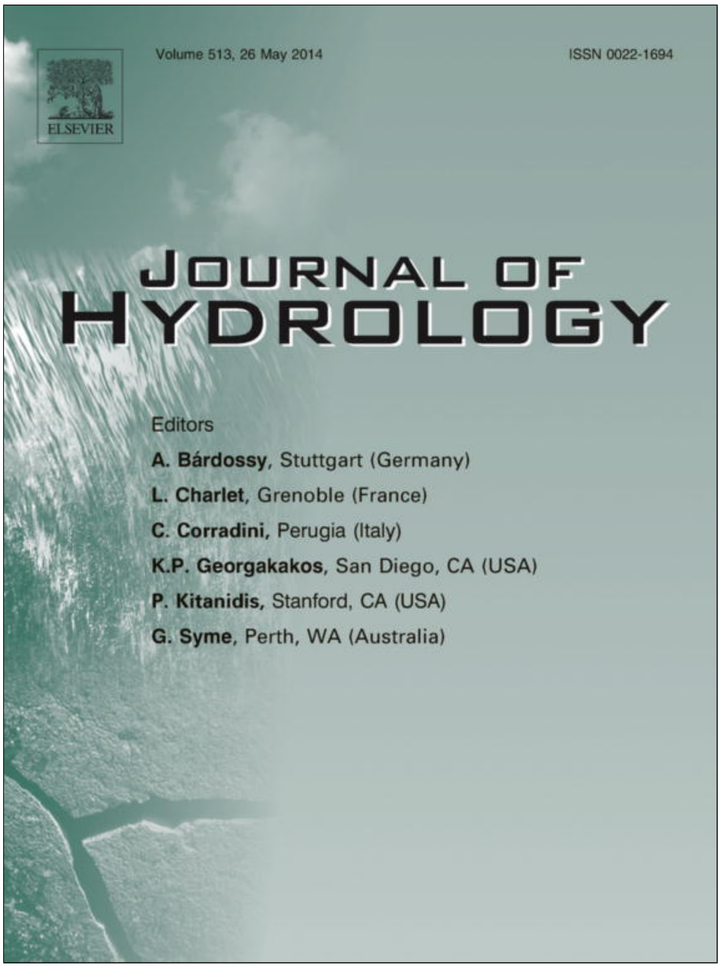
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Exact series solutions of reactive transport models with general initial conditions

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SUMMARY

Exact solutions of partial differential equation models describing the transport and decay of single and coupled multispecies problems can provide insight into the fate and transport of solutes in saturated aquifers. Most previous analytical solutions are based on integral transform techniques, meaning that the initial condition is restricted in the sense that the choice of initial condition has an important impact on whether or not the inverse transform can be calculated exactly. In this work we describe and implement a technique that produces exact solutions for single and multispecies reactive transport problems with more general, smooth initial conditions. We achieve this by using a different method to invert a Laplace transform which produces a power series solution. To demonstrate the utility of this technique, we apply it to two example problems with initial conditions that cannot be solved exactly using traditional transform techniques.

1. Introduction

Mathematical models describing the transport and reaction of dissolved solutes in saturated porous media can play an important role in informing our understanding of contaminant fate and transport processes (Bear, 1972; Domenico, 1987; Remson et al., 1971; Wang and Anderson, 1982; Zheng and Bennett, 2002). For some modeling projects, it is relevant to implement a detailed numerical model that can account for multidimensional, multispecies, nonlinear reactive transport processes (Clement et al., 1998; Clement, 2011; Molz et al., 1986; Zheng and Wang, 1999). In other cases, where insufficient data or finances are available to support the use of a detailed numerical model, a simpler approach, based on an analytical solution of a linear partial differential equation (pde) model, could be more relevant (Clement, 2011; Jones et al., 2006).

Several previous researchers have sought to develop exact solutions to systems of coupled linear advection diffusion reaction equations with decay-chain reaction process. In 1971, Cho (1971) presented an exact solution of a one-dimensional model representing the reactive transport of a system with three components describing nitrification processes. van Genuchten and Wierenga (1976) and van Genuchten (1981, 1985) derived similar exact solutions for decay-chain processes with more complicated inlet boundary conditions and for a system that made an explicit distinction between mobile and immobile species (van Genuchten and Wierenga, 1976; van Genuchten, 1981, 1985). All of these studies were based on solving the governing pde using a Laplace transform technique which meant that the approach was only relevant for relatively simple initial conditions. Both Cho (1971) and van Genuchten and Wierenga (1976, 1981, 1985) focused on problems where the domain was initially free of solutes. Building on these previous investigations, Lunn et al. (1996) presented exact solutions of the system studied by Cho (1971) using a Fourier transform method. This approach allowed Lunn to solve the system for more complicated initial conditions including a constant non-zero initial condition, and an exponentially decaying initial condition.

Further developments of exact or semianalytical solutions of coupled linear advection diffusion reaction equations with decay-chain reaction networks have also been reported. These include extensions to any number of species in the reaction network (Clement, 2000), the presence of distinct equilibrium reactions represented by different retardation factors (Srinivasan and Clement, 2008a,b) as well as dealing with reactive transport processes in two- and three-dimensions (Jones et al., 2006; Sudicky et al., 2013; Wexler, 1992). Approaches based on Green's functions (Kreyszig, 2006) have also been used successfully to analyze two-

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and three-dimensional transport problems with persistent source terms (Leij et al., 2000). More recent developments have included semianalytical solutions for mathematical models where the transport coefficients are spatially variable (Suk, 2013). Regardless of these developments, we note that previously-reported solution methods based on an integral transform technique are restricted in the sense that they require a relatively simple initial condition to permit the exact calculation of the inverse transform. For example, van Genuchten and Wierenga (1976) and van Genuchten (1985) considered a solute-free initial condition; Lunn et al. (1996) considered either a spatially constant or exponentially decaying initial condition; and Srinivasan and Clement (2008a,b) focused on an exponentially decaying initial condition. One of the limitations of these previous methods is that they cannot be applied to other kinds of initial conditions. If, for example, we wished to study the reactive transport of a system with some initial distribution of solute that is neither spatially uniform or decaying exponentially with position, it is impossible to use any of these previous methods to provide an exact solution. These restrictions motivated the recent work by Wang et al. (2011) who proposed an approximate superposition method to solve reactive transport pdes with nonzero initial conditions. While this recent work did not provide any exact solutions to the governing pde model, they did provide insight into conditions where their approximation provided useful information (Wang et al., 2011).

In this work we describe and implement a method that provides an exact power series solution for linear reactive transport problems for more general initial conditions. Our method involves a different way of calculating an inverse Laplace transform and this allows us to consider more general, smooth, non-zero initial conditions, such as nonmonotone functions, which have not been dealt with previously in an exact mathematical framework. In addition to presenting the theoretical aspects of our approach, we also present two example calculations. The first example calculation is for a single species reactive transport model where we consider a nonmonotone initial condition for which traditional transform inversion techniques are not applicable. Second, we consider a coupled problem where again we chose a nonmonotone initial condition which means that traditional exact inverse transform techniques are not applicable. For both cases we compare our truncated power series solutions with numerical calculations to confirm that the proposed method produces accurate results. We conclude by pointing out how our method can be implemented in a very straightforward way using symbolic software and we provide Maple code as supplementary material.

2. Theory

To demonstrate our approach, we first outline how our method allows us to recover a simple function from its Laplace transform without the use of mathematical tables or calculating the inverse transform numerically (e.g., De Hoog et al., 1982). We begin by considering some function $f(t)$, and the Laplace transform of that function, which can be written as

$$\mathcal{L}\{f(t)\} = \int_0^\infty f(t)\mathrm{e}^{-st}\,\mathrm{d}t, \tag{1}$$

where s is the Laplace transform parameter chosen such that the improper integral converges (Beerends et al., 2003; Debnath and Bhatta, 2007; Kreyszig, 2006; Zill and Cullen, 1992). For suitable choices of $f(t)$, such that $\lim_{t\to\infty}\left[\frac{\mathrm{d}^n f(t)}{\mathrm{d}t^n}\mathrm{e}^{-st}\right] = 0$ for all n, repeated application of integration by parts to Eq. (1) gives us

$$\mathcal{L}\{f(t)\} = \frac{1}{s}\left[f(0) + \frac{1}{s}\frac{\mathrm{d}f(0)}{\mathrm{d}t} + \frac{1}{s^2}\frac{\mathrm{d}^2f(0)}{\mathrm{d}t^2} + \frac{1}{s^3}\frac{\mathrm{d}^3f(0)}{\mathrm{d}t^3} + \ldots\right]. \tag{2}$$

Eq. (2) leads to the initial value theorem (Beerends et al., 2003; Debnath and Bhatta, 2007; Ellery et al., 2013)

$$\lim_{s\to\infty}[s\mathcal{L}\{f(t)\}] = f(0), \tag{3}$$

allowing us to calculate the initial value of the function, $f(0)$, directly from $\mathcal{L}\{f(t)\}$ without needing to explicitly invert the Laplace transform. We may extend the initial value theorem by making a change of variables, let $g(t) = \frac{\mathrm{d}^n f(t)}{\mathrm{d}t^n}$, so that we have $\lim_{s\to\infty}[s\mathcal{L}\{g(t)\}] = g(0)$. Re-stating this result in terms of the original variables gives us

$$\lim_{s\to\infty}\left[s\mathcal{L}\left\{\frac{\mathrm{d}^n f(t)}{\mathrm{d}t^n}\right\}\right] = \frac{\mathrm{d}^n f(0)}{\mathrm{d}t^n}, \tag{4}$$

which means that if we know the Laplace transform of the nth derivative of a function, we can evaluate the nth derivative of that function at $t = 0$ without explicitly inverting the transform. Since we know that the Laplace transform of the nth derivative of a function (Beerends et al., 2003, Debnath and Bhatta, 2007, Kreyszig, 2006 and Zill and Cullen, 1992) is given by

$$\mathcal{L}\left\{\frac{\mathrm{d}^n f(t)}{\mathrm{d}t^n}\right\} = s^n\mathcal{L}\{f(t)\} - \sum_{k=1}^{n}\frac{\mathrm{d}^{k-1}f(0)}{\mathrm{d}t^{k-1}}s^{n-k}, \tag{5}$$

we can re-express Eq. (4) as

$$\frac{\mathrm{d}^n f(0)}{\mathrm{d}t^n} = \lim_{s\to\infty}\left[s^{n+1}\mathcal{L}\{f(t)\} - s\sum_{k=1}^{n}\frac{\mathrm{d}^{k-1}f(0)}{\mathrm{d}t^{k-1}}s^{n-k}\right], \tag{6}$$

which means that given $\mathcal{L}\{f(t)\}$, we can calculate all the derivatives of $f(t)$ at $t = 0$. With this information we may then construct a Maclaurin series

$$f(t) = \sum_{i=0}^{\infty}\frac{\mathrm{d}^i f(0)}{\mathrm{d}t^i}\frac{t^i}{i!}. \tag{7}$$

Therefore, for a particular function $f(t)$, for which we can calculate the Laplace transform, $\mathcal{L}\{f(t)\}$, we may reconstruct the function using Eqs. (6) and (7). The reconstruction of $f(t)$ does not depend on calculating the inverse transform. For the practical implementation of the Maclaurin series representation of $f(t)$, we must truncate Eq. (7) after I terms. We will show, by example, that it is often straightforward to obtain reasonably accurate solutions with a relatively modest value of I.

To demonstrate how we might make use of this result, let us consider the straightforward case of $f(t) = \mathrm{e}^{at}$, for which the Laplace transform is $\mathcal{L}\{f(t)\} = 1/(s-a)$, with $s > a$ (Kreyszig, 2006; Zill and Cullen, 1992). Using Eq. (6) we rapidly see that we have

$$\frac{\mathrm{d}f}{\mathrm{d}t}(0) = a,\ \frac{\mathrm{d}^2f}{\mathrm{d}t^2}(0) = a^2,\ \frac{\mathrm{d}^3f}{\mathrm{d}t^3}(0) = a^3,\ \frac{\mathrm{d}^4f}{\mathrm{d}t^4}(0) = a^4, \ldots \tag{8}$$

which, using Eq. (7), allows us to reconstruct the well-known Maclaurin series for the exponential function

$$\mathrm{e}^{at} = 1 + at + \frac{(at)^2}{2!} + \frac{(at)^3}{3!} + \frac{(at)^4}{4!} + \ldots. \tag{9}$$

In summary, Eq. (6) gives us an alternative method for inverting a Laplace transform. Instead of using mathematical tables (Kreyszig, 2006; Zill and Cullen, 1992) or numerical inversion (De Hoog et al., 1982), if we have an explicit formula for $\mathcal{L}\{f(t)\}$, even without any knowledge of $f(t)$, we can recover the Maclaurin series representation of $f(t)$ without difficulty, provided that the function is sufficiently smooth. We note that power series solutions have been used previously to study several practical problems of interest in subsurface hydrology (Philip, 1957a; Philip, 1957b), chemical engineering (Ellery and Simpson, 2011) and bioengineering (Simpson and Ellery, 2012). Although we aim to demonstrate the usefulness of our approach, it is also relevant to point out the conditions under which our approach is invalid. Since we rely on representing the function of interest as a Maclaurin series, we are making an implicit assumption that the solution we seek is smooth. This means that some problems involving nonsmooth initial conditions, such as a Heaviside function, cannot be studied using our approach.

Before we apply our method to study the solution of pde models of a reactive transport process, we will first discuss some differences between our approach and the results described in the previous study by Massouros and Genin (2005) who also described a method for obtaining a power series representation of $f(t)$ from $\mathcal{L}\{f(t)\}$. Massouros and Genin's work follows the same approach as ours except they make a substitution, $t = 1/s$, in Eq. (2) before introducing an iterative algorithm to find the coefficients of a power series representation of $f(t)$ (Massouros and Genin, 2005). There are three main differences between our work and this previous study. First, Massouros and Genin did not apply their technique to solve any kind of pde model. Second, our approach does not require any iterative technique to find the coefficients in the power series solution. Third, Massouros and Genin's technique is limited in the sense that they make the substitution $t = 1/s$, where s is the Laplace transform parameter. We recall that the value of s is typically restricted such that the improper integral definition of the Laplace transform converges. This restriction on the value of s implies that Massouros and Genin's results involve a restriction on the value of t owing to the substitution $t = 1/s$. Our approach does not involve this restriction.

3. Application to single species reactive transport models

We now discuss how to apply Eq. (6) to a linear pde model describing single species reactive transport, given by

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - kC, \quad 0 < x < \infty, \quad t > 0, \quad C(x,0) = h(x), \quad C(0,t) = h(0), \quad \lim_{x\to\infty} C(x,t) = 0, \tag{10}$$

where $C(x,t)$ is the concentration of the solute, x is the spatial coordinate, t is time, D is the diffusivity, v is the advective velocity, k is the decay coefficient and $h(x)$ is the initial distribution of the solute. As we described in Section 1, previous attempts to solve Eq. (10) using transform techniques have been limited to relatively simple choices of $h(x)$ such as constant ($h(x) = H,\ H > 0$) or exponential decaying initial conditions ($h(x) = \mathrm{e}^{-ax}, a > 0$). We will now illustrate that Eq. (6) allows us to construct exact analytical solutions for different choices of $h(x)$. To proceed, we can calculate the Laplace transform of Eq. (10) to arrive at

$$D\frac{\mathrm{d}^2 F}{\mathrm{d}x^2} - v\frac{\mathrm{d}F}{\mathrm{d}x} - (k+s)F = -h(x), \quad 0 < x < \infty, F(0;s) = \frac{h(0)}{s}, \quad \lim_{x\to\infty} F(x;s) = 0, \tag{11}$$

where $F(x;s) = \mathcal{L}\{C(x,t)\}$. The solution of this ordinary differential equation will depend on the form of the initial condition, $h(x)$. Therefore, to make progress at this stage we will consider $h(x) = ax\mathrm{e}^{-bx}$, with $a > 0$ and $b > 0$, which is a nonmonotone function of position with a turning point at $x = \frac{1}{b}$. This kind of initial condition could be used to represent the presence of a pre-existing plume of $C(x,t)$ within the domain. With this choice of initial condition, Eq. (11) can be solved by summing the homogeneous and particular solutions (Kreyszig, 2006; Zill and Cullen, 1992) to give

$$F(x;s) = \frac{a(v+2Db)}{(\phi - s)^2}\left(\mathrm{e}^{mx} - \mathrm{e}^{-bx}\right) - \frac{ax\mathrm{e}^{-bx}}{\phi - s}, \tag{12}$$

where $m = [v - \sqrt{v^2 + 4D(s+k)}]/2D, k+s > 0$ and $\phi = Db^2 + vb - k$. At this stage, a traditional approach to solving this problem (Bear, 1972; Cho, 1971; van Genuchten and Wierenga, 1976; van Genuchten, 1985) would be to calculate the inverse Laplace transform of Eq. (12) to find an exact expression for $C(x,t), C(x,t) = \mathcal{L}^{-1}\{F(x;s)\}$. For this problem, however, the inverse transform of Eq. (12) cannot be obtained using mathematical tables. Furthermore, the symbolic software package Maple could likewise not calculate an exact expression for the inverse Laplace transform. Therefore, a different approach is required.

To make progress, we can combine our expression for $F(x;s)$ with Eqs. (6) and (7) to calculate a power series expression for the solution $C(x,t)$. While the algebra for this procedure is more detailed than the example presented in Section 2, the process of obtaining the power series solution is the same. Furthermore, we present a Maple worksheet as supplementary material to illustrate how the process of calculating the terms in the power series can be automated. The first few terms in this power series are given by

$$C(x,t) = ax\mathrm{e}^{-bx} + a(Db^2x + vbx - kx - 2Db - v)\mathrm{e}^{-bx}t + a\phi(Db^2x + vbx - kx - 4Db - 2v)\mathrm{e}^{-bx}\frac{t^2}{2!} + a\phi^2(Db^2x + vbx - kx - 6Db - 3v)\mathrm{e}^{-bx}\frac{t^3}{3!} + \mathcal{O}(t^4). \tag{13}$$

A more finely truncated power series, up to $\mathcal{O}(t^{10})$, is given in the supplementary material.

We compare how the truncated power series solution performs for this problem by comparing it with a numerical solution of Eq. (10) in Fig. 1. The numerical solution is obtained on the finite domain, $0 < x < L$, with L chosen to be sufficiently large that the finite domain did not influence the numerical solution on the time scale considered. The numerical solution is obtained by uniformly discretizing the spatial domain with step length δx, and we use a standard central difference to approximate the spatial derivative terms on the right of Eq. (10). The resulting system of coupled ordinary differential equations are solved using implicit Euler time stepping with a constant time step of duration δt. The resulting tridiagonal linear systems of equations are solved using the Thomas algorithm (Wang and Anderson, 1982; Zheng and Bennett, 2002).

A comparison between the power series solution and the numerical solution is given in Fig. 1(a) and (b) for a problem which is dominated by the decay term in the mathematical model. The power series solution compares very well with the numerical solution, and at this scale it is impossible to visually distinguish between the two solutions. A second comparison is given in Fig. 1(c) and (d) for a conservative tracer where the advective transport term dominates the diffusive transport term. The influence of the advective transport is evident in the $C(x,t)$ profiles which translate in the positive x direction as time increases. A third comparison in Fig. 1(e) and (f) is given for advection dominant transport with some decay, and again we see that the power series solution compares very well with the numerical calculation.

We conclude this section with a few general comments about our approach for solving Eq. (10). Our power series solution, given by Eq. (13), is very simple to implement since we have an explicit algebraic formula for $C(x,t)$ which we can easily re-evaluate for different choices of $D,\ v,\ k,\ a$ or b to explore the sensitivity of the solution to these parameter values. Furthermore, although we have chosen to present our solution technique for the initial condition $h(x) = ax\mathrm{e}^{-bx}$, we would like to point out that our general approach is also valid for other choices of $h(x)$ provided that the initial condition is smooth and that we can solve Eq. (11) to give an explicit solution for $F(x;s)$.

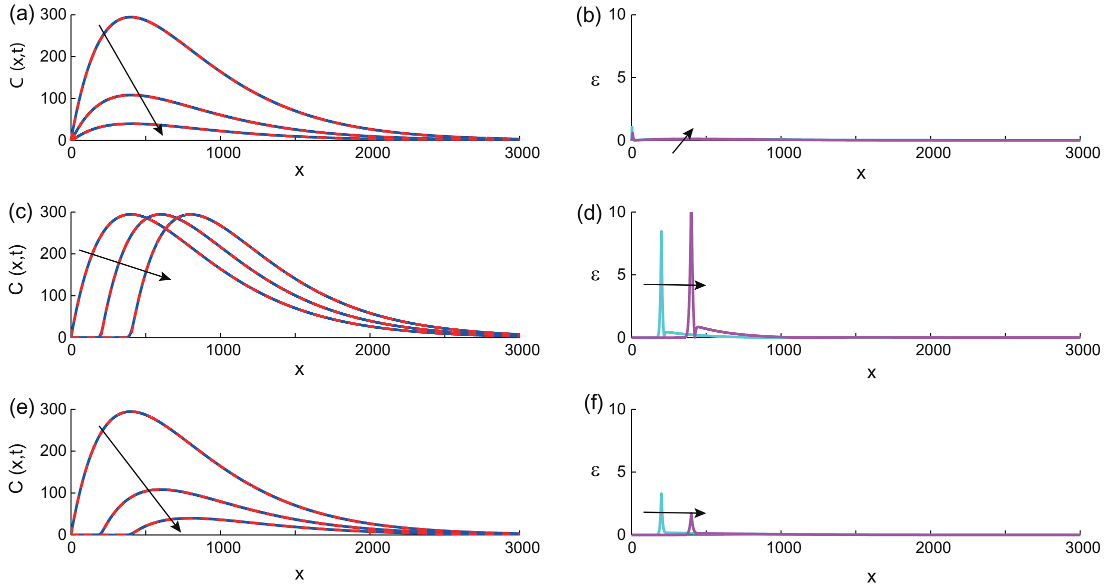

Fig. 1. Solutions of Eq. (10) in (a) and (b) for $D = 0.5,\ v = 0.2,\ k = 0.05$, (c) and (d) for $D = 0.5,\ v = 10,\ k = 0$ and (e) and (f) for $D = 0.5,\ v = 10,\ k = 0.05$. All results correspond to $a = 2$ and $b = 0.0025$. Solutions are shown at $t = 0,\ 20$ and 40, with the arrow showing the direction of increasing t. The power series solution, truncated after $I = 50$ terms, is shown in the dashed (red) curves. A numerical solution of Eq. (10), obtained with $\delta x = 0.1$ and $\delta t = 0.05$ on the truncated domain $0 < x < 10000$, and $0 < C(x,t) < 300$ is shown in the solid (blue) curves. Results in (b), (d) and (f) show $\epsilon = |C_{\text{series}}(x,t) - C_{\text{numerical}}(x,t)|$, where the subscript refers to either the power series solution or the numerical solution. All plots of ϵ show results at $t = 20$ and 40 with the arrow showing the direction of increasing t. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Application to multispecies reactive transport models

We now discuss how to apply Eq. (6) to a system of coupled pdes, given by

$$R\frac{\partial C_1}{\partial t} = D\frac{\partial^2 C_1}{\partial x^2} - v\frac{\partial C_1}{\partial x} - k_1 C_1, \quad 0 < x < \infty, \quad t > 0,$$
$$C_1(x,0) = h_1(x), \quad C_1(0,t) = h_1(0), \quad \lim_{x\to\infty} C_1(x,t) = 0,$$
$$\frac{\partial C_2}{\partial t} = D\frac{\partial^2 C_2}{\partial x^2} - v\frac{\partial C_2}{\partial x} + k_1 C_1 - k_2 C_2, \quad 0 < x < \infty, \quad t > 0,$$
$$C_2(x,0) = h_2(x), \quad C_2(0,t) = h_2(0), \quad \lim_{x\to\infty} C_2(x,t) = 0, \tag{14}$$

where $C_1(x,t)$ is the concentration of the parent species and $C_2(x,t)$ is the concentration of the daughter species. The retardation factor, $R \geqslant 1$, represents a linear equilibrium sorption reaction (Zheng and Bennett, 2002), k_1 is the reaction rate describing the decay of $C_1(x,t)$ and k_2 is the reaction rate describing the decay of $C_2(x,t)$.

We take the Laplace transforms of Eq. (14), where we denote $F_1(x;s) = \mathcal{L}\{C_1(x,t)\}$ and $F_2(x;s) = \mathcal{L}\{C_2(x,t)\}$. This leads to

$$D\frac{d^2F_1}{dx^2} - v\frac{dF_1}{dx} - (k_1 + Rs)F_1(x;s) = -Rh_1(x), \quad 0 < x < \infty,$$
$$F_1(0;s) = \frac{h_1(0)}{s}, \quad \lim_{x\to\infty} F_1(x;s) = 0,$$
$$D\frac{d^2F_2}{dx^2} - v\frac{dF_2}{dx} - (k_2 + s)F_2(x;s) = -k_1F_1(x;s) - h_2(x), \quad 0 < x < \infty,$$
$$F_2(0;s) = \frac{h_2(0)}{s}, \quad \lim_{x\to\infty} F_2(x;s) = 0. \tag{15}$$

The solution of these coupled ordinary differential equations will depend on the initial conditions $h_1(x)$ and $h_2(x)$. To make progress we will consider particular forms for these initial conditions and discuss how our approach can be used for alternative choices for these functions later. For the purposes of this example we consider $h_1(x) = axe^{-bx}$ and $h_2(x) = 0$, with $a > 0$ and $b > 0$. This initial condition could represent an initial plume of $C_1(x,t)$ within the domain and no $C_2(x,t)$ within the domain at $t = 0$. For these initial conditions the exact solution of Eq. (15) is given by

$$F_1(x;s) = \frac{aR(v + 2Db)}{\alpha^2}\left(e^{m_1x} - e^{-bx}\right) - \frac{aRxe^{-bx}}{\alpha},$$
$$F_2(x;s) = \frac{aRk_1(v + 2Db)(\alpha + \beta)}{\alpha^2\beta^2}\left(e^{-bx} - e^{m_2x}\right) + \frac{aRk_1}{\alpha\beta}xe^{-bx} - \frac{aRk_1(v + 2Db)}{\alpha^2(\alpha - \beta)}\left(e^{m_2x} - e^{m_1x}\right), \tag{16}$$

where $m_1 = \left[v - \sqrt{v^2 + 4D(sR + k_1)}\right]/2D, m_2 = \left[v - \sqrt{v^2 + 4D(s + k_2)}\right]/2D, \alpha = Db^2 + vb - sR - k_1, \beta = Db^2 + vb - s - k_2$ and $s > -k_1/R, > -k_2$. At this stage, a traditional approach to solving this problem (Bear, 1972; Cho, 1971; van Genuchten and Wierenga, 1976; van Genuchten, 1985) would be to calculate the inverse Laplace transform of Eq. (16) to find an exact expression for $C_1(x,t)$ and $C_2(x,t)$. Similar to the single species problem in Section 3, we find that the inverse transform cannot be obtained using mathematical tables or Maple.

Combining our expression for $F_1(x;s)$ with Eqs. (6) and (7) allows us to calculate a power series expression for $C_1(x,t)$. Similarly, combining our expression for $F_2(x;s)$ with Eqs. (6) and (7) allows us to calculate a power series expression for $C_2(x,t)$. While the algebra for this procedure is slightly more complicated than the example presented in Section 3, the process is, in principle, exactly the same and we present a Maple worksheet as supplementary material to illustrate how this process can be automated. The first few terms in these power series are given by

$$C_1(x,t) = axe^{-bx} + \frac{ax\phi_1 - a\psi}{R}e^{-bx}t + \frac{a\phi_1(x\phi_1 - 2\psi)}{2R^2}e^{-bx}t^2 + \mathcal{O}(t^3), \tag{17}$$
$$C_2(x,t) = axk_1e^{-bx}t + \frac{ak_1(xR\phi_2 + x\phi_1 - (1+R)\psi)}{2R}e^{-bx}t^2 + \mathcal{O}(t^3), \tag{18}$$

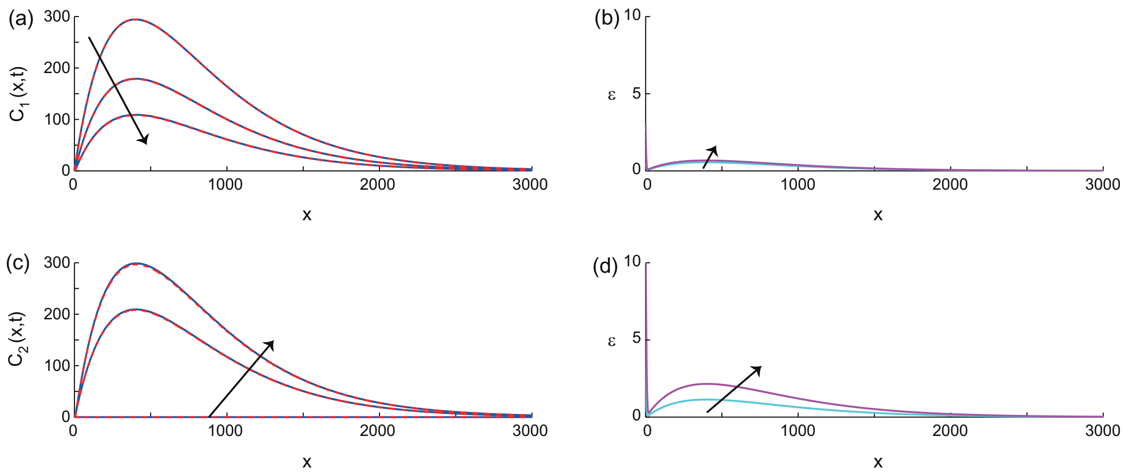

Fig. 2. Solution of Eq. (14) with $R = 2$, $D = 0.5$, $v = 0.2$, $k_1 = 0.05$, $k_2 = 0.01$, $a = 2$ and $b = 0.0025$. Solutions in (a) correspond to $C_1(x,t)$ while solutions in (c) correspond to $C_2(x,t)$. Both the $C_1(x,t)$ and $C_2(x,t)$ solutions are shown at $t = 0, 20$ and 40, with the arrow showing the direction of increasing t. The power series solution, truncated after $I = 50$ terms, is shown in the dashed (red) curves. A numerical solution of Eq. (14), obtained with $\delta x = 0.1$ and $\delta t = 0.05$ on the truncated domain $0 < x < 10000$, $0 < C_1(x,t) < 300$ and $0 < C_2(x,t) < 300$ is shown in the solid (blue) curves in (a) and (c). Results in (b) and (d) show $\epsilon = |C_{\text{series}}(x,t) - C_{\text{numerical}}(x,t)|$, where the subscript refers to either the power series solution or the numerical solution. All plots of ϵ show results at $t = 20$ and 40 with the arrow showing the direction of increasing t. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where $\phi_1 = Db^2 + vb - k_1$, $\phi_2 = Db^2 + vb - k_2$ and $\psi = v + 2Db$. A more finely truncated power series, up to $\mathcal{O}(t^{10})$, for both species, is given in the supplementary material.

To explore how the truncated power series solution performs for this coupled problem we compare it with a numerical solution of Eq. (14) in Fig. 2. The numerical solution is obtained using the same procedure outlined in Section 3. The comparison between the power series solution and the numerical solution in Fig. 2 is excellent.

Although we have presented detailed results for $h_1(x) = axe^{-bx}$ and $h_2(x) = 0$, with $a > 0$ and $b > 0$, our approach is also valid for other choices of $h_1(x)$ and $h_2(x)$. In particular, our approach is relevant for any smooth choice of $h_1(x)$ and $h_2(x)$ provided that we can solve Eq. (15) to give an explicit solution for $F_1(x;s)$ and $F_2(x;s)$.

5. Discussion and conclusions

Exact analytical solutions of pde models describing the transport and reaction of dissolved solutes in saturated porous media can help inform our understanding of contaminant fate and transport processes. Previous analytical solutions have been obtained using integral transform techniques which are limited in the sense that the choice of initial condition has a major impact on whether or not the inverse transform can be computed exactly. For this reason, previous studies (Cho, 1971; Lunn et al., 1996; Srinivasan and Clement, 2008a,b) have focused on relatively simple constant or exponentially decaying initial conditions. Unfortunately, these initial conditions are not always practical. For example, if we consider the situation where we wish to model the transport and reaction of an established plume of solute within the domain where the shape of the initial plume is neither spatially constant or exponentially decaying, none of these previously described models can be used to accurately represent this initial condition.

In this work we have introduced an alternative method for evaluating the inverse of a Laplace transform which generates a power series solution. We apply the technique to both a single species and coupled multispecies reactive transport model in one-dimension. In particular, we focus on initial conditions that represent a pre-existing distribution of solute in the domain that cannot be represented by previous analytical solutions (Cho, 1971; Lunn et al., 1996; Srinivasan and Clement, 2008a,b). Using our technique we obtain a truncated power series solution that compares very well with a numerical solution of the governing pde. In addition to providing the key mathematical steps in this manuscript, we also provide symbolic software algorithms as supplementary material to show how the procedure for calculating additional terms in the power series can be automated. To keep this manuscript as brief as possible we implemented our method for problems with one and two species only; however, our method can also deal with coupled problems with more than two species by following the same procedure outlined in Section 4 and then applying Eq. (6) separately for each additional species.

The main limitation of our approach is that we assume that the solution of the governing equation is sufficiently smooth. This means that our method cannot be used for problems where the solution of the model, the initial conditions or the boundary conditions are not smooth. For these cases where a Maclaurin series representation of the solution is not possible, a different solution technique is required.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2014.03.035.

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