

# Analytical Models of Steady-State Plumes Undergoing Sequential First-Order Degradation

by Daniel K. Burnell<sup>1</sup>, James W. Mercer<sup>2</sup>, and Lawrence S. Sims<sup>3</sup>

---

## Abstract

An exact, closed-form analytical solution is derived for one-dimensional (1D), coupled, steady-state advection-dispersion equations with sequential first-order degradation of three dissolved species in groundwater. Dimensionless and mathematical analyses are used to examine the sensitivity of longitudinal dispersivity in the parent and daughter analytical solutions. The results indicate that the relative error decreases to less than 15% for the 1D advection-dominated and advection-dispersion analytical solutions of the parent and daughter when the Damköhler number of the parent decreases to less than 1 (slow degradation rate) and the Peclet number increases to greater than 6 (advection-dominated). To estimate first-order daughter product rate constants in advection-dominated zones, 1D, two-dimensional (2D), and three-dimensional (3D) steady-state analytical solutions with zero longitudinal dispersivity are also derived for three first-order sequentially degrading compounds. The closed form of these exact analytical solutions has the advantage of having (1) no numerical integration or evaluation of complex-valued error function arguments, (2) computational efficiency compared to problems with long times to reach steady state, and (3) minimal effort for incorporation into spreadsheets. These multispecies analytical solutions indicate that BIOCHLOR produces accurate results for 1D steady-state, applications with longitudinal dispersion. Although BIOCHLOR is inaccurate in multidimensional applications with longitudinal dispersion, these multidimensional multispecies analytical solutions indicate that BIOCHLOR produces accurate steady-state results when the longitudinal dispersion is zero. As an application, the 1D advection-dominated analytical solution is applied to estimate field-scale rate constants of 0.81, 0.74, and 0.69/year for trichloroethene, *cis*-1,2-dichloroethene, and vinyl chloride, respectively, at the Harris Palm Bay, FL, CERCLA site.

---

## Introduction

Degradation rates of daughter products can be a controlling factor on the cleanup rate at some sites with contaminated groundwater. Therefore, obtaining reasonably accurate estimates of rate constants of daughter products is important for estimating the remedial

timeframe particularly for monitored natural attenuation (MNA). Multispecies models have an advantage over single-species models in estimating daughter product rate constants because multispecies models can account for mass accumulation from parent compounds. Many degradation processes either undergo first-order or pseudo first-order sequential reaction kinetics including decay of radionuclides and reductive dechlorination of chlorinated solvents (e.g.,  $\text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE} \rightarrow \text{VC} \rightarrow \text{ethene}$ ). When more mobile, toxic, and/or persistent daughter products such as vinyl chloride (VC) are formed, the application of multispecies analytical solutions with first-order sequential reactions is a useful tool for examining both the potentially greater downgradient plume extent and higher concentration levels of these degradation products at possible exposure points in risk assessments.

---

<sup>1</sup>Corresponding author: Tetra Tech GEO, Inc., 21335 Signal Hill Plaza Suite 100, Sterling, VA 20164; (703) 885-5438; fax: (703) 444-1685; Dan.Burnell@Tetrattech.com

<sup>2</sup>Tetra Tech GEO, Inc., 21335 Signal Hill Plaza Suite 100, Sterling, VA 20164.

<sup>3</sup>L.S. Sims & Associates, 1530 U.S. Highway I, Rockledge, FL 32955.

Received January 2011, accepted July 2011.

© 2011, The Author(s)

Ground Water © 2011, National Ground Water Association.

doi: 10.1111/j.1745-6584.2011.00858.x

The primary objective of this paper is to present practical closed-form, multispecies analytical solutions for use in improving estimates of first-order biodegradation rate constants of sequentially transforming chemicals in steady-state plumes. Advantages of these 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 for use in Monte-Carlo analysis. Given their particular assumptions, these exact analytical solutions are not subject to the significant errors (West et al. 2007) 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 mathematical error when the specified value for the longitudinal dispersion coefficient is nonzero (Srinivasan et al. 2007). In addition, closed-form multidimensional analytical solutions are useful in checking the accuracy of numerical solutions particularly in advection-dominated conditions where artificial numerical dispersion can occur.

In this paper, a closed-form analytical solution is first presented for a one-dimensional (1D) steady-state advection-dispersion equation for three first-order sequentially degrading species. For sites with approximate steady-state plumes of slowly degrading chemicals and relatively high groundwater velocities, dimensionless analyses are presented that indicate longitudinal hydrodynamic dispersion is relatively unimportant, which further reduces the number of required model parameters. Utilizing this conclusion, closed-form analytical solutions are developed for steady-state two-dimensional (2D) and three-dimensional (3D) transport of three sequentially degrading species with constant concentration vertical planar source boundary conditions in advection-dominated aquifers and compared to the BIOCHLOR model. Additional analyses of the 1D analytical solution are performed including: (1) estimating the time to reach steady state; (2) deriving spatial plume moments of the parent and degradation products; and (3) determining both locations and values of maximum concentrations of degradation products. The uncertainty of the 1D multispecies analytical solution is also examined by comparison to plume centerline concentrations of the 2D and 3D multispecies analytical solutions. As a practical example, the closed-form analytical solutions are applied to estimate the field-scale, anaerobic biodegradation rate constants of trichloroethene (TCE), *cis*-1,2-dichloroethene (DCE), and VC at the Harris CERCLA site in Palm Bay, FL.

## 1D Steady-State Analytical Solution to Advection-Dispersion Equations for Three Species Undergoing First-Order Sequential Degradation

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. An exact, closed-form 1D analytical solution for three sequentially degrading species is presented as follows. The governing equations for 1D, steady-state concentrations of three chemicals undergoing advection, hydrodynamic dispersion, and sequential first-order chain decay with a constant concentration point source are:

$$\begin{aligned} \frac{d^2 C_1}{dx^2} - \frac{v}{D_x} \frac{dC_1}{dx} - \frac{k_1 C_1}{D_x} &= 0 \\ \frac{d^2 C_2}{dx^2} - \frac{v}{D_x} \frac{dC_2}{dx} - \frac{k_2 C_2}{D_x} &= -\frac{y_{21} k_1 C_1}{D_x} \\ \frac{d^2 C_3}{dx^2} - \frac{v}{D_x} \frac{dC_3}{dx} - \frac{k_3 C_3}{D_x} &= -\frac{y_{32} k_2 C_2}{D_x} \end{aligned} \quad (1)$$

$$\begin{aligned} C_1(0) &= C_{10} \quad C_1 \rightarrow 0 \text{ as } x \rightarrow \infty \\ C_2(0) &= C_{20} \quad C_2 \rightarrow 0 \text{ as } x \rightarrow \infty \\ C_3(0) &= C_{30} \quad C_3 \rightarrow 0 \text{ as } x \rightarrow \infty \end{aligned}$$

where  $C_1$ ,  $C_2$ , and  $C_3$  are the parent and sequential daughter product concentrations,  $C_{10}$ ,  $C_{20}$ , and  $C_{30}$  are the parent and sequential daughter product concentrations at the source,  $x$  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 degradation rate constants of the parent and sequential daughter products.

These coupled second-order ordinary differential equations can be solved sequentially using the method of undetermined coefficients (Boyce and DiPrima 1977). The general solution (Burnell et al. 2007) is:

$$C_1 = C_{10} e^{r_1 x} \quad (2a)$$

$$C_2 = C_{20} e^{r_2 x} + C_{10} \frac{k_1 y_{21}}{k_1 - k_2} (e^{r_2 x} - e^{r_1 x}) \quad (2b)$$

$$\begin{aligned} C_3 = C_{30} e^{r_3 x} - \frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_1 - k_3)} (e^{r_3 x} - e^{r_1 x}) \\ + \left[ \frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20} k_2 y_{32}}{(k_2 - k_3)} \right] (e^{r_3 x} - e^{r_2 x}) \end{aligned} \quad (2c)$$

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  $r_i < 0$ .

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 1D Advection-Dominated Solution for Parent and Daughter Product

When the longitudinal dispersion coefficient is 0, the governing equations for 1D, steady-state concentrations of parent and daughter chemicals undergoing advection and sequential first-order chain decay with a constant concentration point source are:

$$\frac{dC_1}{dx} + \frac{k_1 C_1}{v_x} = 0 \quad (3a)$$

$$\frac{dC_2}{dx} + \frac{k_2 C_2}{v} = \frac{y_{21} k_1 C_1}{v} \quad (3b)$$

$$C_1(0) = C_{10} \quad C_1 \rightarrow 0 \text{ as } x \rightarrow \infty \quad (3c)$$

$$C_2(0) = 0 \quad C_2 \rightarrow 0 \text{ as } x \rightarrow \infty \quad (3d)$$

In the boundary condition (Equation 3d), the daughter concentration is zero at the source and therefore the daughter compound is only generated by degradation of the parent.

This first-order linear system of differential equations (ODEs) can be solved sequentially using an integrating factor (Boyce and DiPrima 1977). The analytical solution is:

$$C_1 = C_{10} e^{-k_1 x/v} \quad (4a)$$

$$C_2 = C_{10} \frac{k_1 y_{21}}{k_1 - k_2} (e^{-k_2 x/v} - e^{-k_1 x/v}) \quad (4b)$$

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

$$\begin{aligned} C_{D1} &= \frac{C_1}{C_{10}} & C_{D2} &= \frac{C_2}{C_{10} y_{21}} & X_D &= \frac{x}{x_0} \\ Pe &= \frac{v x_0}{D_x} & Da_1 &= \frac{k_1 x_0}{v} & Da_2 &= \frac{k_2 x_0}{v} \end{aligned} \quad (5)$$

where  $C_{D1}$  and  $C_{D2}$  are the relative concentrations of the parent and daughter compounds,  $x_0$  is an arbitrary distance from the source in the  $x$  direction,  $X_D$  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. The Peclet number is a measure of the relative importance of advection compared to longitudinal dispersion. For  $Pe$  defined in Equation 5, 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 degradation 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  $x = x_0$ . On the basis of the dimensionless parameters defined earlier, the analytical solution for advection and sequential first-order sequential

degradation with zero longitudinal dispersion of parent (Equation 4a) and daughter (Equation 4b) is:

$$C_{D1} = e^{-Da_1 X_D} \quad (6a)$$

$$C_{D2} = \frac{Da_1}{Da_1 - Da_2} (e^{-Da_2 X_D} - e^{-Da_1 X_D}) \quad (6b)$$

The analytical solutions for advection, longitudinal dispersion, and sequential first-order degradation of the parent (Equation 2a) and daughter (Equation 2b) compounds in dimensionless form are:

$$C_{D1} = e^{\frac{Pe}{2} \left(1 - \sqrt{1 + 4 \frac{Da_1}{Pe}}\right) X_D} \quad (7a)$$

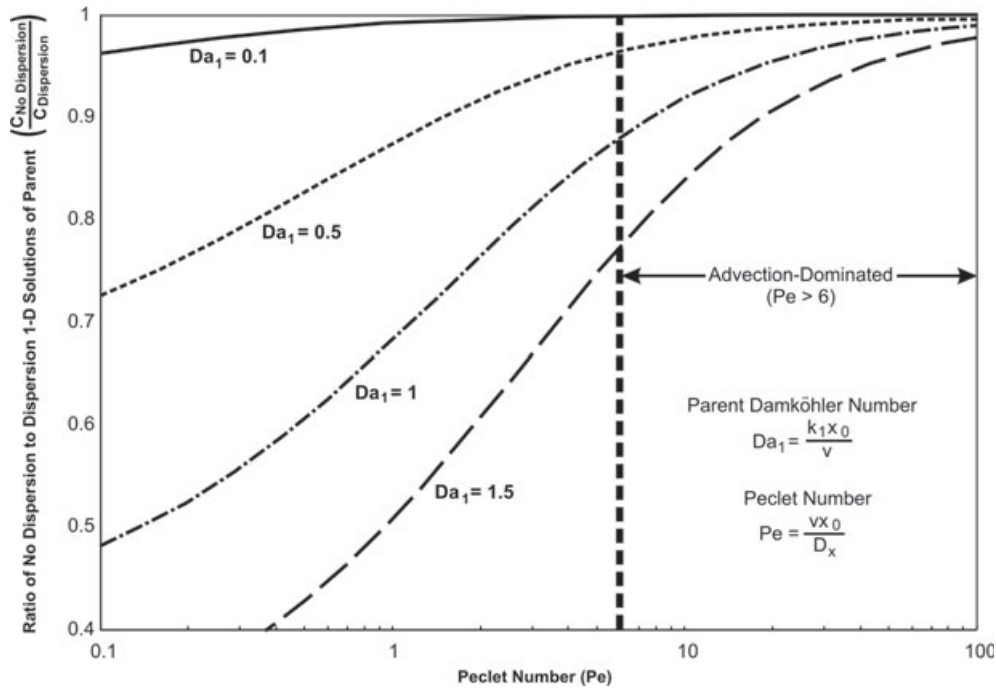
$$\begin{aligned} C_{D2} &= \frac{Da_1}{Da_1 - Da_2} \\ &\times \left[ e^{\frac{Pe}{2} \left(1 - \sqrt{1 + 4 \frac{Da_2}{Pe}}\right) X_D} - e^{\frac{Pe}{2} \left(1 - \sqrt{1 + 4 \frac{Da_1}{Pe}}\right) X_D} \right] \end{aligned} \quad (7b)$$

At sites with relatively high groundwater velocities, the steady-state 1D analytical solutions are less sensitive to longitudinal dispersion. As discussed in Cho (1971), the terms with  $r_i$  in the exponential arguments of Equation 2 can be simplified by expressing  $r_i$  as a generalized binomial series (Abramowitz and Stegun 1972):

$$r_i = \frac{v}{2D_x} \left(1 - \sqrt{1 + 4D_x \frac{k_i}{v^2}}\right) = -\frac{k_i}{v} + a_L \frac{k_i^2}{v^2} + \dots \quad (8)$$

where the free-solution diffusion coefficient is assumed to be 0. An examination of Equation 8 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 2) can be represented using Damköhler numbers  $Da_i = k_i x/v$ , which express the relative importance of reaction vs. 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 (Srinivasan and Clement 2008), the approximation  $r_i \approx -k_i/v$  is also applicable for advection-dominated transport of subsequent degradation product solutions. Many aquifers with chlorinated solvents satisfy this approximation ( $a_L k_i^2 \ll v^2$ ), and in this case, the steady-state plume concentrations can be approximated reasonably well using advection-reaction analytical solutions (Equation 4). 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 1D case was examined using dimensionless plots to more fully analyze when the steady-state, advection-dominated analytical solution (Equation 4) may be applicable. Figure 1 presents a plot of the ratio of the analytical solution (Equation 4a) of the parent for the advection-reaction



**Figure 1. Examination of ratio of 1D steady-state parent analytical solution (Equation 4a) for advection-reaction equation ( $a_L = 0$ ) to the 1D steady-state parent analytical solution (Equation 2a) for advection-dispersion-reaction equation as a function of Peclet number for several values of parent Damköhler numbers.**

equation ( $D_x = 0$ ) to the analytical solution (Equation 2a) for the advection-dispersion-reaction equation as a function of dimensionless Peclet number with several values of dimensionless Damköhler numbers. The percent relative error (%RE) can be determined from the dimensionless plots using  $\%RE = (C_{no\ disp} - C_{disp})/C_{disp} \times 100 = (C_{no\ disp}/C_{disp} - 1) \times 100$ . The dimensionless calculations and Equation 8 indicate that the percent relative error between the advection-dominated and advection-dispersion parent solutions is less than 10% when  $Da_1^2/Pe$  is less than 0.1. Figure 1 also indicates the percent relative error between the two solutions decreases to less than 15% when  $Pe$  increases to values greater than 6 (relatively permeable aquifer) and  $Da_1$  decreases to values less than 1 (relatively slow degradation).

For the 3D steady-state case, West et al. (2007) report percent relative errors ranging from 2.5% to 24% between the parent 3D Domenico solution and exact solution of Wexler (1992) along the plume centerline using parameters defined in an example calculation. Dimensionless analyses by Guyonnet and Neville (2004) observed discrepancies between the steady-state parent Domenico solution and exact solution presented in Sagar (1982) both along and away from the plume centerline 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  $Pe > 6$  and the 3D case with transverse dispersion, Guyonnet and Neville (2004) report relatively small differences between the Domenico and exact 3D parent solution (Sagar 1982) along the plume centerline

particularly when steady-state conditions were reached. For a given Peclet number, the difference between the Domenico and exact 3D parent solutions (Sagar 1982) becomes less as the source dimensions increase. Srinivasan et al. (2007) have shown the Domenico solution approaches the advection-dominated 3D parent solution as the longitudinal dispersivity approaches zero. As shown in these studies, the 3D advection-dominated steady-state parent solution becomes a reasonable approximation to the 3D steady-state advection-dispersion equation at sites where the groundwater velocity is higher and the longitudinal dispersivity is lower.

Figure 2 presents plots of the ratio of the daughter solution (Equation 4b) of the advection-reaction ( $a_L = 0$ ) equation to the daughter solution (Equation 2b) for the 1D advection-dispersion-reaction equation for daughter Damköhler numbers ( $Da_2$ ) ranging from 0 to 100. 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 percent relative error of the advection-reaction solution decreases to less than 15% of the advection-dispersion-reaction equation when the parent Damköhler number is less than 1 (relatively slow degradation) and the Peclet number increases to values greater than 6 (relatively permeable). Dimensionless analyses indicate that this result holds for all daughter Damköhler numbers when  $Da_1 < 1$  and  $Pe > 6$ .

These results indicate that the 1D, steady-state advection-dominated analytical solution (Equation 4) is reasonably accurate for examining the transport of slowly

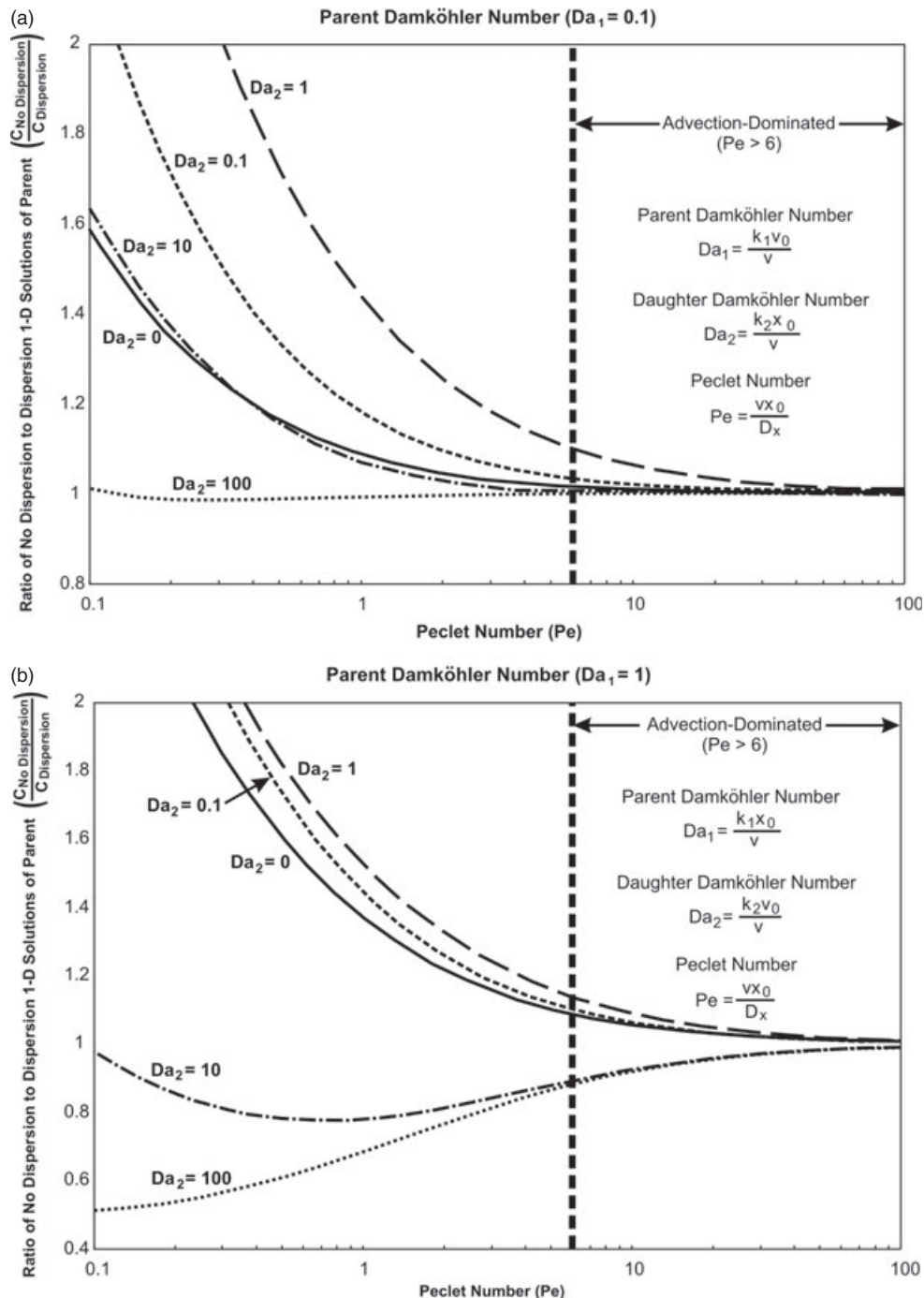


Figure 2. Examination of ratio of 1D daughter analytical solution (Equation 4b) for advection-reaction ( $a_L = 0$ ) to the 1D daughter analytical solution (Equation 2b) for advection-dispersion reaction as a function of Peclet number for several values of daughter Damköhler numbers with: (a) parent  $Da_1 = 0.1$  and (b) parent  $Da_1 = 1.0$ .

sequentially degrading contaminants (e.g., chlorinated solvents) in higher permeability aquifers. Although the relative error of the steady-state, advection-dominated parent solution is relatively small for multidimensional steady-state problems, the errors of the advection-dominated approximation of the parent solutions will be propagated to the daughter solutions. Additional analyses are needed to quantify the accuracy of the steady-state, advection-dominated approximation of daughter products for the 2D and 3D cases.

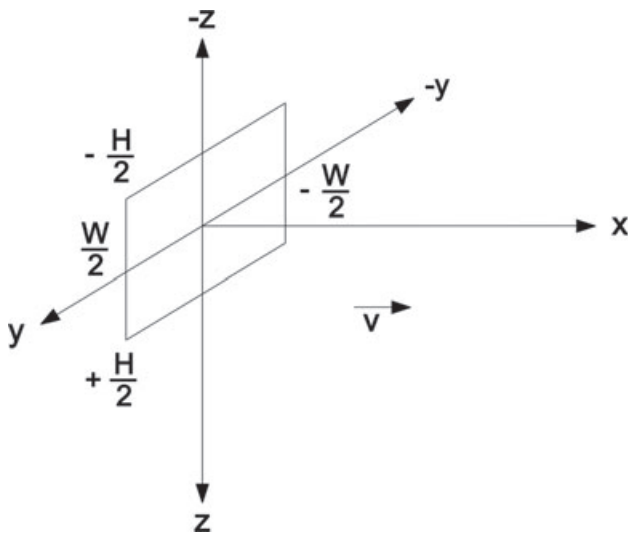
#### Effect of First-Type vs. Third-Type Boundary Condition for Source

In the 1D mathematical model presented earlier, the source was represented using a first-type (Dirichlet) boundary condition in which the concentration of the source is specified at  $x = 0$ . Although the third-type (Cauchy) boundary condition produces no mass balance error at the inlet (Batu 2010), the percent relative error in the mass balance at  $x = 0$  for the parent becomes small (less than 15%) for advection-dominated aquifers

( $Pe > 6$ ) with contaminants having low degradation rates ( $Da < 1$ ). This can be seen by first noting that the dimensionless parameter  $N = D_x R_d k_1 / v^2$  in Batu (2010) is equal to  $Da/Pe$  when degradation is assumed to only occur in the aqueous phase. Inserting  $Da = 1$  and  $Pe = 6$  into  $N = Da/Pe$ , and examining the ratio of the convective mass flux at  $x = 0$  for the first type in Batu (2010, Equation 31) to the third type in Batu (2010, Equation 30) analytical solutions, the ratio of the convective first- to third-type mass flux is calculated to be 1.146. A similar analysis also shows that the percent relative error in the ratio of calculated concentration values for the first- and third-type analytical solutions of the parent is less than 15% at any location in the plume when  $Pa < 6$  and  $Da < 1$ . Given this relatively small difference in concentrations and the typical variability in measured concentrations, the first- and third-type boundary conditions for the source in 1D analytical solutions should yield similar results when estimating rate constants in advection-dominated aquifers with compounds such as chlorinated solvents that degrade relatively slowly.

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

For advection-dominated zones, closed-form 2D and 3D analytical solutions were derived for three species moving at a constant velocity with no longitudinal dispersion ( $D_x = 0$ ), transverse dispersion, and undergoing sequential first-order decay at steady-state plume conditions. A conceptual picture for the 3D problem is present in Figure 3. The governing partial differential



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

equations (PDEs) for the 3D case with a vertical planar source are:

$$v \frac{\partial C_1}{\partial x} = D_y \frac{\partial^2 C_1}{\partial y^2} + D_z \frac{\partial^2 C_1}{\partial z^2} - k_1 C_1 \quad (9a)$$

$$v \frac{\partial C_2}{\partial x} = D_y \frac{\partial^2 C_2}{\partial y^2} + D_z \frac{\partial^2 C_2}{\partial z^2} - k_2 C_2 + k_1 y_{21} C_1 \quad (9b)$$

$$v \frac{\partial C_3}{\partial x} = D_y \frac{\partial^2 C_3}{\partial y^2} + D_z \frac{\partial^2 C_3}{\partial z^2} - k_3 C_3 + k_2 y_{32} C_2 \quad (9c)$$

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

$$C_2(0, y, z) = C_{20} - \frac{W}{2} < y < \frac{W}{2} - \frac{H}{2} < z < \frac{H}{2}$$

$$C_3(0, y, z) = C_{30}$$

$$C_1(0, y, z) = C_2(0, y, z) = C_3(0, y, z) = 0 \text{ elsewhere} \quad (9d)$$

$$\frac{\partial C_1}{\partial x}, \frac{\partial C_2}{\partial x}, \frac{\partial C_3}{\partial x} \rightarrow 0 \text{ as } x \rightarrow \infty$$

$$\frac{\partial C_1}{\partial y}, \frac{\partial C_2}{\partial y}, \frac{\partial C_3}{\partial y} \rightarrow 0 \text{ as } y \rightarrow \pm \infty$$

$$\frac{\partial C_1}{\partial z}, \frac{\partial C_2}{\partial z}, \frac{\partial C_3}{\partial z} \rightarrow 0 \text{ as } z \rightarrow \pm \infty$$

where  $D_y$  is the horizontal transverse dispersion coefficient,  $D_z$  is the vertical transverse dispersion coefficient,  $W$  is the width of the source zone, and  $H$  is the thickness of the source zone. These coupled, linear PDEs can be solved sequentially as shown in the Appendix. The analytical solution for this 3D case is:

**Parent**

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

**Daughter:**

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

**Granddaughter:**

$$C_3 = \frac{1}{4} \cdot \left[ (C_{30} e^{-k_3 x/v} - \frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_1 - k_3)} (e^{-k_3 x/v} - e^{-k_1 x/v})) + \left[ \frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20} k_2 y_{32}}{(k_2 - k_3)} \right] (e^{-k_3 x/v} - e^{-k_2 x/v}) \right]$$

$$\cdot \left[ \operatorname{erf} \left\{ \frac{y + \frac{W}{2}}{2\sqrt{a_y x}} \right\} - \operatorname{erf} \left\{ \frac{y - \frac{W}{2}}{2\sqrt{a_y x}} \right\} \right] \cdot \left[ \operatorname{erf} \left\{ \frac{z + \frac{H}{2}}{2\sqrt{a_z x}} \right\} - \operatorname{erf} \left\{ \frac{z - \frac{H}{2}}{2\sqrt{a_z x}} \right\} \right] \quad (10c)$$

where  $a_y$  and  $a_z$  are the dispersivities in the  $y$  and  $z$  directions, respectively. The parent solution (Equation 10a) 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 10a when the longitudinal dispersivity is 0.

## 2D Advection-Dominated Steady-State Analytical Solution for Three 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 2D model can be used. The governing equations for the 2D mathematical model with no longitudinal hydrodynamic dispersion for a finite-width line source are:

$$v \frac{\partial C_1}{\partial x} = D_y \frac{\partial^2 C_1}{\partial y^2} - k_1 C_1 \quad (11a)$$

$$v \frac{\partial C_2}{\partial x} = D_y \frac{\partial^2 C_2}{\partial y^2} - k_2 C_2 + k_1 y_{21} C_1 \quad (11b)$$

$$v \frac{\partial C_3}{\partial x} = D_y \frac{\partial^2 C_3}{\partial y^2} - k_3 C_3 + k_2 y_{32} C_2 \quad (11c)$$

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

$$C_2(0, y) = C_{20} - \frac{W}{2} < y < \frac{W}{2} \quad (11d)$$

$$C_3(0, y) = C_{30}$$

$$C_1(0, y, z) = C_2(0, y, z) = C_3(0, y, z)$$

$$= 0 \text{ elsewhere}$$

$$\frac{\partial C_1}{\partial x}, \frac{\partial C_2}{\partial x}, \frac{\partial C_3}{\partial x} \rightarrow 0 \text{ as } x \rightarrow \infty$$

$$\frac{\partial C_1}{\partial y}, \frac{\partial C_2}{\partial y}, \frac{\partial C_3}{\partial y} \rightarrow 0 \text{ as } y \rightarrow \pm \infty$$

The derivation for this 2D model is similar to the method for the 3D model discussed in the Appendix. The analytical solution (Burnell et al. 2010) for this 2D model is:

**Parent:**

$$C_1 = \frac{C_{10}}{2} e^{-k_1 x/v} \left[ \operatorname{erf} \left\{ \frac{y + \frac{W}{2}}{2\sqrt{a_y x}} \right\} - \operatorname{erf} \left\{ \frac{y - \frac{W}{2}}{2\sqrt{a_y x}} \right\} \right] \quad (12a)$$

**Daughter:**

$$C_2 = \left[ \frac{C_{20}}{2} e^{-k_2 x/v} + \frac{C_{10}}{2} \frac{k_1 y_{21}}{k_1 - k_2} (e^{-k_2 x/v} - e^{-k_1 x/v}) \right] \cdot \left[ \operatorname{erf} \left\{ \frac{y + \frac{W}{2}}{2\sqrt{a_y x}} \right\} - \operatorname{erf} \left\{ \frac{y - \frac{W}{2}}{2\sqrt{a_y x}} \right\} \right] \quad (12b)$$

**Granddaughter:**

$$C_3 = \left[ \frac{C_{30}}{2} e^{-k_3 x/v} - \frac{C_{10} k_1 y_{21} k_2 y_{32}}{2(k_1 - k_2)(k_1 - k_3)} (e^{-k_3 x/v} - e^{-k_1 x/v}) \right] + \left[ \frac{C_{10} k_1 y_{21} k_2 y_{32}}{2(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20} k_2 y_{32}}{2(k_2 - k_3)} \right] (e^{-k_3 x/v} - e^{-k_2 x/v}) \cdot \left[ \operatorname{erf} \left\{ \frac{y + \frac{W}{2}}{2\sqrt{a_y x}} \right\} - \operatorname{erf} \left\{ \frac{y - \frac{W}{2}}{2\sqrt{a_y x}} \right\} \right] \quad (12c)$$

In the 2D and 3D 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  $i = 1, 2,$  and  $3$ . Because the longitudinal dispersivity is 0, the first- and third-type boundary conditions are identical and there is no error in mass balance at the inlet in these advection-dominated analytical solutions.

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 models based on the Domenico (1987) solution when nonzero values for the longitudinal dispersivity are specified. These steady-state solutions are computationally efficient in comparison to the large run times from multiple time steps that transient analytical solution codes or numerical models may require to reach steady state. These analytical solutions can also be used to examine the accuracy of numerical models that can have errors from artificial dispersion and overshoot oscillations. When longitudinal dispersion is significant, the advection-dominated analytical solutions will not accurately predict concentrations as shown for the Domenico (1987) solution (Srinivasan et al. 2007; West et al. 2007).

## Analysis of 1D, 2D, and 3D Analytical Solutions

### Approximate Time to Reach Steady State for 1D Analytical Solution

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 1D advection-dispersion

equation with first-order decay and constant concentration source (Bear 1972). In general, the second term in the analytical solution presented in Bear (1972, p. 630) is relatively small when  $x/a_L$  is large (Ogata and Banks 1961; Bear 1979). For typical field data values, the general solution can be approximated by:

$$C \cong \frac{C_0}{2} e^{\left(\frac{vx}{2D_x} - \beta x\right)} \operatorname{erfc} \left( \frac{x - \sqrt{v^2/R + 4k_1 D_x/Rt}}{2\sqrt{D_x t/R}} \right) \quad (13)$$

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.

The steady-state concentration ( $C_s$ ) at downgradient distance  $x$  can be found by taking the limit as  $t \rightarrow \infty$  of Equation 13 to obtain:

$$C_s \cong \frac{C_0}{2} e^{\frac{vx}{2D_x} - \beta x} \quad (14)$$

By setting  $C$  equal to  $\alpha C_s$  where  $\alpha$  is the percent of the steady-state concentration, setting  $t = t_s$ , and substituting for  $C_s$  from Equation 14, Equation 13 can be solved (Burnell et al. 2010) for the time ( $t_s$ ) that approximate steady state occurs to give:

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

where  $\eta = \operatorname{erf}^{-1}(2\alpha - 1)$  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  $t = Rx/(v(1 + 4a_x k_1 R/v)^{0.5})$ , which is the time for a given distance  $x$  to reach 50% of its steady-state level (McCallister 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 advective front to reach a given distance as shown in the case study in the following. For the multispecies equations, the highest retardation factor of the chemicals should be used to improve the estimate. Equation 15 indicates that steady-state conditions occur earlier at sites with higher groundwater velocities, lower retardation factors, and higher degradation rates. Equation 15 also shows that concentrations approach steady state first near the source and then sequentially later at increasing downgradient locations after the advective front passes.

### Spatial Moments of 1D Multispecies Plumes

As the normalized concentration can be represented as a probability density function, spatial moments can

be calculated in order to concisely quantify the location and extent of steady-state multispecies plumes. For the 1D constant concentration source analytical solution of the parent (Equation 2a), the zeroth-order moment (total mass  $M_1$  in the plume), first-order moment (centroid  $\hat{x}_1$ ), and second-order moment (mass distribution of the plume about the centroid  $\sigma_1^2$ ) are given by:

$$M_1 = \int_0^\infty C_1(x) dx = \int_0^\infty C_{10} e^{r_1 x} dx = -\frac{C_{10}}{r_1} = C_{10} L_1 \quad (16)$$

$$\hat{x}_1 = \frac{\int_0^\infty x C_1(x) dx}{M_1} = \frac{\int_0^\infty C_{10} x e^{r_1 x} dx}{C_{10} L_1} = \frac{\frac{1}{r_1^2}}{L_1} = L_1 \quad (17)$$

$$\begin{aligned} \sigma_1^2 &= \frac{\int_0^\infty (x - \hat{x}_1)^2 C_1(x) dx}{M_1} \\ &= \frac{\int_0^\infty C_{10} (x - L_1)^2 e^{r_1 x} dx}{C_{10} L_1} = L_1^2 \end{aligned} \quad (18)$$

where  $L_1 = 1/|r_1|$  is the plume centroid and is given by:

$$L_1 = \frac{v + \sqrt{v(v + 4k_1 a_L)}}{2k_1} \quad (19)$$

When  $a_L = 0$  in Equation 19, it is seen that  $L_1 = v/k_1$ . For the steady-state plume concentration of the parent in Equation 2a, Chappelle et al. (2003) refer to  $|r_1|$  as the natural attenuation capacity (NAC), which can be considered the contaminant reducing capacity of an aquifer per unit length along the groundwater flowpath. Thus, the reciprocal of NAC is the plume centroid. When log concentration data are plotted vs. distance from the source in order to estimate rate constants (Buscheck and Alcantar 1995), the plume centroid can also be estimated from the slope ( $r_1 = -1/L_1$ ) of the linear trend fit of log concentration vs. distance. Examination of the log concentration vs. distance slope  $r_1$  in the analytical solution (Equation 2a) indicates that the slope is negative (finite plume centroid distance) when degradation is occurring and is 0 (infinite plume centroid distance) when degradation is not occurring. The slope  $r_1$  is more negative (lower plume centroid distance) with lower values of groundwater velocity, lower values of the hydrodynamic dispersion coefficient, or higher values of the rate constant. Conversely, the plume centroid is larger when the velocity is higher, longitudinal dispersion is higher, or degradation rate is lower for this analytical solution with a first-type boundary condition.

Table 1 displays the zero-, first-, and second-order spatial moments for the parent, daughter, and granddaughter compounds, respectively, for the analytical solution in Equation 2, which has nonzero concentrations for the parent, daughter, and granddaughter species in the source term. Petersen and Sun (2000) provide a summary of sequential first-order reactive plume zero-, first-, and

**Table 1**  
**Spatial Moments of Parent, Daughter, and Granddaughter for 1D Multispecies Analytical Solution for Constant Concentration Source (Equation 2)**

**Zero-Order Plume Mass ( $M_i$ ), First-Order Plume Centroid ( $\hat{x}_i$ ), and Second-Order Plume Distribution About Centroid ( $\sigma_i^2$ ) Spatial Moments**

<b>Parent</b>	$M_1 = C_{10}L_1$ $\hat{x}_1 = L_1$ $\sigma_1^2 = L_1^2$
<b>Daughter</b>	$M_2 = C_{20}L_2 + C_{10}\frac{k_1y_{21}}{k_1 - k_2}(L_2 - L_1)$ $\hat{x}_2 = \frac{C_{10}k_1y_{21}(L_2^2 - L_1^2) + C_{20}L_2^2(k_1 - k_2)}{C_{10}k_1y_{21}(L_2 - L_1) + C_{20}(k_1 - k_2)L_2}$ $\sigma_2^2 = \frac{C_{10}\frac{k_1y_{21}}{k_1 - k_2}[2(L_2^3 - L_1^3) + 2\hat{x}_2(L_1^2 - L_2^2) + \hat{x}_2^2(L_2 - L_1)] + C_{20}(2L_2^3 - 2\hat{x}_2L_2^2 + \hat{x}_2^2L_2)}{C_{10}\frac{k_1y_{21}}{k_1 - k_2}(L_2 - L_1) + C_{20}L_2}$
<b>Granddaughter</b>	$M_3 = C_{30}L_3 - \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_1 - k_3)}(L_3 - L_1) + \left[ \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20}k_2y_{32}}{(k_2 - k_3)} \right] (L_3 - L_2)$ $\hat{x}_3 = \frac{1}{M_3} \cdot \left\{ \left[ \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_1 - k_3)} \right] L_1^2 - \left[ \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20}k_2y_{32}}{(k_2 - k_3)} \right] L_2^2 \right. \\ \left. + \left[ \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_3)(k_2 - k_3)} + \frac{C_{20}k_2y_{32}}{(k_2 - k_3)} + C_{30} \right] L_3^2 \right\}$ $\sigma_3^2 = \frac{1}{M_3} \cdot \left\{ \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_3 - k_1)} [2(L_3^3 - L_1^3) + 2\hat{x}_3(L_1^2 - L_3^2) + \hat{x}_3^2(L_3 - L_1)] \right. \\ \left. + \left[ \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20}k_2y_{32}}{(k_2 - k_3)} \right] \cdot [2(L_3^3 - L_2^3) + 2\hat{x}_3(L_2^2 - L_3^2) + \hat{x}_3^2(L_3 - L_2)] \right. \\ \left. + C_{30}(2L_3^3 - 2\hat{x}_3L_3^2 + \hat{x}_3^2L_3) \right\}$

Note:  $L_i = \frac{v + \sqrt{v(v + 4k_i a_L)}}{2k_i}$ .

second-order statistical moments for four members of the 1D steady-state analytical solution for a constant concentration of parent and zero concentration of daughter products in the source term. As expected, the spatial moments in Table 1 simplify to the spatial moments in Petersen and Sun (2000) when  $C_{20}$  and  $C_{30}$  are 0.

#### Maximum Concentration of Degradation Products in 1D Steady-State Analytical Solution

When a steady-state daughter product plume initially increases and later decreases in concentration away from the source, both the distance to the maximum daughter concentration and the concentration value at this distance can be estimated. By taking the derivative of Equation 2b, setting it equal to 0 and simplifying, the downgradient distance ( $x_{m2}$ ) where the maximum daughter concentration occurs is given by:

$$x_{m2} = \frac{1}{r_2 - r_1} \ln \left[ \frac{C_{10}k_1y_{21}r_1}{r_2C_{10}k_1y_{21} + C_{20}r_2(k_1 - k_2)} \right] \quad (20)$$

where  $\ln$  is the natural log function. The maximum value of the daughter product  $C_{2\max}$ , when it occurs, can

be found by inserting Equation 20 into Equation 2b to give:

$$C_{2\max} = \left( \frac{C_{10}k_1y_{21}}{k_1 - k_2} + C_{20} \right) (b^{r_2/r_2 - r_1} - b^{r_1/r_1 - r_2}) \quad (21)$$

where

$$b = \frac{C_{10}k_1y_{21}r_1}{r_2C_{10}k_1y_{21} + C_{20}r_2(k_1 - k_2)}.$$

When no daughter source is present, a maximum daughter product concentration level will always occur at the downgradient distance

$$x_{m2} = \frac{\ln\left(\frac{r_1}{r_2}\right)}{r_2 - r_1}$$

with a maximum value of:

$$C_{2\max} = \frac{C_{10}k_1y_{21}(r_1 - r_2)}{r_2(k_1 - k_2)} \left( \frac{r_1}{r_2} \right)^{\frac{r_1}{r_2 - r_1}} \quad (22)$$

For the granddaughter product, a similar approach can be used to obtain the distance ( $x_{m3}$ ) to its downgradient maximum value by taking the derivative of Equation 2c and setting equal to 0 to give:

$$\begin{aligned}
& C_{10}e^{r_1x_{m3}} + C_{20}\frac{y_{21}k_1}{k_2 - y_{21}k_1}(r_1e^{r_1x_{m3}} - r_2e^{r_2x_{m3}}) \\
&= C_{30}r_3e^{r_3x_{m3}} - \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_1 - k_3)} \\
&\quad \times (r_3e^{r_3x_{m3}} - r_1e^{r_1x_{m3}}) \quad (23) \\
&\quad + \left[ \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20}k_2y_{32}}{k_2 - k_3} \right] \\
&\quad \times (r_3e^{r_3x_{m3}} - r_2e^{r_2x_{m3}})
\end{aligned}$$

Although this downgradient distance ( $x_{m3}$ ) where the maximum concentration occurs for the granddaughter cannot be solved explicitly, it can still be solved numerically as a root of Equation 23, and the maximum concentration can then be determined using Equation 2c. These equations can be used to estimate the downgradient distance and maximum concentration of degradation products during risk assessment calculations particularly when the degradation products are more toxic than the parent. These equations can also be used to estimate degradation product rate constants (Burnell et al. 2007).

#### Uncertainty of Advection-Dominated 1D Model vs. 2D and 3D Models Along Plume Centerline

Along the plume centerline ( $y = 0$  and  $z = 0$ ), the ratio of the 2D and 3D advection-dominated analytical solutions to the 1D advection-dominated analytical solution is given by  $\text{erf}(W/4\sqrt{a_yx})$  and  $\text{erf}(W/4\sqrt{a_yx})\text{erf}(H/4\sqrt{a_zx})$ , respectively. Because  $\text{erf}(u)$  is less than one for nonzero  $u$ , the 2D and 3D model plume centerline concentrations are always lower than a 1D model at a given downgradient location. The downgradient distance along the plume centerline that the 1D advection-dominated is within  $\alpha$  %RE of the 2D advection-dominated model can be estimated by:

$$x < \frac{W^2}{16a_y[\text{erf}^{-1}(1 - \alpha)]^2} \quad (24)$$

where  $\text{erf}^{-1}$  is the inverse error function. The percent relative error (%RE) for the 1D model approximation of the 3D model plume centerline concentration is:

$$\%RE = \left[ \frac{1}{\text{erf}(W/4\sqrt{a_yx})\text{erf}(H/4\sqrt{a_zx})} - 1 \right] \times 100 \quad (25)$$

For a given  $\alpha$  %RE, Equation 25 can be solved numerically to determine the downgradient distances that are consistent with this level of accuracy. When both  $W/4\sqrt{a_yx}$  and  $H/4\sqrt{a_zx}$  are less than 1, which is

typically the case away from the source

$$\text{erf}(W/4\sqrt{a_yx})\text{erf}(H/4\sqrt{a_zx}) \approx \frac{WH}{16x\sqrt{a_ya_z}}$$

Thus, the ratio of the 1D model to the 3D model plume centerline concentration has an approximate relative error of  $(16x\sqrt{a_ya_z})/WH$ . In addition to errors resulting from the assumption of no longitudinal dispersion, this equation indicates that a 1D advection-dominated model approximation of a 3D advection-dominated model plume centerline concentration will be less accurate for larger downgradient distances, smaller source dimensions, and to a lesser extent for larger horizontal and vertical transverse dispersivity values.

#### Comparison of 1D Advection-Dispersion Analytical Solution with BICHLOR Model

Figure 4 shows a comparison of the steady-state, 1D advection-dispersion multispecies analytical solution (Equation 2) with the BICHLOR model (Aziz et al. 2000) along the plume centerline. The model parameter values are given in Table 2 with a large value ( $10^5$  feet) specified for the source width and depth, and a small value ( $1 \times 10^{-5}$  feet) specified for the vertical and horizontal transverse dispersivity values in order to construct a 1D problem. Results of the comparison show agreement between BIOCHLOR and the 1D advection-dispersion analytical solution. An examination of the transient equations used in BIOCHLOR indicates that they simplify at 1D steady state to the same equations as the 1D analytical solution. Agreement was also observed by Burnell (2002) in a 1D comparison of BIOCHLOR with the numerical multispecies code MT3D<sup>99</sup>. These results indicate that BIOCHLOR can produce accurate solutions in 1D multispecies problems.

#### Comparison of 2D and 3D Advection-Dominated Analytical Solutions with BICHLOR Model

Figure 5 shows a comparison of the steady-state, 3D advection-dispersion multispecies analytical solution (Equation 10) with the BICHLOR model (Aziz et al. 2000) along the plume centerline using the model parameter values in Table 2. In BIOCHLOR, the longitudinal dispersivity value was assigned a low value of 0.0001 feet to represent advection-dominated conditions and a large time value of 1000 years was used to represent steady-state conditions. In addition, the source height was 25 feet in BIOCHLOR to simulate the lower half of the  $z$ -plane. Results of the comparison indicate agreement between BIOCHLOR and the 3D advection-dominated analytical solution. Figure 6 shows a comparison of the 3D analytical solution with BIOCHLOR at  $x = 1000$  feet along the  $y$  axis and  $z$  axis. Results of this comparison also show agreement between the two solutions. An examination of the transient equations used in BIOCHLOR indicates that they simplify at steady state with no longitudinal dispersion to the same equations as the 3D analytical solution.

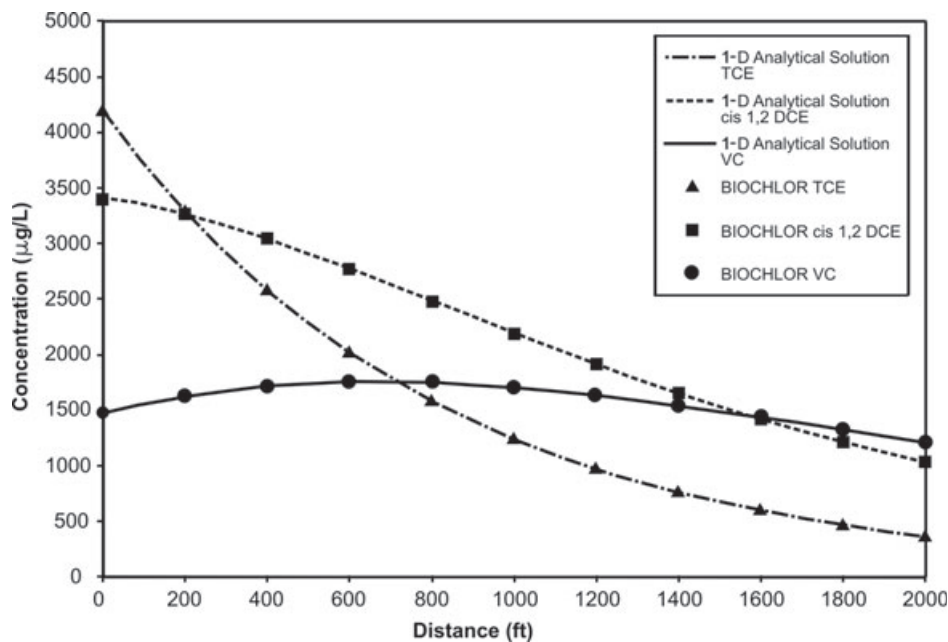


Figure 4. Comparison of 1D advection-dispersion sequential first-order decay multispecies analytical solution (Equation 2) and BIOCHLOR for TCE, DCE, and VC along the plume centerline.

These results indicate that BIOCHLOR can produce accurate 3D steady-state, multispecies model results when the longitudinal dispersivity is 0.

### Application to Estimate Biodegradation Rate Constants

The 1D steady-state advection-dominated analytical solution (Equation 2 with  $r_i \approx -k_i/v$ ) 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 permeable sands and is naturally anaerobic. Both redox and hydrogen data indicate that sulfate reduction is the dominant terminal electron accepting process (TEAP). 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).

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

Model Parameter	Value	References
Source concentration ( $C_{10}$ , $C_{20}$ , and $C_{30}$ )	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/year	Burnell (2002, 2010)
Longitudinal dispersivity ( $a_x$ )	85 ft	Burnell (2002, 2010)
Horizontal transverse dispersivity ( $a_y$ )	1 ft	Estimated based on match of 2D model to observed plume width
Vertical transverse dispersivity ( $a_z$ )	0.1 ft	Estimated based on match of 3D 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.
Parent rate constant ( $k_1$ )	0.81/year	Calibrated value from 1D advection-reaction model
Daughter rate constant ( $k_2$ )	0.74/year	Calibrated value from 1D advection-reaction model
Granddaughter rate constant ( $k_3$ )	0.69/year	Calibrated value from 1D advection-reaction model

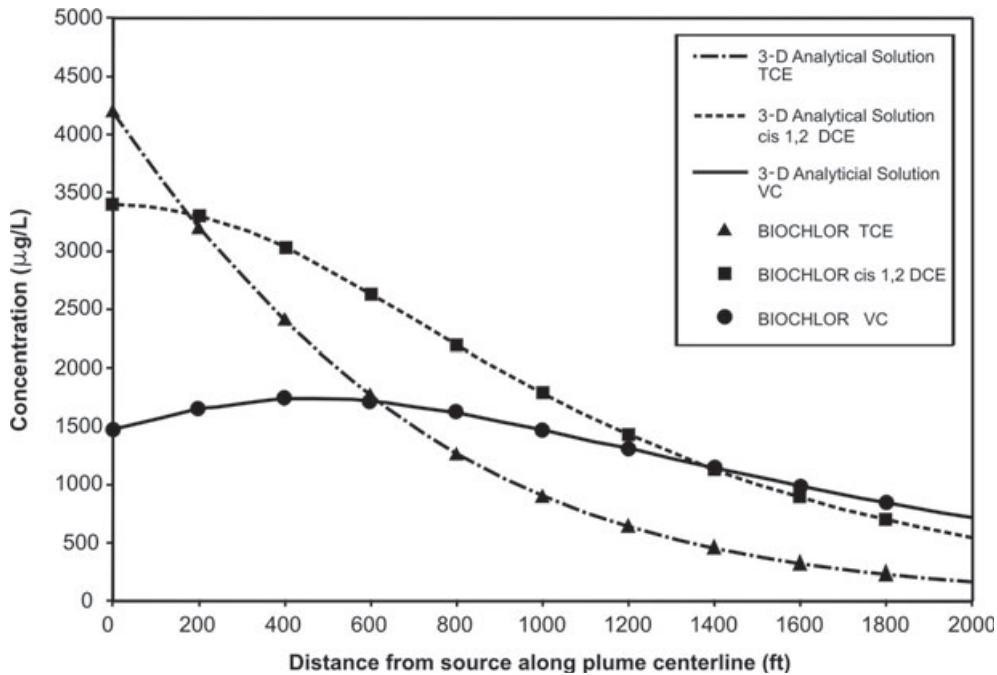


Figure 5. Comparison of 3D advection-dominated (no longitudinal dispersion) sequential first-order decay multispecies analytical solution and BIOCHLOR for TCE, DCE, and VC along the plume centerline.

On the basis of the observed limited organic carbon in the deep zone ( $R = 1$ ), an observed plume distance of 2500 feet, and parameters in Table 2, the estimated time to reach steady-state plume conditions is 5.8 years using Equation 15. Since the TCE spill occurred in 1967, the assumption of steady-state plumes using average concentration data in 1984 is reasonable.

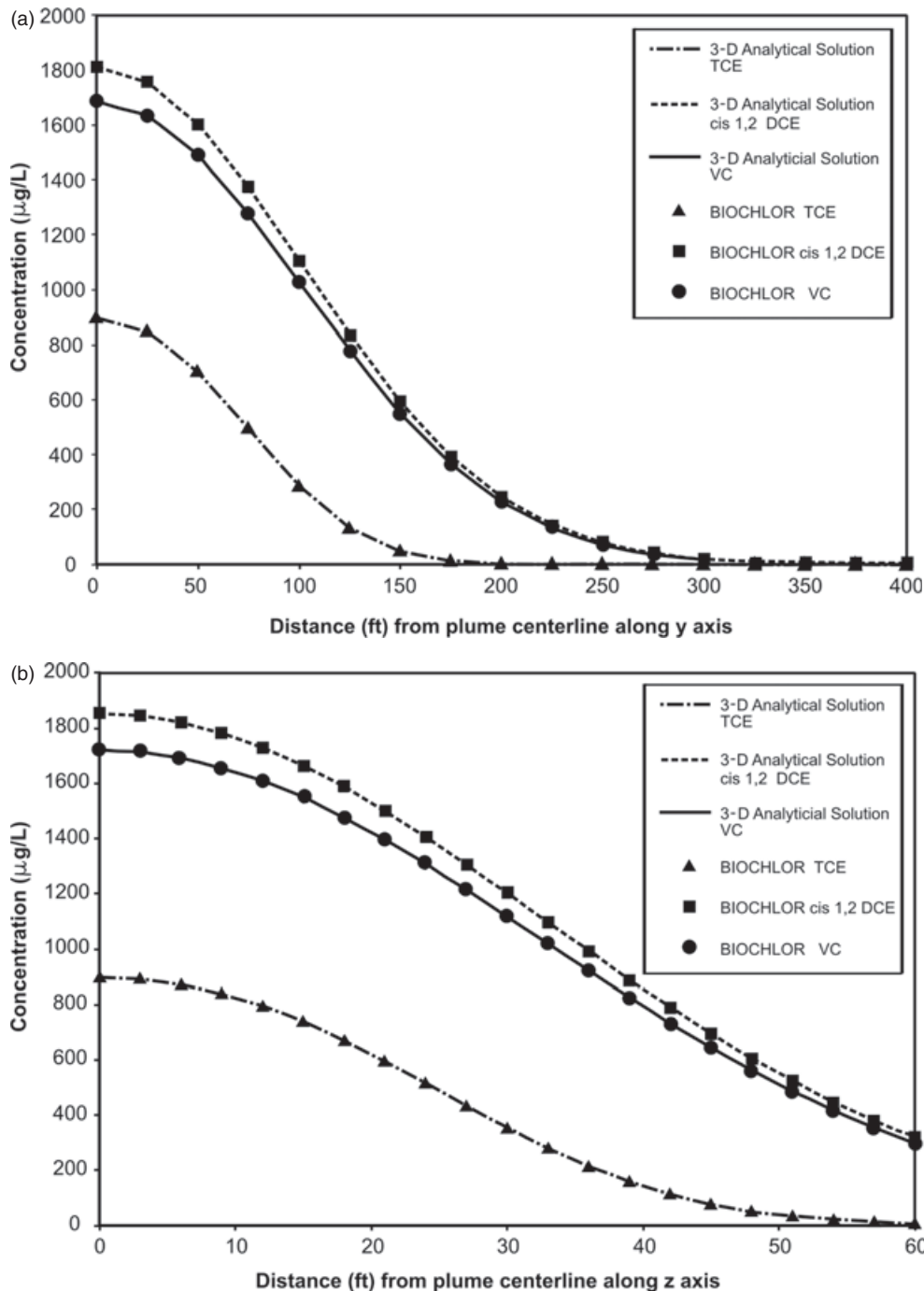
The parameters used for the analytical transport modeling analyses in this study are summarized in Table 2. On the basis of these site-specific parameters and the equations in Table 1, the zeroth-order (plume mass per unit area), first-order (plume centroid), and second-order (plume distribution about centroid) spatial moments for TCE, DCE, and VC plumes are summarized in Table 3. These estimated spatial moments are consistent with the observed plume distribution at the Harris site (Burnell 2002, 2010).

Using estimated ranges of rate constants of TCE, DCE, and VC from other sites in the United States (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 1D steady-state plume concentrations are relatively insensitive to longitudinal dispersivity for the parameter values at this site. The horizontal and vertical transverse dispersivity values were not well constrained. Therefore, the simpler 1D advection-dominated analytical model (Equation 2) with  $r_i = -k_i/v$  was applied to estimate the biodegradation rate constants by varying the rate constants to match average TCE, DCE, and VC data in 1984 from wells located along the plume centerline (Figure 7). Using a least squares approach for the concentration residuals and successive estimation (Sun et al. 2001), the estimated average rate constants

were 0.81, 0.74, and 0.69/year for TCE, DCE, and VC, respectively. Using these rate constants in Equations 2 and 23, a maximum VC concentration of 1830  $\mu\text{g/L}$  was estimated to occur at a downgradient distance of 750 feet, which is consistent with the field data (Figure 7).

The estimated rate constants from a 1D analytic solution are likely overestimated because of the assumption of 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 (Beyer et al. 2007). Additional sources of uncertainty in these estimated rate constants may include deviations from model assumptions, uncertainties in model parameter values, and use of monitor well data that are not screened exactly along the plume centerline (McNab and Dooher 1998). Additional discussion of the applicability of 1D models is provided in Newell et al. (2002) and Zhang and Heathcote (2003). Martian et al. (2003) discusses the sensitivity of estimate rate constants to various parameters for a 2D model. The approximation  $r_i \approx -k_i/v$  in the advection-dominated solutions indicates that the uncertainty in estimated rate constants using 1D, 2D, and 3D advection-dominated models is directly proportional to the uncertainty in the average linear groundwater velocity. Because the uncertainty of the groundwater velocity can be as high as an order of magnitude particularly when slug tests are used to estimate the horizontal hydraulic conductivity, the error in the velocity value can be a primary source of uncertainty in estimated rate constants using analytical solutions.

Using site-specific parameters in Table 2, the 1D advection-dispersion, 2D advection-dominated, and 3D



**Figure 6. Comparison of 3D advection-dominated (no longitudinal dispersion) sequential first-order decay multispecies analytical solution and BIOCHLOR for TCE, DCE, and VC at  $x = 1000$  ft: (a) along the  $y$  axis and (b) along the  $z$  axis.**

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 4. The 1D advection-dispersion model rate constants were higher for TCE and DCE (percent relative differences of 12 and 5.4%, respectively) with similar relative errors for VC in comparison to the 1D advection-dominated model. This occurs because longitudinal dispersion increases downgradient concentrations and therefore higher rate constants are required to match the data. In the 2D and 3D models, the estimated

rate constants of TCE, DCE, and VC were generally lower than the 1D model. For TCE, the 2D and 3D model rate constants were lower with different differences of 6.2 and 11%. For DCE, the 2D and 3D model rate constants were lower by 6.8 and 18%. For VC, the 2D and 3D model rate constants were lower by 20 and 33%.

Figure 7 presents simulated and observed TCE, DCE, and VC plume concentrations along the plume centerline for both the 1D (Equation 2 with  $r_i \approx -k_i/v$ ) and 3D (Equation 10) analytical solutions using the parameters in Table 2. In this plot, the rate constants in the 3D model are

Table 3 Spatial Moments of Parent, Daughter, and Granddaughter Using 1D Analytical Solution (Equation 2) for Plumes at the Harris CERCLA site			
	Plume Mass per Unit Area ( $M_i$ )	Plume Centroid $\hat{x}_i$	Plume Distribution About Centroid ( $\sigma_i$ )
TCE	$M_1 = 0.0902 \text{ kg/ft}^2$	$\hat{x}_1 = 758 \text{ ft}$	$\sigma_1 = 758 \text{ ft}$
DCE	$M_2 = 0.158 \text{ kg/ft}^2$	$\hat{x}_2 = 1235 \text{ ft}$	$\sigma_2 = 1093 \text{ ft}$
VC	$M_3 = 0.142 \text{ kg/ft}^2$	$\hat{x}_3 = 1828 \text{ ft}$	$\sigma_3 = 1431 \text{ ft}$

Table 4 Estimated First-Order Biodegradation Rate Constants for Each Analytical Solution Match to Plume Centerline Data				
	1D Advection-Dispersion	1D Advection-Dominated	2D Advection-Dominated	3D Advection-Dominated
TCE	0.91/year	0.81/year	0.76/year	0.72/year
DCE	0.78/year	0.74/year	0.69/year	0.61/year
VC	0.69/year	0.69/year	0.55/year	0.46/year

given the same values as the 1D model in order to examine the effect of transverse dispersion. An examination of the parent and daughter product concentrations in Figure 7 indicates that the 1D and 3D concentrations are similar

near the source but the 3D concentrations become lower with increasingly downgradient distance because of horizontal and vertical transverse dispersion. The 2D analytical solution curves (not shown) lie between the 1D and 3D curves and therefore have a similar trend but with less difference in concentrations than the 1D and 3D models. Using Equation 24 and the parameters in Table 2, the %RE between the 1D advection-dominated analytical solution and 2D solution is less than 20% for downgradient centerline distances less than 1736 feet, which includes all the data used at this site. For the 1D advection-dominated model approximation of the 3D model plume centerline concentration, Equation 25 shows that the %RE increases from approximately 0% near the source and increases to approximately 50% at the last downgradient data point (Figure 7).

## Discussion of Results

The 1D dimensionless analyses of the advection-dispersion and advection-dominated analytical solutions indicated that the 1D advection-dominated multispecies analytical solution is reasonably accurate for  $Pe > 6$  and  $Da < 1$ . When the longitudinal dispersivity is 0 (plug flow), the front is not sharp because of mass removal by degradation. When the longitudinal dispersivity is nonzero, degradation reduces the amount of longitudinal spreading of the plumes. In other words, although longitudinal dispersion is occurring, the spreading is diminished by degradation and the advection-dominated solution is reasonably accurate when  $Pe > 6$  and  $Da < 1$ . This effect also occurs during aerobic degradation where dispersion causes the contaminants to contact

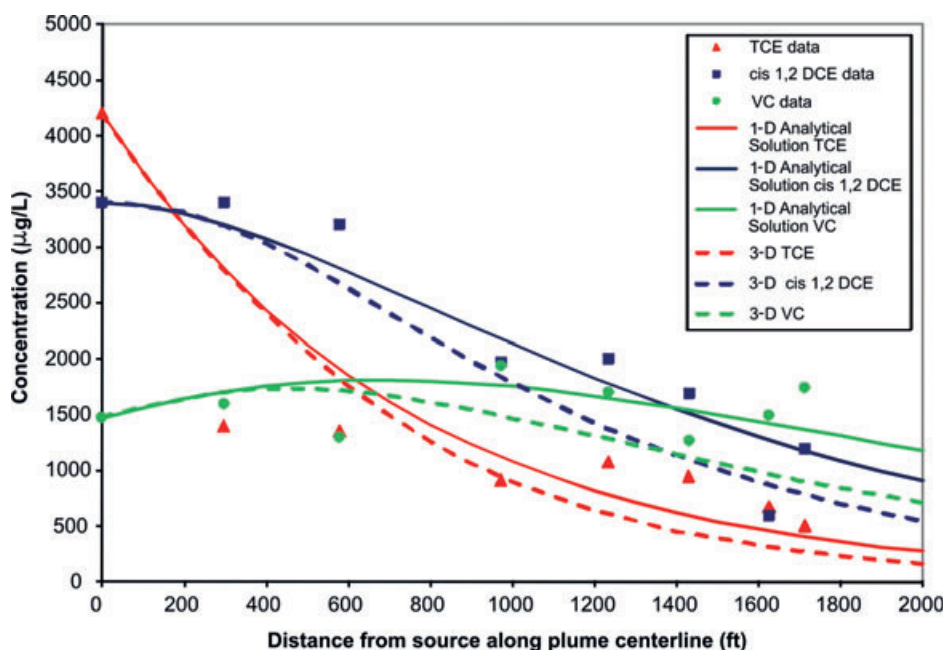


Figure 7. Observed vs. simulated 1984 steady-state concentrations of TCE, *cis* 1,2 DCE, and VC along the plume centerline using 1D and 3D advection-dominated (no longitudinal dispersion) sequential first-order decay multispecies analytical solutions.

more oxygen-rich groundwater (Lester and Mercer 1995).

For the 3D case, sensitivity analyses by Srinivasan et al. (2007) indicated that the 3D 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 exact analytical solution in Wexler (1992). Given that the steady-state modified-Domenico solution is identical to the 3D parent solution (Equation 10a), this 3D advection-dominated analytical solution also will over predict parent plume widths and underestimate parent plume centerline concentrations in comparison to exact analytical solutions that include longitudinal dispersion. This error will be propagated to the daughter compounds. To our knowledge, there are no known exact 3D multispecies analytical solutions for a constant concentration source with longitudinal dispersion that are available for comparison to the 3D multispecies advection-dominated daughter solutions presented in this paper. Numerical modeling, which can include longitudinal dispersion, is recommended to more fully examine the uncertainty of 3D advection-dominated multispecies models.

For a site in Palm Bay, FL, the application of steady-state, 1D advection-dominated analytical solution yielded first-order biodegradation rate constants values of 0.81, 0.74, and 0.69/year, respectively, for TCE, DCE, and VC. These estimated rate constants were higher than the values of 0.46, 0.53, and 0.43/year for TCE, DCE, and VC, respectively, which were estimated using a calibrated 3D numerical model to both transient plume development and dissipation over a 20-year period from 1981 to 2001 (Burnell 2002, 2010). The higher rate constants in the 1D 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 well defined, 2D and 3D models will likely give more accurate answers. When there is significant uncertainty in these parameters, the 1D 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 1D advection-dominated analytical solution, which does not require difficult to determine 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.

## Summary and Conclusions

Multispecies models have an advantage over single species models for estimating daughter product rates constants because multispecies 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 1D steady-state advection-dispersion-reaction analytical solutions of the parent and daughter products are relatively insensitive to longitudinal dispersivity with percent relative errors decreasing to less than 15% between the advection-dominated and advection-dispersion solutions. Given that this difference is generally less than the uncertainty in the average groundwater velocity, which is one of the primary sources of uncertainty in these models, the use of 1D advection-dominated models is reasonable when  $Pe > 6$  and  $Da < 1$ . As an application, a 1D advection-dominated analytical solution is applied to estimate field-scale rate constants of 0.81, 0.74, and 0.69/year for TCE, DCE, and VC, respectively, at the Harris Palm Bay, FL site.

A closed-form 1D steady-state analytical solution for advection, longitudinal dispersion, and sequential first-order transformation of three species is presented for a constant concentration source boundary condition. Zero-, first-, and second-order spatial moments were calculated for this 1D analytical solution. An equation for estimating the time to reach steady-state conditions was also derived. In an example calculation, the 1D, steady-state advection-dispersion analytical solution was found to be in agreement with BIOCHLOR indicating that the BIOCHLOR code produces accurate results for 1D, steady-state simulations with advection and longitudinal dispersion.

For advection-dominated aquifers where source dimensions and transverse dispersivity values are reasonably well defined, steady-state, 2D and 3D advection-dominated (no longitudinal dispersion) multispecies analytical solutions were also 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 multidimensional models can also utilize groundwater data not located along the plume centerline. The 3D, steady-state advection-dominated analytical solution was in agreement with an example calculation using BIOCHLOR indicating that BIOCHLOR produces accurate results in multidimensional, steady-state simulations when the longitudinal dispersivity is zero. Additional analyses are recommended to examine the errors of degradation product concentrations in BIOCHLOR for nonzero values of longitudinal dispersivity.

## Acknowledgments

This work was supported by Harris Corporation and the Tetra Tech GEO Research and Development Fund. We would like to thank Dr. David Loper (FSU) for his valuable advice. The authors also wish to thank the three anonymous reviewers for their thorough technical review and insightful comments, which helped to strengthen and improve this manuscript.

## Appendix

### Derivation of Steady-State 3-D Solution for First-Order Sequentially Degrading Species in Advection-Dominated Zones

For advection-dominated aquifers, the derivation of a steady-state, 3-D closed form analytical solution is presented below. This analytical solution can utilize downgradient data at any location or depth. For the steady-state 3-D case, the governing equations (Equation 9) are solved first for the parent concentration ( $C'_1$ ) of a point source whose boundary condition is specified as:

$$C'_1(0, y, z) = C_{10}\delta(y - y')(z - z') \quad (\text{A1})$$

where  $y'$  and  $z'$  are the location of the point source and  $\delta(y - y')(z - z')$  is the Dirac delta function. Setting  $C_1 = C'_1$  in Equation 9a and taking a double Fourier transform (Haberman 1987) of this equation in  $y$  and  $z$ , the transformed equation is:

$$\frac{\partial \bar{C}'_1}{\partial x} = -a_y w_1^2 \bar{C}'_1 - a_z w_2^2 \bar{C}'_1 - \frac{k_1}{v} \bar{C}'_1 \quad (\text{A2})$$

where  $w_1$  and  $w_2$  are the Fourier transform variables for  $y$  and  $z$ , respectively, and  $\bar{C}'_1$  is the double Fourier transform of  $C'_1$ . The transform of the boundary condition (Equation A1) is:

$$\bar{C}'_1(0, y, z) = \frac{C_{10}}{(2\pi)^2} e^{i(w_1 y' + w_2 z')} \quad (\text{A3})$$

where  $i$  is a complex number. This first order ODE (Equation A2) and boundary condition (Equation A3) can be solved to obtain:

$$\bar{C}'_1 = \frac{C_{10}}{(2\pi)^2} e^{-\left(a_y w_1^2 + a_z w_2^2 + \frac{k_1}{v}\right)x + i w_1 y' + i w_2 z'} \quad (\text{A4})$$

Taking inverse double Fourier transforms (Haberman 1987) of Equation A4 and using the shift property, the point source solution is given as:

$$C'_1 = \frac{C_{10}}{4\pi x \sqrt{a_y a_z}} e^{-\left[\frac{k_1 x}{v} + \frac{(y-y')^2}{4a_y x} + \frac{(z-z')^2}{4a_z x}\right]} \quad (\text{A5})$$

For a constant concentration patch source, we can integrate Equation A5 with respect to  $y'$  from  $-W/2$  to  $W/2$  and with respect to  $z'$  from  $-H/2$  to  $H/2$  using the integration formula in Gradshteyn and Ryzhik (1994, p. 113, Equation 2.33) to obtain Equation 10a. This parent solution (Equation 10a) is in agreement with the transient solution behind the front ( $x < vt$ ), which is at steady state, as presented in Srinivasan et al. (2007).

Once the parent solution is known, the daughter and granddaughter analytical solutions could be found using a transformation procedure (Sun et al. 1999) to uncouple Equations 9a, 9b, and 9c. In this paper, the solution for the daughter product ( $C_2$ ) in Equation 9b is found by first inserting the parent solution (Equation 10a)

into the last term on the right side of Equation 9b, and then using a method similar to the method of undetermined coefficients for differential equations. As discussed in Sneddon (1957), because the daughter PDE (Equation 9b) is nonhomogeneous and linear, one can first solve the homogeneous form of this equation, and then add a particular solution in such a way that the initial and boundary conditions are satisfied. The homogeneous solution of Equation 9b is:

$$C_{2H} = \frac{C_{20}}{4} e^{-k_2 x/v} \left( \operatorname{erf} \left\{ \frac{y + \frac{W}{2}}{2\sqrt{a_y x}} \right\} - \operatorname{erf} \left\{ \frac{y - \frac{W}{2}}{2\sqrt{a_y x}} \right\} \right) \cdot \left( \operatorname{erf} \left\{ \frac{z + \frac{H}{2}}{2\sqrt{a_z x}} \right\} - \operatorname{erf} \left\{ \frac{z - \frac{H}{2}}{2\sqrt{a_z x}} \right\} \right) \quad (\text{A6})$$

The particular solution is found by assuming a solution of the form:

$$C_{2P} = A e^{-k_1 x/v} \left( \operatorname{erf} \left\{ \frac{y + \frac{W}{2}}{2\sqrt{a_y x}} \right\} - \operatorname{erf} \left\{ \frac{y - \frac{W}{2}}{2\sqrt{a_y x}} \right\} \right) \cdot \left( \operatorname{erf} \left\{ \frac{z + \frac{H}{2}}{2\sqrt{a_z x}} \right\} - \operatorname{erf} \left\{ \frac{z - \frac{H}{2}}{2\sqrt{a_z x}} \right\} \right) \quad (\text{A7})$$

By inserting Equation A7 into Equation 9b, the particular solution is found to be:

$$C_{2P} = \frac{C_{10}}{4} \frac{k_1 y_{21}}{k_1 - k_2} e^{-k_1 x/v} \cdot \left( \operatorname{erf} \left\{ \frac{y + \frac{W}{2}}{2\sqrt{a_y x}} \right\} - \operatorname{erf} \left\{ \frac{y - \frac{W}{2}}{2\sqrt{a_y x}} \right\} \right) \cdot \left( \operatorname{erf} \left\{ \frac{z + \frac{H}{2}}{2\sqrt{a_z x}} \right\} - \operatorname{erf} \left\{ \frac{z - \frac{H}{2}}{2\sqrt{a_z x}} \right\} \right) \quad (\text{A8})$$

By applying the initial and boundary conditions, the solution for the daughter product ( $C_2$ ) is then found to be Equation 10b.

The solution for the granddaughter product ( $C_3$ ) is derived by first inserting the daughter solution (Equation 10b) into the last term of Equation 9c. Using the same modified method of undetermined coefficients approach as described earlier, the granddaughter solution is found to be Equation 10c.

## References

- Abramowitz, M., and I.A. Stegun. 1972. *Handbook of Mathematical Functions*, 1046. New York: Dover Publications.
- Aronson, D., and P. Howard. 1997. *Anaerobic Biodegradation of Organic Chemicals in Groundwater: A Summary of Field and Laboratory Studies (SRC TR-96-0223F)*. New York: Environmental Science Center, Syracuse Research Corporation.
- Aziz, C.E., C.J. Newell, J.R. Gonzales, P.E. Haas, and T.P. Clement. 2000. *BIOCHLOR Natural Attenuation Decision Support System, User's Manual Version 1.1, EPA/600/R-00/008*. Washington, D.C.: U.S. EPA Office of Research and Development.

- Batu, V. 2010. Estimation of degradation rates by satisfying mass balance at the inlet. *Ground Water* 48, no. 4: 560–568.
- Bear, J. 1979. *Hydraulics of Groundwater*, 569. New York: McGraw Hill.
- Bear, J. 1972. *Dynamics of Fluids in Porous Media*, 764. New York: Dover.
- Beyer, C., C. Chen, J. Gronewold, O. Kolditz, and S. Bauer. 2007. Determination of first-order degradation rate constants from monitoring networks. *Ground Water* 45, no. 6: 774–785.
- Boyce, W.E., and R.C. DiPrima. 1977. *Elementary Differential Equations and Boundary Value Problems*. 3rd ed., 582. New York: John Wiley & Sons.
- Buscheck, T.E., and C.M. Alcantar. 1995. Regression techniques and analytical solutions to demonstrate intrinsic bioremediation. In *Intrinsic Bioremediation*, ed. R.E. Hinchee, J.T. Wilson, and D.C. Downey, 109–116. Columbus, Ohio: Battelle Press.
- Burnell, D.K. 2010. *Numerical Modeling of TCE Sequential Biodegradation in Groundwater*, 436. Saarbrücken: VDM Verlag.
- Burnell, D.K., J.W. Mercer, and L.S. Sims. 2010. Estimation of sequential biodegradation rate constants in advection-dominated zones. In *Proceedings of the Seventh International Remediation of Chlorinated and Recalcitrant Compounds Symposium*, International Ground Water Modeling Center, Monterey, California.
- Burnell, D.K., J.W. Mercer, and L.S. Sims. 2007. Estimation of sequential biodegradation rate constants. In *Proceedings of the Ninth International in Situ and On-site Bioremediation Symposium*, Monterey, California.
- Burnell, D.K., L.S. Sims, R.P. Lowell, and J.W. Mercer. 2003. Multi-species model calibration and predictive analyses of Trichloroethene, cis-1, 2- Dichloroethene, and Vinyl Chloride decreases over a 20-year period by pump-and-treat and natural biodegradation. In *MODFLOW and More In Remediation/Management Modeling—Conference Proceedings*, 789–793.
- Burnell, D.K. 2002. A groundwater flow and solute transport model of sequential biodegradation of multiple chlorinated solvents in the surficial aquifer. Ph.D. dissertation, Georgia Institute of Technology, Palm Bay, Florida, 412 p.
- Chapelle, F.H., M.A. Widdowson, J.S. Brauner, E. Mendez III, and C.C. Casey. 2003. Methodology for estimating times of remediation associated with monitored natural attenuation. U.S. Geological Survey, Water-Resources Investigation Report 03-4057. Columbia, South Carolina: U.S. Geological Survey, 51 p.
- Cho, C.M. 1971. Convective transport of ammonium with nitrification in soil. *Canadian Journal of Soil Science* 51, 339–350.
- Domenico, P.A. 1987. An analytical model for multidimensional transport of a decaying contaminant species. *Journal of Hydrology* 91, 49–58.
- Geraghty & Miller, Inc. 1987. An Evaluation of the Harris Corporation Ground-Water Recovery System, October, 1987.
- Gradshteyn, I.S., and I.M. Ryzhik. 1994. *Table of Integrals, Series, and Products*. 5th ed., 1204. New York: Academic Press.
- Guyonnet, D., and C. Neville. 2004. Dimensionless analysis of two analytical solutions for 3D solute transport in groundwater. *Journal of Contaminant Hydrology* 75, 141–153.
- Haberman, R. 1987. *Elementary Applied Partial Differential Equations with Fourier Series and Boundary Value Problems*, 2nd ed. Englewood Cliffs, New Jersey: Prentice-Hall.
- Lester, B.H., and J.W. Mercer. 1995. Comparative evaluation of groundwater biodegradation models: summary of the API workshop. NGWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water—Prevention, Detection, and Restoration, Ground Water Publishing Co.
- Martian, P., K.S. Sorenson, and L.N. Petersen. 2003. A critique of the internal tracer method for estimating contaminant degradation rates. *Ground Water* 41, no. 3: 632–639.
- Martyn-Hayden, J., and G.A. Robbins. 1997. Plume distortion and apparent attenuation due to concentration averaging in monitoring wells. *Ground Water* 35, no. 2: 339–346.
- McCallister, P. 1996. Application of screening level approaches for evaluation of BTEX natural attenuation in groundwater, NGWA. In *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals*, 481–494, Houston, Texas, November 1996.
- McNab, W.W., and B.P. Dooher. 1998. A critique of a steady-state method for estimating contaminant degradation rates. *Ground Water* 36, no. 6: 983–987.
- Newell, C.J., H.S. Rifai, J.T. Wilson, J.A. Connor, J.A. Aziz, and M.P. Suarez. 2002. Calculation and use of first-order rate constants for monitored natural attenuation studies. U.S. EPA Ground Water Issue, U.S. EPA/540/S-02/500. Cincinnati, Ohio: U.S. EPA National Risk Management Research Laboratory.
- Newell, C.J., R.K. McLeod, and J. Gonzales. 1996. BIO-SCREEN Natural Attenuation Decision Support System, U.S. Environmental Protection Agency, EPA/600/R-96/087 (August).
- Ogata, A., and R. Banks. 1961. A solution of the differential equation of longitudinal dispersion in porous media. USGS Prof. Pap. No. 411-A. Reston, Virginia: USGS.
- Petersen, J.N., and Y. Sun. 2000. An analytical solution evaluating steady-state plumes of sequentially reactive contaminants. *Transport Porous Media* 41, no. 3: 287–303.
- Pfannkuch, H. 1963. Contribution a l'etude des déplacements de fluides miscibles dans un milieu poreux. Contribution to the study of the displacement of miscible fluids in a porous medium. *Revue de l'Institut Francais du Pétrole* 2, 18.
- Sagar, B. 1982. Dispersion in three dimensions, approximate analytical solutions. *ASCE, Journal of Hydraulics Division* 108, no. 1: 47–62.
- Sneddon, I.N. 1957. *Elements of Partial Differential Equations*, 327. New York: McGraw-Hill.
- Srinivasan, V., and T.P. Clement. 2008. Analytical solutions for sequentially one-dimensional reactive transport problems—Part I: Mathematical derivations. *Advances in Water Resources* 31, 203–218.
- Srinivasan, V., T.P. Clement, and K.K. Lee. 2007. Domenico solution—Is it valid? *Ground Water* 45, no. 2: 136–148.
- Suarez, M.P., and H.S. Rifai. 1999. Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater. *Bioremediation Journal* 3, no. 4: 337–362.
- Sun, Y., J.N. Petersen, and J. Bear. 2001. Successive identification of biodegradation rates for multiple sequentially reactive contaminants in groundwater. *Journal of Contaminant Hydrology* 51, no. 1: 83–95.
- Sun, Y., J.N. Petersen, and T.P. Clement. 1999. A new analytical solution for multiple species reactive transport in multiple dimensions. *Journal of Contaminant Hydrology* 35, no. 4: 429–440.
- West, M.R., B.H. Kueper, and M.J. Unger. 2007. On the use and error of approximation in the Domenico (1987) solution. *Ground Water* 45, no. 2: 126–135.
- Wexler, E.J. 1992. Analytical solutions for one-, two-, and three-dimensional solute transport in ground-water systems with uniform flow. In *TWRI Book 3*, Chap. B7. Reston, Virginia: USGS.
- Zhang, Y.K., and R.C. Heathcote. 2003. An Improved method for estimation of biodegradation rate with field data. *Ground Water Monitoring & Remediation* 23, no. 3: 112–116.