

# Estimation of Daughter Product Biodegradation Rate Constants in Advection-Dominated Aquifers<sup>1</sup>

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## Abstract

Mathematical analyses are used to examine the sensitivity of longitudinal dispersivity in parent and daughter analytical solutions for 1-D, coupled, steady-state advection-dispersion equations with sequential first-order decay. The results indicate that the 1-D advection-dominated analytical solution (zero longitudinal dispersivity) is within 20% of the 1-D advection-dispersion analytical solution when the Damköhler number (importance of biodegradation vs. advection) of parent and daughter compound is less than unity ( $Da < 1$ ) and the Peclet number (importance of advection vs. longitudinal dispersion) is greater than six ( $Pe > 6$ ). To estimate first-order daughter product rate constants in advection-dominated zones, 1-D, 2-D and 3-D multi-species analytical solutions with zero longitudinal dispersivity are derived for 3 sequentially degrading compounds. The closed form of these exact analytical solutions has the advantage of both easy incorporation into spreadsheets and rapid computation without loss of accuracy which occurs in some codes (e.g. BIOCHLOR or BIOSCREEN) based on the Domenico (1987) solution when nonzero values for the longitudinal dispersivity are specified.

As an application, the 1-D advection-dominated analytical solution was applied to estimate field-scale rate constants of  $0.81 \text{ yr}^{-1}$ ,  $0.74 \text{ yr}^{-1}$ , and  $0.69 \text{ yr}^{-1}$  for trichloroethene (TCE), cis-1,2-dichloroethene (DCE), and vinyl chloride (VC), respectively at the Harris Palm Bay, FL site. The 1-D advection-dispersion, 2-D advection-dominated, and 3-D advection-dominated analytical solutions were also fitted to the plume centerline data using a nonlinear least square approach by varying rate constants for comparison to the 1-D advection-dominated model. The 1-D advection-dominated analytical solution yielded slightly lower rate constant values than the 1-D advection-dispersion model because downgradient concentrations from a constant concentration source are increased by longitudinal dispersion. The estimated rate constants were a little higher using the 1-D advection-dominated model compared to the 2-D and 3-D models because concentrations in these models are decreased by transverse dispersion. The uncertainty in estimated rate constants using 1-D, 2-D, and 3-D advection-dominated models is proportional to the uncertainty in the average linear groundwater velocity. For aquifers with high groundwater velocities and source dimensions similar to this site, the simpler 1-D advection-dominated analytical solution, which does not require difficult-to-measure field parameters such as longitudinal and transverse dispersivity or source dimensions, is a useful tool for estimating rate constants of parent and daughter products.

## Introduction

Biodegradation rates of daughter products can be a controlling factor on the cleanup rate at some sites with contaminated groundwater. Therefore, obtaining reasonably accurate rate constants of daughter products is important for estimating the remedial time frame particularly for monitored natural attenuation (MNA). Multi-species models have an advantage over single-species models in estimating daughter product rate constants because multi-species models can account for mass accumulation from parent compounds.

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The primary objective of this paper is to present practical closed-form multi-species analytical solutions for use in improving estimates of first-order biodegradation rate constants of sequentially transforming chemicals in steady-state plumes. Some advantages of closed-form analytical solutions are that they do not require numerical integration, are easy to implement in spreadsheets and other software, and are computationally efficient. In addition, closed-form analytical solutions are useful in examining the accuracy of numerical models that can have significant errors in advection-dominated problems. Given their particular assumptions, these exact analytical solutions are not subject to the significant errors (West and Kuiper, 2004) that can occur in codes such as BIOCHLOR and BIOSCREEN (Newell et al., 1996; Aziz et al., 2000), which incorporate the Domenico (1987) solution, and introduce error when the specified value for the longitudinal dispersion coefficient is nonzero (Srinivasan et al., 2007).

A closed-form analytical solution is first presented for a 1-D steady-state advection-dispersion equation for first-order multiple sequentially degrading species. In many cases, groundwater velocities are high enough in steady-state plumes that longitudinal hydrodynamic dispersion is relatively unimportant, which further reduces the number of required model parameters. For advection-dominated aquifers, closed-form analytical solutions are also developed for steady-state 2-D and 3-D transport of multiple sequentially degrading species with constant concentration source boundary conditions. As an example of their practical utility, closed-form analytical solutions are applied to estimate the field-scale, anaerobic biodegradation rate constants of TCE, DCE, and VC at a site in Palm Bay, FL.

### 1-D Steady-State Analytical Solution to Advection-Dispersion Equations for 3 Sequentially Degrading Species

West et al. (2007) state that significant errors can occur in calculated steady-state plume centerline concentrations in software programs (e.g., BIOSCREEN and BIOCHLOR) based on the Domenico (1987) solution and recommend exact analytical solutions. For 3 compounds undergoing sequential first-order decay and a constant concentration point source, the 1-D exact analytical solution (Burnell et al., 2007) for uniform velocity and longitudinal hydrodynamic dispersion is:

$$C_1 = C_{10} e^{r_1 x} \quad (1a)$$

$$C_2 = C_{20} e^{r_2 x} + C_{10} \frac{k_1 y_{21}}{k_1 - k_2} (e^{r_2 x} - e^{r_1 x}) \quad (1b)$$

$$C_3 = C_{30} e^{r_3 x} - \frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_1 - k_3)} (e^{r_3 x} - e^{r_1 x}) + \left( \frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20} k_2 y_{32}}{(k_2 - k_3)} \right) (e^{r_3 x} - e^{r_2 x}) \quad (1c)$$

where for  $i=1,2,3$

$$r_i = \frac{v}{2D_x} - \sqrt{\frac{v^2}{4D_x^2} + \frac{k_i}{D_x}}$$

and where  $C_1$ ,  $C_2$ , and  $C_3$  are the parent and sequential daughter product concentrations,  $x$  is the downgradient distance from the source,  $v$  is the average linear groundwater velocity,  $D_x$  is the longitudinal dispersion coefficient ( $D_x = D_{oi} \Psi + a_x v$ ),  $a_x$  is the longitudinal dispersivity,  $D_{oi}$  is the free solution diffusion coefficient for species  $i$ ,  $\Psi$  the tortuosity,  $y_{21}$  is the effective yield coefficient indicating the mass of species ( $C_2$ ) produced from its parent ( $C_1$ ),  $y_{32}$  is effective yield coefficient indicating the mass of species ( $C_3$ ) produced from its parent ( $C_2$ ), and  $k_1$ ,  $k_2$ , and  $k_3$ , are the first-order biodegradation rate constants of the parent and sequential daughter products. Biodegradation is assumed to occur only in the aqueous phase. When biodegradation is assumed to occur in both the

aqueous and sorbed phases, the rate constant  $k_i$  should be replaced by  $R_i k_i$  where  $R_i$  is the retardation factor of species  $i$  with  $i = 1, 2$ , and  $3$ . Srinivasan and Clement (2008) present a steady-state, first-order chain decay solution for an arbitrary number of compounds.

### Dimensionless Analysis of 1-D Advection-Dominated Solution for Parent and Daughter Product

When the longitudinal dispersion coefficient is zero, the governing equations for one-dimensional, steady-state concentrations of parent and daughter chemicals undergoing advection and sequential first-order chain decay with a constant concentration point source are:

$$\frac{dC_1}{dx} + \frac{k_1 C_1}{v} = 0 \quad (2a)$$

$$\frac{dC_2}{dx} + \frac{k_2 C_2}{v} = \frac{y_{21} k_1 C_1}{v} \quad (2b)$$

$$\begin{aligned} C_1(0) &= C_{10} \quad C_1 \rightarrow 0 \text{ as } x \rightarrow \infty \\ C_2(0) &= 0 \quad C_2 \rightarrow 0 \text{ as } x \rightarrow \infty \end{aligned} \quad (2c)$$

In the boundary condition (Equations 2c), the daughter concentration is zero at the source and therefore the daughter compound is only generated by biodegradation of the parent.

This first-order linear system of differential equations can be solved sequentially using an integrating factor (Boyce and DiPrima, 1977). The analytical solution for 1-D advection and sequential first-order biodegradation with zero longitudinal dispersion for the parent and daughter is:

$$C_1 = C_{10} e^{-k_1 x/v} \quad (3a)$$

$$C_2 = C_{10} \frac{k_1 y_{21}}{k_1 - k_2} (e^{-k_2 x/v} - e^{-k_1 x/v}) \quad (3b)$$

In order to compare analytical solutions with and without dispersion, the following dimensionless parameters are defined:

$$C_{D1} = \frac{C_1}{C_{10}} \quad C_{D2} = \frac{C_2}{C_{10}} \quad X_D = \frac{x}{x_0} \quad Pe = \frac{v x_0}{D_x} \quad Da_1 = \frac{k_1 x_0}{v} \quad Da_2 = \frac{k_2 x_0}{v} \quad (4)$$

where  $C_{D1}$  and  $C_{D2}$  are the relative concentrations of the parent and daughter concentration,  $X_D$  is the dimensionless distance in the  $x$  direction,  $Pe$  is the Peclet number,  $Da_1$  is the Damköhler number of the parent, and  $Da_2$  is the Damköhler number of the daughter compound. The Peclet number is a measure of the relative importance of advection compared to longitudinal dispersion. For  $Pe$  defined in Equation 4, the free-solution diffusion coefficient, which is relatively unimportant for advection-dominated flow, is assumed to have the same value for each constituent. The Damköhler number measures the relative importance of biodegradation compared to advection. As discussed in Guyonnet and Neville (2004), the dimensionless distance  $X_D$  is defined relative to an arbitrary distance from the source so that taking  $X_D = 1$  implies that the results are applicable to any point  $x = x_0$ . Based on the dimensionless parameters defined above, the analytical solution for advection and sequential first-order sequential biodegradation with zero longitudinal dispersion of parent (Equation 3a) and daughter (Equation 3b) is:

$$C_{D1} = e^{-Da_1 X_D} \quad (5a)$$

$$C_{D2} = \frac{Da_1 y_{21}}{Da_1 - Da_2} (e^{-Da_2 x_D} - e^{-Da_1 x_D}) \quad (5b)$$

The analytical solution for advection, longitudinal dispersion, and sequential first-order biodegradation of the parent (Equation 1a) and daughter (Equation 1b) compounds in dimensionless form is:

$$C_{D1} = e^{\frac{Pe}{2}(1 - \sqrt{1 + 4\frac{Da_2}{Pe}})} \quad (6a)$$

$$C_{D2} = \frac{Da_1 y_{21}}{Da_1 - Da_2} (e^{\frac{Pe}{2}(1 - \sqrt{1 + 4\frac{Da_2}{Pe}})} - e^{\frac{Pe}{2}(1 - \sqrt{1 + 4\frac{Da_1}{Pe}})}) \quad (6b)$$

At sites with relatively high groundwater velocities, the steady-state 1-D analytical solutions are less sensitive to the longitudinal dispersion. As discussed in Cho (1971), the term in the exponential arguments  $r_i$  in Equation 1 can be simplified by expressing it in a generalized binomial series (Abramowitz and Stegun, 1972):

$$r_i = \frac{v}{2D_x} \left[ 1 - \sqrt{1 + 4D_x \frac{k_i}{v^2}} \right] = -\frac{k_i}{v} + a_L \frac{k_i^2}{v^2} + \dots \quad (7)$$

where the free-solution diffusion coefficient is assumed to be zero. An examination of Equation (7) indicates that  $r_i \approx k_i/v$  when  $a_L k_i^2 \ll v^2$ . In advection-dominated zones with relatively slowly degrading compounds, the arguments of the exponential functions in the analytic solution (Equation 1) can be represented using Damköhler numbers  $Da_i = k_i x/v$ , which express the relative importance of reaction versus advection for species  $i$ . Given that  $r_i$  occurs only in the exponential arguments for each chemical of an arbitrary number of members in a decay chain (see Srinivasan and Clement, 2008), the approximation  $r_i \approx k_i/v$  is also applicable for advection-dominated transport of subsequent daughter product solutions. Many aquifers with chlorinated solvents satisfy this approximation ( $a_L k_i^2 \ll v^2$ ) and in this case the concentrations can be approximated reasonably well using advection-reaction analytical solutions (e.g. Equation 3). The advantage of this approximation is the absence of the need for a value of the longitudinal dispersivity value, which is difficult to accurately quantify in the field.

The sensitivity of longitudinal dispersivity for the 1-D case was examined using dimensionless plots to more fully analyze when the advection-dominated analytical solution (Equation 3) is applicable. Figure 1 presents a plot of the ratio of the analytical solution of the parent (Equation 6a) for the advection-dispersion-reaction equation to the analytical solution of the parent (Equation 5a) for the advection-dominated ( $D_x=0$ ) equation as a function of dimensionless Peclet number for several values of dimensionless Damköhler numbers. An examination of this plot indicates the two solutions are within 20% for  $Pe > 6$  (relatively permeable aquifer) and  $Da < 1$  (relatively slow degradation).

For the 3-D case, dimensionless analyses by Guyonnet and Neville (2004) observed discrepancies between the advection-dominated Domenico parent solution and exact parent solution presented in Sagar (1982) for intermediate values of Peclet number between 0.1 and 6. Pfannkuch (1963) indicates this range of  $Pe$  corresponds to the region where hydrodynamic dispersion and molecular diffusion both affect transport. For  $Pe > 6$ , Guyonnet and Neville (2004)

observed relatively small differences in these solutions along the plume centerline particularly when steady-state conditions were reached.

**Figure 1. Examination of ratio of 1-D parent analytical solution (Equation 1a) for advection-dispersion-reaction equation to the 1-D parent analytical solution (Equation 3a) to advection-reaction equation ( $a_L=0$ ) as a function of dimensionless Peclet number for several values of parent Damköhler numbers.**

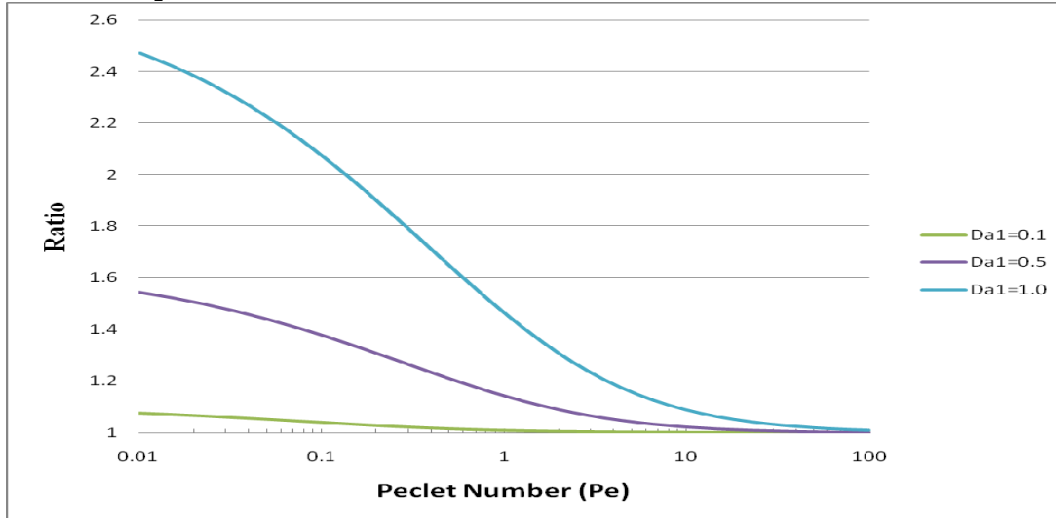
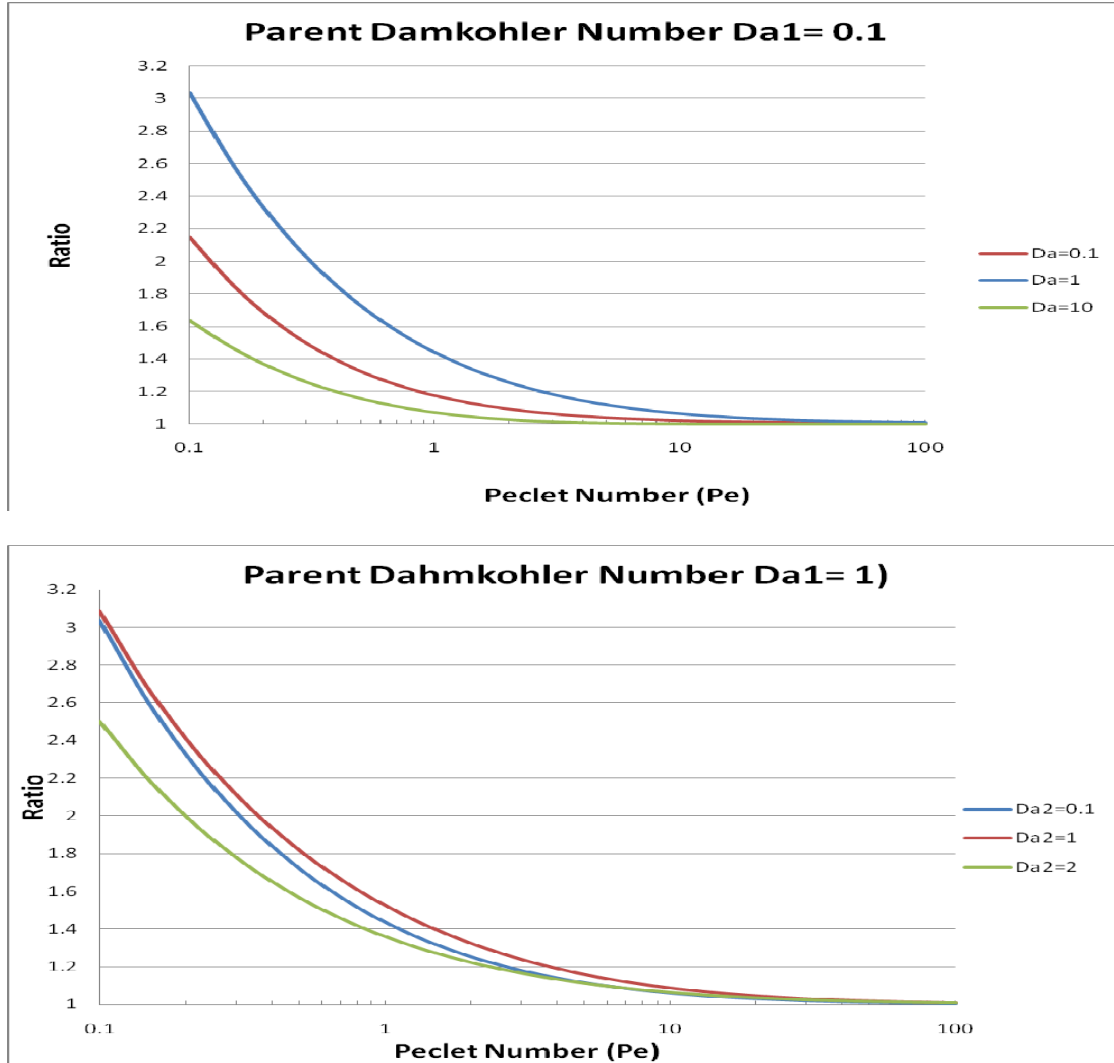


Figure 2 presents plots of the ratio of the daughter solution (Equation 6b) for the 1-D advection-dispersion-reaction equation to the daughter solution (Equation 5b) of the advection-reaction ( $a_L=0$ ) equation for various daughter Damköhler numbers. In the first plot (Figure 2a), the parent Damköhler number ( $Da_1$ ) is equal to 0.1. In the second plot (Figure 2b), the parent Damköhler number ( $Da_1$ ) is equal to 1.0. An examination of these plots also indicates that the advection-reaction solution is less than 20% of the advection-dispersion-reaction equation when the parent Damköhler number  $Da_1 < 1$  and the Peclet number  $Pe > 6$  (relatively permeable). In other words, for 1-D, the steady-state advection-dominated analytical solution (Equation 3) is reasonably accurate for examining the transport of slowly sequentially degrading contaminants (e.g. chlorinated solvents) in higher permeability aquifers.

**Figure 2. Examination of ratio of 1-D daughter analytical solution (Equation 1b) for advection-dispersion-reaction to the 1-D daughter analytical solution (Equation 3b) for advection-reaction ( $a_1=0$ ) as a function of dimensionless Peclet number for several values of daughter Damköhler numbers with: a) parent  $Da_1=0.1$  and b) parent  $Da_1=1.0$ .**



### 3-D Advection-Dominated Steady-State Analytical Solution for 3 Species Undergoing Sequential First-Order Transformations with Vertical Planar Source

For advection-dominated zones, closed-form 2-D and 3-D analytical solutions were derived for three species moving at a constant velocity and undergoing sequential first-order decay at steady-state plume conditions. Figure 3 presents a conceptual picture for the 3-D problem. The governing equations for the 3-D case with a vertical planar source are:

$$v \frac{\partial C_1}{\partial x} = D_y \frac{\partial^2 C_1}{\partial y^2} + D_z \frac{\partial^2 C_1}{\partial z^2} - k_1 C_1 \quad (8a)$$

$$v \frac{\partial C_2}{\partial x} = D_y \frac{\partial^2 C_2}{\partial y^2} + D_z \frac{\partial^2 C_2}{\partial z^2} - k_2 C_2 + k_1 y_{21} C_1 \quad (8b)$$

$$v \frac{\partial C_3}{\partial x} = D_y \frac{\partial^2 C_3}{\partial y^2} + D_z \frac{\partial^2 C_3}{\partial z^2} - k_3 C_3 + k_2 y_{32} C_2 \quad (8c)$$

$$C_1(0, y, z, t) = C_{10}$$

$$C_2(0, y, t) = C_{20} - \frac{W}{2} \leq y \leq \frac{W}{2} - \frac{H}{2} \leq z \leq \frac{H}{2} \quad C_1 \rightarrow 0 \text{ as } x \rightarrow \infty, y \rightarrow \pm \infty, z \rightarrow \pm \infty$$

$$C_3(0, y, t) = C_{30} \quad C_2 \rightarrow 0 \text{ as } x \rightarrow \infty, y \rightarrow \pm \infty, z \rightarrow \pm \infty \quad (8d)$$

$$C_3 \rightarrow 0 \text{ as } x \rightarrow \infty, y \rightarrow \pm \infty, z \rightarrow \pm \infty$$

where  $D_y$  is the horizontal transverse dispersion coefficient,  $D_z$  is the vertical transverse dispersion coefficient,  $W$  is the width of source zone, and  $H$  is the thickness of the source zone. These coupled, linear partial differential equations are solved sequentially. The parent equation (Equation 8a) is homogeneous and is solved first using a double Fourier transform in  $y$  and  $z$ , solving the differential equation, and taking the inverse double Fourier transform (Haberman, 1987). The parent solution (Equation 9a) is in agreement with the solution presented in Srinivasan et al. (2007), which is at steady-state behind the front ( $x < vt$ ). Srinivasan et al. (2007) also showed that the modified-Domenico solution (Martyn-Hayden and Robbins, 1997) is equal to Equation 9a when the longitudinal dispersivity is zero. The daughter and granddaughter (Equations 8b and 8c) are nonhomogeneous and are solved sequentially using a modified method of undetermined coefficients (Sneddon, 1957; Boyce and DiPrima, 1977). The analytical solution for this 3-D case is:

#### Parent

$$C_1 = \frac{C_{10}}{4} (e^{-k_1 x/v}) \left( \operatorname{erf}\left(\frac{y+W}{2\sqrt{a_y x}}\right) - \operatorname{erf}\left(\frac{y-W}{2\sqrt{a_y x}}\right) \right) \left( \operatorname{erf}\left(\frac{z+H}{2\sqrt{a_z x}}\right) - \operatorname{erf}\left(\frac{z-H}{2\sqrt{a_z x}}\right) \right) \quad (9a)$$

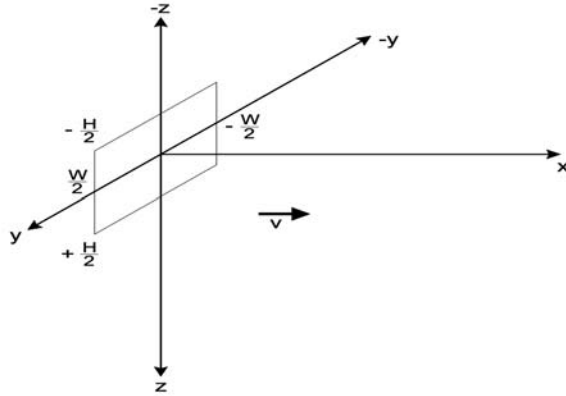
#### Daughter:

$$C_2 = \left( \frac{C_{20}}{4} e^{-k_2 x/v} + \frac{C_{10} k_1 y_{21}}{4(k_1 - k_2)} (e^{-k_2 x/v} - e^{-k_1 x/v}) \right) \left( \operatorname{erf}\left(\frac{y+W}{2\sqrt{a_y x}}\right) - \operatorname{erf}\left(\frac{y-W}{2\sqrt{a_y x}}\right) \right) \left( \operatorname{erf}\left(\frac{z+H}{2\sqrt{a_z x}}\right) - \operatorname{erf}\left(\frac{z-H}{2\sqrt{a_z x}}\right) \right) \quad (9b)$$

#### Granddaughter:

$$C_3 = \frac{1}{4} \left( C_{30} e^{-k_3 x/v} - \frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_1 - k_3)} (e^{-k_3 x/v} - e^{-k_1 x/v}) + \frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20} k_2 y_{32}}{(k_2 - k_3)} (e^{-k_3 x/v} - e^{-k_2 x/v}) \right) \left( \operatorname{erf}\left(\frac{y+W}{2\sqrt{a_y x}}\right) - \operatorname{erf}\left(\frac{y-W}{2\sqrt{a_y x}}\right) \right) \left( \operatorname{erf}\left(\frac{z+H}{2\sqrt{a_z x}}\right) - \operatorname{erf}\left(\frac{z-H}{2\sqrt{a_z x}}\right) \right) \quad (9c)$$

**Figure 3. Conceptual picture of a vertical planar source with only transverse dispersion and a constant velocity in the x direction for the 3-D advection-dominated (no longitudinal dispersion) first-order sequential decay multi-species analytical solution**



**2-D Advection-Dominated Steady-State Analytical Solution for 3 Species Undergoing Sequential First-Order Transformations with Finite-Width Line Source**

For cases where the aquifer thickness is relatively small and concentrations do not vary significantly with depth, a 2-D model can be used. The governing equations for the 2-D mathematical model with no longitudinal hydrodynamic dispersion for a finite-width line source are:

$$v \frac{\partial C_1}{\partial x} = D_y \frac{\partial^2 C_1}{\partial y^2} - k_1 C_1 \tag{10a}$$

$$v \frac{\partial C_2}{\partial x} = D_y \frac{\partial^2 C_2}{\partial y^2} - k_2 C_2 + k_1 y_{21} C_1 \tag{10b}$$

$$v \frac{\partial C_3}{\partial x} = D_y \frac{\partial^2 C_3}{\partial y^2} - k_3 C_3 + k_2 y_{32} C_2 \tag{10c}$$

$$\begin{aligned} C_1(0, y, z) &= C_{10} & x \rightarrow \infty, y \rightarrow \pm \infty, z \rightarrow \pm \infty \\ C_2(0, y) &= C_{20} - \frac{W}{2} \leq y \leq \frac{W}{2} & x \rightarrow \infty, y \rightarrow \pm \infty, z \rightarrow \pm \infty \\ C_3(0, y) &= C_{30} & x \rightarrow \infty, y \rightarrow \pm \infty, z \rightarrow \pm \infty \end{aligned} \tag{10d}$$

The derivation for this 2-D model is similar to the method for the 3-D model. The analytical solution for this 2-D model is:

**Parent:**

$$C_1 = \frac{C_{10}}{2} (e^{-k_1 x/v}) \left( \operatorname{erf} \left( \frac{(y + \frac{W}{2})}{2\sqrt{a_y x}} \right) - \operatorname{erf} \left( \frac{(y - \frac{W}{2})}{2\sqrt{a_y x}} \right) \right) \tag{11a}$$

**Daughter:**

$$C_2 = \left( \frac{C_{20}}{2} e^{-k_2 x/v} + \frac{C_{10}}{2} \frac{k_1 y_{21}}{(k_1 - k_2)} (e^{-k_2 x/v} - e^{-k_1 x/v}) \right) \left( \operatorname{erf} \left( \frac{(y + \frac{W}{2})}{2\sqrt{a_y x}} \right) - \operatorname{erf} \left( \frac{(y - \frac{W}{2})}{2\sqrt{a_y x}} \right) \right) \tag{11b}$$

**Granddaughter:**

$$C_3 = \left( \frac{C_{30}}{2} e^{-k_3 x/v} - \frac{C_{10} k_1 y_{21} k_2 y_{32}}{2(k_1 - k_2)(k_1 - k_3)} (e^{-k_3 x/v} - e^{-k_1 x/v}) \right. \\ \left. + \left( \frac{C_{10} k_1 y_{21} k_2 y_{32}}{2(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20} k_2 y_{32}}{2(k_2 - k_3)} \right) (e^{-k_3 x/v} - e^{-k_2 x/v}) \right) \left( \operatorname{erf} \left( \frac{y + \frac{W}{2}}{2\sqrt{a_y x}} \right) - \operatorname{erf} \left( \frac{y - \frac{W}{2}}{2\sqrt{a_y x}} \right) \right) \quad (11c)$$

In the 2-D and 3-D models, biodegradation is assumed to occur only in the aqueous phase. When biodegradation is assumed to occur in both the aqueous and sorbed phases, the rate constant  $k_i$  should be replaced by  $R_i k_i$  where  $R_i$  is the retardation factor of species  $i$  with  $i = 1, 2, \text{ and } 3$ .

The closed form of these analytical solutions has the advantage of both easy incorporation into spreadsheets and rapid computation without errors from: (1) numerical integration; (2) occurrence of large arguments in exponential functions causing numerical overflow; (3) occurrence of complex numbers in arguments of exponential and error functions; or (4) inaccuracies which occur in codes (e.g. BIOCHLOR or BIOSCREEN) based on the Domenico (1987) solution with nonzero values for the longitudinal dispersivity. These steady-state solutions are computationally efficient in comparison to the large run times of transient simulations for estimating steady-state concentrations. These analytical solutions can also be used to examine the accuracy of numerical models that can have errors from artificial dispersion and overshoot oscillations.

Equations 11a, 11b, and 11c in this 2-D advection-dominated analytical solution are the same as Equations 1a, 1b, and 1c, respectively, in the advection-dispersion solution with the  $r_i \approx k_i/v$  approximation, but divided by 2, and then multiplied by the Domenico (1987) solution spreading term in the  $y$  direction. A similar pattern occurs for the 3-D advection-dominated solution where Equation 1 is multiplied by the spreading terms and divided by 4. In other words, for advection-dominated problems, the effect of increasing the spatial dimension consists of multiplying the 1-D solution by the corresponding Domenico spreading term and dividing by a factor of two.

Along the plume centerline ( $y=0$  and  $z=0$ ), the ratio of the 2-D and 3-D advection-dominated analytical solutions to the 1-D advection-dominated analytical solution is given by  $\operatorname{erf}(W/4\sqrt{a_y x})$  and  $\operatorname{erf}(W/4\sqrt{a_y x}) \operatorname{erf}(H/4\sqrt{a_y x})$  respectively. The downgradient distance along the plume centerline distance where the relative error is less than  $\alpha\%$  for the 1-D advection-dominated model compared to the 2-D advection-dominated model can be estimated by:

$$x < \frac{W^2}{16 a_y \operatorname{erfc}^{-1}(1 - \alpha)} \quad (12)$$

where  $\operatorname{erfc}$  is the complementary error function. In other words, the 1-D advection dispersion model is within  $\alpha\%$  of the 2-D advection-dominated model for downgradient distances indicated by this inequality. Given  $\operatorname{erf}(u) \sim u$  for  $u$  small, when  $W/4\sqrt{a_y x}$  and  $H/4\sqrt{a_y x}$  are both small, a rough approximation for when the 3-D model relative error is not large is given by:

$$x < \frac{WH}{13 \sqrt{a_y a_z}} \quad (13)$$

In other words, the 1-D advection-dominated model will be a reasonable approximation of the 3-D model at downgradient distances given in Equation 13.

## Approximate Time to Reach Steady-State

As observed at numerous sites where degradation is occurring, approximate steady-state conditions are reached when source zones persist over sufficient periods of time for the plumes to grow and stabilize. The time for plumes to reach approximate steady-state conditions over a given downgradient distance can be estimated using the analytical solution to the one-dimensional advection-dispersion equation with first-order decay (e.g. Bear, 1972). In general, the second term in the analytical solution presented in Bear (1972) and others is relatively small for typical field data values (e.g. Ogata and Banks, 1972), and the general solution can be approximated by:

$$C \cong \frac{C_0}{2} e^{\left(\frac{vx}{2D_x} - \beta x\right)} \operatorname{erfc}\left(\frac{x - \sqrt{v^2/R + 4k_1 D_x/R} t}{2\sqrt{D_x t/R}}\right) \quad (14)$$

where  $C$  is the concentration,  $C_0$  is the source concentration,  $\beta = (v^2/R^2 + 4k_1 D_x/R)^{1/2}$ ,  $\operatorname{erfc}$  is the complementary error function,  $x$  is the downgradient distance from the source,  $t$  is time,  $v$  is the average linear groundwater velocity,  $k_1$  is the first order rate constant,  $D_x$  is the longitudinal dispersion coefficient, and  $R$  is the retardation factor. By setting  $C$  equal to  $\alpha C_s$ , where  $\alpha$  is the percent of the steady-state concentration ( $C_s$ ), equation (14) can be solved for the time ( $t_s$ ) that approximate steady-state occurs to give:

$$t_s \cong \frac{R}{\beta} \left( \frac{x\beta^2}{R} + 2z^2 D_x + 2z(xRD_x\beta^2 + z^2 D_x)^{1/2} \right) \quad (15)$$

where  $z = \operatorname{erf}^{-1}(2\alpha - 1)$  and  $z$  is the argument of the error function that gives the value  $2\alpha - 1$ , which is tabulated in Abramowitz and Stegun (1972). For example, by setting  $\alpha = 0.5$ , equation (15) becomes  $t = Rx/(v(1+4\alpha k_1 R/v))^{0.5}$ , which is the time for a given distance  $x$  to reach 50% of its steady-state level (McAllister, 1996). The use of this 50% criterion can significantly underestimate the time to approximate steady-state conditions and may not even give the time for the front to reach a given distance as shown in the case study below. For the multi-species equations, the highest retardation factor of the chemicals should be used to improve the estimate. Steady-state conditions occur earlier at sites with higher groundwater velocities and higher degradation rates. An examination of the solution to the transient one-dimensional advection-dispersion equation also shows that concentrations approach steady-state first near the source and then sequentially later at increasing downgradient locations after the advective front passes.

## Application to Estimate Biodegradation Rate Constants

Given the relatively high groundwater velocity, a steady-state advection-dominated analytical solution was applied to estimate TCE, DCE, and VC first-order rate constants for 1984 quasi-steady state plume conditions at the Harris CERCLA site in Palm Bay, FL. The site consists of relatively homogeneous sands and is naturally anaerobic. Both redox and hydrogen data indicate that sulfate reduction is the dominant terminal electron accepting (TEAP) process. Groundwater sampling confirmed the presence of the *Dehalococcoides* genus, which is likely responsible for the observed sequential transformation of TCE, DCE and VC via reductive dechlorination to ethene (Burnell et al., 2003). Based on the observed limited organic carbon in the deep zone ( $R=1$ ), an observed plume distance of 2500 ft, and parameters in Table 1, the estimated time to reach steady-state plume conditions is 5.8 yr using Equation 15 and has an underestimated value of 3.4 yr using the equation in

McCallister (1996). The advective front reaches this distance of 2500 ft in 4.2 yr, which is also the time for an advection-dominated transient equation to reach steady-state conditions at this distance. Since the TCE spill occurred in 1967, the assumption of steady-state plumes using average concentration data in 1984 is reasonable.

The parameters used for the analytical transport modeling analyses in this study are summarized in Table 1 with the diffusion coefficients set equal to zero given the relatively high groundwater velocity at this site. Using estimated ranges of rate constants of TCE, cis 1,2 DCE, and VC from other sites in the U.S. (Aronson and Howard, 1997; Suarez and Rifai, 1999), the advection-dominated approximation  $a_L k_i^2 \ll v^2$  is met, which indicates that 1-D steady-state plume concentrations are relatively insensitive to longitudinal dispersivity for the parameter values at this site. Therefore, the simpler 1-D advection-dominated analytical model (Equation 1 with  $r_i \approx k_i/v$ ) was applied to estimate the biodegradation rate constants were estimated determined by varying the rate constants to match average TCE, DCE, and VC data in 1984 from wells located along the plume centerline. Using a least squares approach for the concentration residuals, the estimated average rate constants were  $0.81 \text{ yr}^{-1}$ ,  $0.74 \text{ yr}^{-1}$ , and  $0.69 \text{ yr}^{-1}$  for TCE, DCE, and VC, respectively.

In addition to not including effects of longitudinal dispersion, the 1-D advection-dominated solution assumes a point source release with negligible transverse dispersion. This assumption causes overestimates of plume concentrations along the plume centerline with concomitant higher rate constants being needed to match the observed data in comparison to 2-D and 3-D models. Other sources of uncertainty in these estimated rate constants may include deviations from model assumptions, uncertainties in model parameter values, spatial variability in degradation rates, and use of monitor well data that are not screened exactly along the plume centerline. It should be noted that the uncertainty in estimated rate constants using 1-D, 2-D, and 3-D advection-dominated models is directly proportional to the uncertainty in the average linear groundwater velocity. Since the uncertainty of the groundwater velocity can be as high as an order of magnitude, the error in the velocity value is likely to be the primary source of uncertainty in the rate constants.

Using site-specific parameters in Table 1, the 1-D advection-dispersion, 2-D advection-dominated, and 3-D advection-dominated analytical solutions were also matched to the plume centerline data by estimating the rate constants using a nonlinear least square approach. The results are summarized in Table 2. The 1-D advection-dispersion model rate constants were higher for TCE (12 %) and cis 1,2 DCE (relative errors of 12 % and 5.4% respectively) and the same for VC in comparison to the 1-D advection-dominated model. This occurs because longitudinal dispersion increases downgradient concentrations from a source zone with a higher rate constants being required to match the data. In the 2-D and 3-D advection-dominated models, the estimated rate constants of TCE, cis 1,2 DCE, and VC were generally lower than the 1-D advection-dominated model. For TCE, the 2-D and 3-D model rate constants were lower with relative errors of 6.2% and 11%. For cis 1,2 DCE, the 2-D and 3-D model rate constants were lower by 6.8% and 18%. For VC, the 2-D and 3-D model rate constants were lower by 20% and 33%. In order to match the data, the estimated rate constants must be lower in the 2-D and 3-D models in order to offset the lowering of concentrations from transverse dispersion.

Figure 4 presents simulated and observed TCE, DCE, and VC plume concentrations along the plume centerline for both the 1-D (Equation 1 with  $r_i \approx k_i/v$ ) and 3-D (Equation 11) analytical solutions using the parameters in Table 1. In this plot, the rate constants in the 3-D model are the same as the 1-D model in order to examine the effect of horizontal and transverse dispersion.

An examination of the parent and daughter product concentrations in Figure 4 indicates that the 1-D and 3-D concentrations are similar near the source but the 3-D concentrations become lower with increasingly downgradient distance because of horizontal and vertical transverse dispersion. The 2-D analytical solution curves (not shown) lie between the 1-D and 3-D curves and therefore have a similar trend but with less difference in concentrations than the 1-D and 3-D models. Using in

Equation 12, a relative error of  $\alpha=20\%$  and the parameters in Table 1, the ratio of the 1-D advection-dominated analytical solution to the 2-D solution is less than 20% for downgradient centerline distances less than 1736 ft which includes all the data used at this site. For the 3-D model, Equation 13 is satisfied for downgradient distances less than 1544 ft. The relative error of the 1-D compared to the 3-D model is less than 40% for the model parameters in this study.

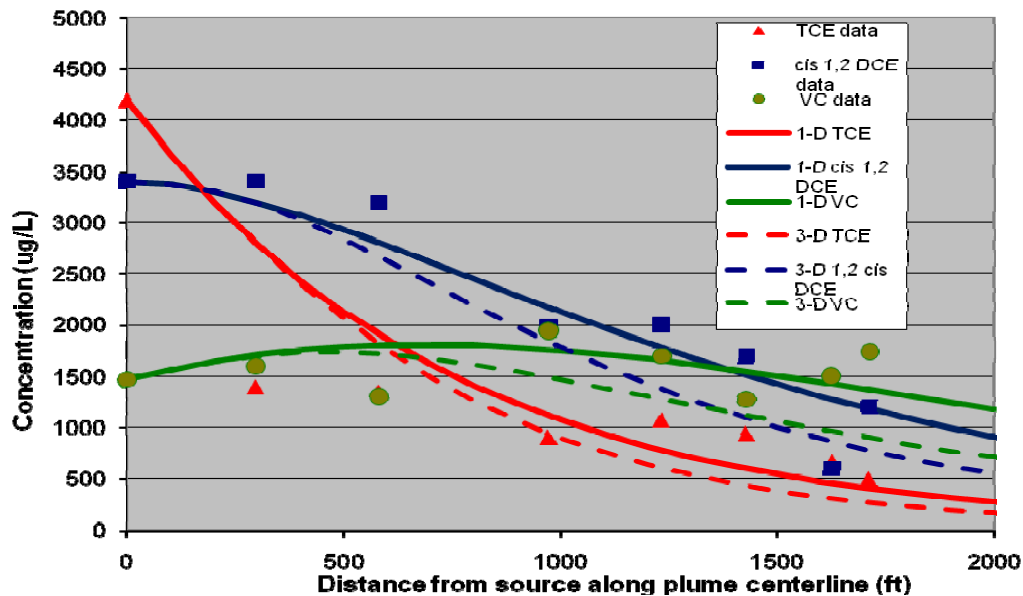
**Table 1. 1-D, 2-D, and 3-D Model Parameter Values.**

Solute Transport Model Parameter	Model Parameter Value	Reference
Source Concentration (C)	4.2 mg/L (TCE) 3.4 mg/L (DCE) 1.47 mg/L (VC)	Average observed total TCE, DCE, and VC at near source well GS-35S in 1984 (Geraghty & Miller, 1987)
Source Width (W)	150 ft	Geraghty & Miller (1987) report
Source Thickness (H)	50 ft	Geraghty & Miller (1987) report
Average Linear Groundwater Velocity (v)	600 ft/yr	Burnell et al. (2002)
Longitudinal, Dispersivity ( $a_x$ )	85 ft,	Estimated based on observed plume transport scale $L = 668$ m in 25 m zone and $a_x = 0.82(\log_{10}L_s)^{2.958}$ regression fit by Xu and Eckstein (1995)
Horizontal Transverse Dispersivity ( $a_y$ )	1 ft	Estimated based on match of 2-D model to observed plume width
Vertical Transverse Dispersivity ( $a_z$ )	0.1 ft	Estimated based on match of 3-D model to observed plume vertical extent
Effective Yield Coefficient ( $Y_{ij}$ )	$y_{21}=0.74$ $y_{32}=0.64$	Calculated stoichiometrically using TCE-to-DCE and DCE-to-VC reactions.

**Table 2. Estimated First-Order Biodegradation Rate Constants for each Analytical Solution Match to Plume Centerline Data**

	1-D Advection-Dispersion	1-D Advection-Dominated	2-D Advection-Dominated	3-D Advection-Dominated
TCE	0.91 yr <sup>-1</sup>	0.81 yr <sup>-1</sup>	0.76 yr <sup>-1</sup>	0.72 yr <sup>-1</sup>
cis 1,2 DCE	0.78 yr <sup>-1</sup>	0.74 yr <sup>-1</sup>	0.69yr <sup>-1</sup>	0.61 yr <sup>-1</sup>
VC	0.69 yr <sup>-1</sup>	0.69 yr <sup>-1</sup>	0.55yr <sup>-1</sup>	0.46 yr <sup>-1</sup>

**Figure 4. Observed vs. simulated 1984 steady-state concentrations of TCE, cis 1,2 DCE, and VC along the plume centerline using 1-D and 3-D advection-dominated (no longitudinal dispersion) sequential first-order decay multi-species analytical solutions**



### Effect of Longitudinal Dispersion

In this study, the 1-D dimensionless analyses of the advection-dispersion and advection-dominated analytical solutions indicated that the 1-D advection-dominated multispecies analytical solution is reasonably accurate for  $Pe > 6$  and  $Da < 1$ . For the 3-D case, sensitivity analyses by Srinivasan et al. (2007) indicated that the 3-D advection-dominated modified-Domenico solution underestimated plume centerline concentrations in comparison to the exact analytical solution (Wexler, 1992). In addition, the widths of the plumes from the advection-dominated solution were wider than the actual solution. Given that the steady-state modified-Domenico solution is identical to the 3-D parent solution (Equation 9a), this 3-D advection-dominated analytical solution will also overpredict parent plume widths and underestimate parent plume centerline concentrations in comparison to exact analytical solutions that include longitudinal dispersion. To our knowledge, there are no known exact 3-D multi-species advection-dispersion analytical solutions available for comparison to the 3-D multi-species advection-dominated daughter solutions presented in this paper. Numerical modeling, which can include longitudinal dispersion, is recommended to more fully examine the uncertainty of 3-D multi-species advection-dominated analytical solutions.

### Summary and Conclusions

Multi-species models are better tools than single species models for estimating daughter product rates constants because multi-species models can account for accumulation from parent compounds. In relatively permeable aquifers ( $Pe > 6$ ) with slowly degrading compounds ( $Da < 1$ ), dimensionless analyses indicate that the 1-D steady-state advection-dominated dispersion-reaction analytical solutions of the parent and daughter products are relatively insensitive to longitudinal

dispersivity with calculated concentration differences of the advection-dominated and advection-dispersion solutions being less than 20%. Given that this difference is generally much less than the uncertainty in the average groundwater velocity, which is the primary source of uncertainty in these models, the use of 1-D advection-dominated models is reasonable when  $Pe > 6$  and  $Da < 1$ . For sites with well known source dimensions and transverse dispersivity values, steady-state, 2-D and 3-D advection-dominated (no longitudinal dispersion) multi-species analytical solutions were derived. These exact closed-form analytic solutions can easily be used in spreadsheets, are computationally efficient, and are useful for examining the accuracy of numerical models. These multi-dimensional models can also utilize groundwater data not located along the plume centerline.

For a site in Palm Bay, FL, the application of steady-state, 1-D advection-dominated analytical solution yielded first-order biodegradation rate constants values of  $0.81 \text{ yr}^{-1}$ ,  $0.74 \text{ yr}^{-1}$ , and  $0.69 \text{ yr}^{-1}$ , respectively, for TCE, DCE, and VC. These estimated rate constants were higher than the values of  $0.46 \text{ yr}^{-1}$ ,  $0.53 \text{ yr}^{-1}$ , and  $0.43 \text{ yr}^{-1}$  for TCE, DCE, and VC, respectively, which were estimated using a calibrated three-dimensional numerical model to both transient plume development and dissipation over a 20 year period from 1981 to 2001 (Burnell, 2002). The higher rate constants in the 1-D analytical solution are likely caused primarily by uncertainty in the groundwater velocity and to a lesser extent by the absence of hydrodynamic dispersion in this model. When source dimensions and the transverse dispersivity values are known, the 2-D and 3-D models will give more accurate answers. When there is significant uncertainty in these parameters, the 1-D model may be preferable because of the sensitivity that different values of transverse dispersivity and source dimensions will have on the results. For aquifers with high groundwater velocities and source dimensions similar to this site, the simpler 1-D advection-dominated analytical solution, which does not require difficult to measure field parameters such as longitudinal and transverse dispersivity or source dimensions, can be a useful tool for estimating rate constants of parent and daughter products.

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