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Analytical solutions for sequentially coupled one-dimensional reactive transport problems – Part I: Mathematical derivations

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Abstract

Multi-species reactive transport equations coupled through sorption and sequential first-order reactions are commonly used to model sites contaminated with radioactive wastes, chlorinated solvents and nitrogenous species. Although researchers have been attempting to solve various forms of these reactive transport equations for over 50 years, a general closed-form analytical solution to this problem is not available in the published literature. In Part I of this two-part article, we derive a closed-form analytical solution to this problem for spatially-varying initial conditions. The proposed solution procedure employs a combination of Laplace and linear transform methods to uncouple and solve the system of partial differential equations. Two distinct solutions are derived for Dirichlet and Cauchy boundary conditions each with Bateman-type source terms. We organize and present the final solutions in a common format that represents the solutions to both boundary conditions. In addition, we provide the mathematical concepts for deriving the solution within a generic framework that can be used for solving similar transport problems.

Keywords: Analytical solution; Radioactive decay; Contaminant transport; First-order decay; Sequential reactions; Reactive transport

1. Introduction

Transport problems involving sequentially decaying contaminants are frequently analyzed by groundwater hydrologists to assess water quality issues associated with environmental and health hazards. Examples of sequentially decaying contaminants include radioactive waste materials, chlorinated solvents, and nitrogenous species [4,8,29]. Several types of models, using both analytical and numerical procedures, have been formulated for solving these sequentially coupled reactive transport problems [9,15]. Although numerical models are capable of solving complex and heterogeneous problems, their performance often needs to be tested against experimental datasets or analytical models. Experimental simulations of complex reactive transport problems are not only time consuming but can also be expensive. Therefore, analytical models provide a convenient, cost-effective alternative to test and validate numerical formulations [11,19,28]. Furthermore, analytical models also provide computationally efficient screening tools for simulating the fate and transport of reactive contaminants in groundwater systems [3,10].

The analytical solution given by McLaren [20] and McLaren [21], which describes the steady-state, one-dimensional transport of a five species nitrogen chain, is one of the first multi-species solutions derived for solving sequentially coupled reactive transport problems. This work assumed that the transport was governed only by advection, and the effects of dispersion and sorption were ignored. Cho [7] developed explicit analytical solutions to a three species transport problem that was subjected to advection, dispersion, linear equilibrium sorption and coupled through sequential first-order reactions.

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Explicit analytical solutions were obtained using Laplace transform procedures for the Dirichlet boundary condition. Misra et al. [22] derived semi-analytical solutions to a problem similar to the one solved by Cho [7] using a pulse source boundary. One of the limitations of these solutions is that only the first species in the chain was subjected to sorption. Burkholder and Rosinger [5] and Lester et al. [18] developed solutions for the advective dispersive transport of radionuclide chains subjected to linear equilibrium sorption. Explicit analytical solutions were presented for a three species problem involving distinct retardation factors for each species, for both impulse and decaying-band release boundary conditions. In addition, they also provided solutions for the case of no dispersion and for the case of identical retardation factors.

Harada et al. [13] published a research report presenting a general format for obtaining semi-analytical solutions to sequentially coupled one-dimensional reactive transport problems of arbitrary chain lengths subjected to arbitrary source release modes. However, one of the major limitations of the solution strategy was that, the semi-analytical solution for a given species in the chain required the computation of its entire predecessor species. This would result in computationally inefficient algorithms especially when analyzing transport problems involving long reactive chains. Harada et al. [13] and Higashi and Pigford [14] also provided explicit closed-form solutions for a set of purely advective (no dispersion) transport problems with various types of boundary conditions.

Gurehian and Jansen [12] presented an analytical solution to a transport problem involving a three member, first-order decay chain in a multi-layered system, subjected to advection, dispersion and linear equilibrium sorption processes for both continuous and band source release conditions. Convolution theorems and Laplace transform techniques were used to obtain semi-analytical solutions for the case involving both advective and dispersive transport and explicit closed-form analytical solutions for the case involving non-dispersive transport. van Genuchten [29] developed explicit analytical solutions to model a sequentially coupled four species transport problem governed by advection, dispersion and linear equilibrium sorption processes involving, first-order reactions. It was assumed that all the species had distinct retardation factors. One of the key contributions of this work is that it considered both Dirichlet and Cauchy boundary conditions. Furthermore, van Genuchten [29] developed a robust computer code (CHAIN) for implementing his analytical solution.

Angelakis et al. [2] developed a semi-analytical solution to a sequentially coupled two-species reactive transport problem governed by advection, dispersion and linear equilibrium sorption subjected to Dirichlet boundary condition. The transport problem assumed that the reactions were first-order and each of the species had different dispersion coefficients and distinct retardation factors. The authors also demonstrated that when the dispersion coefficients of both the species were equal, their solution reduced to the closed-form solution similar to the solutions presented by Cho [7] and Misra et al. [22]. Furthermore, the authors also provided solutions for the no dispersion (pure advection) case. Angelakis et al. [1] developed an interesting semi-analytical solution for a problem involving the coupled transport of two solutes and a gaseous product in soils. The solute migration was governed by advection, dispersion, linear equilibrium sorption and sequential first-order reaction, whereas the gas migration was governed by diffusive transport coupled with reversible linear equilibrium dissolution.

Lunn et al. [19] solved a three-species transport problem, which was similar to the Cho [7] problem, using the Fourier transform method. The authors demonstrated that the use of Fourier transforms enabled them to solve problems having non-zero initial conditions by solving two special case problems. Khandelwal and Rabideau [16] developed semi-analytical solutions for a three species, sequentially-coupled, first-order reactive transport problem. The key contribution of this work was that they addressed cases involving linear, non-equilibrium sorption mechanisms. Eykholt and Li [11] developed a solution method based on kinetic response functions to solve a linearly coupled non-sequential reactive transport problem having different retardation factors. Although, there was no restriction on the number of species in the system, this method required numerical procedures to evaluate the final solution. Furthermore, for the case of the non-ideal plug flow scenarios (advective dispersive transport), the accuracy of this method appears to decrease with decrease in Peclet number.

Sun et al. [26] developed a method that can solve multi-species advective dispersive transport equations coupled with sequential first-order reactions involving arbitrary number of species for different types of initial and boundary conditions. Their method was based on the use of a transformation format to uncouple the system of equations, which could then be solved analytically in the transformed domain. The final solutions are obtained by retransforming the solutions to the original domain. Later, Sun et al. [27] extended the transformation format to solve problems involving a combination of serial and parallel reactions. Clement [8] presented a more general and fundamental approach to derive the Sun et al. [27] solution by employing the similarity transformation method. The approach presented by Clement [8] can solve problems involving serial, parallel, converging, diverging and/or reversible first-order reaction network. However, all of these methods are only applicable for solving problems involving identical retardation factors.

Bauer et al. [4] presented a method to solve one-, two-, and three-dimensional sequentially coupled reactive transport problems with distinct retardation factors. This method was based on transforming the system of equations to a Laplace domain and then obtaining a set of fundamental solutions to each of the equations in the transformed domain. The specific solutions in the Laplace domain can then be obtained through a linear combination of the fundamental solutions. However, in order to accomplish this, the fundamental solutions must be linearly independent. Finally, the Laplace domain solutions can be transformed back to the time domain using the inverse Laplace transform procedure, which could be accomplished either analytically or numerically. Although this method can be applied to solve different types of boundary conditions, the solution procedure is mathematically tedious; specifically obtaining analytical inverse transform expressions for long chain lengths can be a challenge.

Montas [23] developed an analytical procedure to solve a three species, multi-dimensional transport problem coupled by a first-order, non-sequential reaction network subject to a pulse type boundary condition. This procedure involved obtaining a basis solution (of a convoluted form) for the transport equation and then evaluating the basis solution using Laplace transforms. One of the key advantages of this procedure is that it can model transport problems with distinct retardation factors. However, as mentioned earlier, this solution was limited to a three species system.

Quezada et al. [24] extended the approach given by Clement [8] and developed a method that can solve multi-species transport equations coupled with a network of first-order reactions involving distinct retardation factors. This method involves transforming the system of governing equations to a Laplace domain and then solving the transformed system of equations using the Clement [8] approach. The solutions in the Laplace domain are then retransformed to the time domain using an inverse Laplace transform procedure. One of the key limitations of this approach is that, except for a simple two species transport problem, the solutions presented by Quezada et al. [24] are in general semi-analytical since they require a numerical inverse Laplace transform routine to evaluate them.

Our literature review indicates that one-dimensional reactive transport equations coupled through sorption and sequential first-order reactions, have explicit closed-form analytical solutions only for short chains, up to four species. To model transport problems involving longer reaction chains, one has to either use semi-analytical solutions or purely numerical solutions. In this paper, we develop closed-form analytical solutions for the sequential decay problem involving arbitrary number of species subjected to a generic exponentially decaying Bateman-type source boundary, and spatially varying initial conditions.

2. Governing equations

Consider, a one-dimensional transport problem involving n sequentially decaying contaminants simultaneously subjected to advection, dispersion and linear equilibrium adsorption processes. The general governing equation for this transport problem can be expressed as

$$\begin{aligned} R_i\frac{\partial c_i(x,t)}{\partial t}+v\frac{\partial c_i(x,t)}{\partial x}-D_x\frac{\partial^2 c_i(x,t)}{\partial x^2} &= y_i k_{i-1}c_{i-1}(x,t)-k_ic_i(x,t); \quad \forall i=2,3,\ldots,n \\ &= -k_ic_i(x,t); \quad i=1; \\ &\quad \forall t>0 \quad \text{and} \quad 0<x<\infty \end{aligned} \tag{1}$$

where c_i is the concentration of species i [M L^{-3}]; R_i is the retardation coefficient of species i [–]; y_i is the effective yield factor that describes the mass of a species i produced from species $i-1$ [M M^{-1}]; k_i is the first-order decay rate constant of species i [T^{-1}]; v is the transport velocity [L T^{-1}] and D_x is the dispersion coefficient [L^2 T^{-1}]. Eq. (1) is solved for a generic exponentially distributed initial condition given by

$$c_i(x,0)=c_i^0 \mathrm{e}^{-\mu_i x}, \quad 0<x<\infty; \quad \forall i=1,2,\ldots,n \tag{2}$$

where c_i^0 is the initial source concentration of species i at the origin [M L^{-3}] and μ_i is the first-order decay parameter of the initial distribution of species i [L^{-1}]. The boundary condition at ∞ is given as

$$\frac{\partial c_i(\infty,t)}{\partial x}=0, \quad t>0; \quad \forall i=1,2,\ldots n \tag{3}$$

In the following sections, explicit solutions are developed for the two types of inlet (source) conditions involving the Dirichlet (Section 3) and the Cauchy (Section 4) boundaries.

3. Derivation of the solution for the Dirichlet boundary condition

For the case of the Dirichlet boundary condition, the source term is described as follows:

$$c_i(0,t)=\begin{cases} \sum\limits_{i_1=1}^{i} B_i^{i_1}\mathrm{e}^{-\lambda_{i_1}t}, & 0<t\leqslant t_0 \\ 0, t>t_0 \end{cases}; \quad \forall i=1,2,\ldots,n \tag{4}$$

where $B_i^{i_1}$ is the source boundary concentration of specie i_1 that contributes to species i [M L^{-3}] and λ_{i_1} is the first-order decay of the corresponding $B_i^{i_1}$ term [T^{-1}]. Eq. (4) can be conveniently re-written as

$$c_i(0,t) = \sum_{i_1=1}^{i} B_i^{i_1} \mathrm{e}^{-\lambda_{i_1} t}\{u(t) - u(t-t_0)\}, \quad t > 0; \quad \forall i = 1,2,\ldots,n$$

where u is the unit step function given by (5)

$$u(t-a) = \begin{cases} 0, & \text{if } t < a \\ 1, & \text{if } t \geqslant a \end{cases}$$

and 'a' is an arbitrary positive constant

The system of equations given by Eq. (1) can be written in a matrix format as [8,24]:

$$[R]\frac{\partial\{c\}}{\partial t} + v\frac{\partial\{c\}}{\partial x} - D_x\frac{\partial^2\{c\}}{\partial x^2} = [K]\{c\} \tag{6}$$

where [ ] denotes a square matrix and { } denotes a column vector. The corresponding initial and boundary conditions can be written as

$$\{c(x,0)\} = \{c^0\mathrm{e}^{-\mu x}\}, \quad 0 < x < \infty \tag{7}$$

$$\left\{\frac{\partial c(\infty,t)}{\partial x}\right\} = 0, \quad t > 0 \tag{8}$$

$$\{c(0,t)\} = \{\omega\}, \quad t > 0$$

$$\text{where } \omega_i = \sum_{i_1=1}^{i} B_i^{i_1}\mathrm{e}^{-\lambda_{i_1} t}\{u(t) - u(t-t_0)\}, \quad t > 0; \quad \forall i = 1,2,\ldots,n \tag{9}$$

The solution procedure used here is adopted from Quezada [24]. Applying Laplace transform to Eq. (6), we get:

$$[R]s\{p\} - [R]\{c(x,0)\} + v\frac{\mathrm{d}\{p\}}{\mathrm{d}x} - D_x\frac{\mathrm{d}^2\{p\}}{\mathrm{d}x^2} = [K]\{p\} \tag{10}$$

where s is the Laplace variable and p is the Laplace transformed concentration.

Substituting Eq. (7) in Eq. (10) and rearranging we get:

$$\frac{\mathrm{d}^2\{p\}}{\mathrm{d}x^2} - \left(\frac{v}{D_x}\right)\frac{\mathrm{d}\{p\}}{\mathrm{d}x} + \frac{1}{D_x}([K] - [R]s)\{p\} = \frac{-1}{D_x}[R]\{c^0\mathrm{e}^{-\mu x}\} \tag{11}$$

Now in order to uncouple the system of ordinary differential equations (ODEs) given by Eq. (11), we apply the linear transform procedure described by Clement [8] by performing the following matrix operation,

$$\{p\} = [A]\{b\} \tag{12}$$

where $\{b\}$ is the concentration in the doubly transformed domain and $[A]$ is an arbitrary square matrix of order n. Applying this transformation Eq. (11) gets modified as

$$\frac{\mathrm{d}^2[A]\{b\}}{\mathrm{d}x^2} - \left(\frac{v}{D_x}\right)\frac{\mathrm{d}[A]\{b\}}{\mathrm{d}x} + \frac{1}{D_x}([K] - [R]s)[A]\{b\} = \frac{-1}{D_x}[R]\{c^0\mathrm{e}^{-\mu x}\} \tag{13}$$

Pre-multiplying Eq. (13) with $[A]^{-1}$ we get:

$$\frac{\mathrm{d}^2\{b\}}{\mathrm{d}x^2} - \left(\frac{v}{D_x}\right)\frac{\mathrm{d}\{b\}}{\mathrm{d}x} + \frac{1}{D_x}[\widetilde{K}]\{b\} = \frac{-1}{D_x}\left\{\widetilde{C}\right\}$$

$$\text{where } [\widetilde{K}] = [A]^{-1}([K] - [R]s)[A] \quad \text{and } \left\{\widetilde{C}\right\} = [A]^{-1}[R]\{c^0\mathrm{e}^{-\mu x}\} \tag{14}$$

By forcing the columns of the $[A]$ matrix as the eigenvectors of the combined reaction coefficient matrix $\langle [K] - [R]s\rangle$ we can make the $[\widetilde{K}]$ matrix a diagonal matrix and thus uncouple the system of equations; the details of this similarity transformation procedure are illustrated in Clement [8]. The corresponding $[A]$ matrix is

$$[A] = \left[\begin{array}{l} \prod\limits_{i=2}^{n} \frac{-(k_1+sR_1-k_i-sR_i)}{y_i k_{i-1}}, 0, 0, \ldots \\ \prod\limits_{i=3}^{n} \frac{-(k_1+sR_1-k_i-sR_i)}{y_i k_{i-1}}, \prod\limits_{i=3}^{n} \frac{-(k_2+sR_2-k_i-sR_i)}{y_i k_{i-1}}, 0, 0, \ldots \\ \cdot \\ \cdot \\ \prod\limits_{i=n}^{n} \frac{-(k_1+sR_1-k_i-sR_i)}{y_i k_{i-1}}, \prod\limits_{i=n}^{n} \frac{-(k_2+sR_2-k_i-sR_i)}{y_i k_{i-1}}, \ldots, \prod\limits_{i=n}^{n} \frac{-(k_{n-1}+sR_{n-1}-k_i-sR_i)}{y_i k_{i-1}}, 0 \\ 1, 1, \ldots \end{array}\right] \tag{15}$$

The $[A]^{-1}$ matrix is

$$[A]^{-1} = \left[\begin{array}{l} \frac{\prod_{i=2}^{n} y_i k_{i-1}}{\prod_{i=1,(i\neq 1)}^{n} -(k_1+sR_1-k_i-sR_i)}, 0, 0, \ldots \\ \frac{\prod_{i=2}^{n} y_i k_{i-1}}{\prod_{i=1,(i\neq 2)}^{n} -(k_2+sR_2-k_i-sR_i)}, \frac{\prod_{i=3}^{n} y_i k_{i-1}}{\prod_{i=2,(i\neq 2)}^{n} -(k_2+sR_2-k_i-sR_i)}, 0, 0, \ldots \\ \cdot \\ \cdot \\ \frac{\prod_{i=2}^{n} y_i k_{i-1}}{\prod_{i=1,(i\neq n)}^{n} -(k_n+sR_n-k_i-sR_i)}, \frac{\prod_{i=3}^{n} y_i k_{i-1}}{\prod_{i=2,(i\neq n)}^{n} -(k_n+sR_n-k_i-sR_i)}, \ldots, \frac{\prod_{i=n}^{n} y_i k_{i-1}}{\prod_{i=n-1,(i\neq n)}^{n} -(k_n+sR_n-k_i-sR_i)}, 1 \end{array}\right] \tag{16}$$

The corresponding $[\widetilde{K}]$ matrix is

$$[\widetilde{K}] = \left[\begin{array}{l} -k_1 - sR_1, 0, 0, \ldots \\ 0, -k_2 - sR_2, 0, 0, \ldots \\ \cdot \\ \cdot \\ \cdot \\ 0, 0, \ldots (n-1)\text{entries}, -k_n - sR_n \end{array}\right] \tag{17}$$

The corresponding $\{\widetilde{C}\}$ vector is

$$\left\{\widetilde{C}\right\} = \left\{\begin{array}{l} \frac{R_1 c_1^0 \mathrm{e}^{-\mu_1 x} \prod_{i=2}^{n} y_i k_{i-1}}{\prod_{i=1,(i\neq 1)}^{n} -(k_1+sR_1-k_i-sR_i)} \\ \frac{R_1 c_1^0 \mathrm{e}^{-\mu_1 x} \prod_{i=2}^{n} y_i k_{i-1}}{\prod_{i=1,(i\neq 2)}^{n} -(k_2+sR_2-k_i-sR_i)} + \frac{R_2 c_2^0 \mathrm{e}^{-\mu_2 x} \prod_{i=3}^{n} y_i k_{i-1}}{\prod_{i=2,(i\neq 2)}^{n} -(k_2+sR_2-k_i-sR_i)} \\ \cdot \\ \cdot \\ \frac{R_1 c_1^0 \mathrm{e}^{-\mu_1 x} \prod_{i=2}^{n} y_i k_{i-1}}{\prod_{i=1,(i\neq n)}^{n} -(k_n+sR_n-k_i-sR_i)} + \frac{R_2 c_2^0 \mathrm{e}^{-\mu_2 x} \prod_{i=3}^{n} y_i k_{i-1}}{\prod_{i=2,(i\neq n)}^{n} -(k_n+sR_n-k_i-sR_i)} + \ldots + R_n c_n^0 \mathrm{e}^{-\mu_n x} \end{array}\right\} \tag{18}$$

The explicit expression for $\widetilde{C}_i$ in Eq. (18) is

$$\widetilde{C}_i = \sum_{i_1=1}^{i} \left[\frac{R_{i_1} c_{i_1}^0 \mathrm{e}^{-\mu_{i_1} x} \prod_{i_2=i_1+1}^{n} y_{i_2} k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n} - (k_i + sR_i - k_{i_2} - sR_{i_2})} \right]; \quad \forall i = 1, 2, \ldots, n \tag{19}$$

Eq. (14) describes a set of n independent second-order non-homogeneous ODEs the boundary conditions of which are obtained by performing Laplace and linear transforms of the boundary conditions given by Eqs. (8) and (9). Laplace transform of Eqs. (8) and (9) yields:

$$\left\{\frac{\mathrm{d}p(\infty, s)}{\mathrm{d}x}\right\} = 0 \tag{20}$$

$$\{p(0, s)\} = \{\xi\}$$

$$\text{where } \xi_i = \sum_{i_1=1}^{i} \frac{B_i^{i_1}\{1 - \mathrm{e}^{-t_0(s+\lambda_{i_1})}\}}{(s + \lambda_{i_1})}; \quad \forall i = 1, 2, \ldots, n \tag{21}$$

To transform the boundary conditions from p domain to the b domain, we apply the linear transform given by Eq. (12). This yields:

$$\left\{\frac{\mathrm{d}b(\infty,s)}{\mathrm{d}x}\right\}=0 \tag{22}$$

$$\{b(0,s)\}=[A]^{-1}\{\xi\} \tag{23}$$

The explicit expression for $b_i(0,s)$ in Eq. (23) is given as

$$b_i(0,s)=\sum_{i_1=1}^{i}\left[\frac{\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\sum_{i_2=1}^{i_1}\frac{B_{i_1}^{i_2}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_2})}\}}{(s+\lambda_{i_2})}\right];\quad \forall i=1,2,\ldots,n \tag{24}$$

Since Eq. (14) is uncoupled, it can now be written as a set of n independent equations as

$$\frac{\mathrm{d}^2b_i(x,s)}{\mathrm{d}x^2}-\left(\frac{v}{D_x}\right)\frac{\mathrm{d}b_i(x,s)}{\mathrm{d}x}+\frac{1}{D_x}(-k_i-sR_i)b_i(x,s)=\frac{-1}{D_x}\sum_{i_1=1}^{i}\left[\frac{R_{i_1}c_{i_1}^0\mathrm{e}^{-\mu_{i_1}x}\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\right];\quad \forall i=1,2,\ldots,n \tag{25}$$

The general solution to Eq. (25) is given as

$$b_i(x,s)=b_i^{\mathrm{h}}(x,s)+b_i^{\mathrm{p}}(x,s);\quad \forall i=1,2,\ldots n \tag{26}$$

where $b_i^{\mathrm{h}}(x,s)$ is the general solution of the homogeneous part of Eq. (25) and $b_i^{\mathrm{p}}(x,s)$ is a particular solution of Eq. (25). The general solution $b_i^{\mathrm{h}}(x,s)$ can be readily obtained as

$$b_i^{\mathrm{h}}(x,s)=\Psi_i^1\mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}+\sqrt{\frac{v^2}{D_x^2}+\frac{4(k_i+sR_i)}{D_x}}\right\}\right]}+\Psi_i^2\mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}-\sqrt{\frac{v^2}{D_x^2}+\frac{4(k_i+sR_i)}{D_x}}\right\}\right]};\quad \forall i=1,2,\ldots,n \tag{27}$$

where Ψ_i^1 and Ψ_i^2 are constants. The particular solution $b_i^{\mathrm{p}}(x,s)$ is obtained by using the method of undetermined coefficients. The general form of the particular solution is given as

$$b_i^{\mathrm{p}}(x,s)=\frac{-1}{D_x}\sum_{i_1=1}^{i}\left[\frac{M_{i_1}R_{i_1}c_{i_1}^0\mathrm{e}^{-\mu_{i_1}x}\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\right];\quad \forall i=1,2,\ldots n \tag{28}$$

where M_{i_1} is a constant. Substituting Eq. (28) in the governing Eq. (25) and simplifying, we evaluate the constant M_{i_1} as

$$M_{i_1}=\frac{D_x}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_i-sR_i)};\quad \forall i=1,2,\ldots,n \tag{29}$$

Substituting the values of M_{i_1} into Eq. (28) we get the particular solution $b_i^{\mathrm{p}}(x,s)$ to Eq. (25) as

$$b_i^{\mathrm{p}}(x,s)=-\sum_{i_1=1}^{i}\left[\frac{R_{i_1}c_{i_1}^0\mathrm{e}^{-\mu_{i_1}x}\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_i-sR_i)\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\right];\quad \forall i=1,2,\ldots,n \tag{30}$$

Substituting Eqs. (27) and (30) in Eq. (26), we get the general solution to Eq. (25) as

$$\begin{aligned}b_i(x,s)={}&\Psi_i^1\mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}+\sqrt{\frac{v^2}{D_x^2}+\frac{4(k_i+sR_i)}{D_x}}\right\}\right]}+\Psi_i^2\mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}-\sqrt{\frac{v^2}{D_x^2}+\frac{4(k_i+sR_i)}{D_x}}\right\}\right]}\\&-\sum_{i_1=1}^{i}\left[\frac{R_{i_1}c_{i_1}^0\mathrm{e}^{-\mu_{i_1}x}\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_i-sR_i)\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\right];\quad \forall i=1,2,\ldots,n\end{aligned} \tag{31}$$

In order to apply the boundary condition given by Eq. (22), we differentiate the general solution with respect to x. Differentiation of Eq. (31) with respect to x yields:

$$\begin{aligned}\frac{\mathrm{d}b_i(x,s)}{\mathrm{d}x}={}&\Psi_i^1\left[\frac{1}{2}\left\{\frac{v}{D_x}+\sqrt{\frac{v^2}{D_x^2}+\frac{4(k_i+sR_i)}{D_x}}\right\}\right]\mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}+\sqrt{\frac{v^2}{D_x^2}+\frac{4(k_i+sR_i)}{D_x}}\right\}\right]}+\Psi_i^2\left[\frac{1}{2}\left\{\frac{v}{D_x}-\sqrt{\frac{v^2}{D_x^2}+\frac{4(k_i+sR_i)}{D_x}}\right\}\right]\\&\times\mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}-\sqrt{\frac{v^2}{D_x^2}+\frac{4(k_i+sR_i)}{D_x}}\right\}\right]}-\sum_{i_1=1}^{i}\left[\frac{(-\mu_{i_1})R_{i_1}c_{i_1}^0\mathrm{e}^{-\mu_{i_1}x}\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_i-sR_i)\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\right];\quad \forall i=1,2,\ldots,n\end{aligned} \tag{32}$$

To satisfy the boundary condition given by Eq. (22), i.e. when x tends to ∞; the exponential function in the first term tends to ∞, hence Ψ_i^1 must vanish. Eq. (32) now reduces to

$$b_i(x,s)=\Psi_i^2 \mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}-\sqrt{\frac{v^2}{D_x^2}+\frac{4(k_i+sR_i)}{D_x}}\right\}\right]}-\sum_{i_1=1}^{i}\left[\frac{R_{i_1}c_{i_1}^0\mathrm{e}^{-\mu_{i_1}x}\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_i-sR_i)\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\right];\quad \forall i=1,2,\ldots,n \tag{33}$$

Applying the second boundary condition given by Eq. (24), we get:

$$\begin{aligned}\Psi_i^2=&\sum_{i_1=1}^{i}\left[\frac{\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\sum_{i_2=1}^{i_1}\frac{B_{i_1}^{i_2}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_2})}\}}{(s+\lambda_{i_2})}\right]\\&+\sum_{i_1=1}^{i}\left[\frac{R_{i_1}c_{i_1}^0\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_i-sR_i)\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\right];\quad \forall i=1,2,\ldots,n\end{aligned} \tag{34}$$

Therefore, the solution in the b domain is

$$\begin{aligned}b_i(x,s)=&\sum_{i_1=1}^{i}\left[\frac{\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\sum_{i_2=1}^{i_1}\frac{B_{i_1}^{i_2}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_2})}\}}{(s+\lambda_{i_2})}\right]\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_i+sR_i)}\right\}\right]}\\&+\sum_{i_1=1}^{i}\left[\frac{R_{i_1}c_{i_1}^0\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_i+sR_i)}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_i-sR_i)\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\right];\quad \forall i=1,2,\ldots n\end{aligned} \tag{35}$$

Inverse linear transform of Eq. (35) is done to obtain the solution in the Laplace domain (p domain) by using Eq. (12). The solution given by Eq. (35) can be split into two parts and represented as

$$b_i(x,s)=b_i^1(x,s)+b_i^2(x,s)$$

where

$$\begin{aligned}b_i^1(x,s)=&\sum_{i_1=1}^{i}\left[\frac{\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\sum_{i_2=1}^{i_1}\frac{B_{i_1}^{i_2}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_2})}\}}{(s+\lambda_{i_2})}\right]\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_i+sR_i)}\right\}\right]}\\b_i^2(x,s)=&\sum_{i_1=1}^{i}\left[\frac{R_{i_1}c_{i_1}^0\prod_{i_2=i_1+1}^{n}y_{i_2}k_{i_2-1}\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_i+sR_i)}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_i-sR_i)\prod_{i_2=i_1,(i_2\neq i)}^{n}-(k_i+sR_i-k_{i_2}-sR_{i_2})}\right];\quad \forall i=1,2,\ldots n\end{aligned} \tag{36}$$

Using the distributive property of matrix addition, we can apply the inverse linear transform to each of the individual terms and then sum them to get the solution in the p domain. This is expressed as

$$\{p\}=[A]\{b\}=[A]\{b^1\}[A]\{b^2\} \tag{37}$$

The first term $[A]\{b^1\}$ can be evaluated as

$$\{p^1\}=[A]\{b^1\} \tag{38}$$

The explicit expression for $p_i^1(x,s)$ in Eq. (38) is given as

$$p_i^1(x,s)=\sum_{i_1=1}^{i}\left[\left(\prod_{i_2=i_1+1}^{i}y_{i_2}k_{i_2-1}\right)\sum_{i_2=1}^{i_1}\frac{B_{i_1}^{i_2}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_2})}\}}{(s+\lambda_{i_2})}\sum_{i_2=i_1}^{i}\frac{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}}{\prod_{i_3=i_1,(i_3\neq i_2)}^{i}-(k_{i_2}+sR_{i_2}-k_{i_3}-sR_{i_3})}\right];\quad \forall i=1,2,\ldots n \tag{39}$$

Using a similar approach the second term $[A]\{b^2\}$ is evaluated and the explicit expression for $p_i^2(x,s)$ is

$$p_i^2(x,s)=\sum_{i_1=1}^{i}\left[R_{i_1}c_{i_1}^0\left(\prod_{i_2=i_1+1}^{i}y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\frac{\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_{i_2}-sR_{i_2})\prod_{i_3=i_1,(i_3\neq i_2)}^{i}-(k_{i_2}+sR_{i_2}-k_{i_3}-sR_{i_3})}\right];\quad \forall i=1,2,\ldots,n \tag{40}$$

Substituting Eqs. (39) and (40) into Eq. (37) we get the solution in the Laplace domain as

$$
\begin{aligned}
p_i(x,s) = p_i^1(x,s) + p_i^2(x,s) = {} & \sum_{i_1=1}^{i}\left[\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=1}^{i_1}\frac{B_{i_1}^{i_2}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_2})}\}}{(s+\lambda_{i_2})}\sum_{i_2=i_1}^{i}\frac{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}}{\prod_{i_3=i_1,(i_3\neq i_2)}^{i}-(k_{i_2}+sR_{i_2}-k_{i_3}-sR_{i_3})}\right] \\
& + \sum_{i_1=1}^{i}\left[R_{i_1}c_{i_1}^0\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\frac{\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_{i_2}-sR_{i_2})\prod_{i_3=i_1,(i_3\neq i_2)}^{i}-(k_{i_2}+sR_{i_2}-k_{i_3}-sR_{i_3})}\right]; \\
& \forall i = 1,2,\ldots n
\end{aligned}
\tag{41}
$$

The final solution is obtained by taking an inverse Laplace transform of the solution given by Eq. (41). Inverse Laplace transform is performed as follows:

$$
c_i(x,t) = c_i^1(x,t) + c_i^2(x,t) = \mathscr{L}^{-1}\langle p_i^1(x,s)+p_i^2(x,s)\rangle = \mathscr{L}^{-1}\langle p_i^1(x,s)\rangle + \mathscr{L}^{-1}\langle p_i^2(x,s)\rangle; \quad \forall i = 1,2,\ldots n
\tag{42}
$$

In Appendix A, the terms $\mathscr{L}^{-1}\langle p_i^1(x,s)\rangle$ and $\mathscr{L}^{-1}\langle p_i^2(x,s)\rangle$ are evaluated. Substituting Eqs. (A.7) and (A.16) in Eq. (42) we obtain the final solution in the time domain as

$$
\begin{aligned}
c_i(x,t) = {} & \sum_{i_1=1}^{i}\left[\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\sum_{i_3=1}^{i_1}\{G_1^1+h(G_1^1)G_2^1\}\right] + \sum_{i_1=1}^{i}\left[R_{i_1}c_{i_1}^0\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\{G_1^2+h(G_1^2)G_2^2\}\right]; \\
& \forall i = 1,2,\ldots n \\
& \text{where } h(M) = \begin{cases} 1, & \text{if } M \text{ loop is not executed} \\ 0, & \text{if } M \text{ loop is executed} \end{cases}
\end{aligned}
\tag{43}
$$

where the G terms are defined as (See Eqs. (A.7) and (A.16) in Appendix A).

$$
\begin{aligned}
G_1^1 &= \sum_{i_4=i_1,(i_4\neq i_2,R_{i_4}\neq R_{i_2})}^{i}\frac{B_{i_1}^{i_3}\left\langle\begin{array}{l} F_{i_2,i_3,0}[x,t]-u(t-t_0)\mathrm{e}^{(-\lambda_{i_3}t_0)}F_{i_2,i_3,0}[x,(t-t_0)] \\ -F_{i_2,i_2,i_4}[x,t]+u(t-t_0)\mathrm{e}^{(-\lambda_{i_3}t_0)}F_{i_2,i_2,i_4}[x,(t-t_0)] \end{array}\right\rangle}{(a_{i_2,i_4}-\lambda_{i_3})\left(\prod_{i_5=i_1,(i_5\neq i_2,R_{i_5}=R_{i_2})}^{i}-k_{i_2,i_5}\right)(-R_{i_2,i_4})\prod_{i_5=i_1,(i_5\neq i_2,i_5\neq i_4,R_{i_5}\neq R_{i_2})}^{i}-R_{i_2,i_5}(a_{i_2,i_5}-a_{i_2,i_4})} \\
G_2^1 &= \frac{B_{i_1}^{i_3}\langle F_{i_2,i_3,0}[x,t]-u(t-t_0)\mathrm{e}^{(-\lambda_{i_3}t_0)}F_{i_2,i_3,0}[x,(t-t_0)]\rangle}{\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i}-k_{i_2,i_4}} \\
G_1^2 &= \sum_{i_3=i_1,(i_3\neq i_2,R_{i_3}\neq R_{i_2})}^{i}\frac{\langle F_{i_2,i_1,-i_2}[x,t]-\mathrm{e}^{(-\mu_{i_1}x-a_{i_1,-i_2}t)}-F_{i_2,i_2,i_3}[x,t]+\mathrm{e}^{(-\mu_{i_1}x-a_{i_2,i_3}t)}\rangle}{(a_{i_2,i_3}-a_{i_1,-i_2})R_{i_2}\left(\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i}-k_{i_2,i_4}\right)R_{i_2,i_3}\prod_{i_4=i_1,(i_4\neq i_2,i_4\neq i_3,R_{i_4}\neq R_{i_2})}^{i}-R_{i_2,i_4}(a_{i_2,i_4}-a_{i_2,i_3})} \\
G_2^2 &= \frac{-\langle F_{i_2,i_1,-i_2}[x,t]-\mathrm{e}^{(-\mu_{i_1}x-a_{i_1,-i_2}t)}\rangle}{R_{i_2}\prod_{i_3=i_1,(i_3\neq i_2,R_{i_3}=R_{i_2})}^{i}-k_{i_2,i_3}}
\end{aligned}
\tag{44}
$$

where the term F_{i_1,i_2,i_3} is given by (See Eq. (B.8) in Appendix B):

$$
\begin{aligned}
F_{i_1,i_2,i_3}[x,t] &= \frac{\mathrm{e}^{-a_{i_2,i_3}t}\mathrm{e}^{\frac{xv}{2D_x}}}{2}\left[\mathrm{e}^{\frac{-x\omega_{i_1,i_2,i_3}}{2D_x}}\mathrm{erfc}\left\{\frac{R_{i_1}x-\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}+\mathrm{e}^{\frac{x\omega_{i_1,i_2,i_3}}{2D_x}}\mathrm{erfc}\left\{\frac{R_{i_1}x+\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}\right] \\
\text{where } \omega_{i_1,i_2,i_3} &= \sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}
\end{aligned}
\tag{45}
$$

The above expression for F_{i_1,i_2,i_3} is valid only for real values of ω_{i_1,i_2,i_3}. For problems involving complex values for ω_{i_1,i_2,i_3} the F_{i_1,i_2,i_3} term is given as (See Eq. (B.14) in Appendix B):

$$
\begin{aligned}
F_{i_1,i_2,i_3}[x,t] &= \mathrm{e}^{-a_{i_2,i_3}t}\mathrm{e}^{\frac{xv}{2D_x}}\left[A\cos\left(\frac{x\omega_{i_1,i_2,i_3}^*}{2D_x}\right)-B\sin\left(\frac{x\omega_{i_1,i_2,i_3}^*}{2D_x}\right)\right] \\
\text{where } \omega_{i_1,i_2,i_3}^* &= \sqrt{\left|v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)\right|} \text{ and } (A+iB) = \mathrm{erfc}\left\{\frac{R_{i_1}x+i\omega_{i_1,i_2,i_3}^*t}{2\sqrt{R_{i_1}D_xt}}\right\}
\end{aligned}
\tag{46}
$$

4. Derivation of the analytical solution for the Cauchy boundary condition

For the case of the Cauchy boundary condition, the source term is described as follows:

$$-D_x\frac{\partial c_i(0,t)}{\partial x}+vc_i(0,t)=\begin{cases}\sum\limits_{i_1=1}^{i}B_i^{i_1}v\mathrm{e}^{-\lambda_{i_1}t}, & 0<t\leqslant t_0;\quad \forall i=1,2,\ldots,n\\ 0, \quad t>t_0\end{cases} \tag{47}$$

Eq. (47) can be conveniently re-written as

$$-D_x\frac{\partial c_i(0,t)}{\partial x}+vc_i(0,t)=\sum_{i_1=1}^{i}B_i^{i_1}v\mathrm{e}^{-\lambda_{i_1}t}\{u(t)-u(t-t_0)\},\quad t>0;\quad \forall i=1,2,\ldots,n$$

where u is the unit step function given by

$$u(t-a)=\begin{cases}0, & \text{if } t<a\\ 1, & \text{if } t\geqslant a\end{cases} \tag{48}$$

and‘a’ is an arbitrary positive constant

Note that the governing equations, initial conditions and the boundary condition at ∞ for the Cauchy boundary are identical to the Dirichlet boundary. Furthermore, the boundary conditions at the source for both these boundaries share a similar structure. Due to this structural similarity, the solution procedures for the Cauchy boundary will be analogous to that of the Dirichlet boundary. The details of the solution derivation are presented in the supplementary section. The final solution for the Cauchy boundary can also be represented by Eq. (43). However, the terms G associated with the Cauchy boundary are defined as (See (S2.6) and (S2.13) in supplementary section S2):

$$\begin{aligned}
G_1^1&=\sum_{i_4=i_1,(i_4\neq i_2,R_{i_4}\neq R_{i_2})}^{i}\frac{B_{i_1}^{i_3}\left\langle F_{i_2,i_3,0}[x,t]-u(t-t_0)\mathrm{e}^{(-\lambda_{i_3}t_0)}F_{i_2,i_3,0}[x,(t-t_0)]-F_{i_2,i_2,i_4}[x,t]+u(t-t_0)\mathrm{e}^{(-\lambda_{i_3}t_0)}F_{i_2,i_2,i_4}[x,(t-t_0)]\right\rangle}{(a_{i_2,i_4}-\lambda_{i_3})\left(\prod_{i_5=i_1,(i_5\neq i_2,R_{i_5}=R_{i_2})}^{i}-k_{i_2,i_5}\right)(-R_{i_2,i_4})\prod_{i_5=i_1,(i_5\neq i_2,i_5\neq i_4,R_{i_5}\neq R_{i_2})}^{i}-R_{i_2,i_5}(a_{i_2,i_5}-a_{i_2,i_4})}\\
G_2^1&=\frac{B_{i_1}^{i_3}\left\langle F_{i_2,i_3,0}[x,t]-u(t-t_0)\mathrm{e}^{(-\lambda_{i_3}t_0)}F_{i_2,i_3,0}[x,(t-t_0)]\right\rangle}{\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i}-k_{i_2,i_4}}\\
G_1^2&=\sum_{i_3=i_1,(i_3\neq i_2,R_{i_3}\neq R_{i_2})}^{i}\frac{\left\langle\left(1+\frac{\mu_{i_1}D_x}{v}\right)F_{i_2,i_1,-i_2}[x,t]-\mathrm{e}^{(-\mu_{i_1}x-a_{i_1,-i_2}t)}-\left(1+\frac{\mu_{i_1}D_x}{v}\right)F_{i_2,i_2,i_3}[x,t]+\mathrm{e}^{(-\mu_{i_1}x-a_{i_2,i_3}t)}\right\rangle}{(a_{i_2,i_3}-a_{i_1,-i_2})R_{i_2}\left(\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i}-k_{i_2,i_4}\right)R_{i_2,i_3}\prod_{i_4=i_1,(i_4\neq i_2,i_4\neq i_3,R_{i_4}\neq R_{i_2})}^{i}-R_{i_2,i_4}(a_{i_2,i_4}-a_{i_2,i_3})}\\
G_2^2&=\frac{-\left\langle\left(1+\frac{\mu_{i_1}D_x}{v}\right)F_{i_2,i_1,-i_2}[x,t]-\mathrm{e}^{(-\mu_{i_1}x-a_{i_1,-i_2}t)}\right\rangle}{R_{i_2}\prod_{i_3=i_1,(i_3\neq i_2,R_{i_3}=R_{i_2})}^{i}-k_{i_2,i_3}}
\end{aligned} \tag{49}$$

where the term F_{i_1,i_2,i_3} is given by (see (S3.20) in supplementary section S3):

$$\begin{aligned}
F_{i_1,i_2,i_3}[x,t]&=v\mathrm{e}^{-a_{i_2,i_3}t}\mathrm{e}^{\frac{xv}{2D_x}}\left[\frac{\mathrm{e}^{\frac{-x\omega_{i_1,i_2,i_3}}{2D_x}}}{(v+\omega_{i_1,i_2,i_3})}\mathrm{erfc}\left\{\frac{R_{i_1}x-\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}+\frac{\mathrm{e}^{\frac{x\omega_{i_1,i_2,i_3}}{2D_x}}}{(v-\omega_{i_1,i_2,i_3})}\mathrm{erfc}\left\{\frac{R_{i_1}x+\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}\right]\\
&\quad+\frac{2v^2}{(\omega_{i_1,i_2,i_3}^2-v^2)}\mathrm{e}^{\left[\frac{xv}{D_x}-\frac{k_{i_1}t}{R_{i_1}}\right]}\mathrm{erfc}\left\{\frac{R_{i_1}x+vt}{2\sqrt{R_{i_1}D_xt}}\right\};\\
&\text{when } \frac{k_{i_1}}{R_{i_1}}\neq a_{i_2,i_3},\quad \text{and } =\mathrm{e}^{\frac{-k_{i_1}t}{R_{i_1}}}\left[\frac{1}{2}\mathrm{erfc}\left(\frac{R_{i_1}x-vt}{2\sqrt{R_{i_1}D_xt}}\right)+\sqrt{\frac{v^2t}{\pi R_{i_1}D_x}}\mathrm{e}^{\frac{-(R_{i_1}x-vt)^2}{4R_{i_1}D_xt}}-\frac{1}{2}\left(1+\frac{xv}{D_x}+\frac{v^2t}{R_{i_1}D_x}\right)\mathrm{e}^{\frac{xv}{D_x}}\mathrm{erfc}\left(\frac{R_{i_1}x+vt}{2\sqrt{R_{i_1}D_xt}}\right)\right];\\
&\text{when } \frac{k_{i_1}}{R_{i_1}}=a_{i_2,i_3}\quad \text{and } \omega_{i_1,i_2,i_3}=\sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}
\end{aligned} \tag{50}$$

The above expression for F_{i_1,i_2,i_3} is valid only for real values of ω_{i_1,i_2,i_3}. For problems involving complex values for ω_{i_1,i_2,i_3} in the case when $\frac{k_{i_1}}{R_{i_1}}\neq a_{i_2,i_3}$ the F_{i_1,i_2,i_3} term is given as (See (S3.26) in supplementary section S3):

$$F_{i_1,i_2,i_3}[x,t] = \frac{2v}{(v^2+\omega^{*2}_{i_1,i_2,i_3})}\mathrm{e}^{-a_{i_2,i_3}t}\mathrm{e}^{\frac{xv}{2D_x}}\left[\begin{array}{l}(Av - B\omega^*_{i_1,i_2,i_3})\cos\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right)\\ -(A\omega^*_{i_1,i_2,i_3}+Bv)\sin\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right)\end{array}\right] + \frac{v^2}{2R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}} - a_{i_2,i_3}\right)}\mathrm{e}^{\left[\frac{xv}{D_x}-\frac{k_{i_1}t}{R_{i_1}}\right]}\operatorname{erfc}\left\{\frac{R_{i_1}x+vt}{2\sqrt{R_{i_1}D_xt}}\right\}$$

$$\text{where } \omega^*_{i_1,i_2,i_3} = \sqrt{\left|v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}} - a_{i_2,i_3}\right)\right|} \quad \text{and } (A+iB) = \operatorname{erfc}\left\{\frac{R_{i_1}x + i\omega^*_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\} \tag{51}$$

Note: when $\frac{k_{i_1}}{R_{i_1}} = a_{i_2,i_3}$ the F_{i_1,i_2,i_3} terms are unchanged.

Eq. (43) along with Eqs. (44)–(46) and Eqs. (49)–(51) give the complete explicit general solutions to the transport problem described by Eq. (1) subject to the initial condition given by Eq. (2) and the boundary condition at ∞ given by Eq. (3) for the Dirichlet and the Cauchy source boundaries given by Eqs. (4) and (47), respectively.

5. Discussions

In the original governing equation given by Eq. (1), it was assumed that the degradation occurs in the liquid phase only. However, in several practical contaminant transport scenarios (e.g, radioactive transport), decay would occur in both the liquid and solid phases. Under this condition the governing equation should be modified as

$$\begin{aligned} R_i\frac{\partial c_i(x,t)}{\partial t} + v\frac{\partial c_i(x,t)}{\partial x} - D_x\frac{\partial^2 c_i(x,t)}{\partial x^2} &= y_iR_{i-1}k_{i-1}c_{i-1}(x,t) - R_ik_ic_i(x,t); \quad \forall i = 2,3,\ldots,n\\ &= -R_ik_ic_i(x,t); \quad i=1;\\ &\forall t>0 \quad \text{and} \quad 0<x<\infty \end{aligned} \tag{52}$$

Note the additional parameters in the right side of Eq. (52). The solution to the above equation can be readily obtained from the previous solution given by Eq. (43) by substituting the value of k with Rk.

From Sections 3 and 4, it can be seen that the solutions for the Dirichlet and the Cauchy boundaries share a common structure. However, careful observation indicates that the G_1^2 and G_2^2 terms for the Dirichlet boundary (see Eq. (44)) and the Cauchy Boundary (see Eq. (49)) are different. Furthermore, from Eqs. (45) and (46) and Eqs. (50) and (51) it can be observed that the F_{i_1,i_2,i_3} terms involved in the G terms are distinctly different for the two boundary conditions.

It must be noted that the general solution is presented in a format which enables us to directly obtain explicit solutions for any of the species in the chain without involving the computations of its parent chain members. This unique feature makes the general solution computationally efficient. The solutions previously published in the literature have either been restricted to small chain lengths or have been semi analytical solutions for longer chain lengths. The solutions derived in this study overcome both these difficulties. In part II of this two part article, we derive several simpler analytical solutions for specialized transport problems and also develop and test a computer algorithm for implementing these solutions [25].

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Appendix A

The first term $\mathscr{L}^{-1}\langle p_i^1(x,s)\rangle$ can be evaluated as follows. From Eqs. (41) and (42) we get:

$$c_i^1(x,t) = \mathscr{L}^{-1}\langle p_i^1(x,s)\rangle = \mathscr{L}^{-1}\left\langle\sum_{i_1=1}^{i}\left[\left(\prod\nolimits_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=1}^{i_1}\frac{B_{i_1}^{i_2}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_2})}\}}{(s+\lambda_{i_2})}\sum_{i_2=i_1}^{i}\frac{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}}{\prod\nolimits_{i_3=i_1,(i_3\neq i_2)}^{i} - \left(k_{i_2}+sR_{i_2}-k_{i_3}-sR_{i_3}\right)}\right]\right\rangle;$$

$$\forall i = 1,2,\ldots n \tag{A.1}$$

Eq. (A.1) can be rewritten as

$$c_i^1(x,t) = \mathscr{L}^{-1}\left\langle\sum_{i_1=1}^{i}\left[\left(\prod\nolimits_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\sum_{i_3=1}^{i_1}\frac{B_{i_1}^{i_3}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_3})}\}\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}}{(s+a_{i_3,0})\prod\nolimits_{i_4=i_1,(i_4\neq i_2)}^{i} - R_{i_2,i_4}(s+a_{i_2,i_4})}\right]\right\rangle; \quad \forall i = 1,2,\ldots,n$$

$$\text{where } k_{i_1,i_2} = k_{i_1} - k_{i_2}, R_{i_1,i_2} = R_{i_1} - R_{i_2} \quad \text{and } a_{i_1,i_2} = \begin{cases}\frac{k_{i_1,i_2}}{R_{i_1,i_2}}; & \text{when } i_2>0\\ \lambda_{i_1}; & \text{when } i_2 = 0\end{cases} \tag{A.2}$$

It must be noted that for Eq. (A.2) to be valid the condition $R_{i_2,i_4} \neq 0$ must be satisfied. This means that no two species in the transport problem can have identical retardation factors. However, in practice, we do have situations where the retardation factors of some of the species are equal [7]. To overcome this limitation, we reformulate Eq. (A.2) to accommodate a generic case when the transport problem has any number of sets of species having any number of species with identical retardation factors. Incorporating this special case scenario, Eq. (A.2) is reformulated as

$$c_i^1(x,t)=\mathscr{L}^{-1}\left\langle\sum_{i_1=1}^{i}\left[\left(\prod\nolimits_{i_2=i_1+1}^{i}y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\sum_{i_3=1}^{i_1}\frac{B_{i_1}^{i_3}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_3})}\}\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}}{(s+a_{i_3,0})\left(\prod\nolimits_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i}-k_{i_2,i_4}\right)\prod\nolimits_{i_4=i_1,(i_4\neq i_2,R_{i_4}\neq R_{i_2})}^{i}-R_{i_2,i_4}(s+a_{i_2,i_4})}\right]\right\rangle;$$

$$\forall i=1,2,\ldots n \tag{A.3}$$

Note that in Eq. (A.3) the condition $k_{i_2,i_4} \neq 0$ must be satisfied for the solution to be determinate. Factorization of Eq. (A.3) gives:

$$c_i^1(x,t)=\mathscr{L}^{-1}\left\langle\sum_{i_1=1}^{i}\left[\left(\prod\nolimits_{i_2=i_1+1}^{i}y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\sum_{i_3=1}^{i_1}\left\{\begin{array}{c}\dfrac{B_{i_1}^{i_3}\{1-\mathrm{e}^{-t_0(s+\lambda_{i_3})}\}\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}}{(s+a_{i_3,0})\prod\nolimits_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i}-k_{i_2,i_4}}\\ \displaystyle\sum_{i_4=i_1,(i_4\neq i_2,R_{i_4}\neq R_{i_2})}^{i}\frac{1}{-R_{i_2,i_4}(s+a_{i_2,i_4})\prod\nolimits_{i_5=i_1,(i_5\neq i_2,i_5\neq i_4,R_{i_5}\neq R_{i_2})}^{i}-R_{i_2,i_5}(a_{i_2,i_5}-a_{i_2,i_4})}\end{array}\right\}\right]\right\rangle;$$

$$\forall i=1,2,\ldots n \tag{A.4}$$

It must be noted that the solution formulation as given by Eq. (A.4) is valid only when the condition $a_{i_2,i_5} \neq a_{i_2,i_4}$ is satisfied. Eq. (A.4) can be further factorized and simplified as

$$c_i^1(x,t)=\sum_{i_1=1}^{i}\left[\left(\prod\nolimits_{i_2=i_1+1}^{i}y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\sum_{i_3=1}^{i_1}\{G_1^1+h(G_1^1)G_2^1\}\right];\quad \forall i=1,2,\ldots n$$

where

$$G_1^1=\sum_{i_4=i_1,(i_4\neq i_2,R_{i_4}\neq R_{i_2})}^{i}\frac{B_{i_1}^{i_3}\mathrm{e}^{\frac{xv}{2D_x}}\mathscr{L}^{-1}\left\langle\frac{\{1-\mathrm{e}^{-t_0(s+\lambda_{i_3})}\}\mathrm{e}^{\left[\frac{-x}{2D_x}\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right]}}{(s+a_{i_3,0})(s+a_{i_2,i_4})}\right\rangle}{\left(\prod\nolimits_{i_5=i_1,(i_5\neq i_2,R_{i_5}=R_{i_2})}^{i}-k_{i_2,i_5}\right)(-R_{i_2,i_4})\prod\nolimits_{i_5=i_1,(i_5\neq i_2,i_5\neq i_4,R_{i_5}\neq R_{i_2})}^{i}-R_{i_2,i_5}(a_{i_2,i_5}-a_{i_2,i_4})} \tag{A.5}$$

$$G_2^1=\frac{B_{i_1}^{i_3}\mathrm{e}^{\frac{xv}{2D_x}}\mathscr{L}^{-1}\left\langle\frac{\left\{1-\mathrm{e}^{-t_0(s+\lambda_{i_3})}\right\}\mathrm{e}^{\left[\frac{-x}{2D_x}\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right]}}{(s+a_{i_3,0})}\right\rangle}{\prod\nolimits_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i}-k_{i_2,i_4}}$$

$$h(M)=\begin{cases}1, & \text{if } M \text{ loop is not executed}\\ 0, & \text{if } M \text{ loop is executed}\end{cases}$$

The term G_1^1 in Eq. (A.5) can be further factorized and simplified as

$$G_1^1=\sum_{i_4=i_1,(i_4\neq i_2,R_{i_5}=R_{i_2})}^{i}\frac{B_{i_1}^{i_3}\mathrm{e}^{\frac{xv}{2D_x}}\left[\mathscr{L}^{-1}\left\langle\frac{\{1-\mathrm{e}^{-t_0(s+\lambda_{i_3})}\}\mathrm{e}^{\left[\frac{-x}{2D_x}\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right]}}{(s+a_{i_3,0})}\right\rangle-\mathscr{L}^{-1}\left\langle\frac{\{1-\mathrm{e}^{-t_0(s+\lambda_{i_3})}\}\mathrm{e}^{\left[\frac{-x}{2D_x}\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right]}}{(s+a_{i_2,i_4})}\right\rangle\right]}{(a_{i_2,i_4}-\lambda_{i_3})\left(\prod\nolimits_{i_5=i_1,(i_5\neq i_2,R_{i_5}=R_{i_2})}^{i}-k_{i_2,i_5}\right)(-R_{i_2,i_4})\prod\nolimits_{i_5=i_1,(i_5\neq i_2,i_5\neq i_4,R_{i_5}\neq R_{i_2})}^{i}-R_{i_2,i_5}(a_{i_2,i_5}-a_{i_2,i_4})} \tag{A.6}$$

Again it must be noted that Eq. (A.6) is valid only when the condition $a_{i_2,i_4} \neq a_{i_3,0}$ where $a_{i_3,0}=\lambda_{i_3}$ is satisfied. Using the results from Appendix B, inverse Laplace expressions for the terms G_1^1 and G_2^1 can be evaluated and the solution for $c_i^1(x,t)$ is obtained as

$$c_i^1(x,t)=\sum_{i_1=1}^{i}\left[\left(\prod\nolimits_{i_2=i_1+1}^{i}y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\sum_{i_3=1}^{i_1}\{G_1^1+h(G_1^1)G_2^1\}\right];\quad \forall i=1,2,\ldots,n$$

$$G_1^1=\sum_{i_4=i_1,(i_4\neq i_2,R_{i_4}\neq R_{i_2})}^{i}\frac{B_{i_1}^{i_3}\langle F_{i_2,i_3,0}[x,t]-u(t-t_0)\mathrm{e}^{(-\lambda_{i_3}t_0)}F_{i_2,i_3,0}[x,(t-t_0)]-F_{i_2,i_2,i_4}[x,t]+u(t-t_0)\mathrm{e}^{(-\lambda_{i_3}t_0)}F_{i_2,i_2,i_4}[x,(t-t_0)]\rangle}{(a_{i_2,i_4}-\lambda_{i_3})\left(\prod\nolimits_{i_5=i_1,(i_5\neq i_2,R_{i_5}=R_{i_2})}^{i}-k_{i_2,i_5}\right)(-R_{i_2,i_4})\prod\nolimits_{i_5=i_1,(i_5\neq i_2,i_5\neq i_4,R_{i_5}\neq R_{i_2})}^{i}-R_{i_2,i_5}(a_{i_2,i_5}-a_{i_2,i_4})}$$

$$G_2^1=\frac{B_{i_1}^{i_3}\langle F_{i_2,i_3,0}[x,t]-u(t-t_0)\mathrm{e}^{(-\lambda_{i_3}t_0)}F_{i_2,i_3,0}[x,(t-t_0)]\rangle}{\prod\nolimits_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i}-k_{i_2,i_4}} \tag{A.7}$$

where the term F_{i_1,i_2,i_3} is given by Eq. (B.8) or Eq. (B.14) in Appendix B.

The second term $\mathscr{L}^{-1}\langle p_i^2(x,s)\rangle$ is evaluated as follows. From Eqs. (41) and (42) we get:

$$c_i^2(x,t)=\mathscr{L}^{-1}\langle p_i^2(x,s)\rangle=\mathscr{L}^{-1}\left\langle\sum_{i_1=1}^{i}\left[\begin{array}{c} R_{i_1}c_{i_1}^0\left(\prod_{i_2=i_1+1}^{i}y_{i_2}k_{i_2-1}\right) \\ \sum\limits_{i_2=i_1}^{i}\dfrac{\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{(\mu_{i_1}^2D_x+\mu_{i_1}v-k_{i_2}-sR_{i_2})\prod_{i_3=i_1,(i_3\neq i_2)}^{i}-(k_{i_2}+sR_{i_2}-k_{i_3}-sR_{i_3})}\end{array}\right]\right\rangle;\quad\forall i=1,2,\ldots n \tag{A.8}$$

Eq. (A.8) can be written as

$$c_i^2(x,t)=\mathscr{L}^{-1}\left\langle\sum_{i_1=1}^{i}\left[R_{i_1}c_{i_1}^0\left(\prod_{i_2=i_1+1}^{i}y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\frac{\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{-(s+a_{i_1,-i_2})R_{i_2}\left(\prod_{i_3=i_1,(i_3\neq i_2,R_{i_3}=R_{i_2})}^{i}-k_{i_2,i_3}\right)\prod_{i_3=i_1,(i_3\neq i_2,R_{i_3}\neq R_{i_2})}^{i}-R_{i_2,i_3}(s+a_{i_2,i_3})}\right]\right\rangle;$$
$$\forall i=1,2,\ldots n \tag{A.9}$$

Note: the term a_{i_1,i_2} is modified as

$$a_{i_1,i_2}=\begin{cases}\frac{k_{i_1,i_2}}{R_{i_1,i_2}}; & \text{when } i_2>0\\ \lambda_{i_1}; & \text{when } i_2=0\\ \frac{-\mu_{i_1}^2D_x-\mu_{i_1}v+k_{i_2}}{R_{i_2}}; & \text{when } i_2<0\end{cases} \tag{A.10}$$

Note that the condition $k_{i_2,i_3}\neq 0$ must be satisfied in Eq. (A.9). Factorization of Eq. (A.9) yields:

$$c_i^2(x,t)=\sum_{i_1=1}^{i}\left[R_{i_1}c_{i_1}^0\left(\prod_{i_2=i_1+1}^{i}y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\{G_1^2+h(G_1^2)G_2^2\}\right];\quad\forall i=1,2,\ldots n$$

where

$$G_1^2=\sum_{i_3=i_1,\left(i_3\neq i_2,R_{i_3}\neq R_{i_2}\right)}^{i}\frac{\mathrm{e}^{\frac{xv}{2D_x}}\mathscr{L}^{-1}\left\langle\dfrac{\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x\left(k_{i_2}+sR_{i_2}\right)}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{\left(s+a_{i_1,-i_2}\right)\left(s+a_{i_2,i_3}\right)}\right\rangle}{R_{i_2}\left(\prod_{i_4=i_1,\left(i_4\neq i_2,R_{i_4}=R_{i_2}\right)}^{i}-k_{i_2,i_4}\right)R_{i_2,i_3}\prod_{i_4=i_1,\left(i_4\neq i_2,i_4\neq i_3,R_{i_4}\neq R_{i_2}\right)}^{i}-R_{i_2,i_4}\left(a_{i_2,i_4}-a_{i_2,i_3}\right)}$$
$$G_2^2=\frac{-\mathrm{e}^{\frac{xv}{2D_x}}\mathscr{L}^{-1}\left\langle\dfrac{\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x\left(k_{i_2}+sR_{i_2}\right)}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{\left(s+a_{i_1,-i_2}\right)}\right\rangle}{R_{i_2}\prod_{i_3=i_1,\left(i_3\neq i_2,R_{i_3}=R_{i_2}\right)}^{i}-k_{i_2,i_3}} \tag{A.11}$$

Note that the condition $a_{i_2,i_4}\neq a_{i_2,i_3}$ must be satisfied in Eq. (A.11). The term G_1^2 in Eq. (A.11) can be further factorized and simplified as

$$G_1^2=\sum_{i_3=i_1,(i_3\neq i_2,R_{i_3}\neq R_{i_2})}^{i}\frac{\mathrm{e}^{\frac{xv}{2D_x}}\mathscr{L}^{-1}\left\langle\dfrac{\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{(s+a_{i_1,-i_2})}-\dfrac{\left\{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}-\mathrm{e}^{-\mu_{i_1}x}\right\}}{(s+a_{i_2,i_3})}\right\rangle}{(a_{i_2,i_3}-a_{i_1,-i_2})R_{i_2}\left(\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i}-k_{i_2,i_4}\right)R_{i_2,i_3}\prod_{i_4=i_1,(i_4\neq i_2,i_4\neq i_3,R_{i_4}\neq R_{i_2})}^{i}-R_{i_2,i_4}(a_{i_2,i_4}-a_{i_2,i_3})} \tag{A.12}$$

Note that the condition $a_{i_2,i_4} \neq a_{i_1,-i_2}$ must be satisfied in Eq. (A.12). G_1^2 can be further simplified as

$$G_1^2 = \sum_{i_3=i_1,(i_3\neq i_2,R_{i_3}\neq R_{i_2})}^{i} \mathrm{e}^{\frac{xv}{2D_x}} \times \frac{\left[\mathscr{L}^{-1}\left\langle \frac{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}}{(s+a_{i_1,-i_2})}\right\rangle - \mathrm{e}^{-\mu_{i_1}x}\mathscr{L}^{-1}\left\langle\frac{1}{(s+a_{i_1,-i_2})}\right\rangle - \mathscr{L}^{-1}\left\langle \frac{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x(k_{i_2}+sR_{i_2})}\right\}\right]}}{(s+a_{i_2,i_3})}\right\rangle + \mathrm{e}^{-\mu_{i_1}x}\mathscr{L}^{-1}\left\langle\frac{1}{(s+a_{i_2,i_3})}\right\rangle\right]}{(a_{i_2,i_3}-a_{i_1,-i_2})R_{i_2}\left(\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i} - k_{i_2,i_4}\right)R_{i_2,i_3}\prod_{i_4=i_1,(i_4\neq i_2,i_4\neq i_3,R_{i_4}\neq R_{i_2})}^{i} - R_{i_2,i_4}(a_{i_2,i_4}-a_{i_2,i_3})} \tag{A.13}$$

G_2^2 in Eq. (A.11) can be further simplified as

$$G_2^2 = \frac{-\mathrm{e}^{\frac{xv}{2D_x}}\left[\mathscr{L}^{-1}\left\langle \frac{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_x\left(k_{i_2}+sR_{i_2}\right)}\right\}\right]}}{(s+a_{i_1,-i_2})}\right\rangle - \mathrm{e}^{-\mu_{i_1}x}\mathscr{L}^{-1}\left\langle\frac{1}{(s+a_{i_1,-i_2})}\right\rangle\right]}{R_{i_2}\prod_{i_3=i_1,(i_3\neq i_2,R_{i_3}=R_{i_2})}^{i} - k_{i_2,i_3}} \tag{A.14}$$

From inverse Laplace transform tables we get: [6] (p494, Eq. (3)).

$$\mathscr{L}^{-1}\left\langle\frac{1}{(s+a_{i_1,i_2})}\right\rangle = \mathrm{e}^{-a_{i_1,i_2}t} \tag{A.15}$$

Using Eq. (A.15) and Appendix B, inverse Laplace expressions for the terms G_1^2 and G_2^2 can be evaluated and the solution for $c_i^2(x,t)$ is obtained as

$$c_i^2(x,t) = \sum_{i_1=1}^{i}\left[R_{i_1}c_{i_1}^0\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\{G_1^2 + h(G_1^2)G_2^2\}\right]; \quad \forall i = 1,2,\ldots n$$

where

$$G_1^2 = \sum_{i_3=i_1,(i_3\neq i_2,R_{i_3}\neq R_{i_2})}^{i} \frac{\left\langle F_{i_2,i_1,-i_2}[x,t] - \mathrm{e}^{(-\mu_{i_1}x-a_{i_1,-i_2}t)} - F_{i_2,i_2,i_3}[x,t] + \mathrm{e}^{(-\mu_{i_1}x-a_{i_2,i_3}t)}\right\rangle}{(a_{i_2,i_3}-a_{i_1,-i_2})R_{i_2}\left(\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i} - k_{i_2,i_4}\right)R_{i_2,i_3}\prod_{i_4=i_1,(i_4\neq i_2,i_4\neq i_3,R_{i_4}\neq R_{i_2})}^{i} - R_{i_2,i_4}(a_{i_2,i_4}-a_{i_2,i_3})}$$

$$G_2^2 = \frac{-\left\langle F_{i_2,i_1,-i_2}[x,t] - \mathrm{e}^{(-\mu_{i_1}x-a_{i_1,-i_2}t)}\right\rangle}{R_{i_2}\prod_{i_3=i_1,(i_3\neq i_2,R_{i_3}=R_{i_2})}^{i} - k_{i_2,i_3}} \tag{A.16}$$

where the term F_{i_1,i_2,i_3} is given by Eq. (B.8) or Eq. (B.14) in Appendix B.

Appendix B. Evaluation of inverse Laplace expressions for the Dirichlet boundary condition

$$\chi_{i_1,i_2,i_3,i_4} = \mathrm{e}^{\frac{xv}{2D_x}}\mathscr{L}^{-1}\left\langle\frac{\{1-\mathrm{e}^{-t_0(s+\lambda_{i_4})}\}\mathrm{e}^{\left[\frac{-x}{2D_x}\sqrt{v^2+4D_x(k_{i_1}+sR_{i_1})}\right]}}{(s+a_{i_2,i_3})}\right\rangle \tag{B.1}$$

Eq. (B.1) can be simplified as

$$\chi_{i_1,i_2,i_4,i_3} = \mathrm{e}^{\frac{xv}{2D_x}}(\beta_1-\beta_2)$$

where

$$\beta_1 = \mathscr{L}^{-1}\left\langle\frac{\mathrm{e}^{\left[-x\sqrt{\frac{R_{i_1}}{D_x}}\sqrt{s-\left(\frac{-v^2}{4R_{i_1}D_x}-\frac{k_{i_1}}{R_{i_1}}\right)}\right]}}{\left\{s-\left(\frac{-v^2}{4R_{i_1}D_x}-\frac{k_{i_1}}{R_{i_1}}\right)-\frac{v^2}{4R_{i_1}D_x}-\frac{k_{i_1}}{R_{i_1}}+a_{i_2,i_3}\right\}}\right\rangle \tag{B.2}$$

$$\beta_2 = \mathscr{L}^{-1}\left\langle\frac{\mathrm{e}^{-t_0\lambda_{i_4}}\mathrm{e}^{-t_0s}\mathrm{e}^{\left[-x\sqrt{\frac{R_{i_1}}{D_x}}\sqrt{s-\left(\frac{-v^2}{4R_{i_1}D_x}-\frac{k_{i_1}}{R_{i_1}}\right)}\right]}}{\left\{s-\left(\frac{-v^2}{4R_{i_1}D_x}-\frac{k_{i_1}}{R_{i_1}}\right)-\frac{v^2}{4R_{i_1}D_x}-\frac{k_{i_1}}{R_{i_1}}+a_{i_2,i_3}\right\}}\right\rangle$$

β_1 can be evaluated as follows: invoking the First Shifting Theorem (see [17, p. 253]) we can simplify β_1 as

$$\beta_1 = \mathrm{e}^{\left[\frac{-v^2}{4R_{i_1}D_x} - \frac{k_{i_1}}{R_{i_1}}\right]t}\mathscr{L}^{-1}\left\langle \frac{\mathrm{e}^{\left[-x\sqrt{\frac{R_{i_1}}{D_x}}\sqrt{s}\right]}}{\left\{s - \left(\frac{v^2}{4R_{i_1}D_x} + \frac{k_{i_1}}{R_{i_1}} - a_{i_2,i_3}\right)\right\}}\right\rangle \tag{B.3}$$

The Laplace inverse of Eq. (B.3) can be readily obtained from the tables (see [6, p. 495, Eq. (19)]). Applying this inversion, β_1 can be evaluated as

$$\begin{aligned}\beta_1 = \frac{\mathrm{e}^{-a_{i_2,i_3}t}}{2}\Bigg[&\mathrm{e}^{-x\sqrt{\frac{R_{i_1}}{D_x}}\sqrt{\left(\frac{v^2}{4R_{i_1}D_x}+\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}}\operatorname{erfc}\left\{\frac{x}{2}\sqrt{\frac{R_{i_1}}{D_xt}} - \sqrt{\left(\frac{v^2}{4R_{i_1}D_x}+\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)t}\right\}\\ &+\mathrm{e}^{x\sqrt{\frac{R_{i_1}}{D_x}}\sqrt{\left(\frac{v^2}{4R_{i_1}D_x}+\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}}\operatorname{erfc}\left\{\frac{x}{2}\sqrt{\frac{R_{i_1}}{D_xt}} + \sqrt{\left(\frac{v^2}{4R_{i_1}D_x}+\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)t}\right\}\Bigg]\end{aligned} \tag{B.4}$$

β_1 can be further rearranged and simplified as

$$\beta_1 = \frac{\mathrm{e}^{-a_{i_2,i_3}t}}{2}\left[\begin{aligned}&\mathrm{e}^{\frac{-x}{2D_x}\sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}}\operatorname{erfc}\left\{\frac{R_{i_1}x-\sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}\,t}{2\sqrt{R_{i_1}D_xt}}\right\}\\ &+\mathrm{e}^{\frac{x}{2D_x}\sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}}\operatorname{erfc}\left\{\frac{R_{i_1}x+\sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}\,t}{2\sqrt{R_{i_1}D_xt}}\right\}\end{aligned}\right] \tag{B.5}$$

β_2 is evaluated as follows: β_2 can be simplified as

$$\beta_2 = \mathrm{e}^{-t_0\lambda_{i_4}}\mathscr{L}^{-1}\langle \mathrm{e}^{-t_0s}\mathscr{L}^{-1}(\beta_1)\rangle \tag{B.6}$$

Now, we invoke the Second Shifting Theorem (see [17, p. 265]) and evaluate β_2 as [*Note*: We have already evaluated β_1; Eq. (B.4)]

$$\begin{aligned}\beta_2 = \mathrm{e}^{-\lambda_{i_4}t_0}u(t-t_0)\mathrm{e}^{-a_{i_2,i_3}(t-t_0)}\Bigg[&\mathrm{e}^{\frac{-x}{2D_x}\sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}}\operatorname{erfc}\left\{\frac{R_{i_1}x-\sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}(t-t_0)}{2\sqrt{R_{i_1}D_x(t-t_0)}}\right\}\\ &+\mathrm{e}^{\frac{x}{2D_x}\sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}}\operatorname{erfc}\left\{\frac{R_{i_1}x+\sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)}(t-t_0)}{2\sqrt{R_{i_1}D_x(t-t_0)}}\right\}\Bigg]\end{aligned} \tag{B.7}$$

The final solution can be compactly expressed as

$$\chi_{i_1,i_2,i_3,i_4}[x,t] = F_{i_1,i_2,i_3}[x,t] - u(t-t_0)\mathrm{e}^{-\lambda_{i_4}t_0}F_{i_1,i_2,i_3}[x,(t-t_0)]$$

where

$$F_{i_1,i_2,i_3}[x,t] = \frac{\mathrm{e}^{-a_{i_2,i_3}t}\mathrm{e}^{\frac{xv}{2D_x}}}{2}\left[\mathrm{e}^{\frac{-x\omega_{i_1,i_2,i_3}}{2D_x}}\operatorname{erfc}\left\{\frac{R_{i_1}x-\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\} + \mathrm{e}^{\frac{x\omega_{i_1,i_2,i_3}}{2D_x}}\operatorname{erfc}\left\{\frac{R_{i_1}x+\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}\right] \quad \text{and } \omega_{i_1,i_2,i_3} = \sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)} \tag{B.8}$$

The above expression for F_{i_1,i_2,i_3} is valid only for real values of ω_{i_1,i_2,i_3}. For problems involving complex values for ω_{i_1,i_2,i_3} the F_{i_1,i_2,i_3} term is evaluated as follows:

$$\begin{aligned}&\text{Let, } \omega_{i_1,i_2,i_3} = \sqrt{v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)} = \mathrm{i}\omega^*_{i_1,i_2,i_3}\\ &\text{where } \omega^*_{i_1,i_2,i_3} = \sqrt{\left|v^2+4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}}-a_{i_2,i_3}\right)\right|}\end{aligned} \tag{B.9}$$

Now the F_{i_1,i_2,i_3} terms can be written as

$$F_{i_1,i_2,i_3}[x,t] = \frac{e^{-a_{i_2,i_3}t}e^{\frac{xv}{2D_x}}}{2}\left[e^{\frac{-xi\omega^*_{i_1,i_2,i_3}}{2D_x}}\mathrm{erfc}\left\{\frac{R_{i_1}x - i\omega^*_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\} + e^{\frac{xi\omega^*_{i_1,i_2,i_3}}{2D_x}}\mathrm{erfc}\left\{\frac{R_{i_1}x + i\omega^*_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}\right] \tag{B.10}$$

From the symmetric relations we get:

$$\begin{aligned}&\text{if } \mathrm{erfc}\{a+\mathrm{i}b\} = A + \mathrm{i}B \text{ then } \mathrm{erfc}\{a-\mathrm{i}b\} = A - \mathrm{i}B\\ &\text{where } a,b,A,B \in R\end{aligned} \tag{B.11}$$

Also the exponent of a complex number can be expressed as

$$\begin{aligned}&e^{-\mathrm{i}\theta} = \cos(\theta) - \mathrm{i}\sin(\theta)\\ &e^{\mathrm{i}\theta} = \cos(\theta) + \mathrm{i}\sin(\theta)\end{aligned} \tag{B.12}$$

Using Eqs. (B.11) and (B.12). Eq. (B.10) can be simplified as

$$\begin{aligned}&F_{i_1,i_2,i_3}[x,t] = \frac{e^{-a_{i_2,i_3}t}e^{\frac{xv}{2D_x}}}{2}\left[\begin{array}{l}\left\{\cos\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right) - \mathrm{i}\sin\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right)\right\}(A-\mathrm{i}B)+\\ \left\{\cos\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right) + \mathrm{i}\sin\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right)\right\}(A+\mathrm{i}B)\end{array}\right]\\ &\text{where}\\ &(A-\mathrm{i}B) = \mathrm{erfc}\left\{\frac{R_{i_1}x - i\omega^*_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\} \quad \text{and } (A+\mathrm{i}B) = \mathrm{erfc}\left\{\frac{R_{i_1}x + \mathrm{i}\omega^*_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}\end{aligned} \tag{B.13}$$

Further simplification of Eq. (B.13) yields:

$$\begin{aligned}&F_{i_1,i_2,i_3}[x,t] = e^{-a_{i_2,i_3}t}e^{\frac{xv}{2D_x}}\left[A\cos\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right) - B\sin\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right)\right]\\ &\text{where } \omega^*_{i_1,i_2,i_3} = \sqrt{\left|v^2 + 4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}} - a_{i_2,i_3}\right)\right|} \text{ and } (A+\mathrm{i}B) = \mathrm{erfc}\left\{\frac{R_{i_1}x + \mathrm{i}\omega^*_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}\end{aligned} \tag{B.14}$$

Hence in problems where ω_{i_1,i_2,i_3} is complex the F_{i_1,i_2,i_3} term is given as by Eq. (B.14).

Appendix C. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.advwatres.2007.08.002.

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