

Generalized solution to multi-dimensional multi-species transport equations coupled with a first-order reaction network involving distinct retardation factors

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Abstract

This paper presents a general method for solving coupled multi-dimensional, multi-species reactive transport equations. The new method can be used for solving multi-species transport problems involving first-order kinetic interactions and distinct retardation factors. The solution process employs Laplace transformation and linear transformation steps to uncouple the governing set of coupled partial differential equations. The uncoupled equations are solved using an elementary solution. The details of the solution algorithm are illustrated by deriving an explicit analytical solution to a two-species reactive transport problem. In addition, three one-dimensional problems and two three-dimensional problems are solved to illustrate the use of the method. The proposed solution scheme is a robust procedure for solving a variety of multi-dimensional, multi-species transport problems that are coupled with a first-order reaction network.

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1. Introduction

The need for evaluating the fate and transport of degradable contaminants in groundwater systems has motivated researchers to develop various analytical and numerical solutions to reactive transport equations (e.g., [7,8,15,18,23,30]). Since the early 1950s, several researchers have developed analytical solutions to single-species transport problems in one-dimensional porous media (e.g., [2,20,21,26]). Van Genuchten and Alves [31] provided a comprehensive review of one-dimensional analytical solutions to advection–dispersion equations under various initial and boundary conditions. Multi-dimensional analytical solutions of the transport equation for a single-species are also available in the literature (e.g., [5,14,17,32]).

Cho [4] published one of the pioneering papers that focused on developing analytical solutions to multi-species reactive transport systems. This work provided

an analytical solution to a three-species model that described the fate and transport of ammonium in groundwater systems. In this model, a sequential first-order kinetic reaction description was used to simulate the fate of ammonium which decayed through nitrification and denitrification processes. Similar type of one-dimensional solutions to multi-species, bio-reactive or radioactive transport problems involving a sequential first-order decay reaction chain are also available in the published literature [3,11,16,19,22,30].

All the sequential decay chain solutions described above are limited to one-dimensional problems with either three or four reactive species. Sun and Clement [28] and Sun et al. [29] published general methods for solving multi-dimensional reactive transport equations coupled with a sequential first-order decay chain. These methods, however, cannot solve transport equations with distinct retardation values.

Bauer et al. [1] developed an analytical solution to a multi-species transport problem coupled with a sequential decay chain with different retardation factors. They developed a recursive formula that utilized a fundamental basis solution to build a more complex

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multi-species transport solution. However, the proposed formula is only valid for sequential decay systems and hence the method cannot be used for solving more generalized multi-parent networks involving reversible and/or converging reactions.

Montas [24] derived an explicit analytical solution for solving multi-dimensional reactive transport equations with distinct velocities coupled by first-order interactions. The major advantage of this method is that it can address convergent problems with different transport velocities; the major disadvantage is that the method is restricted to three-species transport.

Clement [6] developed a general solution method that can be used for solving any type of first-order coupled multi-species transport problem in multi-dimensional saturated flow systems. Although this new solution is a highly flexible approach, it has limited use because the method assumes identical retardation values for all the reactive species. The objective of this work is to extend the Clement [6] method for solving reactive transport systems with distinct retardation values.

2. Governing transport equations

This study considers solutions to a set of partial differential equations that describe the transport of multiple reactive species in saturated porous media systems. The kinetics of the reactions are assumed to be first order. The governing set of differential equations that describes the transport of multiple species in a saturated three-dimensional porous medium with uniform steady flow in the x -direction is given as [6]:

$$R_i \frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial x} - D_x \frac{\partial^2 c_i}{\partial x^2} - D_y \frac{\partial^2 c_i}{\partial y^2} - D_z \frac{\partial^2 c_i}{\partial z^2} \\ = \sum_{j=1}^{i-1} y_{i/j} k_j c_j - k_i c_i + \sum_{j=i+1}^n y_{i/j} k_j c_j \quad \forall i = 1, 2, \dots, n \quad (1)$$

where c_i is the i th species concentration [ML^{-3}]; $y_{i/j}$ is the effective yield factor that describes the mass of a species i produced from another species j [MM^{-1}]; k_i is the first-order contaminant destruction rate constant of the i th species [T^{-1}]; v is the transport velocity [LT^{-1}]; D_x, D_y, D_z are the dispersion coefficients [L^2T^{-1}]; and n is the total number of species in the reaction network. Eq. (1) assumes that the degradation reactions occur only in the liquid phase. If we assume degradation reactions to occur in both solid and liquid phases, then (1) should be modified as:

$$R_i \frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial x} - D_x \frac{\partial^2 c_i}{\partial x^2} - D_y \frac{\partial^2 c_i}{\partial y^2} - D_z \frac{\partial^2 c_i}{\partial z^2} \\ = \sum_{j=1}^{i-1} R_j y_{i/j} k_j c_j - R_i k_i c_i + \sum_{j=i+1}^n R_j y_{i/j} k_j c_j \quad \forall i = 1, 2, \dots, n \quad (2)$$

Equations of the form (1) and (2) can be used to model several types of environmental transport problems. For example, Clement et al. [9,10] used similar forms of equation to model the fate and transport of mixed chlorinated solvent plumes; Van Genuchten [30] used it for modeling radionuclide migration; and Cho [4] used it to model the fate and transport of nitrate species in soil–water systems.

In this paper, we propose a three-step process for solving the above set of coupled transport equations. In the first step of the solution process, the Laplace transformation is applied to transform the coupled set of partial differential equations (PDEs) in the concentration/time domain (designated here as c -domain) into a set of PDEs in the Laplace transformed domain (designated here as p -domain). In the second step, the linear transformation procedure described by Clement [6] is used to transform the coupled differential system in the Laplace domain into a set of uncoupled equations in the linear transformed domain (designated here as b -domain). The uncoupled equations are then solved by using an elementary solution to the fundamental differential problem described in the b -domain. The solution is transformed back into the p -domain using an inverse-linear transformation process, and later to the c -domain using the inverse Laplace transform process. The mathematical details of this three-step solution process are developed below.

3. Mathematical details of the solution strategy

Using matrix notation, the governing set of mathematical equations described by (2) can be compactly written in the following format:

$$\left[R \right] \frac{\partial}{\partial t} \{ c \} + v \frac{\partial}{\partial x} \{ c \} - D_x \frac{\partial^2}{\partial x^2} \{ c \} - D_y \frac{\partial^2}{\partial y^2} \{ c \} \\ - D_z \frac{\partial^2}{\partial z^2} \{ c \} = [YK] \{ c \} \quad (3)$$

where $[]$ is used to represent square matrices and $\{ \}$ is used to represent column vectors. Note the matrix $[YK]$ contains all the effective reaction rate coefficients; if the degradation reactions are assumed to occur in both the solid and liquid phase then this matrix will also contain appropriate retardation factors.

Using the Laplace transform method, the time derivative term in Eq. (3) can be written as,

$$\ell \left\{ R \frac{\partial}{\partial t} c(x, y, z, t) \right\} = s \cdot R \cdot p(x, y, z, s) - R \cdot f(x, y, z) \quad (4)$$

where ℓ is the Laplace transform operator; s is the Laplace variable, and $f(x, y, z)$ is the initial concentration of the contaminant in the domain.

Laplace transformation of the entire system of equations given by (3) would yield:

$$s[R]\{p\} - [R]\{f\} + v \frac{\partial}{\partial x} \{p\} - D_x \frac{\partial^2}{\partial x^2} \{p\} - D_y \frac{\partial^2}{\partial y^2} \{p\} - D_z \frac{\partial^2}{\partial z^2} \{p\} = [YK]\{p\} \quad (5)$$

Eq. (5) can be simplified as,

$$v \frac{\partial}{\partial x} \{p\} - D_x \frac{\partial^2}{\partial x^2} \{p\} - D_y \frac{\partial^2}{\partial y^2} \{p\} - D_z \frac{\partial^2}{\partial z^2} \{p\} = \langle [YK] - s[R] \rangle \{p\} + [R]\{f\} \quad (6)$$

where s is the Laplace variable and $\{p\}$ is the Laplace transformed concentration vector $\{c\}$. The elements of $\{p\}$ are defined by the standard Laplace transformation relation:

$$p_i(x, y, z, s) = \int_0^\infty \exp(-st) c_i(x, y, z, t) dt \quad (7)$$

The linear transformation procedure described by Clement [6] can now be used to transform the coupled set of differential equation (6) into an uncoupled format. To accomplish this, let us assume an arbitrary non-singular $n \times n$ matrix $[A]$ and use its inverse to perform the following linear transformation:

$$\{b\} = [A]^{-1} \{p\} \quad (8)$$

Conversely, the above transformation equation can also be written as:

$$\{p\} = [A]\{b\} \quad (9)$$

Substituting (9) into (6) we get,

$$v[A] \frac{\partial}{\partial x} \{b\} - D_x[A] \frac{\partial^2}{\partial x^2} \{b\} - D_y[A] \frac{\partial^2}{\partial y^2} \{b\} - D_z[A] \frac{\partial^2}{\partial z^2} \{b\} = \langle [YK] - s[R] \rangle [A]\{b\} + [R]\{f\} \quad (10)$$

Pre-multiplying the above equation by $[A]^{-1}$ we get,

$$[A]^{-1} v[A] \frac{\partial}{\partial x} \{b\} - [A]^{-1} D_x[A] \frac{\partial^2}{\partial x^2} \{b\} - [A]^{-1} D_y[A] \frac{\partial^2}{\partial y^2} \{b\} - [A]^{-1} D_z[A] \frac{\partial^2}{\partial z^2} \{b\} = [A]^{-1} \langle [YK] - s[R] \rangle [A]\{b\} + [A]^{-1} [R]\{f\} \quad (11)$$

Eq. (11) can be simplified as:

$$v \frac{\partial}{\partial x} \{b\} - D_x \frac{\partial^2}{\partial x^2} \{b\} - D_y \frac{\partial^2}{\partial y^2} \{b\} - D_z \frac{\partial^2}{\partial z^2} \{b\} = [\tilde{K}]\{b\} + [H]\{f\} \quad (12)$$

where, $\tilde{K} = [A]^{-1} \langle [YK] - s[R] \rangle [A]$ and $[H] = [A]^{-1} [R]$. If the columns of the transformation matrix $[A]$ are assigned as the eigenvectors of the combined reaction coefficient matrix $\langle [YK] - s[R] \rangle$ then the matrix $[\tilde{K}]$ will have a diagonal form. Under this condition, Eq. (12)

reduces to a system of n uncoupled differential equations.

Note that the diagonalization process describe above has essentially helped us to transform a system of n coupled equations in the p -domain [described by Eq. (5)] into a set of n uncoupled equation in the linear transformed b -domain [described by Eq. (12)]. The uncoupled set of advection–diffusion–reaction equations can now be independently solved using an elementary solution with transformed initial and boundary conditions.

Transforming the boundary conditions into the b -domain is a two-step process. The boundary conditions defined in the c -domain must first be Laplace transformed into the p -domain and later they must be linear transformed into the b -domain. For example, if constant concentration boundary conditions are assumed for a one-dimensional system then the i th species boundary condition co_i will be expressed in the Laplace transformed p -domain as:

$$po_i = \frac{co_i}{s} \quad (13)$$

To further transform the boundary condition from the p -domain to the b -domain, the following matrix problem should be solved:

$$[A]\{bo\} = \{po\} \quad \text{or} \quad [A]\{bo\} = \{co/s\} \quad (14)$$

In several important environmental transport problems, the transformation matrix $[A]$ will have a lower triangular form (e.g., sequential reaction problems). Under this special condition, the vector $\{bo\}$ can be computed using a simple forward substitution algorithm:

$$bo_i = po_i - \sum_{j=1}^{i-1} A_{ij} bo_j = \frac{co_i}{s} - \sum_{j=1}^{i-1} A_{ij} bo_j \quad (15)$$

where co_i is the constant concentration boundary condition of the i th species in the original c -domain; s is the Laplace variable; and bo_i is the transformed concentration boundary condition of the i th species in the b -domain.

The mathematical details of the uncoupling strategy discussed above are summarized on the left-hand column of Fig. 1. The right-hand column of the figure summarizes the details of the solution vectors derived in various domains. As illustrated in the figure, the first step in the solution process (see the right-hand bottom of Fig. 1) is to compute the solution to the uncoupled differential problem in the b -domain. Then the following matrix operation must be performed on the “ b ” vector to deduce the solution in the p -domain:

$$\{p\} = [A]\{b\} \quad (16)$$

Finally, the solution is transformed to the c -domain by applying the Laplace inversion operation on the “ p ” vector. The Laplace inversion step can be completed either by using an analytical procedure or by using a

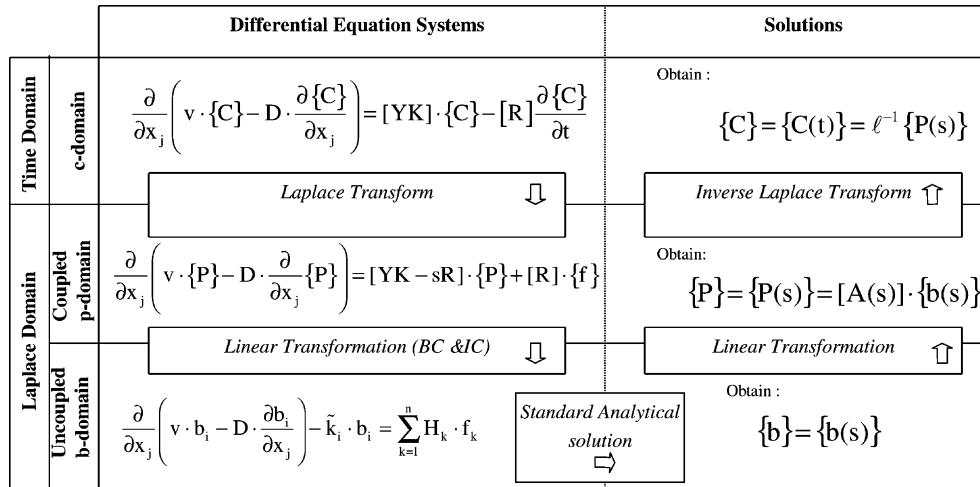


Fig. 1. Summary of various mathematical steps used in the solution procedure.

numerical procedure. A computational algorithm for implementing the proposed solution procedure is summarized in Fig. 2. A one-dimensional, two-species

reactive transport problem is used in the section below to describe the details of computational steps listed in the figure.

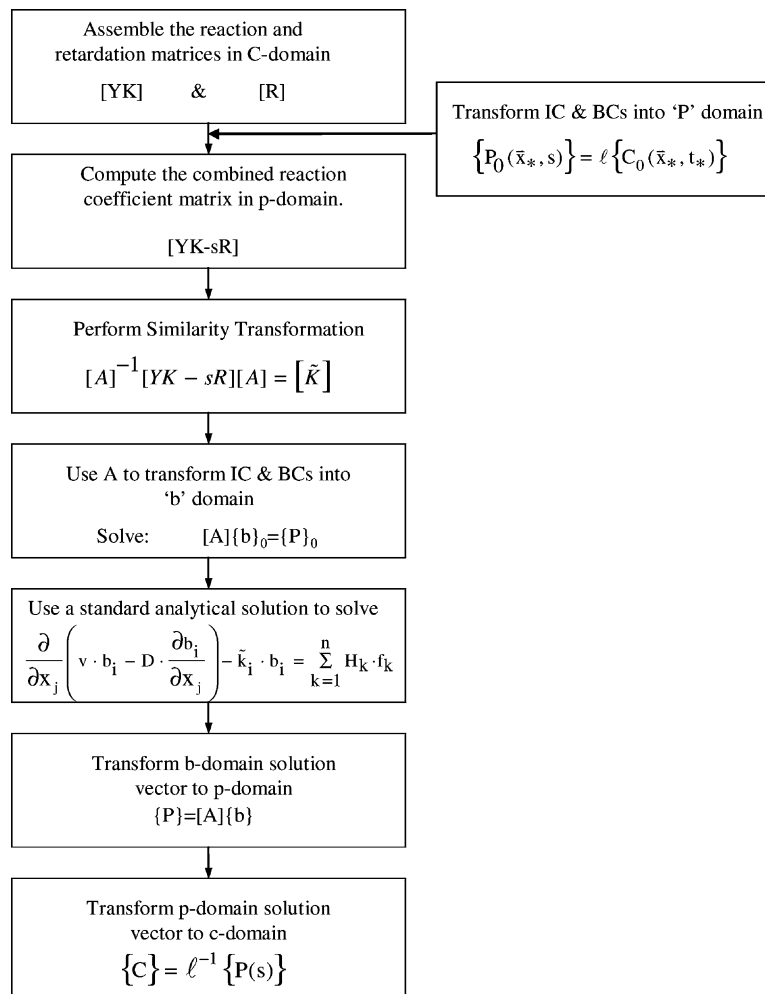


Fig. 2. Computational algorithm for the generalized solution procedure.

4. Derivation of analytical solution for a two-species example

Consider a one-dimensional reactive transport problem that describes the fate of two reactive contaminants mediated by sequential first-order reactions. The governing equations for the problem are:

$$\begin{aligned}
 R_1 \frac{\partial c_1}{\partial t} + v \frac{\partial c_1}{\partial x} - D_x \frac{\partial^2 c_1}{\partial x^2} &= -k_1 c_1 \\
 R_2 \frac{\partial c_2}{\partial t} + v \frac{\partial c_2}{\partial x} - D_x \frac{\partial^2 c_2}{\partial x^2} &= k_1 c_1 - k_2 c_2
 \end{aligned}
 \tag{17}$$

The initial and boundary conditions for the problem are:

$$\begin{aligned}
 \text{At } t = 0, \quad c_i(x, 0) &= 0 \quad i = 1, \dots, 2 \\
 \text{At } x = 0, \quad c_i(0, t) &= \text{co}_i \quad i = 1, \dots, 2 \\
 \lim_{x \rightarrow \infty} c_i(x, t) &= 0 \quad i = 1, \dots, 2
 \end{aligned}
 \tag{18}$$

Using matrix notation, Eq. (17) can be written as:

$$\begin{aligned}
 \begin{bmatrix} R_1 & 0 \\ 0 & R_2 \end{bmatrix} \frac{\partial}{\partial t} \begin{Bmatrix} c_1 \\ c_2 \end{Bmatrix} + v \frac{\partial}{\partial x} \begin{Bmatrix} c_1 \\ c_2 \end{Bmatrix} - D_x \frac{\partial^2}{\partial x^2} \begin{Bmatrix} c_1 \\ c_2 \end{Bmatrix} \\
 = \begin{bmatrix} -k_1 & 0 \\ k_1 & -k_2 \end{bmatrix} \begin{Bmatrix} c_1 \\ c_2 \end{Bmatrix}
 \end{aligned}
 \tag{19}$$

Applying Laplace transform to the above equation we get,

$$\begin{aligned}
 s \begin{bmatrix} R_1 & 0 \\ 0 & R_2 \end{bmatrix} \begin{Bmatrix} p_1 \\ p_2 \end{Bmatrix} + v \frac{\partial}{\partial x} \begin{Bmatrix} p_1 \\ p_2 \end{Bmatrix} - D_x \frac{\partial^2}{\partial x^2} \begin{Bmatrix} p_1 \\ p_2 \end{Bmatrix} \\
 = \begin{bmatrix} -k_1 & 0 \\ k_1 & -k_2 \end{bmatrix} \begin{Bmatrix} p_1 \\ p_2 \end{Bmatrix}
 \end{aligned}
 \tag{20}$$

where p_1 and p_2 are the concentration of species in the Laplace domain.

The boundary conditions of the problem can be transferred to the p -domain as:

$$p_i(0, s) = \text{po}_i = \frac{\text{co}_i}{s} \quad i = 1, \dots, 2
 \tag{21}$$

$$\lim_{x \rightarrow \infty} p_i(x, s) = 0 \quad i = 1, \dots, 2
 \tag{22}$$

Eq. (20) can be rearranged as,

$$\begin{aligned}
 v \frac{\partial}{\partial x} \begin{Bmatrix} p_1 \\ p_2 \end{Bmatrix} - D_x \frac{\partial^2}{\partial x^2} \begin{Bmatrix} p_1 \\ p_2 \end{Bmatrix} \\
 = \begin{bmatrix} -k_1 - sR_1 & 0 \\ k_1 & -k_2 - sR_2 \end{bmatrix} \begin{Bmatrix} p_1 \\ p_2 \end{Bmatrix}
 \end{aligned}
 \tag{23}$$

Comparing the above equation with (6), one can identify the combined reaction coefficient matrix for the system as:

$$\langle [YK] - s[R] \rangle = \begin{bmatrix} -k_1 - sR_1 & 0 \\ k_1 & -k_2 - sR_2 \end{bmatrix}
 \tag{24}$$

The next step in the solution process involves the computation of the linear transformation matrix $[A]$. We

know that the columns of $[A]$ should have the eigenvectors of the combined reaction coefficient matrix. The eigenvalues and eigenvectors of $\langle [YK] - s[R] \rangle$ can be written as:

$$\begin{aligned}
 \lambda_1 &= -k_1 - sR_1; \quad x_1 = \begin{Bmatrix} A_{11} \\ \frac{k_1 A_{11}}{s(R_2 - R_1) + k_2 - k_1} \end{Bmatrix} \\
 \lambda_2 &= -k_2 - sR_2; \quad x_2 = \begin{Bmatrix} 0 \\ A_{22} \end{Bmatrix}
 \end{aligned}
 \tag{25}$$

where λ_1 and λ_2 are the eigenvalues, and A_{11} and A_{22} are arbitrary constants. For simplicity, let us set the values of A_{11} and A_{22} to unity. Then, using (25) the transformation matrix $[A]$ and the diagonal matrix $[\tilde{K}]$ can be written as:

$$\begin{aligned}
 [A] &= \begin{bmatrix} 1 & 0 \\ \frac{k_1}{s(R_2 - R_1) + k_2 - k_1} & 1 \end{bmatrix} \\
 [\tilde{K}] &= \begin{bmatrix} -k_1 - sR_1 & 0 \\ 0 & -k_2 - sR_2 \end{bmatrix}
 \end{aligned}
 \tag{26}$$

The matrix $[A]$ can be used to perform the following linear transformation:

$$\begin{Bmatrix} P_1 \\ P_2 \end{Bmatrix} = \begin{bmatrix} 1 & 0 \\ \frac{k_1}{s(R_2 - R_1) + k_2 - k_1} & 1 \end{bmatrix} \begin{Bmatrix} b_1 \\ b_2 \end{Bmatrix}
 \tag{27}$$

Applying the above linear transformation step, Eq. (23) can be written in the b -domain as:

$$\begin{aligned}
 v \frac{\partial}{\partial x} \begin{Bmatrix} b_1 \\ b_2 \end{Bmatrix} - D_x \frac{\partial^2}{\partial x^2} \begin{Bmatrix} b_1 \\ b_2 \end{Bmatrix} \\
 = \begin{bmatrix} -k_1 - sR_1 & 0 \\ 0 & -k_2 - sR_2 \end{bmatrix} \begin{Bmatrix} b_1 \\ b_2 \end{Bmatrix}
 \end{aligned}
 \tag{28}$$

Note that Eq. (28) represents two independent, steady-state, advection–dispersion equations with a first-order decay term. An explicit solution to these two independent equations can be computed using the analytical expression:

$$\begin{aligned}
 b_i(s, x) &= \text{bo}_i \exp \left[\left(\frac{v - \sqrt{v^2 + 4D_x(R_i s + k_i)}}{2D_x} \right) x \right] \\
 x > 0, \quad i &= 1, \dots, 2
 \end{aligned}
 \tag{29}$$

where bo_i is the boundary condition of the species i in the b -domain. Since the $[A]$ matrix of our problem has a lower triangular form, we can use (15) to write the transformed boundary conditions in the b -domain as:

$$\begin{aligned}
 \text{bo}_1 &= \frac{\text{co}_1}{s} \\
 \text{bo}_2 &= \frac{\text{co}_2}{s} - A_{21} \text{bo}_1 = \frac{\text{co}_2}{s} - \frac{k_1 \text{co}_1}{[s(R_2 - R_1) + k_2 - k_1]s}
 \end{aligned}
 \tag{30}$$

After solving the problem in the b -domain, Eq. (16) can be used to transform the solution vector back to the p -domain as:

$$\begin{aligned}
 p_1(s, x) &= \frac{cO_1}{s} M_1 \\
 p_2(s, x) &= \frac{cO_2}{s} M_2 + \frac{k_1 cO_1}{s[s(R_2 - R_1) + k_2 - k_1]} (M_1 - M_2)
 \end{aligned}
 \quad (31)$$

where M is defined as:

$$M_i(s, x) = \exp \left[\left(\frac{v - \sqrt{v^2 + 4D_x(R_i s + k_i)}}{2D_x} \right) x \right]$$

$$x > 0, \quad i = 1, \dots, 2 \quad (32)$$

Finally, to derive the solution in c -domain, an inverse Laplace transform must be applied to the above equation. This step can be summarized as:

$$\begin{aligned}
 c_1(x, t) &= \ell^{-1}(p_1(s, x)) = cO_1 \ell^{-1} \left(\frac{M_1}{s} \right) \\
 c_2(x, t) &= \ell^{-1}[p_2(s, x)] = cO_2 \ell^{-1} \left(\frac{M_2}{s} \right) \\
 &+ k_1 cO_1 \cdot \ell^{-1} \left(\frac{(M_1 - M_2)}{s[s(R_2 - R_1) + k_2 - k_1]} \right)
 \end{aligned}
 \quad (33)$$

Analytical expressions for the inverse Laplace transforms can be obtained from a standard table [25]. Using these expressions we can write the final solution as,

$$c_1(x, t) = cO_1 H_1 \quad (34)$$

$$c_2(x, t) = cO_2 H_2 + \frac{k_1 cO_1}{k_2 - k_1} (H_1 - H_2 - Q_1 + Q_2) \quad (35)$$

where,

$$\begin{aligned}
 H_i &= \frac{\text{Exp}\left(\frac{vx}{2D_x}\right)}{2} \left[\text{Exp}(-a_i b_i) \text{Erfc}\left(\frac{a_i}{2} t^{-\frac{1}{2}} - b_i t^{\frac{1}{2}}\right) \right. \\
 &+ \left. \text{Exp}(a_i b_i) \cdot \text{Erfc}\left(\frac{a_i}{2} t^{-\frac{1}{2}} + b_i t^{\frac{1}{2}}\right) \right]
 \end{aligned}
 \quad (36)$$

$$a_i = \sqrt{\frac{R_i}{D_x}} x, \quad b_i = \sqrt{\frac{v^2}{4D_x R_i} + \frac{k_i}{R_i}} \quad (37)$$

$$\begin{aligned}
 Q_i(x, t) &= \ell^{-1} \left(\frac{M_i}{s + \frac{\beta}{\gamma}} \right) = \frac{\text{Exp}\left(\frac{vx}{2D_x}\right)}{2} \text{Exp}\left(\frac{-(k_2 - k_1)}{R_2 - R_1} t\right) \\
 &\times \left[\text{Exp}(-e_i f_i) \text{Erfc}\left(\frac{e_i}{2} t^{-\frac{1}{2}} - f_i t^{\frac{1}{2}}\right) \right. \\
 &+ \left. \text{Exp}(e_i f_i) \cdot \text{Erfc}\left(\frac{e_i}{2} t^{-\frac{1}{2}} + f_i t^{\frac{1}{2}}\right) \right]
 \end{aligned}
 \quad (38)$$

$$e_i = \sqrt{\frac{R_i}{D_x}} x \quad \text{and} \quad f_i = \sqrt{\frac{v^2}{4D_x R_i} + \frac{k_i}{R_i} - \left(\frac{k_2 - k_1}{R_2 - R_1} \right)} \quad (39)$$

Eqs. (34) and (35) along with various definitions [Eqs. (36)–(39)] are the complete closed form analytical solutions

to the two-species problems. Cho [4] derived an analytical solution to a system similar to (17) using a different analytical procedure. If appropriate equivalent reaction terms are defined, then the analytical expressions published by Cho [4] are identical to the above expressions.

5. Generalization of the solution procedure using numerical-inverse Laplace transform routines

Computing the inverse Laplace transform of the uncoupled solution is the critical step in the proposed solution strategy. In the above example, we accomplished this step by referring to a standard table [25]. In principle, explicit analytical expressions, similar to Eqs. (34)–(39) can be derived for transport problems coupled with any type of first-order reaction network. However, deducing a generic analytical inverse Laplace expression for problems involving a complex network of reactions with an arbitrary number of species is an impossible task. As shown in the two-species example, even for simple problems, the analytical inverse Laplace transform expressions can be fairly complex. Further, developing a general computer code for evaluating these analytical expressions on a case by case can be a tedious process. Use of a numerical-inverse Laplace transformation step can help avoid some of these difficulties. For large reaction networks involving arbitrary number of species, use of a numerical Laplace inversion step provides a flexible framework to develop a generic code. Our test results (given below) indicate that the accuracy of solutions based on a numerical Laplace inversion step is comparable to the accuracy of explicit analytical solutions.

In the literature, several numerical algorithms are available for evaluating inverse Laplace transforms. Davies and Martin [12] tested and compared the performance of different algorithms and concluded that a method based on a Fourier series approximation is the best approach. de Hogg et al. [13] improved the Fourier series method by providing a procedure for accelerating its convergence. The computational details of the Fourier

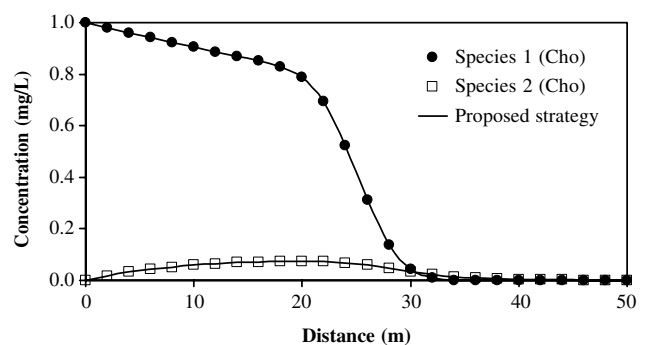


Fig. 3. Comparison of the present solution to the Cho [4] solution for the two-species problem.

Table 1
Parameters used in the two-species test problem

Parameter	Value
C_{01}	1 mg/l
C_{02}	0 mg/l
R_1	2
R_2	1
K_1	0.01 h ⁻¹
K_2	0.1 h ⁻¹
Time	50 h
v	1 cm h ⁻¹
D	0.18 cm ² h ⁻¹

series based inverse Laplace procedure are given de Hogg et al. [13], and also discussed thoroughly in Quezada [27].

Fig. 3 compares the solutions to the two-species problem using both the explicit analytical expressions and the numerical-inverse Laplace transform method. The model parameters used for simulation are identical to those given in [4]; these values are summarized in Table 1. The results indicate that the concentration profiles predicted using analytical and numerical inversion methods are almost identical.

6. Solution to one-dimensional test problems

Three example problems were solved to further test the performance of the proposed analytical method. All problems were solved by using the numerical Laplace inversion step. In the first example, a sequential reaction network problem was solved and the results are compared against the results reported in Bauer et al.'s [1] work. In the second example, a more complex reversible reaction network was solved and the results are compared against the results obtained using the numerical reactive transport code RT3D [7]. The third example is similar to the second, but involves non-zero initial conditions.

6.1. Solution to a sequential reaction problem with distinct retardation factors

This problem considers the transport of four reactive species that are degrading in a sequential fashion. The governing transport equations are given as:

$$\begin{aligned}
 R_1 \frac{\partial C_1}{\partial t} + v \frac{\partial C_1}{\partial x} - D_x \frac{\partial^2 C_1}{\partial x^2} &= -k_1 R_1 C_1 \\
 R_2 \frac{\partial C_2}{\partial t} + v \frac{\partial C_2}{\partial x} - D_x \frac{\partial^2 C_2}{\partial x^2} &= k_1 R_1 C_1 - k_2 R_2 C_2 \\
 R_3 \frac{\partial C_3}{\partial t} + v \frac{\partial C_3}{\partial x} - D_x \frac{\partial^2 C_3}{\partial x^2} &= k_2 R_2 C_2 - k_3 R_3 C_3 \\
 R_4 \frac{\partial C_4}{\partial t} + v \frac{\partial C_4}{\partial x} - D_x \frac{\partial^2 C_4}{\partial x^2} &= k_3 R_3 C_3 - k_4 R_4 C_4
 \end{aligned}
 \tag{40}$$

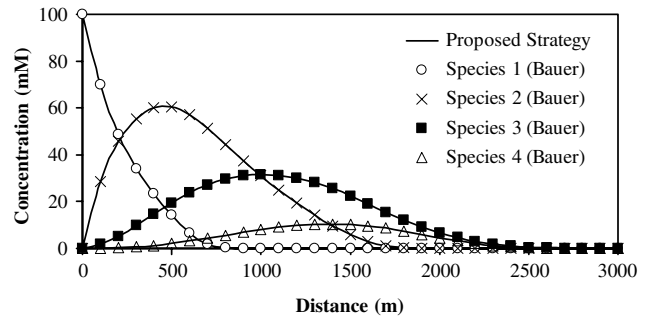


Fig. 4. Comparison of the present solution and the analytical solution of Bauer et al. [1] for the sequential decay problem. $T = 3000$ days, $K = (7, 5, 4.5, 3.8) \times 10^{-4}$ day⁻¹, $R(5.3, 1.9, 1.2, 1.3)$, $v = 1$ m day⁻¹, $\alpha_x = 10$ m.

The length of the column is assumed to be 3000 m and the initial concentrations of all four species are assumed to be zero. The concentration of the first species at the inlet boundary was fixed at 100 mM and the others are fixed at zero. The total simulation time for this example is 3000 days. Other details used for this one-dimensional test problem are identical to a test problem discussed in Bauer et al. [1]. The solution to the problem using the proposed method is compared against the Bauer et al. results in Fig. 4. The results show that concentration profiles predicted by the present solution are in excellent agreement with Bauer et al. results.

6.2. Solution to a reversible reaction problem with distinct retardation factors

The purpose of this example is to demonstrate the capability of the proposed method for solving transport problems involving reversible reactions. The network of reactions considered in the test problem is shown in Fig. 5. This example is similar to a test problem proposed by Clement [6], except this new version of the problem involves distinct retardation values. The governing transport equations for the problem are given as:

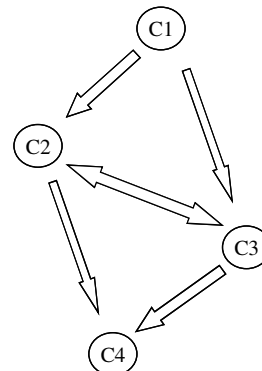


Fig. 5. Schematic of the reversible reaction network.

$$\begin{aligned}
 R_1 \frac{\partial C_1}{\partial t} + v \frac{\partial C_1}{\partial x} - D_x \frac{\partial^2 C_1}{\partial x^2} &= -k_1 C_1 \\
 R_2 \frac{\partial C_2}{\partial t} + v \frac{\partial C_2}{\partial x} - D_x \frac{\partial^2 C_2}{\partial x^2} \\
 &= F_{c2/e1} Y_{c2/e1} k_1 C_1 - k_2 C_2 + F_{c2/e3} Y_{c2/e3} k_3 C_3 \\
 R_3 \frac{\partial C_3}{\partial t} + v \frac{\partial C_3}{\partial x} - D_x \frac{\partial^2 C_3}{\partial x^2} \\
 &= F_{c3/e1} Y_{c3/e1} k_1 C_1 + F_{c3/e2} Y_{c3/e2} k_2 C_2 - k_3 C_3 \\
 R_4 \frac{\partial C_4}{\partial t} + v \frac{\partial C_4}{\partial x} - D_x \frac{\partial^2 C_4}{\partial x^2} \\
 &= F_{c4/e2} Y_{c4/e2} k_2 C_2 + F_{c4/e3} Y_{c4/e3} k_3 C_3 - k_4 C_4
 \end{aligned} \tag{41}$$

The values of various model parameters assumed are given in Table 2. Fig. 6 compares the analytical results computed using the present approach and the numerical results computed using the RT3D code [7]. The results indicate that the concentration profiles predicted by

Table 2
Parameters used in the one-dimensional reversible reaction problem

Parameter	Value
Column length L	40.0 m
Longitudinal dispersivity	0.2 m
Velocity v	0.4 m d ⁻¹
Singularity parameter α	0.1
Retardation factor R_1	1.0
Retardation factor R_2	2.0
Retardation factor R_3	3.0
Retardation factor R_4	4.0
K_1	0.075 d ⁻¹
K_2	0.05 d ⁻¹
K_3	0.02 d ⁻¹
K_4	0.045 d ⁻¹
Yield Y (all of them)	1.0
$F_{c2/e1}$	0.75
$F_{c3/e1}$	0.25
$F_{c3/e2}$	0.5
$F_{c4/e2}$	0.5
$F_{c2/e3}$	0.9
$F_{c4/e3}$	0.1
Boundary cond.—species 1 (constant)	1.0 mol l ⁻¹
Boundary cond.—species 2–4	0.0 mol l ⁻¹
Simulation time	50 d

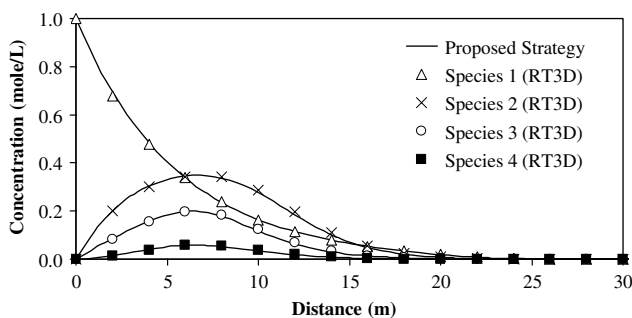


Fig. 6. Comparison of the present analytical solution and the numerical solution of RT3D for the reversible reaction problem.

both methods are almost identical. It should be noted that none of the solution strategies currently available in the publish literature have the capability to analytically solve the coupled reactive transport problem posed in this example. However, the numerical-inverse transformed based semi-analytical method proposed in this work is general enough to solve these types of reversible reaction coupled transport problems for an arbitrary number of species.

6.3. Solution to a test problem involving distinct retardation factors and non-zero initial conditions

The problem discussed in Section 6.2 is solved here for non-zero initial conditions. As shown in Eq. (12), non-zero initial conditions lead to additional non-homogeneous terms in the set of uncoupled differential equations. To solve these equations one would require a basis solution that accounts for the non-homogeneous terms. In Appendix A, we derive a new basis solution for solving a test problem in which the initial concentration distribution is described by an exponential function of the form:

$$f_i(x) = bc_i \cdot \exp(-\beta_i \cdot x) \tag{42}$$

The new basis solution derived in Appendix A was used to solve a test problem. Table 3 summarizes the values of bc_i and β_i assumed in the problem. Other model parameters assumed, including the boundary conditions, are similar to those discussed in Section 6.2.

Simulations were completed to predict the concentration profiles of four reactive species after 3000 days of transport. The concentration profiles computed using the present analytical procedure and the numerical data

Table 3
Parameters used in the one-dimensional non-zero initial condition problem

Parameter	Species 1	Species 2	Species 3	Species 4
bc_i	0.50	0.30	0.35	0.20
β_i	0.05	0.02	0.01	0.01

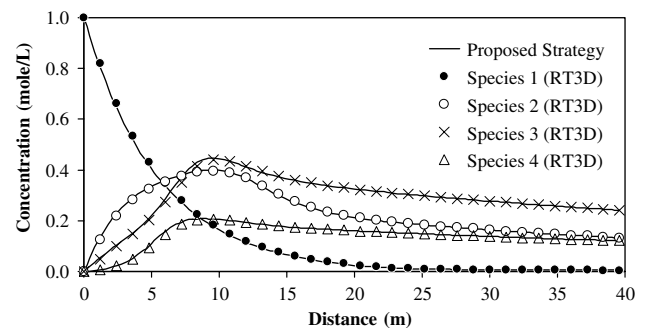


Fig. 7. Comparison of the present solution to the numerical solution of RT3D for the non-zero initial condition problem.

computed using the RT3D code are shown in Fig. 7. The results show that both methods predict similar concentration distribution.

7. Solution to three-dimensional test problems

In this section, three-dimensional examples are solved to demonstrate the use of the proposed analytical solution strategy for solving multi-dimensional problems. These three-dimensional examples assume presence of an instantaneous point source at the origin and zero initial conditions. The first example considers reactive transport from a sequential reactive network; this problem is similar to the one presented in Bauer et al. [1]. The second example considers transport from a complex reaction network involving a set of sequential-parallel reactions.

7.1. Strategy for modeling reactive instantaneous point source

The governing equation for modeling an instantaneous, multi-species, point source within a three-dimensional domain can be written as:

$$c_i(x, y, z, 0) = \frac{\hat{m}_i}{\phi} \cdot \delta(x, y, z) \quad \forall i = 1, \dots, n$$

where c_i is the i th species concentration [ML⁻³]; \hat{m}_i is the total mass of the i th species released at the beginning of the simulation [M]; δ is the delta function; and n is the total number of species in the reaction network.

Using the proposed analytical strategy, the governing set of three-dimensional reactive transport equations can be written in the uncoupled b -domain as:

$$v \frac{\partial}{\partial x} \{b\} - D_x \frac{\partial^2}{\partial x^2} \{b\} - D_y \frac{\partial^2}{\partial y^2} \{b\} - D_z \frac{\partial^2}{\partial z^2} \{b\} = [\tilde{K}] \{b\} \tag{43}$$

where $[\tilde{K}] = [A]^{-1} \{ [YK] - s[R] \} [A]$ is a diagonal matrix. For a given species, the solution to differential equation (43) can be deduced from an analytical function given by Bauer et al. [1]. The analytical function can be written in the form:

$$b_i(s, x, y, z) = b_{0i} \cdot f_i(x, y, z, s)$$

where

$$f_i(x, y, z, s) = \frac{\sqrt{\alpha_x v}}{\sqrt{x^2 + \frac{z_x}{\alpha_y} y^2 + \frac{z_x}{\alpha_z} z^2}} \cdot \exp \left[\frac{x - \sqrt{\left(1 - \frac{4z_x \tilde{K}_i}{v}\right) \left(x^2 + \frac{z_x}{\alpha_y} y^2 + \frac{z_x}{\alpha_z} z^2\right)}}{2\alpha_x} \right] \cdot \exp \left[-\frac{v}{2\alpha_x} \left(x + \sqrt{\left(1 - \frac{4z_x \tilde{K}_i}{v}\right) \left(x^2 + \frac{z_x}{\alpha_y} y^2 + \frac{z_x}{\alpha_z} z^2\right)} \right) \right] \tag{44}$$

$-\infty < y, z < \infty, \quad x > 0$

where \tilde{K}_i is the i th element of the diagonal matrix $[\tilde{K}]$; α_i is the dispersivity in the i th direction [L]; and b_{0i} is the mass loading term of the i th species expressed in the b -domain.

Determination of the mass loading term in the b -domain (the values of b_0), requires the use of mass balance conditions. Assuming the degradation process occurs only in aqueous phase, the mass balance for the i th species can be written as,

$$R_i \cdot \frac{dm_i}{dt} = \sum_{j=1}^{i-1} y_{i/j} \cdot k_j \cdot m_j - k_i \cdot m_i + \sum_{j=i+1}^n y_{i/j} \cdot k_j \cdot m_j + \hat{m}_i \cdot \delta(t) \tag{45}$$

where m_i is the mass of the i th species [M]; R_i is the retardation factor i th species; $y_{i/j}$ is the effective yield factor that describes the mass of a species i produced from another species j [MM⁻¹]; k_i is the first-order contaminant destruction rate constant of the i th species [T⁻¹]; and \hat{m}_i is the total mass of i th contaminant released from the point source [M]. Note if degradation is assumed to occur in both aqueous and solid phases then the three reaction terms in the right-hand side of Eq. (45) should be multiplied by the corresponding retardation values R_j .

Using matrix notation, the above mass balance condition for a reaction network can be compactly written in the following format:

$$[R] \frac{d}{dt} \{m\} = [YK] \{m\} + \{\hat{m}\} \delta(t) \tag{46}$$

where $[R]$ is a diagonal matrix, and $[YK]$ may have arbitrary entries depending on the reaction network. If the aquifer is considered to be initially free of contaminant, then Laplace transformation of (46) can be written as:

$$s[R] \{M\} = [YK] \{M\} + \{\hat{m}\} \tag{47}$$

where M_i is the Laplace transformed mass of i th species [M] expressed as,

$$M_i(s) = \int_0^\infty \exp(-st) m_i(t) dt \tag{48}$$

Grouping common terms

$$[s[R] - [YK]] \{M\} = \{\hat{m}\} \tag{49}$$

The matrix equation (49) can be solved for the vector $\{M\}$, which will provide the total mass of all the species in the Laplace transformed p -domain.

The total mass of the i th species (M_i) can also be obtained by integrating the Laplace transformed concentration distribution (p_i) over the entire domain,

$$\phi \cdot \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_i \cdot dx dy dz = M_i \quad (50)$$

where, ϕ is the porosity. Eq. (50) can be written for every species and the values can be used to assemble the vector $\{M\}$, purely from a mass balance perspective.

The next step is to use the linear transformation procedure to transform the mass balance equation (50) into the uncoupled b -domain. This linear transformation step can be written for the i th species as,

$$p_i = \sum_{j=1}^n A_{ij} \cdot b_j \quad (51)$$

Substituting expressions (51) and (44) into (50) we get,

$$\begin{aligned} \phi \cdot \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_i \cdot dx dy dz \\ = \phi \cdot \sum_{j=1}^n A_{ij} \cdot \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} b_j \cdot dx dy dz \\ = \phi \cdot \sum_{j=1}^n A_{ij} \cdot \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} b_{0j} \cdot f_j(x, y, z, s) \cdot dx dy dz = M_i \end{aligned} \quad (52)$$

The integral on the right-hand side can be evaluated as:

$$\begin{aligned} I_i = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_i(x, y, z, s) \cdot dx dy dz \\ = \frac{-4 \cdot \pi \cdot \sqrt{v^3 \cdot \alpha_x \cdot \alpha_y \cdot \alpha_z}}{\tilde{k}_i} \end{aligned} \quad (53)$$

Substituting (53) into (52) we get,

$$\phi \cdot \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_i \cdot dx dy dz = \phi \cdot \sum_{j=1}^n A_{ij} \cdot b_{0j} \cdot I_j = M_i \quad (54)$$

Using matrix notations,

$$[A][I] \cdot \{b_0\} = \frac{1}{\phi} \{M\} \quad (55)$$

where $[I]$ is a diagonal matrix and its entries are defined by the integral equation (53), $[A]$ is the linear transformation matrix of the reaction problem (see Section 3), and the vector $\{M\}$ can be computed from (49). The matrix equation (55) can be directly solved to evaluate the vector $\{b_0\}$.

7.2. Solution to a three-dimensional problem involving sequential reactions

The problem considers four reactive species that are degrading in a sequential fashion in a three-dimensional aquifer. The governing transport equations are:

$$\begin{aligned} R_1 \frac{\partial C_1}{\partial t} + v \frac{\partial C_1}{\partial x} - D_x \frac{\partial^2 C_1}{\partial x^2} - D_y \frac{\partial^2 C_1}{\partial y^2} - D_z \frac{\partial^2 C_1}{\partial z^2} &= -k_1 R_1 C_1 \\ R_2 \frac{\partial C_2}{\partial t} + v \frac{\partial C_2}{\partial x} - D_x \frac{\partial^2 C_2}{\partial x^2} - D_y \frac{\partial^2 C_2}{\partial y^2} - D_z \frac{\partial^2 C_2}{\partial z^2} \\ &= k_1 R_1 C_1 - k_2 R_2 C_2 \\ R_3 \frac{\partial C_3}{\partial t} + v \frac{\partial C_3}{\partial x} - D_x \frac{\partial^2 C_3}{\partial x^2} - D_y \frac{\partial^2 C_3}{\partial y^2} - D_z \frac{\partial^2 C_3}{\partial z^2} \\ &= k_2 R_2 C_2 - k_3 R_3 C_3 \\ R_4 \frac{\partial C_4}{\partial t} + v \frac{\partial C_4}{\partial x} - D_x \frac{\partial^2 C_4}{\partial x^2} - D_y \frac{\partial^2 C_4}{\partial y^2} - D_z \frac{\partial^2 C_4}{\partial z^2} \\ &= k_3 R_3 C_3 - k_4 R_4 C_4 \end{aligned} \quad (56)$$

Subject to

$$c_i(x, y, z, 0) = \frac{\hat{m}_i}{\phi} \cdot \delta(x, y, z) \quad \forall i = 1, \dots, 4$$

In this example, degradation reactions are assumed to occur in both solid and liquid phases. A summary of the model parameters utilized in this example problem are given in Table 4. At time $t = 0$, it is assumed that 1000 mol of species-1 is released within the origin node. The total amount of transport time is 3000 days. In Fig. 8, we compare the analytical results computed for the centerline of the plume against the results reported in Bauer et al. [1]. Results show that concentration profiles predicted by the present solution are in excellent agreement with Bauer's solution.

Table 4
Parameters used in the three-dimensional sequential reaction problem

Parameter	Value
Longitudinal dispersivity	10.0 m
Transversal dispersivity	1.0 m
Vertical dispersivity	1.0 m
Velocity v	1.0 m d ⁻¹
Retardation factor—species 1 (R_1)	5.3
Retardation factor—species 2 (R_2)	1.9
Retardation factor—species 3 (R_3)	1.2
Retardation factor—species 4 (R_4)	1.3
K_1	7e-4 d ⁻¹
K_2	5e-4 d ⁻¹
K_3	4.5e-4 d ⁻¹
K_4	3.8e-4 d ⁻¹
Yield Y (all of them)	1.0
Boundary cond.—species 1 (instantaneous)	1000 mol
Boundary cond.—species 2-4	0.0
Porosity	0.15
Simulation time	3000 d

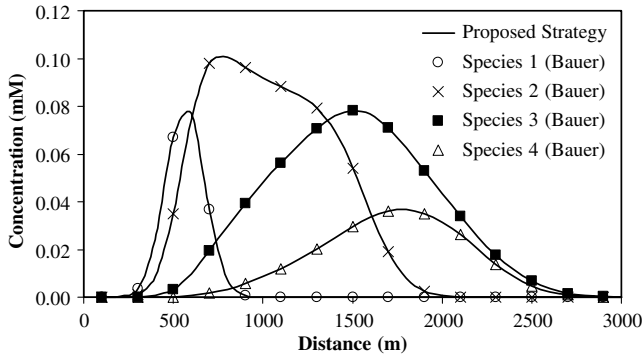


Fig. 8. Comparison of the present solution to the analytical solution of Bauer et al. [1] for the three-dimensional sequential decay problem. $T = 3000$ days, $K = (7, 5, 4.5, 3.8) \times 10^{-4}$ day $^{-1}$, $R = (5.3, 1.9, 1.2, 1.3)$, $v = 1$ m day $^{-1}$, $\alpha_x = 10$ m, $\alpha_y = 1$ m, $\alpha_z = 1$ m, $m = (1000, 0, 0, 0)$ mol, $\phi = 0.15$.

7.3. Solution to a three-dimensional problem involving serial-parallel reactions

The purpose of this example is to demonstrate the capability of the proposed method for solving three-dimensional transport problems involving serial and parallel reactions. The network of reactions considered in the test problem is shown in Fig. 9. The governing transport equations for the problem are given as:

$$\begin{aligned}
 R_1 \frac{\partial C_1}{\partial t} + v \frac{\partial C_1}{\partial x} - D_x \frac{\partial^2 C_1}{\partial x^2} - D_y \frac{\partial^2 C_1}{\partial y^2} - D_z \frac{\partial^2 C_1}{\partial z^2} &= -k_1 R_1 C_1 \\
 R_2 \frac{\partial C_2}{\partial t} + v \frac{\partial C_2}{\partial x} - D_x \frac{\partial^2 C_2}{\partial x^2} - D_y \frac{\partial^2 C_2}{\partial y^2} - D_z \frac{\partial^2 C_2}{\partial z^2} &= F_{c2/c1} Y_{c2/c1} k_1 R_1 C_1 - k_2 R_2 C_2 \\
 R_3 \frac{\partial C_3}{\partial t} + v \frac{\partial C_3}{\partial x} - D_x \frac{\partial^2 C_3}{\partial x^2} - D_y \frac{\partial^2 C_3}{\partial y^2} - D_z \frac{\partial^2 C_3}{\partial z^2} &= F_{c3/c1} Y_{c3/c1} k_1 R_1 C_1 + F_{c3/c2} Y_{c3/c2} k_2 R_2 C_2 - k_3 R_3 C_3 \\
 R_4 \frac{\partial C_4}{\partial t} + v \frac{\partial C_4}{\partial x} - D_x \frac{\partial^2 C_4}{\partial x^2} - D_y \frac{\partial^2 C_4}{\partial y^2} - D_z \frac{\partial^2 C_4}{\partial z^2} &= F_{c4/c2} Y_{c4/c2} k_2 R_2 C_2 + F_{c4/c3} Y_{c4/c3} k_3 R_3 C_3 - k_4 R_4 C_4
 \end{aligned}
 \tag{57}$$

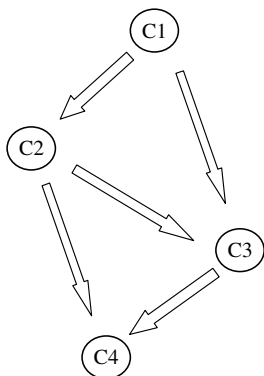


Fig. 9. Schematic of the sequential-parallel reaction network.

Table 5
Parameters used in the three-dimensional serial-parallel reaction problem

Parameter	Value
Longitudinal dispersivity	0.2 m
Transversal dispersivity	0.02 m
Vertical dispersivity	0.02 m
Velocity v	0.44 m d $^{-1}$
Retardation factor—species 1 (R_1)	1.0
Retardation factor—species 2 (R_2)	2.0
Retardation factor—species 3 (R_3)	3.0
Retardation factor—species 4 (R_4)	4.0
K_1	0.075 d $^{-1}$
K_2	0.05 d $^{-1}$
K_3	0.02 d $^{-1}$
K_4	0.045 d $^{-1}$
Yield Y (all of them)	1.0
$F_{c2/c1}$	0.25
$F_{c3/c1}$	0.75
$F_{c3/c2}$	0.5
$F_{c4/c2}$	0.5
$F_{c4/c3}$	1.0
Boundary cond.—species 1 (instantaneous)	1000 mol
Boundary cond.—species $i = 2-4$	0.0
Porosity	0.3
Simulation time	50 d

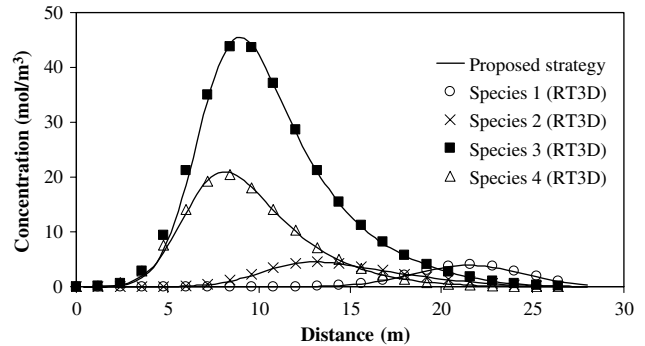


Fig. 10. Comparison of the centerline profile of the present solution against the numerical solution of RT3D for the three-dimensional sequential-parallel reaction problem.

Similar to the previous problem, a point source was released instantaneously at the origin. The values of various model parameters assumed in this test problem are given in Table 5. Figs. 10 and 11 compare the analytical results computed using the present approach against the numerical results computed using the RT3D code. Results indicate that the concentration profiles predicted by both models are almost identical.

8. Summary and conclusions

A general solution methodology is presented for solving multi-dimensional, multi-species transport equations coupled with a first-order kinetic reaction

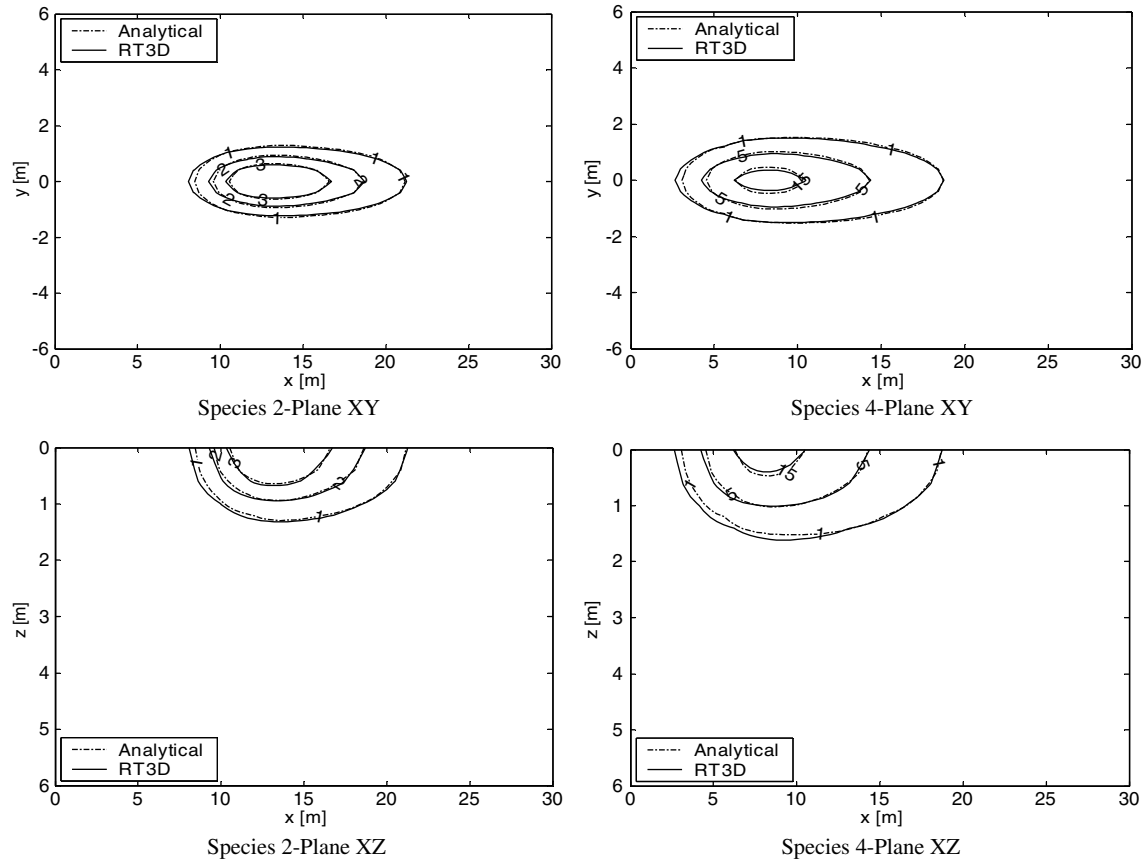


Fig. 11. Comparison of the present solution against the numerical solution of RT3D for the three-dimensional sequential-parallel reaction problem (XY and XZ cross sectional contours displayed for species-2 at 1, 2, and 3 mol m⁻³ and species-4 at 1, 5, and 15 mol m⁻³).

network. The solution employs a three-step transformation process, where Laplace and linear transformation procedures are applied sequentially to uncouple the governing set of coupled partial differential equations. This allows the problem to be solved using an elementary solution in the uncoupled domain. The computed concentration values are then inverted using inverse-linear and inverse-Laplace transform steps to compute the final results. The inverse Laplace transform step, which can be completed either analytically or numerically, is the critical step in the proposed analytical solution strategy. While the analytical inversion step will help derive explicit solutions, the inverse Laplace transforms could be difficult to deduce for several problem involving complex reactions and multiple number of species. The numerical-inverse transform based semi-analytical procedure, proposed in this work, is a more general method for solving any type first-order reaction coupled transport problems involving arbitrary number of species.

The details of the proposed method are illustrated by deriving an explicit analytical solution to a two-species transport problem. Further, several one- and three-dimensional test problems are solved and the results compared against other published analytical solutions,

and also against the numerical solutions generated using the RT3D code [7]. The simulation results show that the proposed solution scheme is a robust procedure for solving different types of multi-dimensional, multi-species problems that are coupled with various types of first-order kinetic reactions.

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Appendix A. Derivation of the fundamental solution for the non-zero initial condition problem

One-dimensional, multi-species transport equations for a system involving non-uniform initial conditions can be written in matrix notation as (from Eq. (12)):

$$v \frac{\partial}{\partial x} \{b\} - D_x \frac{\partial^2}{\partial x^2} \{b\} = [\tilde{K}]\{b\} + [H]\{f\} \quad (\text{A.1})$$

Since the above equations are uncoupled, their solution can be deduced independently for each species and later assembled to construct the solution vector $\{b\}$. In the non-zero initial condition problem discussed in Section 6.3, we assume the initial concentration of every species to have the following functional form:

$$f_i(x) = bc_i \cdot \exp(-\beta_i \cdot x) \quad (\text{A.2})$$

Using above initial condition function, the non-homogeneous differential equation for the i th species is written as:

$$\frac{\partial^2 b_i}{\partial x^2} - \frac{v}{D_x} \frac{\partial b_i}{\partial x} + \frac{\tilde{k}}{D_x} b_i = g_i \quad \text{where,} \\ g_i = -\frac{1}{D_x} \sum_{j=1}^n H_{ij} \cdot bc_j \cdot e^{-\beta_j \cdot x} \quad (\text{A.3})$$

General solution to Eq. (A.3) is composed of a homogeneous solution and a particular solution. The homogeneous solution for a species i (designated as Y_{hi}) can be written as:

$$Y_{hi} = C_1 y_1 + C_2 y_2 \quad \text{where } y_1 = e^{r_{1i} \cdot x}, \quad y_2 = e^{r_{2i} \cdot x} \quad (\text{A.4})$$

In Eq. (A.4), C_1 and C_2 are arbitrary constants and the terms r_{1i} and r_{2i} are defined as,

$$r_{1i} = \frac{v}{2D_x} + \sqrt{\left(\frac{v}{2D_x}\right)^2 - \frac{\tilde{k}_i}{D_x}} \quad \text{and} \\ r_{2i} = \frac{v}{2D_x} - \sqrt{\left(\frac{v}{2D_x}\right)^2 - \frac{\tilde{k}_i}{D_x}} \quad (\text{A.5})$$

The particular solution (Y_{pi}) is written using the variation parameter method as:

$$Y_{pi} = u_1 \cdot y_1 + u_2 \cdot y_2 \quad (\text{A.6})$$

where,

$$\frac{du_1}{dx} = \frac{-y_2 \cdot g_i}{W} \quad \text{and} \quad \frac{du_2}{dx} = \frac{y_1 \cdot g_i}{W} \quad (\text{A.7})$$

and W is the Wronskian of the systems written as:

$$W = \begin{vmatrix} y_1 & y_2 \\ y_1' & y_2' \end{vmatrix} \quad (\text{A.8})$$

Evaluating Eq. (A.7) after substituting the value of g_i and W from (A.3) and (A.8), respectively, we get

$$u_1 = \frac{-1}{D_x \cdot (r_{2i} - r_{1i})} \cdot \sum_{j=1}^n \frac{H_{ij} \cdot bc_j \cdot e^{-(r_{1i} + \beta_j) \cdot x}}{(r_{1i} + \beta_j)} \quad \text{and} \\ u_2 = \frac{1}{D_x \cdot (r_{2i} - r_{1i})} \cdot \sum_{j=1}^n \frac{H_{ij} \cdot bc_j \cdot e^{-(r_{2i} + \beta_j) \cdot x}}{(r_{2i} + \beta_j)} \quad (\text{A.9})$$

From (A.6), the particular solution for the problem can now be written as,

$$Y_{pi} = \frac{-1}{D_x} \cdot \sum_{j=1}^n \frac{H_{ij} \cdot bc_j \cdot e^{-\beta_j \cdot x}}{(r_{1i} + \beta_j)(r_{2i} + \beta_j)} \quad (\text{A.10})$$

The final solution is the sum of the homogeneous solution and the particular solution and can be written as:

$$b_i = Y_{hi} + Y_{pi} \\ = C_1 \cdot e^{r_{1i} \cdot x} + C_2 \cdot e^{r_{2i} \cdot x} - \frac{1}{D_x} \cdot \sum_{j=1}^n \frac{H_{ij} \cdot bc_j \cdot e^{-\beta_j \cdot x}}{(r_{1i} + \beta_j)(r_{2i} + \beta_j)} \quad (\text{A.11})$$

The boundary conditions for the test problem are:

$$\lim_{x \rightarrow \infty} b_i = 0 \quad \text{and} \quad b_i(x=0) = b_{i0} \quad (\text{A.12})$$

Using above boundary conditions, the analytical solution to the differential equation (A.3) can be written as:

$$b_i = b_{i0} \cdot e^{r_{2i} \cdot x} + \frac{1}{D_x} \cdot \sum_{j=1}^n \frac{H_{ij} \cdot bc_j \cdot \{e^{r_{2i} \cdot x} - e^{-\beta_j \cdot x}\}}{(r_{1i} + \beta_j)(r_{2i} + \beta_j)} \quad (\text{A.13})$$

The above expression was used as the basis solution for solving the test problem discussed in Section 6.3.

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