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A semi-analytical solution for the transport of solutes with complex sequences of first-order reactions

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ABSTRACT

A semi-analytical solution for one-dimensional transport of multiple species along a reaction chain is introduced. The DECAY solution considers advection, dispersion, equilibrium sorption, and arbitrarily complex sequences of first-order reactions. The treatment of branching accommodates transport that potentially involves multiple parents and daughter products. The solution is general in that the individual species may have different dispersion and sorption coefficients and different decay rates specified in the dissolved and sorbed phases for each species. Yield coefficients can be specified so that the calculations can be conducted in terms of concentrations expressed in units of either mass or moles per unit volume of water. The DECAY solution accommodates Dirichlet and Cauchy inflow boundary conditions with general influent concentration histories. The concentrations of each species are evaluated by accurate and efficient numerical inversion of the Laplace-transform solutions. The semi-analytical solution has been tested extensively and verified against existing analytical solutions and numerical simulations.

1. Introduction

The fate and transport of species along a reaction sequence is of considerable environmental interest. The original motivation for the analysis of multiple species arose in the context of radionuclide transport; in these applications the daughter products along a straight decay chain may be more hazardous and longer-lived than the parent (Lester et al., 1975; Higashi and Pigford, 1980). Attention has been focused recently on the transport of fuels and chlorinated solvents and the products of their biodegradation (see for example Suarez and Rifai, 1999; Hwang et al., 2015). At many contaminated sites it is the distribution and concentrations of daughter products that provide a primary line of evidence for the assessment of natural attenuation (Wiedemeier et al., 1999). Two reaction chains of environment significance, involving reaction sequences that are more complex than straight chains are illustrated in Fig. 1a and b.

Several analytical, semi-analytical and numerical approaches have been developed to support the analysis of multi-species transport along straight reaction chains. Important analytical contributions include those of van Genuchten (1985), Sun et al. (1999), Quezada et al. (2004) and Srinivasan and Clement (2008a, b).

This paper has been prepared to document the derivation and implementation of a semi-analytical approach for the simulation of one-dimensional transport of multiple species along complex reaction sequences. The solution is evaluated by efficient and accurate numerical inversion of the Laplace transform solutions for each species, implemented in the code DECAY.

The theory underlying the DECAY solution is not new. The van Genuchten (1985) solution for chain decay is the starting point for the DECAY solution. The DECAY solution generalizes the analysis of van Genuchten (1985) to consider arbitrarily complex first-order reaction sequences. The DECAY solution extends the capabilities of the van Genuchten (1985) solution for more complex reaction pathways. The full development for three-dimensional transport is presented in Sudicky et al. (2013). The Sudicky et al. (2013) solution considers three-dimensional transport with uniform uni-directional groundwater flow, but requires numerical inversion of a Laplace-transform solution expressed in terms of an infinite, complex-valued integral containing an infinite series. The capability to consider species-dependent dispersion coefficients is particularly important when the Darcy velocity is low and hydrodynamic dispersion becomes controlled by diffusion. For example, as indicated on Table 1 below, the diffusion coefficients among the chlorinated solvents reaction pathway from PCE to vinyl chloride vary by about one order of magnitude (U.S. EPA, 1996). The differences in the dispersion coefficients for relatively small groundwater velocities are magnified when sorption is considered (as quantified by the organic

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[1] Guided the design of the study, provided the foundation of the analysis, and edited the version of the manuscript to be published.

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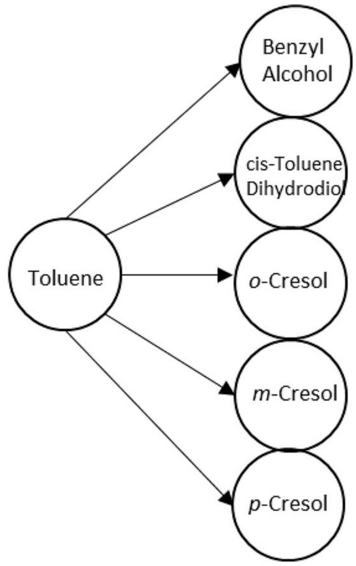
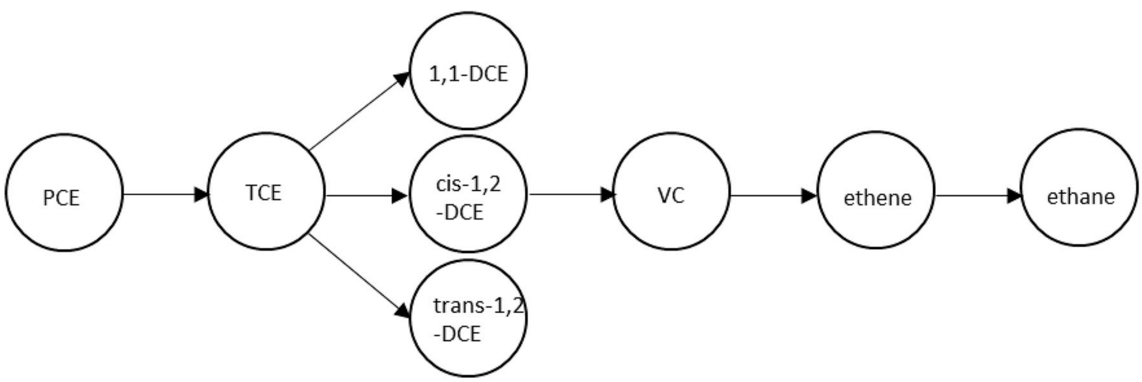


a Example of a parallel reaction sequence (Alvarez and Illman, 2006)

Fig. 1a. Example of a parallel reaction sequence (Alvarez and Illman, 2006).



b Examples of a serial-parallel reaction sequence (Wiedemeier et al., 1999)

Fig. 1b. Examples of a serial-parallel reaction sequence (Wiedemeier et al., 1999).

Table 1
Diffusion and partitioning coefficient for species along the PCE degradation pathway.

Chemical	Diffusion coefficient in water (cm^2/s)	Organic carbon-water partitioning coefficient (L/kg)
PCE	8.2×10^{-6}	155
TCE	9.1×10^{-6}	166
1,1-DCE	1.04×10^{-5}	58.9
Cis-1,2-DCE	1.13×10^{-5}	35.5
Trans-1,2-DCE	1.19×10^{-5}	52.5
Vinyl chloride	1.23×10^{-6}	18.6

carbon-water partitioning coefficient, K_{oc}).

The solution approach described here results in the development of solutions relatively general within a rigorous framework that is straightforward to extend to arbitrarily complex reaction sequences. The approach is relatively general in that it accommodates first-order reactions along chains with complex branching, and incorporates flexibility with respect to the specification of dispersion/diffusion parameters, retardation factors, and reaction rates in the dissolved and the sorbed phases. The solution also accommodates both Type I (Dirichlet) and Type III (Cauchy) inflow boundary conditions with arbitrary concentration histories.

The DECAY solution is evaluated by efficient and accurate numerical inversion of the Laplace transform solutions for each species. The solution is particularly useful for screening-level applications and to support the interpretation of data for monitored natural attenuations. In complex settings, the solution may be useful to support the design and checking of numerical models. The DECAY solution has been tested extensively. For this paper, benchmarking analyses have been selected specifically to illustrate the simulation of reactions with branching.

The DECAY code is written in the FORTRAN language. DECAY is freely accessible from the website www.sspa.com. The DECAY package includes complete documentation that includes results for extensive testing.

2. Development of the DECAY solution

2.1. a. Conceptual model

The DECAY solution considers advection, mechanical dispersion and molecular diffusion, equilibrium sorption, and first-order degradation and production reactions. The solution can accommodate both sequential and branching decay with no limitation on the number of species. The DECAY code is currently limited to three levels of reactions, with the level referring to the sequential order of decay reactions along a branching decay chain (for the starting species of a decay chain, its LEVEL equals to zero). However, with the Laplace transform approach it is straightforward to add more levels of reaction. The treatment of branching accommodates the transport of species that may have more than one parent and multiple daughter products. Yield coefficients are included as input, to allow concentrations to be expressed in terms of either mass or moles per unit volume of water. The branching ratios allow specification of the fraction of parent transforming into particular daughter products.

Goode (1999) discussed the application of first-order reaction kinetics to represent chemical decomposition or biodegradation of organic species. The DECAY solution provides the flexibility to assign different values of reaction rates in the dissolved and sorbed phases for each species. The DECAY solution accommodates Dirichlet and Cauchy inflow boundary conditions with general influent concentration histories.

2.2. b. Governing equation

Assuming steady flow along a homogeneous aquifer, the statement of mass conservation for the ith species along a decay chain, accounting for one-dimensional advection, dispersion, sorption and a first-order transformation reaction is written as:

$$R_i\phi\frac{\partial C_i}{\partial t} = -q\frac{\partial C_i}{\partial x} + \phi D_i\frac{\partial^2 C_i}{\partial x^2} - \left(\phi\lambda_{d_i} + \rho_b K_{d_i}\lambda_{s_i}\right)C_i + Y_{j\to i}\eta_{j\to i}\left(\phi\lambda_{d_j} + \rho_b K_{d_j}\lambda_{s_j}\right)C_j \quad (1)$$

Here C is the dissolved concentration (ML^{-3}), x is distance (L), t is time (T), ϕ is the porosity of the porous medium (dimensionless), q is the Darcy flux (LT^{-1}), D is the dispersion coefficient (L^2T^{-1}), λ_d is the first-order decay rate in the dissolved phase (T^{-1}), λ_s is the first-order decay rate in the sorbed phase (T^{-1}), ρ_b is the bulk density of the porous media (ML^{-3}), and K_d is the equilibrium sorption coefficient ($M^{-1}L^3$). The last term of Equation (1) represents the generation of species i from the transformation of parent species j, with $Y_{j\to i}$ the yield coefficient between parent j and species i. Further details on the interpretation of the yield coefficient are presented in the demonstration analysis. The parameter $\eta_{j\to i}$ denotes the branching ratio, that is, the fraction of parent j that transforms into species i. The retardation factor R and the dispersion coefficient D for species i are defined as:

$$R_i = 1 + \frac{\rho_b K_{d_i}}{\phi} \quad (2)$$

$$D_i = \alpha_i|v| + D^* \quad (3)$$

Here α is the longitudinal dispersivity (L), v is the average linear groundwater velocity (LT^{-1}), and D^* is the effective molecular diffusion coefficient (LT^{-2}). The hydrodynamic dispersion coefficient reflects the contributions of mechanical dispersion and molecular diffusion. The dispersivity quantifies the effects of mechanical dispersion due to variations in groundwater velocity along the flowpath. The dispersivity is considered to be a characteristic of the porous medium while the effective diffusion coefficient incorporates the properties of each solute and the tortuosity of the porous medium.

2.3. c. Initial and boundary conditions

The DECAY solution assumes that the domain is initially devoid of solute:

$$C_i(x, 0) = 0 \quad (4)$$

The DECAY solution can handle a general inflow boundary expressed as:

$$-\phi\delta D_i\frac{\partial C_i}{\partial x} + qC_i|_{x=0} = qC_i^0(t) \quad (5)$$

When $\delta = 0$, Equation (5) collapses to a Type I (specified concentration) boundary condition:

$$c_i(0, t) = c_i^0(t) \quad (6a)$$

When $\delta = 1$, Equation (5) becomes a Type III (specified mass flux) boundary condition for a well-mixed reservoir:

$$-\phi D_i\frac{\partial c_i(0, t)}{\partial x} + qc_i(0, t) = qc_i^0(t) \quad (6b)$$

The domain is assumed to be semi-infinite and the outflow boundary condition is written:

$$\frac{\partial C_i}{\partial x}(\infty, t) = 0 \quad (7)$$

2.4. d. Derivation and evaluation of the solution

The partial differential equation Eq. (1) is solved by applying the Laplace transform with respect to time. The mathematical derivation of the solution is presented in detail in Appendix A. The general solution of the concentration of species i in the Laplace domain for a sequential decay reaction can be written as:

$$\bar{C}_i = \frac{1}{-\phi\delta D_i\beta_i + q}\left[q\bar{C}_i^0(p) - \phi\delta\mu_{i-1}Y_{i-1\to i}\eta_{i-1\to i}\sum_{j=1}^{i-1}\frac{\overline{K_{i-1,i-j}^*}\beta_j}{(\beta_j-\beta_i)(\beta_j-\alpha_i)} + \frac{q\mu_{i-1}Y_{i-1\to i}\eta_{i-1\to i}}{D_i}\sum_{j=1}^{i-1}\frac{\overline{K_{i-1,i-j}^*}}{(\beta_j-\beta_i)(\beta_j-\alpha_i)}\right]Exp\{\beta_i x\} - \frac{\mu_{i-1}Y_{i-1\to i}\eta_{i-1\to i}}{D_i}\sum_{j=1}^{i-1}\frac{\overline{K_{i-1,i-j}^*}Exp\{\beta_j x\}}{(\beta_j-\beta_i)(\beta_j-\alpha_i)} \quad (8)$$

Here $\overline{K_{i-1,i-j}^*}$ is the coefficient of $Exp\{\beta_{j+1}x\}$ ($j = 1, \ldots, i$-1) in the general solution of $\bar{C}_{i-1}$; $\bar{C}_i^0(p)$ is the initial concentration of species i at the inflow boundary in the Laplace domain; μ_i can be expressed as,

$$\mu_i = \lambda_{d_i} + \frac{\rho_b K_{d_i}\lambda_{s_i}}{\phi} \quad (9)$$

and α_i, β_i are the general solutions for a homogeneous second order ODE in the form of

$$\bar{C}_{i_H} = A_i Exp\{\alpha_i x\} + B_i Exp\{\beta_i x\} \quad (10)$$

The solution is in the Laplace domain and the final solution involves retransforming to the time domain using an inverse Laplace transform procedure. The inversion of the Laplace transform is accomplished numerically using the algorithm of De Hoog et al. (1982). The solution for branching decay reactions is obtained by tracking the reaction history of a species. The run time varies with the number of species in the decay chain. For a typical 4-species reaction, the execution time is typically a few seconds.

3. Benchmarking analyses

The DECAY solution has been extensively tested and the test examples are provided in the user's guide (Wang and Neville, 2016). Three examples have been selected to be presented here to illustrate

Table 2
Common basic parameters for the three examples.

Parameters	
Darcy flux q (m/day)	0.01
Porosity ϕ (−)	0.1
Bulk density ρ_b (g/cm^3)	1.0
Dispersion coefficient D (m^2/day)	0.18

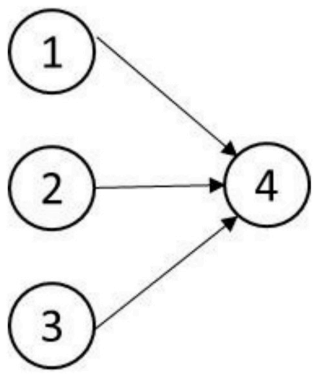


Fig. 2. Decay pathways of Benchmark Analysis 1.

branching pathways for which analyses have not been reported previously in the literature. The results of the DECAY solution are compared against the numerical results from a solute transport model, MT3D-USGS (Bedekar et al., 2016) for the three examples. It is assumed that the reactions occur only in the dissolved phase. The values of Darcy flux, porosity, bulk density and dispersion coefficient are identical for the three examples and are presented on Table 2. The test example with variable dispersion coefficients among different species is not presented here, but has been provided in the user's guide (Wang and Neville, 2016).

3.1. a. Benchmark Analysis 1

This analysis is designed to demonstrate the capability of the DECAY solution to handle reactions with multiple parents. The reaction pathway for Analysis 1 is illustrated in Fig. 2. The input parameters for this example are tabulated on Table 3.

The results obtained with the DECAY solution and MT3D-USGS are shown in Fig. 3. In general, the results match closely; the slight mismatches at the ends of the profiles arise because the analytical solution assumes a semi-infinite domain whereas the numerical model terminates with a zero dispersive-flux boundary condition. The parent species 1, 2 and 3 have decreasing concentrations over time. The daughter species 4 first increases, then stabilizes after reaching a plateau, and eventually decreases at the later time.

3.2. b. Benchmark Analysis 2

Four species are also considered in Analysis 2; however, the reaction sequence is reversed with respect to Analysis 1. As shown in Fig. 4, one parent is split into three daughter products. The input parameters for the analysis are listed on Table 4.

The results obtained with the DECAY solution and MT3D-USGS are shown in Fig. 5. The results obtained with the semi-analytical and numerical solutions match closely. In this analysis, the concentration of the parent species (1) decreases over time, and the concentrations of the daughter products (2, 3 and 4) exhibit similar trends, initially increasing, followed by a period of stabilization and then long-term decline.

3.3. c. Benchmark Analysis 3

This decay reaction for Benchmark Analysis 3 is illustrated in Fig. 6. The reaction sequence occurs at three levels and involves six species. Species 1 and 4 have two daughter products with different fractions of transformation; and species 2 and 3 have only one daughter product. The input parameters for this example are presented on Table 5.

The results calculated from the DECAY program and MT3D-USGS are plotted in Fig. 7. A logarithmic scale is selected for the concentration axis as the range of concentrations among the decay species is wide, extending over four orders of magnitude. The figure again shows a perfect agreement between the two results, but with a slight discrepancy for each species at the end of the profile. Species 2 and 3 are the daughter products of species 1; species 4 is the only daughter product of species 2 and 3; and species 5 and 6 are the daughter products of species 4. The concentration profiles obtained with the semi-analytical and numerical solutions are consistent.

4. Conclusions

The DECAY program is an extended semi-analytical solution for contaminant transport involving advection, dispersion, equilibrium sorption, and first-order straight-chain and branching decay reactions. Numerical inversion of the Laplace-transform is applied providing an accurate and efficient solution. The DECAY solution allows different dispersion coefficients and sorption coefficients resulting in different retardation factors for each species. Unlike van-Genuchten (1985) solution, the solution accommodates the specification of different decay rates for the dissolved and sorbed phases for each species, which is usually the case for chemical decomposition or biodegradation of organic compounds given that the sorbed phase is present. Yield coefficients are implemented in the solution assisting in the calculations in terms of converting concentrations expressed in units of either mass or moles per unit volume of water. Branching ratio is introduced representing the fraction of parent species that transforms into daughter species. The DECAY solution can handle general initial and boundary conditions, including Dirichlet and Cauchy inflow boundary conditions with Bateman-type source histories. The number species involved in decay reactions is not limited in the DECAY solution, but a maximum of

Table 3
Other input parameters for Example 1.

Parameters	Species 1	Species 2	Species 3	Species 4
Sorption coefficient K_d (cm^3/g)	0.0	0.0	0.0	0.0
Dissolved phase decay rate (day^{-1})	6.93×10^{-3}	3.47×10^{-3}	1.16×10^{-3}	1.00×10^{-3}
Yield coefficient (−)	0.0	0.0	0.0	{1.0,1.0,1.0}
Branching ratio (−)	1.0	1.0	1.0	{1.0,1.0,1.0}
Initial concentration (−)	1.0	1.0	1.0	0.0

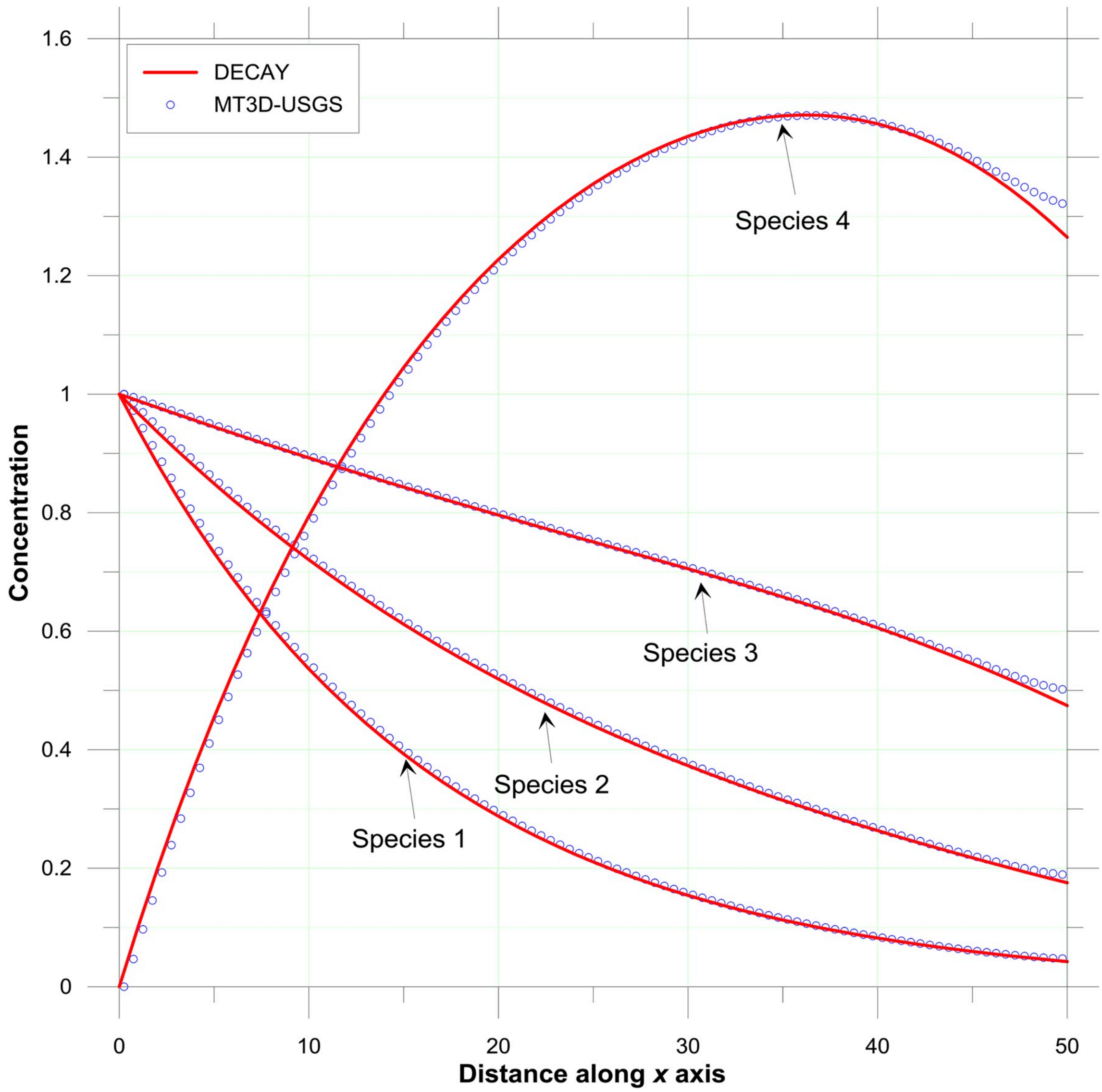


Fig. 3. Concentration profiles at 600 days for Benchmark Analysis 1.

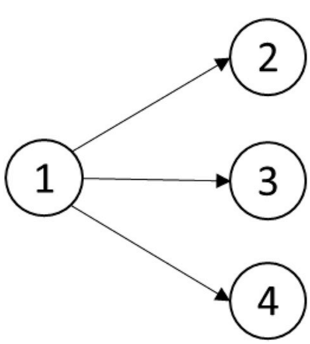


Fig. 4. Decay pathway of Benchmark Analysis 2.

Table 4
Other input parameters for Example 2.

Parameters	Species 1	Species 2	Species 3	Species 4
Dissolved phase decay rate (day^{-1})	6.93×10^{-3}	3.47×10^{-3}	1.16×10^{-3}	1.00×10^{-3}
Yield coefficient (−)	0.0	1.0	1.0	1.0
Branching ratio (−)	1.0	0.5	0.3	0.2
Initial concentration (−)	1.0	0.0	0.0	0.0

three reaction levels is implemented in the current version of the solution. The use of the Laplace transform enables straightforward extension of reaction levels.

Extensive testing has been conducted to verify the DECAY solution. The three examples presented in the paper are representative of complex decay pathways and have not been reported previously. The results generated by DECAY were compared against the numerical simulations by MT3D-USGS. The results showed good agreements for all three examples, which suggest a high performance and robustness of the DECAY solution.

Because the DECAY solution is applicable to one-dimensional solute transport calculation, the ideal application will be along the centerline of a plume. Despite its limitation, DECAY is capable of mimicking

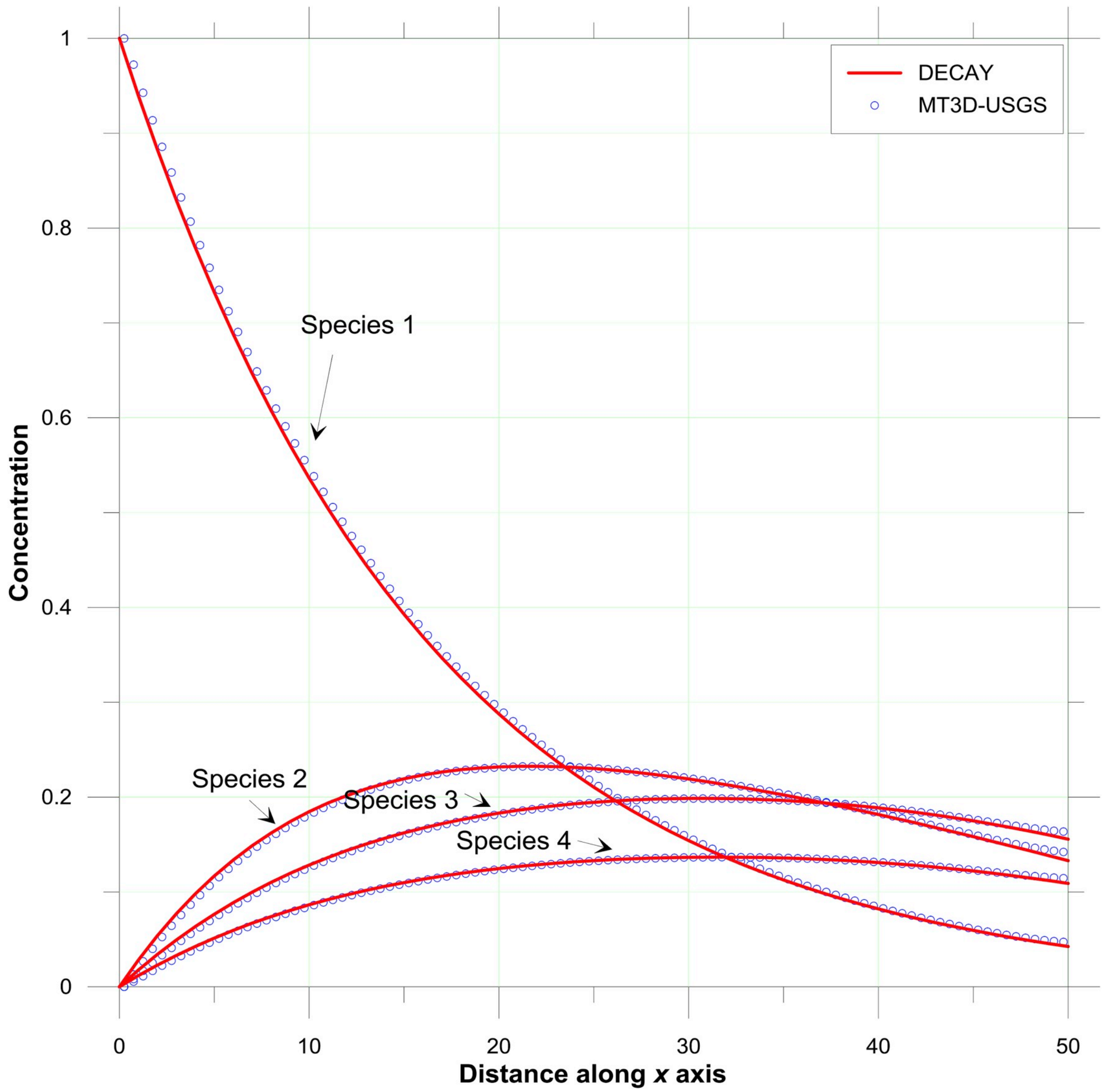


Fig. 5. Concentration profiles at 600 days for Benchmark Analysis 2.

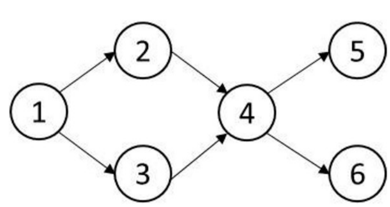


Fig. 6. Decay pathways of Benchmark Analysis 3.

various complicated reactive pathways. The implementation is more flexible and easier than numerical models. The DECAY program is available to everyone via the website www.sspa.com. DECAY is an excellent tool for making screen-level calculations for contaminant transport involving advection, dispersion, sorption and first-order decay reactions with branching.

Table 5
Other input parameters for Benchmark Analysis 3.

Parameters	Species 1	Species 2	Species 3	Species 4	Species 5	Species 6
Dissolved phase decay rate (day^{-1})	5.0×10^{-3}	3.0×10^{-3}	1.5×10^{-3}	2.0×10^{-3}	1.0×10^{-3}	5.0×10^{-4}
Yield coefficient (−)	0.0	1.0	1.0	{1.0,1.0}	1.0	1.0
Branching ratio (−)	1.0	0.6	0.4	{1.0,1.0}	0.6	0.4
Initial concentration (−)	0.0	0.0	0.0	0.0	0.0	1.0

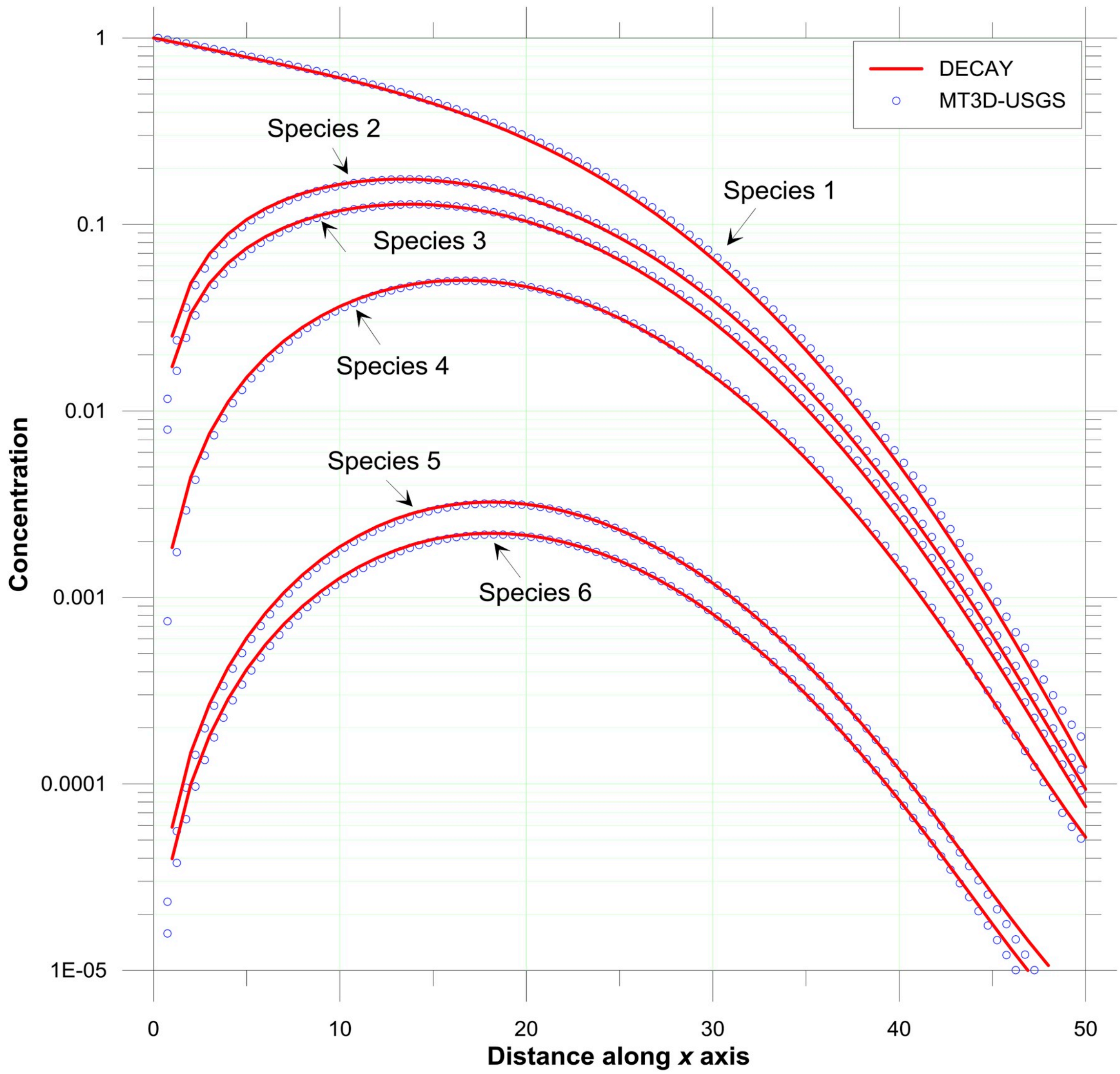


Fig. 7. Concentration profiles at 200 days for Benchmark Analysis 3.

Author Contributions

Derived and implemented the analytical solutions, prepared all figures, and wrote the draft manuscript.

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Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cageo.2018.11.013.

Appenix A. Mathematical Derivation

1 Governing equation

Assuming steady flow along a homogeneous aquifer, the statements of mass conservation for the species along a straight-decay chain, accounting for one-dimensional advection, dispersion, sorption and a first-order transformation reaction are written as:

i. Species 1 -

$$R_1\phi\frac{\partial C_1}{\partial t} = \phi D_1\frac{\partial^2 C_1}{\partial x^2} - q\frac{\partial C_1}{\partial x} - \phi\lambda_{d_1}C_1 - \rho_b K_{d1}\lambda_{s_1}C_1 \quad [A1]$$

ii. Species 2 –

$$R_2\phi\frac{\partial C_2}{\partial t} = \phi D_2\frac{\partial^2 C_2}{\partial x^2} - q\frac{\partial C_2}{\partial x} - \phi\lambda_{d_2}C_2 - \rho_b K_{d_2}\lambda_{s_2}C_2 + \phi\lambda_{d_1}Y_{1\to 2}C_1 + \rho_b K_{d_1}\lambda_{s_1}Y_{1\to 2}C_1 \quad \text{[A2]}$$

iii. Species i –

$$R_i\phi\frac{\partial C_i}{\partial t} = \phi D_i\frac{\partial^2 C_i}{\partial x^2} - q\frac{\partial C_i}{\partial x} - \phi\lambda_{d_i}C_i - \rho_b K_{d_i}\lambda_{s_i}C_i + \phi\lambda_{d_j}Y_{j\to i}C_j + \rho_b K_{d_j}\lambda_{s_j}Y_{j\to i}C_j \quad \text{[A3]}$$

where

$j = i$-1
C_i = dissolved concentration for species i (ML^{-3})
x = distance (L)
t = time (T)
ϕ = porosity of the porous medium (−)
q = Darcy flux (LT^{-1})
D_i = dispersion coefficient for species i (L^2T^{-1})
λ_{d_i} = the first-order decay rate in the dissolved phase for species i (T^{-1})
λ_{s_i} = the first-order decay rate in the sorbed phase for species i (T^{-1})
ρ_b = bulk density of the porous medium (ML^{-3})
K_{d_i} = equilibrium sorption coefficient for species i ($M^{-1}L^3$)
$Y_{j\to i}$ = yield coefficient from species i to j
$R_i = 1 + \frac{\rho_b}{\phi}K_{d_i}$

2 Simplification of the governing equations

Eqs. [A1], [A2], and [A3] are simplified as follows:

i. $$R_1\phi\frac{\partial C_1}{\partial t} = \phi D_1\frac{\partial^2 C_1}{\partial x^2} - q\frac{\partial C_1}{\partial x} - \phi\left(\lambda_{d_1} + \frac{\rho_b K_{d_1}}{\phi}\lambda_{s_1}\right)C_1 \quad \text{[A4]}$$

ii. $$R_2\phi\frac{\partial C_2}{\partial t} = \phi D_2\frac{\partial^2 C_2}{\partial x^2} - q\frac{\partial C_2}{\partial x} - \phi\left(\lambda_{d_2} + \frac{\rho_b K_{d_2}}{\phi}\lambda_{s_2}\right)C_2 + \phi\left(\lambda_{d_1} + \frac{\rho_b K_{d_1}}{\phi}\lambda_{s_1}\right)Y_{1\to 2}C_1 \quad \text{[A5]}$$

iii. $$R_i\phi\frac{\partial C_i}{\partial t} = \phi D_i\frac{\partial^2 C_i}{\partial x^2} - q\frac{\partial C_i}{\partial x} - \phi\left(\lambda_{d_i} + \frac{\rho_b K_{d_i}}{\phi}\lambda_{s_i}\right)C_i + \phi\left(\lambda_{d_j} + \frac{\rho_b K_{d_j}}{\phi}\lambda_{s_j}\right)Y_{j\to i}C_j \quad \text{[A6]}$$

Defining

$$\mu_i = \lambda_{d_i} + \frac{\rho_b K_{d_i}}{\phi}\lambda_{s_i} \quad \text{[A7]}$$

and the governing equations can be re-written as

i. $$R_i\phi\frac{\partial C_i}{\partial t} = \phi D_i\frac{\partial^2 C_i}{\partial x^2} - q\frac{\partial C_i}{\partial x} - \phi\left(\lambda_{d_i} + \frac{\rho_b K_{d_i}}{\phi}\lambda_{s_i}\right)C_i + \phi\left(\lambda_{d_j} + \frac{\rho_b K_{d_j}}{\phi}\lambda_{s_j}\right)Y_{j\to i}C_j R_1\phi\frac{\partial C_1}{\partial t} = \phi D_1\frac{\partial^2 C_1}{\partial x^2} - q\frac{\partial C_1}{\partial x} - \phi\mu_1 C_1 \quad \text{[A8]}$$

ii. $$R_2\phi\frac{\partial C_2}{\partial t} = \phi D_2\frac{\partial^2 C_2}{\partial x^2} - q\frac{\partial C_2}{\partial x} - \phi\mu_2 C_2 + \phi\mu_1 Y_{1\to 2}C_1 \quad \text{[A9]}$$

iii. $$R_i\phi\frac{\partial C_i}{\partial t} = \phi D_i\frac{\partial^2 C_i}{\partial x^2} - q\frac{\partial C_i}{\partial x} - \phi\mu_i C_i + \phi\mu_j Y_{j\to i}C_j \quad \text{[A10]}$$

3 'End members' for decay in sorbed phase

It assumes that the first-order decay rate in the sorbed phase is considered to have two case values.

Case 1. The decay in sorbed phase proceeds at the same rate as in dissolved phase

$\lambda_{d_i} = \lambda_{s_i}$

$$\mu_i = \lambda_{d_i} + \frac{\rho_b K_{d_i}}{\phi}\lambda_{s_i} = \left(1 + \frac{\rho_b K_{d_i}}{\phi}\right)\lambda_{d_i} = R_i\lambda_{d_i} \quad \text{[A11]}$$

Case 2. The decay in sorbed phase is zero

$\lambda_{s_i} = 0$

$$\mu_i = \lambda_{d_i} \quad \text{[A12]}$$

4 Initial and boundary conditions

1) Inflow boundary conditions

$$-\phi\delta D_i\frac{\partial C_i}{\partial x} + qC_i|_{x=0} = qC_i^0(t) \qquad [A13]$$

$\delta = 0 \rightarrow$ Type I inflow boundary conditions: $C_i(0,t) = C_i^0(t)$.
$\delta = 1 \rightarrow$ Type III inflow boundary conditions: $-\phi D_i\frac{\partial C_i(0,t)}{\partial x} + qC_i(0,t) = qC_i^0(t)$.

2) Outflow boundary conditions

$$\frac{\partial C_i}{\partial x}(\infty, t) = 0 \qquad [A14]$$

3) Initial conditions

The solution assumes that the domain is initially devoid of solute:

$$C_i(x, 0) = 0 \qquad [A15]$$

5 Solution in the Laplace domain: Species 1

Apply the Laplace transform to the governing equation for species 1 (Eq. [A4]),

$$R_1\phi[p\bar{C}_1 - C_1(x,0)] = \phi D_1\frac{\partial^2\bar{C}_1}{\partial x^2} - q\frac{\partial\bar{C}_1}{\partial x} - \phi\mu_1\bar{C}_1 \qquad [A16]$$

Rearranging,

$$\frac{d^2\bar{C}_1}{dx^2} - \frac{q}{\phi D_1}\frac{d\bar{C}_1}{dx} - \frac{1}{\phi D_1}(R_1\phi p + \phi\mu_1)\bar{C}_1 = 0 \qquad [A17]$$

The general solution for this equation is:

$$\bar{C}_1 = A_1 Exp\{\alpha_1 x\} + B_1 Exp\{\beta_1 x\} \qquad [A18]$$

where

$$\alpha_1 = \frac{q}{2\phi D_1} + \frac{1}{2}\sqrt{\left(\frac{q}{\phi D_1}\right)^2 + \frac{4}{\phi D_1}(R_1\phi p + \phi\mu_1)} \qquad [A19]$$

$$\beta_1 = \frac{q}{2\phi D_1} - \frac{1}{2}\sqrt{\left(\frac{q}{\phi D_1}\right)^2 + \frac{4}{\phi D_1}(R_1\phi p + \phi\mu_1)} \qquad [A20]$$

Subject to the inflow and outflow boundary conditions,

$$-\phi\delta D_1\frac{d\bar{C}_1}{dx}(0,p) + q\bar{C}_1(0,p) = q\bar{C}_1^0(p) \qquad [A21]$$

$$\frac{d\bar{C}_1}{dx}(\infty, p) = 0 \qquad [A22]$$

Since the solution is bounded, $A_1 = 0$.
Eq. [A21] can be rewritten as:

$$-\phi\delta D_1\frac{d}{dx}(B_1 Exp\{\beta_1 x\}) + q(B_1 Exp\{\beta_1 x\})\Big|_{x=0} = q\bar{C}_1^0(p) \qquad [A23]$$

$$\rightarrow -\phi\delta D_1 B_1\beta_1 + qB_1 = q\bar{C}_1^0(p)$$

Solving for B_1 yields,

$$B_1 = \frac{q\bar{C}_1^0(p)}{-\phi\delta D_1\beta_1 + q} \qquad [A24]$$

Substituting Eq. [A24] into Eq. [A18], we obtain

$$\bar{C}_1 = \frac{q\bar{C}_1^0(p)}{-\phi\delta D_1\beta_1 + q}Exp\{\beta_1 x\} \qquad [A25]$$

If Type I boundary condition is applied, $\delta = 0$, the solution for species 1 is:

$$\bar{C}_1 = \bar{C}_1^0(p)Exp\{\beta_1 x\} \qquad [A26]$$

To simplify the solution, let us introduce a parameter $\overline{K_{1,1}^*}$,

$$\overline{K_{1,1}^{*}} = \frac{q\bar{C}_1^{0}(p)}{-\phi\delta D_1\beta_1 + q} \qquad [A27]$$

Substituting Eq. [A27] into the solution, we get

$$\bar{C}_1 = \overline{K_{1,1}^{*}}Exp\{\beta_1 x\} \qquad [A28]$$

When $\delta = 0$, $\overline{K_{1,1}^{*}} = \bar{C}_1^{0}(p)$.

6 Solution in the Laplace domain: Species 2

Apply the Laplace transform to the governing equation for species 2 (Eq. [A5]),

$$R_2\phi[p\bar{C}_2 - C_2(x,0)] = \phi D_2\frac{d^2\bar{C}_2}{dx^2} - q\frac{d\bar{C}_2}{dx} - \phi\mu_2\bar{C}_2 + \phi\mu_1 Y_{1\to2}\bar{C}_1 \qquad [A29]$$

Rearranging,

$$\frac{d^2\bar{C}_2}{dx^2} - \frac{q}{\phi D_2}\frac{d\bar{C}_2}{dx} - \frac{1}{\phi D_2}(R_2\phi p + \phi\mu_2)\bar{C}_2 = \frac{-\phi\mu_1 Y_{1\to2}\bar{C}_1}{\phi D_2} \qquad [A30]$$

The transformed governing equation for $\bar{C}_2$ is a non-homogeneous, second-order ODE. The general solution is the combination of the complementary homogeneous solution and the particular solution for the non-homogeneous part.

$$\bar{C}_2 = \bar{C}_{2H} + \bar{C}_{2P} \qquad [A31]$$

The solution for the complementary homogeneous equation is:

$$\bar{C}_{2H} = A_2 Exp\{\alpha_2 x\} + B_2 Exp\{\beta_2 x\} \qquad [A32]$$

where

$$\alpha_2 = \frac{q}{2\phi D_2} + \frac{1}{2}\sqrt{\left(\frac{q}{\phi D_2}\right)^2 + \frac{4}{\phi D_2}(R_2\phi p + \phi\mu_2)} \qquad [A33]$$

$$\beta_2 = \frac{q}{2\phi D_2} - \frac{1}{2}\sqrt{\left(\frac{q}{\phi D_2}\right)^2 + \frac{4}{\phi D_2}(R_2\phi p + \phi\mu_2)} \qquad [A34]$$

The particular solution for the non-homogeneous part of the solution can be derived using the method of operators:

$$\bar{C}_{2P} = Exp\{-p_1 x\}\int^{x} Exp\{p_1\xi\}[Exp\{-p_2\xi\}\int_{\xi} Exp\{p_2\chi\}f(\chi)d\chi]d\xi \qquad [A35]$$

Here,

$$p_1 = -\alpha_2$$

$$p_2 = -\beta_2$$

$$f(x) = \frac{-\phi\mu_1 Y_{1\to2}\bar{C}_1}{\phi D_2}$$

Substituting Eq. [A28] into the equation, we have

$$f(x) = -\frac{\mu_1 Y_{1\to2}}{D_2}\overline{K_{1,1}^{*}}Exp\{\beta_1 x\} \qquad [A36]$$

The inner integral becomes

$$\int^{\xi} Exp\{p_2\chi\}f(\chi)d\chi = \int^{\xi} Exp\{-\beta_2\chi\}\frac{-\mu_1 Y_{1\to2}}{D_2}\overline{K_{1,1}^{*}}\mathrm{Exp}\{\beta_1\chi\}d\chi$$

$$= -\frac{\mu_1 Y_{1\to2}}{D_2}\overline{K_{1,1}^{*}}\int^{\xi} Exp\{(\beta_1 - \beta_2)\chi\}d\chi$$

$$= -\frac{\mu_1 Y_{1\to2}}{D_2(\beta_1 - \beta_2)}\overline{K_{1,1}^{*}}Exp\{(\beta_1 - \beta_2)\xi\} \qquad [A37]$$

The particular solution, Eq. [A35] is equal to

$$\bar{C}_{2P} = Exp\{\alpha_2 x\}\int^{x} Exp\{-\alpha_2\xi\}\left[Exp\{\beta_2\xi\}\frac{-\mu_1 Y_{1\to2}}{D_2(\beta_1-\beta_2)}\overline{K_{1,1}^{*}}Exp\{(\beta_1 - \beta_2)\xi\}\right]d\xi$$

$$= -\frac{\mu_1 Y_{1\to2}\overline{K_{1,1}^{*}}}{D_2(\beta_1-\beta_2)}Exp\{\alpha_2 x\}\int^{x} Exp\{(\beta_1 - \alpha_2)\xi\}d\xi$$

$$= -\frac{\mu_1 Y_{1\to2}\overline{K_{1,1}^{*}}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)}Exp\{\beta_1 x\} \qquad [A38]$$

The complete solution is therefore,

$$\bar{C}_2 = \bar{C}_{2H} + \bar{C}_{2P} = A_2 Exp\{\alpha_2 x\} + B_2 Exp\{\beta_2 x\} - \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)} Exp\{\beta_1 x\} \quad [A39]$$

The boundary conditions for species 2 are:

$$-\phi\delta D_2 \frac{d\bar{C}_2(0,p)}{dx} + q\bar{C}_2(0,p) = q\bar{C}_2^0(p) \quad [A40]$$

$$\frac{d\bar{C}_2}{dx}(\infty,p) = 0 \quad [A41]$$

Since the solution is bounded, $A_2 = 0$.
Eq. [A40] becomes,

$$-\phi\delta D_2 \frac{d}{dx}\left[B_2 Exp\{\beta_2 x\} - \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)} Exp\{\beta_1 x\}\right] + q\left[B_2 - \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)}\right] = q\bar{C}_2^0(p)$$

Evaluating the derivative yields,

$$-\phi\delta D_2\left[B_2\beta_2 - \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}\,\beta_1}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)}\right] + q\left[B_2 - \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)}\right] = q\bar{C}_2^0(p) \quad [A42]$$

Solving for B_2 yields,

$$B_2 = \frac{1}{-\phi\delta D_2\beta_2 + q}\left[q\bar{C}_2^0(p) - \phi\delta\mu_1 Y_{1\to 2}\frac{\beta_1\overline{K_{1,1}^*}}{(\beta_1-\beta_2)(\beta_1-\alpha_2)} + q\frac{\mu_1 Y_{1\to 2}}{D_2}\frac{\overline{K_{1,1}^*}}{(\beta_1-\beta_2)(\beta_1-\alpha_2)}\right] \quad [A43]$$

Substituting B_2 in the general solution for species 2,

$$\bar{C}_2 = \frac{1}{-\phi\delta D_2\beta_2 + q}\left[q\bar{C}_2^0(p) - \phi\delta\mu_1 Y_{1\to 2}\frac{\beta_1\overline{K_{1,1}^*}}{(\beta_1-\beta_2)(\beta_1-\alpha_2)} + q\frac{\mu_1 Y_{1\to 2}}{D_2}\frac{\overline{K_{1,1}^*}}{(\beta_1-\beta_2)(\beta_1-\alpha_2)}\right] Exp\{\beta_2 x\} - \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)} Exp\{\beta_1 x\} \quad [A44]$$

If Type I boundary condition is applied, $\delta = 0$, the solution for species 2 is:

$$\bar{C}_2 = \left[\bar{C}_2^0(p) + \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)}\right] Exp\{\beta_2 x\} - \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)} Exp\{\beta_1 x\} = \bar{C}_2^0(p) Exp\{\beta_2 x\} + \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)} Exp\{(\beta_2-\beta_1)x\} \quad [A45]$$

To simplify the solution, let $\overline{K_{2,1}^*}$ be the coefficient on $Exp\{\beta_2 x\}$, and let $\overline{K_{2,2}^*}$ be the coefficient on $Exp\{\beta_1 x\}$.
The general solution, Eq. [A44] can be rewritten as,

$$\bar{C}_2 = \overline{K_{2,1}^*} Exp\{\beta_2 x\} + \overline{K_{2,2}^*} Exp\{\beta_1 x\} \quad [A46]$$

7 Solution in the Laplace domain: Species 3

The general solution in Laplace domain for species 3 according to Eqs. [A31] and [A32],

$$\bar{C}_3 = \bar{C}_{3H} + \bar{C}_{3P} = A_3 Exp\{\alpha_3 x\} + B_3 Exp\{\beta_3 x\} + \bar{C}_{3P} \quad [A47]$$

with

$$\alpha_3 = \frac{q}{2\phi D_3} + \frac{1}{2}\sqrt{\left(\frac{q}{\phi D_3}\right)^2 + \frac{4}{\phi D_3}(R_3\phi p + \phi\mu_3)}$$

$$\beta_3 = \frac{q}{2\phi D_3} - \frac{1}{2}\sqrt{\left(\frac{q}{\phi D_3}\right)^2 + \frac{4}{\phi D_3}(R_3\phi p + \phi\mu_3)}$$

The particular solution of the non-homogeneous part for species 3 according to Eq. [A35] is,

$$\bar{C}_{3P} = Exp\{\alpha_3 x\}\int^x Exp\{-\alpha_3\xi\}\left[Exp\{\beta_3\xi\}\int^\xi Exp\{-\beta_3\chi\} f(\chi)d\chi\right]d\xi \quad [A48]$$

where

$$f(\chi) = \frac{-\mu_2 Y_{2\to 3}\bar{C}_2}{D_3} \quad [A49]$$

Substituting for $f(\chi)$ and $\bar{C}_2$, the inner integral is,

$$\int^{\xi} Exp\{-\beta_3\chi\}f(\chi)d\chi = \int^{\xi} Exp\{-\beta_3\chi\}\frac{-\mu_2 Y_{2\to3}\bar{C}_2}{D_3}d\chi$$
$$= \int^{\xi} Exp\{-\beta_3\chi\}\frac{-\mu_2 Y_{2\to3}}{D_3}(\overline{K^*_{2,1}}Exp\{\beta_2\chi\} + \overline{K^*_{2,2}}\ Exp\{\beta_1\chi\})d\chi$$
$$= \frac{-\mu_2 Y_{2\to3}}{D_3}\int^{\xi} (\overline{K^*_{2,1}}Exp\{(\beta_2-\beta_3)x\} + \overline{K^*_{2,2}}\ Exp\{(\beta_1-\beta_3)x\})d\chi$$
$$= \frac{-\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{\beta_2-\beta_3}Exp\{(\beta_2-\beta_3)\xi\} + \frac{\overline{K^*_{2,2}}}{\beta_1-\beta_3}\ Exp\{(\beta_1-\beta_3)\xi\}\right] \quad \text{[A50]}$$

Substituting into Eq. [A48],

$$\bar{C}_{3P} = Exp\{\alpha_3 x\}\int^{x} Exp\{(\beta_3-\alpha_3)\xi\}\frac{-\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{\beta_2-\beta_3}Exp\{(\beta_2-\beta_3)\xi\} + \frac{\overline{K^*_{2,2}}}{\beta_1-\beta_3}\ Exp\{(\beta_1-\beta_3)\xi\}\right]d\xi$$
$$= -\frac{\mu_2 Y_{2\to3}}{D_3}Exp\{\alpha_3 x\}\int^{x}\left[\frac{\overline{K^*_{2,1}}}{\beta_2-\beta_3}Exp\{(\beta_2-\alpha_3)\xi\} + \frac{\overline{K^*_{2,2}}}{\beta_1-\beta_3}\ Exp\{(\beta_1-\alpha_3)\xi\}\right]d\xi=$$
$$= -\frac{\mu_2 Y_{2\to3}}{D_3}Exp\{\alpha_3 x\}\left[\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)}Exp\{(\beta_2-\alpha_3)x\} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\ Exp\{(\beta_1-\alpha_3)x\}\right]=$$
$$= -\frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\ Exp\{\beta_1 x\}\right] \quad \text{[A51]}$$

The full solution for species 3 is therefore,

$$\bar{C}_3 = A_3 Exp\{\alpha_3 x\} + B_3 Exp\{\beta_3 x\} - \frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\ Exp\{\beta_1 x\}\right] \quad \text{[A52]}$$

The boundary conditions for species 3 are:

$$-\phi\delta D_3\frac{d\bar{C}_3(0,p)}{dx} + q\bar{C}_3(0,p) = q\bar{C}^0_3(p) \quad \text{[A53]}$$

$$\frac{d\bar{C}_3}{dx}(\infty,p) = 0 \quad \text{[A54]}$$

Since the solution is bounded, $A_3 = 0$, Eq. [A53] becomes,

$$-\phi\delta D_3\frac{d}{dx}\left[B_3 Exp\{\beta_3 x\} - \frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\ Exp\{\beta_1 x\}\right]\right]$$
$$+ q\left[B_3 - \frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right]\right] = q\bar{C}^0_3(p)$$

$$-\phi\delta D_3\left[B_3\beta_3 - \frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\beta_2\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\beta_1\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right]\right] + q\left[B_3 - \frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right]\right] = q\bar{C}^0_3(p)$$

$$(-\phi\delta D_3\beta_3 + q)B_3 + \phi\delta D_3\frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\beta_2\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\beta_1\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right] - q\frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right] = q\bar{C}^0_3(p) \quad \text{[A55]}$$

Solving for B_3,

$$B_3 = \frac{1}{-\phi\delta D_3\beta_3 + q}\left[q\bar{C}^0_3(p) - \phi\delta\mu_2 Y_{2\to3}\left(\frac{\beta_2\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\beta_1\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right) + q\frac{\mu_2 Y_{2\to3}}{D_3}\left(\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right)\right] \quad \text{[A56]}$$

The general solution for $\bar{C}_3$ is:

$$\bar{C}_3 = \frac{1}{-\phi\delta D_3\beta_3 + q}\left[q\bar{C}^0_3(p) - \phi\delta\mu_2 Y_{2\to3}\left(\frac{\beta_2\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\beta_1\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right) + q\frac{\mu_2 Y_{2\to3}}{D_3}\left(\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right)\right]Exp\{\beta_3 x\}$$
$$-\frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\ Exp\{\beta_1 x\}\right] \quad \text{[A57]}$$

If Type I boundary condition is applied, $\delta = 0$, the solution for species 3 is:

$$\bar{C}_3 = \left[\bar{C}^0_3(p) + \frac{\mu_2 Y_{2\to3}}{D_3}\left(\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right)\right]Exp\{\beta_3 x\} - \frac{\mu_2 Y_{2\to3}}{D_3}\left[\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\ Exp\{\beta_1 x\}\right] \quad \text{[A58]}$$

To simplify the solution, let $\overline{K^*_{3,1}}$ be the coefficient on $Exp\{\beta_3 x\}$, $\overline{K^*_{3,2}}$ be the coefficient on $Exp\{\beta_2 x\}$, and let $\overline{K^*_{3,3}}$ be the coefficient on $Exp\{\beta_1 x\}$. The general solution, Eq. [A57] can be rewritten as,

$$\bar{C}_3 = \overline{K^*_{3,1}}Exp\{\beta_3 x\} + \overline{K^*_{3,2}}Exp\{\beta_2 x\} + \overline{K^*_{3,3}}\ Exp\{\beta_1 x\} \quad \text{[A59]}$$

8 Solution in the Laplace domain: Species 4

The general solution for species 4 is

$$\bar{C}_4 = \bar{C}_{4H} + \bar{C}_{4P} = A_4 Exp\{\alpha_4 x\} + B_4 Exp\{\beta_4 x\} + \bar{C}_{4P} \quad [A60]$$

with

$$\alpha_4 = \frac{q}{2\phi D_4} + \frac{1}{2}\sqrt{\left(\frac{q}{\phi D_4}\right)^2 + \frac{4}{\phi D_4}(R_4\phi p + \phi\mu_4)}$$

$$\beta_4 = \frac{q}{2\phi D_4} - \frac{1}{2}\sqrt{\left(\frac{q}{\phi D_4}\right)^2 + \frac{4}{\phi D_4}(R_4\phi p + \phi\mu_4)}$$

The particular solution of the non-homogeneous part for species 4 is,

$$\bar{C}_{4P} = Exp\{\alpha_4 x\}\int^x Exp\{-\alpha_4\xi\}\left[Exp\{\beta_4\xi\}\int^\xi Exp\{-\beta_4\chi\}f(\chi)d\chi\right]d\xi \quad [A61]$$

where

$$f(\chi) = \frac{-\mu_3 Y_{3\to4}\bar{C}_3}{D_4} \quad [A62]$$

Substituting for $f(\chi)$ and $\bar{C}_3$ using Eq. [A59], the inner integral is,

$$\int^\xi Exp\{-\beta_4\chi\}f(\chi)d\chi = \int^\xi Exp\{-\beta_4\chi\}\frac{-\mu_3 Y_{3\to4}\bar{C}_3}{D_4}d\chi$$
$$= \frac{-\mu_3 Y_{3\to4}}{D_4}\int^\xi Exp\{-\beta_4\chi\}(\overline{K^*_{3,1}}Exp\{\beta_3\chi\} + \overline{K^*_{3,2}}Exp\{\beta_2\chi\} + \overline{K^*_{3,3}}\ Exp\{\beta_1\chi\})d\chi$$
$$= \frac{-\mu_3 Y_{3\to4}}{D_4}\int^\xi (\overline{K^*_{3,1}}Exp\{(\beta_3 - \beta_4)\chi\} + \overline{K^*_{3,2}}Exp\{(\beta_2 - \beta_4)\chi\} + \overline{K^*_{3,3}}\ Exp\{(\beta_1 - \beta_4)\chi\})d\chi$$
$$= \frac{-\mu_3 Y_{3\to4}}{D_4}\left[\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)}Exp\{(\beta_3 - \beta_4)\xi\} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)}Exp\{(\beta_2 - \beta_4)\xi\} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)}Exp\{(\beta_1 - \beta_4)\xi\}\right] \quad [A63]$$

Carrying out the outer integration:

$$\bar{C}_{4P} = Exp\{\alpha_4 x\}\int^x Exp\{-\alpha_4\xi\}Exp\{\beta_4\xi\}\frac{-\mu_3 Y_{3\to4}}{D_4}\left[\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)}Exp\{(\beta_3 - \beta_4)\xi\} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)}Exp\{(\beta_2 - \beta_4)\xi\} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)}Exp\{(\beta_1 - \beta_4)\xi\}\right]d\xi$$
$$= \frac{-\mu_3 Y_{3\to4}}{D_4}Exp\{\alpha_4 x\}\int^x\left[\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)}Exp\{(\beta_3 - \alpha_4)\xi\} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)}Exp\{(\beta_2 - \alpha_4)\xi\} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)}Exp\{(\beta_1 - \alpha_4)\xi\}\right]d\xi$$
$$= -\frac{\mu_3 Y_{3\to4}}{D_4}\left[\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)}Exp\{\beta_3 x\} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)}Exp\{\beta_2 x\}\right. \quad [A64]$$

The full solution in Laplace domain for species 4 is:

$$\bar{C}_4 = A_4 Exp\{\alpha_4 x\} + B_4 Exp\{\beta_4 x\} - \frac{\mu_3 Y_{3\to4}}{D_4}\left[\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)}Exp\{\beta_3 x\} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}Exp\{\beta_1 x\}\right] \quad [A65]$$

The boundary conditions for Species 4 are:

$$-\phi\delta D_4\frac{d\bar{C}_4(0, p)}{dx} + q\bar{C}_4(0, p) = q\bar{C}_4^0(p) \quad [A66]$$

$$\frac{d\bar{C}_4}{dx}(\infty, p) = 0 \quad [A67]$$

Since the solution is bounded, $A_4 = 0$, Eq. [A66] becomes,

$$-\phi\delta D_4\frac{d}{dx}\left[B_4 Exp\{\beta_4 x\} - \frac{\mu_3 Y_{3\to4}}{D_4}\left(\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)}Exp\{\beta_3 x\} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}Exp\{\beta_1 x\}\right)\right] + q\left(B_4 Exp\{\beta_4 x\}\right.$$
$$\left.- \frac{\mu_3 Y_{3\to4}}{D_4}\left[\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)}Exp\{\beta_3 x\} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}Exp\{\beta_1 x\}\right)\right]$$
$$= q\bar{C}_4^0(p)$$

$$-\phi\delta D_4 B_4\beta_4 + \phi\delta\mu_3 Y_{3\to4}\left[\frac{\beta_3\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\beta_2\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\beta_1\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right] + qB_4$$
$$- \frac{\mu_3 Y_{3\to4}}{D_4}q\left[\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right]$$
$$= q\bar{C}_4^0(p) \quad [A68]$$

Solving for B_4,

$$B_4 = \frac{1}{-\phi\delta D_4\beta_4 + q}\left[q\bar{C}_4^0(p) - \phi\delta\mu_3 Y_{3\to4}\left(\frac{\beta_3\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\beta_2\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\beta_1\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right) + q\frac{\mu_3 Y_{3\to4}}{D_4}\left(\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right)\right] \qquad \text{[A69]}$$

Substituting for B_4 in the general solution:

$$\bar{C}_4 = \frac{1}{-\phi\delta D_4\beta_4 + q}\left[q\bar{C}_4^0(p) - \phi\delta\mu_3 Y_{3\to4}\left(\frac{\beta_3\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\beta_2\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\beta_1\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right) + q\frac{\mu_3 Y_{3\to4}}{D_4}\left(\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right)\right] Exp\{\beta_4 x\} - \frac{\mu_3 Y_{3\to4}}{D_4}\left[\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)}Exp\{\beta_3 x\} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}Exp\{\beta_1 x\}\right] \qquad \text{[A70]}$$

If Type I boundary condition is applied, $\delta = 0$, the solution for species 4 is:

$$\bar{C}_4 = \left[\bar{C}_4^0(p) + \frac{\mu_3 Y_{3\to4}}{D_4}\left(\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right)\right] Exp\{\beta_4 x\} - \frac{\mu_3 Y_{3\to4}}{D_4}\left[\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)}Exp\{\beta_3 x\} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)}Exp\{\beta_2 x\} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}Exp\{\beta_1 x\}\right] \qquad \text{[A71]}$$

To simplify the solution, let $\overline{K^*_{4,1}}$ be the coefficient on $Exp\{\beta_4 x\}$, $\overline{K^*_{4,2}}$ be the coefficient on $Exp\{\beta_3 x\}$, $\overline{K^*_{4,3}}$ be the coefficient on $Exp\{\beta_2 x\}$, and let $\overline{K^*_{4,4}}$ be the coefficient on $Exp\{\beta_1 x\}$.

The general solution, Eq. [A70] can be rewritten as,

$$\bar{C}_4 = \overline{K^*_{4,1}}Exp\{\beta_4 x\} + \overline{K^*_{4,2}}Exp\{\beta_3 x\} + \overline{K^*_{4,3}}Exp\{\beta_2 x\} + \overline{K^*_{4,4}}\,Exp\{\beta_1 x\} \qquad \text{[A72]}$$

The solution coefficients for species 1–4 are summarized:

$$\overline{K^*_{1,1}} = \frac{q\bar{C}_1^0(p)}{-\phi\delta D_1\beta_1 + q}$$

$$\overline{K^*_{2,1}} = \frac{1}{-\phi\delta D_2\beta_2 + q}\left[q\bar{C}_2^0(p) - \phi\delta\mu_1 Y_{1\to2}\frac{\beta_1\overline{K^*_{1,1}}}{(\beta_1-\beta_2)(\beta_1-\alpha_2)} + q\frac{\mu_1 Y_{1\to2}}{D_2}\frac{\overline{K^*_{1,1}}}{(\beta_1-\beta_2)(\beta_1-\alpha_2)}\right]$$

$$\overline{K^*_{2,1}} = -\frac{\mu_1 Y_{1\to2}\overline{K^*_{1,1}}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)}$$

$$\overline{K^*_{3,1}} = \frac{1}{-\phi\delta D_3\beta_3 + q}\left[q\bar{C}_3^0(p) - \phi\delta\mu_2 Y_{2\to3}\left(\frac{\beta_2\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\beta_1\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right) + q\frac{\mu_2 Y_{2\to3}}{D_3}\left(\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right)\right]$$

$$\overline{K^*_{3,2}} = -\frac{\mu_2 Y_{2\to3}}{D_3}\frac{\overline{K^*_{2,1}}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)}$$

$$\overline{K^*_{3,3}} = -\frac{\mu_2 Y_{2\to3}}{D_3}\frac{\overline{K^*_{2,2}}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}$$

$$\overline{K^*_{4,1}} = \frac{1}{-\phi\delta D_4\beta_4 + q}\left[q\bar{C}_4^0(p) - \phi\delta\mu_3 Y_{3\to4}\left(\frac{\beta_3\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\beta_2\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\beta_1\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right) + q\frac{\mu_3 Y_{3\to4}}{D_4}\left(\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right)\right]$$

$$\overline{K^*_{4,2}} = -\frac{\mu_3 Y_{3\to4}}{D_4}\frac{\overline{K^*_{3,1}}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)}$$

$$\overline{K^*_{4,3}} = -\frac{\mu_3 Y_{3\to4}}{D_4}\frac{\overline{K^*_{3,2}}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)}$$

$$\overline{K^*_{4,4}} = -\frac{\mu_3 Y_{3\to4}}{D_4}\frac{\overline{K^*_{3,3}}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}$$

Noting that when $\delta = 0$,

$$\overline{K_{1,1}^*} = \bar{C}_1^0(p)$$

$$\overline{K_{2,1}^*} = \bar{C}_2^0(p) + \frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)}$$

$$\overline{K_{2,2}^*} = -\frac{\mu_1 Y_{1\to 2}\overline{K_{1,1}^*}}{D_2(\beta_1-\beta_2)(\beta_1-\alpha_2)}$$

$$\overline{K_{3,1}^*} = \bar{C}_3^0(p) + \frac{\mu_2 Y_{2\to 3}}{D_3}\left[\frac{\overline{K_{2,1}^*}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)} + \frac{\overline{K_{2,2}^*}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}\right]$$

$$\overline{K_{3,2}^*} = -\frac{\mu_2 Y_{2\to 3}}{D_3}\frac{\overline{K_{2,1}^*}}{(\beta_2-\beta_3)(\beta_2-\alpha_3)}$$

$$\overline{K_{3,3}^*} = -\frac{\mu_2 Y_{2\to 3}}{D_3}\frac{\overline{K_{2,2}^*}}{(\beta_1-\beta_3)(\beta_1-\alpha_3)}$$

$$\overline{K_{4,1}^*} = \bar{C}_4^0(p) + \frac{\mu_3 Y_{3\to 4}}{D_4}\left[\frac{\overline{K_{3,1}^*}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)} + \frac{\overline{K_{3,2}^*}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)} + \frac{\overline{K_{3,3}^*}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}\right]$$

$$\overline{K_{4,2}^*} = -\frac{\mu_3 Y_{3\to 4}}{D_4}\frac{\overline{K_{3,1}^*}}{(\beta_3-\beta_4)(\beta_3-\alpha_4)}$$

$$\overline{K_{4,3}^*} = -\frac{\mu_3 Y_{3\to 4}}{D_4}\frac{\overline{K_{3,2}^*}}{(\beta_2-\beta_4)(\beta_2-\alpha_4)}$$

$$\overline{K_{4,4}^*} = -\frac{\mu_3 Y_{3\to 4}}{D_4}\frac{\overline{K_{3,3}^*}}{(\beta_1-\beta_4)(\beta_1-\alpha_4)}$$

9 Solution in the Laplace domain: Species 5 and beyond

The general solution for species i in the Laplace domain is:

$$\bar{C}_i = \overline{K_{i,1}^*}Exp\{\beta_i x\} + \overline{K_{i,2}^*}Exp\{\beta_{i-1} x\} + \overline{K_{i,3}^*}Exp\{\beta_{i-2} x\} + \cdots + \overline{K_{i,i-1}^*}\,Exp\{\beta_2 x\} + \overline{K_{i,i}^*}\,Exp\{\beta_1 x\} \quad \text{[A73]}$$

where

$$\overline{K_{i,1}^*} = \frac{1}{-\phi\delta D_i\beta_i + q}\left[q\bar{C}_i^0(p) - \phi\delta\mu_{i-1}Y_{i-1\to i}\left(\frac{\beta_{i-1}\overline{K_{i-1,1}^*}}{(\beta_{i-1}-\beta_i)(\beta_{i-1}-\alpha_i)} + \frac{\beta_{i-2}\overline{K_{i-1,2}^*}}{(\beta_{i-2}-\beta_i)(\beta_{i-2}-\alpha_i)} + \ldots + \frac{\beta_1\overline{K_{i-1,i-1}^*}}{(\beta_1-\beta_i)(\beta_1-\alpha_i)}\right)\right.$$
$$\left. + \frac{q\mu_{i-1}Y_{i-1\to i}}{D_i}\left(\frac{\overline{K_{i-1,1}^*}}{(\beta_{i-1}-\beta_i)(\beta_{i-1}-\alpha_i)} + \frac{\overline{K_{i-1,2}^*}}{(\beta_{i-2}-\beta_i)(\beta_{i-2}-\alpha_i)} + \ldots + \frac{\overline{K_{i-1,i-1}^*}}{(\beta_1-\beta_i)(\beta_1-\alpha_i)}\right)\right]$$

$$\overline{K_{i,2}^*} = -\frac{\mu_{i-1}Y_{i-1\to i}}{D_i}\frac{\overline{K_{i-1,1}^*}}{(\beta_{i-1}-\beta_i)(\beta_{i-1}-\alpha_i)}$$

$$\overline{K_{i,3}^*} = -\frac{\mu_{i-1}Y_{i-1\to i}}{D_i}\frac{\overline{K_{i-1,2}^*}}{(\beta_{i-2}-\beta_i)(\beta_{i-2}-\alpha_i)}$$

…

$$\overline{K_{i,i-1}^*} = -\frac{\mu_{i-1}Y_{i-1\to i}}{D_i}\frac{\overline{K_{i-1,i-2}^*}}{(\beta_2-\beta_i)(\beta_2-\alpha_i)}$$

$$\overline{K_{i,i}^*} = -\frac{\mu_{i-1}Y_{i-1\to i}}{D_i}\frac{\overline{K_{i-1,i-1}^*}}{(\beta_1-\beta_i)(\beta_1-\alpha_i)}$$

In summary, the general solution for the ith species is:

$$\bar{C}_i = \frac{1}{-\phi\delta D_i\beta_i + q}\left[q\bar{C}_i^0(p) - \phi\delta\mu_{i-1}Y_{i-1\to i}\sum_{j=1}^{i-1}\frac{\overline{K_{i-1,i-j}^*}\beta_j}{(\beta_j-\beta_i)(\beta_j-\alpha_i)} + \frac{q\mu_{i-1}Y_{i-1\to i}}{D_i}\sum_{j=1}^{i-1}\frac{\overline{K_{i-1,i-j}^*}}{(\beta_j-\beta_i)(\beta_j-\alpha_i)}\right]Exp\{\beta_i x\} - \frac{\mu_{i-1}Y_{i-1\to i}}{D_i}\sum_{j=1}^{i-1}\frac{\overline{K_{i-1,i-j}^*}Exp\{\beta_j x\}}{(\beta_j-\beta_i)(\beta_j-\alpha_i)} \quad \text{[A74]}$$

10 Solution for branching decay chain

A new parameter, $\eta_{j\to i}$, is introduced that denotes the branching ratio, that is, the fraction of parent j that transforms into species i. If species i has n parents, the simplified governing equation of Eq. [A6] becomes

$$R_i\phi\frac{\partial C_i}{\partial t} = \phi D_i\frac{\partial^2 C_i}{\partial x^2} - q\frac{\partial C_i}{\partial x} - \phi\left(\lambda_{d_i} + \frac{\rho_b K_{d_i}}{\phi}\lambda_{s_i}\right)C_i + \sum_{j=1}^{n}\phi\left(\lambda_{d_j} + \frac{\rho_b K_{d_j}}{\phi}\lambda_{s_j}\right)Y_{j\to i}\eta_{j\to i}C_j \quad \text{[A75]}$$

The general solution of species i with branching reactions is the same as the solution for straight-chain decay, Eq. [A74], except replacing $Y_{j\to i}$ with $Y_{j\to i}\eta_{j\to i}$ and accounting for all the straight-chain paths that yield species i.

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