SEMI-ANALYTICAL SOLUTIONS OF ONE-DIMENSIONAL MULTISPECIES REACTIVE TRANSPORT IN A PERMEABLE REACTIVE BARRIER-AQUIFER SYSTEM

A Thesis

by

JOHN MICHAEL MIELES

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2011

Major Subject: Geology

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Approved by:

Chair of Committee,	Hongbin Zhan
Committee Members,	Bill Batchelor
	David Sparks
Head of Department,	Andreas Kronenberg

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ABSTRACT

Semi-Analytical Solutions of One-Dimensional Multispecies Reactive Transport in a Permeable Reactive Barrier-Aquifer System. (May 2011)

John Michael Mieles, B.S., University of Rochester

Chair of Advisory Committee: Dr. Hongbin Zhan

At many sites it has become apparent that most chemicals of concern (COCs) in groundwater are persistent and not effectively treated by conventional remediation methods. In recent years, the permeable reactive barrier (PRB) technology has proven to be more cost-efficient in the long-run and capable of rapidly reducing COC concentrations by up to several orders of magnitude. In its simplest form, the PRB is a vertically emplaced rectangular porous medium in which impacted groundwater passively enters a narrow treatment zone. In the treatment zone dissolved COCs are rapidly degraded as they come in contact with the reactive material. As a result, the effluent groundwater contains significantly lower solute concentrations as it re-enters the aquifer and flows towards the plane of compliance (POC). Effective implementation of the PRB relies on accurate site characterization to identify the existing COCs, their interactions, and their required residence time in the PRB and aquifer. Ensuring adequate residence time in the PRB-aquifer system allows COCs to react longer, hence improving the probability that regulatory concentrations are achieved at the POC.

In this study, the Park and Zhan solution technique is used to derive steady-state analytical and transient semi-analytical solutions to multispecies reactive transport in a permeable reactive barrier-aquifer (dual domain) system. The advantage of the dual domain model is that it can account for the potential existence of natural degradation in the aquifer, when designing the required PRB thickness. Also, like the single-species Park and Zhan solution, the solutions presented here were derived using the total mass flux (third-type) boundary condition in PRB-aquifer system. The study focuses primarily on the steady-state analytical solutions of the tetrachloroethylene (PCE) serial degradation pathway and secondly on the analytical solutions of the parallel degradation pathway.

Lastly, the solutions in this study are not restricted solely to the PRB-aquifer model. They can also be applied to other types of dual domain systems with distinct flow and transport properties, and up to four other species reacting in serial or parallel degradation pathways. Although the solutions are long, the results of this study are novel in that the solutions provide improved modeling flexibility. For example: 1) every species can have unique first-order reaction rates and unique retardation factors, 2) higher order daughter species can be modeled solely as byproducts by neglecting their input concentrations, 3) entire segments of the parallel degradation pathway can be neglected depending on the desired degradation pathway model, and 4) converging multi-parent reactions can be modeled. As part of the study, separate Excel spreadsheet programs were created to facilitate prompt application of the steady-state analytical solutions, for both the serial and parallel degradation pathways. The spreadsheet programs are included as supplementary material.

DEDICATION

To my wife

ACKNOWLEDGEMENTS

I would like to thank my committee members: Dr. Sparks and Dr. Batchelor. Their quiet confidence in my ability to complete the Masters program carried me through rough times. This ultimately meant more to me than they know. I am especially thankful to my advisor, Dr. Hongbin Zhan. Dr. Zhan's faith in me and my potential never faltered, even as mine wavered in the hardest of times. Only through his steady guidance, personal warmth, and patience did I achieve some of the potential he saw.

Finally, I thank my wife and family. Without them I would not know the rewards that come with struggle and perseverance. I thank them for reminding me of this valuable lesson during these past two years.

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1. INTRODUCTION

At many sites it has become apparent that most chemicals of concern (COCs) in groundwater are persistent and not effectively treated by conventional, large-scale remediation methods. In recent years, the permeable reactive barrier (PRB) technology has proven to be more cost-efficient in the long-run and capable of rapidly reducing COC concentrations by up to several orders of magnitude. The purpose of a PRB is not to treat large areas of an impacted aquifer, but rather to manage plume concentrations as groundwater flows away from the source-area. In its simplest form, the PRB is a vertically emplaced rectangular porous medium in which influent groundwater passively enters a narrow treatment zone. As the groundwater flows through the treatment zone, the dissolved COCs come in contact with the reactive material and are rapidly degraded [EPA, 1998]. The effluent groundwater contains significantly lower concentrations as it re-enters the aquifer and flows towards the plane of compliance (POC), as illustrated in Figure 1. It should be noted that effective implementation of the PRB relies on accurate site characterization to identify the existing COCs, their interactions, and their required residence time in the PRB and aquifer. Ensuring adequate residence time in the PRB-aquifer system allows COCs to react longer, hence improving the probability that regulatory or target concentrations are achieved at the POC. Therefore, minimizing performance uncertainties (such as inadequate barrier thickness) in the preliminary design phase is critical in avoiding underperformance of the PRB.

This thesis follows the style of *Water Resources Research.*

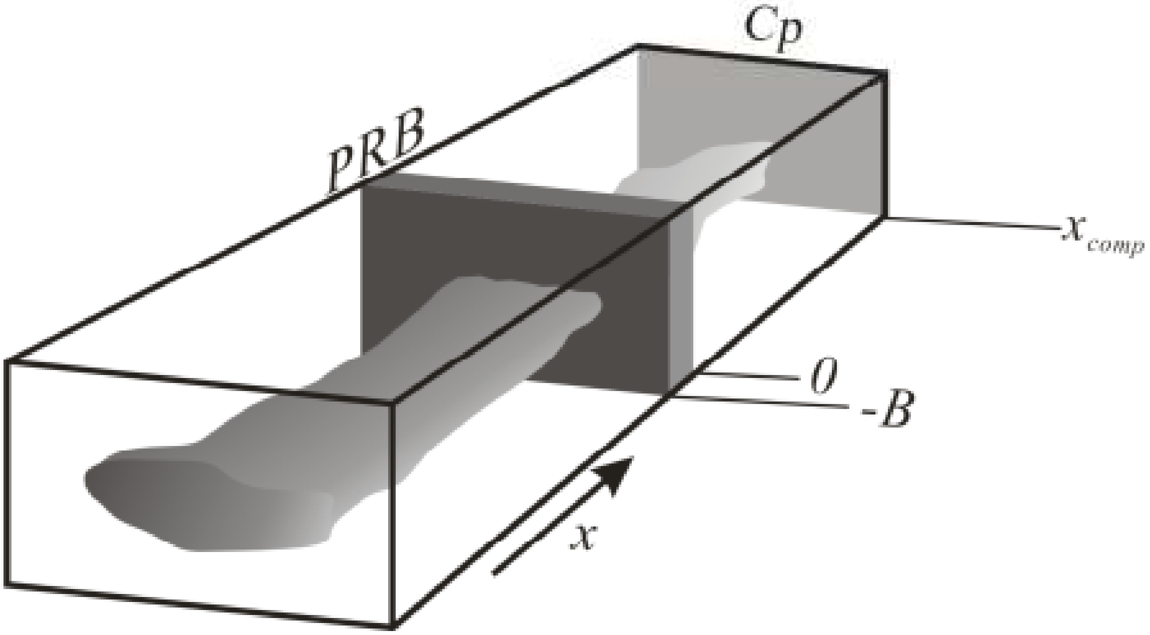


Figure 1: Schematic of installed PRB, solute plume, and aquifer. The *x* axis is along the groundwater flow direction and the PRB is of thickness –*B*. The PRB-aquifer interface is located at *x*=0 and x_{comp} is the plane of compliance (*Cp*), which could be a property boundary or a predetermined location where solute concentrations must achieve a target concentration. Figure adapted from Park and Zhan [2009].

To address design uncertainties, prior research has focused primarily on better understanding 1) the geochemistry of the PRB material [Johnson et al., 1996; Tratnyek et al., 1997; Roberts et al., 1996; Arnold and Roberts, 2000; Allen-King et al., 1997], 2) flow characteristics [Gupta and Fox, 1999], and 3) the minimum PRB thickness as determined from current design equations [Eykholt, 1997; Rabideau et al., 2005; Park and Zhan, 2009]. The one-dimensional design equations presented by Eykholt [1997], Rabideau et al. [2005], and Park and Zhan [2009] utilize the advection-dispersion equation (ADE) with first-order reaction (λ) as the governing equation(s) but differ primarily in their application of the boundary conditions. For example, the two equations of Eykholt [1997] were derived using van Genuchten's [1981] analytical solutions of the ADE with a first-type boundary condition $C(0,t) = C_{in}$ at the influent face of the PRB and a semi-infinite boundary condition $\frac{\partial C}{\partial x}(\infty, t) = 0$ at the effluent face of the PRB, with and without dispersion. The two solutions of Rabideau et al. [2005] were derived using the Sun et al. [1999] transformation procedure: the first assumed a third-type influent boundary condition and semi-infinite effluent condition, while the second solution assumed a first-type influent condition and finite concentration gradient $\frac{\partial C}{\partial x}(B, t) = 0$ effluent condition. The solutions of Eykholt [1997] and the second solution of Rabideau et al. [2005] tend to overestimate mass in the PRB system (particularly at early time) by assuming that the concentration gradient across the influent boundary is initially zero [Wexler, 1992; van Genuchten and Parker, 1984]. However, the second solution of Rabideau et al. [2005] with a finite PRB width forces a zero concentration gradient at B, hence it is useful in that it yields the largest PRB width

[Park and Zhan, 2009]. Alternatively, the first solution of Rabideau et al. [2005] with the third-type or total flux influent condition [Kreft and Zuber, 1978] is more accurate; however, it incorrectly implies that PRBs have large thicknesses with the semi-infinite effluent condition. Additionally, the Eykholt [1997] and Rabideau et al. [2005] design equations are of limited use because they are unable to account for the entirely distinct flow and chemical processes occurring in the downgradient aquifer. For example, solute degradation in the PRB is typically induced by a strong abiotic reaction while the reaction in the aquifer tends to be a weaker biologically driven (natural) attenuation [EPA, 1998]. As such, these solutions are unable to model the solute concentration at the downgradient POC, which is typically in the aquifer.

Both the first solution of Rabideau et al. [2005] and the Park and Zhan [2009] solution consider the influent dissolved solute to be well mixed and therefore described completely by the advective mass flux condition or *flowing concentration flux* [Kreft and Zuber, 1978]. Which upon entering the PRB is subject to both advective and dispersive flux or *total mass flux* [Kreft and Zuber, 1978]; hence the third-type boundary condition is more physically sound and tends to conserve mass [van Genuchten and Parker, 1984] when applied to the ADE, without reaction. The difference between the solutions is that Park and Zhan [2009] assume a finite PRB width, maintain flux and concentration continuity at the PRB-aquifer interface, and assign a separate governing equation to the aquifer, which permits modeling solute concentrations at the POC. The Park and Zhan [2009] solution, however, is currently limited to one reactive species in the PRB-aquifer system. Most groundwater plumes have multiple chemicals present and many plumes have reactive solutes which decay to produce daughter chemicals. A common example is tetrachloroethylene (PCE) which degrades to produce trichloroethylene (TCE), which in turn degrades to dichloroethylene (DCE), with vinyl chloride (VC) as the final chlorinated daughter product. Given this limitation, the objective of this study is to expand the Park and Zhan [2009] model to handle multispecies reactive transport in the PRB-aquifer system. The results will focus on the closed-form steady-state analytical solutions of the aquifer, but it is noted that the transient semi-analytical solutions can be extracted from the derivations with little effort and programmed into a numerical inversion algorithm. Lastly, due to the length of the solutions, an extensive appendix and two Excel programs are separately attached. The Excel spreadsheets are preprogrammed with the steady-state analytical solutions of the serial and parallel degradation pathways.

2. MODEL DEVELOPMENT – SERIAL DEGRADATION SOLUTIONS

Figure 1, adapted from Park and Zhan [2009], is a schematic diagram illustrating the modeled assumption of one-dimensional solute transport perpendicular to the installed PRB and downgradient aquifer. As seen, the PRB is continuous (slab-shaped) and fully submerged with the upgradient and downgradient surfaces positioned normal to the x-axis, the direction of groundwater flow. The thickness of the PRB is B, with the PRB-aquifer interface at $x = 0$ representing the coordinate system origin, and x_{comp} representing a predetermined location where solute concentrations must achieve a regulatory limit; i.e., the POC. Although the PRB-aquifer interface exhibits a common specific discharge (q), the PRB has higher porosity than the adjacent aquifer, and as such pore water velocity is lower in the PRB [Gavaskar et al., 2000]. It should also be noted that the PRB and aquifer have distinct first-order reaction rates and dispersivities; and that subsequent uses of λ_B actually represent an observed first-order reaction rate (λ_{Bobs}) that was properly normalized to the iron surface area concentration in the PRB (see Section 3). Furthermore, note that in a one-dimensional flow and transport model transverse dispersion is neglected; this is a conservative assumption since transverse dispersion dilutes the effluent concentration. Lastly, note that the PRB's ability to induce rapid degradation is key to its design. Therefore, when examining the results of this study one should focus on the large difference between the first-order reaction of the PRB and the aquifer.

For the PRB-aquifer system modeled here, the governing equation of the *first* parent species in the PRB is

$$R_{Bi}\frac{\partial C_{Bi}}{\partial t} = \mathcal{L}(C_{Bi}) - \lambda_{Bi}C_{Bi}\ , \quad \mathcal{L}(C_{Bi}) = D_B\frac{\partial^2 C_{Bi}}{\partial x^2} - u_B\frac{\partial C_{Bi}}{\partial x}\ , \tag{1}$$

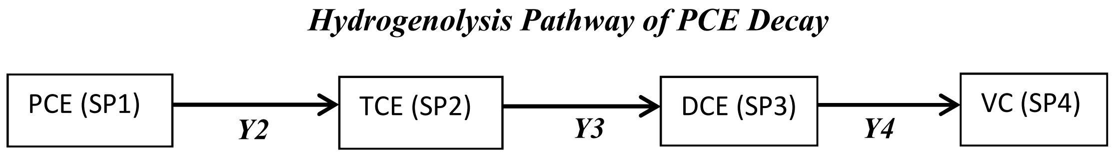
where the subscript "$_B$" denotes the PRB, $\mathcal{L}$ is the advection-dispersion operator, and $i = 1$. For subsequent daughter species the governing equation in the PRB is

$$R_{Bi}\frac{\partial C_{Bi}}{\partial t} = \mathcal{L}(C_{Bi}) - \lambda_{Bi}C_{Bi} + y_i\lambda_{Bi-1}C_{Bi-1}\ , \tag{2}$$

where $i = 2, 3, \cdots, n$ represent the species chain reaction in Figure 2, D_B is the longitudinal dispersion coefficient [L^{2}T^{-1}], u_B is the groundwater flow velocity [LT^{-1}], R_{Bi} is the species-dependent retardation factor for linear sorption [-], C_{Bi} is the species concentration [ML^{-3}], λ_{Bi} is the species-dependent first-order reaction rate constant [T^{-1}], y_i is the stoichiometric yield factor [-] (see Appendix A), x is the spatial variable along the flow direction [L], and t is time [T]. All parameters in Eqs. (1) and (2) pertain to the PRB region; i.e., the distance $-B < x < 0$. At the influent face of the PRB, the solute concentration can be a function of time such that

$$\left(n_B D_B\frac{\partial C_{Bi}}{\partial x} - qC_{Bi}\right)\Big|_{x=-B} = -qC_{i_{in}}(t)\ , \tag{3}$$

where n_B is the porosity of the PRB and $C_{i_{in}}$ is the influent concentration immediately up-stream of the PRB, which can be constant or a temporally variable function. The derivations presented below assume $C_{i_{in}}$ is transient, however, all steady-state results convert $C_{i_{in}}$ to a constant input concentration. Notice that the left-hand side of Eq. (3) represents total mass flux within the PRB while the right-hand side represents the flowing flux entering the PRB. This third-type boundary condition is typically used for laboratory columns with porous media, however, it is reasonable to treat the PRB as analogous to a large-scale column. Another intuitive description of Eq. (3) states simply



Hydrogenolysis Pathway of PCE Decay

Figure 2: Conceptual view of the serial degradation pathway of PCE. ***Y*** – denotes the stoichiometric yield of the daughter product from the parent chemical.

that $C_{i_{in}}\big|_{x=-B^{+}}$ is less than $C_{i_{in}}$ due to the loss of mass by dispersion upon entering the PRB [Danckwerts, 1952].

Since groundwater exiting the PRB enters a medium with entirely different chemical and flow processes a separate ADE is required. Therefore, the governing equations of multi-species reactive transport in the down-gradient aquifer are

$$R_{Li}\frac{\partial C_{Li}}{\partial t} = \mathcal{L}(C_{Li}) - \lambda_{Li}C_{Li}\ , \quad \mathcal{L}(C_{Li}) = D_L\frac{\partial^2 C_{Li}}{\partial x^2} - u_L\frac{\partial C_{Li}}{\partial x} \tag{4}$$

$$R_{Li}\frac{\partial C_{Li}}{\partial t} = \mathcal{L}(C_{Li}) - \lambda_{Li}C_{Li} + y_i\lambda_{Li-1}C_{Li-1}\ , \tag{5}$$

where D_L is the longitudinal dispersion coefficient [L^2T^{-1}], u_L is the groundwater velocity [LT^{-1}], R_{Li} is the species-dependent retardation factor [-], λ_{Li} is the species-dependent first-order reaction rate [T^{-1}], y_i is again the stoichiometric yield factor [-] (equivalent in both media), and C_{Li} is the species concentration [ML^{-3}]. Note that Eqs. (4) and (5) – denoted with subscript "$_L$" – pertain to the aquifer region $0 < x < \infty$, but only Eq. (5) governs the transport of daughter species. It is noted that groundwater flow velocities in the PRB and the aquifer can be determined from a common specific discharge such that $u_B n_B = u_L n_L = q$, where n_B and n_L are the porosities of the PRB and the aquifer, respectively. Additionally, the model assumes the PRB and aquifer are initially free of contamination, thus the initial condition is $C_{Bi}(t=0) = C_{Li}(t=0) = 0$. Lastly, since the PRB-aquifer interface physically represents the transition between two types of porous media the proper boundary conditions to maintain at $x = 0$ are the continuity of solute concentration and the continuity of total mass flux; i.e.,

$$C_{Bi}|_{x=0} = C_{Li}|_{x=0}\ , \tag{6}$$

$$\left(n_B D_B \frac{\partial C_{Bi}}{\partial x} - qC_{Bi}\right)\Big|_{x=0} = \left(n_L D_L \frac{\partial C_{Li}}{\partial x} - qC_{Li}\right)\Big|_{x=0}, \tag{7}$$

and at the positive infinity limit of the aquifer a no-flux boundary condition is assumed

$$\frac{\partial C_{Li}}{\partial x}\Big|_{x=\infty} = 0\,. \tag{8}$$

To facilitate computation, the following dimensionless parameters are introduced:

$$C_{BDi} = \frac{C_{Bi}}{C_S}, C_{Di} = \frac{C_{Li}}{C_S}, x_D = \frac{x}{B}, t_D = \frac{D_B}{B^2}t\,, u_{BD} = \frac{u_B B}{D_B}, u_{LD} = \frac{u_L B}{D_B}, q_D = \frac{qB}{D_B}$$

$$, \delta = \frac{D_L}{D_B}, \lambda_{BDi} = \frac{B^2}{D_B}\lambda_{Bi}\,, \lambda_{LDi} = \frac{B^2}{D_B}\lambda_{Li}\,, \theta = \frac{n_L}{n_B}, \text{and } p = \frac{B^2}{D_B}s \tag{9}$$

where the subscript "$_D$" denotes a dimensionless term, B the PRB thickness [L], S the Laplace variable [T^{-1}], and C_S the solubility [ML^{-3}] of the first species which serves simply as a reference concentration. An alternative reference concentration can be used if desired. Applying the dimensionless parameters defined in Eq. (9) and the Laplace transform to Eqs. (1), (2), (4), and (5) results in the following governing equations:

$$\frac{d^2\overline{C}_{BDi}}{d{x_D}^2} - u_{BD}\frac{d\overline{C}_{BDi}}{dx_D} - (R_{Bi}p + \lambda_{BDi})\overline{C}_{BDi} = 0\,, \tag{10}$$

$$\frac{d^2\overline{C}_{BDi}}{d{x_D}^2} - u_{BD}\frac{d\overline{C}_{BDi}}{dx_D} - (R_{Bi}p + \lambda_{BDi})\overline{C}_{BDi} = -y_i\lambda_{BDi-1}\overline{C}_{BDi-1}\,, \tag{11}$$

$$\delta\frac{d^2\overline{C}_{LDi}}{d{x_D}^2} - u_{LD}\frac{d\overline{C}_{LDi}}{dx_D} - (R_{Li}p + \lambda_{LDi})\overline{C}_{LDi} = 0\,, \tag{12}$$

$$\delta\frac{d^2\overline{C}_{LDi}}{d{x_D}^2} - u_{LD}\frac{d\overline{C}_{LDi}}{dx_D} - (R_{Li}p + \lambda_{LDi})\overline{C}_{LDi} = -y_i\lambda_{LDi-1}\overline{C}_{LDi-1}\,, \tag{13}$$

where the overbar denotes the Laplace domain and p is the dimensionless Laplace variable corresponding to dimensionless time t_D. Notice that the Laplace transform procedure eliminated the time dependency of the original partial differential equations

(PDEs). The resulting equations are second order linear (homogeneous and nonhomogeneous) ordinary differential equations (ODEs), which depend only on the distance from the source concentration [Nagle et al., 2000]. For example, if in Eqs. (11) and (13) *i* is the fourth species then *i*-1 denotes species three, which carries the solutions of species one and two. Applying Eq. (9) and the Laplace transform to the boundary conditions yields

$$\left(\frac{d\overline{C}_{BDi}}{dx_D} - u_{BD}\overline{C}_{BDi}\right)\Bigg|_{x_D=-1} = -u_{BD}\overline{C}_{Di_{in}} \, , \tag{14}$$

$$\overline{C}_{BDi}\Big|_{x_D=0} = \overline{C}_{LDi}\Big|_{x_D=0} \, , \tag{15}$$

$$\left(\frac{d\overline{C}_{BDi}}{dx_D} - q_D\overline{C}_{BDi}\right)\Bigg|_{x_D=0} = \left(\theta\delta\frac{d\overline{C}_{LDi}}{dx_D} - q_D\overline{C}_{LDi}\right)\Bigg|_{x_D=0} \, , \tag{16}$$

$$\frac{d\overline{C}_{LDi}}{dx_D}\Bigg|_{x_D=\infty} = 0 \, . \tag{17}$$

From Park and Zhan [2009], the general solution of Eqs. (10) and (12) in the Laplace domain are

$$\overline{C}_{BDi} = exp\left(\frac{u_{BD}x_D}{2}\right)\left[aexp(v_{Di}x_D) + bexp(-v_{Di}x_D)\right] \, , \tag{18}$$

$$\overline{C}_{LDi} = cexp\left(\frac{u_{LD}-2\omega_{Di}}{2\delta}x_D\right) \, , \tag{19}$$

where $v_{Di}(p) = \sqrt{u_{BD}{}^2/4 + R_{Bi}p + \lambda_{BDi}}$ and $\omega_{Di}(p) = \sqrt{u_{LD}{}^2/4 + \delta(R_{Li}p + \lambda_{LDi})}$, and undetermined coefficients *a*, *b*, and *c* depend on the boundary conditions. Note that Eq. (19) neglects the positive root of the characteristic equation because solute concentrations far from the PRB must be zero, in accordance with boundary condition (17). After applying the boundary conditions, the semi-analytical solution of Eq. (19) for species $i = 1$ is

$$\frac{\overline{C}_{LDi}}{\overline{C}_{Di_{in}}(p)} = 2\upsilon_{Di}u_{BD}E_{Di}exp\left(\frac{u_{LD}-2\omega_{Di}}{2\delta}x_D + \frac{u_{BD}}{2}\right), \tag{20}$$

where $E_{Di} = 1/[(\upsilon_{Di}u_{BD} + 2\theta\omega_{Di}\upsilon_{Di})cosh(\upsilon_{Di}) + (\theta\omega_{Di}u_{BD} + 2\upsilon_{Di}{}^2)sinh(\upsilon_{Di})]$. The complete derivation of Eq. (20) is included in Park and Zhan [2009]. Note that the transient analytical solution of Eq. (20) can be inverted numerically to yield the solution in real-time domain. The steady-state analytical solution, however, can be determined by letting $p \to 0$ (equivalent to $t_D \to \infty$), applying the final value theorem $\lim_{t\to\infty} F(t) = \lim_{p\to 0} pf(p)$ [Dyke, 1999], and assigning a constant influent concentration so that $\overline{C}_{Di_{in}}(p) \to C_{Di_{in}}/p$. The resulting steady-state aquifer solution of Eq. (20) is

$$C_{LDi} = 2\upsilon_{0Di}u_{BD}E_{0Di}C_{Di_{in}}exp\left(\frac{u_{LD}-2\omega_{0Di}}{2\delta}x_D + \frac{u_{BD}}{2}\right), \tag{21}$$

where E_{0Di} now incorporates $\upsilon_{0Di} = \sqrt{u_{BD}{}^2/4 + \lambda_{BDi}}$ and $\omega_{0Di} = \sqrt{u_{LD}{}^2/4 + \delta\lambda_{LDi}}$. The PRB solution is not included here, but is presented in Park and Zhan [2009]. Notice that the PRB solution − although necessary for derivational purposes − is not the end goal. Ultimately, the designer desires to know the solute concentration at the location of the selected POC for a selected PRB thickness. Only the aquifer solution provides this flexibility.

For design purposes Eq. (21) is converted to its dimensional form

$$C_{Li} = 2\upsilon_i u_B E_i C_{i_{in}} exp\left(\frac{u_L - 2D_L\omega_i}{2D_L}x + \frac{u_B B}{2D_B}\right), \tag{22}$$

where $E_i = 1/[(\upsilon_i u_B + 2D_L\theta\omega_i\upsilon_i)cosh(B\upsilon_i) + (\theta\delta\omega_i u_B + 2D_B\upsilon_i{}^2)sinh(B\upsilon_i)]$, and where $\upsilon_i = \sqrt{u_B{}^2/4D_B{}^2 + \lambda_{Bi}/D_B}$ and $\omega_i = \sqrt{u_L{}^2/4D_L{}^2 + \lambda_{Li}/D_L}$. As noted by Park and Zhan [2009], Eq. (22) can be used to determine the species concentration at the downgradient POC given a PRB of thickness B. In its present form Eq. (22) cannot be rearranged to explicitly solve for B, however, assuming the strong first-order reaction in a PRB dominates over dispersion, then $\lambda_{Bi} \gg D_B$ and $Bv_i \gg 1$. This in turn simplifies the hyperbolic function such that $cosh(Bv_i) \approx sinh(Bv_i) \approx exp\,(Bv_i)/2$ and therefore $E_i = 2/exp(Bv_i)(v_i u_B + 2D_L\theta\omega_i v_i + \theta\delta\omega_i u_B + 2D_B {v_i}^2)$. The updated form of Eq. (22) (not presented here for brevity) can now be rearranged to solve explicitly for the required PRB thickness $\left(B_{req}\right)$ given a maximum target concentration to be achieved at the POC, hence:

$$B_{req} = \frac{2D_B}{u_B - 2D_B v_i}\left[ln\left(\frac{C_{i_{MCL}}}{C_{i_{in}}}\right) + \alpha_i - \left(\frac{u_L}{2D_L} - \omega_i\right)x_{comp}\right], \qquad (23)$$

where x_{comp} is the distance to the POC from the PRB-aquifer interface and $\alpha_i = ln((v_i u_B + 2D_L\theta\omega_i v_i + \theta\delta\omega_i u_B + 2D_B {v_i}^2)/4u_B v_i)$, as defined by Park and Zhan [2009]. Utilizing van Genuchten's [1981] solution, Eykholt and Sivavec [1995] and Eykholt [1997] presented a similar design equation,

$$B_{req} = \frac{2D_B}{u_B - 2D_B v_i} ln\left(\frac{C_{i_{MCL}}}{C_{i_{in}}}\right). \qquad (24)$$

Eq. (24) arises from applying a first-type boundary condition $C(0,t) = C_{i_{in}}$ at the influent face of the PRB and a semi-infinite boundary condition $\frac{\partial C}{\partial x}(\infty, t) = 0$ at the effluent face of the PRB. Although Eq. (24) is convenient, it cannot account for the reaction in the aquifer and it is derived with the assumption that PRBs have large thicknesses. Site data compiled by Gavaskar et al. [2000] indicates most PRBs are 1-2 meters thick. Lastly, it is emphasized that Eqs. (23) and (24) apply only to the special case when *i*=1.

For the case when $i = 2$, Eq. (13) becomes

$$\delta \frac{d^2\overline{C}_{LD2}}{dx_D{}^2} - u_{LD}\frac{d\overline{C}_{LD2}}{dx_D} - (R_{L2}p + \lambda_{LD2})\overline{C}_{LD2} = -y_2\lambda_{LD1}\overline{C}_{LD1}\ , \tag{25}$$

where $\overline{C}_{LD1}$ is Eq. (20) but presented in the slightly different form of

$$\overline{C}_{LD1} = 2v_{D1}u_{BD}exp\left(\frac{u_{BD}}{2}\right)E_{D1}\overline{C}_{D1_{in}}exp\left(\frac{u_{LD}-2\omega_{D1}}{2\delta}x_D\right). \tag{26}$$

Hence the particular solution of Eq. (25) is of the form $\overline{C}_{LD2} = \hat{A}_L exp\left(\frac{u_{LD}-2\omega_{D1}}{2\delta}x_D\right)$, where $\hat{A}_L$ is the coefficient for the aquifer that satisfies the homogeneous part of Eq. (25); i.e.,

$$\hat{A}_L = -2v_{D1}y_2u_{BD}exp\left(\frac{u_{BD}}{2}\right)HE_{D1}\overline{C}_{D1_{in}}\ , \tag{27}$$

where $H(p) = \frac{\lambda_{LD1}}{(R_{L1}-R_{L2})p+\lambda_{LD1}-\lambda_{LD2}}$ is a dimensionless ratio of the reactivities in the aquifer. Therefore, the general solution of Eq. (25) is comprised of the complementary and particular solution such that:

$$\overline{C}_{LD2} = \phi exp\left(\frac{u_{LD}-2\omega_{D2}}{2\delta}x_D\right) - 2v_{D1}y_2u_{BD}exp\left(\frac{u_{BD}}{2}\right)HE_{D1}\overline{C}_{D1_{in}}exp\left(\frac{u_{LD}-2\omega_{D1}}{2\delta}x_D\right), \tag{28}$$

where ϕ depends on the boundary conditions. Performing an analogous procedure for the PRB gives

$$\hat{A}_B = y_2u_{BD}exp\left(\frac{u_{BD}}{2}\right)(\theta\omega_{D1} - v_{D1})H_BE_{D1}\overline{C}_{D1_{in}}\ , \tag{29}$$

$$\hat{B}_B = -y_2u_{BD}exp\left(\frac{u_{BD}}{2}\right)(v_{D1} + \theta\omega_{D1})H_BE_{D1}\overline{C}_{D1_{in}}\ , \tag{30}$$

where $H_B(p) = \frac{\lambda_{BD1}}{(R_{B1}-R_{B2})p+\lambda_{BD1}-\lambda_{BD2}}$. Coefficients $\hat{A}_B$ and $\hat{B}_B$ are defined and derived in Eqs. (S1) through (S11) of Appendix A. Notice that they pertain to the particular solution of the PRB when $i = 2$ and must satisfy the homogenous part of Eq. (S1). Therefore, the general solution of the PRB when *i*=2 is

$$\overline{C}_{BD2} = \alpha\exp\left(\frac{u_{BD} + 2\upsilon_{D2}}{2}x_D\right) + \beta\exp\left(\frac{u_{BD} - 2\upsilon_{D2}}{2}x_D\right) + y_2 u_{BD} exp\left(\frac{u_{BD}}{2}\right)(\theta\omega_{D1} - \upsilon_{D1})H_B E_{D1}\overline{C}_{D1_{in}}\exp\left(\frac{u_{BD}+2\upsilon_{D1}}{2}x_D\right) - y_2 u_{BD} exp\left(\frac{u_{BD}}{2}\right)(\upsilon_{D1} + \theta\omega_{D1})H_B E_{D1}\overline{C}_{D1_{in}}\exp\left(\frac{u_{BD}-2\upsilon_{D1}}{2}x_D\right) \quad (31)$$

where α and β depend on the boundary conditions. After applying the boundary conditions to Eqs. (28) and (31) and determining ϕ, the steady-state analytical solution of species *i*=2 in *dimensional* form is

$$C_{L2} = \left[2\upsilon_2 u_B E_2 C_{2_{in}} + \frac{2\upsilon_1\theta y_2 u_B(H-H_B)\delta(\omega_1-\omega_2)(1-\mu_2)E_1}{\upsilon_2+\theta\delta\omega_2}C_{1_{in}} + 2y_2 u_B C_{1_{in}}(\upsilon_2 H_B E_2 + \upsilon_1(H - H_B)E_1)\right] exp\left(\frac{u_L-2D_L\omega_2}{2D_L}x + \frac{u_B B}{2D_B}\right) - 2\upsilon_1 y_2 u_B H E_1 C_{1_{in}} exp\left(\frac{u_L-2D_L\omega_1}{2D_L}x + \frac{u_B B}{2D_B}\right) \quad (32)$$

where x is the distance to the POC from the PRB-aquifer interface, $\mu_2 = E_2\upsilon_2(u_B - 2D_B\upsilon_2)exp(-B\upsilon_2)$ is dimensionless, $H = \lambda_{L1}/(\lambda_{L1} - \lambda_{L2})$ is also dimensionless, and H_B is of equivalent form to H but with the reactivities of the PRB. Notice that retardation values are eliminated when $p \rightarrow 0$, meaning retardation has no effect at steady-state conditions. It should also be noted that if $C_{1_{in}}$ is zero, Eq. (32) reverts to the form of Eq. (22) for a single species; this supports the validity of Eq. (32).

The procedures outlined above were used to derive the steady-state analytical solution of species three and four. For species *i*=3 the steady-state solution in dimensional form is

$$C_{L3} = \Big\{2\upsilon_3 u_B E_3 C_{3_{in}} + \frac{y_3\gamma(I-I_B)}{\upsilon_3+\theta\delta\omega_3}[\upsilon_3 + \theta\delta\omega_2 - \theta\delta(\omega_2-\omega_3)\mu_3](\alpha+\beta) + \frac{y_3\gamma I_B(\upsilon_2+\theta\delta\omega_2)}{\upsilon_3+\theta\delta\omega_3}(1-\mu_3)\psi + \frac{2\upsilon_1 y_3\gamma y_2 u_B E_1\theta\delta(1-\mu_3)C_{1_{in}}}{\upsilon_3+\theta\delta\omega_3}[(\omega_1-\omega_3)(J_B H_B - JH) + (\omega_2-\omega_3)I(H-H_B)] + 2\upsilon_3 y_3\gamma I_B u_B E_3 C_{2_{in}} + 2y_3\gamma y_2 u_B C_{1_{in}}[\upsilon_1 E_1(J_B H_B - JH + IH - IH_B) - \upsilon_3 E_3 H_B(J_B - I_B)]\Big\}\, exp\left(\frac{u_L-2D_L\omega_3}{2D_L}x + \frac{u_B B}{2D_B}\right) - y_3\gamma I\phi exp\left(\frac{u_L-2D_L\omega_2}{2D_L}x + \frac{u_B B}{2D_B}\right) + 2\upsilon_1 y_3\gamma y_2 u_B JHE_1 C_{1_{in}} exp\left(\frac{u_L-2D_L\omega_1}{2D_L}x + \frac{u_B B}{2D_B}\right), \tag{33}$$

where $\alpha,\ \beta$ and ϕ were defined for species two, $\mu_3 = E_3\upsilon_3(u_B - 2D_B\upsilon_3)exp(-B\upsilon_3)$, $I = \lambda_{L2}/(\lambda_{L2}-\lambda_{L3})$, $J = \lambda_{L2}/(\lambda_{L1}-\lambda_{L3})$, and I_B and J_B pertain to the PRB. Also,

$$\psi = \frac{2\upsilon_1\theta y_2 u_B(H-H_B)\delta(\omega_1-\omega_2)E_1}{\upsilon_2+\theta\delta\omega_2}C_{1_{in}}\ . \tag{34}$$

Notice that the branching ratio γ (gamma) must equal one if serial degradation is assumed since no parallel daughter products are produced [Tratnyek et al., 1997; Clement, 2001].

For species *i*=4 the steady-state solution in dimensional form is

$$C_{L4} = \Big\{2\upsilon_4 u_B E_4 C_{4_{in}} + \frac{y_4(K-K_B)}{\upsilon_4+\theta\delta\omega_4}[\upsilon_4 + \theta\delta\omega_3 - \theta\delta(\omega_3-\omega_4)\mu_4](\varepsilon+\iota) + \frac{y_4 K_B(\upsilon_3+\theta\delta\omega_3)}{\upsilon_4+\theta\delta\omega_4}(1-\mu_4)\sigma + \frac{y_4 y_3\gamma\delta}{\upsilon_4+\theta\delta\omega_4}\dot{\Omega}(\alpha+\beta) + \frac{y_4 y_3\gamma L_B I_B(\upsilon_2+\theta\delta\omega_2)(\mu_4-1)}{\upsilon_4+\theta\delta\omega_4}\psi + \frac{2\upsilon_1 y_4 y_3\gamma y_2 u_B\theta\delta E_1(1-\mu_4)}{\upsilon_4+\theta\delta\omega_4}\ddot{\Omega}C_{1_{in}} + 2\upsilon_4 y_4 u_B K_B E_4 C_{3_{in}} + 2\upsilon_4 y_4 y_3\gamma u_B I_B E_4(K_B - L_B)C_{2_{in}} + 2y_4 y_3\gamma y_2 u_B\dddot{\Omega}C_{1_{in}}\Big\} exp\left(\frac{u_L-2D_L\omega_4}{2D_L}x + \frac{u_B B}{2D_B}\right) - y_4 K\zeta exp\left(\frac{u_L-2D_L\omega_3}{2D_L}x + \frac{u_B B}{2D_B}\right) + y_4 y_3\gamma LI\phi exp\left(\frac{u_L-2D_L\omega_2}{2D_L}x + \frac{u_B B}{2D_B}\right) - 2\upsilon_1 y_4 y_3\gamma y_2 u_B JHME_1 C_{1_{in}} exp\left(\frac{u_L-2D_L\omega_1}{2D_L}x + \frac{u_B B}{2D_B}\right), \tag{35}$$

where $\mu_4 = E_4\upsilon_4(u_B - 2D_B\upsilon_4)exp(-B\upsilon_4)$, $K = \lambda_{L3}/(\lambda_{L3}-\lambda_{L4})$, $L = \lambda_{L3}/(\lambda_{L2}-\lambda_{L4})$, $M = \lambda_{L3}/(\lambda_{L1}-\lambda_{L4})$, and K_B, L_B, and M_B pertain to the PRB; and ε, ι, and ζ are large terms pertaining to species three (see Appendix A). Additionally, the following are defined for species four:

$$\sigma = \frac{y_3\gamma\theta(I-I_B)\delta(\omega_2-\omega_3)}{\upsilon_3+\theta\delta\omega_3}(\alpha+\beta) + \frac{y_3\gamma I_B(\upsilon_2+\theta\delta\omega_2)}{\upsilon_3+\theta\delta\omega_3}\psi + \frac{2\upsilon_1 y_3\gamma y_2 u_B\theta\delta E_1}{\upsilon_3+\theta\delta\omega_3}C_{1_{in}}[(\omega_1 - \omega_3)(J_B H_B - JH) + (\omega_2-\omega_3)I(H-H_B)]\,, \tag{36}$$

$$\dot{\Omega} = (L_B I_B - LI)\left(\frac{\upsilon_4}{\delta} + \theta\omega_2 - \theta(\omega_2-\omega_4)\mu_4\right) + K(I_B - I)\left(\theta(\omega_3-\omega_4)\mu_4 - \frac{\upsilon_4}{\delta} - \theta\omega_3\right) \tag{37}$$

$$\ddot{\Omega} = (\omega_1-\omega_4)(JHM - J_B H_B M_B) + LI(\omega_2-\omega_4)(H_B - H) + K(\omega_3-\omega_4)\big(H_B(J_B - I) - H(J-I)\big) \tag{38}$$

$$\dddot{\Omega} = \upsilon_1 E_1\big(J_B H_B(K-M_B) + JH(M-K) + I(H-H_B)(K-L)\big) + \upsilon_4 E_4 H_B\big(I_B(K_B-L_B) + J_B(M_B-K_B)\big) \tag{39}$$

It should also be noted that Eqs. (32), (33), and (35) cannot be solved explicitly for B, hence a coded program or spreadsheet is the most efficient way to utilize the steady-state solutions. Also the denominators of H, H_B, I, I_B, J, J_B, K, K_B, L, L_B, M, and M_B *cannot be zero* in order for the equations to be defined; i.e., in the case when interspecies reaction rate factors equal each other. This restriction, however, does not apply to the transient solutions, unless the interspecies retardation factors equal each other. Detailed derivations of species 2, 3, and 4 are provided in Appendix A.

3. COMPARISON OF THE SERIAL DEGRADATION SOLUTIONS & VMOD

In this section the steady-state analytical solutions presented above are compared to the sequential decay reaction module in the RT3D v2.5 transport engine of Visual MODFLOW (VMOD) 2009. In applying the above equations it is reminded that the transport and flow parameters assigned to the aquifer depend on accurate site characterization while the transport parameters assigned to the PRB are determined using the normalization method proposed by Johnson et al. [1996] and subsequently adopted by the EPA [1998]. A brief review of the normalization method is provided below.

In an extensive review of prior studies on dechlorination by zero-valent iron (ZVI), Johnson et al. [1996] demonstrated that observed first-order reaction rates (λ_{obs}) of any one chemical varied by up to three orders of magnitude. To reduce this apparent variability Johnson et al. [1996] expanded the first-order rate (*R*) model to account for the amount of available metal in the reaction and normalized the reaction rates to the iron surface area concentration (ρ_a); i.e,

$R = -\lambda_{SA} a_s \rho_m C$, or

$$R = -\lambda_{SA} \rho_a C \tag{40}$$

where λ_{SA} is the specific reaction rate constant [L hr^{-1}m^{-2}], a_s is the specific surface area [m^{2}g^{-1}] determined by the Brunauer, Emmett, and Teller (BET) gas adsorption method, ρ_m is the iron mass per *solution* volume or mass concentration [g L^{-1}], and ρ_a is the iron surface area per *solution* volume or surface area concentration [m^{2}L^{-1}]. Therefore, $\lambda_{obs} = \lambda_{SA} \rho_a$ where λ_{SA} is a species-specific rate constant that is determined from the linear regression of λ_{obs} and ρ_a. By repeating this procedure on individual chemicals, Johnson et al. [1996] provided a list of more rigorously derived λ_{SA} values exhibiting differences of one order of magnitude, instead of three orders of magnitude. The list of λ_{SA} constants were not differentiated between column and batch tests. For the purpose of modeling, all subsequent uses of λ imply λ_{obs} was properly derived from λ_{SA}.

To compare the multispecies steady-state analytical solutions with a numerical solution required creating both a spreadsheet program and a finite-difference grid in VMOD to simulate the degradation of PCE → TCE → DCE → VC. The finite-difference grid modeled one-dimensional flow along a 20 m long domain, of which the first 0.5 m was assigned as the thickness (B) of the upgradient PBR zone. The domain also consisted of a 10 m upgradient head, a 9.9 m downgradient head, and a 5 m width. Other flow parameters assigned to the domain included an aquifer effective porosity (n_L) of 0.3, a PRB hydraulic conductivity (k_B) of 60 m/d, and an aquifer hydraulic conductivity (k_L) of 20 m/d. Using the above flow parameters discharge is $Q = k_L A i = 5$ m^3/d. Note that since PRBs are thin, relative to the adjacent aquifer, their effect on the large-scale conductivity of the site is insignificant. Therefore, the discharge value of 5 m^3/d is an acceptable approximation. Also, according to the VMOD geometric multigrid (GMG) flow solver, the seepage velocity in the aquifer is 3.38E-01 m/d. This value can also be confirmed analytically by using the above parameters; i.e., $u_L = k_L i / n_L$= 0.33 m/d. Additionally, since specific discharge at the PRB-aquifer interface is uniform, the seepage velocity in a PRB with effective porosity of n_B =0.5 is $u_B = u_L n_L / n_B$= 0.2 m/d. This value also agrees with the numerical output of 2.03E-01 m/d. It should be noted that although the aquifer conductivity modeled is elevated it was essential in facilitating the convergence of the RT3D engine to steady-state concentrations within a reasonable time limit. Table 1 illustrates the portion of the attached spreadsheet program where the flow parameters (including dispersivity) are designated and others (such as dispersion) are calculated.

Table 1: Modeled Flow Parameters

Domain Parameters		PRB Parameters		Aquifer Parameters	
θ (-)	0.6	$n_{e\text{-}B}$ (-)	0.5	$n_{e\text{-}L}$ (-)	0.3
		B_{req} (m)	0.5	x (m)	0
width (m)	5				
h_{upgrad} (m)	10				
$h_{downgrad}$ (m)	9.9				
L (m)	20				
Grad (-)	0.005				
		k_B (m day^{-1})	60	k_L (m day^{-1})	20
		u_B (m day^{-1})	0.20	u_L (m day^{-1})	0.33
Q (m^3 day^{-1})	5				
		α_B (m)	0.05	α_L (m)	2
δ (-)	66.67	D_B (m^2 day^{-1})	0.01	D_L (m^2 day^{-1})	0.67

The transport parameters such as yield, reaction rate, and influent concentration of each species are presented in Table 2 as they would be entered into the spreadsheet program. At this stage all necessary information is defined and the program conveniently calculates all other constants utilized in the steady-state analytical solutio-

Table 2: Modeled Transport Parameters

Species 1					
E_1 (day)	1.53E-05	λ_{B1} (day^{-1})	2.0	λ_{L1} (day^{-1})	0.2
		v_1 (m^{-1})	1.73E+01	ω_1 (m^{-1})	6.02E-01
Species 2					
E_2 (day)	8.16E-05	λ_{B2} (day^{-1})	1.2	λ_{L2} (day^{-1})	0.05
Y_2 (-)	0.792	v_2 (m^{-1})	1.48E+01	ω_2 (m^{-1})	3.71E-01
		H_B (-)	2.50E+00	H_L (-)	1.33E+00
Species 3					
E_3 (day)	1.05E-04	λ_{B3} (day^{-1})	1.1	λ_{L3} (day^{-1})	0.03
Y_3 (-)	0.738	v_3 (m^{-1})	1.45E+01	ω_3 (m^{-1})	3.28E-01
γ_{branch} (-)	1	I_B (-)	1.20E+01	I_L (-)	2.50E+00
		J_B (-)	1.33E+00	J_L (-)	2.94E-01
Species 4					
E_4 (day)	1.65E-04	λ_{B4} (day^{-1})	0.9	λ_{L4} (day^{-1})	0.02
Y_4 (-)	0.644	v_4 (m^{-1})	1.38E+01	ω_4 (m^{-1})	3.04E-01
		K_B (-)	5.50E+00	K_L (-)	3.00E+00
		L_B (-)	3.67E+00	L_L (-)	1.00E+00
		M_B (-)	1.00E+00	M_L (-)	1.67E-01
C_{1in} (mg L^{-1})	10			**C_{L1} (mg L^{-1})**	1.58E-01
C_{2in} (mg L^{-1})	15			**C_{L2} (mg L^{-1})**	2.14E+00
C_{3in} (mg L^{-1})	5			**C_{L3} (mg L^{-1})**	3.80E+00
C_{4in} (mg L^{-1})	3			**C_{L4} (mg L^{-1})**	3.92E+00

ns. For example, in this scenario the PRB reaction rate constants of species 1, 2, 3, and 4 are 2 d^{-1}, 1.2 d^{-1}, 1.1 d^{-1}, and 0.9 d^{-1} while in the aquifer the weaker reaction rates are 0.2 d^{-1}, 0.05 d^{-1}, 0.03 d^{-1}, and 0.02 d^{-1}. The trend of decreasing reaction rates is intended to simulate the decreasing dechlorination potential of each subsequent daughter species in the aquifer [Wiedemeier et al., 1999] and in the PRB [Matheson and Tratnyek, 1994]. After inputting the reaction rate constants the programs calculate the values of υ_i, ω_i, E_i, and the dimensionless ratios of the reactivities. Lastly, the user inputs the pertinent stoichiometric yields and influent concentrations of each species. The programs then calculate the concentration of each species at the designated POC (the x in Table 1), which is downgradient of the PRB-aquifer interface.

The results of the RT3D numerical solution were exported and the concentration distribution of each species was plotted along with select concentration points from the steady-state analytical solutions of this study. As seen in Figures 3 and 4, the two methods agree particularly well in the aquifer zone where the discrete concentration points coincide with the lines representing the numerical solution. Two additional sets of figures comparing the analytical solutions with VMOD are included in Appendix B.

Applying the spreadsheet programs in a real scenario is straightforward; the designer inputs the site gradient and the conductivity of the aquifer (or groundwater velocity only), the porosity and dispersivity of each medium, and the distance (x) to the downgradient POC. The transport parameters required include the reaction rate constants, stoichiometric yields, and influent concentrations. To determine B_{req}, the designer increases the value of B until all species meet the required concentration at the POC; alternatively, the Microsoft Excel tool *Goal Seek* performs the same function. A minimum input value of B_{req}= 0.5 is recommended for goal seek to return a non-negative width. It is worthwhile to note that these equations can be applied to any other four species reacting in a serial chain reaction and to other types of dual domain systems. For example, the equations can also be used for two adjacent aquifer zones where an oxidizing zone transitions into a reducing zone. As another example, if the reaction

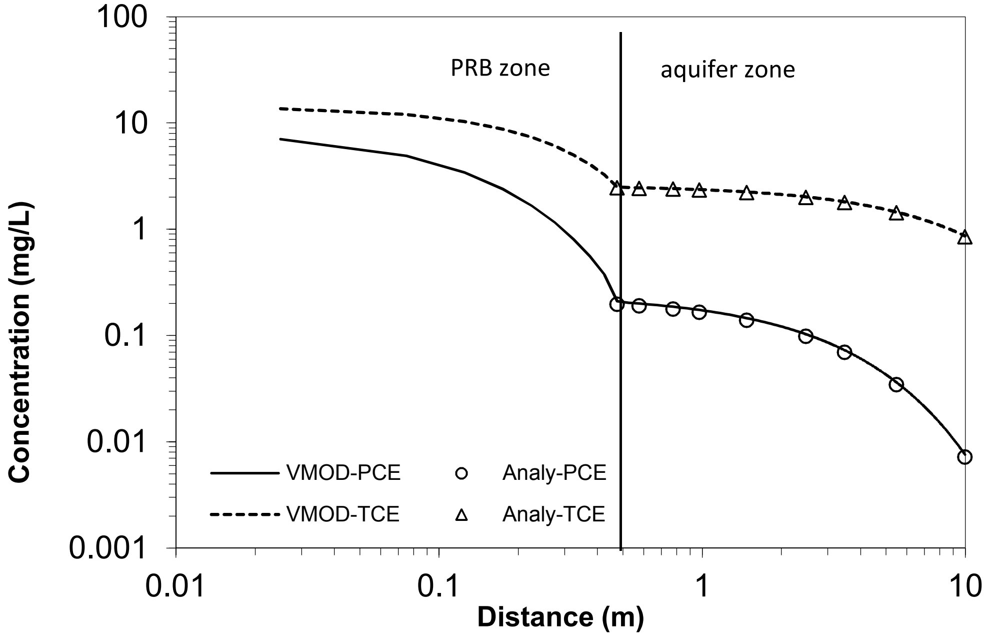


Figure 3: Comparison of the analytical solutions & VMOD: PCE & TCE

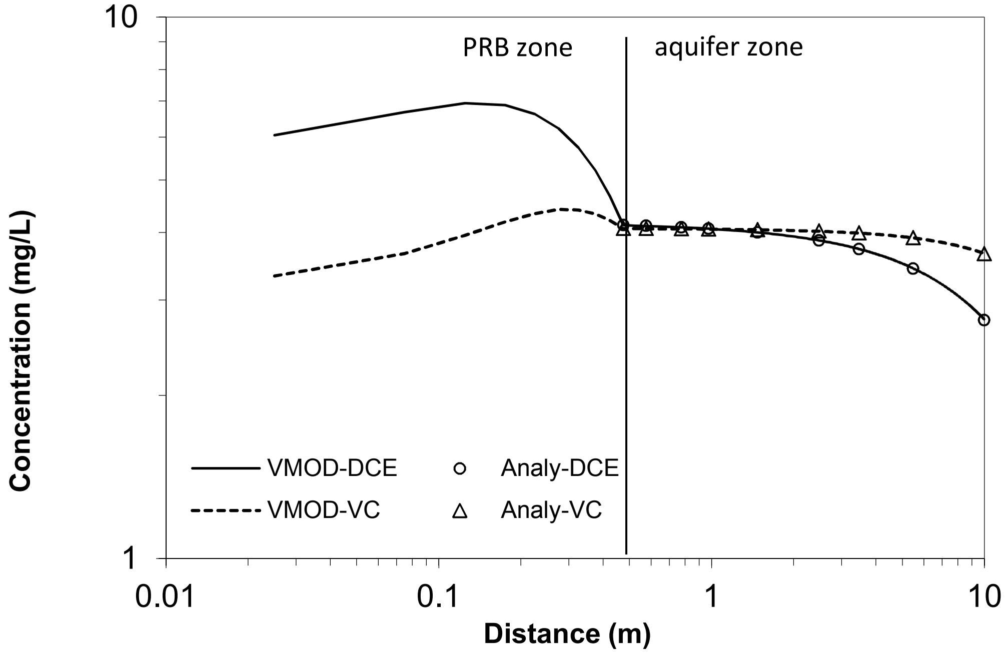


Figure 4: Comparison of the analytical solutions & VMOD: DCE & VC

involves only three species, then both y_4 and $C_{4_{in}}$ are zero, and so on if only two species react. Overall, the multi-species steady-state analytical solutions presented in this study can be quickly implemented using the spreadsheet programs which are cost-effective compared to the standard numerical program, hence the solutions are useful as PRB design equations.

Once the barrier width is calculated the required mass of reactive material in the PRB is currently determined using the EPA [1998] mass estimation calculation, which is fundamentally derived from Eq. (24) without dispersion. For example, if dispersion is neglected Eq. (24) becomes the common plug flow reactor equation

$$B_{req} = -\frac{u_B}{\lambda_{obs}} ln\left(\frac{C_{MCL}}{C_{in}}\right) = -\frac{u_B}{\lambda_{SA} a_s \rho_m} ln\left(\frac{C_{MCL}}{C_{in}}\right) = -\frac{u_B V_w}{\lambda_{SA} a_s M_S} ln\left(\frac{C_{MCL}}{C_{in}}\right), \qquad (41)$$

where M_S is the mass of the solid iron grains and V_w is the solution volume in the PRB, as discussed above. In the case of a continuous PRB, the total volume is simply $V_T = B_{req}A$, where A is the designed area of the PRB normal to the groundwater flow direction. Also, $n = V_w/V_T$ is the PRB porosity, assuming installation in the saturated zone where the volume of air is negligible. Therefore, $V_w = nB_{req}A$ and (41) becomes,

$$M_S = -\frac{u_B n A}{\lambda_{SA} a_s} ln\left(\frac{C_{MCL}}{C_{in}}\right) \Rightarrow \frac{M_S}{A} = -\frac{u_B n}{\lambda_{SA} a_s} ln\left(\frac{C_{MCL}}{C_{in}}\right), \qquad (42)$$

where Eq. (42) is the exact EPA [1998] mass estimation formula and M_S/A is the iron mass per unit area. In this study, an alternative mass estimation calculation is derived. The alternative calculation relies on first determining B_{req} from the attached multispecies-reactive transport spreadsheet programs and subsequently utilizing the relationship

$$V_T = B_{req}A = V_w + V_s \,, \tag{43}$$

where V_s is the volume of iron solids and the volume of air is neglected. Substituting the iron grain (or particle) density $\rho_g = M_s/V_s$ and iron mass concentration $\rho_m = M_s/V_w$ into Eq. (43) yields

$$\frac{M_S}{A} = B_{req}\frac{\rho_g\rho_m}{\rho_g+\rho_m} = B_{req}n\rho_m \text{ , or simply}$$

$$\frac{M_S}{A} = B_{req}\rho_b \,, \tag{44}$$

where $\rho_b = M_s/V_T$ is the dry bulk density of ZVI, of which several values are reported by Gavaskar et al. [2000] and the EPA [1998]. According to the EPA, ZVI bulk density is typically 2.56 g/cm^3. As an example of Eq. (44), the continuous PRB installed in the U.S. Coast Guard (USCG) Support Center near Elizabeth City, North Carolina was designed with a reactive cell height of 5.5 m, length of 46 m, thickness of 0.6 m, and 450 tons (408,233 kg) of granular iron [EPA, 1999]. Based on this data $\frac{M_S}{AB_{req}} = \rho_b = 2.69$ g/cm^3, which is well within the normal range of reported iron bulk densities. Therefore, Eq. (44) can be used to estimate M_S/A once B_{req} and ρ_b are known. Lastly, PRBs tend to be designed with a factor of safety applied to B_{req} [Eykholt, 1997] and a reaction rate correction adjustment factor due to lower subsurface temperatures [Gavaskar et al., 2000]. Note that Eqs. (44) and (40) provide the necessary flexibility to incorporate the factor of safety and the reaction rate adjustment.

4. MODEL DEVELOPMENT – PARALLEL DEGRADATION SOLUTIONS

Several authors including Wiedemeier et al. [1999] have noted the parallel pathway by which TCE degrades to simultaneously produce 1,1-DCE, cis-1,2-DCE, and trans-1,2-DCE. In practice, however, these isomers are typically lumped together into one species. It is important to note that in reality each DCE isomer may have a unique reaction rate and therefore acquire mass and contribute mass at a different rate. The hydrogenolysis degradation model of PCE → TCE → DCE isomers → VC is the sequential replacement of one chlorine atom with one hydrogen atom in which VC acquires mass from convergent multi-parent reactions; i.e., the three DCE isomers degrade to VC. In examining the abiotic reaction between the common chlorinated ethylenes and ZVI, Roberts et al. [1996] and Arnold and Roberts [2000] expanded the hydrogenolysis model to include a separate β-elimination pathway in which PCE → dichloroacetylene → chloroacetylene → acytelene. Degradation in this expanded model is a highly complex network of various multi-parent and multi-daughter reactions where even the hydrogenolysis pathway and the β-elimination (or chlorinated acetylene) pathway exchange mass. Complexity of this level is not practical for the purpose of analytical modeling; hence this study considers the degradation network illustrated in Figure 5 to be a reasonable simplification. The absence of the dichloroacetylene intermediary from Figure 5 is justified since it tends to react very rapidly with ZVI [Roberts et al., 1996; Arnold and Roberts, 2000]. After considering the model in Figure 5, the PRB and aquifer governing equations of species 1 and 2 are unchanged [Rodiguin and Rodiguina, 1964]. However, the governing equations of species DCE1 (SP31),

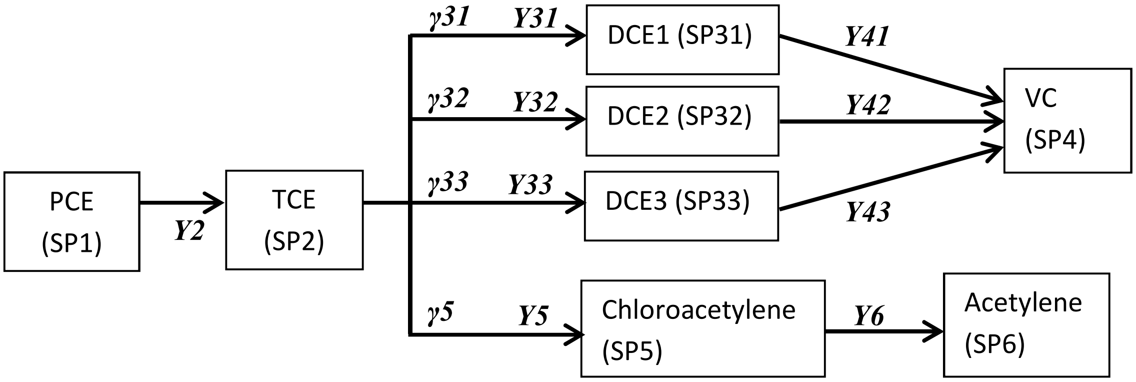


Figure 5: Conceptual view of the parallel degradation pathway of PCE. ***Y*** – denotes the stoichiometric yield of the daughter product from the parent chemical. ***γ*** – gamma denotes the branch factor. Note: the sum of all branch factors should equal 1 to appropriately account for mass.

DCE2 (SP32), DCE3 (SP33), and chloroacetylene (SP5) are revised as follows:

$$R_{B3i}\frac{\partial C_{B3i}}{\partial t}=\mathcal{L}(C_{B3i})-\lambda_{B3i}C_{B3i}+\gamma_{3i}y_{3i}\lambda_{B2}C_{B2}\ , \tag{45}$$

$$R_{B5}\frac{\partial C_{B5}}{\partial t}=\mathcal{L}(C_{B5})-\lambda_{B5}C_{B5}+\gamma_{5}y_{5}\lambda_{B2}C_{B2}\ , \tag{46}$$

for the PRB, and for the aquifer:

$$R_{L3i}\frac{\partial C_{L3i}}{\partial t}=\mathcal{L}(C_{L3i})-\lambda_{L3i}C_{L3i}+\gamma_{3i}y_{3i}\lambda_{L2}C_{L2}\ , \tag{47}$$

$$R_{L5}\frac{\partial C_{L5}}{\partial t}=\mathcal{L}(C_{L5})-\lambda_{L5}C_{L5}+\gamma_{5}y_{5}\lambda_{L2}C_{L2}\ , \tag{48}$$

where i is a counter from 1 to 3 and γ is the branching ratio previously defined, which is now less than one for each species but should satisfy $\gamma_{31}+\gamma_{32}+\gamma_{33}+\gamma_5=1$ [Clement, 2001]. With the exception of the branching ratio not equaling 1, Eqs. (45) through (48) are equivalent in form to Eqs. (2) and (5) of the serial degradation scenario i=3; therefore, the steady-state analytical solution to Eqs. (45) and (47) is equivalent in form to Eq. (33), where α, β and ϕ are unchanged. As seen in Table 3, the major difference arises in the values of the dimensionless reactivity ratios; i.e., $I_{3i}=\lambda_{L2}/(\lambda_{L2}-\lambda_{L3i})$, $J_{3i}=\lambda_{L2}/(\lambda_{L1}-\lambda_{L3i})$, where I_{B3i} and J_{B3i} pertain to the PRB. Similarly, the steady-state dimensional forms of υ and ω are $\upsilon_{3i}=\sqrt{u_B{}^2/4D_B{}^2+\lambda_{B3i}/D_B}$ and $\omega_{3i}=\sqrt{u_L{}^2/4D_L{}^2+\lambda_{L3i}/D_L}$ where i is the counter defined above. (The same analyses apply to $I_5, J_5, I_{B5}, J_{B5}, \upsilon_5$, and ω_5 which pertain to species 5.)

Table 3: Modeled Transport Parameters of SP3*i* and SP5

Species 3-1 (1,1-DCE)					
E_{3-1} (day)	1.05E-04	λ_{B3-1} (day^{-1})	1.10	λ_{L3-1} (day^{-1})	0.03
Y_{3-1} (-)	0.738	v_{3-1} (m^{-1})	1.45E+01	ω_{3-1} (m^{-1})	3.28E-01
γ_{3-1} (-)	0.25	I_{B3-1} (-)	1.20E+01	I_{L3-1} (-)	2.50E+00
		J_{B3-1} (-)	1.33E+00	J_{L3-1} (-)	2.94E-01
Species 3-2 (Cis-1,2-DCE)					
E_{3-2} (day)	1.05E-04	λ_{B3-2} (day^{-1})	1.10	λ_{L3-2} (day^{-1})	0.03
Y_{3-2} (-)	0.738	v_{3-2} (m^{-1})	1.45E+01	ω_{3-2} (m^{-1})	3.28E-01
γ_{3-2} (-)	0.25	I_{B3-2} (-)	1.20E+01	I_{L3-2} (-)	2.50E+00
		J_{B3-2} (-)	1.33E+00	J_{L3-2} (-)	2.94E-01
Species 3-3 (Trans-1,2-DCE)					
E_{3-3} (day)	1.05E-04	λ_{B3-3} (day^{-1})	1.10	λ_{L3-3} (day^{-1})	0.03
Y_{3-3} (-)	0.738	v_{3-3} (m^{-1})	1.45E+01	ω_{3-3} (m^{-1})	3.28E-01
γ_{3-3} (-)	0.25	I_{B3-3} (-)	1.20E+01	I_{L3-3} (-)	2.50E+00
		J_{B3-3} (-)	1.33E+00	J_{L3-3} (-)	2.94E-01
Species 5 (Chloroacetylene)					
E_{5} (day)	1.05E-04	λ_{B5} (day^{-1})	1.10	λ_{L5} (day^{-1})	0.03
Y_{5} (-)	0.460	v_{5} (m^{-1})	1.45E+01	ω_{5} (m^{-1})	3.28E-01
γ_{5} (-)	0.25	I_{B5} (-)	1.20E+01	I_{L5} (-)	2.50E+00
		J_{B5} (-)	1.33E+00	J_{L5} (-)	2.94E-01

The current version of RT3D preprogrammed in VMOD does not include this type of parallel multispecies degradation model. To formally compare the analytical solutions of Eqs. (45)-(48) with a numerical model requires creating a program in the user-defined RT3D reaction module programmed by Clement et al. [1998]. This study presents an alternative method of testing the validity of the (parallel degradation) solutions that is based on the conservation of total concentration between the serial and parallel chains. For example, if each of the four branch factors equals 0.25 and all interspecies stoichiometric yields and first-order reaction rates are equal (as designated in Table 3), then SP3i and SP5 gain and lose moles at the same rate. That is, SP3i and SP5 react (degrade) at the same rate. Therefore, it is expected that 1) at a selected POC SP3i and SP5 exhibit identical concentrations and 2) the total of their summed concentrations is equal to one *effective* SP3 concentration. This *effective* SP3 concentration should exactly equal the SP3 concentration from the serial degradation pathway (discussed in Section 2). A final assumption (which facilitates this test but is not required) is to treat SP3i, SP5, and SP3 as daughter products of weathered TCE; i.e., their influent concentrations are zero. This test was performed on several discrete points and with several decay constants and found to be exactly as predicted. Additionally, it should be pointed out that the spreadsheet program is sufficiently flexible to model only the parallel hydrogenolysis pathway by neglecting the β-elimination pathway altogether. Such an assumption is conservative in dealing with the chlorinated ethylenes and can be accomplished simply by letting y_5, $C_{5_{in}}$, and $C_{6_{in}}$ equal zero and assuring that $\gamma_{31} + \gamma_{32} + \gamma_{33} = 1$. However, caution should be taken in establishing this assumption as the norm. Chlorinated acetylenes are reported to be toxic [Roberts et al., 1996]. Although they degrade rapidly in laboratory studies [Roberts et al., 1996; Arnold and Roberts, 2000], it is uncertain to what extent they accumulate as PRB effluents in the field.

The next chemical in Figure 5, SP4, gains mass from convergent multiparent reactions. In this case the updated governing equations of SP4 are:

$$R_{B4}\frac{\partial C_{B4}}{\partial t} = \mathcal{L}(C_{B4}) - \lambda_{B4}C_{B4} + y_{41}\lambda_{B31}C_{B31} + y_{42}\lambda_{B32}C_{B32} + y_{43}\lambda_{B33}C_{B33}\ , \qquad (49)$$

$$R_{L4}\frac{\partial C_{L4}}{\partial t} = \mathcal{L}(C_{L4}) - \lambda_{L4}C_{L4} + y_{41}\lambda_{L31}C_{L31} + y_{42}\lambda_{L32}C_{L32} + y_{43}\lambda_{L33}C_{L33}\ , \qquad (50)$$

[Rodiguin and Rodiguina, 1964] where y_{41}, y_{42}, and y_{43} are generally distinctive stoichiometric yields, but in this case they are equivalent due to the DCE isomers. Applying the dimensionless parameters in Eq. (9) and the Laplace transform to Eqs. (49) and (50) gives

$$\frac{d^2\overline{C}_{BD4}}{dx_D{}^2} - u_{BD}\frac{d\overline{C}_{BD4}}{dx_D} - (R_{B4}p + \lambda_{BD4})\overline{C}_{BD4} = -y_{41}\lambda_{BD31}\overline{C}_{BD31} - y_{42}\lambda_{BD32}\overline{C}_{BD32} - y_{43}\lambda_{BD33}\overline{C}_{BD33}\,, \tag{51}$$

$$\delta\frac{d^2\overline{C}_{LD4}}{dx_D{}^2} - u_{LD}\frac{d\overline{C}_{LD4}}{dx_D} - (R_{L4}p + \lambda_{LD4})\overline{C}_{LD4} = -y_{41}\lambda_{LD31}\overline{C}_{LD31} - y_{42}\lambda_{LD32}\overline{C}_{LD32} - y_{43}\lambda_{LD33}\overline{C}_{LD33}\,. \tag{52}$$

Recall that in the case of the serial degradation pathway, the steady-state analytical solution of SP4 was presented as Eq. (35). Also recall that in the serial degradation pathway, the boundary conditions were applied once. After comparing the right-hand side of Eqs. (11) and (13) with the right-hand side of Eqs. (51)-(52), it becomes apparent that the general procedure used to determine Eq. (35) can also be used to solve Eqs. (51)-(52), with a slight variation. To solve Eqs. (51)-(52), the boundary conditions are now applied two additional times to the two additional terms on the right-hand side; i.e., the terms associated with $\overline{C}_{D32}$ and $\overline{C}_{D33}$. This realization allows one to quickly deduce the analytical solution of SP4 for the *parallel* degradation pathway and avoid the very long derivation required to manually solve Eqs. (51)-(52). Therefore, the solution to a daughter product that results from a convergent multi-parent reaction can be determined by applying the boundary conditions once to each additional term on the right-hand side. Inevitably, this procedure results in additional terms that are (at every algebraic step) added to the derivation, resulting in a much longer analytical solution. The resulting steady-state analytical solution of SP4 is particularly long and is included in Appendix A.

To test the validity of this solution, the concentration conservation technique introduced above is revisited. In this case the following are assumed: let γ_5 (or y_5) and $C_{3i_{in}}$equal zero, let all y_{4i} equal each other, let $\gamma_{31} = \gamma_{32} = \gamma_{33} = 1/3$, and let all stoichiometric yields and first-order reaction rates pertaining to SP3i equal each other. The physical representation of these assumptions is that SP4 gains the same amount of moles from each SP3i isomer at the same rate. In this case, the SP3i variants again mimic one *effective* SP3 chemical. Therefore, the SP4 concentration from the parallel degradation pathway should exactly equal the SP4 concentration from the serial degradation pathway. This test was performed on several discrete points and with several decay constants and also found to be exactly as predicted. Table 4 below presents the modified inputs of SP4 in the case of the parallel degradation reaction. As seen in Table 4, the rate at which SP4 degrades is unchanged from the serial degradation model; i.e., the values of υ_4 and ω_4 do not change from Table 2 to Table 4. However, the additional terms on the right-hand-side of Eqs. (49) and (50) require that the analytical solution of SP4 account for potentially different rates of mass contribution from each of the three DCE isomers. Hence K_{3i}, L_{3i}, and M_{3i} are defined for the aquifer and K_{B3i}, L_{B3i}, and M_{B3i} pertain to the PRB, where i is the counter from 1 to 3.

Table 4: Modeled Transport Parameters of SP4

Species 4 (VC)					
E_4 (day)	1.65E-04	λ_{B4} (day^{-1})	0.90	λ_{L4} (day^{-1})	0.02
$Y_{4/3\text{-}1}$ (-)	0.644	v_4 (m^{-1})	1.38E+01	ω_4 (m^{-1})	3.04E-01
$Y_{4/3\text{-}2}$ (-)	0.644	$K_{B3\text{-}1}$ (-)	5.50E+00	$K_{L3\text{-}1}$ (-)	3.00E+00
$Y_{4/3\text{-}3}$ (-)	0.644	$L_{B3\text{-}1}$ (-)	3.67E+00	$L_{L3\text{-}1}$ (-)	1.00E+00
		$M_{B3\text{-}1}$ (-)	1.00E+00	$M_{L3\text{-}1}$ (-)	1.67E-01
		$K_{B3\text{-}2}$ (-)	5.50E+00	$K_{L3\text{-}2}$ (-)	3.00E+00
		$L_{B3\text{-}2}$ (-)	3.67E+00	$L_{L3\text{-}2}$ (-)	1.00E+00
		$M_{B3\text{-}2}$ (-)	1.00E+00	$M_{L3\text{-}2}$ (-)	1.67E-01
		$K_{B3\text{-}3}$ (-)	5.50E+00	$K_{L3\text{-}3}$ (-)	3.00E+00
		$L_{B3\text{-}3}$ (-)	3.67E+00	$L_{L3\text{-}3}$ (-)	1.00E+00
		$M_{B3\text{-}3}$ (-)	1.00E+00	$M_{L3\text{-}3}$ (-)	1.67E-01

The final chemical in Figure 5, SP6, results only from the degradation of Chloroacetylene, hence its governing equations are:

$$R_{B6}\frac{\partial C_{B6}}{\partial t} = \mathcal{L}(C_{B6}) - \lambda_{B6}C_{B6} + y_6\lambda_{B5}C_{B5} \tag{53}$$

$$R_{L6}\frac{\partial C_{L6}}{\partial t} = \mathcal{L}(C_{L6}) - \lambda_{L6}C_{L6} + y_6\lambda_{L5}C_{L5} \tag{54}$$

Notice that Eqs. (53) and (54) are equivalent in form to Eqs. (2) and (5) of the serial degradation scenario i=4. Therefore, the steady-state analytical solution of SP6 can be validated by treating the β-elimination pathway as the sole serial degradation pathway and neglecting the hydrogenolysis pathway. That is, let γ_{3i} (or y_{3i}) $= 0$, $\gamma_5 = 1$, allow y_5 and y_6 to equal y_3 and y_4 (respectively), and assign the same reaction rates of SP4 from Table 2 to SP6. In this case, the SP6 analytical solution is validated if SP6 exactly matches the concentration of SP4 in the serial degradation section of this study. This final test was performed on several discrete points and with several decay constants and found to be exactly as predicted.

5. SUMMARY AND CONCLUSIONS

In this study, the Park and Zhan [2009] solution technique is used to derive steady-state analytical and transient semi-analytical solutions to multispecies reactive transport in a PRB-aquifer (dual domain) system. The study focuses primarily on the steady-state analytical solutions of the PCE serial degradation pathway and secondly on the analytical solutions of the parallel degradation pathway. These solutions are not restricted solely to the PRB-aquifer model since they can also be applied to other types of dual domain systems with distinct flow and transport properties and up to four other decaying species. Like the single-species Park and Zhan [2009] solution, these additional solutions maintain flux and concentration continuity at the PRB-aquifer interface and account for the potential existence of natural degradation in the downgradient aquifer. Degradation in the aquifer can be incorporated into the solutions when considering the required PRB thickness so that all species involved in the degradation pathway achieve the regulatory limits at the POC.

In addition to the study, spreadsheet programs and appendices are included to facilitate review of the derivations and prompt application of the steady-state solutions. It is noted that the solution technique results in long equations, particularly in the parallel decay network, but at this expense the solutions provide increased modeling flexibility. For example: every species can have unique reaction rates, higher order daughter species can be modeled solely as byproducts by neglecting their input concentrations, segments of the parallel degradation pathway can be neglected depending on the desired degradation model, and converging multi-parent reactions can be modeled. Additionally, it should be noted that although the transient semi-analytical solutions are not reviewed here, they can be deduced from the derivations provided in Appendix A. However, a numerical inversion program is needed to obtain a solution in the time domain.

Lastly, the transient solutions have the additional flexibility to incorporate species-specific distribution coefficients (Kd_i) and medium-dependent bulk densities; therefore, retardation factors can vary from species to species and also vary due to a change in medium, even if the species is the same. The ability to model with differing retardation factors is an additional benefit of these solutions since differing retardation factors are not possible in the Sun et al. [2004] solution technique and both species-specific retardation factors and convergent reactions are not possible in the Sun et al. [1999] solution.

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APPENDIX A

The derivational details of each species are provided here in supplementary equations for the case of both the serial degradation pathway and the parallel degradation pathway. Some procedures that are repeated for all species were omitted in the derivation of higher order daughter species. Therefore, a more detailed derivation is provided for species 2. Lastly, the semi-analytical solution of species 1 (SP1) – or more generally the homogeneous (complementary) solution – is not included here, see Park and Zhan [2009] for the full derivation.

Serial Degradation Pathway

This section provides the derivational details of SP2, SP3, and SP4 from Figure 2.

Species 2:

The governing equations of species 2 (SP2) can be inferred from Eqs. (2) and (5) when $i = 2$. After applying the dimensionless parameters in Eq. (9) and the Laplace transform, the governing equations become Eqs. (11) and (13) for $i = 2$. Therefore the general solution of the PRB and aquifer are:

$$\overline{C}_{BD2} = \alpha \exp\left(\frac{u_{BD} + 2v_{D2}}{2} x_D\right) + \beta \exp\left(\frac{u_{BD} - 2v_{D2}}{2} x_D\right) + \hat{A}_B exp\left(\frac{u_{BD} + 2v_{D1}}{2} x_D\right) + \hat{B}_B \exp\left(\frac{u_{BD} - 2v_{D1}}{2} x_D\right) \tag{S1}$$

$$\overline{C}_{LD2} = \phi exp\left(\frac{u_{LD} - 2\omega_{D2}}{2\delta} x_D\right) + \hat{A}_L exp\left(\frac{u_{LD} - 2\omega_{D1}}{2\delta} x_D\right). \tag{S2}$$

Notice that the last two terms in Eq. (S1) and the last term in Eq. (S2) represent the particular solutions, hence it is assumed that

$$\overline{C}_{BD2_{part}} = \hat{A}_B exp\left(\frac{u_{BD}+2v_{D1}}{2} x_D\right) + \widehat{B}_B \ \exp\left(\frac{u_{BD}-2v_{D1}}{2} x_D\right), \tag{S3}$$

$$\overline{C}_{LD2_{part}} = \hat{A}_L exp\left(\frac{u_{LD}-2\omega_{D1}}{2\delta} x_D\right), \tag{S4}$$

where the coefficients $\hat{A}_B$, $\widehat{B}_B$, and $\hat{A}_L$ must satisfy their respective homogeneous solution, therefore:

$$\frac{d\overline{C}_{BD2_{part}}}{dx_D} = \hat{A}_B \left(\frac{u_{BD}+2v_{D1}}{2}\right) exp\left(\frac{u_{BD}+2v_{D1}}{2} x_D\right) + \widehat{B}_B \ \left(\frac{u_{BD}-2v_{D1}}{2}\right) \exp\left(\frac{u_{BD}-2v_{D1}}{2} x_D\right), \tag{S5}$$

$$\frac{d^2\overline{C}_{BD2_{part}}}{dx_D{}^2} = \hat{A}_B \left(\frac{u_{BD}+2v_{D1}}{2}\right)^2 exp\left(\frac{u_{BD}+2v_{D1}}{2} x_D\right) + \widehat{B}_B \ \left(\frac{u_{BD}-2v_{D1}}{2}\right)^2 \exp\left(\frac{u_{BD}-2v_{D1}}{2} x_D\right). \tag{S6}$$

To determine $\hat{A}_B$:

$$\hat{A}_B \left(\frac{u_{BD}+2v_{D1}}{2}\right)^2 exp\left(\frac{u_{BD}+2v_{D1}}{2} x_D\right) - \hat{A}_B u_B \left(\frac{u_{BD}+2v_{D1}}{2}\right) exp\left(\frac{u_{BD}+2v_{D1}}{2} x_D\right) - \hat{A}_B (R_{B2}p + \lambda_{BD2}) exp\left(\frac{u_{BD}+2v_{D1}}{2} x_D\right) = -y_2 u_{BD} exp\left(\frac{u_{BD}}{2}\right) (v_{D1} - \theta\omega_{D1}) \lambda_{BD1} E_{D1} \overline{C}_{D1_{in}} exp\left(\frac{u_{BD}+2v_{D1}}{2} x_D\right), \tag{S7}$$

which simplifies to

$$\hat{A}_B = \frac{y_2 u_{BD} exp\left(\frac{u_{BD}}{2}\right)(\theta\omega_{D1} - v_{D1})\lambda_{BD1} E_{D1}}{\left(\frac{u_{BD}+2v_{D1}}{2}\right)^2 - u_B\left(\frac{u_{BD}+2v_{D1}}{2}\right) - (R_{B2}p + \lambda_{BD2})} \overline{C}_{D1_{in}} = \frac{y_2 u_{BD} exp\left(\frac{u_{BD}}{2}\right)(\theta\omega_{D1} - v_{D1})\lambda_{BD1} E_{D1}}{(R_{B1} - R_{B2})p + \lambda_{BD1} - \lambda_{BD2}} \overline{C}_{D1_{in}}, \tag{S8}$$

where the stoichiometric yield y_i is the molecular weight of the daughter divided by the molecular weight of the parent product [Clement et al., 1998]; i.e., one parent does not exactly yield one daughter product. Therefore, the purpose of the stoichiometric yield is to conserve molar concentrations as species react in the model. Also, at this point it is beneficial to define a dimensionless ratio of the reactivities, let $H_B(p) = \lambda_{BD1}/[(R_{B1} - R_{B2})p + \lambda_{BD1} - \lambda_{BD2}]$, therefore

$$\hat{A}_B = y_2 u_{BD} exp\left(\frac{u_{BD}}{2}\right) (\theta\omega_{D1} - v_{D1}) H_B E_{D1} \overline{C}_{D1_{in}}. \tag{S9}$$

Repeating the procedure outlined from Eqs. (S5)-(S9) for $\hat{B}_B$, and $\hat{A}_L$ gives

$$\hat{B}_B = -y_2 u_{BD} exp\left(\frac{u_{BD}}{2}\right)(v_{D1} + \theta\omega_{D1}) H_B E_{D1} \overline{C}_{D1_{in}}, \quad \text{(S10)}$$

$$\hat{A}_L = -2v_{D1} y_2 u_{BD} exp\left(\frac{u_{BD}}{2}\right) H E_{D1} \overline{C}_{D1_{in}}, \quad \text{(S11)}$$

where v_{Di}, ω_{Di}, and E_{Di} were defined previously in this study and where $H(p)$ is similar to $H_B(p)$ but pertains to the aquifer as defined below Eq. (27). With the coefficients $\hat{A}_B$, $\hat{B}_B$, and $\hat{A}_L$ known, Eqs. (S1) and (S2) may now be solved for the unkowns α, β, and ϕ utilizing the transformed boundary conditions of Eqs. (14)-(16). *It is noted that the subscript "D" is henceforth dropped for convenience, the derivation remains dimensionless unless otherwise noted.* Applying boundary condition (14) to Eq. (S1) gives

$$\alpha(u_B - 2v_2) exp(-v_2) + \beta(u_B + 2v_2) exp(v_2) - 2y_2 H_B exp\left(\frac{u_B}{2}\right) u_B \overline{C}_{1_{in}} = 2 exp\left(\frac{u_B}{2}\right) u_B \overline{C}_{2_{in}}. \quad \text{(S12)}$$

Also, applying boundary condition (15) to Eqs. (S1)-(S2) and solving for ϕ gives

$$\phi = \alpha + \beta + 2v_1 y_2 exp\left(\frac{u_B}{2}\right) u_B E_1 (H - H_B) \overline{C}_{1_{in}}. \quad \text{(S13)}$$

Lastly, applying boundary condition (16) to Eqs. (S1)-(S2) and solving for α gives

$$\alpha = \beta \frac{v_2 - \theta\omega_2}{v_2 + \theta\omega_2} + \frac{2v_1 \theta y_2 exp\left(\frac{u_B}{2}\right) u_B E_1 (H - H_B)(\omega_1 - \omega_2)}{v_2 + \theta\omega_2} \overline{C}_{1_{in}}. \quad \text{(S14)}$$

Inserting Eq. (S14) into Eq. (S12) allows Eq. (S12) to be solved explicitly for β; i.e.,

$$\beta = u_B exp\left(\frac{u_B}{2}\right)(v_2 + \theta\omega_2) E_2 \overline{C}_{2_{in}} - v_1 \theta y_2 exp\left(\frac{u_B}{2}\right) u_B E_1 E_2 (H - H_B)(\omega_1 - \omega_2)(u_B - 2v_2) exp(-v_2) \overline{C}_{1_{in}} + y_2 H_B exp\left(\frac{u_B}{2}\right) u_B (v_2 + \theta\omega_2) E_2 \overline{C}_{1_{in}}. \quad \text{(S15)}$$

Inserting Eq. (S15) into Eq. (S14) yields the explicit solution of α

$$\alpha = u_B exp\left(\frac{u_B}{2}\right)(\upsilon_2 - \theta\omega_2)E_2\overline{C}_{2_{in}} + \frac{\upsilon_1\theta y_2 exp\left(\frac{u_B}{2}\right)u_B E_1(H-H_B)(\omega_1-\omega_2)}{\upsilon_2+\theta\omega_2}\overline{C}_{1_{in}}[2 -$$

$$E_2(u_B - 2\upsilon_2)(\upsilon_2 - \theta\omega_2)exp(-\upsilon_2)] + y_2 H_B exp\left(\frac{u_B}{2}\right)u_B(\upsilon_2 - \theta\omega_2)E_2\overline{C}_{1_{in}}, \qquad \text{(S16)}$$

therefore,

$$\alpha + \beta = 2\upsilon_2 u_B exp\left(\frac{u_B}{2}\right)E_2\overline{C}_{2_{in}} + \frac{2\upsilon_1\theta y_2 exp\left(\frac{u_B}{2}\right)u_B E_1(H-H_B)(\omega_1-\omega_2)(1-\mu_2)}{\upsilon_2+\theta\omega_2}\overline{C}_{1_{in}} +$$

$$2\upsilon_2 y_2 H_B exp\left(\frac{u_B}{2}\right)u_B E_2\overline{C}_{1_{in}}\ , \qquad \text{(S17)}$$

where $\mu_2 = E_2\upsilon_2(u_B - 2\upsilon_2)exp(-\upsilon_2)$ is in its *dimensionless* form. With α and β known, Eq. (S1) is now fully determined in the Laplace domain. However, in practice Eq. (S2) is the equation of interest. Therefore, inserting Eq. (S17) into Eq. (S13) gives

$$\phi = 2\upsilon_2 u_B exp\left(\frac{u_B}{2}\right)E_2\overline{C}_{2_{in}} + \frac{2\upsilon_1\theta y_2 exp\left(\frac{u_B}{2}\right)u_B E_1(H-H_B)(\omega_1-\omega_2)(1-\mu_2)}{\upsilon_2+\theta\omega_2}\overline{C}_{1_{in}} +$$

$$2y_2 exp\left(\frac{u_B}{2}\right)u_B[\upsilon_2 E_2 H_B + \upsilon_1 E_1(H - H_B)]\overline{C}_{1_{in}}\ , \qquad \text{(S18)}$$

which in turn is inserted into Eq. (S2) to give the *dimensionless* transient solution in the Laplace domain; i.e.,

$$\overline{C}_{LD2} = \Big[2\upsilon_2 u_B E_2\overline{C}_{2_{in}} + \frac{2\upsilon_1\theta y_2 u_B E_1(H-H_B)(\omega_1-\omega_2)(1-\mu_2)}{\upsilon_2+\theta\omega_2}\overline{C}_{1_{in}} + 2y_2 u_B[\upsilon_2 H_B E_2 +$$

$$\upsilon_1(H - H_B)E_1]\overline{C}_{1_{in}}\Big]exp\left(\frac{u_L-2\omega_2}{2\delta}x + \frac{u_B}{2}\right) - 2\upsilon_1 y_2 u_B H E_1\overline{C}_{1_{in}}exp\left(\frac{u_L-2\omega_1}{2\delta}x + \frac{u_B}{2}\right). \qquad \text{(S19)}$$

This semi-analytical solution can be dimensionalized using Eq. (9) and numerically inverted to obtain a concentration value in the time domain, however, this is beyond the scope of this study. The steady-state analytical solution can be determined by letting $p \to 0$, applying the final value theorem, and assigning a constant influent concentration so that $\overline{C}_{Di_{in}}(p) \to C_{Di_{in}}/p$; i.e.,

$$\lim_{t_D\to\infty} C_{LD2} = \lim_{p\to 0} p\left\{\Big[2\upsilon_{02} u_B E_{02}\frac{C_{2_{in}}}{p} + \frac{2\upsilon_{01}\theta y_2 u_B E_{01}(H-H_B)(\omega_{01}-\omega_{02})(1-\mu_{02})}{\upsilon_{02}+\theta\omega_{02}}\frac{C_{1_{in}}}{p} +\right.$$

$$2y_2u_B[\upsilon_{02}H_BE_{02} + \upsilon_{01}(H - H_B)E_{01}]\frac{C_{1_{in}}}{p}\Big] exp\left(\frac{u_L-2\omega_{02}}{2\delta}x + \frac{u_B}{2}\right) -$$

$$2\upsilon_{01}y_2u_BHE_{01}\frac{C_{1_{in}}}{p}exp\left(\frac{u_L-2\omega_{01}}{2\delta}x + \frac{u_B}{2}\right)\Big\}\,, \qquad \text{(S20)}$$

where p in the denominator cancel out and

$$\upsilon_{0i} = \sqrt{u_B{}^2/4 + \lambda_{Bi}} \text{ and } \omega_{0i} = \sqrt{u_L{}^2/4 + \delta\lambda_{Li}}\,, \qquad \text{(S21)}$$

$$E_{0i} = 1/[(\upsilon_{0i}u_B + 2\theta\omega_{0i}\upsilon_{0i})cosh(\upsilon_{0i}) + (\theta\omega_{0i}u_B + 2\upsilon_{0i}{}^2)sinh(\upsilon_{0i})], \qquad \text{(S22)}$$

$$H = \lambda_{L1}/(\lambda_{L1} - \lambda_{L2}) \text{ and } H_B = \lambda_{B1}/(\lambda_{B1} - \lambda_{B2}), \qquad \text{(S23)}$$

result from letting $p \to 0$. Also, note that $i = 1$ or 2 in Eqs. (S21)-(S23) and $exp\left(\frac{u_B}{2}\right)$ was combined with $exp\left(\frac{u_L-2\omega_{0i}}{2\delta}x\right)$. *Dimensionalizing* Eq. (S20) gives the steady-state analytical solution, see Eq. (32).

Species 3:

The governing equations of species 3 (SP3) can be inferred from Eqs. (2) and (5) when $i = 3$. After applying the dimensionless parameters in Eq. (9) and the Laplace transform the governing equations become Eqs. (11) and (13) for $i = 3$. For the purpose of efficiency, it is beneficial at this point to include the branch ratio $\gamma = 1$ in the governing Eqs. (11) and (13), therefore:

$$\frac{d^2\overline{C}_{BD3}}{dx_D{}^2} - u_{BD}\frac{d\overline{C}_{BD3}}{dx_D} - (R_{B3}p + \lambda_{BD3})\overline{C}_{BD3} = -y_3\gamma\lambda_{BD2}\overline{C}_{BD2}\,, \qquad \text{(S24)}$$

$$\delta\frac{d^2\overline{C}_{LD3}}{dx_D{}^2} - u_{LD}\frac{d\overline{C}_{LD3}}{dx_D} - (R_{L3}p + \lambda_{LD3})\overline{C}_{LD3} = -y_3\gamma\lambda_{LD2}\overline{C}_{LD2}. \qquad \text{(S25)}$$

The general solutions of Eqs. (S24) and (S25) are:

$$\overline{C}_{BD3} = \varepsilon \exp\left(\frac{u_{BD} + 2v_{D3}}{2} x_D\right) + \iota \exp\left(\frac{u_{BD} - 2v_{D3}}{2} x_D\right) + \hat{A}_B exp\left(\frac{u_{BD} + 2v_{D2}}{2} x_D\right)$$
$$+ \hat{B}_B \ \exp\left(\frac{u_{BD} - 2v_{D2}}{2} x_D\right) + \hat{C}_B exp\left(\frac{u_{BD} + 2v_{D1}}{2} x_D\right) + \hat{D}_B \ \exp\left(\frac{u_{BD} - 2v_{D1}}{2} x_D\right) \tag{S26}$$

$$\overline{C}_{LD3} = \zeta exp\left(\frac{u_{LD} - 2\omega_{D3}}{2\delta} x_D\right) + \hat{A}_L exp\left(\frac{u_{LD} - 2\omega_{D2}}{2\delta} x_D\right) + \hat{B}_L exp\left(\frac{u_{LD} - 2\omega_{D1}}{2\delta} x_D\right) \tag{S27}$$

where ε, ι (iota), and ζ (zeta) are the new unknowns to solve for. For convenience the subscript “D” is again dropped until the dimensionalizing procedure. As before, each coefficient $\hat{A}_B$, $\hat{B}_B$, $\hat{C}_B$, $\hat{D}_B$, $\hat{A}_L$, and $\hat{B}_L$ must satisfy its respective homogeneous solution, hence:

$$\hat{A}_B = -y_3 \gamma I_B \alpha \ \text{ and } \ \hat{B}_B = -y_3 \gamma I_B \beta \ , \tag{S28}$$

$$\hat{C}_B = y_3 \gamma y_2 u_B exp\left(\frac{u_B}{2}\right)(v_1 - \theta\omega_1) J_B H_B E_1 \overline{C}_{1_{in}} \ \text{ and}$$

$$\hat{D}_B = y_3 \gamma y_2 u_B exp\left(\frac{u_B}{2}\right)(v_1 + \theta\omega_1) J_B H_B E_1 \overline{C}_{1_{in}} \tag{S29}$$

$$\hat{A}_L = -y_3 \gamma I \phi \ \text{ and } \ \hat{B}_L = 2 v_1 y_3 \gamma y_2 u_B exp\left(\frac{u_B}{2}\right) J H E_1 \overline{C}_{1_{in}} \tag{S30}$$

where α, β, and ϕ are Eqs. (S15), (S16), and (S18) and $I = \lambda_{L2}/[(R_{L2} - R_{L3})p + \lambda_{L2} - \lambda_{L3}]$ and $J = \lambda_{L2}/[(R_{L1} - R_{L3})p + \lambda_{L1} - \lambda_{L3}]$. Note that I_B and J_B are of equivalent form but pertain to the PRB. Applying boundary condition (14) gives

$$\varepsilon(u_B - 2v_3) exp(-v_3) + \iota(u_B + 2v_3) exp(v_3) + y_3 \gamma I_B \alpha (2v_2 - u_B) exp(-v_2) -$$
$$y_3 \gamma I_B \beta (u_B + 2v_2) exp(v_2) + 2 y_3 \gamma y_2 u_B exp\left(\frac{u_B}{2}\right) J_B H_B \overline{C}_{1_{in}} = 2 exp\left(\frac{u_B}{2}\right) u_B \overline{C}_{3_{in}}, \tag{S31}$$

which is inconvenient due to the presence of large terms α and β. However, Eq. (S31) can be simplified further by letting $\alpha = \eta + \psi$ such that

$$\psi = \frac{2 v_1 \theta y_2 exp\left(\frac{u_B}{2}\right) u_B E_1 (H - H_B)(\omega_1 - \omega_2)}{v_2 + \theta \omega_2} \overline{C}_{1_{in}} \ , \tag{S32}$$

$$\eta = u_B exp\left(\frac{u_B}{2}\right)(\upsilon_2 - \theta\omega_2)E_2\overline{C}_{2_{in}} - \frac{\upsilon_1\theta y_2 exp\left(\frac{u_B}{2}\right)u_B E_1 E_2 (H - H_B)(\omega_1 - \omega_2)(u_B - 2\upsilon_2)(\upsilon_2 - \theta\omega_2)exp(-\upsilon_2)}{\upsilon_2 + \theta\omega_2}\overline{C}_{1_{in}} + y_2 H_B exp\left(\frac{u_B}{2}\right)u_B(\upsilon_2 - \theta\omega_2)E_2\overline{C}_{1_{in}}\ , \tag{S33}$$

$$\beta = u_B exp\left(\frac{u_B}{2}\right)(\upsilon_2 + \theta\omega_2)E_2\overline{C}_{2_{in}} - \frac{\upsilon_1\theta y_2 exp\left(\frac{u_B}{2}\right)u_B E_1 E_2 (H - H_B)(\omega_1 - \omega_2)(u_B - 2\upsilon_2)(\upsilon_2 + \theta\omega_2)exp(-\upsilon_2)}{\upsilon_2 + \theta\omega_2}\overline{C}_{1_{in}} + y_2 H_B exp\left(\frac{u_B}{2}\right)u_B(\upsilon_2 + \theta\omega_2)E_2\overline{C}_{1_{in}}. \tag{S34}$$

Notice that Eqs. (S33) and (S34) are equivalent, with the exception of the numerator terms $(\upsilon_2 - \theta\omega_2)$ and $(\upsilon_2 + \theta\omega_2)$. These numerator terms can be factored out along with E_2, hence $\eta = (\upsilon_2 - \theta\omega_2)E_2\tau$ and $\beta = (\upsilon_2 + \theta\omega_2)E_2\tau$ where

$$\tau = u_B exp\left(\frac{u_B}{2}\right)\overline{C}_{2_{in}} - \frac{\upsilon_1\theta y_2 exp\left(\frac{u_B}{2}\right)u_B E_1 (H - H_B)(\omega_1 - \omega_2)(u_B - 2\upsilon_2)exp(-\upsilon_2)}{\upsilon_2 + \theta\omega_2}\overline{C}_{1_{in}} + y_2 H_B exp\left(\frac{u_B}{2}\right)u_B\overline{C}_{1_{in}}, \tag{S35}$$

therefore Eq. (S31) becomes

$$\varepsilon(u_B - 2\upsilon_3)exp(-\upsilon_3) + \iota(u_B + 2\upsilon_3)exp(\upsilon_3) - 2y_3\gamma I_B\tau + y_3\gamma I_B(2\upsilon_2 - u_B)exp(-\upsilon_2)\psi + 2y_3\gamma y_2 u_B exp\left(\frac{u_B}{2}\right)J_B H_B\overline{C}_{1_{in}} = 2exp\left(\frac{u_B}{2}\right)u_B\overline{C}_{3_{in}}. \tag{S36}$$

Note that expanding τ and ψ allows for two large terms to cancel, such that

$$\varepsilon(u_B - 2\upsilon_3)exp(-\upsilon_3) + \iota(u_B + 2\upsilon_3)exp(\upsilon_3) - 2y_3\gamma u_B exp\left(\frac{u_B}{2}\right)I_B\overline{C}_{2_{in}} + 2y_3\gamma y_2 u_B exp\left(\frac{u_B}{2}\right)H_B(J_B - I_B)\overline{C}_{1_{in}} = 2exp\left(\frac{u_B}{2}\right)u_B\overline{C}_{3_{in}}\ , \tag{S37}$$

replaces Eq. (S36). The procedure outlined from Eqs. (S32)-(S37) applies to all subsequent daughter species but for brevity is omitted below. Applying boundary condition (15) gives

$$\varepsilon + \iota - y_3\gamma I_B(\alpha+\beta) + 2v_1 y_3\gamma J_B y_2 H_B u_B exp\left(\frac{u_B}{2}\right) E_1 \overline{C}_{1_{in}} = \zeta - y_3\gamma I\phi + 2v_1 y_3\gamma J y_2 H u_B exp\left(\frac{u_B}{2}\right) E_1 \overline{C}_{1_{in}}\,, \tag{S38}$$

where ϕ is Eq. (S13). Inserting Eq. (S13) into Eq. (S38) and solving for ζ yields

$$\zeta = \varepsilon + \iota + y_3\gamma(I - I_B)(\alpha+\beta) + 2v_1 y_3\gamma y_2 u_B exp\left(\frac{u_B}{2}\right) E_1[J_B H_B - JH + I(H - H_B)]\overline{C}_{1_{in}}. \tag{S39}$$

Lastly, applying boundary condition (16) gives

$$\varepsilon(v_3 + \theta\omega_3) + \iota(\theta\omega_3 - v_3) + y_3\gamma I_B v_2(\beta - \alpha) = y_3\gamma\theta[\omega_2 I - \omega_3(I - I_B)](\alpha+\beta) + 2v_1 y_3\gamma y_2 u_B exp\left(\frac{u_B}{2}\right)\theta E_1\overline{C}_{1_{in}}[\omega_2 I(H - H_B) - \omega_1(JH - J_B H_B) - \omega_3(J_B H_B - JH + IH - IH_B)]\,, \tag{S40}$$

where $(\beta - \alpha)$ is also inconvenient since it was not previously defined. This time using $\alpha = \hat{\eta} + \psi$ where $\hat{\eta} = (v_2 - \theta\omega_2)\hat{\tau}$ and $\beta = (v_2 + \theta\omega_2)\hat{\tau}$ where

$$\hat{\tau} = u_B exp\left(\frac{u_B}{2}\right) E_2\overline{C}_{2_{in}} - \frac{v_1\theta y_2 exp\left(\frac{u_B}{2}\right) u_B E_1 E_2 (H - H_B)(\omega_1 - \omega_2)(u_B - 2v_2) exp(-v_2)}{v_2 + \theta\omega_2}\overline{C}_{1_{in}} + y_2 H_B exp\left(\frac{u_B}{2}\right) u_B E_2\overline{C}_{1_{in}}, \tag{S41}$$

and inserting $0 = y_3\gamma I_B\theta\omega_2\psi - y_3\gamma I_B\theta\omega_2\psi$ in the left-hand-side of Eq. (S40) allows

$$y_3\gamma I_B v_2(\beta - \alpha) + y_3\gamma I_B\theta\omega_2\psi - y_3\gamma I_B\theta\omega_2\psi \rightarrow y_3\gamma I_B\theta\omega_2[2v_2\hat{\tau}] + y_3\gamma I_B\theta\omega_2\psi - y_3\gamma I_B(v_2 + \theta\omega_2)\psi \rightarrow \boldsymbol{y_3\gamma I_B\theta\omega_2(\alpha+\beta) - y_3\gamma I_B(v_2 + \theta\omega_2)\psi}$$

which replaces the third term in Eq. (S40) and is more convenient to work with. Therefore, Eq. (S40) becomes

$$\varepsilon = \iota\,\frac{v_3 - \theta\omega_3}{v_3 + \theta\omega_3} + \frac{y_3\gamma\theta(I - I_B)(\omega_2 - \omega_3)}{v_3 + \theta\omega_3}(\alpha+\beta) + \frac{y_3\gamma I_B(v_2 + \theta\omega_2)}{v_3 + \theta\omega_3}\psi + \frac{2v_1 y_3\gamma y_2 exp\left(\frac{u_B}{2}\right) u_B\theta E_1}{v_3 + \theta\omega_3}\overline{C}_{1_{in}}[(\omega_1 - \omega_3)(J_B H_B - JH) + (\omega_2 - \omega_3)(IH - IH_B)]. \tag{S42}$$

Inserting Eq. (S42) into Eq. (S37) allows Eq. (S37) to be solved explicitly for ι; i.e.,

$$\iota = u_B exp\left(\frac{u_B}{2}\right)(v_3 + \theta\omega_3)E_3\overline{C}_{3_{in}} - \frac{1}{2}y_3\gamma\theta(I - I_B)(\omega_2 - \omega_3)(u_B - 2v_3)E_3 exp(-v_3)(\alpha + \beta) - \frac{1}{2}y_3\gamma I_B(v_2 + \theta\omega_2)(u_B - 2v_3)E_3 exp(-v_3)\psi - v_1 y_3\gamma y_2 exp\left(\frac{u_B}{2}\right)u_B\theta E_1\overline{C}_{1_{in}}[(\omega_1 - \omega_3)(J_B H_B - JH) + (\omega_2 - \omega_3)I(H - H_B)](u_B - 2v_3)E_3 exp(-v_3) + y_3\gamma I_B exp\left(\frac{u_B}{2}\right)u_B(v_3 + \theta\omega_3)E_3\overline{C}_{2_{in}} - y_3\gamma y_2 exp\left(\frac{u_B}{2}\right)u_B H_B E_3(J_B - I_B)(v_3 + \theta\omega_3)\overline{C}_{1_{in}} \ . \tag{S43}$$

Inserting Eq. (S43) into Eq. (S42) yields the explicit solution of ε; i.e.,

$$\varepsilon = u_B exp\left(\frac{u_B}{2}\right)(v_3 - \theta\omega_3)E_3\overline{C}_{3_{in}} + \frac{1}{2}\frac{y_3\gamma\theta(I-I_B)(\omega_2-\omega_3)}{v_3+\theta\omega_3}[2 - E_3(u_B - 2v_3)(v_3 - \theta\omega_3)exp(-v_3)](\alpha + \beta) + \frac{1}{2}\frac{y_3\gamma I_B(v_2+\theta\omega_2)}{v_3+\theta\omega_3}[2 - E_3(u_B - 2v_3)(v_3 - \theta\omega_3)exp(-v_3)]\psi + \frac{v_1 y_3\gamma y_2 exp\left(\frac{u_B}{2}\right)u_B\theta E_1}{v_3+\theta\omega_3}\overline{C}_{1_{in}}[(\omega_1 - \omega_3)(J_B H_B - JH) + (\omega_2 - \omega_3)I(H - H_B)][2 - E_3(u_B - 2v_3)(v_3 - \theta\omega_3)exp(-v_3)] + y_3\gamma I_B exp\left(\frac{u_B}{2}\right)u_B E_3(v_3 - \theta\omega_3)\overline{C}_{2_{in}} - y_3\gamma y_2 exp\left(\frac{u_B}{2}\right)u_B H_B E_3(J_B - I_B)(v_3 - \theta\omega_3)\overline{C}_{1_{in}} \ , \tag{S44}$$

therefore,

$$\varepsilon + \iota = 2v_3 u_B exp\left(\frac{u_B}{2}\right)E_3\overline{C}_{3_{in}} + \frac{y_3\gamma\theta(I-I_B)(\omega_2-\omega_3)(1-\mu_3)}{v_3+\theta\omega_3}(\alpha + \beta) + \frac{y_3\gamma I_B(v_2+\theta\omega_2)(1-\mu_3)}{v_3+\theta\omega_3}\psi + \frac{2v_1 y_3\gamma y_2 exp\left(\frac{u_B}{2}\right)u_B\theta E_1(1-\mu_3)}{v_3+\theta\omega_3}\overline{C}_{1_{in}}[(\omega_1 - \omega_3)(J_B H_B - JH) + (\omega_2 - \omega_3)I(H - H_B)] + 2v_3 y_3\gamma I_B exp\left(\frac{u_B}{2}\right)u_B E_3\overline{C}_{2_{in}} - 2v_3 y_3\gamma y_2 exp\left(\frac{u_B}{2}\right)u_B H_B E_3(J_B - I_B)\overline{C}_{1_{in}} \tag{S45}$$

where $\mu_3 = E_3 v_3(u_B - 2v_3)exp(-v_3)$ is in its *dimensionless* form. Inserting Eq. (S45) into Eq. (S39) yields ζ; i.e.,

$$\zeta = 2v_3 u_B exp\left(\frac{u_B}{2}\right)E_3\overline{C}_{3_{in}} + \frac{y_3\gamma(I-I_B)}{v_3+\theta\omega_3}[v_3 + \theta\omega_2 - \theta(\omega_2 - \omega_3)\mu_3](\alpha + \beta) + \frac{y_3\gamma I_B(v_2+\theta\omega_2)(1-\mu_3)}{v_3+\theta\omega_3}\psi + \frac{2v_1 y_3\gamma y_2 u_B exp\left(\frac{u_B}{2}\right)E_1\theta(1-\mu_3)}{v_3+\theta\omega_3}\overline{C}_{1_{in}}[(\omega_1 - \omega_3)(J_B H_B - JH) + (\omega_2 - \omega_3)I(H - H_B)] + 2v_3 y_3\gamma I_B u_B exp\left(\frac{u_B}{2}\right)E_3\overline{C}_{2_{in}} + 2y_3\gamma y_2 u_B exp\left(\frac{u_B}{2}\right)\overline{C}_{1_{in}}[v_1 E_1(J_B H_B - JH + IH - IH_B) - v_3 E_3 H_B(J_B - I_B)] \ . \tag{S46}$$

The steady-state analytical solution C_{L3} (see Eq. (33)) can be determined by letting $\overline{C}_{Di_{in}}(p) \rightarrow C_{Di_{in}}/p$ and $p \rightarrow 0$ for all applicable terms, applying the final value theorem, combining the two types of exponential terms, dimensionalizing Eq. (S46) and Eq. (S27), and inserting Eq. (S46) into Eq. (S27).

<u>Species 4:</u>

The governing equations of species 4 (SP4) in the Laplace domain are

$$\frac{d^2\overline{C}_{BD4}}{dx_D{}^2} - u_{BD}\frac{d\overline{C}_{BD4}}{dx_D} - (R_{B4}p + \lambda_{BD4})\overline{C}_{BD4} = -y_4\lambda_{BD3}\overline{C}_{BD3}\ , \tag{S47}$$

$$\delta\frac{d^2\overline{C}_{LD4}}{dx_D{}^2} - u_{LD}\frac{d\overline{C}_{LD4}}{dx_D} - (R_{L4}p + \lambda_{LD4})\overline{C}_{LD4} = -y_4\lambda_{LD3}\overline{C}_{LD3}. \tag{S48}$$

The general solutions of Eqs. (S47) and (S48) are:

$$\begin{aligned}\overline{C}_{BD4} = {} & \kappa\exp\left(\frac{u_{BD} + 2v_{D4}}{2}x_D\right) + \xi\exp\left(\frac{u_{BD} - 2v_{D4}}{2}x_D\right) + \hat{A}_B exp\left(\frac{u_{BD} + 2v_{D3}}{2}x_D\right) \\ & + \hat{B}_B\exp\left(\frac{u_{BD} - 2v_{D3}}{2}x_D\right) + \hat{C}_B exp\left(\frac{u_{BD} + 2v_{D2}}{2}x_D\right) + \hat{D}_B\exp\left(\frac{u_{BD} - 2v_{D2}}{2}x_D\right) \\ & + \hat{E}_B exp\left(\frac{u_{BD} + 2v_{D1}}{2}x_D\right) + \hat{F}_B\exp\left(\frac{u_{BD} - 2v_{D1}}{2}x_D\right)\end{aligned} \tag{S49}$$

$$\begin{aligned}\overline{C}_{LD4} = {} & \varrho exp\left(\frac{u_{LD} - 2\omega_{D4}}{2\delta}x_D\right) + \hat{A}_L exp\left(\frac{u_{LD} - 2\omega_{D3}}{2\delta}x_D\right) + \hat{B}_L exp\left(\frac{u_{LD} - 2\omega_{D2}}{2\delta}x_D\right) \\ & + \hat{C}_L exp\left(\frac{u_{LD} - 2\omega_{D1}}{2\delta}x_D\right)\end{aligned} \tag{S50}$$

where κ (kappa), ξ (xi), and ϱ (rho variant) are the new unknowns to solve for. As before, the subscript "D" is dropped and each coefficient $\hat{A}$, $\hat{B}$, $\hat{C}$, $\hat{D}$, $\hat{E}$, and $\hat{F}$ must satisfy its respective homogeneous solution, therefore:

$$\hat{A}_B = -y_4K_B\varepsilon \quad \text{and} \quad \hat{B}_B = -y_4K_B\iota \tag{S51}$$

$$\hat{C}_B = y_4y_3\gamma I_B L_B\alpha \quad \text{and} \quad \hat{D}_B = y_4y_3\gamma I_B L_B\beta \tag{S52}$$

$\hat{E}_B = -y_4y_3\gamma y_2 H_B J_B M_B u_B exp\left(\frac{u_B}{2}\right)(v_1 - \theta\omega_1)E_1\overline{C}_{1_{in}}$ and

$$\hat{F}_B = -y_4 y_3 \gamma y_2 H_B J_B M_B u_B exp\left(\frac{u_B}{2}\right)(v_1 + \theta\omega_1)E_1\overline{C}_{1_{in}} \tag{S53}$$

$$\hat{A}_L = -y_4 K\zeta \tag{S54}$$

$$\hat{B}_L = y_4 y_3 \gamma I L \phi \tag{S55}$$

$$\hat{C}_L = -2v_1 y_4 y_3 \gamma y_2 HJMu_B exp\left(\frac{u_B}{2}\right)E_1\overline{C}_{1_{in}} \tag{S56}$$

where α, β, ε, and ι are Eqs. (S16), (S15), (S44), and (S43), respectively; and ϕ and ζ are Eqs. (S18) and (S46), respectively. In addition, $K = \lambda_{L3}/[(R_{L3} - R_{L4})p + \lambda_{L3} - \lambda_{L4}]$, $L = \lambda_{L3}/[(R_{L2} - R_{L4})p + \lambda_{L2} - \lambda_{L4}]$, and $M = \lambda_{L3}/[(R_{L1} - R_{L4})p + \lambda_{L1} - \lambda_{L4}]$, while K_B, L_B, and M_B pertain to the PRB. Applying boundary condition (14) to Eq. (S49) gives

$$\kappa(u_B - 2v_4)exp(-v_4) + \xi(u_B + 2v_4)exp(v_4) - 2y_4K_Bu_Bexp\left(\frac{u_B}{2}\right)\overline{C}_{3_{in}} + 2y_4y_3\gamma I_Bu_Bexp\left(\frac{u_B}{2}\right)(L_B - K_B)\overline{C}_{2_{in}} + 2y_4y_3\gamma y_2H_Bu_Bexp\left(\frac{u_B}{2}\right)\overline{C}_{1_{in}}[I_B(L_B - K_B) + J_B(K_B - M_B)] = 2exp\left(\frac{u_B}{2}\right)u_B\overline{C}_{4_{in}}\ . \tag{S57}$$

Note that Eq. (S57) is the result of repeating the procedure outlined from Eq. (S32) to (S37) twice. In this process eight large terms cancel out but a new term (similar in purpose to ψ from SP3) is introduced; i.e.,

$$\sigma = \frac{y_3\gamma(I-I_B)\theta(\omega_2-\omega_3)}{v_3+\theta\omega_3}(\alpha+\beta) + \frac{y_3\gamma I_B(v_2+\theta\omega_2)}{v_3+\theta\omega_3}\psi + \frac{2v_1y_3\gamma y_2u_Bexp\left(\frac{u_B}{2}\right)E_1\theta}{v_3+\theta\omega_3}\overline{C}_{1_{in}}[(\omega_1 - \omega_3)(J_BH_B - JH) + (\omega_2 - \omega_3)I(H - H_B)]. \tag{S58}$$

Applying boundary condition (15) and solving for ϱ gives

$$\varrho = \kappa + \xi + y_4(K - K_B)(\varepsilon + \iota) + y_4y_3\gamma[I_B(L_B - K) - I(L - K)](\alpha + \beta) + 2v_1y_4y_3\gamma y_2u_Bexp\left(\frac{u_B}{2}\right)E_1[J_BH_B(K - M_B) - JH(K - M) + I(H - H_B)(K - L)]\overline{C}_{1_{in}}. \tag{S59}$$

Lastly, applying the boundary condition (16) and repeating the procedure outlined from Eqs. (S40) to (S42) twice gives

$$\kappa = \xi\ \frac{\upsilon_4-\theta\omega_4}{\upsilon_4+\theta\omega_4} + \frac{y_4\theta(K-K_B)(\omega_3-\omega_4)}{\upsilon_4+\theta\omega_4}(\varepsilon+\iota) + \frac{y_4K_B(\upsilon_3+\theta\omega_3)}{\upsilon_4+\theta\omega_4}\sigma + \frac{y_4y_3\gamma\theta}{\upsilon_4+\theta\omega_4}[(\omega_2-\omega_4)(L_BI_B - LI) - K(\omega_3-\omega_4)(I_B-I)](\alpha+\beta) - \frac{y_4y_3\gamma L_BI_B(\upsilon_2+\theta\omega_2)}{\upsilon_4+\theta\omega_4}\psi + \frac{2\upsilon_1y_4y_3\gamma y_2 exp\left(\frac{u_B}{2}\right)u_B\theta E_1}{\upsilon_4+\theta\omega_4}\ddot{\Omega}\overline{C}_{1_{in}}\ , \tag{S60}$$

where $\ddot{\Omega}$ is

$$\ddot{\Omega} = (\omega_1-\omega_4)(JHM - J_BH_BM_B) + LI(\omega_2-\omega_4)(H_B-H) + K(\omega_3-\omega_4)\big(H_B(J_B-I) - H(J-I)\big)\ , \tag{S61}$$

and $\dot{\Omega}$ is defined below. Inserting Eqs. (S60) into (S57) allows Eq. (S57) to be solved explicitly for ξ; i.e.,

$$\xi =\ u_B exp\left(\frac{u_B}{2}\right)(\upsilon_4+\theta\omega_4)E_4\overline{C}_{4_{in}} - \frac{1}{2}y_4\theta(K-K_B)(\omega_3-\omega_4)(u_B-2\upsilon_4)E_4 exp(-\upsilon_4)(\varepsilon + \iota) - \frac{1}{2}y_4K_B(\upsilon_3+\theta\omega_3)(u_B-2\upsilon_4)E_4 exp(-\upsilon_4)\sigma - \frac{1}{2}y_4y_3\gamma E_4\theta(u_B-2\upsilon_4)exp(-\upsilon_4)[(\omega_2 - \omega_4)(L_BI_B-LI) - K(\omega_3-\omega_4)(\ I_B-I)](\alpha+\beta) + \frac{1}{2}y_4y_3\gamma L_BI_B(\upsilon_2+\theta\omega_2)(u_B - 2\upsilon_4)E_4 exp(-\upsilon_4)\psi - \upsilon_1y_4y_3\gamma y_2 exp\left(\frac{u_B}{2}\right)u_BE_1E_4\theta(u_B-2\upsilon_4)exp(-\upsilon_4)\ddot{\Omega}\overline{C}_{1_{in}} + y_4K_B exp\left(\frac{u_B}{2}\right)u_B(\upsilon_4+\theta\omega_4)E_4\overline{C}_{3_{in}} - y_4y_3\gamma exp\left(\frac{u_B}{2}\right)u_BI_BE_4(L_B-\ K_B)(\upsilon_4+\theta\omega_4)\overline{C}_{2_{in}} - y_4y_3\gamma y_2 exp\left(\frac{u_B}{2}\right)u_BH_BE_4(\upsilon_4+\theta\omega_4)[I_BL_B+\ K_B(J_B-\ I_B) - M_BJ_B]\overline{C}_{1_{in}}\ . \tag{S62}$$

Inserting Eq. (S62) into Eq. (S60) yields the explicit solution of κ

$$\kappa =\ u_B exp\left(\frac{u_B}{2}\right)(\upsilon_4-\theta\omega_4)E_4\overline{C}_{4_{in}} - \frac{1}{2}y_4\theta(K-K_B)(\omega_3-\omega_4)(u_B-2\upsilon_4)E_4 exp(-\upsilon_4)(\varepsilon + \iota)\frac{(\upsilon_4-\theta\omega_4)}{(\upsilon_4+\theta\omega_4)} - \frac{1}{2}y_4K_B(\upsilon_3+\theta\omega_3)(u_B-2\upsilon_4)E_4 exp(-\upsilon_4)\sigma\frac{(\upsilon_4-\theta\omega_4)}{(\upsilon_4+\theta\omega_4)} - \frac{1}{2}y_4y_3\gamma E_4\theta(u_B - 2\upsilon_4)exp(-\upsilon_4)[(\omega_2-\omega_4)(L_BI_B-LI) - K(\omega_3-\omega_4)(I_B-I)](\alpha+\beta)\frac{(\upsilon_4-\theta\omega_4)}{(\upsilon_4+\theta\omega_4)} + \frac{1}{2}y_4y_3\gamma L_BI_B(\upsilon_2+\theta\omega_2)(u_B-2\upsilon_4)E_4 exp(-\upsilon_4)\psi\frac{(\upsilon_4-\theta\omega_4)}{(\upsilon_4+\theta\omega_4)} -$$

$$v_1 y_4 y_3 \gamma y_2 exp\left(\frac{u_B}{2}\right) u_B E_1 E_4 \theta (u_B - 2v_4) exp(-v_4) \ddot{\Omega} \overline{C}_{1_{in}} \frac{(v_4 - \theta\omega_4)}{(v_4 + \theta\omega_4)} + y_4 K_B exp\left(\frac{u_B}{2}\right) u_B (v_4 - \theta\omega_4) E_4 \overline{C}_{3_{in}} - y_4 y_3 \gamma exp\left(\frac{u_B}{2}\right) u_B I_B E_4 (L_B - K_B)(v_4 - \theta\omega_4) \overline{C}_{2_{in}} - y_4 y_3 \gamma y_2 exp\left(\frac{u_B}{2}\right) u_B H_B E_4 (v_4 - \theta\omega_4)[I_B L_B + K_B(J_B - I_B) - M_B J_B] \overline{C}_{1_{in}} + \frac{y_4 \theta (K - K_B)(\omega_3 - \omega_4)}{v_4 + \theta\omega_4}(\varepsilon + \iota) + \frac{y_4 K_B (v_3 + \theta\omega_3)}{v_4 + \theta\omega_4}\sigma + \frac{y_4 y_3 \gamma \theta}{v_4 + \theta\omega_4}[(\omega_2 - \omega_4)(L_B I_B - LI) - K(\omega_3 - \omega_4)(I_B - I)](\alpha + \beta) - \frac{y_4 y_3 \gamma L_B I_B (v_2 + \theta\omega_2)}{v_4 + \theta\omega_4}\psi + \frac{2v_1 y_4 y_3 \gamma y_2 exp\left(\frac{u_B}{2}\right) u_B \theta E_1}{v_4 + \theta\omega_4} \ddot{\Omega} \overline{C}_{1_{in}} . \qquad \text{(S63)}$$

Therefore,

$$\kappa + \xi = 2v_4 u_B exp\left(\frac{u_B}{2}\right) E_4 \overline{C}_{4_{in}} + \frac{y_4 \theta (K - K_B)(\omega_3 - \omega_4)(1 - \mu_4)}{v_4 + \theta\omega_4}(\varepsilon + \iota) + \frac{y_4 K_B (v_3 + \theta\omega_3)(1 - \mu_4)}{v_4 + \theta\omega_4}\sigma + \frac{y_4 y_3 \gamma \theta (1 - \mu_4)}{v_4 + \theta\omega_4}[(\omega_2 - \omega_4)(L_B I_B - LI) - K(\omega_3 - \omega_4)(I_B - I)](\alpha + \beta) + \frac{y_4 y_3 \gamma L_B I_B (v_2 + \theta\omega_2)(\mu_4 - 1)}{v_4 + \theta\omega_4}\psi + \frac{2v_1 y_4 y_3 \gamma y_2 exp\left(\frac{u_B}{2}\right) u_B E_1 \theta (1 - \mu_4)}{v_4 + \theta\omega_4} \ddot{\Omega} \overline{C}_{1_{in}} + 2v_4 y_4 exp\left(\frac{u_B}{2}\right) u_B K_B E_4 \overline{C}_{3_{in}} + 2v_4 y_4 y_3 \gamma exp\left(\frac{u_B}{2}\right) u_B I_B E_4 (K_B - L_B) \overline{C}_{2_{in}} - 2v_4 y_4 y_3 \gamma y_2 exp\left(\frac{u_B}{2}\right) u_B H_B E_4 [I_B L_B + K_B(J_B - I_B) - M_B J_B] \overline{C}_{1_{in}} , \qquad \text{(S64)}$$

where $\mu_4 = E_4 v_4 (u_B - 2v_4) exp(-v_4)$ is in its *dimensionless* form. Inserting Eq. (S64) into Eq. (S59) yields ϱ; i.e.,

$$\varrho = 2v_4 u_B exp\left(\frac{u_B}{2}\right) E_4 \overline{C}_{4_{in}} + \frac{y_4 (K - K_B)}{v_4 + \theta\omega_4}[v_4 + \theta\omega_3 - \theta(\omega_3 - \omega_4)\mu_4](\varepsilon + \iota) + \frac{y_4 K_B (v_3 + \theta\omega_3)(1 - \mu_4)}{v_4 + \theta\omega_4}\sigma + \frac{y_4 y_3 \gamma}{v_4 + \theta\omega_4}\dot{\Omega}(\alpha + \beta) + \frac{y_4 y_3 \gamma L_B I_B (v_2 + \theta\omega_2)(\mu_4 - 1)}{v_4 + \theta\omega_4}\psi + \frac{2v_1 y_4 y_3 \gamma y_2 exp\left(\frac{u_B}{2}\right) u_B E_1 \theta (1 - \mu_4)}{v_4 + \theta\omega_4} \ddot{\Omega} \overline{C}_{1_{in}} + 2v_4 y_4 K_B exp\left(\frac{u_B}{2}\right) u_B E_4 \overline{C}_{3_{in}} + 2v_4 y_4 y_3 \gamma exp\left(\frac{u_B}{2}\right) u_B I_B E_4 (K_B - L_B) \overline{C}_{2_{in}} + 2y_4 y_3 \gamma y_2 exp\left(\frac{u_B}{2}\right) u_B \dddot{\Omega} \overline{C}_{1_{in}} , \qquad \text{(S65)}$$

where

$$\dot{\Omega} = (L_B I_B - LI)(v_4 + \theta\omega_2 - \theta(\omega_2 - \omega_4)\mu_4) + K(I_B - I)(\theta(\omega_3 - \omega_4)\mu_4 - v_4 - \theta\omega_3), \qquad \text{(S66)}$$

$$\ddot{\Omega} = v_1E_1\big(J_BH_B(K-M_B)+JH(M-K)+I(H-H_B)(K-L)\big)+v_4E_4H_B\big(I_B(K_B-L_B)+J_B(M_B-K_B)\big)\,, \qquad \text{(S67)}$$

are in their dimensionless form and $\ddot{\Omega}$ is defined by Eq. (S61). The steady-state analytical solution of C_{L4} (see Eqs. (35)-(39)) can be determined by letting $\overline{C}_{Di_{in}}(p) \rightarrow C_{Di_{in}}/p$ and $p \rightarrow 0$, applying the final value theorem, combining the two types of exponential terms, dimensionalizing Eqs. (S65) and (S50), and inserting Eq. (S65) into Eq. (S50).

Parallel Degradation Pathway

This section provides the derivational details of SP3i, SP5, SP4, and SP6 if the degradation scenario of Figure 5 is assumed.

Species 3i and 5:

The governing equations of the parallel daughter products SP31, SP32, SP33, and SP5 are Eqs. (45) through (48). Applying the dimensionless parameters in Eq. (9) and the Laplace transform gives the following general solutions:

$$\overline{C}_{BD3\mathrm{i}} = \varepsilon_{3i}\exp\left(\frac{u_{BD}+2v_{D3\mathrm{i}}}{2}x_D\right)+\iota_{3i}\exp\left(\frac{u_{BD}-2v_{D3\mathrm{i}}}{2}x_D\right)+\hat{A}_{B3i}exp\left(\frac{u_{BD}+2v_{D2}}{2}x_D\right)+ \hat{B}_{B3i}\ \exp\left(\frac{u_{BD}-2v_{D2}}{2}x_D\right)+\hat{C}_{B3i}exp\left(\frac{u_{BD}+2v_{D1}}{2}x_D\right)+\widehat{D}_{B3i}\ \exp\left(\frac{u_{BD}-2v_{D1}}{2}x_D\right) \qquad \text{(S68)}$$

$$\overline{C}_{LD3i} = \zeta_{3i}exp\left(\frac{u_{LD}-2\omega_{D3i}}{2\delta}x_D\right)+\hat{A}_{L3i}exp\left(\frac{u_{LD}-2\omega_{D2}}{2\delta}x_D\right)+\hat{B}_{L3i}exp\left(\frac{u_{LD}-2\omega_{D1}}{2\delta}x_D\right) \qquad \text{(S69)}$$

$$\overline{C}_{BD5} = \varepsilon_{5}\exp\left(\frac{u_{BD}+2v_{D5}}{2}x_D\right)+\iota_{5}\exp\left(\frac{u_{BD}-2v_{D5}}{2}x_D\right)+\hat{A}_{B5}exp\left(\frac{u_{BD}+2v_{D2}}{2}x_D\right)+ \hat{B}_{B5}\ \exp\left(\frac{u_{BD}-2v_{D2}}{2}x_D\right)+\hat{C}_{B5}exp\left(\frac{u_{BD}+2v_{D1}}{2}x_D\right)+\widehat{D}_{B5}\ \exp\left(\frac{u_{BD}-2v_{D1}}{2}x_D\right) \qquad \text{(S70)}$$

$$\overline{C}_{LD5} = \zeta_5 exp\left(\frac{u_{LD}-2\omega_{D5}}{2\delta}x_D\right) + \hat{A}_{L5} exp\left(\frac{u_{LD}-2\omega_{D2}}{2\delta}x_D\right) + \hat{B}_{L5} exp\left(\frac{u_{LD}-2\omega_{D1}}{2\delta}x_D\right) \tag{S71}$$

where i is a counter from 1 to 3, $\upsilon_{D3i}(p) = \sqrt{u_{BD}{}^2/4 + R_{B3i}p + \lambda_{BD3i}}$, $\omega_{D3i}(p) = \sqrt{u_{LD}{}^2/4 + \delta(R_{L3i}p + \lambda_{LD3i})}$. Note that ε_{3i}, ι_{3i}, ζ_{3i} and ε_5, ι_5, ζ_5 are the new unknowns to solve for and that each governing equation is solved separately. Dropping the subscript "D" and solving for coefficients $\hat{A}$, $\hat{B}$, $\hat{C}$, and $\hat{D}$ gives:

$$\hat{A}_{B3i} = -y_{3i}\gamma_{3i}I_{B3i}\alpha \quad \text{and} \quad \hat{B}_{B3i} = -y_{3i}\gamma_{3i}I_{B3i}\beta\,, \tag{S72}$$

$$\hat{C}_{B3i} = y_{3i}\gamma_{3i}y_2 u_B exp\left(\frac{u_B}{2}\right)(\upsilon_1 - \theta\omega_1)J_{B3i}H_B E_1\overline{C}_{1_{in}} \text{ and}$$

$$\hat{D}_{B3i} = y_{3i}\gamma_{3i}y_2 u_B exp\left(\frac{u_B}{2}\right)(\upsilon_1 + \theta\omega_1)J_{B3i}H_B E_1\overline{C}_{1_{in}}, \tag{S73}$$

$$\hat{A}_{L3i} = -y_{3i}\gamma_{3i}I_{3i}\phi \quad \text{and} \quad \hat{B}_{L3i} = 2\upsilon_1 y_{3i}\gamma_{3i}y_2 u_B exp\left(\frac{u_B}{2}\right)J_{3i}HE_1\overline{C}_{1_{in}}\,, \tag{S74}$$

where $I_{3i} = \lambda_{L2}/[(R_{L2} - R_{L3i})p + \lambda_{L2} - \lambda_{L3i}]$, $J_{3i} = \lambda_{L2}/[(R_{L1} - R_{L3i})p + \lambda_{L1} - \lambda_{L3i}]$, and I_{B3i} and J_{B3i} are of equivalent form but pertain to the PRB. (The same analyses apply to I_5, J_5, I_{B5}, J_{B5}, υ_5, and ω_5). The procedure to solve for C_{L3i} and C_{L5} is exactly as that of C_{L3} described above. It should be noted that $C_{3i_{in}}$ and $C_{5_{in}}$ can be set to zero such that SP3i and SP5 are effectively treated as byproducts of weathered TCE, however, this is not required and differing input concentrations may be used. Lastly, to appropriately account for mass ensure that $\gamma_{31} + \gamma_{32} + \gamma_{33} + \gamma_5 = 1$ if all parallel species are considered.

Species 4:

As seen in Eqs. (51) and (52) the governing equations of SP4 in a parallel degradation network need to account for mass contributed by all SP3i, hence Eqs. (51) and (52) carry the solutions of the parallel daughter products SP31, SP32, and SP33. As such the general solutions are

$$\overline{C}_{BD4} = \kappa exp\left(\frac{u_{BD}+2\upsilon_{D4}}{2}x_D\right) + \xi exp\left(\frac{u_{BD}-2\upsilon_{D4}}{2}x_D\right) + exp\left(\frac{u_{BD}}{2}x_D\right)\sum_{i=1}^{3}\hat{A}_{B4i}exp(\upsilon_{D3\mathrm{i}}x_D) + \hat{B}_{B4i}\,exp(-\upsilon_{D3\mathrm{i}}x_D) + \hat{C}_{B4i}exp(\upsilon_{D2}x_D) + \widehat{D}_{B4i}\,exp(-\upsilon_{D2}x_D) + \hat{E}_{B4i}exp(\upsilon_{D1}x_D) + \hat{F}_{B4i}\,\mathrm{exp}(-\upsilon_{D1}x_D), \tag{S75}$$

$$\overline{C}_{LD4} = \varrho exp\left(\frac{u_{LD}-2\omega_{D4}}{2\delta}x_D\right) + exp\left(\frac{u_{LD}}{2\delta}x_D\right)\sum_{i=1}^{3}\hat{A}_{L4i}exp\left(\frac{-\omega_{D3i}}{\delta}x_D\right) + \hat{B}_{L4i}exp\left(\frac{-\omega_{D2}}{\delta}x_D\right) + +\hat{C}_{L4i}exp\left(\frac{-\omega_{D1}}{\delta}x_D\right), \tag{S76}$$

It can be seen that the procedure to derive the analytical solution of Eqs. (S75) and (S76) is likely to be very long and tedious. Fortunately, governing equations with the right-hand-side consisting only of $y_{41}\lambda_{BD31}\overline{C}_{BD31}$ and $y_{41}\lambda_{LD31}\overline{C}_{LD31}$ were solved above with general solutions (S49) and (S59), and with Eq. (35) as the steady-state analytical solution. After comparing Eqs. (S49) and (S50) with Eqs. (S75) and (S76) it becomes apparent that the procedure to arrive at Eq. (35) can be repeated at every algebraic step two additional times. This procedure allows one to quickly deduce the form of the solution to SP4, without performing the long derivation. Therefore, as before the subscript "D" is dropped and it can be inferred that each coefficient $\hat{A}_{4i}$, $\hat{B}_{4i}$, $\hat{C}_{4i}$, $\widehat{D}_{4i}$, $\hat{E}_{4i}$, and $\hat{F}_{4i}$ must satisfy its respective homogeneous solution, such that

$$\hat{A}_{B4i} = -y_{4_i}K_{B3i}\varepsilon_{3i} \quad \text{and} \quad \hat{B}_{B4i} = -y_{4_i}K_{B3i}\iota_{3i}\,, \tag{S77}$$

$$\hat{C}_{B4i} = y_{4_i}y_{3_i}\gamma_{3_i}I_{B3i}L_{B3i}\alpha \quad \text{and} \quad \widehat{D}_{B4i} = y_{4_i}y_{3_i}\gamma_{3_i}I_{B3i}L_{B3i}\beta,$$

$$\hat{E}_{B4i} = -y_{4_i}y_{3_i}\gamma_{3_i}y_2H_BJ_{B3_i}M_{B3i}u_Bexp\left(\frac{u_B}{2}\right)(\upsilon_1 - \theta\omega_1)E_1\overline{C}_{1_{in}}\,, \tag{S78}$$

$$\text{and} \quad \hat{F}_{B4i} = -y_{4_i}y_{3_i}\gamma_{3_i}y_2H_BJ_{B3_i}M_{B3i}u_Bexp\left(\frac{u_B}{2}\right)(\upsilon_1 + \theta\omega_1)E_1\overline{C}_{1_{in}}\,, \tag{S79}$$

$$\hat{A}_{L4i} = -y_{4_i}K_{3i}\zeta_{3i}\,, \tag{S80}$$

$$\hat{B}_{L4i} = y_{4_i}y_{3_i}\gamma_{3_i}I_{3i}L_{3i}\phi, \tag{S81}$$

$$\hat{C}_{L4i} = -2\upsilon_1y_{4_i}y_{3_i}\gamma_{3_i}y_2HJ_{3_i}M_{3i}u_Bexp\left(\frac{u_B}{2}\right)E_1\overline{C}_{1_{in}}\,, \tag{S82}$$

where $K_{3i} = \lambda_{L3i}/[(R_{L3i} - R_{L4})p + \lambda_{L3i} - \lambda_{L4}]$, $L_{3i} = \lambda_{L3i}/[(R_{L2} - R_{L4})p + \lambda_{L2} - \lambda_{L4}]$, $M_{3i} = \lambda_{L3i}/[(R_{L1} - R_{L4})p + \lambda_{L1} - \lambda_{L4}]$, and K_{B3i}, L_{B3i}, and M_{B3i} pertain to the PRB. From here on the boundary conditions (14), (15), and (16) are applied to Eqs. (S75) and (S76) in the same manner as they were for the serial degradation pathway. Therefore, the difference in working with a daughter product resulting from a convergent multi-parent reaction is that the boundary conditions are also applied to the two additional terms in the right-hand-side of Eqs. (51) and (52). This results in a significantly longer solution of SP4. Based on these analyses, the *dimensional steady-state* form of ϱ is:

$$\varrho = 2v_4 u_B E_4 C_{4_{in}} + \sum_{i=1}^{3} \frac{y_{4i}(K_{3i}-K_{B3i})}{v_4+\theta\delta\omega_4}[v_4 + \theta\delta\omega_{3i} - \theta\delta(\omega_{3i} - \omega_4)\mu_4](\varepsilon_{3i} + \iota_{3i}) +$$

$$\frac{y_{4i}K_{B3i}(v_{3i}+\theta\delta\omega_{3i})(1-\mu_4)}{v_4+\theta\delta\omega_4}\sigma_{3i} + \frac{y_{4i}y_{3i}\gamma_{3i}\delta}{v_4+\theta\delta\omega_4}\dot{\Omega}_{3i}(\alpha + \beta) + \frac{y_{4i}y_{3i}\gamma_{3i}L_{B3i}I_{B3i}(v_2+\theta\delta\omega_2)(\mu_4-1)}{v_4+\theta\delta\omega_4}\psi +$$

$$\frac{2v_1 y_{4i}y_{3i}\gamma_{3i}y_2 u_B E_1\theta\delta(1-\mu_4)}{v_4+\theta\delta\omega_4}\ddot{\Omega}_{3i}C_{1_{in}} + 2v_4 y_{4i}K_{B3i}u_B E_4 C_{3i_{in}} +$$

$$2v_4 y_{4i}y_{3i}\gamma_{3i}u_B I_{B3i}E_4(K_{B3i} - L_{B3i})C_{2_{in}} + 2y_{4i}y_{3i}\gamma_{3i}y_2 u_B\dddot{\Omega}_{3i}C_{1_{in}}\,, \tag{S83}$$

in which $exp\left(\frac{u_B}{2}\right)$ has been factored out of all applicable terms of Eq. (S83) and combined with the exponential in Eq. (S89). From Eq. (S83) the following are defined:

$$\varepsilon_{3i} + \iota_{3i} =$$

$$2v_{3i}u_B E_{3i}C_{3i_{in}} + \frac{y_{3i}\gamma_{3i}\theta(I_{3i}-I_{B3i})\delta(\omega_2-\omega_{3i})(1-\mu_{3i})}{v_{3i}+\theta\delta\omega_{3i}}(\alpha + \beta) + \frac{y_{3i}\gamma_{3i}I_{B3i}(v_2+\theta\delta\omega_2)(1-\mu_{3i})}{v_{3i}+\theta\delta\omega_{3i}}\psi +$$

$$\frac{2v_1 y_{3i}\gamma_{3i}y_2 u_B\theta E_1\delta(1-\mu_{3i})}{v_{3i}+\theta\delta\omega_{3i}}C_{1_{in}}[(\omega_1 - \omega_{3i})(J_{B3i}H_B - J_{3i}H) + (\omega_2 - \omega_{3i})I_{3i}(H - H_B)] +$$

$$2v_{3\mathrm{i}}y_{3i}\gamma_{3i}I_{B3i}u_B E_{3i}C_{2_{in}} - 2v_{3\mathrm{i}}y_{3i}\gamma_{3i}y_2 u_B H_B E_{3i}(J_{B3i} - I_{B3i})C_{1_{in}}, \tag{S84}$$

$$\sigma_{3i} =$$

$$\frac{y_{3i}\gamma_{3i}(I_{3i}-I_{B3i})\theta\delta(\omega_2-\omega_{3i})}{v_{3i}+\theta\delta\omega_{3i}}(\alpha + \beta) + \frac{y_{3i}\gamma_{3i}I_{B3i}(v_2+\theta\delta\omega_2)}{v_{3i}+\theta\delta\omega_{3i}}\psi + \frac{2v_1 y_{3i}\gamma_{3i}y_2 u_B E_1\theta\delta}{v_{3i}+\theta\delta\omega_{3i}}C_{1_{in}}[(\omega_1 -$$

$$\omega_{3i})(J_{B3i}H_B - J_{3i}H) + (\omega_2 - \omega_{3i})I_{3i}(H - H_B)]\,, \tag{S85}$$

$$\dot{\Omega}_{3i} = (L_{B3i}I_{B3i} - L_{3i}I_{3i})\left(\frac{v_4}{\delta} + \theta\omega_2 - \theta(\omega_2 - \omega_4)\mu_4\right) + K_{3i}(I_{B3i} - I_{3i})\Big(\theta(\omega_{3i} -$$

$$\omega_4)\mu_4 - \frac{v_4}{\delta} - \theta\omega_{3i}\Big)\,, \tag{S86}$$

$$\ddot{\Omega}_{3i} = (\omega_1 - \omega_4)(J_{3i}HM_{3i} - J_{B3i}H_BM_{B3i}) + L_{3i}I_{3i}(\omega_2 - \omega_4)(H_B - H) +$$
$$K_{3i}(\omega_{3i} - \omega_4)\big(H_B(J_{B3i} - I_{3i}) - H(J_{3i} - I_{3i})\big)\,, \tag{S87}$$

$$\dddot{\Omega}_{3i} = \upsilon_1E_1\left(J_{B_{3i}}H_B(K_{3i} - M_{B3i}) + J_{3i}H(M_{3i} - K_{3i}) + I_{3i}(H - H_B)(K_{3i} - L_{3i})\right) +$$
$$\upsilon_4E_4H_B\big(I_{B3i}(K_{B3i} - L_{B3i}) + J_{B3i}(M_{B3i} - K_{B3i})\big)\,, \tag{S88}$$

where υ_{3i}, ω_{3i}, I_{3i}, I_{B3i}, J_{3i}, and J_{B3i} were defined above in SP3i but in Eqs. (S83)-(S88) they are in their steady-state dimensional form. With ϱ completely defined the steady-state analytical solution of C_{L4} (in dimensional form) can now be determined; i.e.,

$$C_{L4} = \varrho exp\left(\frac{u_L - 2D_L\omega_4}{2D_L}x + \frac{u_BB}{2D_B}\right) - \left[\sum_{i=1}^{3} y_{4i}K_{3i}\zeta_{3i}exp(-\omega_{3i}x)\right]exp\left(\frac{u_L}{2D_L}x + \frac{u_BB}{2D_B}\right) +$$
$$\phi\left[\sum_{i=1}^{3} y_{4i}y_{3i}\gamma_{3i}I_{3i}L_{3i}\right]\left(\frac{u_L - 2D_L\omega_2}{2D_L}x + \frac{u_BB}{2D_B}\right) -$$
$$2\upsilon_1y_2u_BHE_1C_{1_{in}}\left[\sum_{i=1}^{3} y_{4i}y_{3i}\gamma_{3i}\,J_{3i}M_{3i}\right]exp\left(\frac{u_L - 2D_L\omega_1}{2D_L}x + \frac{u_BB}{2D_B}\right)\,, \tag{S89}$$

where ϱ is Eq. (S83), ϕ is the dimensional steady-state version of (S18), and ζ_{3i} is

$$\zeta_{3i} = 2\upsilon_{3i}u_BE_{3i}C_{3i_{in}} + \frac{y_{3i}\gamma_{3i}(I_{3i} - I_{B3i})}{\upsilon_{3i} + \theta\delta\omega_{3i}}[\upsilon_{3i} + \theta\delta\omega_2 - \theta\delta(\omega_2 - \omega_{3i})\mu_{3i}](\alpha + \beta) +$$
$$\frac{y_{3i}\gamma_{3i}I_{B3i}(\upsilon_2 + \theta\delta\omega_2)(1 - \mu_{3i})}{\upsilon_{3i} + \theta\delta\omega_{3i}}\psi + \frac{2\upsilon_1y_{3i}\gamma_{3i}y_2u_BE_1\theta\delta(1 - \mu_{3i})}{\upsilon_{3i} + \theta\delta\omega_{3i}}C_{1_{in}}[(\omega_1 - \omega_{3i})(J_{B3i}H_B - J_{3i}H) +$$
$$(\omega_2 - \omega_{3i})I_{3i}(H - H_B)] + 2\upsilon_{3i}y_{3i}\gamma_{3i}I_{B3i}u_BE_{3i}C_{2_{in}} + 2y_{3i}\gamma_{3i}y_2u_BC_{1_{in}}\big[\upsilon_1E_1\big(J_{B3i}H_B -$$
$$J_{3i}H + I_{3i}(H - H_B)\big) - \upsilon_{3i}E_{3i}H_B(J_{B3i} - I_{B3i})\big]\,, \tag{S90}$$

where $\mu_{3i} = E_{3i}\upsilon_{3i}(u_B - 2D_B\upsilon_{3i})exp(-B\upsilon_{3i})$, and ψ and $\alpha + \beta$ are all in their respective steady-state dimensional forms.

Species 6:

The governing equations of SP6 are Eqs. (53) and (54). Applying the dimensionless parameters in Eq. (9) and the Laplace transform gives the following general solutions:

$$\overline{C}_{BD6} = \kappa_6 \exp\left(\frac{u_{BD}+2v_{D6}}{2}x_D\right) + \xi_6 \exp\left(\frac{u_{BD}-2v_{D6}}{2}x_D\right) + \hat{A}_B exp\left(\frac{u_{BD}+2v_{D5}}{2}x_D\right) +$$
$$\hat{B}_B \exp\left(\frac{u_{BD}-2v_{D5}}{2}x_D\right) + \hat{C}_B exp\left(\frac{u_{BD}+2v_{D2}}{2}x_D\right) + \hat{D}_B \exp\left(\frac{u_{BD}-2v_{D2}}{2}x_D\right) +$$
$$\hat{E}_B exp\left(\frac{u_{BD}+2v_{D1}}{2}x_D\right) + \hat{F}_B \exp\left(\frac{u_{BD}-2v_{D1}}{2}x_D\right) \tag{S91}$$

$$\overline{C}_{LD6} = \varrho_6 exp\left(\frac{u_{LD}-2\omega_{D6}}{2\delta}x_D\right) + \hat{A}_L exp\left(\frac{u_{LD}-2\omega_{D5}}{2\delta}x_D\right) + \hat{B}_L exp\left(\frac{u_{LD}-2\omega_{D2}}{2\delta}x_D\right)$$
$$+ \hat{C}_L exp\left(\frac{u_{LD}-2\omega_{D1}}{2\delta}x_D\right) \tag{S92}$$

The subscript "D" is dropped and each coefficient $\hat{A}$, $\hat{B}$, $\hat{C}$, $\hat{D}$, $\hat{E}$, and $\hat{F}$ must satisfy its respective homogeneous solution, therefore:

$$\hat{A}_B = -y_6 K_{B5}\varepsilon_5 \quad \text{and} \quad \hat{B}_B = -y_6 K_{B5}\iota_5 \,, \tag{S93}$$

$$\hat{C}_B = y_6 y_5 \gamma_5 I_{B5} L_{B5}\alpha \quad \text{and} \quad \hat{D}_B = y_6 y_5 \gamma_5 I_{B5} L_{B5}\beta, \tag{S94}$$

$$\hat{E}_B = -y_6 y_5 \gamma_5 y_2 H_B J_{B5} M_{B5} u_B exp\left(\frac{u_B}{2}\right)(v_1 - \theta\omega_1)E_1 \overline{C}_{1_{in}} \,,$$

$$\text{and } \hat{F}_B = -y_6 y_5 \gamma_5 y_2 H_B J_{B5} M_{B5} u_B exp\left(\frac{u_B}{2}\right)(v_1 + \theta\omega_1)E_1 \overline{C}_{1_{in}} \,, \tag{S95}$$

$$\hat{A}_L = -y_6 K_5 \zeta_5 \,, \tag{S96}$$

$$\hat{B}_L = y_6 y_5 \gamma_5 I_5 L_5 \phi \,, \tag{S97}$$

$$\hat{C}_L = -2v_1 y_6 y_5 \gamma_5 y_2 H J_5 M_5 u_B exp\left(\frac{u_B}{2}\right) E_1 \overline{C}_{1_{in}} \,, \tag{S98}$$

where $K_5 = \lambda_{L5}/[(R_{L5} - R_{L6})p + \lambda_{L5} - \lambda_{L6}]$, $L_5 = \lambda_{L5}/[(R_{L2} - R_{L6})p + \lambda_{L2} - \lambda_{L6}]$, $M_5 = \lambda_{L5}/[(R_{L1} - R_{L6})p + \lambda_{L1} - \lambda_{L6}]$, and K_{B5}, L_{B5}, and M_{B5} pertain to the PRB. Also, $I_5 = \lambda_{L2}/[(R_{L2} - R_{L5})p + \lambda_{L2} - \lambda_{L5}]$, $J_5 = \lambda_{L2}/[(R_{L1} - R_{L5})p + \lambda_{L1} - \lambda_{L5}]$, where I_{B5} and J_{B5} pertain to the PRB. From here on the derivation procedure is equivalent to SP4 of the serial degradation scenario. Applying boundary condition (14) to Eq. (S91) gives

$$\kappa_6(u_B - 2\upsilon_6)exp(-\upsilon_6) + \xi_6(u_B + 2\upsilon_6)exp(\upsilon_6) - 2y_6K_{B5}u_Bexp\left(\frac{u_B}{2}\right)\overline{C}_{5_{in}} + 2y_6y_5\gamma_5I_{B5}u_Bexp\left(\frac{u_B}{2}\right)(L_{B5} - K_{B5})\overline{C}_{2_{in}} + 2y_6y_5\gamma_5y_2H_Bu_Bexp\left(\frac{u_B}{2}\right)\overline{C}_{1_{in}}[I_{B5}(L_{B5} - K_{B5}) + J_{B5}(K_{B5} - M_{B5})] = 2exp\left(\frac{u_B}{2}\right)u_B\overline{C}_{6_{in}} \,, \tag{S99}$$

Applying boundary condition (15) and solving for ϱ_6 gives

$$\varrho_6 = \kappa_6 + \xi_6 + y_6(K_5 - K_{B5})(\varepsilon_5 + \iota_5) + y_6y_5\gamma_5[I_{B5}(L_{B5} - K_5) - I_5(L_5 - K_5)](\alpha + \beta) + 2\upsilon_1y_6y_5\gamma_5y_2u_Bexp\left(\frac{u_B}{2}\right)E_1[J_{B5}H_B(K_5 - M_{B5}) - J_5H(K_5 - M_5) + I_5(H - H_B)(K_5 - L_5)]\overline{C}_{1_{in}}. \tag{S100}$$

Lastly, applying the boundary condition (16) and repeating the procedure outlined from Eqs. (S40) to (S42) twice gives

$$\kappa_6 = \xi_6\frac{\upsilon_6-\theta\omega_6}{\upsilon_6+\theta\omega_6} + \frac{y_6\theta(K_5-K_{B5})(\omega_5-\omega_6)}{\upsilon_6+\theta\omega_6}(\varepsilon_5 + \iota_5) + \frac{y_6K_{B5}(\upsilon_5+\theta\omega_5)}{\upsilon_6+\theta\omega_6}\sigma_5 + \frac{y_6y_5\gamma_5\theta}{\upsilon_6+\theta\omega_6}[(\omega_2 - \omega_6)(L_{B5}I_{B5} - L_5I_5) - K_5(\omega_5 - \omega_6)(I_{B5} - I_5)](\alpha + \beta) - \frac{y_6y_5\gamma_5L_{B5}I_{B5}(\upsilon_2+\theta\omega_2)}{\upsilon_6+\theta\omega_6}\psi + \frac{2\upsilon_1y_6y_5\gamma_5y_2exp\left(\frac{u_B}{2}\right)u_B\theta E_1}{\upsilon_6+\theta\omega_6}\ddot{\Omega}_5\overline{C}_{1_{in}} \,, \tag{S101}$$

After solving for κ_6, ξ_6, and ϱ_6 the (dimensional) steady-state analytical solution C_{L6} can be determined; i.e.,

$$C_{L6} = \left\{2\upsilon_6u_BE_6C_{6_{in}} + \frac{y_6(K_5-K_{B5})}{\upsilon_6+\theta\delta\omega_6}[\upsilon_6 + \theta\delta\omega_5 - \theta\delta(\omega_5 - \omega_6)\mu_6](\varepsilon_5 + \iota_5) + \frac{y_6K_{B5}(\upsilon_5+\theta\delta\omega_5)(1-\mu_6)}{\upsilon_6+\theta\delta\omega_6}\sigma_5 + \frac{y_6y_5\gamma_5\delta}{\upsilon_6+\theta\delta\omega_6}\dot{\Omega}_5(\alpha + \beta) + \frac{y_6y_5\gamma_5L_{B5}I_{B5}(\upsilon_2+\theta\delta\omega_2)(\mu_6-1)}{\upsilon_6+\theta\delta\omega_6}\psi + \frac{2\upsilon_1y_6y_5\gamma_5y_2u_BE_1\theta\delta(1-\mu_6)}{\upsilon_6+\theta\delta\omega_6}\ddot{\Omega}_5C_{1_{in}} + 2\upsilon_6y_6K_{B5}u_BE_6C_{5_{in}} + 2\upsilon_6y_6y_5\gamma_5u_BI_{B5}E_6(K_{B5} - L_{B5})C_{2_{in}} + 2y_6y_5\gamma_5y_2u_B\dddot{\Omega}_5C_{1_{in}}\right\}exp\left(\frac{u_L-2D_L\omega_6}{2D_L}x + \frac{u_BB}{2D_B}\right) - y_6K_5\zeta_5exp\left(\frac{u_L-2D_L\omega_5}{2D_L}x + \frac{u_BB}{2D_B}\right) + y_6y_5\gamma_5L_5I_5\phi exp\left(\frac{u_L-2D_L\omega_2}{2D_L}x + \frac{u_BB}{2D_B}\right) - 2\upsilon_1y_6y_5\gamma_5y_2u_BHJ_5M_5E_1C_{1_{in}}exp\left(\frac{u_L-2D_L\omega_1}{2D_L}x + \frac{u_BB}{2D_B}\right) \,, \tag{S102}$$

where $\mu_6 = E_6 \upsilon_6 (u_B - 2D_B \upsilon_6) exp(-B\upsilon_6)$ and where $\varepsilon_5 + \iota_5$, σ_5, $\dot{\Omega}_5$, $\ddot{\Omega}_5$, $\dddot{\Omega}_5$, and ζ_5 are Eqs. (S84), (S85), (S86), (S87), (S88), and (S90) in which subscript “5” replaces all “$3i$” subscripts and subscript “6” replaces all “4” subscripts where applicable.

APPENDIX B

Two additional sets of figures comparing the analytical solutions with VMOD are presented below. In addition, the tables below present the transport parameters used to generate the figures. Note that other parameters such as discharge, gradient, conductivity, porosity, groundwater seepage velocity, and stoichiometric yields did not change from that of Table 1 and are not included in Tables B-1 and B-2.

Table B-1	
B_{req} (m)	1
α_B (m)	0.1
α_L (m)	2
λ_{B1} (day^{-1})	1.5
λ_{L1} (day^{-1})	0.15
λ_{B2} (day^{-1})	1.8
λ_{L2} (day^{-1})	0.2
λ_{B3} (day^{-1})	0.5
λ_{L3} (day^{-1})	0.03
λ_{B4} (day^{-1})	1
λ_{L4} (day^{-1})	0.05
C_{1in} (mg L^{-1})	10
C_{2in} (mg L^{-1})	5
C_{3in} (mg L^{-1})	8
C_{4in} (mg L^{-1})	2

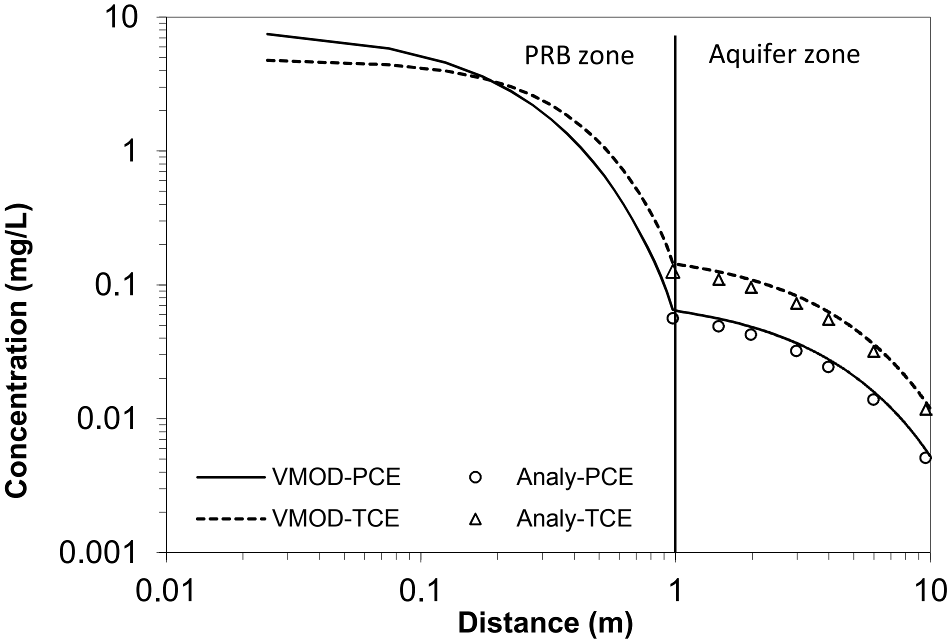

Figure B-1A: Comparison of the analytical solutions & VMOD: PCE & TCE

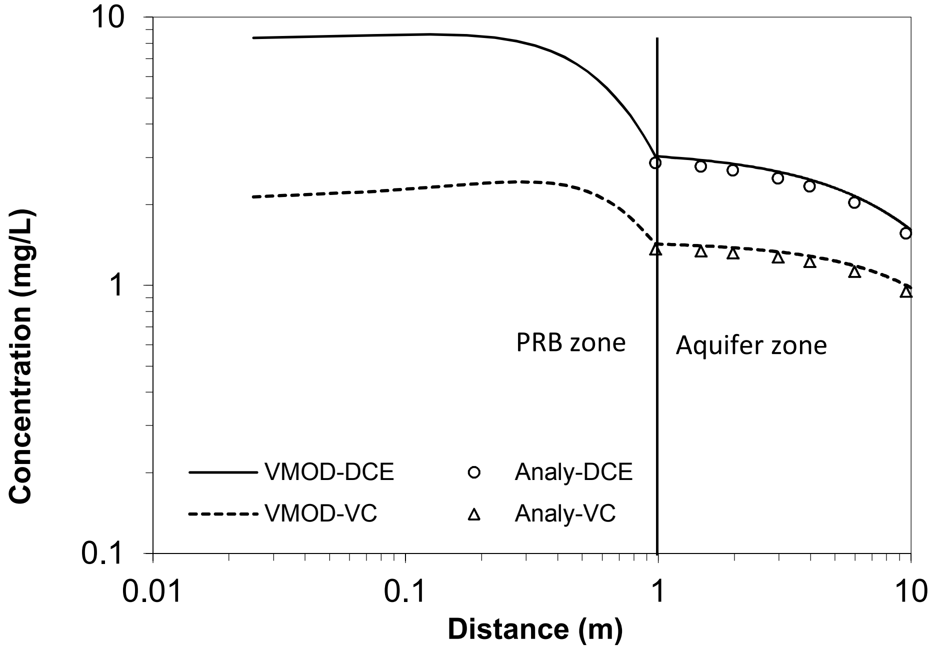

Figure B-1B: Comparison of the analytical solutions & VMOD: DCE & VC

Table B-2	
B_{req} (m)	1.5
α_B (m)	0.15
α_L (m)	2
λ_{B1} (day^{-1})	1.3
λ_{L1} (day^{-1})	0.25
λ_{B2} (day^{-1})	0.9
λ_{L2} (day^{-1})	0.09
λ_{B3} (day^{-1})	1.1
λ_{L3} (day^{-1})	0.15
λ_{B4} (day^{-1})	0.6
λ_{L4} (day^{-1})	0.03
C_{1in} (mg L^{-1})	8
C_{2in} (mg L^{-1})	6
C_{3in} (mg L^{-1})	2
C_{4in} (mg L^{-1})	3

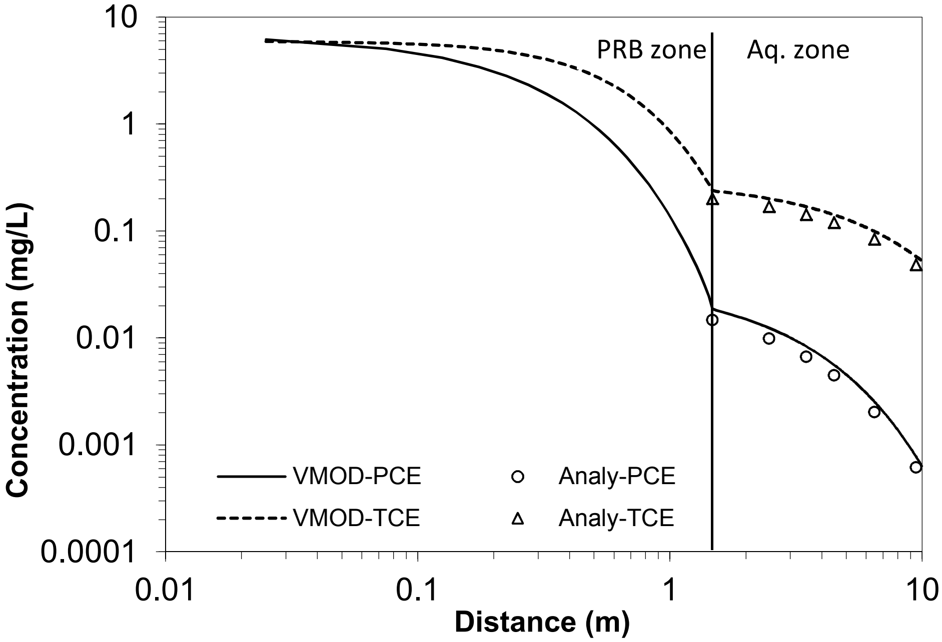

Figure B-2A: Comparison of the analytical solutions & VMOD: PCE & TCE

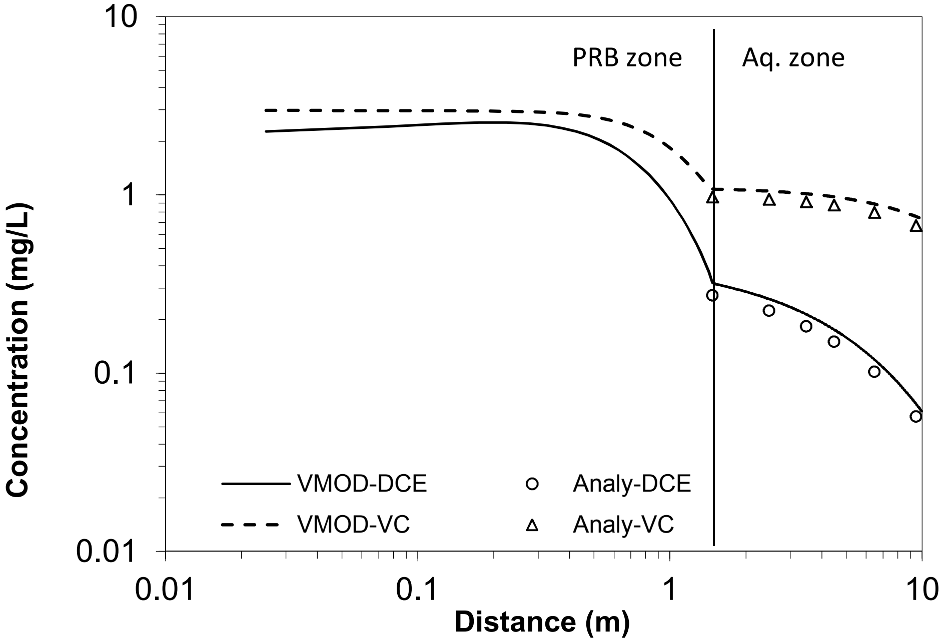

Figure B-2B: Comparison of the analytical solutions & VMOD: DCE & VC

VITA

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