

# Estimation of Parent and Daughter Product Biodegradation Rate Constants Using Time Series Plots

*Daniel K. Burnell* (dan.burnell@tetratech.com), James W. Mercer (Tetra Tech GEO, Sterling, VA) and Scott R. Anderson, (Tetra Tech NUS, Pittsburg, PA)

Todd H. Wiedemeier, T.H. Wiedemeier & Associates, LLC, Denver, CO

**ABSTRACT:** At many sites, the source zone mass flux changes over time and therefore the downgradient concentrations observed in site monitoring wells also vary with time. At sites where steady-state plume analysis analytical tools (e.g., Buscheck and Alcantar method) are not appropriate and plume concentrations change significantly over time, time-series plots have been applied to estimate biodegradation rate constants using linear regression of log concentration data vs. time in monitoring wells. However, in many cases, the concentration-versus-time data of degradation products may initially increase and later decrease and an exponential curve cannot be fit to the data. In order to analyze data with nonlinear log concentration trends, this paper presents a new method for estimating rate constants of parent and degradation products for transient sequentially degrading plumes when concentration vs. time data are available for at least two monitoring wells located along a groundwater flow path. A stochastic view point is also presented to provide additional insight into first-order degradation reactions. Given that BIOCHLOR assumes the same retardation factor for parent and degradation products, a new 1-D transient analytical multi-species solute transport analytical solution is derived for an exponentially-decaying source that can account for different breakthrough times of parent and daughter compounds in downgradient wells. As an application, this analytical solution is used to estimate biodegradation rate constants of TCE and cis 1,2 DCE based on their concentration-vs.-time data from downgradient monitoring wells at the former Naval Battalion Center Site in North Kingstown, RI.

## INTRODUCTION

For steady-state parent plumes, the Buscheck and Alcantar (1995) method can be used to estimate first-order degradation rate constants for parent compounds. Because this method is based on the parent analytical solution of the 1-D steady-state advection-dispersion equation, it does not account for mass accumulation from parent compounds and should not be used for degradation products. In order to estimate rate constants of degradation products (e.g. cis 1,2 DCE and VC), simple 1-D, 2-D, and 3-D steady-state multispecies analytical solutions in spreadsheets (Burnell et al. 2007; 2011), approximate spreadsheet models based on the Domenico solution (e.g. BIOCHOR), and computer programs (e.g. MT3DMS and ART3D) can be utilized. At many sites, the source mass flux changes significantly over time and the plumes are not at steady-state. In this case, concentrations of parent and daughter products vary over time and steady-state analytical solutions cannot be used.

The primary objective of this paper is to present a new analytical solution that can be used to estimate rate constants of parent and degradation products for transient, sequentially-degrading plumes in which the source decays exponentially with time. A 1-D steady-state analytical solution is first presented for a parent and its daughter product. A stochastic view point is then developed to give additional insights into first-order degradation reactions in steady-state parent plumes. Although the BIOCHLOR code can

simulate transient plume development, it assumes the same retardation factor for parent and degradation products (Aziz et al., 2000). Therefore, BIOCHLOR cannot simulate differences in parent and daughter plume velocities and their different breakthrough times in monitoring wells. To address this limitation, a 1-D transient, advection-dominated multi-species analytical solution is derived that accounts for different retardation factors of a parent and its daughter product. The simple closed form of this analytical solution allows one to use spreadsheets to examine the different breakthrough times of the parent and its degradation product in downgradient observation wells. This new spreadsheet modeling tool is applied to estimate biodegradation rate constants for TCE and cis 1,2 DCE based on time series data in downgradient wells at the former Naval Battalion Center Site in North Kingstown, RI.

### 1-D STEADY-STATE, ADVECTION AND HYDRODYNAMIC DISPERSION OF PARENT AND DAUGHTER COMPOUNDS

After a spill, contaminant plumes grow until approximate steady-state plume conditions occur in which the rate of mass added to the plume (from source zones and any parent compounds) is equal to the rate that mass is removed by degradation. The advection-dispersion equations for 1-D steady-state plumes of a parent and its daughter product both undergoing first-order sequential degradation are:

$$\frac{d^2 C_1}{dx^2} - \frac{v}{D_x} \frac{dC_1}{dx} - \frac{k_1 C_1}{D_x} = 0 \quad (1a)$$

$$\frac{d^2 C_2}{dx^2} - \frac{v}{D_x} \frac{dC_2}{dx} - \frac{k_2 C_2}{D_x} = - \frac{y_{21} k_1 C_1}{D_x} \quad (1b)$$

$$C_1(0) = C_{10} \quad C_1 \rightarrow 0 \quad \text{as } x \rightarrow \infty \quad (1c)$$

$$C_2(0) = C_{20} \quad C_2 \rightarrow 0 \quad \text{as } x \rightarrow \infty \quad (1d)$$

where  $C_1$  and  $C_2$  are the parent and daughter product concentrations,  $C_{10}$  and  $C_{20}$  are the parent and daughter product concentrations at the source,  $x$  is the downgradient distance from the source,  $k_1$  and  $k_2$  are the biodegradation rate constants of the parent and daughter,  $y_{12}$  is the yield coefficient, and  $v$  is the average linear groundwater velocity.

This first-order linear system of ordinary differential equations (ODEs) can be solved sequentially using the method of undetermined coefficients (Boyce and DiPrima, 1977). The analytical solution is:

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

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

where for  $i=1,2,3$

$$r_i = \frac{v}{2D_x} - \sqrt{\frac{v^2}{4D_x^2} + \frac{k_i}{D_x}} \quad \text{and} \quad r_i < 0$$

Biodegradation is assumed to occur only in the aqueous phase. When biodegradation occurs 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  $3$ . Burnell et al. (2007) present a steady-state analytical solution for three compounds. Srinivasan and Clement (2008) present a steady-state, first-order chain decay solution for an arbitrary number of compounds. Multi-dimensional steady-state analytical solutions for three species for advection-dominated aquifers are presented in Burnell et al. (2011).

## STOCHASTIC ANALYSIS AND MEAN 1-D STEADY-STATE PLUME LENGTH OF PARENT

From a deterministic view point, first-order reactions over time  $t$  are represented mathematically using exponential decay functions ( $C=C_0e^{-k_1t}$ ) that assume contaminants (initially at concentration  $C_0$ ) decrease at a rate proportional to the concentration level. When contaminants move at a constant velocity with longitudinal dispersion, the steady-state plume distribution is given by Equation 2a. Additional insights of first-order degradation of contaminants moving at a constant velocity in groundwater can be obtained by taking a stochastic point of view as discussed below.

In reality, the distance that a contaminant molecule migrates until it biodegrades is uncertain and depends on a chance encounter with a microbe. Consider 1-D transport with first-order decay and let  $N$  be a discrete random variable from a Poisson distribution that represents the number of sequential decays that a contaminant molecule undergoes during its migration from the source ( $x=0$ ) to some downgradient distance  $x$ . A Poisson process has the following assumptions (Hogg and Tanis, 1993): (1) number of sequential transformations in non-overlapping length intervals is independent; (2) probability of one transformation occurring in a short interval  $h$  is  $\lambda h$ ; and (3) probability of two or more changes over a short length is essentially zero. The probability density function for the number of decay events  $N$  is given by  $P(N)=\frac{(\lambda x)^N e^{-\lambda x}}{N!}$  where  $\lambda$  is the average number of decays that occur per unit length. Using this equation, the probability that a particle does not decay ( $N=0$ ) over some migration distance  $x$  is  $e^{-\lambda x}$ . By letting  $\lambda=|r_1|$ , the normalized parent concentration  $C_1/C_{10} = e^{-|r_1|x}$  in Equation (2a) can be interpreted as the probability that the parent particle does not degrade as it is transported by advection and macroscopic hydrodynamic dispersion over a distance  $x$  from the source at steady-state plume conditions.

The distance between decay events in a Poisson process is exponentially distributed (Hogg and Tanis, 1993). To examine this, let  $X$  be a continuous random variable from a Poisson process where  $X$  represents the distance a parent particle migrates until it degrades and undergoes a transformation. For  $x \geq 0$ , the distribution function for the random distance  $X$  is given by:

$$F(x)=P(X \leq x)=1-P(X > x)=1-e^{-|r_1|x} \quad (3)$$

For  $x < 0$ , the distribution function  $F(x) = 0$ . Because the probability density function (pdf) of  $f(x) = F'(x)$ , it is found to be:

$$f(x) = |r_1| e^{-|r_1|x} = \frac{1}{L_1} e^{-\frac{x}{L_1}} \quad (4)$$

for  $x \geq 0$ , which is the probability density function for the exponential distribution.

Therefore, the distance traveled until the first decay in a Poisson process has an exponential distribution where  $L_1 = 1/|r_1|$  can be interpreted as the mean migration distance of the particles in a steady-state parent plume. Using the distribution function  $F(x) = 1 - \exp(-x/L_1)$ , the median plume distance of the parent ( $m_1$ ) is calculated to be  $m_1 = -L_1 \ln(0.5)$ . The variance of the random plume distance  $X$  is  $\sigma^2 = L_1^2 = 1/r_1^2$ .

For the steady-state plume concentration of the parent in Equation (2a), Chapelle et al. (2003) refer to  $|r_1|$  as the natural attenuation capacity, which can be considered the contaminant reducing capacity of an aquifer per unit length along the groundwater flow path. The statistical viewpoint presented above indicates that  $L_1 = 1/|r_1|$  can be interpreted as the mean migration distance of the parent plume particles. The mean steady-state plume distance can be simplified to be:

$$L_1 = \frac{v + \sqrt{v(v + 4k_1 a_L)}}{2k_1} \quad (5)$$

When  $a_L$  is small,  $L_1 \sim v/k_1$  and therefore the mean steady-state plume length is larger for higher groundwater velocities and slower degradation rates. It should be noted that the mean 1-D migration distance of a parent particle from its source is equal to the 1-D plume centroid for the 1-D analytical solution (Equation 2a) as discussed in Burnell et al. (2011).

### **ADVECTION-DOMINATED PLUME ANALYTICAL SOLUTION OF PARENT AND DAUGHTER PRODUCT FOR EXPONENTIAL DECAYING POINT SOURCE, SORPTION, AND STEADY-STATE INITIAL PLUMES**

Over time, the amount of contaminant source DNAPL mass diminishes as a result of many processes including dissolution that form the dissolved plume. As indicated in laboratory studies (e.g. Jawitz et al. 2005) and source zone flushing models (e.g. Falta et al., 2005a; 2005b), the source mass flux may decrease exponentially with time when there is a linear relationship between the source mass remaining and the mass flux. This corresponds to  $\Gamma=1$  in power function models (Rao et al., 2001; Parker and Park, 2004; Zhu and Sykes, 2004). As discussed in Newell and Adamson (2005), the long “tail” of source function exponential decay curves approximates the effects of various processes including DNAPL dissolution, matrix diffusion, complex desorption processes, and stagnant zones over time.

In order to simulate an exponentially decaying source, a 1-D multi-species analytical solution was developed for advection-dominated water bearing zones with different retardation factors for the parent and daughter. The initial concentrations of parent and daughter (Equation 6c and 6d) are assumed to be equal to the steady-state plumes for advection-dominated conditions (Equation 2 with  $r_1 = k_1/v$ ). The mathematical model is summarized below:

$$\frac{\partial C_1}{\partial t} + \frac{v}{R_1} \frac{\partial C_1}{\partial x} = -\frac{k_1}{R_1} C_1 \quad (6a)$$

$$\frac{\partial C_2}{\partial t} + \frac{v}{R_2} \frac{\partial C_2}{\partial x} = -\frac{k_2}{R_2} C_2 + \frac{k_1 y_{21}}{R_2} C_1 \quad (6b)$$

$$C_1(x,0) = C_{10} e^{-\frac{k_1}{v}x} \quad (6c)$$

$$C_2(x,0) = C_{20} e^{-\frac{k_2}{v}x} + C_{10} \frac{k_1 y_{21}}{k_1 - k_2} (e^{-\frac{k_2}{v}x} - e^{-\frac{k_1}{v}x}) \quad (6d)$$

$$C_1(0,t) = C_{10} e^{-\gamma_1 t}$$

$$C_2(0,t) = C_{20} e^{-\gamma_2 t} \quad (6e)$$

$$C_1 \rightarrow 0 \text{ as } x \rightarrow \infty$$

$$C_2 \rightarrow 0 \text{ as } x \rightarrow \infty$$

where  $\gamma_i$  is the rate that source concentration decreases exponentially with time for each contaminant  $i$ ,

As shown in Appendix A, the solution of the parent and daughter product can be found by Laplace transforms (Boyce and Diprima, 1977) with the use of inverse Laplace transform tables given in Abramowitz and Stegun (1972). The general solution is:

#### PARENT:

$$C_1 = C_{10} e^{-\frac{k_1 x}{v}} \quad t \leq \frac{xR_1}{v} \quad (7a)$$

$$= C_{10} e^{-\gamma_1 (t - \frac{R_1 x}{v}) - \frac{k_1 x}{v}} \quad t > \frac{xR_1}{v} \quad (7b)$$

#### DAUGHTER:

$$C_2 = C_{20} e^{-k_2 x/v} + C_{10} \frac{k_1 y_{21}}{(k_1 - k_2)} (e^{-k_2 x/v} - e^{-k_1 x/v}) \quad t \leq \frac{xR_2}{v} \quad (7c)$$

$$C_2 = C_{20} e^{-\gamma_2 (t - \frac{R_2 x}{v}) - k_2 x/v} + \frac{C_{10} k_1 \gamma_{21}}{k_1 - k_2} (e^{-k_2 x - \frac{(k_2 - k_1)}{R_2 - R_1} (t - \frac{R_2 x}{v})} - e^{-k_1 x}) \quad (7d)$$

$$+ \frac{C_{10} k_1 \gamma_{21}}{k_1 - k_2 + \gamma_1 (R_2 - R_1)} (e^{-\gamma_1 (t - \frac{R_2 x}{v})} - e^{-\frac{(k_2 - k_1)}{R_2 - R_1} (t - \frac{R_2 x}{v})}) \quad \frac{xR_2}{v} < t \leq \frac{xR_1}{v}$$

$$C_2 = C_{20} e^{-\gamma_2 (t - \frac{R_2 x}{v}) - k_2 x/v}$$

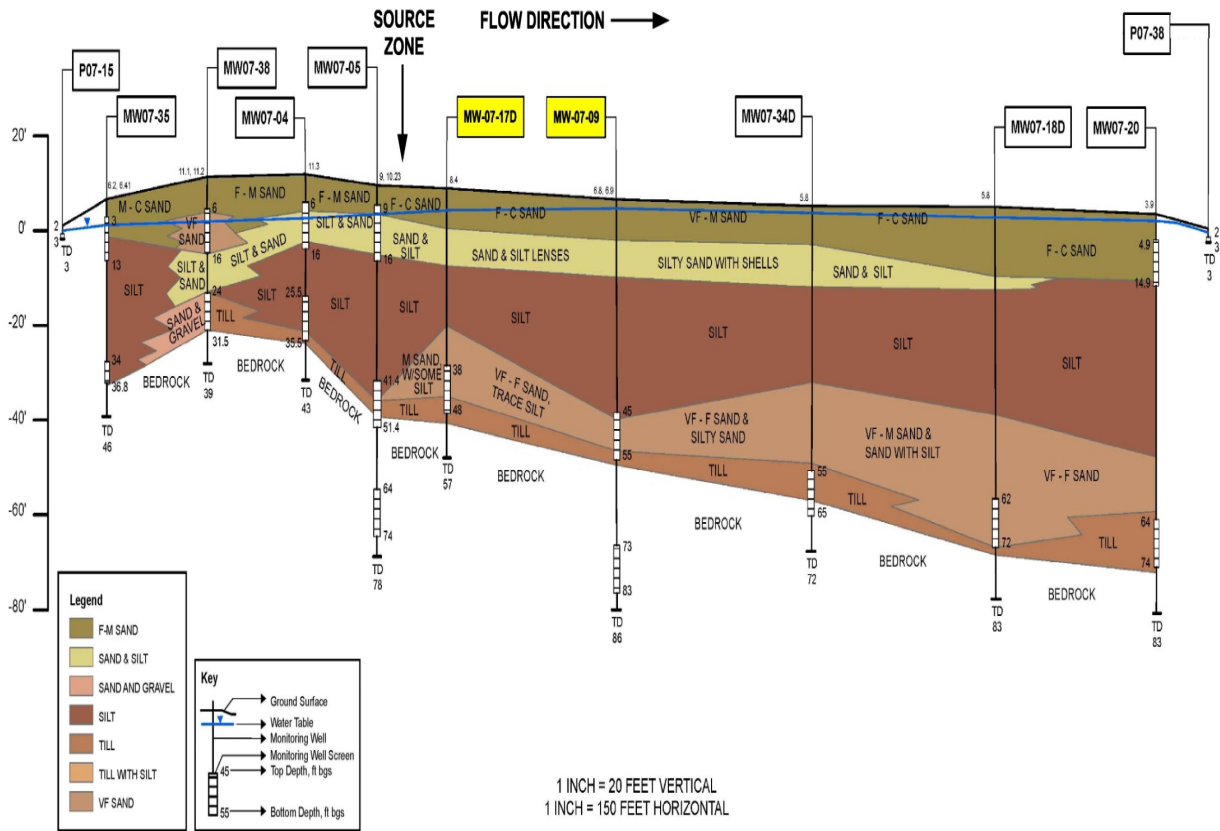
$$+ \frac{C_{10} k_1 \gamma_{21}}{k_1 - k_2 + \gamma_1 (R_2 - R_1)} (e^{-\frac{k_2 x}{v}} (e^{-\gamma_1 (t - \frac{R_2 x}{v})} - e^{-\frac{(k_2 - k_1)}{R_2 - R_1} (t - \frac{R_2 x}{v})}) - e^{-\frac{k_1 x}{v}} (e^{-\gamma_1 (t - \frac{R_1 x}{v})} - e^{-\frac{(k_2 - k_1)}{R_2 - R_1} (t - \frac{R_1 x}{v})})) \quad (7e)$$

$$+ \frac{C_{10} k_1 \gamma_{21}}{k_1 - k_2} (e^{-\frac{k_2 x}{v} - \frac{(k_2 - k_1)}{R_2 - R_1} (t - \frac{R_2 x}{v})} - e^{-\frac{k_1 x}{v} - \frac{(k_2 - k_1)}{R_2 - R_1} (t - \frac{R_1 x}{v})}) \quad t > \frac{xR_1}{v}$$

where  $C_1$  and  $C_2$  represent the parent (TCE) and daughter (cis 1,2 DC) species. Srinivasan and Clement (2007) derived a general solution for an arbitrary number of compounds when the initial concentrations of both the parent and daughter decrease exponentially with distance from the source. Both the steady-state (Equation 2) and transient (Equation 7) analytical solutions are available in the Sequential Plume Spreadsheet Analyzer (SPSA) toolkit (Burnell et al., 2011). Both Harada et al. 1980 and Higashi and Pigford (1980) derived analytical solutions when the initial concentrations are zero. In contrast to the BIOCHLOR and REMCHLOR models, this analytical solution can simulate the different plume velocities of the parent and its daughter product, which allows one to examine the different breakthrough times of parent and daughter products that are commonly observed in concentration vs. time in site monitor wells.

### APPLICATION TO ESTIMATE TCE AND CIS 1,2 DCE BIODEGRADATION RATE CONSTANTS

The 1-D transient advection-dominated analytical solution (Equation 7) was applied to estimate TCE and cis 1,2 DCE first-order rate constants based on time series data in monitor well MW-07-17D located near the source and in the downgradient well MW-07-9D at the former Naval Battalion Center Site in North Kingstown, RI. As seen in Figure 1, the site data show that the contaminants are migrating primarily within a thin (<1 ft to 30 ft thick), relatively permeable sand zone that is underlain by a lower permeability clay till unit. Both ORP and DO data indicate that iron reduction is the dominant terminal electron accepting (TEAP) process with localized zones of both sulfate reducing and methanogenic conditions. The presence of cis 1,2 DCE and VC degradation products of TCE indicate that reductive dechlorination is occurring. The relatively lower levels of



**FIGURE 1. Vertical cross section along the groundwater flow direction at former Navy Battalion Center Site in North Kingstown, RI.**

VC compared to cis 1,2 DCE suggest that direct oxidation of DCE may be occurring. A detailed discussion of the site is given in Tetra Tech (2010).

### 1-D TRANSIENT MULTI-SPECIES MODEL SIMULATION

The parameters used for the analytical transport modeling analyses in this study are summarized in Table 1. The TCE source zone mass flux decrease over time was simulated by fitting an exponential curve to the TCE time series data from 1996 to 2010 in near source well MW-07-17D (Figure 2). The estimated source function half life was 7.5 yr. The TCE and cis 1,2 DCE rate constants were then varied in order to match the analytical solution (Equation 7) to observed trends in downgradient well MW-07-9D, which is located approximately 300 ft downgradient from MW-07-17D. The simulated parent and daughter plume plume centerline concentrations for various times are presented in Figure 3 and Figure 4, respectively.

Figure 5 shows a good match between simulated and observed TCE and cis 1,2 DCE data in downgradient well MW-07-09D. The estimated rate constants of TCE and cis 1,2 DCE were 0.35 yr<sup>-1</sup> and 0.99 yr<sup>-1</sup>, respectively. With the plumes being initially at

steady-state in the model, the concentrations do not change in this well until the effect of source depletion reaches this location. In the model, the concentration does not change right away in this well because higher initial upgradient plume concentrations decrease over time during their downgradient movement and eventually become equal to the initial

**TABLE 1. 1-D Multi-Species Advection-Reaction Model Parameter Values.**

Solute Transport Model Parameter	Model Parameter Value	Reference
Source Concentration of parent ( $C_{10}$ ) and daughter ( $C_{20}$ )	$C_{10} = 1,100$ mg/L (TCE) $C_{20} = 7.8$ mg/L (cis 1,2 DCE)	Observed TCE and cis 1,2 DCE in near source well MW-07-17D in Jan. 1996 (Tetra Tech, 2010)
Parent ( $\gamma_1$ ) and Daughter ( $\gamma_2$ ) Source Decay Rate	$\gamma_1 = \gamma_2 = 0.091$ yr <sup>-1</sup> (Half life=7.5 yr)	Exponential curve fit to observed TCE trend in near source well MW-07-17D (Tetra Tech, 2010)
Average Linear Groundwater Velocity (v)	40 ft/yr	Site data (Tetra Tech, 2010)
Effective Yield Coefficient ( $y_{21}$ )	$y_{21} = 0.74$	Calculated stoichiometrically using TCE-to-DCE reaction
Parent (TCE) Retardation Factor ( $R_1$ )	$R_1 = 1.3$	Site data (Tetra Tech, 2010)
Daughter (cis 1,2 DCE) Retardation Factor ( $R_2$ )	$R_2 = 1.0$	Site data (Tetra Tech, 2010)
Parent (TCE) Rate Constant ( $k_1$ )	$0.35$ yr <sup>-1</sup> (Half life=2.0 yr)	Calibrated value based on fit of 1-D advection-reaction multi-species model to TCE and cis 1,2 DCE data in MW-07-09D
Daughter (cis 1,2 DCE) Rate Constant ( $k_2$ )	$0.99$ yr <sup>-1</sup> (Half life = 0.70 yr)	Calibrated value based on fit of 1-D advection-reaction multi-species model to TCE and cis 1,2 DCE data in MW-07-09D

steady-state concentration level at this location. Thus, concentrations remain constant until the effects of source depletion reach this location. It is seen that effect of the decaying source is not seen in this well until 10 yr later for the parent and 8.5 yr later for the daughter. The effect of the source depletion is first observed for cis 1,2 DCE because it moves faster in groundwater than TCE. These simulation plots also indicate that effects of source remediation can take long periods of time to be seen in downgradient wells particularly when the groundwater velocity is relatively low and sorption is important.

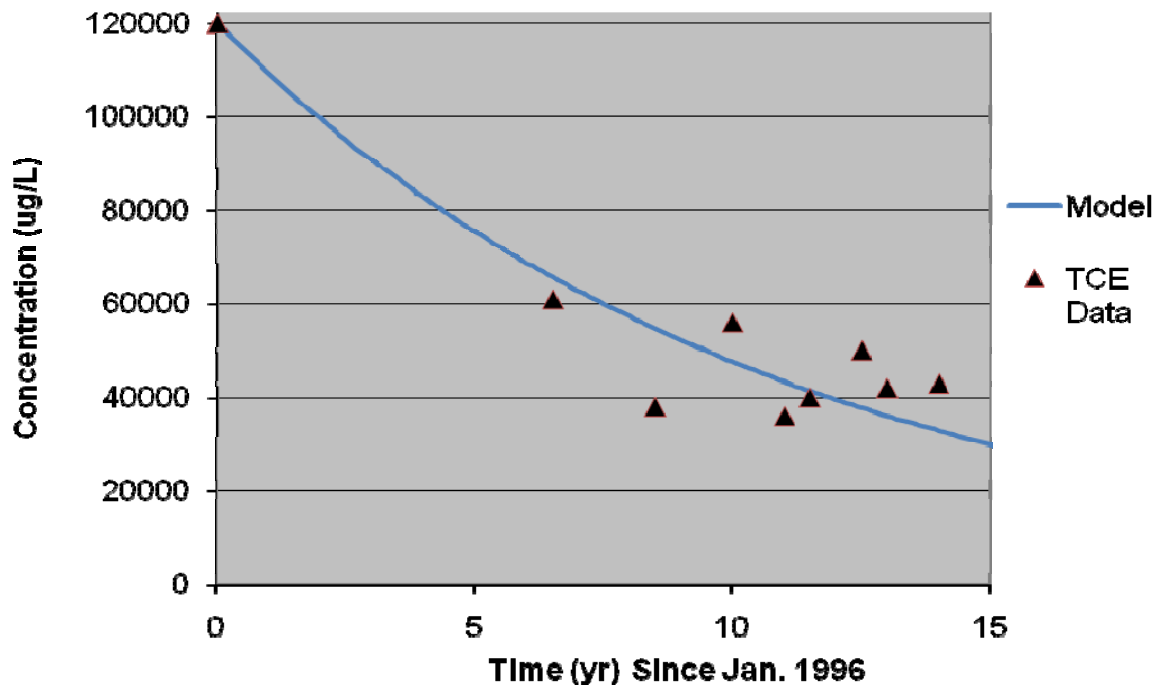


FIGURE 2. Observed vs. simulated concentrations of TCE in near source monitor well MW-07-179D using 1-D, transient advection-dominated multi-species model.

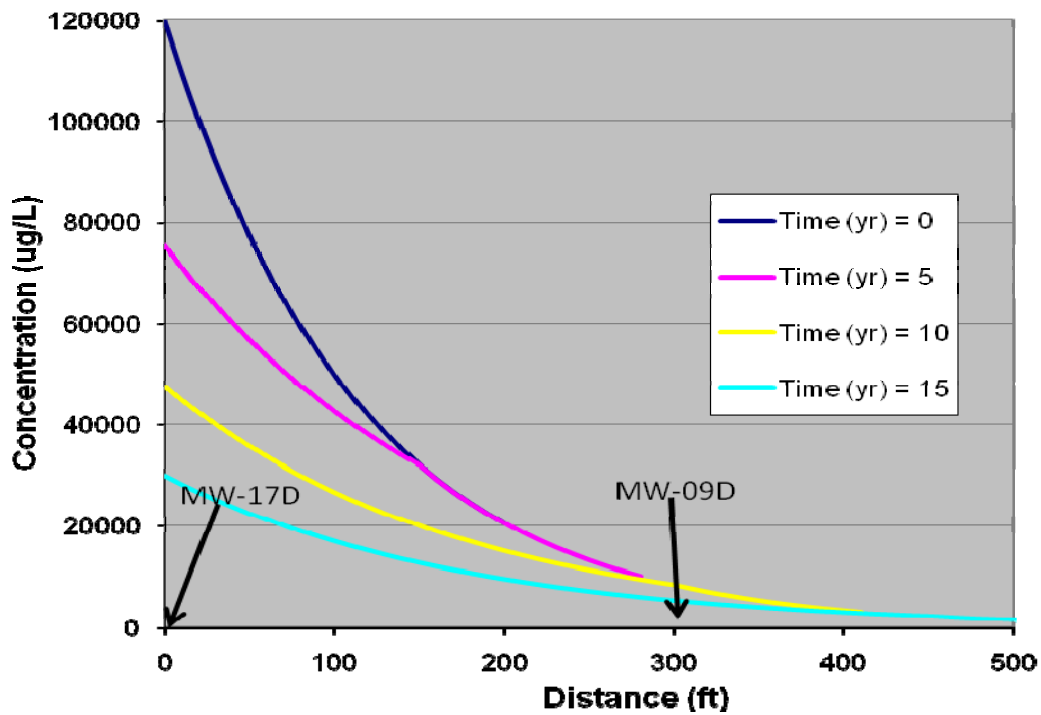


FIGURE 3. Simulated TCE concentration vs. distance along plume centerline for various times since 1996.

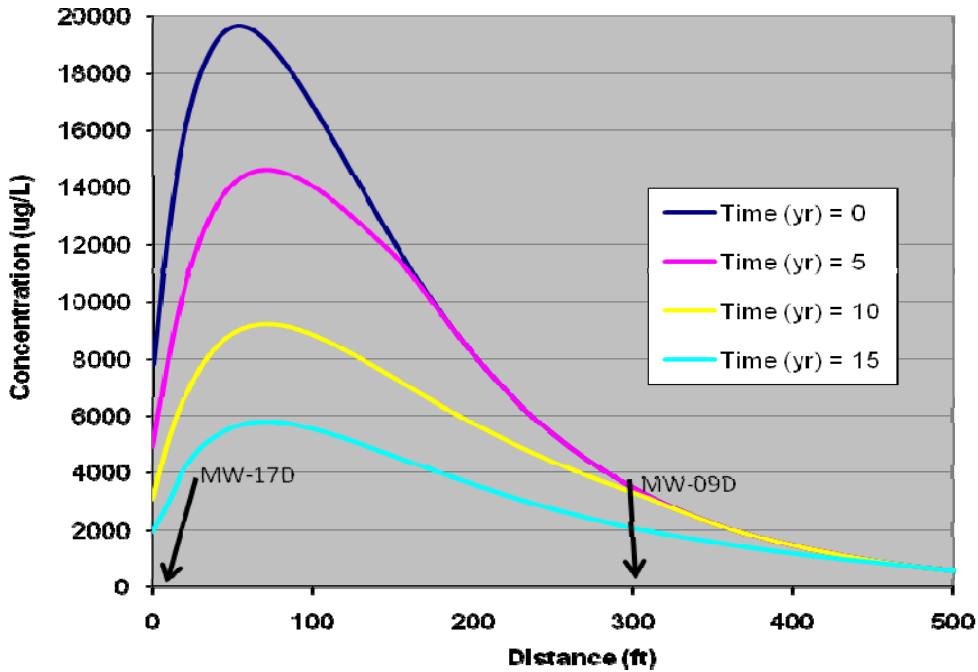


FIGURE 4. Simulated cis 1,2 DCE concentration vs. distance along plume centerline for various times since 1996.

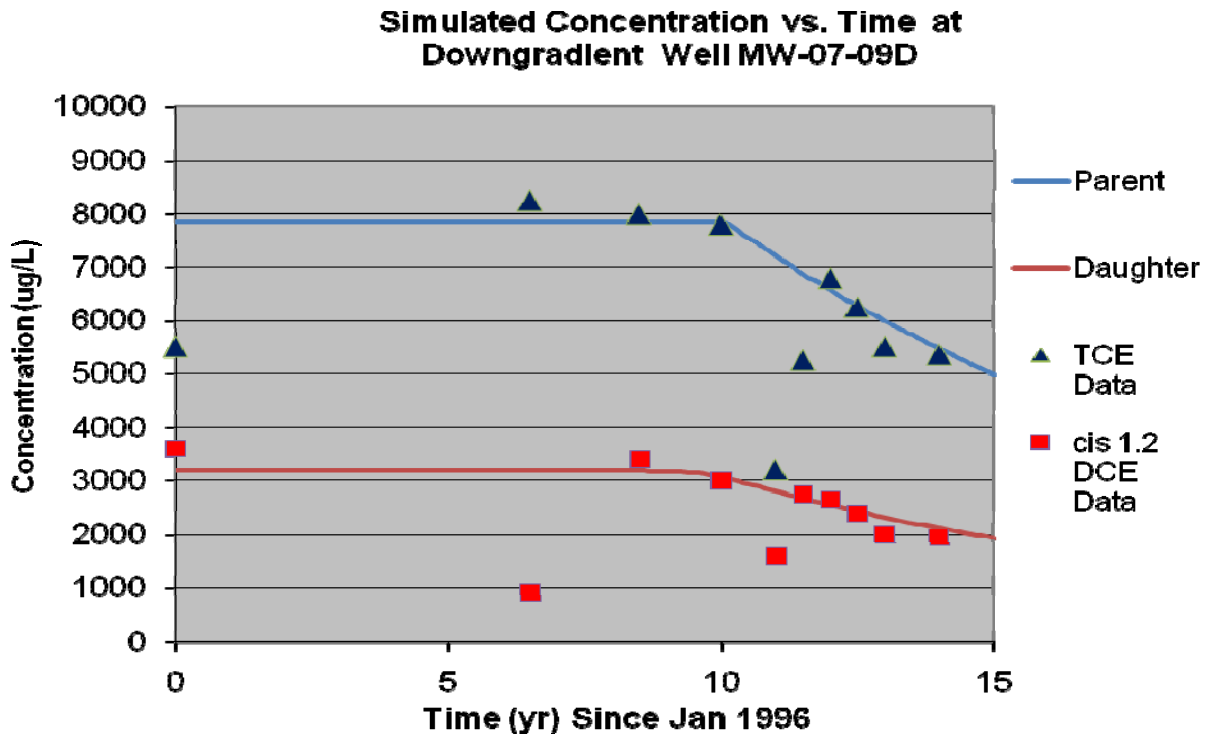


FIGURE 5. Observed vs. simulated concentration of TCE and cis 1,2 DCE in downgradient well MW-07-09D using 1-D, transient advection-dominated multi-species model.

## **EFFECT OF HYDRODYNAMIC DISPERSION**

Using dimensionless plots, Burnell et al. (2010; 2011) showed that longitudinal dispersion is relatively unimportant in 1-D steady-state plumes when aquifers are relatively permeable (Peclet number  $Pe > 6$ ) and contaminants (e.g. chlorinated solvents) degrade relatively slowly (Damköhler number  $Da < 1$ ). Further analyses indicated that when  $a_L k_i^2 \ll v^2$ , advection-reaction equations ( $a_L = 0$ ) can be used for steady-state multispecies plumes where  $a_L$  is the longitudinal dispersivity,  $k_i$  is the biodegradation of species  $i$ , and  $v$  is the average linear groundwater velocity. For transient plumes, effects of hydrodynamic dispersion can be important and additional analyses using analytical (e.g. ART3D) and numerical (e.g. MT3DMS, RT3D) are recommended to examine the effect of the assumption that hydrodynamic dispersion is zero. Effects of longitudinal dispersion can be approximated using the streamtube approach in REMCHLOR. Effects of vertical and horizontal transverse dispersion can be approximated by multiplication of the analytical solutions in Equation 7 by the Domenico (1987) spreading terms.

The estimated rate constants from a one-dimensional analytic solution are likely overestimated because of the assumption of a point source release with negligible longitudinal and 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.

## **SUMMARY AND CONCLUSIONS**

Taking a stochastic viewpoint of steady-state plumes with contaminants undergoing first-order biodegradation, the distance that a contaminant parent particle migrates from a source zone until it is degraded can be viewed as a random Poisson process that depends on a chance encounter with a contaminant-specific degrading microbe. Under the assumption that the biodegradation rate constant is constant, the distance a contaminant particle travels via advection and dispersion until it is biodegraded can be represented as an exponential random variable during steady-state plume conditions. On a plot of the log parent concentration data versus distance along the 1-D flow path, the reciprocal of the slope of the line of best fit is its expected mean plume length or plume centroid. The reciprocal of the expected plume length (plume centroid) has also been defined as the natural attenuation capacity (NAC).

Multi-species analytical solutions, which obey conservation of mass between parent and degradation products, are useful tools for estimating parent and degradation product rate constants. When plume concentrations change over time in near source wells as a result of time-dependent changes in source zone mass flux, the effect of this source depletion and any mass balance changes between parent and daughter products along the flow path will eventually be seen in downgradient monitor wells. To examine effects of an exponential decaying source, a 1-D transient analytical solution was derived for advection, sorption, and first-order degradation of a parent and daughter compound. In contrast to BIOCHLOR and REMCHLOR, this analytical solution can account for different retardation factors of the parent and daughter, which allows one to examine different breakthrough times for parent and daughter products at downgradient

monitoring points.

As an application at the former Naval Battalion Center Site in RI, this analytical solution was applied to estimate TCE and cis 1,2 DCE rate constants of  $0.35 \text{ yr}^{-1}$  and  $0.99 \text{ yr}^{-1}$ , respectively, based on concentration-vs.-time data from a well located near the source and a downgradient well. These estimated rate constants are consistent with estimated ranges of rate constants from other sites in the U.S (Aronson and Howard, 1997; Suarez and Rifai, 1999; Wiedemeier et al., 1999). The higher rate constant of cis 1,2 DCE compared to TCE may be caused by more rapid oxygen-rated mineralization mechanisms that can occur in zones with relatively low levels of DO (Bradley, 2011; Bradley and Chapelle, 2011).

## ACKNOWLEDGMENTS

This work was supported by the Mid-Atlantic Naval Facilities Engineering Command with special thanks to Jeffrey M. Dale and David A. Barney.

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**APPENDIX A: DERIVATION OF 1-D, TRANSIENT SOLUTION OF PARENT AND DAUGHTER COMPOUNDS UNDERGOING FIRST-ORDER DEGRADATION WITH AN EXPONENTIALLY DECAYING SOURCE**

**PARENT:**

Taking the Laplace transforms of the parent (Equation 6a) and its boundary condition (Equation 6c), respectively, we get:

$$p\bar{v}_1 - C_{10}e^{-\frac{k_1 x}{v}} + \frac{v}{R_1} \frac{d\bar{v}_1}{dx} = -\frac{k_1}{R_1} \bar{v}_1 \quad (\text{A1})$$

$$\bar{v}_1(0) = \frac{C_{10}}{p + \gamma_1} \quad (\text{A2})$$

where  $\bar{v}_1$  is the Laplace transform of  $C_1$  and  $p$  is the Laplace transform variable. This first-order linear ODE and boundary condition can be solved using an integrating factor to get:

$$\bar{v}_1 = \frac{C_{10}}{p} e^{-\frac{k_1 x}{v}} + \frac{C_{10}}{p + \gamma_1} e^{-\frac{(k_1 + R_1 p)x}{v}} - \frac{C_{10} e^{-\frac{(k_1 + R_1 p)x}{v}}}{p} \quad (\text{A3})$$

Taking inverse Laplace transforms of both side of Equation A3 and simplifying using tables in Abramowitz and Stegun (1972), we get:

$$C_1 = C_{10} e^{-\frac{k_1 x}{v}} (1 + U_{\frac{R_1 x}{v}}(t) (e^{-\gamma_1(t - \frac{R_1 x}{v})} - 1)) \quad (\text{A4})$$

where  $U_{\frac{R_1 x}{v}}(t) = \begin{cases} 0 & t \leq \frac{R_1 x}{v} \\ 1 & t > \frac{R_1 x}{v} \end{cases}$  is the unit step function (Boyce and Diprima, 1977).

Using this definition of the unit step function, Equation A4 can be written as Equation 7a and 7b.

**DAUGHTER:**

Although the methods of characteristics could have been used, the Laplace transform is particularly useful to find a solution for the daughter (Equation 6b) because of the discontinuous nature of the parent solution (e.g. Equation 7a and 7b). Inserting instead The parent solution (Equation A4) into the Equation 6b and taking the Laplace transform of both sides, we get:

$$p\bar{v}_2 - C_{20} e^{-\frac{k_2 x}{v}} - \frac{C_{10}}{k_1 - k_2} \frac{k_1 y_{12}}{v} e^{-k_2 x} + \frac{C_{10}}{k_1 - k_2} \frac{k_1 y_{12}}{v} e^{-\frac{k_1 x}{v}} + \frac{v}{R_2} \frac{d\bar{v}_2}{dx} = \quad (\text{A5})$$

$$-\frac{k_2}{R_2} \bar{v}_2 + \frac{C_{10}}{R_2 p} \frac{k_1 y_{12}}{v} e^{-\frac{k_1 x}{v}} - \frac{C_{10}}{R_2 p} \frac{k_1 y_{12}}{v} e^{-\frac{(k_1 x + R_1 p)}{v}} + \frac{C_{10}}{R_2 (p + \gamma_1)} \frac{k_1 y_{12}}{v} e^{-\frac{(k_1 + R_1)p x}{v}}$$

$$\bar{v}_2(0) = \frac{C_{20}}{p + \gamma_2} \quad (\text{A6})$$

where  $\bar{v}_2$  is the Laplace transform of  $C_2$ . The first-order linear ODE (Equation A5) and boundary condition (Equation A6) can be solved using an integrating factor to get:

$$\begin{aligned} \bar{v}_2 = & \frac{C_{20}}{p} e^{-\frac{k_2}{v}x} + \frac{C_{10} k_1 y_{12}}{p(k_1 - k_2)} e^{-k_2 x} - \frac{C_{10} k_1 y_{12} R_2}{(k_1 - k_2)(k_2 - k_1 + R_2 p)} e^{-\frac{k_1 x}{v}} + \frac{C_{10} k_1 y_{12}}{p(k_2 - k_1 + R_2 p)} e^{-\frac{k_1 x}{v}} \\ & - \frac{C_{10} k_1 y_{12}}{p(k_2 - k_1 + (R_2 - R_1)p)} e^{-\frac{(k_1 + R_1)x}{v}} + \frac{C_{10} k_1 y_{12}}{(p + \gamma_1)(k_2 - k_1 + (R_2 - R_1)p)} e^{-\frac{(k_1 + R_1)x}{v}} + \frac{C_{20}}{p + \gamma_2} e^{-\frac{(k_2 + R_2 p)x}{v}} \\ & - \frac{C_{20}}{p} e^{-\frac{(k_2 + R_2 p)x}{v}} - \frac{C_{10} k_1 y_{12}}{p(k_2 - k_1)} e^{-\frac{(k_2 + R_2 p)x}{v}} + \frac{C_{10} k_1 y_{12} R_2}{(k_1 - k_2)(k_2 - k_1 + R_2 p)} e^{-\frac{(k_2 + R_2 p)x}{v}} \\ & - \frac{C_{10} k_1 y_{12}}{p(k_2 - k_1 + R_2 p)} e^{-\frac{(k_2 + R_2 p)x}{v}} + \frac{C_{10} k_1 y_{12}}{p(k_2 - k_1 + (R_2 - R_1)p)} e^{-\frac{(k_2 + R_2 p)x}{v}} - \frac{C_{10} k_1 y_{12}}{(p + \gamma_1)(k_2 - k_1 + (R_2 - R_1)p)} e^{-\frac{(k_2 + R_2 p)x}{v}} \end{aligned} \quad (\text{A7})$$

Taking inverse Laplace transforms of both side of Equation A7 and simplifying using tables in Abramowitz and Stegun (1972), we get:

$$\begin{aligned} C_2 = & C_{20} e^{-\frac{k_2 x}{v}} + \frac{C_{10} k_1 y_{12}}{k_1 - k_2} (e^{-\frac{k_2 x}{v}} - e^{-\frac{k_1 x}{v}}) \\ & + \left[ \frac{C_{10} k_1 y_{12}}{k_2 - k_1} e^{-\frac{k_1 x}{v}} \left( 1 - e^{-\frac{(k_2 - k_1)(t - \frac{R_1 x}{v})}{R_2 - R_1}} \right) + \frac{C_{10} k_1 y_{12}}{k_2 - k_1 - \gamma_1(R_2 - R_1)} e^{-\frac{k_1 x}{v}} \left( e^{-\gamma_1(t - \frac{R_1 x}{v})} - e^{-\frac{(k_2 - k_1)(t - \frac{R_1 x}{v})}{R_2 - R_1}} \right) \right] \cdot U_{\frac{R_1 x}{v}}(t) \\ & + \left[ C_{20} e^{-\frac{k_2 x}{v} - \gamma_2(t - \frac{R_2 x}{v})} - C_{20} e^{-\frac{k_2 x}{v}} - \frac{C_{10} k_1 y_{12}}{k_1 - k_2} e^{-\frac{k_2 x}{v}} + \frac{C_{10} k_1 y_{12}}{k_1 - k_2} e^{-\frac{k_2 x}{v}} - \frac{(k_2 - k_1)(t - \frac{R_2 x}{v})}{R_2} \right] \cdot U_{\frac{R_2 x}{v}}(t) \\ & + \left[ \frac{C_{10} k_1 y_{12}}{k_2 - k_1} e^{-\frac{k_2 x}{v}} \left( 1 - e^{-\frac{(k_2 - k_1)(t - \frac{R_2 x}{v})}{R_2}} \right) + \frac{C_{10} k_1 y_{12}}{k_2 - k_1} e^{-\frac{k_2 x}{v}} \left( 1 - e^{-\frac{(k_2 - k_1)(t - \frac{R_2 x}{v})}{R_2 - R_1}} \right) \right] \cdot U_{\frac{R_2 x}{v}}(t) \\ & - \left[ \frac{C_{10} k_1 y_{12}}{k_2 - k_1 - \gamma_1(R_2 - R_1)} e^{-\frac{k_2 x}{v}} \left( e^{-\gamma_1(t - \frac{R_2 x}{v})} - e^{-\frac{(k_2 - k_1)(t - \frac{R_2 x}{v})}{R_2 - R_1}} \right) \right] \cdot U_{\frac{R_2 x}{v}}(t) \end{aligned} \quad (\text{A8})$$

When  $R_1 > R_2$ , the daughter solution (Equation A8) can be expressed in the form given by Equations 7c to 7e.