following equations for the unknown field $T_j(x,t)$:

$$R_j\frac{\partial T_j}{\partial t} = \frac{1}{Pe}\frac{\partial^2 T_j}{\partial x^2} - \frac{\partial T_j}{\partial x} - \gamma_j T_j + \gamma_{j-1}T_{j-1}; \quad j = 1, 2, 3, \ldots \tag{10a}$$

Note that in this expression all terms involving F_j vanished due to Eq. 4a. The initial and boundary conditions are respectively:

$$T_j(x,0) = g_j(x) - F_j(x) \tag{10b}$$

$$-\frac{\partial T_j(0,t)}{\partial x} + Pe\, T_j(0,t) = 0 \tag{10c}$$

$$\frac{\partial T_j(1,t)}{\partial x} = 0 \tag{10d}$$

The structure of Eq. 10 is the same as that of Eq. 3, with no additional source terms being created by the homogenization procedure. As shown in Appendix A, it is possible to transform Eq. 10 from an advection-diffusion equation into a diffusion equation using the following algebraic substitution (Ozisik 1980; Pérez Guerrero et al. 2009):

$$T_j(x,t) = \theta_j(x,t)\exp(px + q_j t) \tag{11}$$

where:

$$p = \frac{Pe}{2}; \quad q_j = -\frac{1}{R_j}\left(\frac{Pe}{4} + \gamma_j\right) \tag{12}$$

The substitution produces the diffusion equation:

$$R_j\frac{\partial \theta_j}{\partial t} = \frac{1}{Pe}\frac{\partial^2 \theta_j}{\partial x^2} + \gamma_{j-1}T_{j-1}(x,t)\exp(-px - q_j t); \quad j = 1, 2, 3, \ldots \tag{13a}$$

The initial and boundary condition for the unknown function $\theta_j(x,t)$ are, respectively:

$$\theta_j(x,0) = \exp(-px)[g_j(x) - F_j(x)] \tag{13b}$$

$$-\frac{\partial\theta_j(0,t)}{\partial x} + \frac{Pe}{2}\theta_j(0,t) = 0 \tag{13c}$$

$$\frac{\partial\theta_j(1,t)}{\partial x} + \frac{Pe}{2}\theta_j(1,t) = 0 \tag{13d}$$

Note that both boundary conditions (Eq. 10c, 10d) were modified as a consequence of the algebraic substitution given by Eq. 11.

3.3 Solution via CITT

The problem defined by Eq. 13b can be solved using the CITT. Following the procedure outlined above, we select a Sturm–Liouville type problem as the auxiliary eigenvalue problem:

$$\frac{d^2\psi_i(x)}{\mathrm{d}x^2} + \beta_i^2\psi_i(x) = 0; \tag{14a}$$

$$\beta_i^2 = \frac{\mu_i^2}{(1/Pe)} \tag{14b}$$

with boundary conditions:

$$-\frac{\mathrm{d}\psi_i(0)}{\mathrm{d}x} + \frac{Pe}{2}\psi_i(0) = 0 \tag{14c}$$

$$\frac{\mathrm{d}\psi_i(1)}{\mathrm{d}x} + \frac{Pe}{2}\psi_i(1) = 0 \tag{14d}$$

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

$$\psi_i = \beta_i\cos(\beta_i x) + H_1\sin(\beta_i x) \tag{15}$$

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

$$N_i = \frac{(\beta_i^2 + H_1^2) + H_1 + H_2}{2} \tag{16}$$

$$\tan(\beta_i) = \frac{\beta_i(H_1 + H_2)}{\beta_i^2 - H_1H_2} \tag{17}$$

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

The normalized eigenfunction and the orthogonality property are, respectively:

$$\tilde{\psi}_i(x) = \frac{\psi_i(x)}{N_i^{1/2}} \tag{18}$$

$$\int_0^1 \tilde{\psi}_i(x)\tilde{\psi}_k(x)\mathrm{d}x = \delta_{ik} \tag{19}$$

where δ_{ik} is the Kronecker delta.

At this point, we represent the unknown function $\theta_j(x,t)$ as a series expansion in terms of the eigenfunctions:

$$\theta_j(x,t) = \sum_{i=1}^{\infty} \tilde{\psi}_i(x)\bar{\theta}_{ji}(t) \quad (Inverse) \tag{20a}$$

where $\bar{\theta}_{ji}(t)$ is the transformed potential. An explicit definition for the transformed potential is obtained by applying the operator $\int_0^1 \tilde{\psi}_i(x)\mathrm{d}x$ to both sides of Eq. 20a and then invoking the orthogonality property given by Eq. 19 (Ozisik 1980; Cotta 1993). This results in:

$$\bar{\theta}_{ji}(t) = \int_0^1 \tilde{\psi}_i(x)\theta_j(x,t)\mathrm{d}x \quad (Transform) \tag{20b}$$

Equation 20b is the formula of the integral transformation which we use to transform Eq. 13b into a system of ordinary differential equations with dependent variables $\bar{\theta}_{ji}(t)$. Once that system is solved, $\theta_j(x,t)$ is obtained using the inverse transform, Eq. 20a.

Thus, we now apply the operator $\int_0^1 \tilde{\psi}_i(x)\mathrm{d}x$ to Eq. 13b and invoke the integral transform defined by Eq. 20b to obtain the following system of decoupled ordinary differential equations:

$$R_j \frac{d\bar{\theta}_{ji}(t)}{\mathrm{d}t} + \mu_i^2 \bar{\theta}_{ji}(t) = \bar{S}_{ji}(t); \quad i,j = 1,2,3,\ldots \tag{21a}$$

$$\bar{\theta}_{ji}(t=0) = \bar{f}_{ji} \tag{21b}$$

$$\bar{f}_{ji} = \int_0^1 \tilde{\psi}_i(x)\exp(-px)[g_j(x) - F_j(x)]\mathrm{d}x \tag{21c}$$

The integral coefficient $\bar{f}_{ji}$ can be evaluated analytically in some cases; in others, it is necessary to calculate this coefficient numerically within a prescribed error tolerance. The term $\bar{S}_{ji}(t)$ is the transformed source term and is defined by the integral:

$$\bar{S}_{ji}(t) = \int_0^1 \tilde{\psi}_i(x)\gamma_{j-1}T_{j-1}(x,t)\exp(-px - q_j t)\mathrm{d}x \tag{22a}$$

This expression can be simplified to the form:

$$\bar{S}_{ji}(t) = \gamma_{j-1}\bar{\theta}_{j-1\,i}(t)\exp[(q_{j-1} - q_j)t] \tag{22b}$$

Equation 21 is an ordinary differential equation whose analytical solution is:

$$\bar{\theta}_{ji}(t) = \exp\left(-\frac{\mu_i^2}{R_j}t\right)\left[\bar{f}_{ji} + \frac{1}{R_j}\int_0^t \bar{S}_{ji}(\tau)\exp\left(\frac{\mu_i^2}{R_j}\tau\right)\mathrm{d}\tau\right] \tag{23}$$

This expression gives a recursive rule [$\bar{S}_{ji}(t)$ depends on $\bar{\theta}_{j-1\,i}(t)$] for obtaining the transformed field for each species. Now, invoking Eqs. 9, 11, 20a, and 23, we obtain the explicit analytical expression for the dimensionless concentration:

$$c_j(x,t) = F_j(x) + \exp(px + q_j t)\sum_{i=1}^{\infty} \tilde{\psi}_i(x)\bar{\theta}_{ji}(t); \quad j = 1,2,3,\ldots \tag{24}$$

Table 1 Parameter values for the nitrification chain problem

Description	NH_4^+ ($j=1$)	NO_2^- ($j=2$)	NO_3^- ($j=3$)
Retardation coefficient (R_j)	2	1	1
Decay constant, λ_j (h^{-1})	0	0.1	0
Pore velocity: $U=1\,cm\,h^{-1}$	Dispersion coefficient: $D=0.18\,cm^2\,h^{-1}$		

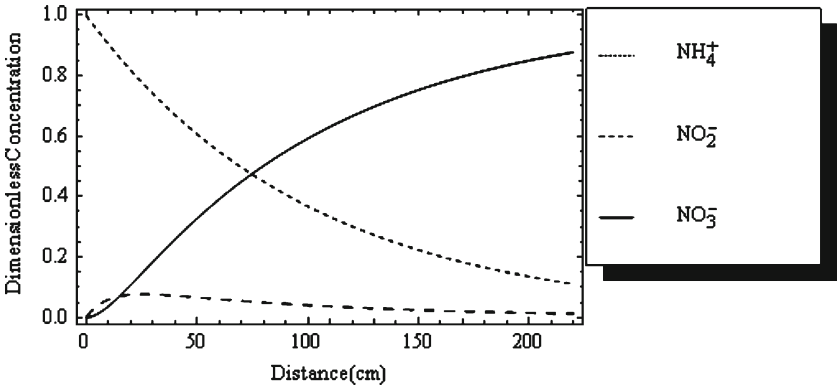

Fig. 1 Steady-state concentration for all the nitrogen species ($L=220\,cm$)

4 Test Case

The analytical solution presented above for the sequential decay problem was implemented in a Mathematica (2007) program. Analytical expressions were developed for the transformed fields using Eqs. 22b and 23 for an arbitrary number of species. A generic analytical expression for the integral coefficients $\bar{f}_{ji}$ was also developed. All analytical and functional expressions were implemented for numerical evaluation. To calculate a specific set of eigenvalues β_i, the transcendental Eq. 17 was solved numerically using the Mathematica (2007) built-in function "FindRoot".

The Mathematica program was first used to solve the three-species nitrification chain ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) transport problem as solved previously by van Genuchten (1985). The parameter values for this problem are specified in Table 1. Assuming a transport domain of length of $L=220\,cm$, we calculated the steady-state concentration field for the three nitrogen species (Fig. 1) using Eqs. 5, 6 and 8. The strategy of Sun et al. (1999a,b) and Sun and Clement (1999) as implemented here proved to be very efficient for obtaining the steady-state solution.

Table 2 shows the convergence behavior of the NH_4^+ concentration computed for time $T=200\,h$, $L=220\,cm$, and $Pe=1,222$. Table 2 indicates that for this problem, $N=450$ terms were needed to reach convergence throughout the spatial domain. Convergence is defined here as having obtained the correct values up to 10 significant digits. Note that with $N=250$, convergence was achieved for $X \leq 120\,cm$, but not beyond that location. Convergence progressed slowly along the domain as N was increased from $N=250$–450. The region where convergence was slower ($X > 120\,cm$) corresponded to those parts of the domain where the concentration of NH_4^+ was very close to zero. Table 3 shows the

Table 2 Solution convergence for the three-species nitrification transport problem assuming $L = 220$ cm and $T = 200$ h (N = Number of terms summed)

X (cm)	Dimensionless concentration for NH_4^+			
	$N = 250$	$N = 350$	$N = 450$	$N = 500$
0	0.9982064510	0.9982064510	0.9982064510	0.9982064510
5	0.9496085026	0.9496085026	0.9496085026	0.9496085026
10	0.9033765583	0.9033765583	0.9033765583	0.9033765583
15	0.8593954286	0.8593954286	0.8593954286	0.8593954286
20	0.8175555319	0.8175555319	0.8175555319	0.8175555319
25	0.7777526219	0.7777526219	0.7777526219	0.7777526219
30	0.7398875272	0.7398875272	0.7398875272	0.7398875272
35	0.7038659047	0.7038659047	0.7038659047	0.7038659047
40	0.6695980046	0.6695980046	0.6695980046	0.6695980046
45	0.6369984464	0.6369984464	0.6369984464	0.6369984464
50	0.6059860065	0.6059860065	0.6059860065	0.6059860065
55	0.5764834154	0.5764834154	0.5764834154	0.5764834154
60	0.5484171659	0.5484171659	0.5484171659	0.5484171659
65	0.5217173284	0.5217173284	0.5217173284	0.5217173284
70	0.4963172806	0.4963172806	0.4963172806	0.4963172806
75	0.4721485541	0.4721485541	0.4721485541	0.4721485541
80	0.4490140056	0.4490140056	0.4490140056	0.4490140056
85	0.4250786668	0.4250786668	0.4250786668	0.4250786668
90	0.3894312160	0.3894312160	0.3894312160	0.3894312160
95	0.3149047564	0.3149047564	0.3149047564	0.3149047564
100	0.1927162768	0.1927162768	0.1927162768	0.1927162768
105	0.07678511830	0.07678511830	0.07678511830	0.07678511830
110	0.01794434192	0.01794434192	0.01794434192	0.01794434192
115	0.002312432594	0.002312432594	0.002312432594	0.002312432594
120	0.0001586398313	0.0001586398313	0.0001586398313	0.0001586398313
125	5.675790084E-6	5.675789878E-6	5.675789878E-6	5.675789878E-6
130	3.007974339E-7	1.045824992E-7	1.045824992E-7	1.045824992E-7
135	0.001083916543	9.845112917E-10	9.845112917E-10	9.845112917E-10
140	−221818.1891	4.709534978E-12	4.709534978E-12	4.709534978E-12
145	−2.668137442E11	1.140537819E-14	1.140537819E-14	1.140537819E-14
150	−6.668710815E16	1.394604866E-17	1.394604866E-17	1.394604866E-17
155	2.244041842E23	8.592942476E-21	8.592942476E-21	8.592942476E-21
160	3.445925381E29	2.663974946E-24	2.663974946E-24	2.663974946E-24
165	1.558852171E35	4.150608044E-28	4.150608044E-28	4.150608044E-28
170	−2.075877104E41	3.247053381E-32	3.247053381E-32	3.247053381E-32
175	−4.268009016E47	1.274515591E-36	1.274515591E-36	1.274515591E-36
180	−2.727350336E53	2.513402272E-41	2.508537003E-41	2.508537003E-41
185	1.633178059E59	1.480383980E-37	2.474588289E-46	2.474588289E-46
190	5.087387277E65	2.595176680E-31	1.222969535E-51	1.222969535E-51
195	4.212543655E71	3.825694352E-25	3.026982697E-57	3.026982697E-57
200	−8.120405055E76	5.163387350E-19	3.751109863E-63	3.751109863E-63
205	−5.828191022E83	6.596017284E-13	2.326790851E-69	2.326790851E-69
210	−6.048183034E89	8.107330268E-7	7.222868392E-76	7.222868392E-76
215	−5.189939507E94	0.9676763723	1.121853644E-82	1.121853644E-82
220	6.373088273E101	1.127919833E6	1.199389159E-89	1.199389159E-89

converged values for the three-species nitrification chain ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$). With a domain length of $L = 220$ cm, the computed concentrations in this table for approximately $X < 200$ cm were identical to those obtained previously by van Genuchten (1985) for a semi-infinite domain. Closer to the exit boundary, the computed concentrations diverged from those computed for the semi-infinite case.

Table 3 Converged dimensionless concentration for the three nitrogen species ($L = 220$ cm and $T = 200$ h)

X (cm)	Dimensionless concentration		
	NH_4^+	NO_2^-	NO_3^-
0	0.9982064510	0.001731801827	0.00006174718691
5	0.9496085026	0.03871306202	0.01167843542
10	0.9033765583	0.05950592502	0.03711751672
15	0.8593954286	0.07048358153	0.07012098991
20	0.8175555319	0.07554095946	0.1069035086
25	0.7777526219	0.07705693685	0.1451904413
30	0.7398875272	0.07648303679	0.1836294360
35	0.7038659047	0.07470359556	0.2214304997
40	0.6695980046	0.07225611283	0.2581458825
45	0.6369984464	0.06946605852	0.2935354950
50	0.6059860065	0.06652934238	0.3274846512
55	0.5764834154	0.06356276291	0.3599538217
60	0.5484171659	0.06063486556	0.3909479685
65	0.5217173284	0.05778481534	0.4204978553
70	0.4963172806	0.05503393446	0.4486486814
75	0.4721485541	0.05239263717	0.4754531577
80	0.4490140056	0.04986128376	0.5009661232
85	0.4250786668	0.04738367837	0.5252204386
90	0.3894312160	0.04453022133	0.5480350476
95	0.3149047564	0.03978515558	0.5682353216
100	0.1927162768	0.03122025618	0.5826020944
105	0.07678511830	0.01994781008	0.5871394638
110	0.01794434192	0.01024425185	0.5808288008
115	0.002312432594	0.004491732945	0.5663503702
120	0.0001586398313	0.001831048663	0.5470470018
125	5.675789878E-6	0.0007320388051	0.5249781425
130	1.045824992E-7	0.0002918152583	0.5010561015
135	9.845112917E-10	0.0001162802778	0.4756178471
140	4.709534978E-12	0.00004632002377	0.4487583366
145	1.140537819E-14	0.00001844287785	0.4204734822
150	1.394604866E-17	7.337981865E-6	0.3907175422
155	8.592942476E-21	2.916377722E-6	0.3594259040
160	2.663974946E-24	1.157092755E-6	0.3265240692
165	4.150608044E-28	4.578688461E-7	0.2919313874
170	3.247053381E-32	1.804342084E-7	0.2555653614
175	1.274515591E-36	7.064376319E-8	0.2173648817
180	2.508537003E-41	2.737358199E-8	0.1774058936
185	2.474588289E-46	1.043032216E-8	0.1362795622
190	1.222969535E-51	3.865819869E-9	0.09580638645
195	3.026982697E-57	1.368811897E-9	0.05947262630
200	3.751109863E-63	4.505102185E-10	0.03133947460
205	2.326790851E-69	1.328924131E-10	0.01349921247
210	7.222868392E-76	3.370995078E-11	0.004600992689
215	1.121853644E-82	7.061392726E-12	0.001209079344
220	1.199389159E-89	1.255589051E-12	0.0002545665546

Table 4 illustrates for different domain lengths the divergence of the concentration at the exit boundary from the semi-infinite results. Table 4 shows converged dimensionless concentrations for $X = L$, $T = 200$ h, and domain lengths $L = 100$, $L = 160$, and $L = 200$ cm, as well as results reported by van Genuchten (1985) for the same time T and position X but with a semi-infinite domain. For all three of these domain lengths, the computed concentrations for positions $X < (L - 5)$ cm were identical to the semi-infinite case (and results not shown).

Table 4 For time $T = 200$ h and various finite domain lengths L, comparison of dimensionless concentrations at $X = L$ with results obtained by van Genuchten (1985) for position X and a semi-infinite domain

X (cm)	L (cm)	Dimensionless concentration		
		NH_4^+	NO_2^-	NO_3^-
100	100	0.1974489849	0.03160207912	0.5822557877
	∞	0.19272	0.03122	0.58260
160	160	3.284869976E-24	1.194407808E-6	0.3277406677
	∞	0.00000	0.00001	0.32652
200	200	5.005954795E-63	4.686175169E-10	0.03215551034
	∞	0.00000	0.00000	0.03134

Table 5 Calculated dimensionless concentration for $T = 50$ h and $L = 110$ cm

X (cm)	Dimensionless concentration		
	NH_4^+	NO_2^-	NO_3^-
0	0.9982064510	0.001731801827	0.00006174718691
5	0.9496085026	0.03871306202	0.01167843542
10	0.9033763767	0.05950592248	0.03711751630
15	0.8590855526	0.07047834522	0.07011995330
20	0.7813793474	0.07471180447	0.1066758904
25	0.3980357655	0.06321867920	0.1389760794
30	0.03721508150	0.03218574711	0.1463644870
35	0.0003259844933	0.01199491648	0.1251952903
40	2.116560254E-7	0.004038071439	0.08898433433
45	9.362204927E-12	0.001163571008	0.04786979317
50	2.720387050E-17	0.0002378086225	0.01540368887
55	5.098177485E-24	0.00002569193818	0.002211598187
60	6.098329323E-32	1.106360548E-6	0.0001125983943
65	4.626179563E-41	1.571458652E-8	1.768548405E-6
70	2.216160379E-51	6.608912388E-11	7.926994338E-9
75	6.684354841E-63	7.749196672E-14	9.700019589E-12
80	1.266667903E-75	2.446642598E-17	3.155992504E-15
85	1.505598773E-89	2.036299547E-21	2.685192944E-19
90	1.121133343E-104	4.406821766E-26	5.908976694E-24
95	5.224910888E-121	2.457022876E-31	3.337684639E-29
100	1.522752711E-138	3.506493253E-37	4.812926628E-35
105	2.773488562E-157	1.274872527E-43	1.764637898E-41
110	5.1438380E-177	1.622019705E-50	2.260630087E-48

At the exit boundary, the computed concentrations diverged from the semi-infinite results (Table 4). Convergence for $L = 160$ cm was achieved with $N = 250$ terms in the series while $L = 220$ cm required $N = 450$ terms. With all other parameters constant, the number the terms required for convergence was found to depend on the domain length. This is because the domain length is contained inside of the Peclet number. Increasing L makes the effective diffusion coefficient ($1/Pe$) in Eq. 13a is smaller, which necessitates the use of more terms in the series to achieve convergence. Similar finding were obtained by van Genuchten and Alves (1982) for single-species transport in a finite domain.

For benchmark purposes, Table 5 represents the concentration fields for the three nitrogen species at a much smaller time ($T = 50$ h) and a domain L of 110 cm.

5 Conclusion

Using the algebraic substitution given by Eq. 11 within the CITT, it was possible to obtain an analytical solution of a multi-species advection-dispersion transport equation featuring sequential first-order decay reactions, distinct linear sorption reactions for each species, a finite domain, and steady-state boundary conditions. The convergence properties of the solution were examined using a classic test case involving a three-species nitrification chain. Results showed that the solution for each species converged to previously reported literature values. The presented solution procedure can be extended to decay chain problems subject to transient boundary conditions. Because of the scarcity of available solutions for finite domains, the solution procedure and the results presented in this study should be especially useful for testing numerical solutions.

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Appendix A

Consider the following advection-diffusion equation with constant coefficients R, A_1, A_2, B_1, and source term $S(x,t)$:

$$R\frac{\partial M}{\partial t} = A_2\frac{\partial^2 M}{\partial x^2} - A_1\frac{\partial M}{\partial x} - A_0 M + S(x,t) \tag{25}$$

Using the algebraic substitution:

$$M(x,t) = \overline{M}(x,t)\exp(px+qt) \tag{26}$$

Equation 25 can be reformulated as a diffusion equation in terms of $\overline{M}(x,t)$:

$$R\frac{\partial \overline{M}}{\partial t} = A_2\frac{\partial^2 \overline{M}}{\partial x^2} + S(x,t)\exp(px+qt) \tag{27}$$

where the coefficients p and q are given by:

$$p = \frac{A_1}{2A_2};\quad q = -\frac{1}{R}\left(\frac{A_1^2}{4A_2} + A_0\right) \tag{28}$$

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