

# A chloride transport model for identifying sequential bioreactive systems of chlorinated solvents

Yunwei Sun

Lawrence Livermore National Laboratory, Livermore, California 94551, USA

Xinjian Lu

Department of Management, California State University, East Bay, California 94542-3067, USA

## ABSTRACT

Chlorinated solvents, such as tetrachloroethylene (PCE) and trichloroethylene (TCE), are often biodegraded to produce daughter species under aerobic and anaerobic conditions. During the biodegradation, chloride is produced in groundwater as a byproduct. For this reason, chloride concentrations in contaminant plumes are elevated relative to background concentrations. Because of the neutral chemical behavior of chloride, it can be treated as an indicator to identify the sources of contaminants and to estimate biodegradation rates of chlorinated solvents. However, chloride is produced from multiple reactions in the PCE/TCE reaction chain. The partial differential equation of chloride transport, which is coupled with four reactants, can only be solved numerically. In this paper, we use singular value decomposition (SVD) to decouple the coupled partial differential equations into independent subsystems. Then, we derive the analytical solution of chloride transport and use it, in turn, as a handy tool to quantify biodegradation of chlorinated solvents.

**Keywords:** chloride, convergent reaction, chlorinated solvent, transport, first order.

## INTRODUCTION

Biodegradation of chlorinated solvents is usually demonstrated by the presence of daughter products (Semprini et al., 1990; Wiedemeier et al., 1996). However, daughter products may not be easily measured because they may be consumed by further reactions. Reduction of chlorinated solvent concentrations is caused by both transport (dilution) and bioreactions. To accurately quantify bioreactions

and identify contaminant sources, in addition to chlorinated solvent concentrations, the biodegradation byproduct, chloride, can be used as an indicator. During the biodegradation of chlorinated hydrocarbons, chloride is released into groundwater. For this reason, chloride concentration in contaminant plume areas is elevated relative to background concentrations. Although chloride is not considered as a contaminant, its behavior has been qualitatively used to estimate biodegradation rates (Wiedemeier et al., 1996). Clement et al. (2000) simulated the chloride transport together with tetrachloroethylene (PCE) and trichloroethylene (TCE) sequential biodegradation in their numerical model. The bioreaction rates were calibrated using field chloride concentrations. Because of the lack of screening tools for modeling chloride transport and production, the field-observed data of chloride concentration cannot be easily utilized to interpret biodegradation processes of chlorinated solvents. A handy solution is required not only for verifying numerical codes and validating conceptual models of biodegradation of chlorinated solvents, but also for quantitatively evaluating reaction rates and pathways.

Sun et al. (1999) developed a linear transform for deriving analytical solutions of sequential reactive transport (dashed-line box in Fig. 1). Using the singular value decomposition (SVD), Clement (2001) further derived semi-analytical solutions of transport with convergent reactions. Later, Lu et al. (2003) and Sun et al. (2004) developed closed-forms of SVD transforms for the reaction network of chlorinated solvents. However, the chloride concentration is not considered quantitatively as supplemental information for identifying the reactive transport system of chlorinated solvents.

The purpose of this paper is to present an

analytical solution of chloride transport and production during chlorinated solvent biodegradation. Assuming first-order reactions, all vectors in the reaction matrix can be transformed into components on some coordinate system, on which new vectors are orthogonal to each other. The partial differential equations coupled by the reaction matrix are transformed into a set of independent partial differential equations. Then, the multiple-species transport system with the coupled reaction network (see Fig. 1) is simplified as a group of single-species transport subsystems, for which analytical solutions may be available or easily derived. Finally, the analytical solution of chloride transport and production is derived using an inverse transform.

## MATHEMATICAL MODEL AND SOLUTION METHOD

### Mathematical Model

The mass balance equations governing the transport with the reaction network (Fig. 1) in groundwater are given by

$$\frac{\partial \mathbf{c}}{\partial t} + L(\mathbf{c}) = \mathbf{A}\mathbf{c},$$
$$L(\mathbf{c}) = -D_L \frac{\partial^2}{\partial x^2} - D_T \frac{\partial^2}{\partial y^2} - D_V \frac{\partial^2}{\partial z^2} + v \frac{\partial}{\partial x}, \quad (1)$$

where  $\mathbf{c}$  is the vector of concentrations;  $t$  is time (T);  $x$ ,  $y$ , and  $z$  are the coordinates (L);  $D_L$ ,  $D_T$ , and  $D_V$  are the longitudinal, transverse, and vertical dispersion coefficients ( $L^2 T^{-1}$ ), respectively;  $v$  is the groundwater velocity ( $LT^{-1}$ ); and  $\mathbf{A}$  is the first-order reaction matrix. Specifically,

$$\mathbf{A} = \begin{bmatrix} -k_1 & 0 & 0 & 0 & 0 & 0 \\ y_1 k_1 & -k_2 & 0 & 0 & 0 & 0 \\ 0 & y_2 k_2 & -k_3 & 0 & 0 & 0 \\ 0 & 0 & y_3 k_3 & -k_4 & 0 & 0 \\ 0 & 0 & 0 & y_4 k_4 & -k_5 & 0 \\ \alpha_1 k_1 & \alpha_2 k_2 & \alpha_3 k_3 & \alpha_4 k_4 & 0 & -k_6 \end{bmatrix} \quad (2)$$

The conceptual model can be summarized as the transport of chloride and chlorinated solvents using the following assumptions: (1) homogeneous and isotropic porous medium; (2) the same retardation factor for all species; (3) zero-initial condition (concentrations); (4) sequentially first-order reactions; (5) temporally and spatially constant reaction rates; and (6) sequential biodegradation of chlorinated solvents.

**Solution Method**

Since equation 2 is diagonalizable, it can be decomposed as

$$\mathbf{A} = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1}, \quad (3)$$

where  $\mathbf{\Lambda} = \text{diag}([-k_1 -k_2 \dots -k_6])$  is a diagonal matrix containing the eigenvalues of  $\mathbf{A}$ , and  $\mathbf{S}$  is a matrix that has columns that are linearly independent eigenvectors of  $\mathbf{A}$ , such that

describes the reaction network in Figure 1, where  $k_i, \forall i = 1, 2, \dots, 5$  are the first-order reaction rates;  $y_i, \forall i = 1, \dots, 4$  are yield coefficients from parent reactant to daughter product; and  $\alpha_i, \forall i = 1, \dots, 4$  are yield coefficients from each reaction to chloride. Except for PCE, the reaction term of species  $c_i$  ( $1 < i \leq 5$ ) is combined by the gain from the degradation of its parent species,  $y_{i-1} k_{i-1} c_{i-1}$ , and the loss to the first-order reaction of itself,  $-k_i c_i$ . The reaction term of chloride is composed of four reaction steps

$$\frac{\partial c_6}{\partial t} = \sum_{i=1}^4 [\alpha_i k_i c_i] - k_6 c_6.$$

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ \frac{y_1 k_1}{k_2 - k_1} & 1 & 0 & 0 & 0 & 0 \\ \prod_{i=1}^2 \frac{y_i k_i}{k_{i+1} - k_i} & \frac{y_2 k_2}{k_3 - k_2} & 1 & 0 & 0 & 0 \\ \prod_{i=1}^3 \frac{y_i k_i}{k_{i+1} - k_i} & \prod_{i=2}^3 \frac{y_i k_i}{k_{i+1} - k_i} & \frac{y_3 k_3}{k_4 - k_3} & 1 & 0 & 0 \\ \prod_{i=1}^4 \frac{y_i k_i}{k_{i+1} - k_i} & \prod_{i=2}^4 \frac{y_i k_i}{k_{i+1} - k_i} & \prod_{i=3}^4 \frac{y_i k_i}{k_{i+1} - k_i} & \frac{y_4 k_4}{k_5 - k_4} & 1 & 0 \\ F_1 & F_2 & F_3 & F_4 & F_5 & 1 \end{bmatrix} \quad (4)$$

and  $\mathbf{S}^{-1}$  is the inverse matrix of  $\mathbf{S}$ ,

$$\mathbf{S}^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ \frac{y_1 k_1}{k_1 - k_2} & 1 & 0 & 0 & 0 & 0 \\ \prod_{i=1}^2 \frac{y_i k_i}{k_i - k_3} & \frac{y_2 k_2}{k_2 - k_3} & 1 & 0 & 0 & 0 \\ \prod_{i=1}^3 \frac{y_i k_i}{k_i - k_4} & \prod_{i=2}^3 \frac{y_i k_i}{k_i - k_4} & \frac{y_3 k_3}{k_3 - k_4} & 1 & 0 & 0 \\ \prod_{i=1}^4 \frac{y_i k_i}{k_i - k_5} & \prod_{i=2}^4 \frac{y_i k_i}{k_i - k_5} & \prod_{i=3}^4 \frac{y_i k_i}{k_i - k_5} & \frac{y_4 k_4}{k_4 - k_5} & 1 & 0 \\ G_1 & G_2 & G_3 & G_4 & G_5 & 1 \end{bmatrix}. \quad (5)$$

In  $\mathbf{S}$  and  $\mathbf{S}^{-1}$  matrices,  $F$  and  $G$  are defined as

$$F_\xi = \frac{1}{k_6 - k_\xi} \sum_{i=\xi}^5 \left[ \alpha_i \prod_{l=\xi}^{i-1} \frac{y_l}{k_{l+1} - k_\xi} \prod_{l=\xi}^i k_l \right],$$

and

$$G_\xi = \sum_{i=\xi}^5 \left[ \alpha_i \prod_{l=\xi}^{i-1} y_l \prod_{l=\xi}^i \frac{k_l}{k_l - k_6} \right],$$

where  $\prod_{l=\xi}^i () = 1, \forall i < \xi$ . Substituting equation 3 into equation 1 yields

$$\frac{\partial \mathbf{c}}{\partial t} + L(\mathbf{c}) = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1}\mathbf{c} \quad (6)$$

and multiplying by  $\mathbf{S}^{-1}$ , equation 6 becomes

$$\frac{\partial \mathbf{a}}{\partial t} + L(\mathbf{a}) = \mathbf{\Lambda}\mathbf{a}, \quad \mathbf{a} = \mathbf{S}^{-1}\mathbf{c}. \quad (7)$$

Each partial differential equation in expression 7 is independent of the other partial differential equations. Analytical solutions for equation 7, in terms of  $a_i \in \mathbf{a}$ , are available for a variety of boundary conditions. Finally, the solution of  $\mathbf{c}$  can be derived as  $\mathbf{c} = \mathbf{S}\mathbf{a}$ . To avoid the singularity in equations 4 and 5 when two species have the same reaction rates (say  $k_i - k_j = 0$ ), a negligible small value of  $10^{-3}k_i$  is used instead of  $k_i - k_j$ .

**SOLUTIONS AND APPLICATION**

Although we are not limiting ourselves to a one-dimensional description, in order to simplify the demonstration of the solution implementation, we start with a one-dimensional case. The analytical solution of a single species transport with first-order decay in a semi-infinite column (Bear, 1979) is used as a basic function in the transformed domain,

$$a_i = a_i^o f_i, \quad \mathbf{a}^o = \mathbf{S}^{-1}\mathbf{c}^o, \quad (8)$$

where

$$f_i(x, t) = \frac{1}{2} \exp\left(\frac{vx}{2D}\right) [\exp(-\beta_i x) \text{erfc } \gamma_i^- + \exp(\beta_i x) \text{erfc } \gamma_i^+]$$

$$\beta_i = \left( \frac{v^2}{4D^2} + \frac{k_i}{D} \right)^{1/2},$$

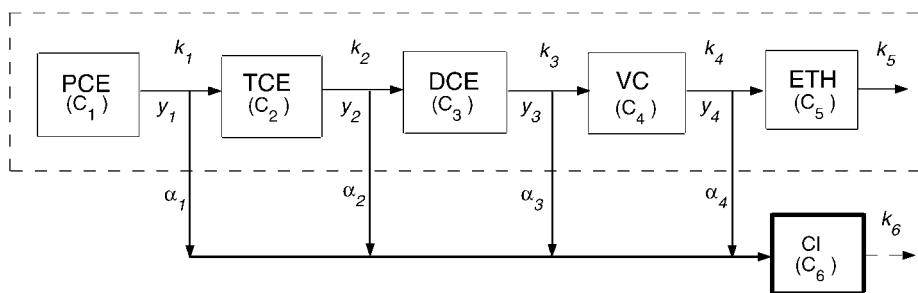
$$\begin{aligned} \text{erfc}(\eta) &= 1 - \text{erf}(\eta) \\ &= \frac{2}{\sqrt{\pi}} \int_{\eta}^{\infty} \exp(-\tau^2) d\tau \end{aligned}$$

$$\gamma_i^- = \frac{x - (v + 4k_i D)^{1/2} t}{2(Dt)^{1/2}},$$

$$\gamma_i^+ = \frac{x + (v + 4k_i D)^{1/2} t}{2(Dt)^{1/2}}. \quad (9)$$

TABLE 1. SYSTEM PARAMETERS

Parameter	Value	Parameter	Value
$v$	0.1 m d <sup>-1</sup>	$D_L$	0.4 m <sup>2</sup> d <sup>-1</sup>
$k_1$	0.075 d <sup>-1</sup>	$k_2$	0.050 d <sup>-1</sup>
$k_3$	0.030 d <sup>-1</sup>	$k_4$	0.020 d <sup>-1</sup>
$k_5$	0.010 d <sup>-1</sup>		
$y_1$	0.79	$y_2$	0.74
$y_3$	0.64	$y_4$	0.45
$\alpha_1$	0.2195	$\alpha_2$	0.2769
$\alpha_3$	0.3750	$\alpha_4$	0.5806



Function  $f_i$  reaches steady state at a large time,  $t$ ,

$$f_i(x, \infty) = \begin{cases} \exp\left[\left\{\frac{v}{2D} - \left(\frac{v^2}{4D^2} + \frac{k_i}{D}\right)^{1/2}\right\}x\right] & \forall k_i \neq 0 \\ 1.0 & \forall k_i = 0. \end{cases} \quad (10)$$

The solution of the reactive transport system in the real concentration domain is expressed as

$$c_i = \sum_{j=1}^6 (S_{i,j} a_j) = \sum_{j=1}^6 \left[ S_{i,j} f_j \sum_{l=1}^6 (S_{l,j}^{-1} c_l^0) \right]. \quad (11)$$

In equation 9,  $f_i(x,t)$  (Bear, 1979) represents the basic solution of a single-species transport in one dimension. Similarly, two- or three-dimensional solutions of chloride transport and production can be obtained when two-dimensional basic solutions,  $f_i(x,y,t)$ , for single-species transport with a first-order reaction (e.g., Wilson and Miller, 1978) or three-dimensional basic solutions ( $f_i(x,y,z,t)$ ; e.g., Domenico, 1987) are used.

**Comparison with Semi-Analytical and Numerical Solutions**

Here we compare, the analytical solution derived in this paper with a semi-analytical solution and a numerical solution for the first-order reactive transport in a semi-infinite homogeneous column. The  $S$  and  $S^{-1}$  matrices in the semi-analytical solution can be calculated numerically using the *eigs* function in MATLAB (MathWorks, 2000). Physical and reaction parameters for this problem are given in Table 1. Initial concentrations of all species are assumed to be zero. Constant concentration boundary conditions with  $c_i^0 = 1.0$  and  $c_i^0 = 0.0, i \geq 2$  are assumed at the inlet boundary. Both the analytical and semi-analytical solutions are computed for a column of 40 m

Figure 1. Tetrachloroethylene (PCE) and trichloroethylene (TCE) degradation pathway, where  $k_i, \forall i = 1, 2, \dots, 5$  are the first-order reaction rates;  $y_i, \forall i = 1, \dots, 4$  are yield coefficients from parent reactant to daughter product; and  $\alpha_i, \forall i = 1, \dots, 4$  are yield coefficients from each reaction to chloride. DCE, VC, and ETH represent dichloroethylene, vinyl chloride, and ethylene, respectively.

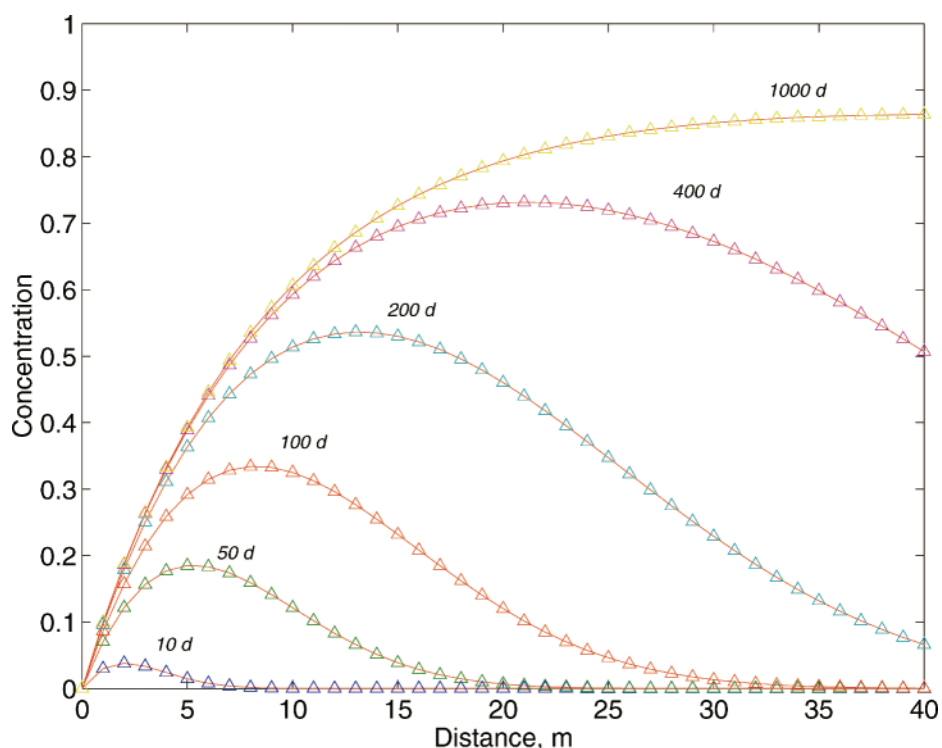


Figure 2. Concentration profiles of chloride at six different times using the transport parameters and reaction rates given in Table 1. The solid lines and triangles represent analytical solutions and semi-analytical results, respectively. Concentrations are normalized by the tetrachloroethylene (PCE) boundary concentration.

discretized using 40 evenly spaced elements. Figure 2 shows the comparison of the analytical and semi-analytical solutions for six given times.

Using the same system parameters (Table 1), the analytical solution is compared against the RT3D solution (Clement et al., 1998). For the purpose of comparison, all species concentrations are computed at 200 d. Since species 1–5 are not coupled with chloride concentration, the solution for the first five

species concentrations is identical to that of Sun et al. (1999). The comparison shown in Figure 3 indicates a good agreement between analytical and numerical solutions.

**Peak Chloride Concentrations**

One advantage of analytical solutions is that the derivatives of concentrations can be easily derived. The compact information of plume characteristics, such as peak concentration and

its location, can be obtained using relatively simple manipulation. Solving  $dc_o/dt = 0$ , the peak concentration, as well as its location, is expressed as a function of time, as shown in Figure 4. For the given physical and reaction parameters (Table 1) and constant boundary condition  $c_1^i = 1.0$  and  $c_i^e = 0.0, i \geq 2$ , the peak concentration reaches steady state. However, the location of the peak concentration never gets to steady state. This indicates that a long-term contaminant source can elevate chloride concentration at a large distance downstream from the source.

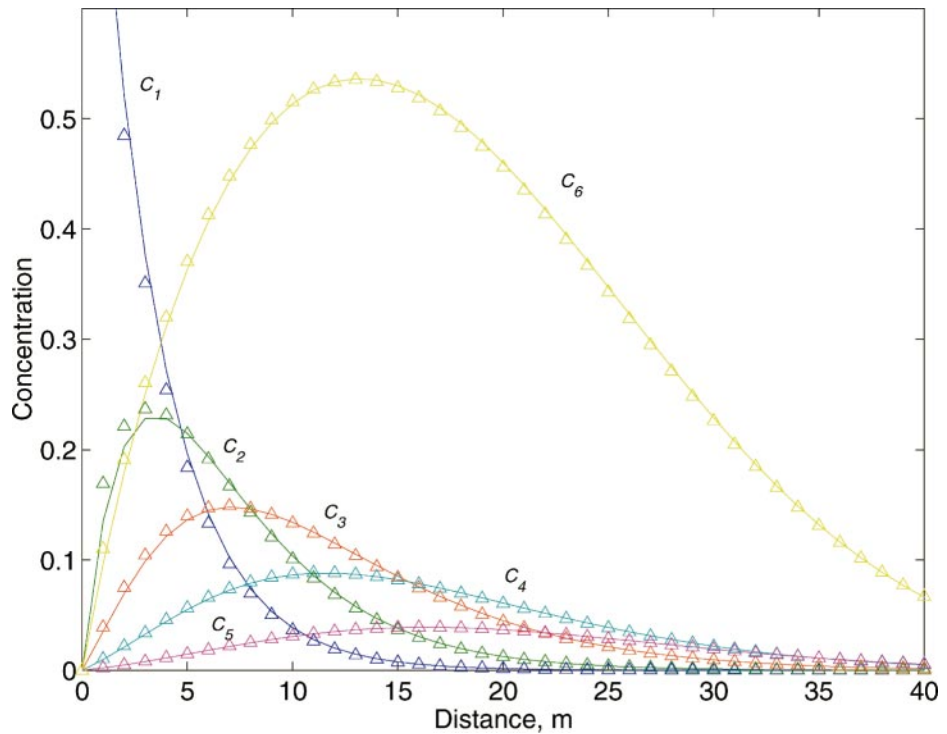
**Chloride Transport and Production in Two Dimensions**

To demonstrate the application of the solution for multidimensional problems, Wilson and Miller's (1978) solution is used here to replace the basic solution given in equation 9. The reactive transport problem was simulated in a confined aquifer with  $x \times y$  dimensions of  $500 \text{ m} \times 310 \text{ m}$ . A continuous source at  $10 \text{ m}^3/\text{d}$  and  $1.0 \text{ mg/L}$  source concentration of the first species was assumed at (155, 155). The same reaction parameters given in Table 1 were used, and transport parameters were assumed as  $v = 0.4 \text{ m/d}$ ,  $D_L = 4.0$ , and  $D_T = 1.2 \text{ m}^2 \text{ d}^{-1}$ . The contours of chloride concentrations predicted by the analytical solution are shown in Figure 5.

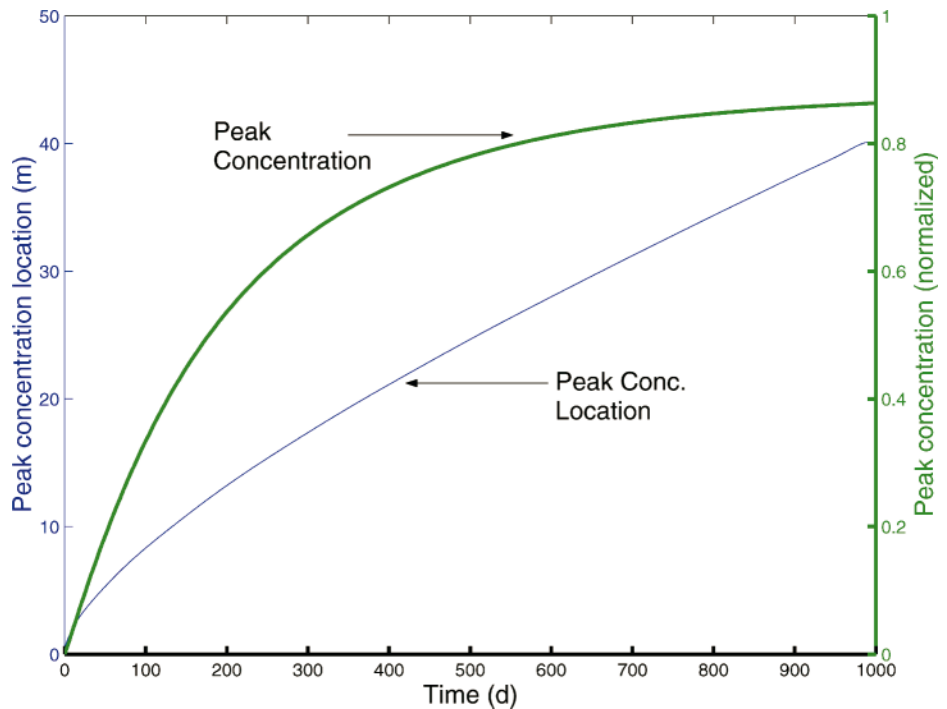
**CONCLUSIONS AND DISCUSSION**

We have presented an analytical solution of chloride transport and production during the biodegradation of chlorinated solvents. This solution quantitatively provides additional information for demonstrating biodegradation and for distinguishing bioreactions from dilution. By using singular value decomposition analytically, the closed form of  $\mathbf{S}$  and  $\mathbf{S}^-$  matrices is provided for the sequential first-order reactions. The solutions are compared against semi-analytical and numerical solutions. Under various initial and boundary conditions, previously published analytical solutions of a single-species transport with the first-order decay can be used as the basic solution,  $f_b$ , to construct the solution of chloride transport.

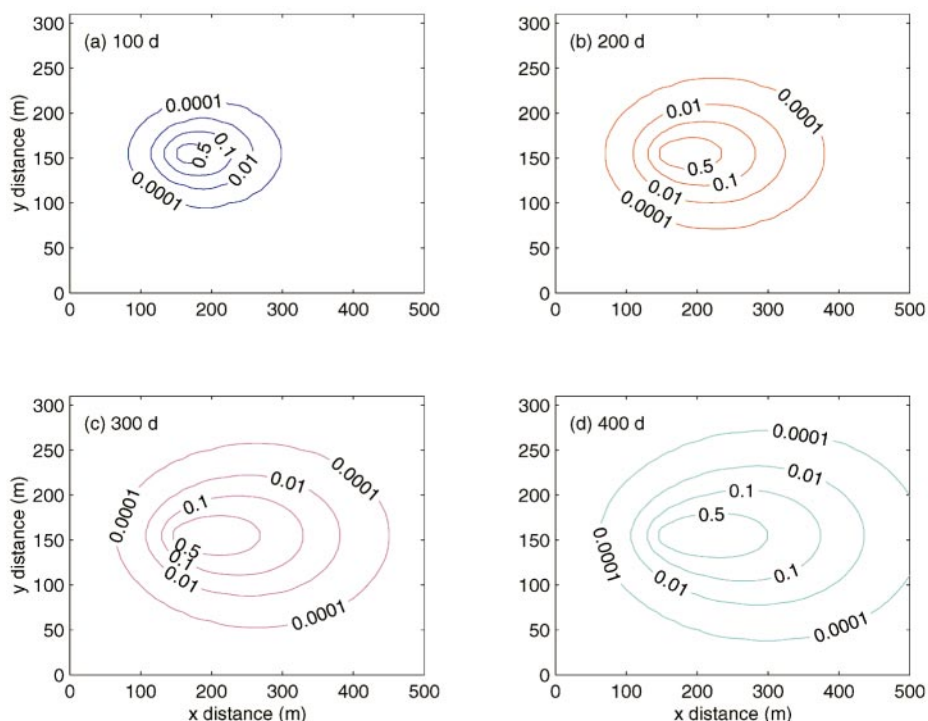
The solution developed in this paper can be implemented and used as a screen tool for modeling chloride production and transport during the biodegradation of chlorinated solvents. However, the conceptual model is limited to the same retardation factor for all species and zero-initial concentration condition. In reality, background chloride concentrations may need numerical computer codes, such as



**Figure 3. Concentration profiles of six species. The solid lines and triangles represent analytical solutions and RT3D (Clement et al., 1998) results, respectively, and  $\Delta x = 1.0 \text{ m}$  and  $\Delta t = 1.0 \text{ d}$  were used in the numerical simulation. Concentrations are normalized by the tetrachloroethylene (PCE) boundary concentration.**



**Figure 4. Peak chloride concentration and its location as a function of time.**



**Figure 5. Contour plots of chloride concentration at different times. Reaction parameters in Table 1 were used, and transport parameters are defined as  $v = 0.4$  m/d,  $D_L = 4.0$ , and  $D_T = 1.2$  m<sup>2</sup> d<sup>-1</sup>. Concentrations are normalized by the tetrachloroethylene (PCE) boundary concentration.**

RT3D, for simulating biodegradation and reactive transport. The use of numerical and analytical solutions should be viewed as mutually complementary. Because of the relative ease of use and speed in providing insight into biodegradation processes, this analytical solution can be used to estimate biodegradation and natural attenuation at the screening and planning stages.

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