

Estimation of Sequential Biodegradation Product Rate Constants

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ABSTRACT: The use of single-species analytical solute transport modeling approaches (e.g., Buscheck and Alcantar method) can lead to underestimated values of biodegradation product rate constants because these approaches do not include biodegradation product accumulation along the groundwater flow path. In order to improve estimates of daughter product biodegradation rate constants, the steady-state solution of the one-dimensional advection-dispersion equation for a point source with first-order chain reaction of three species was derived. This solution can be calibrated to concentration versus distance data of approximate steady-state plumes of both parent and daughter products in order to estimate their field-scale rate constants. An analysis of the analytical solution also indicates that the downgradient locations of both cross-over points (where parent and daughter concentration versus distance data intersect) and maximum points (distance where highest concentration levels occur) can be used to directly interpret field data and estimate daughter product rate constants.

As an application, this one-dimensional, multi-species analytical solution was calibrated to quasi-steady state trichloroethene (TCE), cis-1,2-dichloroethene (DCE), and vinyl chloride (VC) plume conditions at a site in Palm Bay, FL in order to estimate their field-scale, first-order biodegradation rate constants. The estimated first-order rate constant values for the steady-state plumes by the analytical solution were 0.88 yr^{-1} , 0.82 yr^{-1} , and 0.87 yr^{-1} for TCE, DCE, and VC, respectively. These rate constant values are upper bound estimates because the assumption of a point source release with negligible transverse dispersion leads to higher calculated plume centerline concentrations with concomitant higher calibrated rate constants in order to match the observed data. Although the source width and transverse dispersivity values are not typically well defined in the field, a two- or three-dimensional model could be applied when justifiable in order to reduce the uncertainty of these estimated rate constants.

INTRODUCTION

Estimation of biodegradation rates from field data have been performed using (1) graphical extraction (Ellis, 1996), (2) Buscheck and Alcantar method (Buscheck and Alcantar, 1995), (3) Wiedemeier et al. method (Wiedemeier et al., 1996), and (4) using semi-analytical and numerical models (see e.g., Jones et al. 2006 [ART3D]; Newell et al., 1996 [BIOSCREEN]; Aziz et al., 2000 [BIOCHLOR]; Srinivasan and Mercer, 1988 [BIO1D]; Zheng and Wang, 1999 [MT3DMS]). The graphical method overestimates first-order decay because the determined decay constant accounts for the effects of all processes (dispersion, matrix diffusion, sorption, volatilization and degradation) that decrease the concentration along the flow path. The Buscheck and Alcantar method improves on graphical extraction because it incorporates information about dispersion (in the direction of flow) and sorption, and distinguishes these effects from degradation. The Buscheck and Alcantar method does not account for transverse dispersivity or volatilization, and if these processes are important,

first-order decay could be overestimated. The Wiedemeier et al. method estimates first-order decay between two points along a flow path by normalizing the concentration of the chemical of interest to that of a tracer. This method provides a decay constant that does not include the effects of sorption or dispersion; however, the method requires a tracer. Use of numerical models can provide an estimate of degradation that is independent of abiotic processes, but can be computationally intensive.

The Buscheck and Alcantar method has been used frequently to estimate biodegradation rate constants. For this approach, it is assumed that the dissolved plume is at steady state. Although this method originally was developed for dissolved petroleum plumes (BTEX), it can be applied to dissolved chlorinated solvents as well (Chapelle et al., 2003). For chlorinated solvents, however, this procedure yields apparent degradation rate constants for biodegradation products that underestimate actual degradation rate constants because the method does not account for generation of the daughter products. This limitation can be overcome by using a multispecies, solute transport numerical model such as MT3DMS or a semi-analytical model for multispecies transport (e.g., BIOCHLOR).

In this paper, an alternative analytical model for multispecies transport is presented and applied to a field site that has been previously modeled using MT3DMS (Burnell et al., 2003). The analytical model provides a steady-state solution of the one-dimensional solute transport equation with first-order chain reaction of each chemical. The analytical model provides a convenient way to estimate biodegradation rate constants at field sites where biodegradation is occurring and daughter products are being formed and subsequently biodegraded.

MODEL DESCRIPTION

At steady-state, the coupled one-dimensional advection-dispersion equations for a three-member system with first-order chain decay and a constant concentration point source can be written as:

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

$$\begin{aligned} C_1(0) &= C_{10} \quad C_1 \rightarrow 0 \text{ as } x \rightarrow \infty \\ C_2(0) &= C_{20} \quad C_2 \rightarrow 0 \text{ as } x \rightarrow \infty \\ C_3(0) &= C_{30} \quad C_3 \rightarrow 0 \text{ as } x \rightarrow \infty \end{aligned} \quad (2)$$

where C_1 , C_2 , and C_3 are the parent and sequential daughter product concentrations, x is the downgradient distance from the source, v is the average linear groundwater velocity, D_x is the longitudinal dispersion coefficient ($D_x = a_x v$), a_x is the longitudinal dispersivity, y_{21} is the effective yield coefficient that indicates the mass of species (C_2) produced from its parent (C_1), y_{32} is effective yield coefficient that indicates the mass of species (C_3) produced from its parent (C_2), and k_1 , k_2 , and k_3 , are the first-order biodegradation rate constants of the parent and sequential daughter products. Biodegradation is assumed to occur only in the

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

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

$$C_1 = C_{10} e^{r_1 x} \quad (3a)$$

$$C_2 = C_{20} e^{r_2 x} + C_{10} \frac{k_1 y_{21}}{k_1 - k_2} (e^{r_2 x} - e^{r_1 x}) \quad (3b)$$

$$C_3 = C_{30} e^{r_3 x} - \frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_1 - k_3)} (e^{r_3 x} - e^{r_1 x}) + \left(\frac{C_{10} k_1 y_{21} k_2 y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20} k_2 y_{32}}{(k_2 - k_3)} \right) (e^{r_3 x} - e^{r_2 x}) \quad (3c)$$

where for $i=1,2,3$:

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

A generating function for the analytical solution of an n member chain is given in Quezada et al. (2004) as part of a transient, multi-dimensional general solution.

MODEL APPLICATION

The one-dimensional analytical model was applied to estimate TCE, DCE, and VC first-order rate constants for quasi-steady state plume conditions at a site in Palm Bay, FL. The site consists of relatively homogeneous beach sand deposits and is naturally anaerobic. Both redox and hydrogen data indicate that sulfate reduction is the dominant terminal electron accepting (TEAP) process. Groundwater sampling confirmed the presence of the Dehalococcoides group, which are likely responsible for the observed sequential transformation of TCE, DCE and VC via reductive dechlorination to ethene (Burnell et al., 2003).

The main assumptions of this modeling approach are: (1) a uniform ground-water velocity; (2) rate constants are uniform and first-order; (3) steady-state plume conditions; (4) the source release is a continuous point source at a constant concentration; and (5) effects of transverse dispersion are relatively unimportant.

The parameters used for this analytical transport model are summarized in Table 1. Because of uncertainties in the degradation rate, the value of the degradation rate was determined by varying its value and calibrating the analytical model (equation 3) to observed average TCE, DCE, and VC data along the plume centerline during pre-remedial pumping conditions in 1984. For the calculation of plume concentrations along the centerline of the plumes, the source concentration was set equal to average 1984 observed concentrations of TCE, DCE, and VC in monitor well GS-35S located near and downgradient of the source area. The longitudinal dispersivity value used in the model was determined based on the transport scale-dependent relationship given in Xu and Eckstein (1995).

Figure 1 shows the calibrated TCE, DCE, and VC plumes (lines) and observed values versus distance from the source along the centerline of the plumes. The calibrated values for the first-order biodegradation half lives of TCE, DCE, and VC were 0.88 yr^{-1} , 0.82 yr^{-1} , and 0.87 yr^{-1} , respectively. The calculated plumes demonstrate a good match to both the trends

and observed concentration values of each compound.

Table 1. Model Parameter Values.

Solute Transport Model Parameter	Model Parameter Value	Reference
Source Concentration (C)	4.2 mg/L (TCE) 3.4 mg/L (DCE) 1.47 mg/L (VC)	Average observed total TCE, DCE, and VC at near source well GS-35S in 1984 (Geraghty & Miller, 1987)
Average Linear Groundwater Velocity (v)	594 ft/yr	Burnell et al. (2002)
Longitudinal Dispersivity (a_x)	85 ft	Estimated based on observed plume transport scale $L = 668$ m in 25 m zone and $a_x = 0.82(\log_{10}L_s)^{2.958}$ regression fit by Xu and Eckstein (1995)
Effective Yield Coefficient (y_{ij})	$y_{21}=0.74$ $y_{32}=0.64$	Calculated stoichiometrically using TCE-to-DCE and DCE-to-VC reactions.
TCE First-order Biodegradation Rate Constant (k_1) and Half Life	$k_1 = 0.88 \text{ yr}^{-1}$ Half Life = 0.79 yr	Estimated TCE half life range of 0.77 yr to 13 yr (Wiedemeier et al., 1999; Suarez and Rifai, 1999; Aronson and Howard, 1997).
DCE First-order Biodegradation Rate (k_2) and Half Life	$k_2 = 0.82 \text{ yr}^{-1}$ Half Life = 0.85 yr	Estimated cis 1,2 DCE half life range of 0.21 yr to 3.9 yr (Wiedemeier et al., 1999; Suarez and Rifai, 1999; Aronson and Howard, 1997)
VC First-order Biodegradation Rate (k_3) and Half Life	$k_3 = 0.87 \text{ yr}^{-1}$ Half Life = 0.80 yr	Estimated VC half life range of 0.27 yr to 5.8 yr (Wiedemeier et al., 1999; Suarez and Rifai, 1999; Aronson and Howard, 1997).

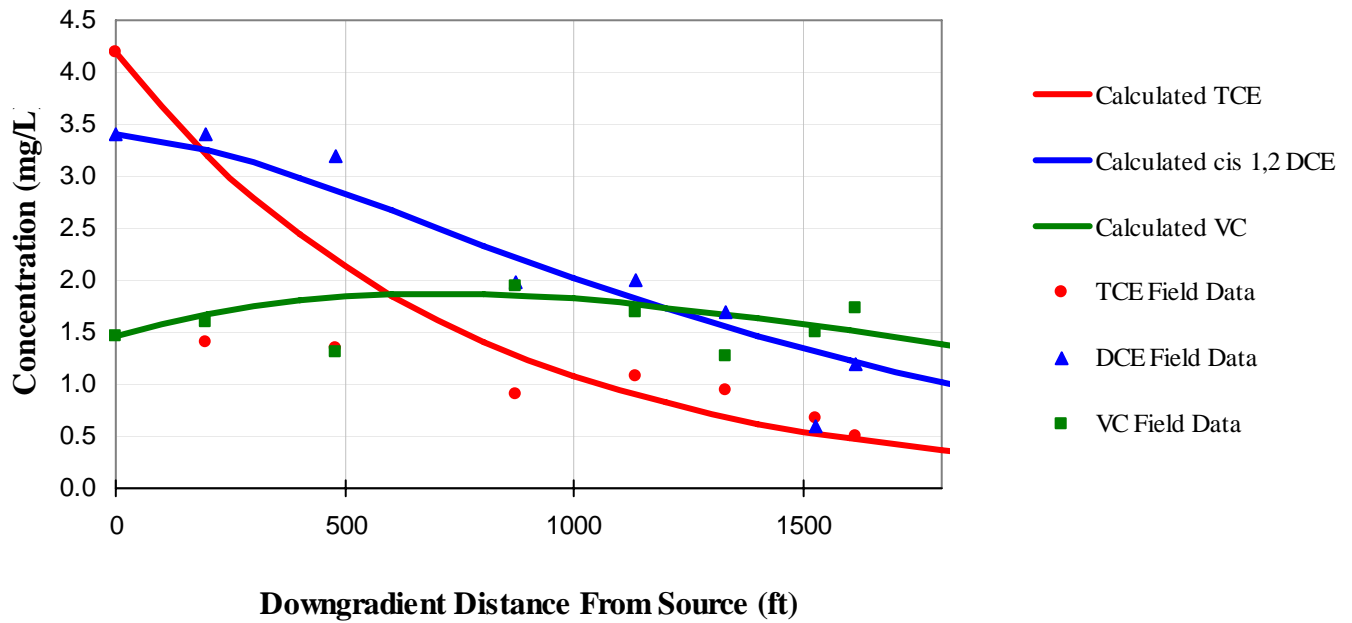


Figure 1. 1-D Multi-Species Analytical Solution and Field Data at Palm Bay, FL Site.

These estimated rate constants were higher than the values of 0.46 yr⁻¹, 0.53 yr⁻¹, and 0.43 yr⁻¹ for TCE, DCE, and VC, respectively, which were estimated using a calibrated three-dimensional numerical model to both transient plume development and dissipation over a 20 year period from 1981 to 2001. In addition to possible changes in the biodegradation rate over time, the higher rate constants in the one-dimensional analytic solution are likely caused by 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. Additional sources of uncertainty in these estimated rate constants may include deviations from the other model assumptions given above, uncertainties in model parameter values, and use of monitor well data that are not screened exactly along the plume centerline. Although a higher dimensional model may reduce the uncertainty, its usefulness depends on the level of accuracy of the source dimensions and both vertical and transverse dispersivity values, which are typically not well defined in the field.

CROSS-OVER AND MAXIMUM POINT METHOD

The locations of intersection and maximum points on the concentration versus distance plots of multiple sequentially degrading species data also can be used to estimate the daughter product rate constants. In this method, the parent rate constant is first estimated by fitting an exponential model to its downgradient concentration trend. The daughter products can then be estimated sequentially using the intersection and maximum match points.

Intersection Points. By setting equations (3a) and (3b) equal to each other and setting $x = x_{12}$, the intersection point (x_{12}) of the species 1 and species 2 curves is given by:

$$C_{10}e^{\tau_1 x_{12}} = C_{20}e^{\tau_2 x_{12}} + C_{10} \frac{y_{21}k_1}{k_1 - k_2} (e^{\tau_2 x_{12}} - e^{\tau_1 x_{12}}) \quad (4a)$$

Because the cross-over point x_{12} is given by field data and all the other parameters including the rate constant of the parent species 1 are known, the rate constant of species 2 can be determined by solving equation (4a) iteratively for k_2 . By setting equations (3b) and (3c) equal to each other and setting $x = x_{23}$, a relationship that includes the intersection point (x_{23}) of the species 2 and species 3 curves is given by:

$$C_{20}e^{\tau_2 x_{23}} + C_{10} \frac{y_{21}k_1}{k_1 - k_2} (e^{\tau_2 x_{23}} - e^{\tau_1 x_{23}}) = C_{30}e^{\tau_3 x_{23}} - \frac{C_{10}k_1 y_{21}k_2 y_{32}}{(k_1 - k_2)(k_1 - k_3)} (e^{\tau_3 x_{23}} - e^{\tau_1 x_{23}}) + \left(\frac{C_{10}k_1 y_{21}k_2 y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20}k_2 y_{32}}{(k_2 - k_3)} \right) (e^{\tau_3 x_{23}} - e^{\tau_2 x_{23}}) \quad (4b)$$

Because all the other parameters are known, the rate constant for species 3 can then be determined. By setting equations (3a) and (3c) equal to each other and setting $x = x_{13}$, a relationship that includes the intersection point (x_{13}) of the species 1 and species 3 curves is given by:

$$C_{10}e^{\tau_1 x_{13}} = C_{30}e^{\tau_3 x_{13}} - \frac{C_{10}k_1 y_{21}k_2 y_{32}}{(k_1 - k_2)(k_1 - k_3)} (e^{\tau_3 x_{13}} - e^{\tau_1 x_{13}}) + \left(\frac{C_{10}k_1 y_{21}k_2 y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20}k_2 y_{32}}{(k_2 - k_3)} \right) (e^{\tau_3 x_{13}} - e^{\tau_2 x_{13}}) \quad (4c)$$

The intersection point (x_{13}) provides an additional check on the estimated species 3 rate constant.

Maximum Points. When a steady-state daughter product plume initially increases and later decreases in concentration levels away from the source, the distance to the maximum concentration can be used to estimate its rate constant. By taking the derivative of equation (3b), setting it equal to zero and simplifying, the downgradient distance (x_{m2}) where the maximum concentration occurs for species 2 is given by:

$$x_{m2} = \frac{1}{(r_2 - r_1)} \ln\left(\frac{(C_{10}k_1y_{21}r_1)}{(r_2C_{10}k_1y_{21} + C_{20}r_2(k_1 - k_2))}\right) \quad (5a)$$

where \ln is the natural log function. Because all the other parameters are known, the rate constant for species 2 can be found iteratively using equation (5a). A similar approach can be used for species 3 by taking the derivative of equation (3c) and setting equal to zero to give:

$$C_{10}e^{r_1x_{m3}} + C_{20}\frac{y_{21}k_1}{k_2 - y_{21}k_1}(r_1e^{r_1x_{m3}} - r_2e^{r_2x_{m3}}) = C_{30}r_3e^{r_3x_{m3}} - \frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_1 - k_3)}(r_3e^{r_3x_{m3}} - r_1e^{r_1x_{m3}}) \\ + \left(\frac{C_{10}k_1y_{21}k_2y_{32}}{(k_1 - k_2)(k_2 - k_3)} + \frac{C_{20}k_2y_{32}}{(k_2 - k_3)}\right)(r_3e^{r_3x_{m3}} - r_2e^{r_2x_{m3}}) \quad (5b)$$

Although the downgradient distance (x_{m3}) where the maximum concentration occurs for species 3 cannot be solved for explicitly, the rate constant for species 3 can still be solved iteratively using equation (5b).

Application of Cross-over and Maximum Point Method. This intersection and maximum point method was also applied to the data at the Palm Bay, FL site in order to estimate the rate constants for TCE, DCE, and VC. The first step in this method is to plot best fit curves for the concentration vs. distance plots of TCE, DCE, and VC in the same graph in order to determine the downgradient distance for all intersection and maximum concentration points. For the parent compound, an exponential curve was fitted to the concentration versus distance data located downgradient from the source zone to give a value of 0.88 yr^{-1} . Because of the effects of both accumulation (from biodegradation of parent) and biodegradation, the sequential biodegradation product curves will be nonlinear even on log scale plots of concentration versus downgradient distance from the source. For the sequential biodegradation products, hand drawn curves were used to match the data trends of the sequential biodegradation products (Figure 2).

The second step in this method is to determine the rate constant of the first daughter product. Because DCE does not have any downgradient maximum points (see Figure 2), the intersection point of the TCE and DCE curves was used to estimate the rate constant for DCE. Using the TCE-DCE intersection point ($x_{12} = 200 \text{ ft}$), TCE rate constant value, and other parameters in Table 1, equation (4b) is solved iteratively to obtain an estimated DCE rate constant value of 0.85 yr^{-1} .

The third step is to estimate the rate constant of the next biodegradation product (VC). In a similar manner, the DCE-VC intersection point ($x_{23} = 600 \text{ ft}$), estimated TCE and DCE rate constants, and other parameters in Table 1 were inserted into equation (4c). This equation is solved iteratively for k_3 to obtain a VC rate constant value of 0.85 yr^{-1} .

Because there is an additional intersection point (x_{13}) for the TCE-VC curves and a VC downgradient maximum point, each of these can be used to refine and check the estimated rate constant values. Using this intersection point ($x_{13} = 1150$ ft), TCE rate constant value, and other parameters in Table 1, equation (4c) is solved iteratively to obtain an estimated VC rate constant value of 0.81 yr^{-1} . Using the VC maximum point, inserting into equation (5b), and solving iteratively with the other parameters, the VC rate constant is estimated to be 0.88 yr^{-1} . The similar values for each of the VC rate constants gives increased confidence that similar analytical solution type curves were used to estimate its rate constant.

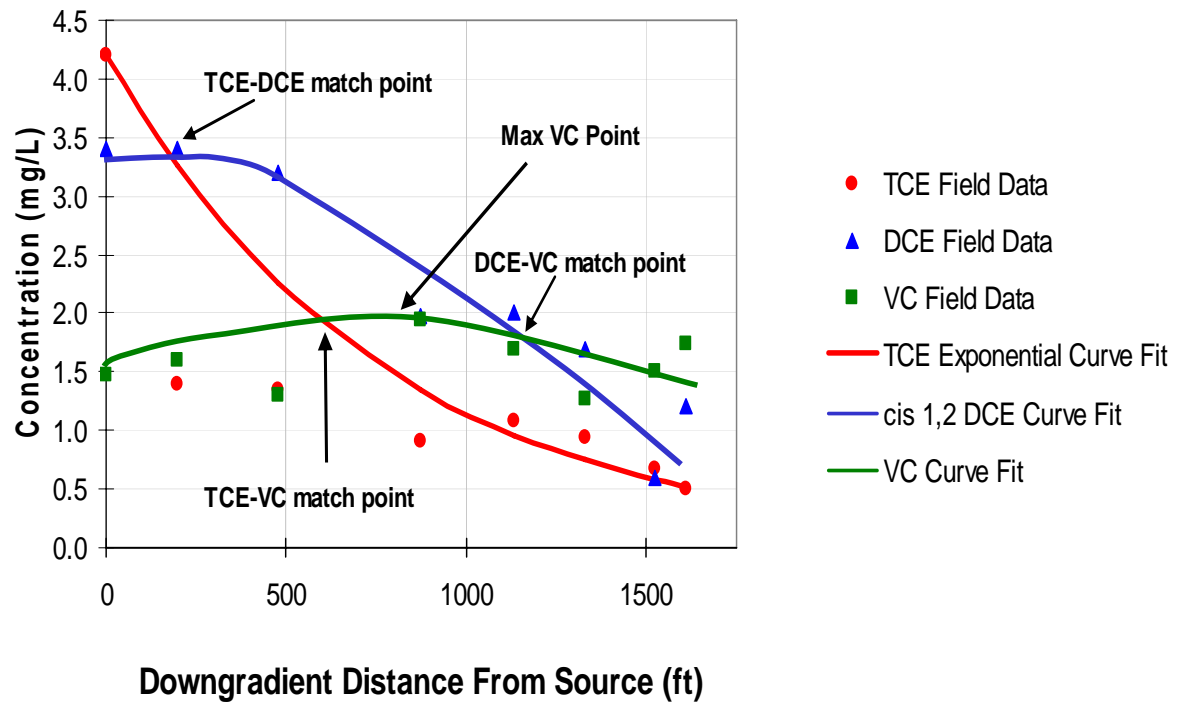


Figure 2. Estimated Curve Fits and Match Point Locations Using Intersection and Maximum Point Method to Determine Rate Constants of TCE, DCE, and VC.

For comparison, the Buscheck and Alcantar solution was applied to TCE and yielded a lower rate constant value of 0.52 yr^{-1} . This lower value was caused by its regression curve underestimating the source concentration, which lead to a lower slope through the data. When the concentration near the source is known, it is recommended to estimate only the slope in the data and to set the y-intercept equal to the source concentration as performed for TCE in Figure 2. Given the nonlinear daughter product curves, the Buscheck and Alcantar method could not be applied. When an apparent linear trend exists at log scale, this method will overestimate the daughter product rate constants because it assumes no accumulation from biodegradation of the parent component.

SUMMARY AND CONCLUSIONS

Because the biodegradation rates of daughter products can be a controlling factor on the cleanup rate at some sites with contaminated groundwater, obtaining reasonably accurate rate constants of daughter products is essential in order to estimate the remedial time frame. The steady-state, one-dimensional, multi-species analytical solution presented in this paper provides an improved method to estimate daughter product biodegradation rate constants in comparison to single-species analytical solute transport modeling approaches (e.g. Buscheck and Alcantar, 1995), which do not include biodegradation product accumulation along the groundwater flow path. This analytical solution can be applied at field sites where the degradation rate constant does not significantly vary spatially. For a site in Palm Bay, FL, the analytical model was calibrated to observed quasi-steady state plume data. Results of this analysis yielded values for the first-order biodegradation rate constants for TCE, DCE, and VC of 0.88 yr^{-1} , 0.82 yr^{-1} , and 0.87 yr^{-1} , respectively. These values are consistent with values for other sites in the U.S. (Aronson and Howard, 1997; Suarez and Rifai, 1999). The similar rate constant values in the parent and daughter products may indicate that a similar group of microbes (*D. Ethenogenes*) is playing a key role in the biodegradation process. Both cross-over points and maximum distance points also can be used to facilitate field data analyses and estimate the daughter product rate constants. Although the one-dimensional multi-species analytical solution overestimates biodegradation rate constants, it is more computationally efficient and uses less parameters than multi-dimensional analytical solutions, which require values for the transverse dispersivity (horizontal and vertical) and source dimensions that are difficult to accurately quantify in the field.

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