



Assessment of a non-traditional operator split algorithm for simulation of reactive transport

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Abstract

A non-traditional operator split (OS) scheme for the solution of the advection-diffusion-reaction (ADR) equation is proposed. The scheme is implemented with the recently published central scheme [A. Kurganov, E. Tadmor, New high-resolution central schemes for non-linear conservation laws and convection-diffusion equations, *J. Comput. Phys.* 160 (2000) 241–282] to accurately simulate advection-reaction processes. The governing partial differential equation (PDE) is split into two PDEs, which are solved sequentially within each time step. Unlike traditional methods, the proposed scheme provides a very efficient method to solve the ADR equation for any value of the grid-Péclet number. An analytical mass balance error analysis shows that the proposed non-traditional scheme incurs a splitting error, which behaves differently to the splitting error incurred in traditional OS schemes. Numerical results are presented to illustrate the robustness of the proposed scheme.

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1. Introduction

The operator split (OS) technique provides a convenient means of solving the advection-diffusion-reaction (ADR) equation:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} + f(c), \quad (1)$$

where c [ML^{-3}] is the solute concentration, D [L^2T^{-1}] the diffusion coefficient, v [LT^{-1}] the advective velocity, x [L] the spatial variable and t [T] is time. The function $f(c)$ represents kinetic processes within the system; for some applications, non-linearities in the system are confined to $f(c)$. For the purposes of this manuscript, we will interpret $f(c)$ as a reaction.

The standard two-step OS scheme used to simulate (1) involves splitting the reaction part from the equation, yielding a simpler linear PDE and a linear or non-linear system of ordinary differential equations (ODE) [5,9,12,20,24,25,28,30]:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}, \quad (2)$$

$$\frac{dc}{dt} = f(c). \quad (3)$$

Traditionally, the linear advection-diffusion equation (2) is solved using a standard finite difference or finite element approach [20,30], while the reaction equation (3) is solved using an ODE solution technique that is appropriate for the particular form of $f(c)$ [20,30]. We refer to this scheme as the DA-R scheme.

The use of OS schemes have become widespread because of the flexibility offered by choosing different solution techniques to suit the various terms in the conservation equation [24]. OS schemes are also advantageous because the decoupling of reaction and transport discretisations permits different reaction types to be simulated with minimal recoding [13,14]. Obtaining numerical solutions using an OS technique can increase the computational efficiency compared to solving the full system and also provides opportunities for parallel computation [16,19]. OS schemes are particularly attractive for coupled multi-species problems or problems with non-linear kinetics [11,18]. Possible extensions of the traditional OS technique, such as the alternating OS scheme [20,25,30], the iterative OS scheme [18] and specialised schemes that combine OS with LU factorisation [9] have been proposed. This work, however, focuses on a sequential OS scheme as this is the most widely used approach [8,14,32,35]. Previous investigations have shown that solving the ADR equation with the traditional two-step OS scheme can introduce an error, which is minimised by choosing Δt sufficiently small [20,25,30].

Traditional OS schemes can provide several advantages over solving the full conservation equation [30]. However, if the transport part of the equation is solved with standard Eulerian techniques, then the overall accuracy is limited by the well-known grid Péclet number restriction. The grid Péclet number restriction for mass-lumped linear finite element or finite difference solutions of the advection-diffusion equation requires $Pe_{\text{grid}} = \frac{v \Delta x}{D} \leq 2$ in order to prevent spurious oscillations and excessive numerical diffusion [8]. For advection-dominated problems, the grid Péclet number restriction can be quite severe, requiring excessively fine grids to prevent numerical errors.

In addition to the traditional DA-R scheme (2) and (3), previous analyses have used a three-step splitting scheme, whereby the diffusion, advection and reaction steps are all separated (D-A-R) [13,14,32,35]:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad (4)$$

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x}, \quad (5)$$

$$\frac{dc}{dt} = f(c). \quad (6)$$

The D-A-R procedure has been successfully used to simulate the ADR equation, where the advection term is typically simulated using particle tracking or front tracking techniques [13,14,32,35]. These methods have been invoked to help overcome the grid Péclet number restriction of traditional Eulerian approaches. The advantage of the D-A-R method is that the original PDE is split into two linear PDEs and a linear or non-linear ODE system. Each of these steps can be solved by a solution technique appropriate to the nature of each term.

Overcoming the traditional difficulties associated with solving the ADR equation under advection-dominated conditions has been an active area of research. Investigations of alternative Eulerian algorithms that minimise numerical error for advection-dominated conditions have yielded a wide range of improved schemes. A survey of the developments of alternative difference schemes can be found in Yeh [6], Leonard [34] and Christon et al. [33]; similar developments based on weighted residual strategies are surveyed by Yeh [6] and Donea and Huerta [2].

Recent advances in solving hyperbolic conservation laws with central schemes and flux limiters provide high accuracy alternatives to standard Eulerian solutions to the advective transport equation [33]. In this work, the recent central scheme proposed by Kurganov and Tadmor (KT) [21] is used to solve the advection-reaction part of the ADR equation. The KT discretisation permits a semi-discrete form, which is explicitly integrated with a Runge–Kutta method. It is therefore convenient to simply incorporate any reaction terms into this integration process thereby temporally integrating both the advection and reaction terms simultaneously. Following this argument, we propose a “non-traditional” OS scheme, whereby the ADR equation is split:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad (7)$$

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + f(c). \quad (8)$$

This non-traditional OS scheme (D-AR) at first appears more complicated than the traditional OS schemes as the single linear or non-linear PDE has been split into two PDEs: the first is a linear diffusion equation and the second is a linear or non-linear advection-reaction equation. The reason for splitting a single PDE into two other PDEs is that the KT algorithm requires explicit temporal integration [21]. In general, temporal integration of the diffusion term cannot be completed explicitly because of the well-known stability criteria due to the stiffness of the discretised form of the diffusion operator [1,8]. Therefore, to maintain generality, the diffusion equation is to be solved implicitly using a standard finite difference or finite element approach.

The impetus for splitting the ADR equation according to (7) and (8) originated through simulating cell migration problems. For models of cell migration by haptotaxis [23,26] and chemotaxis [22], the advection term is non-linear. In these cases, the advective velocity is proportional to the spatial gradient of a signalling (chemotaxis) or adhesive (haptotaxis) substance. The advective velocity can be temporally and spatially variable and is determined as a part of the solution. This complication results in a non-linear advection term [22]. Under these conditions, traditional splitting (2) and (3) does not convert the non-linear PDE into a linear transport PDE and linear or non-linear ODE pair. This is an important point that distinguishes the application of OS strategies to non-linear advection problems from classical linear advection problems such as those encountered in contaminant transport analyses within aquifer systems [6,8].

Previous work by Marchant et al. [23] investigated the influence of adding diffusion to the pure haptotactic tumour invasion problem described by Perumpanani et al. [26]. Marchant et al.’s numerical simulations were limited by stability constraints owing to the explicit temporal integration of the diffusion equation within the KT algorithm. Therefore, only small amounts of diffusion were added [23]. Recent work by Landman et al. [22] successfully used an OS scheme analogous to the proposed non-traditional splitting (7) and (8) to perform numerical simulations of a combined diffusion and chemotaxis cell invasion problem. Landman et al. simulated any combination of diffusion or chemotaxis without any stability constraints associated with the diffusive migration [22]. This previous work successfully investigated the interactions of diffusive and chemotactic migration, and all simulations were performed with a non-traditional splitting scheme similar to that which is to be analysed here.

The objective of this work is to explore the robustness of D-AR splitting scheme for solving the ADR equation. The explicit KT central scheme is used to solve the advection-reaction part of the conservation equation. The diffusion term is split and solved implicitly. Because the D-AR OS scheme is different from all standard OS approaches, the convergence behaviour of the proposed OS scheme is investigated. In addition, the mass balance error (MBE) incurred by the proposed D-AR scheme is investigated analytically and compared to the MBE for standard DA-R and D-A-R approaches. This analytical error analysis is particularly important as previous analytical analyses of OS errors have been restricted to standard sequential and alternating forms of traditional two-step OS schemes [20,25,30].

2. Results

2.1. Implicit finite difference solution of the diffusion equation

The first step in the D-AR OS scheme is to solve (7). The diffusion equation is solved using a standard implicit finite difference approach [1,3]. The domain is uniformly discretised with nodes spaced Δx apart. The nodes are indexed $i = 1, \dots, N$. Temporal integration can be performed with a time-weighted scheme, which yields the discretised form of the diffusion equation at a central node:

$$\frac{c_i^{j+1} - c_i^j}{\Delta t} = \omega D \left\{ \frac{c_{i+1}^{j+1} - 2c_i^{j+1} + c_{i-1}^{j+1}}{(\Delta x)^2} \right\} + (1 - \omega) D \left\{ \frac{c_{i+1}^j - 2c_i^j + c_{i-1}^j}{(\Delta x)^2} \right\},$$

$$i = 2, \dots, N - 1, \quad j = 0, \dots, T, \tag{9}$$

where the subscript i represents the spatial discretisation and the superscript j represents the temporal discretisation. N is the number of spatial nodes and T is the number of temporal steps. A time weighting factor ω is introduced. The weighting factor is restricted to $0 < \omega \leq 1$. Common choices of ω include the fully implicit $\omega = 1$ and Crank–Nicolson $\omega = 0.5$ schemes [3]. For simplicity, all computations in this work correspond to the fully implicit method, which is known to produce good results [13]. The linear system (9) is assembled into a tridiagonal form and efficiently solved using the Thomas algorithm. The numerical scheme, (9) with $\omega = 1$, is unconditionally stable [3].

2.2. Kurganov–Tadmor central scheme

The solution of the second step in the D-AR OS scheme is obtained using Kurganov and Tadmor’s central scheme [21]. To apply the KT scheme, the conservation system must be in the form:

$$\frac{\partial \mathbf{W}}{\partial t} + \frac{\partial \mathbf{F}(\mathbf{W})}{\partial x} = \mathbf{Z}(\mathbf{W}), \quad (10)$$

where \mathbf{W} is the vector of conserved variables, \mathbf{F} is the flux vector and \mathbf{Z} is the vector of kinetic terms. The components are immediately recognised:

$$\mathbf{W} = [c], \quad \mathbf{F} = [vc] \quad \text{and} \quad \mathbf{Z} = [f(c)].$$

The KT algorithm is applied to (10) by computing derivatives with a MINMOD flux limiter [21,33] on a uniformly discretised domain. Details of the implementation of the KT scheme for a general conservation system are given in Appendix A. Temporal integration is achieved by recognising that the KT algorithm permits a semi-discrete form:

$$\frac{d\mathbf{W}}{dt} = \mathbf{\Lambda}(\mathbf{W}) + \mathbf{Z}(\mathbf{W}), \quad (11)$$

where $\mathbf{\Lambda}$ is the spatial operator associated with the KT discretisation procedure. The time integration of (11) is performed explicitly with the third-order TVD Runge–Kutta method described by Shu and Osher [29]. The stability of this scheme is limited by the Courant constraint; $\text{Cr} = \frac{v \Delta t}{\Delta x} \leq 1$. Therefore, time steps must be chosen sufficiently small such that this constraint is satisfied. Note that, in general, the same Courant constraint is applied to traditional finite element and finite difference solutions of the advection-diffusion equation (2) when the temporal integration is done with a backward Euler method [8]. Therefore, this limitation is no more restrictive than a standard approach.

2.3. Comparison of D-AR operator split and analytical solutions for a reactive Gaussian hill problem

To demonstrate the accuracy and flexibility of the proposed D-AR algorithm, a reactive Gaussian hill problem is simulated [2]. We consider equation (1) with the initial condition:

$$c(x, 0) = \exp \left\{ - \left(\frac{x - x_0}{l} \right)^2 \right\}. \quad (12)$$

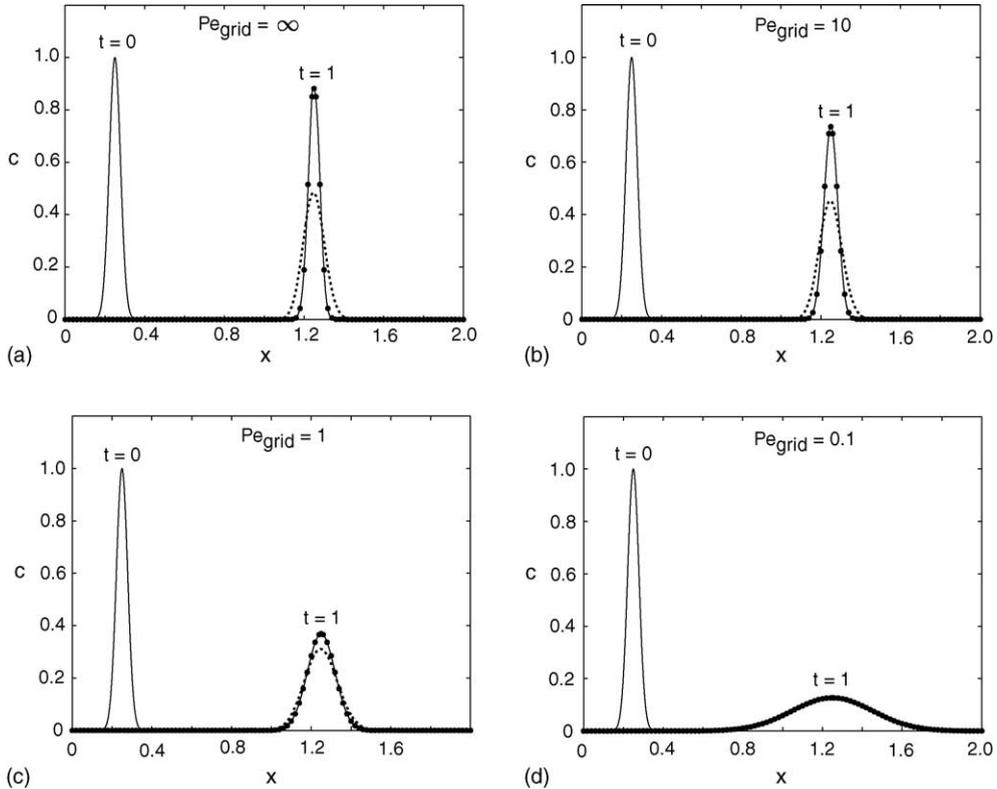


Fig. 1. Reactive Gaussian hill problem at $t = 1$ simulated with the D-AR operator split scheme for reactive transport with $k = 0.1$. Operator Split numerical solution (—) and standard central difference numerical solution (....) are compared with the analytical solution (•) over a range of grid Péclet numbers: (a) $Pe_{\text{grid}} = \infty$, (b) $Pe_{\text{grid}} = 10$, (c) $Pe_{\text{grid}} = 1$ and (d) $Pe_{\text{grid}} = 0.1$. Computations are for $x_0 = \frac{1}{4}$, $l = \frac{1}{25}$ and $v = 1$. The numerical discretisation is $\Delta x = \Delta t = 2 \times 10^{-3}$.

For linear decay, $f(c) = -kc$, the analytical solution on $-\infty < x < \infty$ is [2]:

$$c(x, t) = \frac{\exp(-kt)}{\sigma(t)} \exp \left\{ - \left(\frac{x - x_0 - vt}{l\sigma(t)} \right)^2 \right\}, \quad \sigma(t) = \sqrt{1 + \frac{4Dt}{l^2}}. \tag{13}$$

Numerical computations are performed on the truncated domain, $0 < x < 2$, with boundary conditions $c(0, t) = c(2, t) = 0$. Two reaction rates are considered, $k = 0.1$ and 1.0 . A range of diffusion coefficients are used to show the performance of the algorithm over a wide range of grid Péclet numbers. The range of grid Péclet numbers investigated here includes $0.1 \leq Pe_{\text{grid}} \leq \infty$. The upper limit $Pe_{\text{grid}} = \infty$ is included for completeness. Note that in this case, $D = 0$ and no operator splitting is required; however, it is convenient to include this case as it is relevant for certain problems [26] and known to be a major failing of standard Eulerian approaches. Figs. 1 and 2 compare the numerical and analytical solutions for the reactive Gaussian hill problem.

The numerical profiles for both the reactive Gaussian hill problems are indistinguishable from the analytical results (Figs. 1 and 2). The D-AR OS scheme performs well over the wide range of grid Péclet

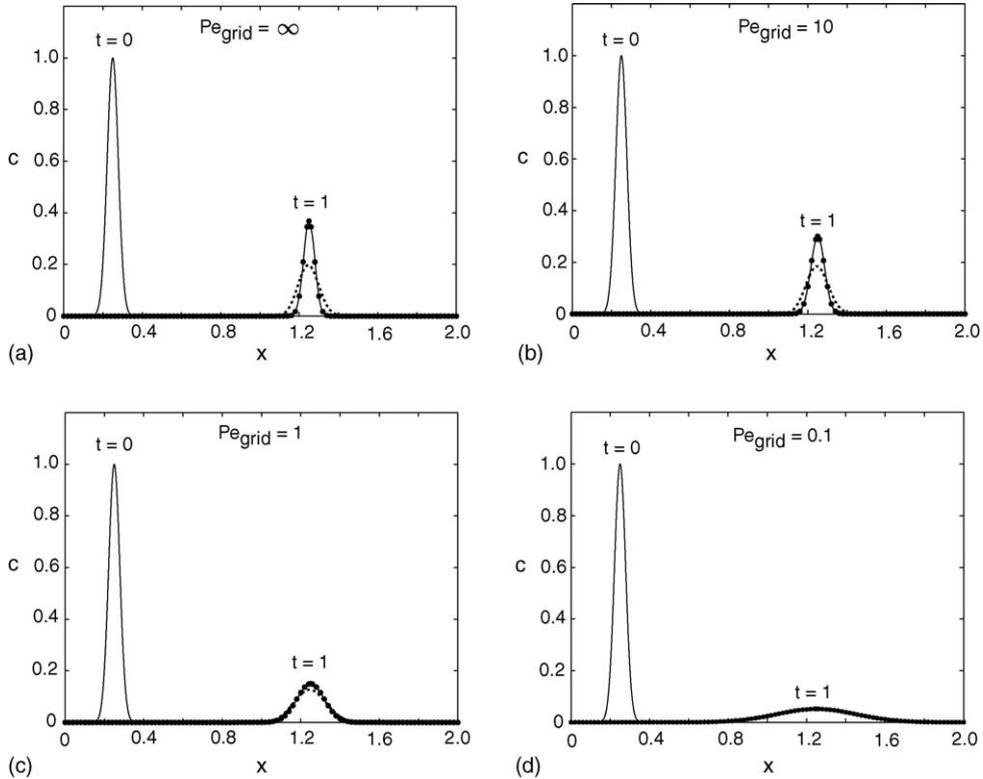


Fig. 2. Reactive Gaussian hill problem at $t = 1$ simulated with the D-AR operator split scheme for reactive transport with $k = 1.0$. Operator Split numerical solution (—) and standard central difference numerical solution (...) are compared with the analytical solution (●) over a range of grid Péclet numbers: (a) $Pe_{\text{grid}} = \infty$, (b) $Pe_{\text{grid}} = 10$, (c) $Pe_{\text{grid}} = 1$ and (d) $Pe_{\text{grid}} = 0.1$. Calculations are for $x_0 = \frac{1}{4}$ and $l = \frac{1}{25}$ and $v = 1$. The numerical discretisation is $\Delta x = \Delta t = 2 \times 10^{-3}$.

numbers as the KT algorithm does not suffer from the spurious oscillations and excessive numerical diffusion, which can be present in standard numerical solutions [8].

For comparison purposes a standard finite difference solution is also presented in Figs. 1 and 2. The standard solution corresponds to a central difference approximation for the advection term and fully implicit Euler time stepping. The finite difference algorithm performs poorly at the same spatial and temporal discretisations. For the high grid Péclet numbers the standard solutions are excessively dissipative and the peak concentration is totally obscured by numerical diffusion. Typically, standard solutions of the ADR equation are limited to $Pe_{\text{grid}} = \frac{v\Delta x}{D} \leq 2$ [8]. This restriction can be quite severe when advection processes dominate the overall transport mechanism. For example, in the case, where $D = 2 \times 10^{-4}$ (Figs. 1b and 2b), a standard Eulerian algorithm would require $\Delta x \leq 4 \times 10^{-4}$ in order to meet the grid Péclet number constraint. Reducing the spatial discretisation then requires $\Delta t \leq \Delta x$ such that the Courant constraint is satisfied. In the case, where $D = 0$ (Figs. 1a and 2a), a standard finite element or finite difference discretisation can never satisfy the grid Péclet number constraint.

2.4. Analytical analysis of the operator split mass balance error

Traditional OS schemes are known to incur an error when a non-zero mass flux across the domain boundary is present within a particular time step [20,25,30]. The OS error is innate and independent of numerical errors. The reactive Gaussian hill problem presented in Section 2.3 did not engender any OS error as there was no mass flux across the boundaries [10]. Therefore, any discrepancy between the numerical and analytical solutions for this particular problem were due to numerical error alone. Alternatively, to examine the OS error in isolation from numerical errors, it is convenient to conduct an analytical analysis of a problem where an OS error is known to occur.

For those problems where the OS error is encountered, it is possible to analytically analyse the error for simple cases of $f(c)$. Because the D-AR OS scheme proposed here is different from traditional schemes, we expect that the OS error will behave differently. Therefore, it is appropriate to investigate the nature of the error and compare the errors associated with the DA-R, D-A-R and D-AR OS schemes. Here, we perform this analysis using exact analytical solutions to the full ADR equation [16,20,25,30]. Alternative methods of analysis, such as conducting numerical–numerical comparisons or Taylor series analysis of numerical schemes [9–12] are not attempted since the analytical analysis enables us to exactly isolate the OS errors from other sources of error, such as numerical error. Furthermore, numerical–numerical comparisons are typically limited by the grid Péclet restriction, which is avoided with the analytical analysis.

To demonstrate the OS error, the ADR equation with linear decay, $f(c) = -kc$, is considered. To generalise the results it is convenient to work in dimensionless variables. Introducing a length, time and concentration scales (L , T and c_{\max}), the variables are non-dimensionalised: $c' = \frac{c}{c_{\max}}$, $x' = \frac{x}{L}$, and $t' = \frac{t}{T}$. After substituting into the dimensional ADR equation, dropping the apostrophe notation and choosing $\frac{L}{T} = v$, the dimensionless governing equation is:

$$\frac{\partial c}{\partial t} = \frac{1}{Pe} \frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial x} - D_a c, \tag{14}$$

where $Pe = \frac{vL}{D}$ is the general Péclet number and $D_a = \frac{kL}{v}$ is the Damköhler number. Note that the general Péclet number is equivalent to the grid Péclet number when $L = \Delta x$.

Analysis of traditional DA-R OS scheme have shown that the splitting error increases with the magnitude of the reaction term D_a [20,30]. We anticipate that the behaviour of the D-A-R and D-AR splitting error will be more complex than for the DA-R scheme as the advection and diffusion operators are split. Therefore, it is reasonable to expect that the accuracy of the D-A-R and D-AR OS schemes will exhibit some interaction between the Damköhler and general Péclet numbers.

To investigate the splitting errors, we consider (14) on the semi-infinite domain $0 < x < \infty$ with the initial condition $c(x, 0) = 0$. A Dirichlet boundary condition is imposed at the origin, $c(0, t) = 1$ for $t > 0$. An exact analytical solution for the concentration distribution is available [31]:

$$c_A(x, t) = \frac{1}{2} \exp \left[\frac{x(1-u)}{\frac{2}{Pe}} \right] \operatorname{erfc} \left[\frac{x-ut}{2\sqrt{\frac{t}{Pe}}} \right] + \frac{1}{2} \exp \left[\frac{x(1+u)}{\frac{2}{Pe}} \right] \operatorname{erfc} \left[\frac{x+ut}{2\sqrt{\frac{t}{Pe}}} \right],$$

$$u = \sqrt{1 + \frac{4D_a}{Pe}}, \tag{15}$$

all analytical expressions are evaluated using the approximations for the error function given by Zhang and Jin [7].

To simulate the DA-R OS solution analytically, first the intermediate solution is obtained by using the full analytical solution with $D_a = 0$, and then performing the reaction step separately:

$$c_{(\text{DA-R})\text{Step 1}}(x, t) = \frac{1}{2} \operatorname{erfc} \left[\frac{x-t}{2\sqrt{\frac{t}{Pe}}} \right] + \frac{1}{2} \exp[xPe] \operatorname{erfc} \left[\frac{x+t}{2\sqrt{\frac{t}{Pe}}} \right], \quad (16)$$

$$c_{(\text{DA-R})\text{Step 2}}(x, t) = c_{(\text{DA-R})\text{Step 1}}(x, t) \times \exp(-D_a t). \quad (17)$$

Once these two steps have been evaluated sequentially, the resulting concentration profile will correspond to the DA-R OS solution.

The D-AR OS scheme can also be evaluated analytically. For the first step, the solution of the diffusion equation takes on the well-known form [1]:

$$c_{(\text{D-AR})\text{Step 1}}(x, t) = \operatorname{erfc} \left[\frac{x}{2\sqrt{\frac{t}{Pe}}} \right]. \quad (18)$$

Once the first part of the D-AR OS scheme is obtained, the solution of the remaining advection-reaction equation can be computed with the method of characteristics (MOC) [4]. The characteristics are lines in the (x, t) coordinate space such that $\frac{dx}{dt} = 1$, and along these characteristics, the concentration changes according to $\frac{dc}{dt} = -D_a c$. Once these steps are completed, the D-AR OS concentration $c_{(\text{D-AR})\text{Step 2}}(x, t)$ is known and the profile can be compared to the analytical solution for the full problem, as well as comparing it to the DA-R OS solution.

The D-A-R OS scheme (4)–(6) is also analytically evaluated here. First, the solution to the diffusion equation (18) is calculated to give $c_{(\text{D-A-R})\text{Step 1}}(x, t)$. Secondly, the resulting profile is advected using the MOC along the characteristics $\frac{dx}{dt} = 1$, to give the second intermediate profile $c_{(\text{D-A-R})\text{Step 2}}(x, t)$. Finally, the reaction step is completed by degrading the advected profile according to the linear decay model to yield the final result $c_{(\text{D-A-R})\text{Step 3}}(x, t)$. Note that the only difference between the D-AR scheme and the D-A-R scheme is that the reaction and advection operators are split. For the particular case, where $D_a = 0$, the proposed non-traditional scheme is identical to the three-step scheme.

The first stage in analysing the performance of the proposed D-AR OS scheme is to demonstrate the convergence behaviour of the solution. To do this, we choose to express the OS error in terms of a mass balance error (MBE) [30]. Expressions for the mass of solute in the domain at $t = \Delta t$ are determined using $M = \int_0^\infty c(x, t) dx$, and summarised in Appendix B. These expressions have been evaluated for the exact analytical case, and each of the three OS techniques. The MBE is then defined:

$$\text{MBE}(Pe, D_a, \Delta t) = M_{\text{analytical}} - M_{\text{OS}}, \quad (19)$$

where $M_{\text{analytical}}$ is the exact mass and M_{OS} is the OS mass. Values of the MBE for the proposed D-AR scheme are evaluated over a range of Damköhler and general Péclet numbers for various values of Δt and summarised in Table 1.

The MBE trends (Table 1) demonstrate that the D-AR OS scheme converges with decreasing Δt . Convergence of the MBE occurs over the entire range of general Péclet and Damköhler numbers inves-

Table 1
D-AR OS scheme: convergence of MBE with decreasing Δt

$t = \Delta t$	$Pe = 1, D_a = 1$	$Pe = 1, D_a = 10$	$Pe = 1, D_a = 0.1$	$Pe = 10, D_a = 1$	$Pe = 0.1, D_a = 1$
1×10^0	1.638×10^{-1}	2.701×10^{-1}	-3.185×10^{-1}	-3.982×10^{-2}	1.053×10^0
1×10^{-1}	-2.238×10^{-2}	1.053×10^{-1}	-4.444×10^{-2}	-3.185×10^{-2}	2.417×10^{-2}
1×10^{-2}	-4.134×10^{-3}	2.417×10^{-3}	-4.828×10^{-3}	-4.444×10^{-3}	-2.581×10^{-3}
1×10^{-3}	-4.730×10^{-4}	-2.581×10^{-4}	-4.946×10^{-4}	-4.828×10^{-4}	-4.236×10^{-4}

tigated. Therefore, in practice, the D-AR OS scheme should produce accurate results for a sufficiently small choice of Δt . We note that for different parameterisations the D-AR scheme can both underestimate (MBE > 0) and overestimate (MBE < 0) the solute mass in the domain.

In addition to evaluating the MBE for the D-AR OS scheme, it is possible to explore the nature of the D-AR MBE asymptotically in the limit $\Delta t \rightarrow 0$. By expanding the expression for the D-AR MBE (19) in powers of Δt , we obtain:

$$MBE_{D-AR} = -\frac{\Delta t}{2} + \frac{1}{6\sqrt{\pi}} \left[\frac{8D_a}{\sqrt{Pe}} + \sqrt{Pe} \right] (\Delta t)^{3/2} + \dots \tag{20}$$

This asymptotic expansion confirms the convergence behaviour demonstrated in Table 1. In addition, the expansion is insightful as it explicitly shows how the general Péclet and Damköhler interact to govern the D-AR MBE for small Δt .

Now that the convergence behaviour of the D-AR OS scheme has been demonstrated, it is instructive to compare the MBE of the D-AR, DA-R and D-A-R schemes. Comparisons are made by evaluating the MBE as a function of D_a for several fixed values of the general Péclet number. The MBEs are compared at time $t = \Delta t = 1 \times 10^{-1}$ (Fig. 3).

The differences between the DA-R, D-A-R and the D-AR MBE trends are quite distinct. In general, the MBE is largest for the smallest general Péclet number (Fig. 3a) corresponding to the highest mass flux through the inlet boundary. Conversely, the MBE is smallest for the largest general Péclet number (Fig. 3c) corresponding to the smallest mass flux through the inlet boundary. For the DA-R scheme, the MBE is always positive. Therefore, the DA-R scheme always underestimates the amount of mass in the domain. This result has also been reported by Valocchi and Malmstead [30]. This previous study presented the DA-R MBE for a different inlet boundary condition.

The behaviour of the D-AR MBE differs significantly from the DA-R scheme. For $D_a = 0$, the D-AR MBE is negative indicating that splitting the diffusion and advection steps alone overestimates the amount of mass in the domain. As D_a increases, the D-AR MBE increases reaching zero for some positive value of D_a . Therefore, we can identify two interacting processes that contribute in opposing ways to the overall MBE. Splitting advection and diffusion overestimates the mass in the domain, while splitting reaction from transport underestimates the mass in the domain. These two competing processes interact in the D-AR scheme such that it is possible to either underestimate or overestimate the mass depending upon the particular parameterisation. This behaviour is more complex than the simpler DA-R scheme.

The D-A-R scheme also has a zero MBE for some positive value of D_a . As for the D-AR scheme, the overestimation of mass in the domain for small D_a is caused by the splitting of the diffusion and advection. This overestimation of mass is reduced as D_a increases, and eventually the MBE is positive for

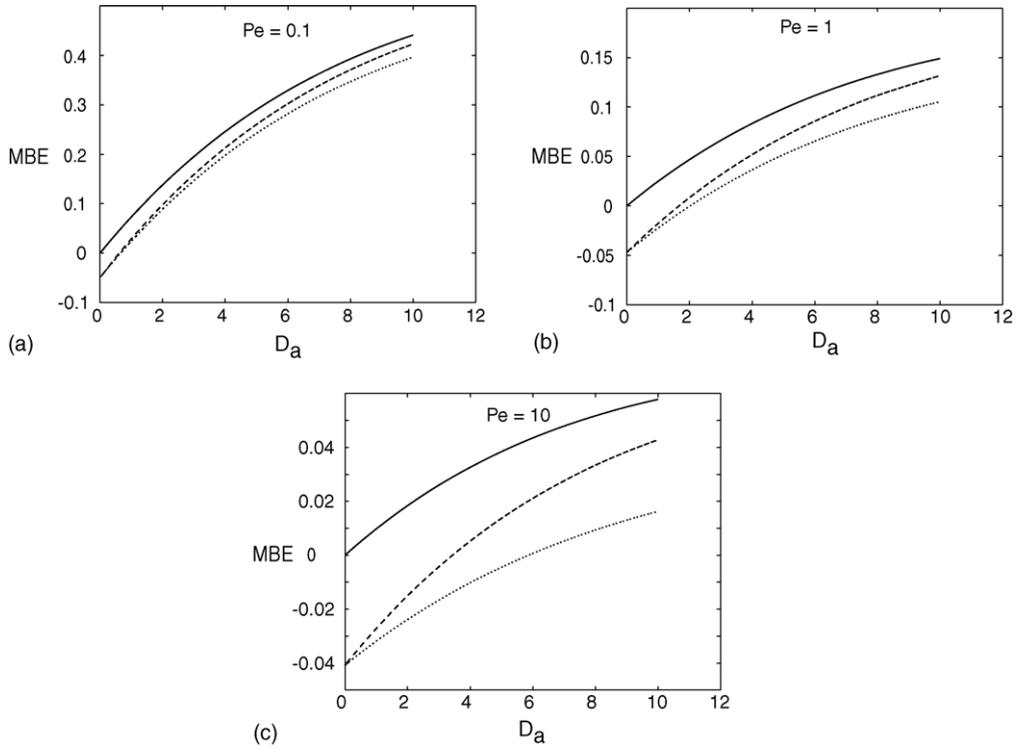


Fig. 3. Innate OS MBE: DA-R splitting (—), D-A-R splitting (---) and the proposed D-AR scheme (···) are compared over the range $0 \leq D_a \leq 10$, for (a) $Pe = 0.1$, (b) $Pe = 1$, (c) $Pe = 10$. Results are compared at $t = \Delta t = 1 \times 10^{-1}$.

sufficiently fast reactions. It should be noted that all of the results in Fig. 3 are computed at $t = \Delta t = 1 \times 10^{-1}$, in addition further profiles at $t = \Delta t = 1 \times 10^{-2}$ were evaluated and the same general trends were observed.

The D-A-R scheme and proposed D-AR scheme behave identically for $D_a = 0$ and diverge for large D_a . This behaviour can be explained physically. During the time interval Δt mass is transported into the domain at $x = 0$. This mass undergoes simultaneous transport and decay. Therefore, the mass transported into the domain near the beginning of the time interval undergoes more decay than the mass transported into the domain near the end of the time interval [30]. The D-A-R scheme simulates mass transport into the domain through two separated steps: (1) by diffusion and (2) by advection. These two processes yield a particular amount of mass in the domain, which is then decayed for the entire duration of the time interval. This has the effect of overestimating the amount of decay because the mass nearest the inlet boundary is assumed to undergo decay for the same amount of time as the mass farthest from the inlet boundary. The first step in the D-AR scheme is identical to the first step in the D-A-R scheme, where a particular mass of solute is transported across the inlet boundary by diffusion. The remaining advection and reaction processes are combined so that the mass advected into the domain near the beginning of the time interval undergoes more decay than the mass advected into the domain at the end of the time interval. Therefore, the proposed D-AR scheme also overestimates the amount of decay associated with the diffused mass. However, there is no overestimation of the decay associated with the advected mass.

This physical argument suggests that the differences between the D-AR and D-A-R schemes will be pronounced when advection is the dominant transport mechanism (high general Péclet number) and where the reaction rate is high (high Damköhler number). These trends correspond with the quantitative results presented in Fig. 3.

For completeness, we also analytically analysed the case where the proposed scheme was implemented in the reverse order, namely AR-D. This analysis, which is significantly more algebraically intensive, indicated that reversing the order of splitting yielded no obvious advantage in terms of the MBE. Therefore, the analysis in this work focuses on the D-AR ordering since the analytical analysis for this case is straightforward.

In general, it is difficult to conclude which splitting scheme is preferable. For slow reactions, the DA-R scheme is more accurate. Conversely, for fast reactions, the proposed D-AR scheme outperforms both DA-R and D-A-R. For practical purposes, the single species linear decay analysis presented here can only act as a guide to the nature of the MBE. This analysis does not apply for the more general case, where multi-species transport or non-linear problems might be of interest. Although the MBE analysis presented here enables us to glean some insight into the behaviour of the proposed splitting scheme, for practical purposes, the sensitivity of results to the time step Δt should always be checked to ensure that the simulated results are grid-independent.

2.5. General applications: coupled transport with distinct retardation factors

To demonstrate the generality of the proposed D-AR OS scheme, a problem is solved where a positive mass flux through the inlet boundary is present, and therefore the numerical results are subject to an OS MBE. We consider a coupled two-species problem [15,27]:

$$R_1 \frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial x^2} - v \frac{\partial c_1}{\partial x} - k_1 c_1, \quad (21)$$

$$R_2 \frac{\partial c_2}{\partial t} = D \frac{\partial^2 c_2}{\partial x^2} - v \frac{\partial c_2}{\partial x} + k_1 c_1 - k_2 c_2. \quad (22)$$

The two-species model is considered here with the initial condition, $c_1(x, 0) = c_2(x, 0) = 0$. The boundary conditions are $c_1(0, t) = 1$ and $c_2(0, t) = 0$. It is convenient to consider this system as an analytical solution is available. Quezada et al. [27] derived the analytical solution for (21) and (22) on the semi-infinite domain $0 < x < \infty$. Numerical computations are performed on a truncated domain $0 < x < L$, where L is chosen sufficiently large to avoid boundary effects. A range of diffusion coefficients is considered in order to simulate a range of grid Péclet numbers. In the case of pure advection, $D = 0$, the analytical solution of Quezada et al. [27] is not applicable; however, the analytical solution can be evaluated using the MOC. Numerical and analytical results are summarised in Fig. 4.

The choice of parameters used in Fig. 4 requires some discussion. Fig. 4a shows the limiting case with $D = 0$ and $Pe_{\text{grid}} = \infty$. The numerical results and MOC results are in good agreement; the KT algorithm correctly predicts the position of the sharp front and resolves the steep gradient accurately. This particular case is useful since there is no OS MBE and any discrepancy between the numerical and analytical results are limited to numerical errors alone. For the remaining cases, we focus on situations where the OS MBE is present. Previous analysis (Fig. 3) showed that, in general, the OS MBE was largest when the mass flux across the inlet boundary was increased. Here we focus

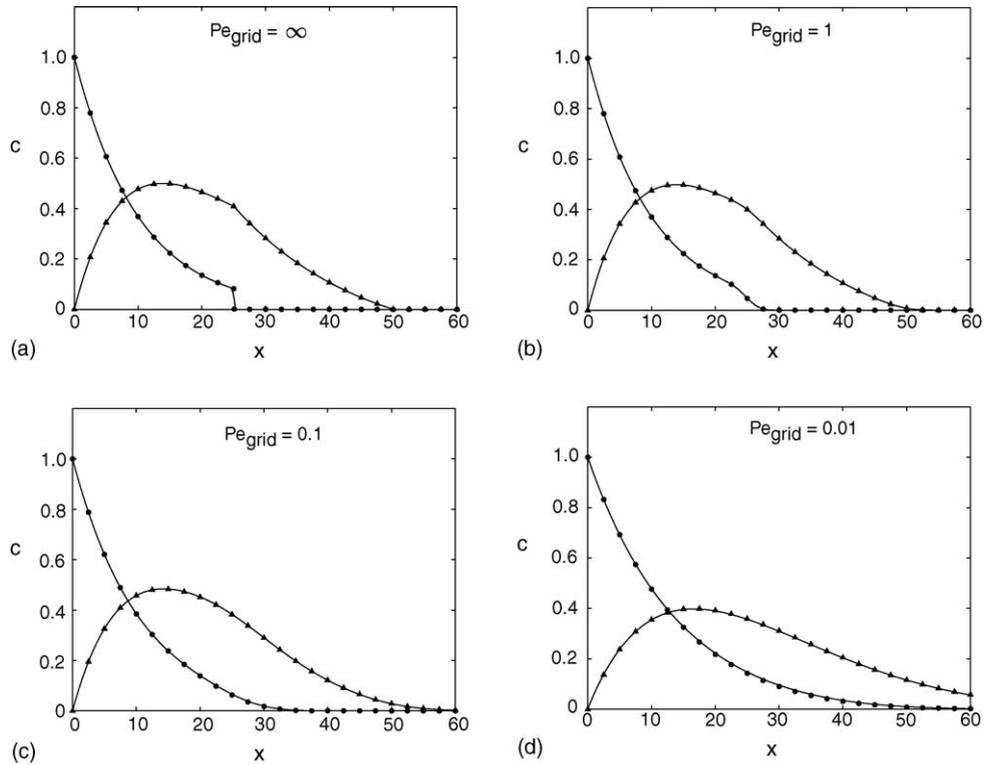


Fig. 4. Comparison of D-AR OS numerical profiles (—) and analytical solution for species 1 (●) and species 2 (▲) at $t = 50$. A range of grid Péclet numbers are shown: (a) $Pe_{\text{grid}} = \infty$, (b) $Pe_{\text{grid}} = 1$ and (c) $Pe_{\text{grid}} = 0.1$ (d) $Pe_{\text{grid}} = 0.01$. The problem is parameterised with $v = 1$, $R_1 = 2$, $R_2 = 1$, $k_1 = 0.1$ and $k_2 = 0.05$, numerical computations are evaluated with the discretisation $\Delta x = \Delta t = 5 \times 10^{-2}$.

on diffusion dominant problems to increase the mass flux across the inlet boundary. These diffusion dominant cases (Fig. 4b–d) present a worst case scenario as the separation of advection-reaction and diffusion mechanisms is exaggerated. Although we have deliberately chosen to focus on cases where the OS MBE is pronounced, the comparisons between the numerical and analytical profiles (Fig. 4b–d) show excellent agreement thereby demonstrating the versatility of the proposed D-AR scheme.

3. Discussion and conclusion

This work has extended the applicability of the KT central scheme to be used in conjunction with an OS technique to simulate ADR systems. The algorithm presented here is likely to be of interest to researchers analysing reactive transport problems, which are ubiquitous throughout all applied science disciplines. The KT central scheme is typically implemented with an explicit method for the temporal integration of the discretised equations. Therefore, to develop a general algorithm for the solution of the ADR equation with the KT scheme an OS step is introduced. In the proposed scheme the diffusion operator

is split from the advection-reaction terms and solved implicitly. This splitting is non-traditional as the governing PDE is split into two PDEs; the first representing diffusive transport and the second representing simultaneous advection and reaction. This OS scheme is different to standard OS schemes, where the governing PDE is typically split into a PDE/ODE pair [11,12,20,25,30] or a three-step PDE/PDE/ODE sequence [13,14,32,35].

An analysis of a standard linear decay problem showed that the OS MBE for the D-AR scheme approaches zero as $\Delta t \rightarrow 0$. Convergence of the MBE occurs for any values of the general Péclet and Damköhler numbers. Comparing the OS MBE indicated that the standard DA-R OS technique is more accurate at low Damköhler numbers (slow reactions), while the proposed D-AR scheme is more accurate at high Damköhler number conditions (fast reactions).

The analytical analysis in this work is only possible for one-dimensional conditions; however, OS MBE also occurs in higher dimensions, and therefore the trends established in this work are also relevant for two- and three-dimensional problems. In general, for more complex multi-species or non-linear reactions it is difficult to analytically analyse the OS MBE. For these more general cases, the proposed scheme should always be used in conjunction with a grid convergence analysis. The applicability of the algorithm for such problems was demonstrated by simulating a coupled two-species transport problem with distinct retardation factors. This problem was accurately solved across a wide range of grid Péclet numbers.

Using the KT central scheme to solve the advection-reaction portion of the ADR equation is very powerful as this scheme is known to be accurate and highly flexible [21,33]. Incorporating a central scheme to simulate advective transport means that the algorithm can also be used to simulate transport phenomena involving non-linear advection problems. Therefore, the same algorithm can be applied to a wide range of physical processes including models of haptotactic and chemotactic cell migration [22,23,26], fluid flow in open channels [17], gas dynamics [33] and glacier migration [21]. Furthermore, presenting results from the KT algorithm with an OS scheme to include diffusive transport is novel as most previous implementations of KT have been limited to either pure advection-reaction systems [17,33] or systems with small diffusion coefficients [21,23] such that OS was not required.

In summary, the proposed D-AR OS scheme implemented with the KT algorithm provides a very general and versatile means of solving the ADR equation. The incorporation of the central scheme developed by Kurganov and Tadmor [21] for the advection-reaction terms enables the algorithm to solve the ADR equation for any value of the grid Péclet number. Simulating diffusive transport implicitly through an OS step means that the numerical scheme avoids any stability issues associated with explicit solutions of the diffusion equation. This benefit, however, comes at the expense of an OS MBE. An analytical analysis indicates that the D-AR MBE behaves differently to traditional splitting schemes and can always be controlled by choosing Δt sufficiently small.

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Appendix A. Kurganov–Tadmor central scheme

The semi-discrete formulation of the KT scheme applied to (10) can be summarised as:

$$\frac{d}{dt} W_i(t) = -\frac{H_{i+(1/2)}(t) - H_{i-(1/2)}(t)}{\Delta x} + Z(W_i(t)). \quad (\text{A.1})$$

The numerical fluxes are given as:

$$H_{i+(1/2)}(t) = \frac{F(W_{i+(1/2)}^+(t)) + F(W_{i+(1/2)}^-(t))}{2} - \frac{\lambda_{i+(1/2)}(t)}{2} [W_{i+(1/2)}^+(t) - W_{i+(1/2)}^-(t)], \quad (\text{A.2})$$

$$H_{i-(1/2)}(t) = \frac{F(W_{i-(1/2)}^+(t)) + F(W_{i-(1/2)}^-(t))}{2} - \frac{\lambda_{i-(1/2)}(t)}{2} [W_{i-(1/2)}^+(t) - W_{i-(1/2)}^-(t)], \quad (\text{A.3})$$

where λ_i is the maximum speed of propagation of the hyperbolic system at position i and F denotes the flux. The values of the conserved variable at the cell faces are given by:

$$W_{i+(1/2)}^+(t) = W_{i+1}(t) - \frac{\Delta x}{2} \left(\frac{\partial W(t)}{\partial x} \right)_{i+1}, \quad (\text{A.4})$$

$$W_{i+(1/2)}^-(t) = W_i(t) + \frac{\Delta x}{2} \left(\frac{\partial W(t)}{\partial x} \right)_i, \quad (\text{A.5})$$

$$W_{i-(1/2)}^+(t) = W_i(t) - \frac{\Delta x}{2} \left(\frac{\partial W(t)}{\partial x} \right)_i, \quad (\text{A.6})$$

$$W_{i-(1/2)}^-(t) = W_{i-1}(t) + \frac{\Delta x}{2} \left(\frac{\partial W(t)}{\partial x} \right)_{i-1}. \quad (\text{A.7})$$

The gradient terms used to compute the values of W at the cell faces are evaluated using a numerical limiter:

$$\frac{\partial W}{\partial x} = \text{MM} \left\{ \left[\theta \frac{W_{i+1} - W_i}{\Delta x}, \frac{W_{i+1} - W_{i-1}}{2 \Delta x}, \theta \frac{W_i - W_{i-1}}{\Delta x} \right] \right\}, \quad (\text{A.8})$$

where MM denotes the standard MINMOD limiter [33] and the parameter θ satisfies $1 \leq \theta \leq 2$. All computations in this study were performed with $\theta = 1.99$.

Appendix B. Mass balance equations

To compute the mass of solute in the domain, it is necessary to evaluate $M(t) = \int_0^\infty c(x, t) dx$. Four cases are presented corresponding to the exact analytical case $M_{\text{analytical}}(t)$ and the three OS cases $M_{(\text{D-A-R})}(t)$, $M_{(\text{D-A-R})}(t)$ and $M_{(\text{D-AR})}(t)$. Each expression is evaluated at $t = \Delta t$.

The exact analytical case yields:

$$\begin{aligned} M_{\text{analytical}}(\Delta t) = & \frac{1}{2\alpha_1} \exp\left(\alpha_1 \beta + \frac{\alpha_1^2 \gamma^2}{4}\right) \left[\text{erf}\left(\frac{\beta}{\gamma} + \frac{\alpha_1 \gamma}{2}\right) + 1 \right] - \frac{1}{2\alpha_1} \left[\text{erf}\left(\frac{\beta}{\gamma}\right) + 1 \right] \\ & + \frac{1}{2\alpha_2} \exp\left(-\alpha_2 \beta + \frac{\alpha_2^2 \gamma^2}{4}\right) \left[1 - \text{erf}\left(\frac{\beta}{\gamma} - \frac{\alpha_2 \gamma}{2}\right) \right] - \frac{1}{2\alpha_2} \left[1 - \text{erf}\left(\frac{\beta}{\gamma}\right) \right], \quad (\text{B.1}) \end{aligned}$$

where

$$u = \sqrt{1 + \frac{4D_a}{Pe}}, \quad \alpha_1 = \frac{Pe(1-u)}{2}, \quad \alpha_2 = \frac{Pe(1+u)}{2}, \quad \beta = u \Delta t, \quad \gamma = 2\sqrt{\frac{\Delta t}{Pe}}.$$

The expression for the standard DA-R scheme is:

$$M_{(DA-R)}(\Delta t) = \frac{1}{2} \exp(-D_a \Delta t) \left[\frac{\gamma}{\sqrt{\pi}} \exp\left(-\frac{\beta^2}{\gamma^2}\right) + \beta \operatorname{erf}\left(\frac{\beta}{\gamma}\right) + \beta \right] + \frac{1}{2\alpha} \exp(-D_a \Delta t) \\ \times \left[\exp\left(\frac{\alpha^2 \gamma^2}{4} - \alpha\beta\right) \left\{ 1 - \operatorname{erf}\left(\frac{\beta}{\gamma} - \frac{\alpha\gamma}{2}\right) \right\} - 1 + \operatorname{erf}\left(\frac{\beta}{\gamma}\right) \right], \quad (\text{B.2})$$

where

$$\alpha = Pe, \quad \beta = \Delta t, \quad \gamma = 2\sqrt{\frac{\Delta t}{Pe}}.$$

The two remaining cases are:

$$M_{(D-A-R)}(\Delta t) = \exp(-D_a \Delta t) \left[\frac{1}{\alpha\sqrt{\pi}} + \Delta t \right], \quad (\text{B.3})$$

$$M_{(D-AR)}(\Delta t) = \frac{\exp(-D_a \Delta t)}{\alpha\sqrt{\pi}} + \frac{[1 - \exp(-D_a \Delta t)]}{D_a}, \quad (\text{B.4})$$

where

$$\alpha = \frac{1}{2} \sqrt{\frac{Pe}{\Delta t}}.$$

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