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A semi-analytical solution for simulating contaminant transport subject to chain-decay reactions

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ABSTRACT

We present a set of new, semi-analytical solutions to simulate three-dimensional contaminant transport subject to first-order chain-decay reactions. The aquifer is assumed to be areally semi-infinite, but finite in thickness. The analytical solution can treat the transformation of contaminants into daughter products, leading to decay chains consisting of multiple contaminant species and various reaction pathways. The solution in its current form is capable of accounting for up to seven species and four decay levels. The complex pathways are represented by means of first-order decay and production terms, while branching ratios account for decay stoichiometry. Besides advection, dispersion, bio-chemical or radioactive decay and daughter product formation, the model also accounts for sorption of contaminants on the aquifer solid phase with each species having a different retardation factor. First-type contaminant boundary conditions are utilized at the source (x=0 m) and can be either constant-in-time for each species, or the concentration can be allowed to undergo first-order decay. The solutions are obtained by exponential Fourier, Fourier cosine and Laplace transforms. Limiting forms of the solutions can be obtained in closed form, but we evaluate the general solutions by numerically inverting the analytical solutions in exponential Fourier and Laplace transform spaces. Various cases are generated and the solutions are verified against the HydroGeoSphere numerical model.

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1. Introduction

Contaminants released in the subsurface are transported by various physical processes such as diffusion, advection, and dispersion. The contaminants may also react and cause them to transform into other species. In such a case, the traditional treatment of contaminant transport does not apply because of sorption and mass loss processes that are not accounted. However, many contaminants are reactive with other contaminants within fluids or with the porous medium, which necessitates that one explicitly accounts for

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these processes. In particular, reactive contaminant transport is a topic of great interest to account for processes involving denitrification, degradation of pesticides and their products, radioactive decay, and bioremediation of organic compounds. Comprehensive numerical models (e.g., Clement, 1997; Simunek et al., 1994; Therrien et al., 2005; Widdowson et al., 2002; Yu et al., 2009; Zheng and Wang, 1999) have been developed to account for these complexities, but analytical solutions are still necessary to verify these numerical models and to perform scoping calculations. In addition, accurate solutions from analytical or semi-analytical models (e.g., Clement, 2001; Khandelwal and Rabideau, 1999; Lu and Sun, 2008; Neville et al., 2000; Samper-Calvete and Yang, 2007) can be computed more efficiently than numerical models. The

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solutions may also be used for predicting contaminant concentrations and for analyzing laboratory or field data to determine solute transport parameters. One other important reason may be that because of their relative simplicity, analytical solutions still have an important role in screening studies (Alvarez and Illman, 2006) and to assess the performance of natural attenuation and bioremediation (Illman and Alvarez, 2009). More recently, such solutions have been used in the analysis of permeable reactive barriers (e.g., Mieles and Zhan, 2012; Park and Zhan, 2009; Rabideau et al., 2005). An additional benefit is that analytical solutions can be readily used for Monte Carlo probabilistic simulations of contaminant transport to account for uncertainties in groundwater velocity, transport parameters, and contaminant source boundary conditions, among other factors (e.g., Eykholt et al., 1999).

Various analytical solutions have been developed to accommodate chain-decay reactive transport problems. In particular, Cho (1971) utilized Laplace transforms to derive a one-dimensional solution for advective-dispersive transport of ammonium with nitrification and denitrification in soil assuming a first-order reaction rates. Meanwhile, van Genuchten (1985) developed a one-dimensional analytical solution that considers the transport of four species involved in a consecutive (or serial) first-order decay chain using Laplace transforms and implemented the solution in a computer program called CHAIN. Lunn et al. (1996) then utilized the Fourier sine transform (as opposed to the Laplace transform) to obtain the one-dimensional solution of Cho (1971) in a simpler way. One of the key advantages of using the Fourier sine transform approach was in the flexibility to introduce new initial and boundary conditions which allows for developing new solutions for different conditions.

Sun et al. (1999a,b) and Sun and Clement (1999) developed a general method to derive analytical solutions of any number of species with first-order sequential degradation in multiple dimensions. In particular, they presented a substitution method to transform the multiple species transport equations into a decoupled set of transport equations for single species. This implies that any previously derived analytical solutions for single-species transport with firstorder reactions rate can be directly used for multiple species transport problems. Sun et al. (1999a) demonstrated the approach by obtaining an analytical solution for a five species serial-parallel reactive transport system. Results from the analytical solution compared very favourably with a previously developed numerical code. Sun et al. (1999b) then used the solution for a single radioactive tracer decay solution from Bear (1979) to obtain a solution for three-species transport with first-order reactions. More recently, Clement (2001) presented a generalized approach to derive analytical solutions to multispecies transport following the approach of Sun et al. (1999a). Clement's (2001) approach relies on a similarity transformation method that can handle wider ranging problems involving serial, parallel, converging, diverging and/or reversible first-order reaction systems. It is important to note that the methods developed to this point are only applicable to all species having identical retardation factors.

New analytical solutions that consider different retardation factors for each species have been developed more recently. For example, Bauer et al. (2001) obtained analytical

solutions for one-, two, and three-dimensional contaminant transport of decay chains for a homogeneous medium. Their solution was unique in a sense that variable retardation coefficients can be included and that their analysis extended to multiple porosity media. Quezada et al. (2004) extended the approach developed by Clement (2001) and presented a generalized method for solving coupled, multi-dimensional, multi-species reactive transport equations. As in Bauer et al. (2001), the solutions can handle distinct retardation factors, but the solution was limited to a three-species system. To extend the number of species that the solution can handle, Srinivasan and Clement (2008a,b) then developed closedform analytical solutions for the chain decay problem with an arbitrary number of species with spatially varying initial conditions and an exponentially decaying Bateman-type source condition. One limitation of this approach was that it was limited to a one-dimensional system. More recently, Guerrero et al. (2009) developed a one-dimensional analytical solution for multi-species transport in a finite domain with constant boundary conditions. Similar to other recent solutions, the Guerrero et al. (2009) solution allows for various contaminant species to have different retardation factors; however, it is one-dimensional and can handle only sequential chain decay problems. Guerrero et al. (2010) then extended Guerrero et al. (2009)'s work to handle timevarying boundary conditions. Most recently, Mieles and Zhan (2012) published a one-dimensional, steady-state, analytical solution for serial and parallel degradation pathways with unique first-order reaction rates as well as retardation factors.

Our review suggests that there is currently a lack of a multidimensional analytical solution to the chain-decay reactive transport problem that can handle varying retardation factors for individual species and various reaction pathways in multiple dimensions. Therefore, the main objective of this paper is to present a set of new, semianalytical solutions to simulate three-dimensional contaminant transport subject to first-order chain-decay reactions. The three dimensional domain considered is semi-infinite in areal extent and the aquifer is taken to be of finite thickness. The solutions can treat the transformation of contaminants into daughter products, leading to decay chains consisting of multiple contaminant species and various reaction pathways that can be either straight or branching. The model in its current form is capable of accounting for up to seven species and four decay levels. The complex pathways are represented by means of first-order decay and first-order production terms, while branching ratios account for decay stoichiometry. Besides advection, dispersion, bio-chemical decay and daughter product formation, the model also accounts for sorption of contaminants onto the aquifer solid phase with each species having a different retardation factor. The solutions are obtained by exponential Fourier, Fourier cosine and Laplace transforms. Similar limiting forms of the solutions can be obtained analytically, but we obtain almost all solutions by numerically inverting the analytical solutions obtained in Laplace and exponential Fourier space. Various test cases are presented and the solutions are verified against a previously-derived analytical model and a more sophisticated numerical model. Finally, we discuss the potential utilities of this solution.

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2. Statement of problem

2.1. Modeling scenarios

A schematic view of a waste disposal facility and contaminant migration pathways under consideration is shown in Fig. 1. Contaminants leaching from the disposal facility are considered to migrate vertically downward through the unsaturated zone until they reach the saturated zone. Groundwater flow in the saturated zone is assumed to be essentially one-dimensional in the horizontal plane with a constant groundwater velocity, v. After they enter the saturated zone at the water table, contaminants migrate by one-dimensional advection with flowing groundwater and by three-dimensional dispersion. Due to mixing processes, the contaminant plume as it reaches the edge of the waste facility, will have reached a thickness *H* below the water table and will show an approximately Gaussian distribution in the lateral (y-) direction. Alternately, we also consider the case where the width of the souce in the *y*-direction is a step function rather than Gaussian in shape.

The new analytical solution can model the transformation of contaminants into daughter products, leading to decay chains consisting of multiple contaminant species. Example of decay chains that can be handled is shown in Fig. 2. Besides advection, dispersion, bio-chemical decay and daughter product formation, this new model also accounts for sorption of contaminants on the the aquifer solid phase with retardation factors that can be different for each species.

2.2. Governing equations

The governing equation for the i^{th} member of a decay chain can be written as:

$$D_{x}\frac{\partial^{2}c_{i}}{\partial x^{2}} + D_{y}\frac{\partial^{2}c_{i}}{\partial y^{2}} + D_{z}\frac{\partial^{2}c_{i}}{\partial z^{2}} - \nu\frac{\partial c_{i}}{\partial x} + \lambda_{i}R_{i}c_{i} - \sum_{j=1}^{m_{i}}\eta_{ij}\lambda_{j}R_{j}c_{j} = R_{i}\frac{\partial c_{i}}{\partial t}$$
(1)

where c_i = dissolved concentration in the *i*th contaminant species, *x*, *y*, *z* = Cartesian coordinates, *t* = time, D_x , D_y , D_z = dispersion coefficients, *v* = average linear groundwater velocity, λ_i = first-order decay coefficient of *i*th species, R_i = retardation coefficient of *i*th species, λ_j = first-order decay coefficient of parent species *j*, η_{ij} = fraction of parent *j* that transforms into species *i*, and m_i = number of immediate parents of species *i*. The dispersion coefficients are related to



Fig. 1. Schematic view of a waste disposal facility and subsurface contaminant migration.



Fig. 2. Example decay chains representing contaminant transformation and daughter product formation: (a) straight decay chain; (b) diverging decay chain; (c) converging decay chain; (d) four-member branched decay chain; and (e) seven-member branched decay chain.

the groundwater velocity, *v*, through the dispersivities, α_x , α_y , α_z , as

$$D_x = \alpha_x |v| + D^*$$

$$D_y = \alpha_y |v| + D^*$$

$$D_z = \alpha_z |v| + D^*$$
(2)

where D^* is the effective molecular diffusion coefficient. Implicit in the way (1) and (2) are written is the assumption that all members of the decay chain are consider to have the same mechanical dispersion and molecular diffusion characteristics. This assumption could be relaxed but is a reasonable assumption since diffusion coefficients for many contaminants do not vary markedly. The summation term in (1) represents the contribution of all immediate parents *j* to the production of species *i*. For straight decay chains, the number of parent species, m_i , and the decay fraction η_{ij} , are both equal to unity. For branched decay chains on the other hand, m_i , may be greater than one, but the contribution of each parent, η_{ij} , is typically less than one.

Initial and boundary conditions associated with (1) are

$$c_i(x, y, z, 0) = 0 \tag{3}$$

$$\frac{\partial c_i}{\partial t}(0, y, z, t) + \gamma_i c_i(0, y, z, t) - \sum_{j=1}^{m_i} \eta_{ij} \gamma_j c_j = 0$$
(4a)

$$c_{i}(0, y, z, 0) = c_{pi} \left\{ \exp\left(-\frac{y^{2}}{2S_{i}^{2}}\right) \right\} \cdot [H(z - H_{1}) - H(z - H_{2})] \quad (4b)$$

$$c_i(\infty, y, z, t) = 0 \tag{4c}$$

$$c_i(x, \pm \infty, z, t) = 0 \tag{4d}$$

$$\frac{\partial c_i}{\partial z}(x, y, 0, t) = 0 \tag{4e}$$

$$\frac{\partial c_i}{\partial z}(x, y, B, t) = 0 \tag{4f}$$

where γ_i is the source decay constant. Initial condition (3) specifies an initially contaminant free aquifer. Boundary conditions (4a) and (4b) describe the decay and production of contaminant at the source (x=0 m) and the spatial distribution of concentration along the source plane, respectively. A value of the coefficient $\gamma_i = 0$ corresponds to the case of a constant source concentration. Boundary condition (4b) describes a source concentration that is vertically uniform between elevations H_1 and H_2 and equal to zero elsewhere in the vertical plane where $H(z - H_i)$ is the Heaviside step function. The source concentration profile in the y-direction is described by a Gaussian distribution with standard deviation S_i and c_{pi} is the peak concentration value at the center of the Gaussian distribution. If a rectangular patch source-zone is desired in the y-z plane, then the right-hand side of (4b) would be replaced by $c_{pi}[H(y+y_0)-H(y-y_0)]$. $[H(z-H_1)-H(z-H_2)]$. Eqs. (4c)–(4f) complete the description of boundary conditions for the aquifer system which is semi-infinite in the *x*-direction, infinite in the *y*-direction and finite in the *z*-direction.

The solution to (1)-(4) for each species is given in Appendix A. The solution is obtained through application of Fourier transforms to treat the *y*- and *z*-coordinates and use of the Laplace transform to remove the time dependence of the transport equation. The final solution is obtained by numerical inversion of the Laplace-transformed solutions, using the algorithm developed by de Hoog et al. (1982), and by integrating the exponential Fourier transform by Gauss quadrature.

The general three-dimensional transport Eq. (1) can be readily simplified to describe the cases of one- or twodimensional transport, as well as the steady-state solutions for cases involving a constant source by applying the finalvalue theorem to the Laplace-transformed solutions as shown in Appendix A.

3. Verification tests

In this section, the results for a number of verification problems are presented. The tests were designed to test the accuracy of the multi-species transport solution and the correctness of the computer code Chain-decay Multispecies Model (CMM) used to compute the various solutions presented here. The developed code was also tested against various published computer codes for a range of problems which test different aspects of the transport solution.

3.1. One-dimensional transport of three-member radionuclide decay chain

The first problem analyzed is that of the three-member radionuclide decay chain:

$$U^{234} \rightarrow Th^{230} \rightarrow Ra^{226}$$

This problem involves one-dimensional transport with a constant source. Model parameters for this problem are listed in Table 1. Our solution is verified with HydroGeoSphere (Therrien et al., 2005), a fully-integrated surface–subsurface flow and transport simulator. The results for this verification problem are presented in Fig. 3. Depicted are the concentration profiles of the three radionuclides at time t = 10,000 years. The CMM results are represented by the solid lines, while the symbols represent the solution obtained with HydroGeoSphere. The agreement between the two solutions is excellent for all three species. Fig. 3 shows that at distances greater than about 220 m from the source, the concentrations of both U²³⁴ and Th²³⁰ become very small. At large distances, the dominant species is Ra²²⁶. The different behaviour of

Table 1Transport parameters for one-dimensional radionuclide transport problem.

Parameter	Units	Value
Groundwater velocity, v	m/year	100
Dispersion coefficient, D_x	m ² /year	1,000
Dispersion coefficient, D_{y}	m ² /year	0.0
Dispersion coefficient, D_z	m²/year	0
Retardation factor, R		
U ²³⁴		1.43×10^{4}
Th ²³⁰		5.0×10^{4}
Ra ²²⁶		5.0×10^{2}
Decay coefficient, λ		
U ²³⁴	year ⁻¹	2.83×10^{-6}
Th ²³⁰	year ⁻¹	9.00×10^{-6}
Ra ²²⁶	year ⁻¹	4.33×10^{-6}
Source decay coefficient, γ		
U ²³⁴	year ⁻¹	0.0
Th ²³⁰	year ⁻¹	0.0
Ra ²²⁶	year ⁻¹	0.0
Initial source concentration, c _p		
U ²³⁴		1.0
Th ²³⁰		0.0
Ra ²²⁶		0.0



Fig. 3. Comparison between CMM (curves) and HydroGeoSphere (symbols) for one-dimensional transport of radionuclide decay chain.

Ra²²⁶ compared to U²³⁴ and Th²³⁰ reflects the fact that Ra²²⁶ is weakly sorbed compared to U²³⁴ and Th²³⁰ because of its lower retardation factor. This example illustrates the importance of a model being able to account for different retardation factors for different contaminant species.

3.2. One-dimensional transport of a 4-member, branched decay chain

The second test problem was designed to verify the ability of our solution to correctly handle the case of a branching

 Table 2

 Transport parameters for one-dimensional branched decay chain problem.

Parameter	Units	Value
Groundwater velocity, v	m/year	0.3
Dispersion coefficient, D_x	m ² /year	3.0
Dispersion coefficient, D_{y}	m ² /year	0.0
Dispersion coefficient, D_z	m²/year	0.0
Retardation factor, R		
Species 1		1.50
Species 2		2.0
Species 3		1.0
Species 4		1.0
Decay coefficient, λ		
Species 1	year ⁻¹	6.93×10^{-3}
Species 2	year ⁻¹	3.47×10^{-3}
Species 3	year ⁻¹	1.16×10^{-3}
Species 4	year ⁻¹	1.00×10^{-3}
Source decay coefficient, γ		
Species 1	year ⁻¹	0.0
Species 2	year ⁻¹	0.0
Species 3	year ⁻¹	0.0
Species 4	year ⁻¹	0.0
Initial source concentration, <i>c</i> _p		
Species 1		1.0
Species 2		0.0
Species 3		0.0
Species 4		0.0



Fig. 4. Comparison between CMM (curves) and HydroGeoSphere (symbols) for 1D transport of a 4-member branched decay chain.

decay chain. This problem involves the one-dimensional transport of the following hypothetical branched decay chain (Fig. 2d):



In other words, the parent component Species 1 transforms completely into daughter component Species 2; Species 2, in turn, transforms into two granddaughter components, Species 3 and Species 4, with equal decay fractions $\eta_{32} = \eta_{42} = 0.5$. The model parameters for this problem are listed in Table 2. In contrast to the first problem, the second test problem includes a decaying source boundary condition. Our solution for this test



Fig. 5. Schematic of simulation domain: contaminant source is assigned to the gray rectangular patch zone with a dimension of $-10 \text{ m} \le y \le 10 \text{ m}$ and $9 \text{ m} \le z \le 10 \text{ m}$ at x = 0 m.

problem was again compared against HydroGeoSphere. For the numerical simulations using HydroGeoSphere, a onedimensional homogeneous domain of size 120 m is used and the domain is discretized using a 1 m nodal spacing. For the flow problem, boundary conditions and medium properties were assigned values to obtain a uniform linear groundwater velocity equal to 0.3 m/year. For transport, a specified concentration ($C_{sp.1} = 1.0$) was assigned at x = 0 m. The comparison is presented in Fig. 4 which shows concentration profiles for the 4 members of the decay chain at a time of t = 600 years. The solid and dashed lines again represent the CMM solution, while the HydroGeoSphere solution is represented by the symbols. Agreement between the two solutions is very good, except that the concentration values obtained with HydroGeoSphere for Species 1, 2, 3 and 4 are very slightly lower than the CMM results at the end of the simulation domain. The maximum difference between two models is 2.3×10^{-2} . The results that are displayed in Fig. 4 again illustrate the potential significance of incorporating hazardous daughter production formation in contaminant fate and transport analyses. While the concentration of the original product, Species 1, decreases exponentially,

Table 3

Transport parameters for three-dimensional, seven-member decay chain simulation problem.

Parameter	Units	Value
Groundwater velocity, v	m/year	20.0
Dispersion coefficient, D_x	m ² /year	20.0
Dispersion coefficient, D_{y}	m ² /year	2.0
Dispersion coefficient, D_z	m ² /year	1.0
Source width $(=2y_0)$	m	20.0
Aquifer thickness, B	m	10.0
Source elevation, H_1	m	9.0
Source elevation, H_2	m	10.0
Source standard deviation, S	m	0.0
Retardation factor, R		
Species 1		1.0
Species 2		2.0
Species 3		3.0
Species 4		4.0
Species 5		5.0
Species 6		6.0
Species 7		7.0
Decay coefficient, λ	year ⁻¹	
Species 1		0.07
Species 2		0.06
Species 3		0.05
Species 4		0.04
Species 5		0.03
Species 6		0.02
Species 7		0.00
Source decay coefficient, γ	year ⁻¹	
Species 1		0.0
Species 2		0.0
Species 3		0.0
Species 4		0.0
Species 5		0.0
Species 6		0.0
Species 7		0.0
Initial source concentration, <i>c</i> _p		
Species 1		1.0
Species 2		0.0
Species 3		0.0
Species 4		0.0
Species 5		0.0
Species 6		0.0
Species 7		0.0

its daughter, Species 2, and granddaughters, Species 3 and 4, products increase with distance from the source zone (x = 0 m) until they reach a maximum concentration. The granddaughter products are produced at the same rate and also have similar decay and sorption coefficients, with the decay rate coefficient of Species 3 being slightly higher. Both the CMM and HydroGeoSphere codes produce the expected results that the concentration profiles of Species 3 and 4 are similar with Species 4 having somewhat higher concentrations.

3.3. Three dimensional transport of a 7-member decay chain

The third verification problem was designed to test a number of remaining features of our solution, including threedimensional transport of a complex decay chain. The results from our solution are again compared to HydroGeoSphere. This problem involves a 7-member branched decay chain (Fig. 2e).



Time = 5 years Species 3 <u>CMM</u> HydroGeoSphere 10^{-3} 10^{-2} 150 10^{-2} 10^{-2} The parent component Species 1 transforms equally into two daughter products, Species 2 and 3, each of which subsequently transform into two granddaughter products, Species, 4, 5 and Species 6, 7, respectively, with

$$\eta_{42} = \eta_{52} = \eta_{63} = \eta_{73} = 0.5$$

A schematic view of the modeling scenario is shown in Fig. 5. The problem involves a 1 m thick source at the top of the aquifer a total saturated zone thickness of B = 10 m. The width of the patch source is 20 m and it is centered at y = 0 m. The transport parameters for this problem are listed in Table 3. In the HydroGeoSphere model, the problem is simulated in a domain of size 200 m × 40 m × 10 m and the domain is discretized using 1 m × 1 m × 0.5 m hexahedral elements. A specified concentration boundary condition ($C_{sp.1} = 1.0$) is assigned to the nodes located in the rectangular patch source at x = 0 m. The simulation results



Fig. 6. Comparison between CMM (solid curves) and HydroGeoSphere (dashed curves) solutions for a seven-member decay chain problem at 5 years.

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obtained using the CMM model are compared to those of HydroGeoSphere. A three-dimensional view of the simulation results obtained using CMM and HydroGeoSphere is shown in Fig. 6. The concentration distributions for the simulations are symmetric with respect to y = 0 m because the flow field of the simulation is steady state and uniform. The CMM results (solid curves) each of the seven species at t=5 years match well with those obtained with HydroGeoSphere (dashed curves), although there is a small difference for species 1 and 2 on the y-z plane at x = 0 m. This slight discrepancy is mainly due to difficulties in the Fourier transform inversions in the vicinity of the patch source.

4. Summary and conclusions

We presented a set of new, semi-analytical solutions to simulate three-dimensional contaminant transport subject to first-order chain-decay reactions and equilibrium sorption. The analytical solutions can treat the transformation of contaminants into daughter products by first-order decay and the increasing concentrations of transformation species, leading to decay chains consisting of multiple contaminant species and various reaction pathways. The solutions in their current forms are capable of accounting for up to seven species and four decay levels. Complex branching transformation pathways can be accomodated using branching ratios to account for decay stoichiometry. Besides advection, dispersion, bio-chemical or radioactive decay and daughter product formation, the model also accounts for sorption of contaminants on the aquifer solid phase with each species being allowed to have a different retardation factor. The solutions are obtained by exponential Fourier, finite Fourier cosine and Laplace transforms. Limiting forms of the solutions, such as steady state cases, can be obtained analytically, but we evaluate most of the solutions by

numerically inverting the analytical solutions in Laplace space and by integrating the exponential Fourier transforms by Gauss quadrature.

The semi-analytical solutions were verified by comparing the results from three different test cases to those generated by the HydroGeoSphere numerical model. In general, we conclude that the agreement between the two approaches is very good suggesting the high accuracy of the semi-analytical model. While the comparison was very good, minor discrepancies between the semi-analytical and HydroGeoSphere models arose in certain situations. We note that to improve the accuracy of the numerical solutions, we took the following steps: (1) reducing grid sizes based on the Peclet number, (2) assigning upstream weighting and fully implicit conditions, and (3) setting small transport solver convergence criteria (i.e. 10^{-10}). Therefore, we attribute the minor discrepancies to slight difficulties in evaluating the semianalytical solutions near the contaminant source.

The advent of numerical models (e.g., Clement, 1997; Simunek et al., 1994; Therrien et al., 2005; Widdowson et al., 2002; Yu et al., 2009; Zheng and Wang, 1999) and the development of user-friendly interfaces have accelerated the use of these models to capture contaminant transport behavior and once captured, utilized in predictive modes. Numerical models are considered to be more flexible than analytical solutions such as those presented here because they can handle complexities associated with natural systems such as the space- and time-varying nature of forcing functions and subsurface heterogeneity. However, while there are a number of comprehensive numerical models that account for such complexities, analytical solutions are still necessary to verify these numerical models. In addition, accurate solutions from analytical models that can be computed efficiently are thus useful as screening tools for the assessment of contaminant plume behaviour (e.g., Illman and Alvarez, 2009), and the analysis of permeable reactive barriers (e.g., Mieles and Zhan, 2012; Park and Zhan, 2009; Rabideau et al., 2005). In particular, the ability of this model to consider decay chains consisting of multiple contaminant species, various reaction pathways, unique branching ratios, and retardation factors for different members makes it ideal for use in these screening studies.

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Appendix A. Analytical solution for 3-D transport of a straight and branching chain of decaying solutes in groundwater

Consider the straight decay chain $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow$, ... and the following problem geometry (Fig. A.1), where c_{pi} is the source peak concentration, S_i is the source standard deviation in *y*-direction for a Gaussian-shaped source in the *y*-direction, *v* is the average linear groundwater velocity, *n* is porosity, D_x , D_y , D_z are the dispersion coefficients in the *x*, *y*, and *z* directions, R_i is the retardation factor, λ_i is the decay constant, γ_i is the source decay constant (can equal λ_i or 0). Note that the subscript *i* in the above definitions refer to the *i*th member of the chain and assume that



Fig. A.1. Problem geometry for the analytical solution for three-dimensional transport of straight and branching chains of decaying solutes in groundwater.

That is, all species have the same dispersion coefficient, which implies the same mechanical dispersion and molecular diffusion coefficient.

Species 1

The boundary value problem governing the reactive transport of species 1 is:

$$R_1 \frac{\partial c_1}{\partial t} + v \frac{\partial c_1}{\partial x} - D_x \frac{\partial^2 c_1}{\partial x^2} - D_y \frac{\partial^2 c_1}{\partial y^2} - D_z \frac{\partial^2 c_1}{\partial z^2} - \lambda_1 R_1 c_1 = 0$$
(A1)

$$c_1(x, y, z, 0) = 0$$
 (A2a)

$$\frac{\partial c_1}{\partial t}(0, y, z, t) + \gamma_1 c_1(0, y, z, t) = 0 \tag{A2b}$$

$$c_1(0, y, z, 0) = c_{p_1} \varpi_1(y) [H(z - H_1) - H(z - H_2)]$$
(A2c)

where

$$\varpi_{1}(y) = \begin{cases} \exp\left(-\frac{y^{2}}{2S_{1}^{2}}\right) & \text{Gaussian type} \\ [H(y+y_{0})-H(y-y_{0})] & \text{Rectangular patch type} \end{cases}$$
$$H(y-y_{0}) = \begin{cases} 0 & y < y_{0} \\ 1 & y > y_{0} \\ H(z-H_{i}) = \begin{cases} 0 & z < H_{i} \\ 1 & z > H_{i} \end{cases}$$

$$c_1(\infty, y, z, t) = 0 \tag{A2d}$$

$$c_1(x,\pm\infty,z,t) = 0 \tag{A2e}$$

$$\frac{\partial c_1}{\partial z}(x, y, 0, t) = 0 \tag{A2f}$$

$$\frac{\partial c_1}{\partial z}(x, y, B, t) = 0 \tag{A2g}$$

Define the Fourier transform in *y* as

$$\mathscr{F}[c_1(x,y,z,t)] = \bar{c}_1(x,\alpha,z,t) = \int_{-\infty}^{\infty} e^{-i\alpha y} c_1 dy$$
(A3)

and apply it to (A1), and associated conditions (A2), to get

$$\frac{R_1\partial\bar{c}_1}{\partial t} + \nu\frac{\partial\bar{c}_1}{\partial x} - D_x\frac{\partial^2\bar{c}_1}{\partial x^2} + \alpha^2 D_y\bar{c} - D_z\frac{\partial^2\bar{c}_1}{\partial z^2} - \lambda_1 R_1\bar{c}_1 = 0$$
(A4)

subject to

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$$\bar{c}_1(x,\alpha,z,0) = 0 \tag{A5a}$$

 $\frac{\partial \bar{c}_1}{\partial t}(0,\alpha,z,t) + \gamma_1 \bar{c}_1(0,\alpha,z,t) = 0$ (A5b)

$$\bar{c}_{1}(0,\alpha,z,0) = c_{p_{1}}\zeta_{1}(\alpha) \cdot [H(z-H_{1}) - H(z-H_{2})]$$
(A5c)

$$\bar{c}_1(\infty,\alpha,z,t) = 0 \tag{A5d}$$

$$\frac{\partial \bar{c}_1}{\partial z}(x,\alpha,0,t) = 0 \tag{A5e}$$

$$\frac{\partial \bar{c}_1}{\partial z}(z, \alpha, B, t) = 0 \tag{A5f}$$

where $\zeta(\alpha)$ is the Fourier transform of the source type function ($\varpi(y)$). $\zeta(\alpha)$ can be expressed according to the source type: Gaussian-type can be transformed using (Churchill, 1972, p.472):

$$\mathscr{F}\left[\exp\left(-\frac{y^2}{2S_1^2}\right)\right] = (2\pi)^{1/2} S_1 \exp\left(-\frac{S_1^2 \alpha^2}{2}\right) \tag{A6a}$$

The rectangular patch type, which is the boxcar function, in *y* is defined as:

$$\mathscr{F}[H(y+y_0)-H(y-y_0)] = \frac{2}{\alpha}\sin(\alpha y_0)$$
(A6b)

Now apply the finite Fourier cosine transform in *z*, defined as:

$$\mathscr{F}_{c}[\bar{c}_{1}(x,\alpha,z,t)] = \bar{\bar{c}}_{1}(x,\alpha,n,t) = \int_{0}^{B} \bar{c}_{1}\cos\left(\frac{n\pi z}{B}\right) dz \tag{A7}$$

To get:

$$R_1 \frac{\partial \bar{c}_1}{\partial t} + \nu \frac{\partial \bar{c}_1}{\partial x} - D_x \frac{\partial^2 \bar{c}_1}{\partial x^2} + \left(\alpha^2 D_y + \frac{n^2 \pi^2}{B^2} D_z + \lambda_1 R_1 \right) \bar{c}_1 = 0$$
(A8)

$$\bar{\bar{c}}_1(x,\alpha,n,0) = 0 \tag{A9a}$$

$$\frac{\partial \bar{c}_1}{\partial t}(0,\alpha,n,t) + \gamma_1 \bar{c}_1(0,\alpha,n,t) = 0$$
(A9b)

$$\bar{\bar{c}}_1(0,\alpha,n,0) = c_{p_1}\zeta_1(\alpha) \times \begin{cases} (H_2 - H_1) & n = 0\\ \frac{B}{n\pi} \left[\sin\left(\frac{n\pi H_2}{B}\right) - \sin\left(\frac{n\pi H_1}{B}\right) \right] & n > 0 \end{cases}$$
(A9c)

where:

$$\zeta_{1}(\alpha) = \begin{cases} (2\pi)^{1/2} S_{1} \exp\left(-\frac{S_{1}^{2} \alpha^{2}}{2}\right) & \text{Gaussian type} \\ \frac{2}{\alpha} \sin(\alpha y_{0}) & \text{Rectangular patch type} \end{cases}$$
(A9d)

$$\bar{\bar{c}}_1(\infty,\alpha,n,t) = 0 \tag{A9e}$$

Finally, apply the Laplace transform in *t* defined as:

$$\mathscr{L}\left[\bar{\bar{c}}_{1}(x,\alpha,n,t)\right] = \bar{\bar{c}}_{1}(x,\alpha,n,p) = \int_{0}^{\infty} \bar{\bar{c}}_{1}e^{-pt}dt$$
(A10)

to obtain:

$$\frac{d^2\bar{\bar{c}}_1}{dx^2} - \frac{v}{D_x}\frac{d\bar{\bar{c}}_1}{\partial x} - \frac{1}{D_x}\left[R_1(p+\lambda_1) + \alpha^2 D_y + \frac{n^2\pi^2 D_z}{B^2}\right]\bar{\bar{c}}_1 = 0$$

or

$$\frac{d^2\bar{\bar{c}}_1}{dx^2} - \phi \frac{d\bar{\bar{c}}_1}{dx} - \omega_1(\alpha, n, p)\bar{\bar{c}}_1 = 0$$
(A11)

$$\bar{\bar{c}}_1(0,\alpha,n,p) = c_{p_1}\zeta_1(\alpha)\kappa_1(n)\cdot\frac{1}{p+\gamma_1}$$
(A12a)

$$\bar{\bar{c}}_1(\infty,\alpha,n,p) = 0 \tag{A12b}$$

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where

$$\begin{split} \phi &= \frac{v}{D_x} \\ \omega_1(\alpha, n, p) &= \frac{1}{D_x} \left[R_1(p + \lambda_1) + \alpha^2 D_y + \frac{n^2 \pi^2 D_z}{B^2} \right] \\ \kappa_1(n) &= \begin{cases} (H_2 - H_1) & n = 0 \\ \frac{B}{n\pi} \left[\sin\left(\frac{n\pi H_2}{B}\right) - \sin\left(\frac{n\pi H_1}{B}\right) \right] & n > 0 \end{cases} \end{split}$$
(A12c)

The general solution to (A11), subject to (A12a, b) is easily shown to be

$$\bar{\bar{c}}_1 = \frac{c_{p_1}\zeta_1(\alpha)\kappa_1(n)}{p+\gamma_1} \exp\{b_1^-(\alpha,n,p)x\}$$
(A13)

where

$$b_1^-(\alpha, n, p) = \frac{\phi}{2} \left[1 - \left\{ 1 + \frac{4\omega_1(\alpha, n, p)}{\phi^2} \right\}^{1/2} \right]$$

The task that remains is the inversion of the transforms. Analytical inversion steps and the form of $c_1(x, y, z, t)$ is given in Appendix B. However, here we will follow a different approach to yield a solution for the Laplace-transformed solution $\bar{c}_i(x, y, z, p)$ that will be inverted numerically. We do this because it facilitates the determination of $c_i(x, y, z, t)$ for i > 1. First, we define the inverse Fourier cosine transform:

$$\mathcal{F}_{c}^{-1}\left[\bar{\bar{c}}_{1}(x,\alpha,n,p)\right] = \bar{\bar{c}}_{1}(x,\alpha,z,p)$$

$$= \frac{\bar{\bar{c}}_{1}(x,\alpha,n=0,p)}{B} + \frac{2}{B} \sum_{n=1}^{\infty} \bar{\bar{c}}_{1}(x,\alpha,n,p) \cos\left(\frac{n\pi z}{B}\right)$$
(A14)

Now let's invert the exponential Fourier transform using the general formula:

$$\mathscr{F}^{-1}[\bar{f}(\alpha)] = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\alpha y} \bar{f}(\alpha) d\alpha = f(y)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} [\cos(\alpha y) + i\sin(\alpha y)] \bar{f}(\alpha) d\alpha$$
(A15)

If f(y) is an even function in y then (A15) reduces to:

$$f(y) = \frac{1}{\pi} \int_{0}^{\infty} \cos(\alpha y) \bar{f}(\alpha) d\alpha$$
(A16)

since $sin(\alpha y)$ is odd and $cos(-\alpha y) = cos(\alpha y)$. Given that $c_i(x, y, z, t)$ is even (i.e., $c_i(x, -y, z, t) = c_i(x, y, z, t)$), we obtain, by applying (A16) to (A14)

$$\bar{c}_1(x,y,z,p) = \frac{1}{\pi B} \int_0^\infty \left[\bar{\bar{c}}_1(x,\alpha,n=0,p) + 2\sum_{n=1}^\infty \bar{\bar{c}}_1(x,\alpha,n,p) \cos\left(\frac{n\pi z}{B}\right) \right] \cos(\alpha y) d\alpha \tag{A17}$$

with $\overline{\overline{c}}_1(x, \alpha, n, p)$ given by (A13). Caution should be taken to ensure that the appropriate form of $\kappa(\alpha, n, p)$ given by (A12c) is used since its form for n = 0 is different from that for n > 0. Finally, denoting \mathscr{L}^{-1} as the inverse Laplace transform operator, we can write

$$c_1(x, y, z, t) = \mathscr{L}^{-1}[\bar{c}_1(x, y, z, p)]$$
(A18)

This step can be efficiently and accurately performed using the de Hoog et al. (1982) numerical algorithm.

Species 2

$$R_2 \frac{\partial c_2}{\partial t} + \nu \frac{\partial c_2}{\partial x} - D_x \frac{\partial^2 c_2}{\partial x^2} - D_y \frac{\partial^2 c_2}{\partial y^2} - D_z \frac{\partial^2 c_2}{\partial z^2} + \lambda_2 R_2 c_2 - \lambda_1 R_1 c_1 = 0$$
(A19)

$$c_2(x, y, z, 0) = 0$$
 (A20a)

$$\frac{\partial c_2}{\partial t}(0, y, z, t) + \gamma_2 c_2(0, y, z, t) - \gamma_1 c_1(0, y, z, t) = 0$$
(A20b)

$$c_2(0, y, z, 0) = c_{p_2} \varpi_2(y) \cdot [H(z - H_1) - H(z - H_2)]$$
(A20c)

$$c_2(\infty, y, z, t) = 0 \tag{A20d}$$

$$c_2(x, \pm \infty, z, t) = 0 \tag{A20e}$$

$$\frac{\partial c_2}{\partial z}(x, y, 0, t) = 0 \tag{A20f}$$

$$\frac{\partial c_2}{\partial z}(x, y, B, t) = 0 \tag{A20g}$$

Similar to species 1, the source type function can be expressed as:

$$\varpi_2(y) = \begin{cases} \exp\left(-\frac{y^2}{2S_2^2}\right) & \text{Gaussian type} \\ [H(y+y_0) - H(y-y_0)] & \text{Rectangular patch type} \end{cases}$$
(A20h)

In solving for c_2 , we will follow exactly the same steps as we did for c_1 . The only difference is the nonhomogeneous term involving $\lambda_1 R_1 c_1$ in (A19) which is easily accommodated. We must also take care of the integral transformations of (A20b) subject to initial condition (A20c). After applications of the Fourier transforms \mathscr{F} and \mathscr{F}_c , they become:

$$\frac{\partial \bar{c}_2}{\partial t}(0,\alpha,n,t) + \gamma_2 \bar{\bar{c}}_2(0,\alpha,n,t) - \gamma_1 \bar{\bar{c}}_1(0,\alpha,n,t) = 0$$
(A21)

subject to:

$$\bar{\bar{c}}_2(0,\alpha,n,0) = c_{p_2}\zeta_2(\alpha)\kappa_2(n)$$

where:

$$\zeta_{2}(\alpha) = \begin{cases} (2\pi)^{1/2} S_{2} \exp\left(-\frac{S_{2}^{2} \alpha^{2}}{2}\right) & \text{Gaussian type} \\ \frac{2}{\alpha} \sin(\alpha y_{0}) & \text{Rectangular patch type} \end{cases}$$
(A22a)

$$\kappa_2(n) = \begin{cases} (H_2 - H_1) & n = 0\\ \frac{B}{n\pi} \left[\sin\left(\frac{n\pi H_2}{B}\right) - \sin\left(\frac{n\pi H_1}{B}\right) \right] & n > 0 \end{cases}$$
(A22b)

Application of the Laplace transform to (A21) gives:

$$\bar{\bar{c}}_{2}(0,\alpha,n,p) = \frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \frac{\gamma_{1}}{p+\gamma_{2}}\bar{\bar{c}}_{1}(0,\alpha,n,p)$$

$$= \frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \frac{\gamma_{1}}{p+\gamma_{2}} \cdot \frac{c_{p_{1}}\zeta_{1}(\alpha)\kappa_{1}(n)}{p+\gamma_{1}}$$
(A23)

where (A12a) has been substituted for $\overline{\overline{c}}_1(0, \alpha, n, p)$. We obtain the following ordinary differential equation describing $\overline{\overline{c}}_2(x, \alpha, n, p)$:

$$\frac{d^2\bar{\bar{c}}_2}{dx^2} - \phi \frac{d\bar{\bar{c}}_2}{dx} - \omega_2(\alpha, n, p)\bar{\bar{c}}_2 = \beta_1\bar{\bar{c}}_1 \tag{A24}$$

$$\bar{\bar{c}}_{2}(0,\alpha,n,p) = \frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \frac{c_{p_{1}}\gamma_{1}\zeta_{1}(\alpha)\kappa_{1}(n)}{(p+\gamma_{2})(p+\gamma_{1})}$$
(A25a)

$$\bar{\bar{c}}_2(\infty,\alpha,n,p) = 0 \tag{A25b}$$

where $\phi = v/D_x$ as before and

$$\begin{split} \omega_2(\alpha,n,p) &= \frac{1}{D_x} \left[R_2(p+\lambda_2) + \alpha^2 D_y + \frac{n^2 \pi^2 D_z}{B^2} \right] \\ \beta_1 &= -\frac{\lambda_1 R_1}{D_x} \end{split}$$

Upon substituting (A13) for $\overline{\overline{c}}_1$ into (A21) and using the result given in Appendix C, the general solution to (A21) is

$$\bar{\bar{c}}_{2} = A \exp\{b_{2}^{-}(\alpha, n, p)x\} + B \exp\{b_{2}^{+}(\alpha, n, p)x\} + \frac{\beta_{1}c_{p_{1}}\zeta_{1}(\alpha)\kappa_{1}(n)}{p + \gamma_{1}} \cdot \frac{1}{\omega_{1} - \omega_{2}}\exp\{b_{1}^{-}(\alpha, n, p)x\}$$

$$= A \exp\{b_{2}^{-}x\} + B \exp\{b_{2}^{+}x\} + \frac{\beta_{1}}{\omega_{1} - \omega_{2}} \cdot \bar{\bar{c}}_{1}(x, \alpha, n, p)$$

$$(A26)$$

$$b_{2}^{\pm} = \frac{\phi}{2} \left[1 \pm \left\{\frac{4\omega_{2}}{\phi^{2}}\right\}^{1/2}\right]$$

provided that

$$\omega_1 \neq \omega_2 \quad (i.e., R_1 \lambda_1 \neq R_2 \lambda_2)$$

Requiring that the solution be bounded according to (A25b) implies that B = 0. Making use of (A25a) yields:

$$\frac{c_{p_2}\zeta_2(\alpha)\kappa_2(n)}{p+\gamma_2} + \frac{c_{p_1}\gamma_1\zeta_1(\alpha)\kappa_1(n)}{(p+\gamma_1)(p+\gamma_2)} = A + \frac{\beta_1c_{p_1}\zeta_1(\alpha)\kappa_1(n)}{p+\gamma_1} \cdot \frac{1}{\omega_1 - \omega_2}$$

or

$$A = \frac{c_{p_2}\zeta_2(\alpha)\kappa_2(n)}{p+\gamma_2} + \frac{c_{p_1}\gamma_1\zeta_1(\alpha)\kappa_1(n)}{(p+\gamma_1)(p+\gamma_2)} - \frac{c_{p_1}\beta_1\zeta_1(\alpha)\kappa_1(n)}{p+\gamma_1} \cdot \frac{1}{\omega_1 - \omega_2}$$
(A27)

Thus, substituting for A and B in (A26) gives

$$\bar{\bar{c}}_{2} = \left[\frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \frac{c_{p_{1}}\gamma_{1}\zeta_{1}(\alpha)\kappa_{1}(n)}{(p+\gamma_{2})(p+\gamma_{1})} \right] \exp\{b_{2}^{-}(\alpha,n,p,x)\}$$

$$+ \frac{c_{p_{1}}\zeta_{1}(\alpha)\kappa_{1}(n)}{p+\gamma_{1}} \cdot \beta_{1} \cdot \frac{1}{\omega_{1}-\omega_{2}} \left[\exp\{b_{1}^{-}(\alpha,n,p)x\} - \exp\{b_{2}^{-}(\alpha,n,p)x\} \right]$$

$$(A28)$$

or

$$\bar{\bar{c}}_{2} = \left[\frac{c_{p_{2}} \zeta_{2}(\alpha) \kappa_{2}(n)}{p + \gamma_{2}} + \left\{ \frac{\gamma_{1}}{p + \gamma_{2}} - \frac{\beta_{1}}{\omega_{1} - \omega_{2}} \right\} \bar{\bar{c}}_{1}(0, \alpha, n, p) \right] \exp\{b_{2}^{-}x\}$$

$$+ \frac{\beta_{1}}{\omega_{1} - \omega_{2}} \bar{\bar{c}}_{1}(x, \alpha, n, p)$$
(A28a)

provided that

 $\omega_1 \neq \omega_2 \quad (i.e., R_1\lambda_1 \neq R_2\lambda_2)$

It can be seen that the first term on the right-hand side of (A25) involving c_{p_2} is of the same form as (A13) for $\overline{\overline{c}}_1$. If we have the special case that $\omega_1 = \omega_2$ (*i. e.*, $R_1\lambda_1 = R_2\lambda_2$), then a modified general solution must be used (Appendix C, Eq. C8), which yields:

$$\bar{\bar{c}}_{2} = \left[\frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \frac{c_{p_{1}}\gamma_{1}\zeta_{1}(\alpha)\kappa_{1}(n)}{(p+\gamma_{2})(p+\gamma_{1})}\right]\exp\{b_{2}^{-}(\alpha,n,p)x\} + \frac{xc_{p_{1}}\beta_{1}\zeta_{1}(\alpha)\kappa_{1}(n)}{(p+\gamma_{1})(b_{2}^{+}-b_{2}^{-})}\exp\{b_{2}^{-}(\alpha,n,p)x\}$$
(A29)

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for the case $\omega_1 = \omega_2$ or

$$\bar{\bar{c}}_2 = \left[\frac{c_{p_2} \zeta_2(\alpha) \kappa_2(n)}{p + \gamma_2} + \frac{\gamma_1}{p + \gamma_2} \bar{\bar{c}}_1(0, \alpha, n, p) \right] \exp\{b_2^- x\}$$

$$- \frac{\beta_1 x}{b_2^+ - b_2^-} \bar{\bar{c}}_1(x, \alpha, n, p)$$
(A29a)

Finally, making use of the inversion results (A17) and (A18), we can write:

$$c_{2}(x,y,z,t) = \mathscr{L}^{-1}\left[\frac{1}{\pi B}\int_{0}^{\infty} \left[\bar{\bar{c}}_{2}(x,\alpha,n=0,p) + 2\sum_{n=1}^{\infty}\bar{\bar{\bar{c}}}_{1}(x,\alpha,n,p)\cos\left(\frac{n\pi z}{B}\right)\right]\cos(\alpha y)d\alpha\right]$$
(A30)

where either (A28a) or (A29a) is substituted.

Species 3

$$R_3 \frac{\partial c_3}{\partial t} + v \frac{\partial c_3}{\partial x} - D_x \frac{\partial^2 c_3}{\partial x^2} - D_y \frac{\partial^2 c_3}{\partial y^2} - D_z \frac{\partial^2 c_3}{\partial z^2} + \lambda_3 R_3 c_3 - \lambda_2 R_2 c_2 = 0$$
(A31)

$$c_3(x, y, z, 0) = 0$$
 (A32a)

$$\frac{\partial c_3}{\partial t}(0, y, z, t) + \gamma_3 c_3(0, y, z, t) - \gamma_2 c_2(0, y, z, t) = 0$$
(A32b)

$$c_3(0, y, z, 0) = c_{p_3} \varpi(y) \cdot [H(z - H_1) - H(z - H_2)]$$
(A32c)

$$c_3(\infty, y, z, t) = 0 \tag{A32d}$$

$$c_3(x, \pm \infty, z, t) = 0 \tag{A32e}$$

$$\frac{\partial c_3}{\partial x}(x, y, 0, t) = 0 \tag{A32f}$$

$$\partial z = (x, y, 0, t) = 0$$

$$\frac{\partial c_3}{\partial z}(x, y, B, t) = 0 \tag{A32g}$$

Application of the Fourier transforms \mathscr{F} and \mathscr{F}_c and the Laplace transform transforms \mathscr{L} to the system (A31) and (A32) leads to

$$\frac{d^2\bar{\bar{c}}_3}{dx^2} - \phi \frac{d\bar{\bar{c}}_3}{dx} - \omega_3(\alpha, n, p)\bar{\bar{c}}_3 = \beta_2\bar{\bar{c}}_2 \tag{A33}$$

$$(p+\gamma_3)\overline{\overline{c}}_3(0,\alpha,n,p) = c_{p_3}\zeta_3(\alpha)\kappa_3(n) + \gamma_2\overline{\overline{c}}_2(0,\alpha,n,p)$$
(A34)

$$\bar{\bar{c}}_{3}(0,\alpha,n,p) = \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p+\gamma_{3}} + \frac{\gamma_{2}}{p+\gamma_{3}} \left[\frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \frac{c_{p_{1}}\gamma_{1}\zeta_{1}(\alpha)\kappa_{1}(n)}{(p+\gamma_{2})(p+\gamma_{1})} \right]$$
(A35a)

$$\bar{\bar{c}}_{3}(\infty,\alpha,n,p) = 0 \tag{A35b}$$

where:

$$\begin{split} \omega_{3}(\alpha,n,p) &= \frac{1}{D_{x}} \left[R_{3}(p+\lambda_{3}) + \alpha^{2}D_{y} + \frac{n^{2}\pi^{2}D_{z}}{B^{2}} \right] \\ \beta_{2} &= -\frac{\lambda_{2}R_{2}}{D_{x}} \\ \zeta_{3}(\alpha) &= \begin{cases} (2\pi)^{1/2}S_{3}\exp\left(-\frac{S_{3}^{2}\alpha^{2}}{2}\right) & \text{Gaussian type} \\ \frac{2}{\alpha}\sin(\alpha y_{0}) & \text{Rectangular patch type} \\ \frac{R_{3}(n)}{B} &= \begin{cases} (H_{2}-H_{1}) & n=0 \\ \frac{B}{n\pi} \left[\sin\left(\frac{n\pi H_{2}}{B}\right) - \sin\left(\frac{n\pi H_{1}}{B}\right)\right] & n > 0 \end{cases} \end{split}$$

The general solution of (A33) after substituting for $\overline{\overline{c}}_2$ using (A28a) is (again using the results of Appendix B):

$$\begin{split} \bar{\bar{c}}_{3} &= A \exp\{b_{3}^{-}(\alpha,n,p)x\} + B \exp\{b_{3}^{+}(\alpha,n,p)x\} \\ &+ \frac{\beta_{2}}{\omega_{2} - \omega_{3}} \left[\frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p + \gamma_{2}} + \left\{\frac{\gamma_{1}}{p + \gamma_{2}} - \frac{\beta_{1}}{\omega_{1} - \omega_{2}}\right\} \bar{\bar{c}}_{1}(0,\alpha,n,p)\right] \exp\{b_{2}^{-}(\alpha,n,p)x\} \\ &+ \frac{\beta_{1}\beta_{2}}{(\omega_{1} - \omega_{2})(\omega_{1} - \omega_{3})} \bar{\bar{c}}_{1}(x,\alpha,n,p) \end{split}$$
(A36)

provided that

$$\omega_1 \neq \omega_2, \omega_1 \neq \omega_3, \omega_2 \neq \omega_3$$

The parameters b_3^- and b_3^+ are defined analogously to those for species 1 or 2 defined earlier except that λ_3 and R_3 are substituted. Boundary condition (A35b) gives B = 0 and (A35a) yields:

$$A = \frac{c_{p_3}\zeta_3(\alpha)\kappa_3(n)}{p+\gamma_3} + \frac{\gamma_2}{p+\gamma_3}\bar{\bar{c}}_2(0,\alpha,n,p)$$

$$-\frac{\beta_2}{\omega_2-\omega_3} \left[\frac{c_{p_2}\zeta_2(\alpha)\kappa_2(n)}{p+\gamma_2} + \left\{ \frac{\gamma_1}{p+\gamma_2} - \frac{\beta_1}{\omega_1-\omega_2} \right\} \bar{\bar{c}}_1(0,\alpha,n,p) \right]$$

$$-\frac{\beta_1\beta_2}{(\omega_1-\omega_2)(\omega_1-\omega_3)}\bar{\bar{c}}_1(0,\alpha,n,p)$$
(A37)

Now, substitute (A37) into (A36) to get

$$\bar{\bar{c}}_{3} = \begin{bmatrix} \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p+\gamma_{3}} + \frac{\gamma_{2}}{p+\gamma_{3}}\bar{\bar{c}}_{2}(0,\alpha,n,p) \\ -\frac{\beta_{2}}{\omega_{2}-\omega_{3}} \left(\frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \left\{\frac{\gamma_{1}}{p+\gamma_{2}} - \frac{\beta_{1}}{\omega_{1}-\omega_{2}}\right\}\bar{\bar{c}}_{1}(0,\alpha,n,p) \\ -\frac{\beta_{1}\beta_{2}}{(\omega_{1}-\omega_{2})(\omega_{1}-\omega_{3})}\bar{\bar{c}}_{1}(0,\alpha,n,p) \\ + \frac{\beta_{2}}{\omega_{2}-\omega_{3}} \left[\frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \left\{\frac{\gamma_{1}}{p+\gamma_{2}} - \frac{\beta_{1}}{\omega_{1}-\omega_{2}}\right\}\bar{\bar{c}}_{1}(0,\alpha,n,p) \right] \exp\{b_{2}^{-}x\} \\ + \frac{\beta_{1}\beta_{2}}{(\omega_{1}-\omega_{2})(\omega_{1}-\omega_{3})}\bar{\bar{c}}_{1}(x,\alpha,n,p)$$
(A38)

$$\omega_1 \neq \omega_2, \omega_1 \neq \omega_3, \omega_2 \neq \omega_3$$

If on the other hand $\omega_2 = \omega_3$ (i.e., $R_2\lambda_2 = R_3\lambda_3$) but then we have $\omega_2 \neq \omega_3$ using (B8) in Appendix B:

$$\begin{split} \bar{\bar{c}}_{3} &= A \exp\{b_{3}^{-}x\} + B \exp\{b_{3}^{-}x\} \\ &- \beta_{2} \Big[\frac{c_{p_{2}} \zeta_{2}(\alpha) \kappa_{2}(n)}{p + \gamma_{2}} + \Big\{ \frac{\gamma_{1}}{p + \gamma_{2}} - \frac{\beta_{1}}{\omega_{1} - \omega_{2}} \Big\} \bar{\bar{c}}_{1}(0, \alpha, n, p) \Big] \\ &\cdot \Big[\frac{1}{b_{3}^{+} - b_{3}^{-}} + x \Big] \frac{1}{b_{3}^{+} - b_{3}^{-}} \exp(b_{3}^{-}x) \\ &+ \frac{\beta_{1} \beta_{2}}{(\omega_{3} - \omega_{1})(\omega_{2} - \omega_{1})} \bar{\bar{c}}_{1}(x, \alpha, n, p) \end{split}$$
(A39)

$$\omega_1 \neq \omega_2, \omega_1 \neq \omega_3, \omega_2 \neq \omega_3$$

Application of the boundary conditions (A34 or A35a) and (A35b) gives B = 0 and

$$A = \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p+\gamma_{3}} + \frac{\gamma_{2}}{p+\gamma_{3}}\bar{\bar{c}}_{2}(0,\alpha,n,p) + \beta_{2}\left[\frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \left\{\frac{\gamma_{1}}{p+\gamma_{2}} - \frac{\beta_{1}}{\omega_{1}-\omega_{2}}\right\}\bar{\bar{c}}_{1}(0,\alpha,n,p) \cdot \frac{1}{(b_{3}^{+}-b_{3}^{-})^{2}}\right] - \frac{\beta_{1}\beta_{2}}{(\omega_{3}-\omega_{1})(\omega_{2}-\omega_{1})}\bar{\bar{c}}_{1}(0,\alpha,n,p)$$
(A40)

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Substituting (A40) into (A39) for A and letting B = 0 gives:

$$\bar{\bar{c}}_{3} = \begin{bmatrix} \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p+\gamma_{3}} + \frac{\gamma_{2}}{p+\gamma_{3}}\bar{\bar{c}}_{2}(0,\alpha,n,p) \\ -\frac{\beta_{1}\beta_{2}}{(\omega_{3}-\omega_{1})(\omega_{2}-\omega_{1})}\bar{\bar{c}}_{1}(0,\alpha,n,p) \end{bmatrix} \exp\{b_{3}^{-}x\}$$

$$-\frac{\beta_{2}x}{b_{3}^{+}-b_{3}^{-}} \begin{bmatrix} \frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p+\gamma_{2}} + \left\{\frac{\gamma_{1}}{p+\gamma_{2}} - \frac{\beta_{1}}{\omega_{1}-\omega_{2}}\right\}\bar{\bar{c}}_{1}(0,\alpha,n,p) \end{bmatrix} \exp\{b_{3}^{-}x\}$$

$$+\frac{\beta_{1}\beta_{2}}{(\omega_{3}-\omega_{1})(\omega_{2}-\omega_{1})}\bar{\bar{c}}_{1}(x,\alpha,n,p)$$
(A41a)

or

$$\bar{\bar{c}}_{3} = \begin{bmatrix} \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p+\gamma_{3}} + \frac{\gamma_{2}}{p+\gamma_{3}}\bar{\bar{c}}_{2}(0,\alpha,n,p) \\ -\frac{\beta_{1}\beta_{2}}{(\omega_{3}-\omega_{1})(\omega_{2}-\omega_{1})}\bar{\bar{c}}_{1}(0,\alpha,n,p) \end{bmatrix} \exp\{b_{3}^{-}x\}$$

$$-\frac{\beta_{2}x}{b_{3}^{+}-b_{3}^{-}} \left[\bar{\bar{c}}_{2}(x,\alpha,n,p) - \frac{\beta_{1}}{\omega_{1}-\omega_{2}}\bar{\bar{c}}_{1}(x,\alpha,n,p)\right] \\ + \frac{\beta_{1}\beta_{2}}{(\omega_{3}-\omega_{1})(\omega_{2}-\omega_{1})}\bar{\bar{c}}_{1}(x,\alpha,n,p)$$
(A41b)

where

$$\omega_3 = \omega_2, \omega_2 \neq \omega_1, \omega_3 \neq \omega_1$$

and (A28a) is used to express the second term in (A41a).

If we have $\omega_3 \neq \omega_1$, then using (A29a) for $\overline{\overline{c}}_3$ in (A33) leads to:

$$\begin{split} \bar{\bar{c}}_{3} &= A \exp\{b_{3}^{-}x\} + B \exp\{b_{3}^{+}x\} \end{split}$$
(A42)

$$&+ \frac{\beta_{2}}{\omega_{2} - \omega_{3}} \left[\frac{c_{p_{2}} \zeta_{2}(\alpha) \kappa_{2}(n)}{p + \gamma_{2}} + \frac{\gamma_{1}}{p + \gamma_{2}} \bar{\bar{c}}_{1}(0, \alpha, n, p) \right] \exp\{b_{2}^{-}x\}$$
(A42)

$$&- \frac{\beta_{1}\beta_{2}}{\omega_{1} - \omega_{3}} \cdot \frac{1}{b_{2}^{+} - b_{2}^{-}} \left[x - \frac{1}{b_{2}^{-} - b_{3}^{+}} \right] \bar{\bar{c}}_{1}(x, \alpha, n, p)$$

$$&= A \exp\{b_{3}^{-}x\} + B \exp\{b_{3}^{+}x\}$$

$$&+ \frac{\beta_{2}}{\omega_{2} - \omega_{3}} \left[\bar{\bar{c}}_{2}(x, \alpha, n, p) + \frac{\beta_{1} \bar{\bar{c}}_{1}(0, \alpha, n, p)}{(b_{2}^{+} - b_{2}^{-})(b_{2}^{-} - b_{3}^{+})} \right]$$

$$&\omega_{2} = \omega_{1}, \omega_{3} \neq \omega_{1}, \omega_{2} \neq \omega_{3} \end{split}$$

where use has been made of the result (B11) in Appendix B and also (A29a). Application of the boundary conditions yields B = 0 and

$$A = \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p + \gamma_{3}} + \frac{\gamma_{2}}{p + \gamma_{3}}\bar{\bar{c}}_{2}(0, \alpha, n, p) - \frac{\beta_{2}}{\omega_{2} - \omega_{3}} \left[\bar{\bar{c}}_{2}(0, \alpha, n, p) + \frac{\beta_{1}\bar{\bar{c}}_{1}(0, \alpha, n, p)}{(b_{2}^{+} - b_{2}^{-})(b_{2}^{-} - b_{3}^{+})}\right]$$
(A43)

Using (A43) in (A442) gives

$$\bar{\bar{c}}_{3} = \begin{bmatrix} \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p+\gamma_{3}} + \left(\frac{\gamma_{2}}{p+\gamma_{3}} - \frac{\beta_{2}}{\omega_{2}-\omega_{3}}\right)\bar{\bar{c}}_{2}(0,\alpha,n,p) \\ - \frac{\beta_{2}\beta_{1}}{\omega_{2}-\omega_{3}} \cdot \frac{1}{(b_{2}^{+}-b_{2}^{-})(b_{2}^{-}-b_{3}^{+})}\bar{\bar{c}}_{1}(0,\alpha,n,p) \\ + \frac{\beta_{2}}{\omega_{2}-\omega_{3}} \left[\bar{\bar{c}}_{2}(x,\alpha,n,p) + \frac{\beta_{1}\bar{\bar{c}}_{1}(x,\alpha,n,p)}{(b_{2}^{+}-b_{2}^{-})(b_{2}^{-}-b_{3}^{+})}\right]$$
(A44)

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$$\omega_2 = \omega_1, \omega_3 \neq \omega_1, \omega_2 \neq \omega_3$$

Finally, if $\omega_1 = \omega_2 = \omega_3$

$$\begin{split} \bar{\bar{c}}_{3} &= A \exp\{b_{3}^{-}x\} + B \exp\left\{b_{3}^{+}x\right\} \\ &\quad - \frac{\beta_{2}}{b_{3}^{+} - b_{3}^{-}} \left[\frac{1}{b_{3}^{+} - b_{3}^{-}} + x\right] \left[\frac{c_{p_{2}}}{p + \gamma_{2}} + \frac{\gamma_{1}}{p + \gamma_{2}} \bar{\bar{c}}_{1}(0, \alpha, n, p)\right] \exp\{b_{3}^{-}x\} \\ &\quad - \frac{\beta_{2}\beta_{1}}{(b_{3}^{+} - b_{3}^{-})^{2}} \left[\frac{1}{b_{3}^{-} - b_{3}^{+}} \left(x - \frac{1}{b_{3}^{-} - b_{3}^{+}}\right) - \frac{x^{2}}{2}\right] \bar{\bar{c}}_{1}(x, \alpha, n, p) \end{split}$$
(A45)

Now, making use of the boundary conditions for $\bar{\bar{c}}_3$ gives B = 0 and

$$A = \frac{c_{p_3}\zeta_3(\alpha)\kappa_3(n)}{p+\gamma_3} + \frac{\gamma_2}{p+\gamma_3}\bar{\bar{c}}_2(0,\alpha,n,p)$$

$$+ \frac{\beta_2}{(b_3^+ - b_3^-)^2} \left[\frac{c_{p_2}}{p+\gamma_2} + \frac{\gamma_1}{p+\gamma_2} \bar{\bar{c}}_1(0,\alpha,n,p) \right]$$

$$- \frac{\beta_1\beta_2}{(b_3^+ - b_3^-)^2} \frac{1}{(b_3^- - b_3^+)^2} \bar{\bar{c}}_1(0,\alpha,n,p)$$
(A46)

Finally, substituting for A and B in (A45) gives

$$\bar{\bar{c}}_{3} = \begin{bmatrix} \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p+\gamma_{3}} + \frac{\gamma_{2}}{p+\gamma_{3}}\bar{\bar{c}}_{2}(0,\alpha,n,p) \\ + \frac{\beta_{2}}{(b_{3}^{+}-b_{3}^{-})^{2}} \left\{ \frac{c_{p_{2}}}{p+\gamma_{2}} + \left(\frac{\gamma_{1}}{p+\gamma_{2}} \frac{\beta_{1}}{(b_{3}^{+}-b_{3}^{-})^{2}} \right) \bar{\bar{c}}_{1}(0,\alpha,n,p) \right\} \end{bmatrix} \exp\{b_{3}^{-}x\}$$

$$- \frac{\beta_{2}}{b_{3}^{+}-b_{3}^{-}} \left[\frac{1}{b_{3}^{+}-b_{3}^{-}} + x \right] \left[\frac{c_{p_{2}}}{p+\gamma_{2}} + \frac{\gamma_{1}}{p+\gamma_{2}} \bar{\bar{c}}_{2}(0,\alpha,n,p) \right] \exp\{b_{3}^{-}x\}$$

$$- \frac{\beta_{1}\beta_{2}}{(b_{3}^{+}-b_{3}^{-})^{2}} \left[\frac{1}{b_{3}^{-}-b_{3}^{+}} \left(x - \frac{1}{b_{3}^{-}-b_{3}^{+}} \right) - \frac{x^{2}}{2} \right] \bar{\bar{c}}_{1}(x,\alpha,n,p)$$

$$(A47)$$

Or, upon simplifying (A47):

$$\bar{\bar{c}}_{3} = \begin{bmatrix} \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p+\gamma_{3}} + \frac{\gamma_{2}}{p+\gamma_{3}}\bar{\bar{c}}_{2}(0,\alpha,n,p) \\ -\frac{\beta_{2}\beta_{1}}{(b_{3}^{+}-b_{3}^{-})^{2}}\bar{\bar{c}}_{1}(0,\alpha,n,p) \end{bmatrix} \exp\{b_{3}^{-}x\}$$

$$-\frac{\beta_{2}}{b_{3}^{+}-b_{3}^{-}} \left[x \left(\frac{c_{p_{2}}}{p+\gamma_{2}} + \frac{\gamma_{1}}{p+\gamma_{2}}\bar{\bar{c}}_{1}(0,\alpha,n,p) \right) \right] \exp\{b_{3}^{-}x\}$$

$$-\frac{\beta_{2}\beta_{1}}{(b_{3}^{+}-b_{3}^{-})^{2}} \left[\frac{1}{b_{3}^{-}-b_{3}^{+}} \left(x - \frac{1}{b_{3}^{-}-b_{3}^{+}} \right) - \frac{x^{2}}{2} \right] \bar{\bar{c}}_{1}(x,\alpha,n,p)$$

$$(A48)$$

The inverse transform of $\overline{\overline{c}}_3$ is given by substituting either (A38), (A41b), (A44) or (A48) into:

$$c_{3}(x,y,z,t) = \mathscr{L}^{-1}\left[\frac{1}{\pi B}\int_{0}^{\infty} \left[\bar{\bar{c}}_{3}(x,\alpha,n=0,p) + 2\sum_{n=1}^{\infty}\bar{\bar{c}}_{3}(x,\alpha,n,p)\cos\left(\frac{n\pi z}{B}\right)\right]\cos(\alpha y)d\alpha\right]$$
(A49)

Species 4

$$R_4 \frac{\partial c_4}{\partial t} + \nu \frac{\partial c_4}{\partial x} - D_x \frac{\partial^2 c_4}{\partial x^2} - D_y \frac{\partial^2 c_4}{\partial y^2} - D_z \frac{\partial^2 c_4}{\partial z^2} + \lambda_4 R_4 c_4 - \lambda_3 R_3 c_3 = 0$$
(A50)

$$c_4(x, y, z, 0) = 0$$
 (A51a)

$$\frac{\partial c_4}{\partial t}(0, y, z, t) + \gamma_4 c_4(0, y, z, t) - \gamma_3 c_3(0, y, z, t) = 0$$
(A51b)

$$c_4(0, y, z, 0) = c_{p_4} \varpi_4(y) \cdot [H(z - H_1) - H(z - H_2)]$$
(A51c)

$$c_4(\infty, y, z, t) = 0 \tag{A51d}$$

$$c_4(x, \pm \infty, z, t) = 0 \tag{A51e}$$

$$\frac{\partial c_4}{\partial z}(x, y, 0, t) = 0 \tag{A51f}$$

$$\frac{\partial c_4}{\partial z}(x, y, B, t) = 0 \tag{A51g}$$

Application of the transformations transforms \mathscr{F} , \mathscr{F}_c and \mathscr{L} to the system (A50) and (A51) leads to

$$\frac{d^2\bar{\bar{c}}_4}{dx^2} - \phi \frac{d\bar{\bar{c}}_4}{dx} - \omega_4(\alpha, n, p)\bar{\bar{c}}_4 = \beta_3\bar{\bar{c}}_3$$
(A52)

$$\bar{\bar{\bar{c}}}_4(0,\alpha,n,p) = \frac{c_{p_4}\zeta_4(\alpha)\kappa_4(n)}{p+\gamma_4} + \frac{\gamma_3}{p+\gamma_4}\bar{\bar{\bar{c}}}_3(0,\alpha,n,p)$$
(A53a)

$$\overline{\overline{c}}_4(\infty,\alpha,n,p) = 0 \tag{A53b}$$

where:

$$\begin{split} \omega_4(\alpha,n,p) &= \frac{1}{D_x} \left[R_4(p+\lambda_4) + \alpha^2 D_y + \frac{n^2 \pi^2 D_z}{B^2} \right] \\ \beta_3 &= -\frac{\lambda_3 R_3}{D_x} \\ \zeta_4(\alpha) &= \begin{cases} (2\pi)^{1/2} S_4 \exp\left(-\frac{S_4^2 \alpha^2}{2}\right) & \text{Gaussian type} \\ \frac{2}{\alpha} \sin(\alpha y_0) & \text{Rectangular patch type} \\ \frac{R_4(n)}{B} &= \begin{cases} (H_2 - H_1) & n = 0 \\ \frac{B}{n\pi} \left[\sin\left(\frac{n\pi H_2}{B}\right) - \sin\left(\frac{n\pi H_1}{B}\right) \right] & n > 0 \end{cases} \end{split}$$

Upon substituting (A38) for $\overline{\overline{c}}_3$ in (A52) and (A28a) for $\overline{\overline{c}}_2$ in (A38), the general solution to (A52) is:

$$\begin{split} \bar{\bar{c}}_{4} &= A \exp\{b_{4}^{-}x\} + B \exp\{b_{4}^{+}x\} \\ &+ \frac{\beta_{3}}{\omega_{3} - \omega_{4}} \begin{bmatrix} \frac{c_{p_{3}}\zeta_{3}(\alpha)\kappa_{3}(n)}{p + \gamma_{3}} + \frac{\gamma_{2}}{p + \gamma_{3}} \bar{\bar{c}}_{2}(0, \alpha, n, p) \\ &- \frac{\beta_{2}}{\omega_{2} - \omega_{3}} \left(\frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p + \gamma_{2}} + \left\{ \frac{\gamma_{1}}{p + \gamma_{2}} - \frac{\beta_{1}}{\omega_{1} - \omega_{2}} \right\} \bar{\bar{c}}_{1}(0, \alpha, n, p) \\ &- \frac{\beta_{1}\beta_{2}}{(\omega_{1} - \omega_{2})(\omega_{1} - \omega_{3})} \bar{\bar{c}}_{1}(0, \alpha, n, p) \\ &+ \frac{\beta_{2}\beta_{3}}{(\omega_{2} - \omega_{3})(\omega_{2} - \omega_{4})} \left[\frac{c_{p_{2}}\zeta_{2}(\alpha)\kappa_{2}(n)}{p + \gamma_{2}} + \left\{ \frac{\gamma_{1}}{p + \gamma_{2}} - \frac{\beta_{1}}{\omega_{1} - \omega_{2}} \right\} \bar{\bar{c}}_{1}(0, \alpha, n, p) \right] \exp\{b_{2}^{-}x\} \\ &+ \frac{\beta_{1}\beta_{2}\beta_{3}}{(\omega_{1} - \omega_{2})(\omega_{1} - \omega_{3})(\omega_{1} - \omega_{4})} \bar{\bar{c}}_{1}(x, \alpha, n, p) \end{split}$$
(A54)

for the case

 $\omega_1 \neq \omega_2 \neq \omega_3 \neq \omega_4$

Boundary condition (A53b) gives B = 0 and (A53a) yields:

$$A = \frac{c_{p_4}\zeta_4(\alpha)\kappa_4(n)}{p + \gamma_4} + \frac{\gamma_3}{p + \gamma_4}\bar{\bar{c}}_3(0,\alpha,n,p) - \frac{\beta_3}{\omega_3 - \omega_4} \begin{bmatrix} \frac{c_{p_3}\zeta_3(\alpha)\kappa_3(n)}{p + \gamma_3} + \frac{\gamma_2}{p + \gamma_3}\bar{\bar{c}}_2(0,\alpha,n,p) \\ - \frac{\beta_2}{\omega_2 - \omega_3} \left(\frac{c_{p_2}\zeta_2(\alpha)\kappa_2(n)}{p + \gamma_2} + \left\{ \frac{\gamma_1}{p + \gamma_2} - \frac{\beta_1}{\omega_1 - \omega_2} \right\} \bar{\bar{c}}_1(0,\alpha,n,p) \\ - \frac{\beta_1\beta_2}{(\omega_1 - \omega_2)(\omega_1 - \omega_3)}\bar{\bar{c}}_1(0,\alpha,n,p) \\ - \frac{\beta_2\beta_3}{(\omega_2 - \omega_3)(\omega_2 - \omega_4)} \left[\frac{c_{p_2}\zeta_2(\alpha)\kappa_2(n)}{p + \gamma_2} + \left\{ \frac{\gamma_1}{p + \gamma_2} - \frac{\beta_1}{\omega_1 - \omega_2} \right\} \bar{\bar{c}}_1(0,\alpha,n,p) \\ - \frac{\beta_1\beta_2\beta_3}{(\omega_1 - \omega_2)(\omega_1 - \omega_3)} \bar{\bar{c}}_1(0,\alpha,n,p) \end{bmatrix}$$
(A55)

Substituting (A55) for A into (A54) and letting B = 0 yields the final solution for $\overline{\overline{c}}_4$ for the case $\omega_1 \neq \omega_2 \neq \omega_3 \neq \omega_4$. Due to the large number of combinations of special case solutions for $\omega_4 = \omega_3$, etc., this solution will not be derived here. Finally using the inversion formula, we can write:

$$c_4(x, y, z, t) = \mathscr{L}^{-1}\left[\frac{1}{\pi B}\int_0^{\infty} \left[\bar{\bar{c}}_4(x, \alpha, n=0, p) + 2\sum_{n=1}^{\infty} \bar{\bar{c}}_4(x, \alpha, n, p)\cos\left(\frac{n\pi z}{B}\right)\right]\cos(\alpha y)d\alpha\right]$$
(A56)

Steady-state solutions

For any species *c_i*, the steady-state solution follows from the final-value theorem for the Laplace transformation given by:

$$c_{i}(x,y,z) = \lim_{p \to 0} p \bar{c}_{i}(x,y,z,p)$$

$$= \frac{1}{\pi B} \int_{0}^{\infty} \left[\lim_{p \to 0} \left(p \cdot \bar{\bar{c}}_{i}(x,\alpha,n=0,p) \right) + 2 \sum_{n=1}^{\infty} \cos\left(\frac{n\pi z}{B}\right) \lim_{p \to 0} p \cdot \bar{\bar{c}}_{i}(x,\alpha,n,p) \right] \cos(\alpha y) dx$$
(A57)

Note that the contributions of a decaying boundary condition at x = 0 for any of the parents leading to c_i is zero, including the concentration of c_{p_i} if it decays also. The limits appearing in (14) are easily written down.

Solution for simple splitting chains

Consider the parent-daughter splitting reaction as illustrated in Fig. 2b. Here, η_{1j} is a splitting factor with j = 2, 3, 4, ... and

$$\sum_{j=1}^{\rm ND} \eta_{1j} = 1$$

where ND is the number of daughters. We have

$$\bar{\bar{c}}_1 = \frac{c_{p_1}\zeta_1(\alpha)\kappa_1(n)}{p+\gamma_1}\exp(\bar{b}_1 x)$$
(A58)

as usual (e.g., see A13).

For the case shown here, the solution for $\overline{\overline{c}}_1$ is:

$$\bar{\bar{c}}_{i} = \left[\frac{c_{p_{i}}\zeta_{i}(\alpha)\kappa_{i}(n)}{p+\gamma_{i}} + \left\{\frac{\gamma_{1i}}{p+\gamma_{i}} - \frac{\beta_{1i}}{\omega_{1}+\omega_{i}}\right\}\bar{\bar{c}}_{1}(0,\alpha,n,p)\right]\exp(b_{i}^{-}x) + \frac{\beta_{1i}}{\omega_{1}+\omega_{i}}\bar{\bar{c}}_{1}(x,\alpha,n,p)$$
(A59)

provided that

 $\omega_1 \neq \omega_i, i = 2, 3, \dots$

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The assumption of unequal coefficients ω_i is the same as before (see A28a). For the special case where $\omega_1 = \omega_i$, where i = 2, 3, ..., the solution becomes (see A29a).

$$\bar{\bar{c}}_{i} = \left[\frac{c_{p_{i}}\zeta_{i}(\alpha)\kappa_{i}(n)}{p+\gamma_{i}} + \frac{\gamma_{1i}}{p+\gamma_{i}}\bar{\bar{c}}_{1}(0,\alpha,n,p)\right]\exp(b_{i}^{-}x) + \frac{\beta_{1i}x}{b_{i}^{+}-b_{i}^{-}}\bar{\bar{c}}_{1}(x,\alpha,n,p)$$
(A60)

if

 $\omega_i = \omega_i$, where i = 2, 3, ...

In the above, we have defined $\gamma_{1i} = \eta_{1i}\gamma_1$, $\beta_{1i} = \eta_{1i}\beta_1$ and normally we would use $\gamma_1 = \lambda_1$.

Solution for simple converging chains

Consider the parent-daughter converging reaction as illustrated in Fig. 2c. Here, η_{1j} is a splitting factor with j = 2, 3, 4, ... and

$$\bar{\bar{c}}_i = \frac{c_{p_i} \zeta_i(\alpha) \kappa_i(n)}{p + \gamma_i} \exp(b_i^- x) \qquad i = 1, 2, \dots N - 1$$
(A61)

$$\bar{\bar{c}}_{N} = \left[\frac{c_{p_{N}} \zeta_{N}(\alpha) \kappa_{N}(n)}{p + \gamma_{N}} + \sum_{i=1}^{N-1} \left(\frac{c_{p_{i}} \gamma_{i}}{p + \gamma_{N}} - \frac{\beta_{i}}{\omega_{i} - \omega_{N}} \right) \bar{\bar{c}}_{i}(0, \alpha, n, p) \right] \exp(b_{N}^{-} x)$$

$$+ \sum_{i=1}^{N-1} \frac{\beta_{i} x}{\omega_{i} - \omega_{N}} \bar{\bar{c}}_{i}(x, \alpha, n, p)$$
(A62)

for the case $\omega_i \neq \omega_N$ and

$$\bar{\bar{c}}_{N} = \left[\frac{c_{p_{N}}\zeta_{N}(\alpha)\kappa_{N}(n)}{p+\gamma_{N}} + \sum_{i=1}^{N-1}\frac{\gamma_{i}}{p+\gamma_{N}}\bar{\bar{c}}_{i}(0,\alpha,n,p)\right]\exp(b_{N}^{-}x) - \frac{x}{b_{N}^{+}-b_{N}^{-}}\sum_{i=1}^{N-1}\frac{\beta_{i}}{\omega_{i}-\omega_{N}}\bar{\bar{c}}_{i}(x,\alpha,n,p)$$
(A63)

for the case $\omega_i = \omega_N$. Eq (A62) and (A63) for \overline{c}_N are simply based on superposition using (A28a) and (A29a).

Solution for a seven-member branching chain

Consider the seven-member branching chain as shown in Fig. 2e:

Member 1: as Eq. (A17) with $\overline{\overline{c}}(x, \alpha, n, p)$ given by (A13)

- Member 1: as Eq. (A17) with $c(x, \alpha, n, p)$ given by (A13) Member 2: as Eq. (A28a) or (A28), but with β_1 replaced by β_{12} where $\beta_{12} = \eta_{12}\beta_1$. Because the mass from the decay of member 1 splits at x = 0 also, then the term $\frac{\gamma_1}{p + \gamma_2}$ in (A28a) must be replaced by $\frac{\eta_{12}\gamma_1}{p + \gamma_2}$. Member 3: as Eq. (A28a) or (A28), but with β_1 replaced by β_{13} where $\beta_{13} = \eta_{13}\beta_1$. Also, replace $\frac{\gamma_1}{p + \gamma_2}$ by $\frac{\eta_{13}\gamma_1}{p + \gamma_2}$ noting that all subscripts involving "2" now become "3" to denote member 3 in (A28a). Member 4: same as (A38) but replace $\frac{\gamma_2}{p + \gamma_3}$ by $\frac{\eta_{24}\gamma_2}{p + \gamma_3}$, β_2 by $\eta_{24}\beta_2$, $\frac{\gamma_1}{p + \gamma_2}$ by $\frac{\eta_{12}\gamma_1}{p + \gamma_2}$, and β_1 by $\eta_{12}\beta_1$. Note that all subscripts "3" will become "4" to denote member 4.

- will become "4" to denote member 4. Member 5: same as (A38) but replace $\frac{\gamma_2}{p + \gamma_3}$ by $\frac{\eta_{25}\gamma_2}{p + \gamma_3}$, β_2 by $\eta_{25}\beta_2$, $\frac{\gamma_1}{p + \gamma_2}$ by $\frac{\eta_{12}\gamma_1}{p + \gamma_2}$, and β_1 by $\eta_{12}\beta_1$. Note that all subscripts "3" will become "5" to denote member 5. Member 6: same as (A38) but replace $\frac{\gamma_2}{p + \gamma_3}$ by $\frac{\eta_{36}\gamma_2}{p + \gamma_3}$, β_2 by $\eta_{36}\beta_2$, $\frac{\gamma_1}{p + \gamma_2}$ by $\frac{\eta_{13}\gamma_1}{p + \gamma_2}$, and β_1 by $\eta_{13}\beta_1$. Note that all subscripts "3" will become "6" to denote member 6 and all subscripts "2" will refer to member 3 which is the parent of 6. Member 7: same as (A38) but replace $\frac{\gamma_2}{p + \gamma_3}$ by $\frac{\eta_{37}\gamma_2}{p + \gamma_3}$, β_2 by $\eta_{37}\beta_2$, $\frac{\gamma_1}{p + \gamma_2}$ by $\frac{\eta_{13}\gamma_1}{p + \gamma_2}$, and β_1 by $\eta_{13}\beta_1$. Note that all subscripts "3" will become "6" to denote member 6 and all subscripts "2" will refer to member 3 which is the parent of 6. Member 7: same as (A38) but replace $\frac{\gamma_2}{p + \gamma_3}$ by $\frac{\eta_{37}\gamma_2}{p + \gamma_3}$, β_2 by $\eta_{37}\beta_2$, $\frac{\gamma_1}{p + \gamma_2}$ by $\frac{\eta_{13}\gamma_1}{p + \gamma_2}$, and β_1 by $\eta_{13}\beta_1$. Note that all subscripts "3" will become "7" to denote member 7 and all subscripts "2" will refer to member 3 which is the parent of 7.

Appendix B. Analytical inversion of $\overline{\overline{c}}_1(x, \alpha, n, p)$

From Eq. (A13) and using the definitions of $\omega(\alpha,n,p)$, ϕ , $\zeta_1(\alpha)$ and $\kappa_1(n)$, (A13) can be expressed as

$$\bar{\bar{c}}_{1} = c_{p_{1}}\zeta_{1}(\alpha)\kappa_{1}(n)\exp\left(\frac{\nu x}{2D_{x}}\right) \\
\cdot \frac{1}{p+\gamma_{1}}\exp\left[-\left\{p+\lambda_{1}+\frac{\nu^{2}}{4R_{1}D_{x}}+\frac{\alpha^{2}D_{y}}{R_{1}}+\frac{n^{2}\pi^{2}D_{z}}{R_{1}B^{2}}\right\}^{1/2}\left(\frac{R_{1}}{D_{x}}\right)^{1/2}x\right]$$
(B1)

Where

$$\zeta_1(\alpha) = \begin{cases} (2\pi)^{1/2} S_1 \exp\left(-\frac{S_1^2 \alpha^2}{2}\right) & \text{Gaussian type} \\ \frac{2}{\alpha} \sin(\alpha y_0) & \text{Rectangular patch type} \end{cases}$$

$$\kappa_1(n) = \begin{cases} (H_2 - H_1) & n = 0\\ \frac{B}{n\pi} \left[\sin\left(\frac{n\pi H_2}{B}\right) - \sin\left(\frac{n\pi H_1}{B}\right) \right] & n > 0 \end{cases}$$

Now define the following inverse Laplace transforms:

$$\mathscr{L}^{-1}\left[\exp\left\{-a(p+b)^{1/2}\right\}\right] = \frac{a}{2\pi^{1/2}t^{3/2}}\exp(-bt)\exp\left(-\frac{a^2}{4t}\right) \qquad a > 0$$
(B2)
$$\mathscr{L}^{-1}\left[\frac{1}{p+a}\right] = \exp(-at)$$
(B3)

And the convolution theorem:

$$\mathscr{L}^{-1}\left[\bar{f}_{1}(p)^{*}\bar{f}_{2}(p)\right] = \int_{0}^{t} f_{1}(\tau) \cdot f_{2}(t-\tau)d\tau$$
(B4)

Using (B2) - (B4) we get:

$$\bar{\bar{c}}_{11}(x,\alpha,n,t) = \frac{c_{p_1}R_1^{1/2}x}{2(\pi D_x)^{1/2}} \cdot \zeta_1(\alpha) \cdot \kappa_1(n) \exp\left(\frac{vx}{2D_x}\right)$$

$$\cdot \int_0^t \frac{1}{\tau^{3/2}} \exp\left\{-\left(\frac{v^2}{4R_1D_x} + \frac{\alpha^2 D_y}{R_1} + \frac{n^2\pi^2 D_z}{R_1B^2} + \lambda_1\right)\tau - \frac{R_1x^2}{4D_x\tau}\right\}$$

$$\cdot \exp\{-\gamma_1(t-\tau)\}d\tau$$
(B5a)

Depending on the source types, (B5a) can be expressed as two types. If $\zeta_1(\alpha)$ is the Gaussian source type, then:

$$= \frac{c_{p_1} S_1 R_1^{1/2} x}{(2D_x)^{1/2}} \cdot \exp\left(\frac{vx}{2D_x}\right) \cdot \kappa_1(n) \exp(-\gamma_1 t) \\ \cdot \int_0^t \frac{1}{\tau^{3/2}} \exp\left\{-\left(\frac{v^2}{4R_1 D_x} + \frac{n^2 \pi^2 D_z}{R_1 B^2} + \lambda_1 - \gamma_1\right) \tau - \frac{R_1 x^2}{4D_x \tau}\right\}$$
(B5b)
$$\cdot \exp\left\{-\alpha^2 \left(\frac{D_y \tau}{R_1} + \frac{S_1^2}{2}\right)\right\} d\tau$$

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or if $\zeta_1(\alpha)$ is the rectangular patch source type, then:

$$= \frac{c_{p_1} R_1^{1/2} x}{2(\pi D_x)^{1/2}} \cdot \exp\left(\frac{vx}{2D_x}\right) \cdot \kappa_1(n) \exp(-\gamma_1 t)$$

$$\cdot \int_0^t \frac{1}{\tau^{3/2}} \exp\left\{-\left(\frac{v^2}{4R_1 D_x} + \frac{n^2 \pi^2 D_z}{R_1 B^2} + \lambda_1 - \gamma_1\right) \tau - \frac{R_1 x^2}{4D_x \tau}\right\}$$

$$\cdot \frac{2}{\alpha} \sin(\alpha y_0) \cdot \exp\left(-\frac{\alpha^2 D_y \tau}{R_1}\right) d\tau$$
(B5c)

We can use the following inverse Fourier transform \mathscr{F}^{-1} :

$$\mathscr{F}^{-1}\left[\exp\left\{-a\alpha^{2}\right\}\right] = \frac{1}{2(\pi a)^{1/2}}\exp\left(-\frac{y^{2}}{4a}\right) \tag{B6a}$$

$$\mathscr{F}^{-1}\left[\frac{2}{\alpha}\sin(\alpha y_0)\right] = H(y+y_0) - H(y-y_0)$$
(B6b)

And the convolution theorem:

$$\mathscr{F}^{-1}\left[\bar{f}(\alpha)^*\bar{g}(\alpha)\right] = \int_{-\infty}^{\infty} f(\xi) \cdot g(y-\xi)d\xi$$
(B6c)

To invert the Fourier transform involving α . For (B5b), making use of (B6a) yields

$$\bar{c}_{1}(x,y,n,t) = \frac{c_{p_{1}}S_{1}R_{1}^{1/2}x}{2(2\pi D_{x})^{1/2}}\exp\left(\frac{\nu x}{2D_{x}}\right)\exp(-\gamma_{1}t)\kappa_{1}(n)$$

$$\cdot \int_{0}^{t} \frac{1}{\tau^{3/2}\left(D_{y}\tau/R_{1}+S_{1}^{2}/2\right)^{1/2}}\exp\left\{ -\frac{R_{1}x^{2}}{4D_{x}\tau} - \frac{y^{2}}{4\left(D_{y}\tau/R_{1}+S_{1}^{2}/2\right)} - \left(\frac{\nu^{2}}{4R_{1}D_{x}} + \frac{n^{2}\pi^{2}D_{z}}{R_{1}B^{2}} + \lambda_{1} - \gamma_{1}\right)\tau \right\} d\tau$$
(B7a)

Similarly, using (B6b) and (B6c), (B5c) can be transformed:

$$\bar{c}_{1}(x, y, n, t) = \frac{c_{p_{1}}R_{1}^{1/2}x}{4(\pi D_{x})^{1/2}}\exp\left(\frac{vx}{2D_{x}}\right)\exp(-\gamma_{1}t)\kappa_{1}(n)$$

$$\cdot \int_{0}^{t} \frac{1}{\tau^{3/2}} \left[erfc\left\{\frac{y-y_{0}}{2\left(D_{y}\tau\right)^{1/2}}\right\} - erfc\left\{\frac{y+y_{0}}{2\left(D_{y}\tau\right)^{1/2}}\right\} \right]$$

$$\cdot \exp\left\{-\left(\frac{R_{1}x^{2}}{4D_{x}\tau} + \frac{v^{2}}{4R_{1}D_{x}} - \frac{n^{2}\pi^{2}D_{z}}{R_{1}B^{2}} + \lambda_{1} - \gamma_{1}\right)\tau\right\} d\tau$$
(B7b)

Finally making use of the inverse Fourier cosine transform (A14) to obtain: A. Case for Gaussian source type:

$$c_{1}(x, y, z, t) = \frac{c_{p_{1}}S_{1}R_{1}^{1/2}x}{2B(2\pi D_{x})^{1/2}}\exp\left(\frac{\nu x}{2D_{x}}\right)\exp(-\gamma_{1}t)$$

$$\cdot \int_{0}^{t} \left[(H_{2}-H_{1}) + \frac{2B}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\left\{\sin\left(\frac{n\pi H_{2}}{B}\right) - \sin\left(\frac{n\pi H_{1}}{B}\right)\right\}\cos\left(\frac{n\pi z}{B}\right)\exp\left\{-\frac{n^{2}\pi^{2}D_{z}\tau}{R_{1}B^{2}}\right\}\right]$$

$$\cdot \frac{1}{\tau^{3/2}\left(D_{y}\tau/R_{1} + S_{1}^{2}/2\right)^{1/2}}\exp\left\{-\frac{R_{1}x^{2}}{4D_{x}\tau} + \left[\frac{y^{2}}{4\left(D_{y}\tau/R_{1} + S_{1}^{2}/2\right)} + \frac{\nu^{2}}{4R_{1}D_{x}} + \lambda_{1}-\gamma_{1}\right]\tau\right\}d\tau$$
(B8a)

B. Case for rectangular patch source type:

.

$$c_{1}(x, y, z, t) = \frac{c_{p_{1}}R_{1}^{1/2}x}{4B(\pi D_{x})^{1/2}} \exp\left(\frac{vx}{2D_{x}}\right) \exp(-\gamma_{1}t)$$

$$\cdot \int_{0}^{t} \left[(H_{2}-H_{1}) + \frac{2B}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \left\{ \sin\left(\frac{n\pi H_{2}}{B}\right) - \sin\left(\frac{n\pi H_{1}}{B}\right) \right\} \cos\left(\frac{n\pi z}{B}\right) \exp\left(-\frac{n^{2}\pi^{2}D_{z}\tau}{R_{1}B^{2}}\right) \right]$$

$$\cdot \frac{1}{\tau^{3/2}} \exp\left\{ -\left(\frac{R_{1}x^{2}}{4D_{x}\tau} - \frac{v^{2}}{4R_{1}D_{x}} + \lambda_{1} - \gamma_{1}\right)\tau \right\} \left[erfc\left\{\frac{y-y_{0}}{2\left(D_{y}\tau\right)^{1/2}}\right\} - erfc\left\{\frac{y+y_{0}}{2\left(D_{y}\tau\right)^{1/2}}\right\} \right] d\tau$$
(B8b)

Eqs. (B8a) and (B8b) are the final form of the solution for c_1 with Gaussian and rectangular patch source types, respectively.

Appendix C. Solution to the nonhomogeneous ordinary differential equation

Given the nonhomogeneous ordinary differential equation:

$$\frac{d^2\bar{\bar{c}}_i}{dx^2} - \phi \frac{d\bar{\bar{c}}_i}{dx} - \omega_i(\alpha, n, p)\bar{\bar{c}}_i = \beta_k \bar{\bar{c}}_k \qquad i \ge 2$$
(C1)

we seek a general solution of the form:

$$\overline{\overline{c}}_{i} = A\exp\{b_{1}^{-}(\alpha, n, p)x\} + B\exp\{b_{1}^{+}(\alpha, n, p)x\} + \overline{\overline{c}}_{i}^{p}(x, \alpha, n, p)$$
(C2)

where

$$b_1^{\pm}(\alpha, n, p) = \frac{\phi}{2} \left[1 \pm \left\{ 1 + \frac{4\omega_i}{\phi^2} \right\}^{1/2} \right]$$

and $\bar{\bar{c}}_i^p$ is the particular solution arising from the nonhomogeneous term $\beta_k \bar{\bar{c}}_k(x, \alpha, n, p)$. The solution for $\bar{\bar{c}}_i^p$ is given by:

$$\bar{\bar{c}}_{i}^{p} = \beta_{k} \int \frac{\left[\exp(b_{i}^{-}\zeta)\exp(b_{i}^{+}x) - \exp(b_{i}^{+}\zeta)\exp(b_{i}^{-}x)\right]}{W(\zeta)} \bar{\bar{c}}_{k}(\zeta, \alpha, n, p)d\zeta$$
(C3)

where the Wronskian W(x) is given by

$$W(x) = \begin{vmatrix} e^{b_i^- x} & e^{b_i^+ x} \\ b_i^- e^{b_i^- x} & b_i^+ e^{b_i^- x} \end{vmatrix} = (b_i^+ - b_i^-) \exp\{(b_i^- + b_i^+)x\}$$
(C4)

We note that the solution for $\overline{\overline{c}}_k$ will be of the form:

$$\bar{\bar{c}}_k = F \exp\{b_k \bar{x}\}$$
(C5)

where F is some function (usually independent of x). Substitution of (C4) and (C5) into (C3) yields, after minor algebra:

$$\begin{split} \bar{\bar{c}}_{i}^{p} &= F\beta_{k} \cdot \frac{1}{b_{i}^{+} - b_{i}^{-}} \int \left[\exp\left(b_{i}^{+}(x - \zeta)\right) - \exp(b_{i}^{-}(x - \zeta)) \right] \exp(b_{k}^{-}\zeta) d\zeta \\ &= F\beta_{k} \frac{1}{b_{i}^{+} - b_{i}^{-}} \left[\exp\left(b_{i}^{+}x\right)^{x} \left[\exp\left(\left(b_{k}^{-} - b_{i}^{+}\right)\zeta\right) d\zeta \right] - \exp(b_{i}^{-}x)^{x} \int \exp\left(\left(b_{k}^{-} - b_{i}^{+}\right)\zeta\right) d\zeta \right] \\ &= F\beta_{k} \frac{1}{b_{i}^{+} - b_{i}^{-}} \left[\frac{1}{b_{k}^{-} - b_{i}^{+}} - \frac{1}{b_{k}^{-} - b_{i}^{-}} \right] \exp(b_{k}^{-}x) \quad if \ b_{k}^{-} \neq b_{i}^{-} \end{split}$$
(C6a)

$$= F\beta_{k} \frac{1}{(b_{k}^{-} - b_{i}^{+})(b_{k}^{-} - b_{i}^{-})} \exp(b_{k}^{-}x) \qquad \text{if } b_{k}^{-} \neq b_{i}^{-}$$
(C6b)

Upon writing b_k^- , b_i^- , and b_i^+ in the denominator of (C6) in terms of ϕ , ω_i , and ω_k , (C6) can be simplified to:

$$\bar{\bar{c}}_{i}^{p} = F\beta_{k}\frac{1}{\omega_{k} - \omega_{i}}\exp(b_{k}^{-}x)$$
(C7)

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if we have

$$b_k^- \neq b_i^-$$
 (*i.e.*, $R_k \lambda_k \neq R_i \lambda_i$)

If, however $\omega_k = \omega_i$ (*i. e.*, $R_k \lambda_k = R_i \lambda_i$), we must use:

$$\begin{split} \bar{\bar{c}}_{i}^{p} &= F\beta_{i-1}\frac{1}{b_{i}^{+}-b_{i}^{-}}\left[\frac{\exp(b_{k}^{-}x)}{b_{k}^{-}-b_{i}^{+}}-\exp(b_{i}^{-}x)\int_{0}^{x}d\zeta\right] = F\beta_{i-1}\frac{1}{b_{i}^{+}-b_{i}^{-}}\left[\frac{\exp(b_{k}^{-}x)}{b_{k}^{-}-b_{i}^{+}}-x\exp(b_{i}^{-}x)\right] \\ &= -F\beta_{i-1}\left[\frac{1}{b_{i}^{+}-b_{i}^{-}}+x\right]\frac{1}{b_{i}^{+}-b_{i}^{-}}\exp(b_{i}^{-}x) \end{split}$$
(C8)

We can also have the case where $\overline{\overline{c}}_k$ is the form:

$$\bar{\bar{c}}_k = Fx \exp\{b_k - x\} \tag{C9}$$

For which we need to evaluate:

$$\begin{split} \bar{\bar{c}}_{i}^{p} &= F\beta_{k} \frac{1}{b_{i}^{+} - b_{i}^{-}} \left[\exp\left(b_{i}^{+}x\right)^{x} \zeta \exp\left(\left(b_{k}^{-} - b_{i}^{+}\right)\zeta\right) d\zeta - \exp(b_{i}^{-}x) \int \zeta \exp((b_{k}^{-} - b_{i}^{-})\zeta) d\zeta \right] \\ &= F\beta_{k} \frac{1}{b_{i}^{+} - b_{i}^{-}} \left[\exp\left(b_{i}^{+}x\right) \left\{ \frac{1}{b_{k}^{-} - b_{i}^{+}} \left(x \exp\left(\left(b_{k}^{-} - b_{i}^{+}\right)x\right) - \int \exp\left(\left(b_{k}^{-} - b_{i}^{+}\right)\zeta\right) d\zeta \right) \right\} \right] \\ &- \exp(b_{i}^{-}x) \left\{ \frac{1}{b_{k}^{-} - b_{i}^{-}} \left(x \exp((b_{k}^{-} - b_{i}^{-})x) - \int \exp((b_{k}^{-} - b_{i}^{-})\zeta) d\zeta \right) \right\} \right] \\ &= F\beta_{k} \frac{1}{b_{i}^{+} - b_{i}^{-}} \left[\frac{1}{b_{k}^{-} - b_{i}^{+}} \left(x - \frac{1}{b_{k}^{-} - b_{i}^{+}} \right) \exp(b_{k}^{-}x) - \frac{1}{b_{k}^{-} - b_{i}^{-}} \left(x - \frac{1}{b_{k}^{-} - b_{i}^{-}} \right) \exp(b_{k}^{-}x) \\ &= F\beta_{k} \frac{1}{b_{i}^{+} - b_{i}^{-}} \left[\frac{1}{b_{k}^{-} - b_{i}^{+}} \left(x - \frac{1}{b_{k}^{-} - b_{i}^{+}} \right) - \frac{1}{b_{k}^{-} - b_{i}^{-}} \left(x - \frac{1}{b_{k}^{-} - b_{i}^{-}} \right) \right] \exp(b_{k}^{-}x) \end{split}$$
(C10)

if

$$b_k^- \neq b_i^-$$

but:

$$\frac{1}{b_i^+ - b_i^-} \left[\frac{1}{b_k^- - b_i^+} - \frac{1}{b_k^- - b_i^-} \right] = \frac{1}{\omega_k - \omega_i}$$

in which case (C10) can be written as:

$$\bar{\bar{c}}_{i}^{p} = F\beta_{k}\frac{1}{\omega_{k}-\omega_{i}}\left[x-\frac{1}{b_{k}^{-}-b_{i}^{+}}\right]\exp(b_{k}^{-}x)$$
(C11)

for the case when

$$b_k^- \neq b_i^-$$
, (*i.e.*, $\omega_k \neq \omega_i$)

If $\overline{\overline{c}}_k$ is of the form of (C9) and $b_k^- = b_i^-$, then:

$$\bar{\bar{c}}_{i}^{p} = \frac{F\beta_{k}}{b_{i}^{+} - b_{i}^{-}} \left[\frac{1}{b_{k}^{-} - b_{i}^{+}} \left(x - \frac{1}{b_{k}^{-} - b_{i}^{+}} \right) \exp(b_{k}^{-} x) - \frac{x^{2}}{2} \exp(b_{k}^{-} x) \right]$$
(C12)

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