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Analytical solutions for sequentially coupled one-dimensional reactive transport problems – Part II: Special cases, implementation and testing

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Abstract

This is Part-II of a two-part article that presents analytical solutions to multi-species reactive transport equations coupled through sorption and sequential first-order reactions. In Part-I, we provide the mathematical derivations and in this article we discuss the computational techniques for implementing these solutions. We adopt these techniques to develop a general computer code and use it to verify the solutions. We also simplify the general solutions for various special-case transport scenarios involving zero initial condition, identical retardation factors and zero advection. In addition to this, we derive specialized solution expressions for zero dispersion and steady-state conditions. Whereever possible, we compare these special-case solutions against previously published analytical solutions to establish the validity of the new solution. Finally, we test the new solution against other published analytical and semi-analytical solutions using a set of example problems.

Keywords: Reactive transport; Radio-active decay; Sequential reactions; Coupled reactive transport; Multispecies transport; Model validation; Analytical solution

1. Introduction

In Part-I of this two part manuscript a new closed-form analytical solution which solves the one dimensional transport of sequentially decaying contaminants was presented. The governing equation for the transport problem considered is [12]:

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

where c_i is the concentration of species i [ML^{-3}]; R_i is the retardation coefficient of species i [Dimensionless]; y_i is the effective yield factor that describes the mass of a species i produced from species $i-1$ [MM^{-1}]; k_i is the first-order decay rate constant of species i [T^{-1}]; v is the transport velocity [LT^{-1}] and D_x is the dispersion coefficient [L^2T^{-1}].

Eq. (1) was solved for a generic exponential type spatially varying initial conditions and a Bateman type Dirichlet and Cauchy boundary conditions. The details of these initial and boundary conditions including the notations can be obtained from Srinivasan and Clement [12]. The general solution for both Dirichlet and Cauchy boundaries is expressed as [12]

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

where

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

The G terms in Eq. (2) are defined in Eq. (44) for the Dirichlet boundary condition and Eq. (49) for the Cauchy boundary condition in Srinivasan and Clement [12]. Note that appropriate expressions for the G terms have to be applied based on the type of boundary condition considered.

To test the general solution, one can either compare it analytically against other closed-form solutions or compare the results of its simulation against other analytical or numerical simulations. While testing the general solution using example simulations requires its implementation on a computational platform, analytical comparisons are viable only when we have suitable solutions that solve an identical transport problem. Since explicit closed-form solutions are available only for simplified transport scenarios, we need to simplify the general solution to these special cases in order to compare them with previously published closed-form solutions. The objective of this manuscript is to: (1) discuss the computational implementation of the new analytical solution; (2) test and validate the solution against published analytical and numerical results; (3) deduce solutions for zero initial condition, identical retardation factors and zero advection velocity from the general solution expression, and derive new solutions for zero dispersion coefficient and steady state conditions; and (4) evaluate the salient features and limitations of the solution. In the following sections our general solutions are first simplified and analytically compared against the solution expressions presented by van Genuchten [16] and Higashi and Pigford [9] for specialized transport scenarios. To further test the solutions, we perform several example simulations and compare the results of the general solution against the results generated from the semi-analytical solution given by Quezada et al. [11].

2. Implementation of the solution

To develop a computer code for the general solution, one has to formulate an algorithm based on the looping structure presented in Eq. (2). In order to evaluate the summation loops, one has to compute all the G terms in Eq. (2), which are defined in Eqs. (44) and (49) in Srinivasan and Clement [12]. From these equations one can observe that the G terms require the evaluation of F_{i_1,i_2,i_3} terms. These F_{i_1,i_2,i_3} terms, which are defined in Eqs. (45), (46), (50) and (51) in Srinivasan and Clement [12], involve computations of the product of complementary error functions and exponential functions. After evaluating the F_{i_1,i_2,i_3} terms, one can then compute the G terms. The general solution can then be implemented by substituting the values for the corresponding G terms in the summation loop described by Eq. (2). Although the above procedure appears to be a straightforward task, round-off errors and underflow/overflow errors that occur during the computations of the G and F_{i_1,i_2,i_3} terms, can cause severe stability problems even for short chain lengths involving four species [16]. These computational errors are further aggravated when solving problems involving the Cauchy boundary condition for long chain lengths and/or large simulation times.

As pointed out by van Genuchten [16], the round-off errors arise due to the approximations involved in the computation of the complementary error functions (ERFC) in the F_{i_1,i_2,i_3} terms, especially when employing the Cauchy boundary condition, for large retardation factors and long simulation distances or simulation times. Typically, ERFC is evaluated by approximating it either as a closed-form analytical expression [7] or as an infinite summation series [6]. Van Genuchten [16] suggested that this round-off error could be considerably limited by first substituting the approximate expressions for the ERFCs into the F_{i_1,i_2,i_3} terms and then combining and simplifying the resulting terms. The mathematical details of this strategy can be obtained from the computer code CHAIN [16]. Although this strategy significantly improves the round-off errors, it involves extensive book keeping. It must be noted that van Genuchten [16] used the Gautschi [7,6] approximations for computing the ERFC terms. Using a more accurate approximation for the ERFC function, such as the Cody [4] Chebyshev approximation, would also provide additional improvement to the round-off errors.

Another important computational challenge encountered in implementing this solution is the handling of very large and/or very small numbers while computing the exponential and Π functions. These numbers arise when solving problems involving long chain lengths and/or large simulation times. For example, consider the computations involved in evaluating the G_1^2 term in Eq. (2) (see Appendix A [12])

$$G_1^2 = \sum_{i_3=i_1,(i_3\neq i_2,R_{i_3}\neq R_{i_2})}^{i} \frac{\left\langle F_{i_2,i_1,-i_2}[x,t] - \mathrm{e}^{(-\mu_{i_1}x - a_{i_1,-i_2}t)} - F_{i_2,i_2,i_3}[x,t] + \mathrm{e}^{(-\mu_{i_1}x - a_{i_2,i_3}t)}\right\rangle}{(a_{i_2,i_3} - a_{i_1,-i_2})R_{i_2}\left(\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i} - k_{i_2,i_4}\right)R_{i_2,i_3}\prod_{i_4=i_1,(i_4\neq i_2,i_4\neq i_3,R_{i_4}\neq R_{i_2})}^{i} - R_{i_2,i_4}(a_{i_2,i_4} - a_{i_2,i_3})} \tag{3}$$

From Eq. (3) one can observe that the denominator term involves the computation of two independent product loops. Under certain parameter combinations, each of the arguments within these product loops can assume very small values (e.g., <1E−5); when this loop is run for long chain lengths (e.g., >10) the product of these arguments results in an extremely small number (<1E−50). Performing division by a small number of this order, results in very large arguments which cannot be represented accurately by using a finite computer precision. Furthermore, mathematical operations (additions and/or subtractions) of these large arguments can result in severe round-off errors. Note that this problem is not only restricted to the G_1^2 term, but can also apply to the other G terms. Similarly, one can also observe that the numerator of the G_1^2 terms in Eq. (3) involves the computation of exponential functions. While performing simulations for large times at small distances, one may encounter very large arguments within these exponential functions that cannot be represented by finite computer precision. Therefore, it is common to observe overflow errors when solving problems involving large simulation times. A powerful solution to tackle these two problems involving long chain lengths and large simulation times is to use a log based formulation. The log based formulation involves transforming the arguments whose products have to be evaluated in to the log space. Within the log space the products are evaluated by performing a set of additions. Finally, the evaluated product is inverse transformed from the log scale to the linear scale. By employing the proposed log based formulation, the underflow and/or overflow errors related to evaluating the Π terms can be virtually eliminated. However, the proposed log based formulation can only be applied to compute product terms and cannot be used to compute summation terms. To tackle the problem of overflow errors while evaluating summation terms, one can make use of the symmetrical property of the F_{i_1,i_2,i_3} terms. This involves combining the F_{i_1,i_2,i_3} terms that have identical i_2 and i_3 values and then evaluating the sum of these combination terms separately and then substituting them in the main solution, as described by van Genuchten [16]. Although, this method seems to have a direct approach, the algebraic manipulation involved in combining the various F_{i_1,i_2,i_3} terms requires the reformulation of the final solution in a different format. This reformulation can be a mathematically tedious process involving extensive book keeping, especially for problems having long chain lengths.

One can use the log formulation and other computational techniques suggested above for developing a computer code for the general solution. In the section below, we also present another alternative where analytical solutions for several simpler and more practical cases that are computationally less challenging to implement are deduced. These special-case solutions are particularly useful for developing screening level models. Furthermore, some of these simple solutions can be directly compared against analytical solutions presented in the literature to provide powerful arguments for demonstrating the validity of the general solution.

3. Special cases

In this section, solutions to several simplified transport scenarios are presented and where ever possible, these solutions are validated against previously published analytical solutions. It should be noted that for some of these special cases, a more rigorous mathematical analysis (rather than simple substitution) is required to derive these simplified solutions. Furthermore, unlike the general solution these special case solutions impose fewer limitations on the transport parameter values and hence are easier to compute. These limitations are pointed out in Appendix A and Supplementary Section S2 in Srinivasan and Clement [12], and also summarized in Table 4.

3.1. Deduced solution for zero initial condition

The general solution can be readily simplified to solve transport scenarios where the initial concentrations of all the contaminants are zero. This is done by substituting the value of c^o as zero. For this case, the general solution simplifies to:

$$c_i(x,t) = \sum_{i_1=1}^{i}\left[\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\sum_{i_3=1}^{i_1}\{G_1^1 + h(G_1^1)G_2^1\}\right]; \quad \forall i = 1,2,\ldots,n \tag{4}$$

where a_{i_1,i_2} is given by:

$$a_{i_1,i_2} = \begin{cases} \frac{k_{i_1,i_2}}{R_{i_1,i_2}}; & \text{when } i_2 > 0 \\ \lambda_{i_1}; & \text{when } i_2 = 0 \end{cases} \tag{5}$$

Note that the G_1^1 and G_2^1 terms in Eq. (4) defined in Srinivasan and Clement [12] remain unchanged. It can be shown that the expressions for the first four species of this special case solution match the solutions given by van Genuchten [16]. Furthermore, from Eq. (4), one can observe that, for the zero initial condition case the second term of the general solution given by Eq. (2) is absent. This not only relaxes some of the restrictions on the transport parameter values but also helps in reducing the round off errors, especially during large simulation times.

3.2. Deduced solution for identical retardation factors

Special cases arise when the retardation factors of all the species in the transport problem are identical (for example, the transport of non-sorbing set of sequentially decaying contaminants, where the retardation factors of all the species will be 1). One can obtain the solution for this problem from the general solution by simple substitution. The modified solution for this special case problem for both types of boundary conditions is given as

$$c_i(x,t) = \sum_{i_1=1}^{i}\left[\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\sum_{i_3=1}^{i_1}\{G_2^1\}\right] + \sum_{i_1=1}^{i}\left[R_{i_1}c_{i_1}^{\mathrm{o}}\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\{G_2^2\}\right];\quad \forall i=1,2,\ldots,n \tag{6}$$

Note that the G_2^1 and G_2^2 terms defined in Srinivasan and Clement [12] remain unchanged. The exclusion of the G_1^1 and G_1^2 terms helps in obtaining a computationally more stable solution for longer chain lengths. Additionally, this solution imposes lesser restriction on the transport parameter values. Sun et al. [14] solved a transport problem similar to the above problem assuming zero initial conditions. However, Sun et al. [14] did not provide an explicit closed-form expression, instead they only present a computational algorithm to obtain the concentration profiles.

3.3. Deduced solution for zero advection velocity

In several chemical processes, the transport of contaminants is purely governed by diffusion. The solutions to this problem are obtained by setting the advection velocity to zero. These specialized solutions can be directly applied to model reactive transport scenarios involving chemical and nuclear repository leakage through diffusion.

The solution for this condition is identical to the general solution given by Eq. (2), except that the F_{i_1,i_2,i_3} terms will be modified. For the Dirichlet boundary condition, the F_{i_1,i_2,i_3} term is given as

$$F_{i_1,i_2,i_3}[x,t] = \frac{\mathrm{e}^{-a_{i_2,i_3}t}}{2}\left[\begin{array}{l}\mathrm{e}^{\frac{-x\omega_{i_1,i_2,i_3}}{2D_x}}\operatorname{erfc}\left\{\frac{R_{i_1}x-\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}\\ +\mathrm{e}^{\frac{x\omega_{i_1,i_2,i_3}}{2D_x}}\operatorname{erfc}\left\{\frac{R_{i_1}x-\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}\end{array}\right] \tag{7}$$

where

$$\omega_{i_1,i_2,i_3} = \sqrt{4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}} - a_{i_2,i_3}\right)}$$

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

$$F_{i_1,i_2,i_3}[x,t] = \mathrm{e}^{-a_{i_2,i_3}t}\left[A\cos\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right) - B\sin\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right)\right] \tag{8}$$

where

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

For the case of the Cauchy boundary condition, forcing the advection velocity to be zero would result in a zero boundary condition. To avoid this, we assume that the boundary condition at the source does not involve the v term and modify Cauchy source boundary condition as

$$-D_x\frac{\partial c_i(0,t)}{\partial x} = \begin{cases}\sum_{i_1=1}^{i} B_i^{i_1}\mathrm{e}^{-\lambda_{i_1}t}, & 0 < t \leqslant t_o\\ 0, & t > t_o\end{cases};\quad \forall i=1,2,\ldots,n \tag{9}$$

For this condition, the F_{i_1,i_2,i_3} term is modified as

$$F_{i_1,i_2,i_3}[x,t] = \mathrm{e}^{-a_{i_2,i_3}t}\left[\begin{array}{l}\frac{\mathrm{e}^{\frac{-x\omega_{i_1,i_2,i_3}}{2D_x}}}{\omega_{i_1,i_2,i_3}}\mathrm{erfc}\left\{\frac{R_{i_1}x-\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}+\\ \frac{\mathrm{e}^{\frac{x\omega_{i_1,i_2,i_3}}{2D_x}}}{-\omega_{i_1,i_2,i_3}}\mathrm{erfc}\left\{\frac{R_{i_1}x+\omega_{i_1,i_2,i_3}t}{2\sqrt{R_{i_1}D_xt}}\right\}\end{array}\right]; \quad \text{when } \frac{k_{i_1}}{R_{i_1}} \neq a_{i_2,i_3}, \quad \text{and}$$

$$= \mathrm{e}^{\frac{-k_{i_1}t}{R_{i_1}}}\left[\sqrt{\frac{t}{\pi R_{i_1}D_x}}\mathrm{e}^{\frac{-(R_{i_1}x-vt)^2}{4R_{i_1}D_xt}} - \frac{x}{2D_x}\mathrm{erfc}\left(\frac{R_{i_1}x}{2\sqrt{R_{i_1}D_xt}}\right)\right]; \quad \text{when } \frac{k_{i_1}}{R_{i_1}} = a_{i_2,i_3}$$

where

$$\omega_{i_1,i_2,i_3} = \sqrt{4R_{i_1}D_x\left(\frac{k_{i_1}}{R_{i_1}} - a_{i_2,i_3}\right)} \tag{10}$$

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

$$F_{i_1,i_2,i_3}[x,t] = \frac{2}{\omega^{*\,2}_{i_1,i_2,i_3}}\mathrm{e}^{-a_{i_2,i_3}t}\mathrm{e}^{\frac{xv}{2D_x}}\left[\begin{array}{l}-B\omega^*_{i_1,i_2,i_3}\cos\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right)\\ -A\omega^*_{i_1,i_2,i_3}\sin\left(\frac{x\omega^*_{i_1,i_2,i_3}}{2D_x}\right)\end{array}\right] \tag{11}$$

where

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

3.4. Derived solution for steady state

The behavior of a contaminant plume under steady state conditions is of special interest especially while analyzing monitored natural attenuation (MNA) processes. Computationally, steady state solutions avoid the problems related to overflow errors which occur when employing the general solution to solve for large simulation times. Although this problem can be tackled by using the algebraic manipulation technique suggested in Section 2, it can be a tedious effort. Furthermore, numerical codes (e.g., RT3D [3]) and semi-analytical solutions (e.g., Quezada et al. [11]), require large amounts of computational resources to accurately model steady state solutions. For these reasons, it is very useful to have explicit solutions for steady state conditions. It must be noted that unlike previous special cases, it is not possible to deduce the steady state solution by direct substitution. Therefore, we derive the steady state solution by solving the steady state form of the governing assuming a constant source for the Dirichlet and Cauchy boundaries conditions. Since the time term is absent in the governing equations, Laplace transform techniques are not involved, and we can directly use the linear transform method given by Clement [2] to uncouple the system of equations. The detailed solution procedure is given in Appendix A.

The steady state solution for the Dirichlet boundary is given as

$$c_i(x) = \sum_{i_1=1}^{i}\left[\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\left(\sum_{i_2=1}^{i_1} B_{i_1}^{i_2}\right)\sum_{i_2=i_1}^{i}\frac{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_xk_{i_2}}\right\}\right]}}{\prod\limits_{i_3=i_1,(i_3\neq i_2)}^{i} -(k_{i_2}-k_{i_3})}\right]; \quad \forall i = 1,2,\ldots n \tag{12}$$

The corresponding steady state solution for the Cauchy boundary condition is given as

$$c_i(x) = \sum_{i_1=1}^{i}\left[\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\left(\sum_{i_2=1}^{i_1} B_{i_1}^{i_2}\right)\sum_{i_2=i_1}^{i}\frac{v\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_xk_{i_2}}\right\}\right]}}{\left\{\frac{v}{2}+\frac{1}{2}\sqrt{v^2+4D_xk_{i_2}}\right\}\prod\limits_{i_3=i_1,(i_3\neq i_2)}^{i} -(k_{i_2}-k_{i_3})}\right]; \quad \forall i = 1,2,\ldots n \tag{13}$$

From Eqs. (12) and (13) it can be observed that the steady state solutions are less complex compared to the generic transient solutions since they do not involve the ERFC terms.

3.5. Derived solution for zero dispersion coefficient

If we ignore the effects of diffusion and dispersion, the governing transport simplifies to:

$$
\begin{aligned}
R_i \frac{\partial c_i(x,t)}{\partial t} + v \frac{\partial c_i(x,t)}{\partial x} &= y_{i-1} k_{i-1} c_{i-1}(x,t) - k_i c_i(x,t); \quad \forall i = 2,3,\ldots,n \\
&= -k_i c_i(x,t); \;\; i = 1; \\
&\quad \forall t > 0 \quad \text{and} \quad 0 < x < \infty
\end{aligned} \tag{14}
$$

Note that in the absence of dispersion, the Cauchy boundary condition will be identical to the Dirichlet boundary condition. In the Supplementary section we solve the above problem for a generic exponential initial condition. The solution for the no dispersion condition can also be represented by equation. However, the G terms associated with this solution are defined as: (see Eqs. (S1.29) and (S1.38) in the Supplementary section S1)

$$
\begin{aligned}
G_1^1 &= \sum_{i_4=i_1,(i_4\neq i_2,R_{i_4}\neq R_{i_2})}^{i} \frac{B_{i_1}^{i_3}\left\langle \begin{array}{l} F_{i_2,i_3,0}[x,t] - \mathrm{e}^{-t_o\lambda_{i_3}} F_{i_1,i_2,i_3}[x,(t-t_o)] \\ -F_{i_2,i_2,i_4}[x,t] + \mathrm{e}^{-t_o\lambda_{i_3}} F_{i_2,i_2,i_4}[x,(t-t_o)] \end{array} \right\rangle}{(a_{i_2,i_4} - \lambda_{i_3})\left(\prod_{i_5=i_1,(i_5\neq i_2,R_{i_5}=R_{i_2})}^{i} - k_{i_2,i_5}\right)(-R_{i_2,i_4})\prod_{i_5=i_1,(i_5\neq i_2,i_5\neq i_4,R_{i_5}\neq R_{i_2})}^{i} - R_{i_2,i_5}(a_{i_2,i_5} - a_{i_2,i_4})} \\
G_2^1 &= \frac{B_{i_1}^{i_3}\left\langle F_{i_2,i_3,0}[x,t] - \mathrm{e}^{-t_o\lambda_{i_3}} F_{i_1,i_2,i_3}[x,(t-t_o)] \right\rangle}{\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i} - k_{i_2,i_4}} \\
G_1^2 &= \sum_{i_3=i_1,(i_3\neq i_2,R_{i_3}\neq R_{i_2})}^{i} \frac{\left\langle F_{i_2,i_1,-i_2}[x,t] - \mathrm{e}^{(-\mu_{i_1}x - a_{i_1,-i_2}t)} - F_{i_2,i_2,i_3}[x,t] + \mathrm{e}^{(-\mu_{i_1}x - a_{i_2,i_3}t)} \right\rangle}{(a_{i_2,i_3} - a_{i_1,-i_2})R_{i_2}\left(\prod_{i_4=i_1,(i_4\neq i_2,R_{i_4}=R_{i_2})}^{i} - k_{i_2,i_4}\right)R_{i_2,i_3}\prod_{i_4=i_1,(i_4\neq i_2,i_4\neq i_3,R_{i_4}\neq R_{i_2})}^{i} - R_{i_2,i_4}(a_{i_2,i_4} - a_{i_2,i_3})} \\
G_2^2 &= \frac{-\left\langle F_{i_2,i_1,-i_2}[x,t] - \mathrm{e}^{(-\mu_{i_1}x - a_{i_1,-i_2}t)} \right\rangle}{R_{i_2}\prod_{i_3=i_1,(i_3\neq i_2,R_{i_3}=R_{i_2})}^{i} - k_{i_2,i_3}}
\end{aligned} \tag{15}
$$

where the term F_{i_1,i_2,i_3} is given by: (see Eq. (S2.5) in Supplementary section S2)

$$
F_{i_1,i_2,i_3}[x,t] = u\left(t - \frac{R_{i_1}x}{v}\right)\mathrm{e}^{-a_{i_2,i_3}\left(t - \frac{R_{i_1}x}{v}\right)} \tag{16}
$$

It can be shown that, in the absence of initial contaminant distributions the solutions derived in this section are identical to those published in Harada et al. [8] and Higashi and Pigford [9]. Note that, although the solution for the no dispersion case appears to be identical in structure to the general solution, the F_{i_1,i_2,i_3} terms involved in this solution, defined in equation, are distinctly different from that of the general solution. These new F_{i_1,i_2,i_3} terms do not involve the ERFC terms and hence are easier to compute.

4. Example problems

A general computer code that implements Eq. (2) was developed based on the computational algorithm provided in Section 2. Using this code, the general solution is first tested against two published example problems: one involving the Dirichlet boundary and the other involving the Cauchy boundary. The example problem for the Dirichlet boundary condition is taken from Cho [1]. The parameters used in this problem are summarized in Table 1. The results of the general

Table 1
Parameters used in the Cho [1] example problem

Parameter	Value
Velocity; v (cm/h)	1
Dispersion coefficient; D_x (cm^2/h)	0.18
Simulation time; t (h)	200
Pulse time; t_o (h)	200
Retardation factors; R, 1–3	2, 1, 1
First-order decay coefficients k, 1–3 (1/h)	0.01, 0.1, 0
Yield coefficients; y, 1–2	1, 1
First-order source decay coefficients; λ, 1–3 (1/h)	0, 0, 0
Boundary constant value species 1; B, 1–1	1
Boundary constant value species 2; B, 1–2	0, 0
Boundary constant value species 3; B, 1–3	0, 0, 0
Initial condition constant; c^o, 1 to 3	0, 0, 0
Initial condition exponent; μ, 1–3 (1/cm)	0, 0, 0

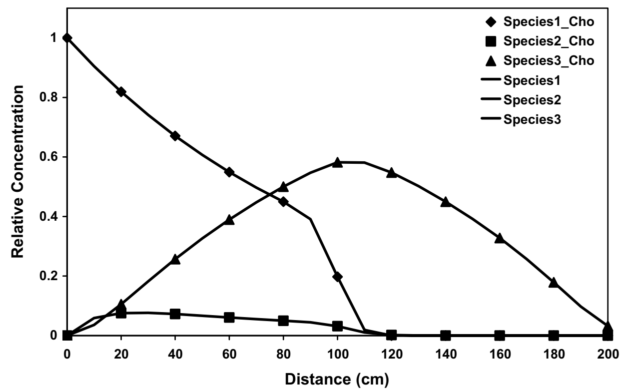

Fig. 1. Comparison of the concentration profiles of the general solution with the Cho [1] solution (3 species, Dirichlet boundary condition).

solution are compared against the results given in Cho [1]. Fig. 1 compares the concentration profiles of the two solutions. It can be observed that the two solutions give identical results.

The Cauchy boundary example problem is taken from van Genuchten [16]. This problem is a modified version of the problem given by Higashi and Pigford [9]. Here the source is modeled as a step source and decay is assumed to occur in both phases. The transport parameters used in this problem are summarized in Table 2. The results of the general solution are compared against the van Genuchten [16] solution and are summarized in Fig. 2. Observation of the concentration profiles given in Fig. 2 indicates that there is an excellent match between the two solutions.

Table 2
Parameters used in the modified Higashi and Pigford [9] example problem as given by van Genuchten [16]

Parameter	Value
Velocity; v (m/year)	100
Dispersion coefficient; D_x (m^2/year)	10
Simulation time; t (year)	1.0E+5
Pulse time; t_o (year)	1.0E+4
Retardation factors; R, 1–4	1.0E+4, 1.4E+4, 5.0E+4, 5.0E+2
First-order decay coefficients k, 1–4 (1/year)	7.9E−3, 2.8E−6, 8.71E−6, 4.3E−4
Yield coefficients; y, 1–3	1,1,1
First-order source decay coefficients; λ, 1–4 (1/year)	8.9E−3, 1.0028E−3, 1.0087E−3, 1.43E−3
Boundary constant value species 1; B, 1–1	1.25
Boundary constant value species 2; B, 1–2	−1.2504, 1.2504
Boundary constant value species 3; B, 1–3	4.43684E−4, 5.93431E−1, −5.93874E−1
Boundary constant value species 4; B, 1–4	−5.1674E−6, 1.20853E−2, −1.22637E−2, 1.78958E−4
Initial condition constant; c^o, 1–4	0, 0, 0, 0
Initial condition exponent; μ, 1–4 (1/m)	0, 0, 0, 0

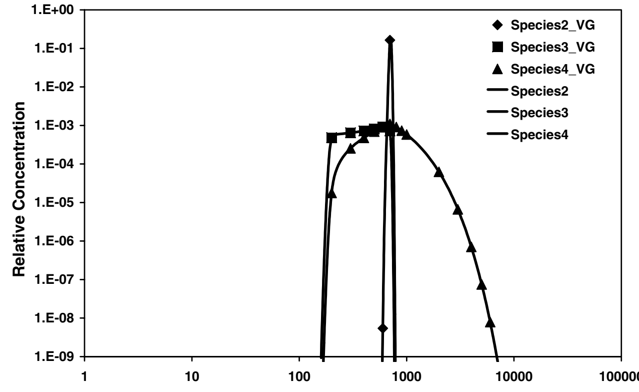

Fig. 2. Comparison of the concentration profiles of the general solution with the van Genuchten [16] solution (4 species, Cauchy boundary condition).

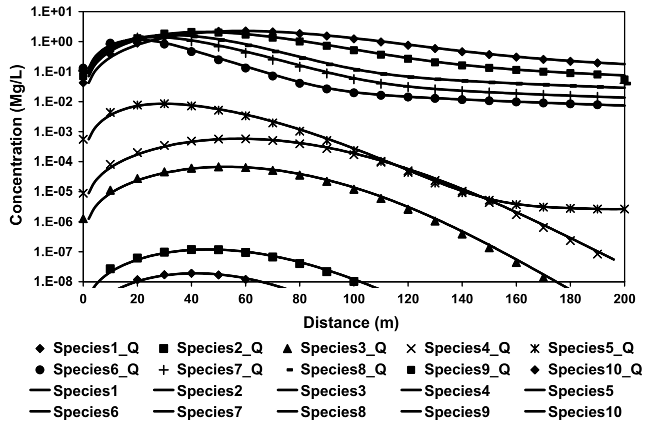

Fig. 3. Comparison of the concentration profiles of the general solution with the Quezada et al. [11] semi-analytical solution (10 species, Dirichlet boundary condition).

The above example problems only considered the transport of a limited number of species in the absence of initial conditions. To further test the performance of the general solution, a hypothetical 10 species problem was formulated that included exponentially decaying boundary conditions along with spatially varying initial contaminant distributions. Decay is assumed to occur only in the liquid phase only. Furthermore, the retardation factors of some of the species were made equal. Table 3 summarizes the model parameters used in this problem. The above problem was solved for a Dirichlet boundary condition assuming a pulse time for the source release t_o as 10 years. The results of the general solution were compared against the semi-analytical solution given by Quezada et al. [11]. Fig. 3 shows the concentration distributions of all the species. These results indicate that the two solutions match well. An identical problem with a source pulse time t_o of 20 years was formulated for a Cauchy boundary. The concentration distributions of all the species were compared against the Quezada et al. [11] solution. Fig. 4 compares the profiles of both these solutions. Again, it can be seen that the profiles predicted by the two solutions have a good match. These simulations further validate the performance of the general solution for transport problems involving long chain lengths.

Finally, the steady state solution derived in this study is tested against the transient version of the general code developed in this study using an example problem. The transient codes were simulated for large simulation times in order to achieve near steady state conditions. The example problem chosen for this simulation is the steady state version of the Cho [1] problem (see Table 1). Fig. 5 compares the profiles generated by the steady state solution and the transient solution. It can be observed that both these solution match well. It must be noted that unlike the computations involved in the tran-

Table 3
Parameters used in the new 10 species example problem

Parameter (Should be updated)	Value
Velocity; v (m/year)	5
Dispersion coefficient; D_x (m^2/year)	50
Simulation time; t (year)	20
Pulse Time; t_o (year)	10 (For Dirichlet) and 20 (For Cauchy)
Retardation factors; R, 1–10	1.9, 1, 1.4, 1, 5, 8, 1.4, 3.1, 1,1
First-order decay coefficients k, 1–10 (1/year)	3, 2, 1.5, 1.25, 2.75, 1, 0.75, 0.5, 0.25, 0.1
Yield coefficients; y, 1–9	1, 2, 1.5, 0.4, 1, 1, 0.7, 0.9, 1
First-order source decay coefficients; λ, 1–10 (1/year)	0.1, 0.75, 0.5, 0.25, 0, 0, 0.3, 1, 0, 0.65
Boundary constant value species 1; B, 1–1 (Mg/L)	10
Boundary constant value species 2; B, 1–2 (Mg/L)	0, 5
Boundary constant value species 3; B, 1–3 (Mg/L)	0, 0, 2.5
Boundary constant value species 4; B, 1–4 (Mg/L)	0, 0, 0, 0
Boundary constant value species 5; B, 1–5 (Mg/L)	0, 0, 0, 0, 10
Boundary constant value species 6; B, 1–6 (Mg/L)	0, 0, 0, 0, 0, 5
Boundary constant value species 7; B, 1–7 (Mg/L)	0, 0, 0, 0, 0, 0, 2.5
Boundary constant value species 8; B, 1–8 (Mg/L)	0, 0, 0, 0, 0, 0, 0, 0
Boundary constant value species 9; B, 1–9 (Mg/L)	0, 0, 0, 0, 0, 0, 0, 0, 0
Boundary constant value species 10; B, 1–10 (Mg/L)	0, 0, 0, 0, 0, 0, 0, 0, 0, 0
Initial condition constant; c^o, 1–10 (Mg/L)	0, 0.1, 0.2, 0, 0.25, 0.3, 0.15, 0, 0, 0
Initial condition exponent; μ, 1–10 (1/m)	0, 0.01, 0, 0, 0.02, 0.01, 0.1, 0, 0, 0

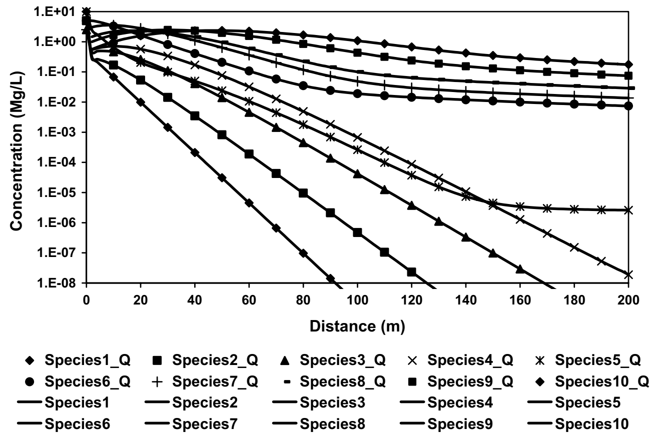

Fig. 4. Comparison of the concentration profiles of the general solution with the Quezada et al. [11] semi-analytical solution (10 species, Cauchy boundary condition).

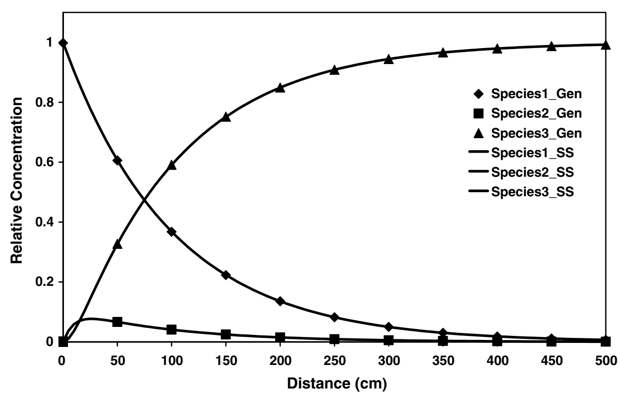

Fig. 5. Comparison of the concentration profiles of the steady state solution with the general transient solution (3 species, Dirichlet boundary condition).

sient codes, the computations in the steady state code do not have any stability issues. Hence the steady state solutions provide a powerful alternative to simulate the long term performance of contaminated sites.

5. Discussions

5.1. Salient features of the general solution

One of the most important features of the general solution is that can solve an arbitrary number of species. The final solution is given in an explicit closed-form format that avoids numerical methods. In addition, the general solution is formulated and presented in format such that the solutions for both the Dirichlet and Cauchy boundaries share a common structure. This enables the implementation of both these solutions within one code that shares several common routines with the capability to easily switch between the two boundary conditions.

Another interesting advantage of this solution is that it can be used to directly obtain the solution for a particular species in the chain without involving the computations of other species. This is extremely efficient when modeling scenarios where there the daughter product would be more toxic or more mobile than the parent compound. In this case, one would be interested in obtaining the concentration profiles for the daughter product only. Solving this problem numerically would involve the computation of all the predecessor species and this can be time consuming. A similar situation also arises when employing the recursive type semi-analytical solutions presented by Harada et al. [8] (see Eq. 4.20 in [8]). Their solution expression for any species $i > 1$ involves the concentration term of its predecessor $i - 1$th species.

The third feature of this solution is that it can be readily extended to a general diverging reaction network. As pointed out by Sun et al. [15], one can conceptualize a diverging network as a superposition of a series of parallel reaction networks

Table 4
Summary of parameter limitations

$k_{i_1,i_2} \neq 0; \quad \forall i_1, i_2 = 1, 2, \ldots n$
where $i_1 \neq i_2$
$a_{i_1,i_2} \neq a_{i_1,i_3}; \quad \forall i_1, i_2, i_3 = 1, 2, \ldots n$
where $i_1 \neq i_2, i_1 \neq i_3, i_2 \neq i_3, R_{i_1} \neq R_{i_2}$ and $R_{i_1} \neq R_{i_3}$
$a_{i_1,i_2} \neq \lambda_{i_3}; i \leqslant i_1, i_2 \leqslant n; 1 \leqslant i_3 \leqslant i; \quad \forall i = 1, 2, \ldots n$
where $i_1 \neq i_2$ and $R_{i_1} \neq R_{i_2}$
$a_{i_1,i_2} \neq a_{i,-i_1}; i \leqslant i_1, i_2 \leqslant n; \quad \forall i = 1, 2, \ldots n$
where $i_1 \neq i_2$ and $R_{i_1} \neq R_{i_2}$

each of which can be solved independently. It must be noted that one diverging species will have no effect on the other diverging species and hence they can be considered independent of each other. Hence in order to solve a diverging reaction network, one has to split the network into a set of parallel sequential reaction networks and solve each sequential chain independently.

The one dimensional solutions presented in this work can be readily extended to solve multi-dimensional transport problems involving transverse dispersion terms using the approximate Domenico solution [5]. The mathematical details of this extension strategy are provided in Quezada [10]. As pointed out by Srinivasan et al. [13], this strategy can provide reasonable estimates for multi-dimensional transport problems.

5.2. Limitations of the general solution

Despite its advantages, the general solution and its simplified solutions have some key limitations. As with the case of all analytical solutions, these solutions can model idealized transport problems only. Situations involving heterogeneity, variation in the flow field, presence of source/sink terms, etc. cannot be modeled using these solutions. Furthermore, these solutions are restricted to modeling first-order kinetic reactions only. Although this is highly suitable for modeling radioactive waste transport and certain types of simplified chemical reactions, these solutions cannot capture the more generic reaction kinetics such as the Monod kinetics.

The general solution places several limitations on the values of the transport parameters which are summarized in Table 4. The details/origins of these limitations can be obtained from Srinivasan and Clement [12], Appendix A and Supplementary section S2. These limiting conditions arise when factorizing the denominator of the G terms during the computation of the inverse Laplace transforms. An easy approach to tackle this problem is to marginally perturb the individual model parameters such that the limiting conditions are averted [16]. This would enable us to tackle the problem using the general code. However, this perturbation technique can potentially aggravate some of the existing computational problems related to overflow/under flow errors. Another more rigorous approach to tackle this problem would be to perform a mathematical analysis incorporating these special cases and evaluating the corresponding alternate expressions, similar to the analysis used to handle the case of identical retardation factors. This analysis would involve modifying the factorization of the G terms to include the limiting conditions and performing generalized inverse Laplace transform operations on the alternate expressions.

Finally, it must be noted that unlike the semi-analytical solutions presented by Clement [2] or Quezada et al. [11] which can model arbitrary reaction networks, the general solution can only model sequential and/or diverging reaction networks. However, it is possible to extend this solution to solve systems involving complex reaction networks using a similar approach. The key step required to perform this extension would be to obtain generalized expressions for the linear transform matrices used to uncouple the coupled system of equations.

6. Conclusions

In this two-part article we develop a set of analytical solutions to multi-species reactive transport equations that are coupled through sorption and sequential first-order reactions. In Part-I of this work, we provide the mathematical derivations of the general solution which incorporates a generic Bateman type exponentially decaying Dirichlet and Cauchy source boundary conditions and a spatially varying initial condition. In Part-II, we test the validity of the general solution and also discuss the computational techniques for implementing the solutions. In addition, several special-case solutions for simpler transport problems involving zero initial condition, identical retardation factors, zero advection, zero dispersion and steady-state condition are presented. The solutions proposed in this study can be used to develop screening tools for assessing ground water quality issues at sites contaminated with chemicals undergoing first-order decay reactions.

Acknowledgements

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Appendix A. Derivation of the steady state solutions

A.1. Dirichlet boundary

The system of governing transport equations can be written in a matrix format as [2,11]

$$v\frac{\mathrm{d}\{c\}}{\mathrm{d}x} - D_x\frac{\mathrm{d}^2\{c\}}{\mathrm{d}x^2} = [K]\{c\} \tag{A.1}$$

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

$$\left\{\frac{\mathrm{d}c(\infty)}{\mathrm{d}x}\right\} = 0 \tag{A.2}$$

$$\{c(0)\} = \{\omega\}$$

where

$$\omega_i = \sum_{i_1=1}^{i} B_i^{i_1}; \quad \forall i = 1, 2, \ldots, n \tag{A.3}$$

Now in order to uncouple the system of ordinary differential equations (ODEs) given by equation, we apply a linear transform procedure described by Clement [2], i.e. we perform the following matrix operation.

$$\{c\} = [A]\{b\} \tag{A.4}$$

where $\{b\}$ is the concentration in the transformed domain. Applying this transformation equation gets modified as

$$\frac{\mathrm{d}^2[A]\{b\}}{\mathrm{d}x^2} - \left(\frac{v}{D_x}\right)\frac{\mathrm{d}[A]\{b\}}{\mathrm{d}x} + \frac{1}{D_x}([K])[A]\{b\} = 0 \tag{A.5}$$

Pre-multiplying equation with $[A]^{-1}$ we get:

$$\frac{\mathrm{d}^2\{b\}}{\mathrm{d}x^2} - \left(\frac{v}{D_x}\right)\frac{\mathrm{d}\{b\}}{\mathrm{d}x} + \frac{1}{D_x}[\widetilde{K}]\{b\} = 0 \tag{A.6}$$

where

$$[\widetilde{K}] = [A]^{-1}[K][A]$$

By forcing the columns of the $[A]$ matrix as the eigenvectors of the $[K]$ matrix, we can make $[\widetilde{K}]$ a diagonal matrix and thus uncouple the system of equations; the details of this similarity transformation procedure are illustrated in Clement [2]. The corresponding $[A]$ matrix is given as

$$[A] = \begin{bmatrix} \prod_{i=2}^{n} \frac{-(k_1-k_i)}{y_i k_{i-1}}, 0, 0, \ldots \\ \prod_{i=3}^{n} \frac{-(k_1-k_i)}{y_i k_{i-1}}, \prod_{i=3}^{n} \frac{-(k_2-k_i)}{y_i k_{i-1}}, 0, 0, \ldots \\ \cdot \\ \cdot \\ \prod_{i=n}^{n} \frac{-(k_{11}-k_i)}{y_i k_{i-1}}, \prod_{i=n}^{n} \frac{-(k_2-k_i)}{y_i k_{i-1}}, \ldots, \prod_{i=n}^{n} \frac{-(k_{n-1}-k_i)}{y_i k_{i-1}}, 0 \\ 1, 1, \ldots \end{bmatrix} \tag{A.7}$$

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

$$[A]^{-1} = \begin{bmatrix} \frac{\prod_{i=2}^{n} y_i k_{i-1}}{\prod_{i=1,(i\neq 1)}^{n} -(k_1-k_i)}, 0, 0, \ldots \\ \frac{\prod_{i=2}^{n} y_i k_{i-1}}{\prod_{i=1,(i\neq 2)}^{n} -(k_2-k_i)}, \frac{\prod_{i=3}^{n} y_i k_{i-1}}{\prod_{i=2,(i\neq 2)}^{n} -(k_2-k_i)}, 0, 0, \ldots \\ . \\ . \\ \frac{\prod_{i=2}^{n} y_i k_{i-1}}{\prod_{i=1,(i\neq n)}^{n} -(k_n-k_i)}, \frac{\prod_{i=3}^{n} y_i k_{i-1}}{\prod_{i=2,(i\neq n)}^{n} -(k_n-k_i)}, \ldots, \frac{\prod_{i=n}^{n} y_i k_{i-1}}{\prod_{i=n-1,(i\neq n)}^{n} -(k_n-k_i)}, 1 \end{bmatrix} \tag{A.8}$$

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

$$\left[\widetilde{K}\right] = \begin{bmatrix} -k_1, 0, 0, \ldots \\ 0, -k_2, 0, 0, \ldots \\ . \\ . \\ . \\ 0, 0, \ldots (n-1) \text{ entries}, -k_n \end{bmatrix} \tag{A.9}$$

Eq. (A.5) describes a set of n independent second-order homogeneous ODEs the boundary conditions of which are obtained by linear transforming Eqs. (A.2) and (A.3). This yields:

$$\left\{\frac{\mathrm{d}b(\infty)}{\mathrm{d}x}\right\} = 0 \tag{A.10}$$

$$b_i(0) = \sum_{i_1=1}^{i}\left[\frac{\prod_{i_2=i_1+1}^{n} y_{i_2} k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n} -(k_i - k_{i_2})} \sum_{i_2=1}^{i_1} B_{i_1}^{i_2}\right]; \quad \forall i = 1, 2, \ldots, n \tag{A.11}$$

Since Eq. (A.5) is uncoupled, it can now be written as a set of n independent equations as

$$\frac{\mathrm{d}^2 b_i(x)}{\mathrm{d}x^2} - \left(\frac{v}{D_x}\right)\frac{\mathrm{d}b_i(x)}{\mathrm{d}x} + \frac{1}{D_x}(-k_i)b_i(x) = 0; \quad \forall i = 1, 2, \ldots, n \tag{A.12}$$

The general solution to Eq. (A.12) is given as

$$b_i(x) = \Psi_i^1 \mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}+\sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]} + \Psi_i^2 \mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}-\sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]}; \quad \forall i = 1, 2, \ldots, n \tag{A.13}$$

where Ψ_i^1 and Ψ_i^2 are constants. In order to apply the boundary condition given by Eq. (A.10) we differentiate the general solution with respect to x. Differentiation of Eq. (A.13) with respect to x yields:

$$\frac{\mathrm{d}b_i(x)}{\mathrm{d}x} = \Psi_i^1\left[\frac{1}{2}\left\{\frac{v}{D_x}+\sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]\mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}+\sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]} + \Psi_i^2\left[\frac{1}{2}\left\{\frac{v}{D_x}-\sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]\mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}-\sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]}; \quad \forall i = 1, 2, \ldots, n \tag{A.14}$$

To satisfy the boundary condition given by Eq. (A.10), i.e. when x tends to ∞; the exponential function in the first term tends to ∞, hence Ψ_i^1 must vanish. Eq. (A.13) now reduces to:

$$b_i(x) = \Psi_i^2 \mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x}-\sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]}; \quad \forall i = 1, 2, \ldots, n \tag{A.15}$$

Applying the second boundary condition given by Eq. (A.11), we get:

$$\Psi_i^2 = \sum_{i_1=1}^{i}\left[\frac{\prod_{i_2=i_1+1}^{n} y_{i_2} k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n} -(k_i - k_{i_2})} \sum_{i_2=1}^{i_1} B_{i_1}^{i_2}\right]; \quad \forall i = 1, 2, \ldots, n \tag{A.16}$$

Note that the condition $k_{i_1,i_2} \neq 0$, where $1 \leqslant i_1, i_2 \leqslant n$ and $i_1 \neq i_2$ must be satisfied for Eq. (A.16) to be valid. Therefore, the solution in the b domain is:

$$b_i(x) = \sum_{i_1=1}^{i} \left[\frac{\prod\limits_{i_2=i_1+1}^{n} y_{i_2} k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n} - (k_i - k_{i_2})} \sum_{i_2=1}^{i_1} B_{i_1}^{i_2} \right] \mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x} - \sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]}; \quad \forall i = 1,2,\ldots,n \tag{A.17}$$

Inverse linear transform of Eq. (A.17) is done to obtain the solution in the c domain by using Eq. (A.4). The final steady state solution for the Dirichlet boundary is:

$$c_i(x) = \sum_{i_1=1}^{i} \left[\left(\prod_{i_2=i_1+1}^{i} y_{i_2} k_{i_2-1} \right) \left(\sum_{i_2=1}^{i_1} B_{i_1}^{i_2} \right) \sum_{i_2=i_1}^{i} \frac{\mathrm{e}^{\left[\frac{x}{2D_x}\left\{v - \sqrt{v^2+4D_x k_{i_2}}\right\}\right]}}{\prod\limits_{i_3=i_1,(i_3\neq i_2)}^{i} -(k_{i_2} - k_{i_3})} \right]; \quad \forall i = 1,2,\ldots,n \tag{A.18}$$

A.2. Cauchy boundary

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

$$-D_x \frac{\mathrm{d}c_i(0)}{\mathrm{d}x} + v c_i(0) = \sum_{i_1=1}^{i} B_i^{i_1} v; \quad \forall i = 1,2,\ldots,n \tag{A.19}$$

Since the governing equations and the boundary condition at ∞ are identical for the Dirichlet and the Cauchy boundaries, the procedures involved in uncoupling the system of equations will be identical and hence we can use the previous section to obtain the semi-determined general solution and the linear transform matrices $[A]$ and $[A]^{-1}$. The semi-determined general solution [identical to equation] is given by:

$$b_i(x) = \Psi_i^2 \mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x} - \sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]}; \quad \forall i = 1,2,\ldots,n \tag{A.20}$$

The linear transform matrices $[A]$ and $[A]^{-1}$ are given by Eqs. (A.7) and (A.8) respectively. The constant Ψ_i^2 in Eq. (A.19) is evaluated by using the boundary condition given by Eq. (A.20) after transforming them into the b domain by applying the linear transform given by Eq. (A.4). The transformed boundary condition can be expressed as

$$-D_x \frac{\mathrm{d}b_i(0)}{\mathrm{d}x} + v b_i(0) = \sum_{i_1=1}^{i} \left[\frac{v \prod_{i_2=i_1+1}^{n} y_{i_2} k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n} - (k_i - k_{i_2})} \sum_{i_2=1}^{i_1} B_{i_1}^{i_2} \right]; \quad \forall i = 1,2,\ldots,n \tag{A.21}$$

Note that the condition $k_{i_1,i_2} \neq 0$, where $1 \leqslant i_1, i_2 \leqslant n$ and $i_1 \neq i_2$ must be satisfied for Eq. (A.21) to be valid. Substituting the expression for $b_i(x,s)$ from the semi-determined general solution given by Eq. (A.20) into the transformed boundary condition given by Eq. (A.21), we can evaluate the constant Ψ_i^2 as follows:

$$-D_x \Psi_i^2 \left[\frac{1}{2} \left\{ \frac{v}{D_x} - \sqrt{\frac{v^2}{D_x^2} + \frac{4k_i}{D_x}} \right\} \right] + v\Psi_i^2 = \sum_{i_1=1}^{i} \left[\frac{v \prod_{i_2=i_1+1}^{n} y_{i_2} k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n} - (k_i - k_{i_2})} \sum_{i_2=1}^{i_1} B_{i_1}^{i_2} \right]; \quad \forall i = 1,2,\ldots,n \tag{A.22}$$

From Eq. (A.22) Ψ_i^2 is evaluated as

$$\Psi_i^2 = \frac{\sum\limits_{i_1=1}^{i} \left[\frac{v \prod_{i_2=i_1+1}^{n} y_{i_2} k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n} -(k_i - k_{i_2})} \sum\limits_{i_2=1}^{i_1} B_{i_1}^{i_2} \right]}{\left\{ \frac{v}{2} + \frac{1}{2}\sqrt{v^2 + 4D_x k_i} \right\}}; \quad \forall i = 1,2,\ldots,n \tag{A.23}$$

Therefore, the solution in the b domain is:

$$b_i(x) = \sum_{i_1=1}^{i} \left[\frac{\prod_{i_2=i_1+1}^{n} y_{i_2} k_{i_2-1}}{\prod_{i_2=i_1,(i_2\neq i)}^{n} - (k_i - k_{i_2})} \sum_{i_2=1}^{i_1} B_{i_1}^{i_2} \right] \frac{v \mathrm{e}^{\left[\frac{x}{2}\left\{\frac{v}{D_x} - \sqrt{\frac{v^2}{D_x^2}+\frac{4k_i}{D_x}}\right\}\right]}}{\left\{ \frac{v}{2} + \frac{1}{2}\sqrt{v^2 + 4D_x k_i} \right\}}; \quad \forall i = 1,2,\ldots,n \tag{A.24}$$

Inverse Linear transform of Eq. (A.24) is done to obtain the solution in the c domain by using Eq. (A.4). The final steady state solution for the Cauchy boundary is:

$$c_i(x) = \sum_{i_1=1}^{i}\left[\left(\prod_{i_2=i_1+1}^{i} y_{i_2}k_{i_2-1}\right)\left(\sum_{i_2=1}^{i_1} B_{i_1}^{i_2}\right)\sum_{i_2=i_1}^{i}\frac{v e^{\left[\frac{x}{2D_x}\left\{v-\sqrt{v^2+4D_xk_{i_2}}\right\}\right]}}{\left\{\frac{v}{2}+\frac{1}{2}\sqrt{v^2+4D_xk_{i_2}}\right\}\prod_{i_3=i_1,(i_3\neq i_2)}^{i} - (k_{i_2}-k_{i_3})}\right];\quad \forall i=1,2,\ldots,n \tag{A.25}$$

Appendix B. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.advwatres.2007.08.001.

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