Transport in Porous Media **37:** 327–346, 1999.

A Decomposition Method for Solving Coupled Multi-Species Reactive Transport Problems

YUNWEI SUN and T. PRABHAKAR CLEMENT
Pacific Northwest National Laboratory, Richland, WA 99352, U.S.A.

(Received: 6 July 1998)

Abstract. Concerns over the problems associated with mixed waste groundwater contamination have created a need for more complex models that can represent reactive contaminant fate and transport in the subsurface. In the literature, partial differential equations describing solute transport in porous media are solved either for a single reactive species in one, two or three dimensions, or for a limited number of reactive species in one dimension. Those solutions are constrained by many simplifying assumptions. Often, it is desirable to simulate transport in two or three dimensions for a more practical system that might have multiple reactive species. This paper presents a decomposition method to solve the partial differential equations of multi-dimensional, multi-species transport problems that are coupled by linear reactions. A matrix method is suggested as a tool for describing the reaction network. In this way, the level of complexity required to solve the multi-species reactive transport problem is significantly reduced.

Key words: analytical solution, partial differential equation, reactive transport, multi-species, decomposition.

1. Introduction

Analytical models are powerful tools for expressing enormous amounts of information within a compact mathematical framework. However, analytical solutions to several transport problems of practical interest may not be feasible because of the complexities associated with nonlinear boundary conditions and inhomogeneous aquifer properties. Ogata (1958) and Bear (1960) were the first to derive analytical solutions to contaminant transport equations for one-dimensional problems. Van Genuchten and Alves (1982) and Toride *et al.* (1995) compiled various analytical solutions available for solving one-dimensional solute transport equations. Beljin (1991) reviewed analytical solute transport models for three-dimensional groundwater systems. However, in all of the above references the fundamental partial differential equations represent the transport of either a nonreactive species or a single reactive species.

In recent years, increased interest in the fate and transport of reactive contaminants in the subsurface environment has created a need for mathematical tools to solve multi-species transport problems. For example, chlorinated solvent contaminants such as PCE (tetrachloroethylene) and TCE (trichloroethylene) are known to degrade and produce daughter products such as DCE (dichloroethylene) and VC (vinyl chloride). One of the most challenging aspects of managing chlorinated solvent contaminants is the fact that the degradation daughter product VC is more toxic than the parent contaminant. Simple analytical models that predict the transport of single reactive species cannot be used to describe the formation of daughter products and quantify their adverse effects.

In literature, analytical solutions to multi-species reactive transport equations are available only for one-dimensional problems with a limited number of species. Van Genuchten (1985) used the Laplace transform method to derive one-dimensional analytical solution to a four-species transport problem, which is coupled by first-order reactions. Lunn *et al.* (1996) used the Fourier transform method to derive analytical solutions to three-species transport equations that are coupled with first-order reactions. Both of the analytical solutions are limited to sequential first-order reactions.

More recently, Sun *et al.* (1997, 1998) derived an analytical solution strategy that can be used to solve any number of reactive species that are coupled by sequential, first-order reactions. However, in real problems, the species may not necessarily be coupled in a sequential pattern. In this manuscript, Sun *et al.*'s (1997) work is extended to develop a more general matrix method to solve any number of reactive species that are coupled by a complex reaction network. Using the matrix method, a general transformation methodology is developed to solve the system of multiple partial differential equations (PDEs), which are coupled by sequential or parallel first-order reactions. The coupled PDEs are decomposed into multiple independent subsystems corresponding to each species in the reaction network. In the decomposed domain, each subsystem becomes identical to a single-species first-order reactive transport equation. Therefore, previously published analytical solutions to single-species first-order reactive problems can be directly utilized to solve the coupled reactive transport problem.

2. Governing Equations and Solution Strategy

The general mass balance equation for predicting the fate and transport of a chemical species in a system of multiple reacting contaminants that are coupled by first-order reactions can be written as

$$\frac{\partial c_i}{\partial t} = L(c_i) + y_i k_p c_p - k_i c_i, \quad \forall i = 1, 2, \cdots, n, \tag{1}$$

where c_i and c_p [ML^{-3}] are the concentrations of species i and species p; p represents parent-species index of species i; y_i is the stoichiometric yield factor for the reaction of species p to produce species i; k_p [T^{-1}] represents the contaminant destruction rate for the species p which is the parent-species of i; k_i is the contaminant destruction rate for ith species, n is the total number of species; and L is the advection–dispersion operator:

$$L(c_i) = -\nabla \cdot (c_i \mathbf{v} - \mathbf{D}\nabla c_i), \tag{2}$$

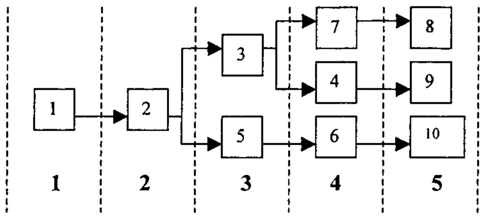


Figure 1. An example of a reaction family tree.

where **D** $[L^2T^{-1}]$ is the tensor of hydrodynamic dispersion coefficient and **v** $[LT^{-1}]$ is the vector of contaminant transport velocity. The value of y_i is assumed to be zero when species i is the very first species.

As an example problem, let us consider a complex reaction network where the relationship among multiple species can be described by a *reaction family tree* shown in Figure 1. It should be noted that the reactions considered in this manuscript assume presence of a limiting reactant, at every reaction step (or generation), that controls the overall reaction rate of the reaction step. Concentrations of all other (nonlimiting) reactants involved in the reactions are assumed to be in excess. Therefore, the kinetics of each reaction step can be approximated using a first-order reaction model.

In the example problem shown in Figure 1, the very first species, species 1, in the first generation reacts to produce species 2 in the second generation; and species 2 reacts to produce species 3 and species 5 in the third generation. There are ten species and five generations in this example problem. Note that each species has a unique parent, but has one or more daughter species. Representing reactions in this type of network format is designated in this manuscript as the *reaction family tree*. Using the information in the family tree, every species in the network can be tracked back to its very first ancestor. The concentration of every species depends on the concentrations of its ancestor species. Sun *et al.* (1998) manually decomposed a relatively simple reaction system, similar to this one, into several sequential reaction chains and successively derived analytical solutions to the corresponding PDEs. In this work, Sun *et al.*'s (1997) method is extended to provide a general-purpose matrix transformation method to solve reactive transport systems with any number of species in multiple dimensions with nonuniform initial and boundary conditions. This matrix transform method can be used to systematically derive analytical solutions for all the reacting species simultaneously, without any manual decomposition.

2.1. DEFINITION OF SPECIES–SPECIES (F) MATRIX

To numerically represent the reaction network in Figure 1, we define a species–species (or family) matrix as

$$F(j,i) = \begin{cases} g_j & \text{if species } j \text{ is an ancestor of species } i, \\ g_j & \text{if } i = j, \\ 0 & \text{if species } j \text{ is not an ancestor of species } i, \end{cases} \tag{3}$$

where g_j is the generation number of species j. For the reactive system shown in Figure 1, the **F** matrix can be expressed as

Species	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$	$j = 6$	$j = 7$	$j = 8$	$j = 9$	$j = 10$
$i = 1$	1	0	0	0	0	0	0	0	0	0
$i = 2$	1	2	0	0	0	0	0	0	0	0
$i = 3$	1	2	3	0	0	0	0	0	0	0
$i = 4$	1	2	3	4	0	0	0	0	0	0
$i = 5$	1	2	0	0	3	0	0	0	0	0
$i = 6$	1	2	0	0	3	4	0	0	0	0
$i = 7$	1	2	3	0	0	0	4	0	0	0
$i = 8$	1	2	3	0	0	0	**4**	5	0	0
$i = 9$	1	2	3	4	0	0	0	0	5	0
$i = 10$	1	2	0	0	3	4	0	0	0	5

The species–species matrix (**F**-matrix) provides a compact way to store the information about the connections between the species, and the generation numbers of each species in the network. Each nonzero entry in the **F** matrix represents a generation number, and location of the entry (i.e. the row and column numbers) represents the parent–daughter relationship. For example, the boldface entry '4' in row 8 and column 7 represents that species 7 is the parent of species 8 and is in the 4th generation.

2.2. DEFINITION OF SPECIES-GENERATION (G) MATRIX

From the **F**-matrix, the information of all ancestor species in all generations can be extracted and assembled into a species–generation matrix (**G**-matrix). The elements of **G**-matrix are defined as

$$G(j, i) = \begin{cases} l, & \forall F(l, i) = j, \quad l = 1, 2, \cdots n, \\ 0, & \forall F(l, i) \neq j, \quad l = 1, 2, \cdots n, \end{cases} \tag{4}$$

where i denotes species index, j is generation index in **G** matrix, and l is a dummy index. The generation matrix for the example problem is

Species	Generation				
	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$
$i = 1$	1	0	0	0	0
$i = 2$	1	2	0	0	0
$i = 3$	1	2	3	0	0
$i = 4$	1	2	3	4	0
$i = 5$	1	2	5	0	0
$i = 6$	1	2	5	6	0
$i = 7$	1	2	3	7	0
$i = 8$	1	2	3	7	8
$i = 9$	1	2	3	4	9
$i = 10$	1	2	5	6	**10**

Each non-zero entry in the **G**-matrix represents a species number. Each row in **G** matrix provides species numbers of all ancestor species and identifies their generation number. For example, row 10 provides information on species10. As we go from right to left in row 10, we can backward track species 6, 5, 2, 1 (also see Figure 1) as ancestors of species 10, and they are, respectively, present in generations 4, 3, 2, and 1 (column locations).

Although species number in a family tree can be assigned arbitrarily, different numbering scheme will produce different sparse matrix structure, which in turn would affect the computational efficiency. The most efficient (in terms of storage and structure) **F** and **G** matrices can be produced if the species are numbered systematically from the very first generation to later generations.

2.3. REACTION RATE AND STOICHIOMETRIC YIELD VECTORS

Assuming first-order kinetics, the reactive fate-and-transport of various contaminants involved in the reaction network, represented by Figure 1, can be predicted by solving the following system of partial differential equations:

$$\begin{aligned}
&\frac{\partial c_1}{\partial t} = L(c_1) - k_1 c_1, &&\frac{\partial c_2}{\partial t} = L(c_2) - k_2 c_2 + y_2 k_1 c_1,\\
&\frac{\partial c_3}{\partial t} = L(c_3) - k_3 c_3 + y_3 k_2 c_2, &&\frac{\partial c_4}{\partial t} = L(c_4) - k_4 c_4 + y_4 k_3 c_3,\\
&\frac{\partial c_5}{\partial t} = L(c_5) - k_5 c_5 + y_5 k_2 c_2, &&\frac{\partial c_6}{\partial t} = L(c_6) - k_6 c_6 + y_6 k_5 c_5,\\
&\frac{\partial c_7}{\partial t} = L(c_7) - k_7 c_7 + y_7 k_3 c_3, &&\frac{\partial c_8}{\partial t} = L(c_8) - k_8 c_8 + y_8 k_7 c_7,\\
&\frac{\partial c_9}{\partial t} = L(c_9) - k_9 c_9 + y_9 k_4 c_4, &&\frac{\partial c_{10}}{\partial t} = L(c_{10}) - k_{10} c_{10} + y_{10} k_6 c_6.
\end{aligned} \tag{5}$$

Note that each transport equation has its own first-order reaction rate and a stoichiometric yield factor. The stoichiometric yield factor represents production of a species from its parent species. For example, if c_1 is used to represent PCE and c_2 is used to represent TCE, then y_2 would represent the amount of TCE (in grams) produced per gram of PCE destroyed, which can be estimated from the reaction stoichiometry as 0.79.

To store the values of reaction rates and yield values, a reaction rate vector (designated as the **k**-vector) and a yield vector (designated as the **y**-vector) are used. For the example problem, the vectors can be defined as

Species	1	2	3	4	5	6	7	8	9	10
k	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	k_9	k_{10}
y	0	y_2	y_3	y_4	y_5	y_6	y_7	y_8	y_9	y_{10}

These two vectors are used to define all the reaction properties of the coupled reactive transport system.

2.4. LINEAR TRANSFORMATION AND SYSTEM DECOMPOSITION

Sun *et al.* (1998) provided the following transformation format that can be used for uncoupling a sequential system of partial differential equations that are coupled by first-order reactions:

$$a_i = c_i + \sum_{j=1}^{i-1} \left[\prod_{l=j}^{i-1} \frac{y_l k_l}{k_l - k_i} \right] c_j, \quad \forall i = 2, \cdots, n. \tag{6}$$

The format can be used to transform a set of coupled PDEs, similar to (5), into a set of independent PDEs. An application of Sun *et al.*'s (1998) method for a simple two-species problem is given in Appendix A. In this work, we use matrix notations to generalize the transformation methodology in a linear algebraic format

$$\mathbf{a} = \mathbf{P}\mathbf{c}, \tag{7}$$

where **a** is the vector of auxiliary concentrations in the transformed domain, **c** is the vector of real concentrations, and **P** is the system transforming matrix. The matrix **P** is used to decompose the set of coupled partial differential equations (5) into a set of independent partial differential equations. The elements of **P** are calculated using the elements of **F** and **G** matrices as

$$P(j,i) = \begin{cases} 0, & \forall F(j,i) = 0, \\ \displaystyle\prod_{l=F(j,i)}^{F(i,i)-1} \frac{y_{G(l+1,i)} k_{G(l,i)}}{(k_{G(l,i)} - k_i)}, & \forall F(j,i) \neq 0 \quad \text{and } j \neq i, \\ 1, & \forall j = i, \end{cases} \tag{8}$$

where **F** and **G** denote species–species and species–generation matrices, respectively, as defined in (3) and (4). For example, for $i = 10$, $j = 5$, $F(i,i) = 5$, $F(j,i) = 3$, $G(F(j,i),i) = 5$, $G(F(j,i)+1,i) = 6$,

$$P(5,10) = \prod_{l=3}^{5-1} \frac{y_{G(l+1,10)} k_{G(l,10)}}{(k_{G(l,10)} - k_{10})} = \frac{y_6 y_{10} k_5 k_6}{(k_5 - k_{10})(k_6 - k_{10})} \tag{9}$$

and for $i = 10$, $j = 2$, $F(i,i) = 5$, $F(j,i) = 2$, $G(F(j,i),i) = 2$, $G(F(j,i)+1,i) = 5$, $G(F(j,i)+2,i) = 6$,

$$P(2,10) = \prod_{l=2}^{5-1} \frac{y_{G(l+1,10)} k_{G(l,10)}}{(k_{G(l,10)} - k_{10})} = \frac{y_5 y_6 y_{10} k_2 k_5 k_6}{(k_2 - k_{10})(k_5 - k_{10})(k_6 - k_{10})}. \tag{10}$$

Note that the matrix **P** is simply a generalized representation of the transformation format represented by (6).

For the example problem, we define the following **k** and **y** vectors to store the values of reaction rates (day^{-1}) and stoichiometric yields

$$\begin{aligned} \mathbf{k} &= [0.03\ 0.02\ 0.015\ 0.01\ 0.011\ 0.006\ 0.002\ 0.0015\ 0.003\ 0.002]^{\mathrm{T}}, \\ \mathbf{y} &= [0.0\ 0.79\ 0.50\ 0.45\ 0.74\ 0.64\ 0.37\ 0.51\ 0.51\ 0.45]^{\mathrm{T}}. \end{aligned} \tag{11}$$

Using the above reaction parameters, the system transformation matrix **P** for the example problem can be assembled and the system transformation can be expressed in a linear format as

$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \\ a_6 \\ a_7 \\ a_8 \\ a_9 \\ a_{10} \end{bmatrix} = \begin{bmatrix} 1.000 & .000 & .000 & .000 & .000 & .000 & .000 & .000 & .000 & .000 \\ 2.370 & 1.000 & .000 & .000 & .000 & .000 & .000 & .000 & .000 & .000 \\ 3.160 & 2.000 & 1.000 & .000 & .000 & .000 & .000 & .000 & .000 & .000 \\ 1.600 & 1.350 & 1.350 & 1.000 & .000 & .000 & .000 & .000 & .000 & .000 \\ 2.051 & 1.644 & .000 & .000 & 1.000 & .000 & .000 & .000 & .000 & .000 \\ 1.470 & 1.488 & .000 & .000 & 1.408 & 1.000 & .000 & .000 & .000 & .000 \\ .201 & .237 & .427 & .000 & .000 & .000 & 1.000 & .000 & .000 & .000 \\ .377 & .453 & .839 & .000 & .000 & .000 & 2.040 & 1.000 & .000 & .000 \\ .212 & .241 & .410 & .729 & .000 & .000 & .000 & .000 & 1.000 & .000 \\ .367 & .434 & .000 & .000 & .528 & .675 & .000 & .000 & .000 & 1.000 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \\ c_7 \\ c_8 \\ c_9 \\ c_{10} \end{bmatrix} \tag{12}$$

Using the above system transformation equation, the set of PDEs (5), which are coupled in the 'c' domain, can be written as the following set of independent transport equations in the 'a' domain (see Appendices A and B for detailed derivations):

$$\begin{aligned} \frac{\partial a_1}{\partial t} &= L(a_1) - k_1 a_1, & \frac{\partial a_2}{\partial t} &= L(a_2) - k_2 a_2, \\ \frac{\partial a_3}{\partial t} &= L(a_3) - k_3 a_3, & \frac{\partial a_4}{\partial t} &= L(a_4) - k_4 a_4, \\ \frac{\partial a_5}{\partial t} &= L(a_5) - k_5 a_5, & \frac{\partial a_6}{\partial t} &= L(a_6) - k_6 a_6, \\ \frac{\partial a_7}{\partial t} &= L(a_7) - k_7 a_7, & \frac{\partial a_8}{\partial t} &= L(a_8) - k_8 a_8, \\ \frac{\partial a_9}{\partial t} &= L(a_9) - k_9 a_9, & \frac{\partial a_{10}}{\partial t} &= L(a_{10}) - k_{10} a_{10}. \end{aligned} \tag{13}$$

Note that Equation (13) has a general form:

$$\frac{\partial a_i}{\partial t} = L(a_i) - k_i a_i, \quad \forall i = 1, 2, \cdots, n. \tag{14}$$

Therefore, in the transformed domain all the PDEs can be solved independently using any single-species reactive transport solution. However, it is important to note that the initial and boundary conditions should also be transformed using (7) before computing the concentration profiles in the 'a' domain. After solving the problem in the 'a' domain, the concentrations can be converted back to the real 'c' domain using the inverse transformation:

$$\mathbf{c} = \mathbf{P}^{-1}\mathbf{a}. \tag{15}$$

If a systematic species-numbering scheme is used, the **P** matrix will be in a triangular form and standard backward substitution procedures can be used to perform the matrix inversion.

3. Applications

3.1. ONE-DIMENSIONAL PROBLEM

To illustrate the solution procedure, the reactive transport problem described by Equation (5) is first solved in one dimension. Analytical solutions were computed for a column of length 500 ft discretized using 50 evenly spaced nodal points. The one-dimensional analytical solution to single-species transport given in Bear (1979) (see Appendix C) was used as the base solution for analytically solving the problem. A uniform groundwater transport velocity of 0.5 ft/day was assumed. Other transport parameters used are summarized in Table I. Initial conditions for all the species were assumed to be zero. The boundary conditions assumed are similar to those used in deriving the basic analytical solution (Bear, 1979).

In addition, for comparison purposes, the problem was also solved by the numerical code RT3D (Clement *et al.*, 1998). Boundary conditions, similar to those used in the analytical solution, were also simulated in the numerical model by setting appropriate concentrations at the boundary nodes. A constant concentration condition (first species at 100 mg/L and 0 mg/L for all other species) was set at the inlet node and a free boundary condition was set at the exit node. A constant time step size of 10 days was used.

The analytical and numerical results for the one-dimensional example are compared in Figure 2. In the figure, for illustration purposes, we only present the spatial concentration distribution of three species (species 1, 5 and 10). The results shown in the figure indicate good agreement between the solutions.

3.2. TWO-DIMENSIONAL PROBLEM

In order to verify the application of the solution strategy for multi-dimensional problems, Equation (5) was solved in a two-dimensional rectangular domain. An analytical solution developed by Wilson and Miller's (1978) (see Appendix C) was used as the base solution to solve the two-dimensional problem. The analytical solution was implemented to predict contaminant concentration values over an evenly spaced (10 ft $\times$ 10 ft) rectangular grid of 50 columns and 31 rows. The groundwater transport velocity was assumed to be 0.5 ft/day. Other transport parameters assumed are given in Table I. Initial conditions for all the species were assumed to be zero.

Table I. Transport parameters

Parameter	Symbol	Assumed value
Effective porosity	ϕ	0.2
Longitudinal dispersivity	α_x	10.0 ft
Horizontal transverse dispersivity	α_y	3.0 ft
Vertical transverse dispersivity	α_z	3.0 ft

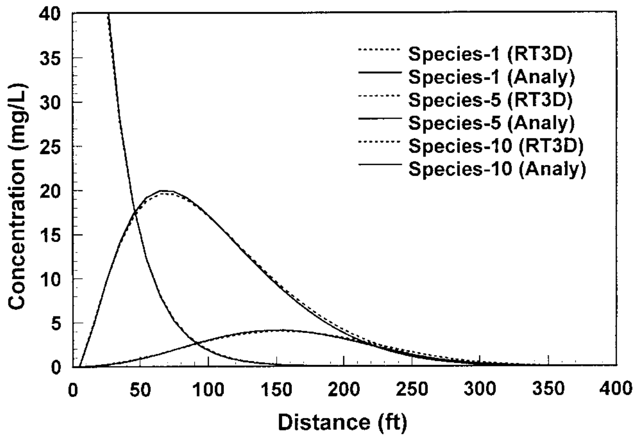


Figure 2. Concentration profiles of species 1, 5, and 10 in a one-dimensional column simulated by the analytical and numerical solutions.

For comparison purposes, the problem was also solved by the RT3D numerical code. In the numerical model, reactive transport was simulated in a 10 ft thick (one layer) confined aquifer with x-y dimensions of 500 ft $\times$ 310 ft. A continuous source, injecting contaminated water at the rate of 1 ft^3/day in a grid cell centered at $x = 155$ ft and $y = 155$ ft, was used to simulate a point source. The concentration of species 1 in the contaminant water was 100 mg/L. A uniform time step size of 20 days was used in the numerical model.

The concentration contours predicted by the analytical and numerical models are compared in Figure 3. Similar to the one-dimensional example, only the results for species 1, 5 and 10 are presented here. The results show good agreement between the solutions. Some minor differences, which can be observed near the source, are primarily due to the approximations involved in representing the point source using a finite sized grid within the numerical modeling framework.

3.3. THREE-DIMENSIONAL PROBLEM

To implement the proposed solution strategy for solving three-dimensional problems, an analytical solution developed by Kim *et al.* (1988) (see Appendix C) was used. The solution was originally developed for modeling decaying single-species transport from a continuous point source in a three-dimensional domain. The analytical solution was coded to predict the contaminant concentration values over an evenly spaced (10 ft $\times$ 10 ft $\times$ 10 ft) three-dimensional grid of 50 columns, 31 rows, and 21 layers. A uniform groundwater transport velocity of 0.5 ft/day was assumed. Other transport parameters assumed are summarized in Table I. Initial conditions for all the species were assumed to be zero.

To verify the results, the problem was also solved numerically using the RT3D code. In the numerical model, reactive transport in a 210 ft thick (21 layers) confined

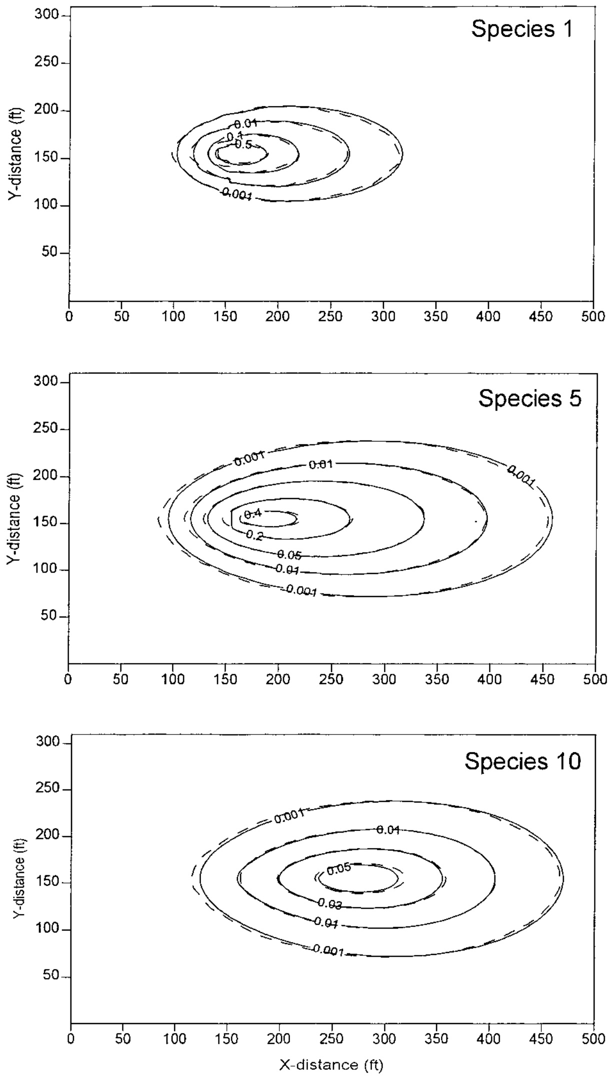


Figure 3. Concentration distributions of species 1, 5, and 10 in a two-dimensional aquifer predicted by the analytical and numerical solutions. Dashed and solid lines represent RT3D and analytical results, respectively.

aquifer with x-y dimensions of 500 ft $\times$ 310 ft was simulated. A continuous source injecting species-1 contaminated water, with a concentration of 100 mg/L and at the rate of 1 ft^3/day, in a grid cell centered at $x = 155$ ft and $y = 155$ ft, $z = 105$ ft was assumed. A uniform time step size of 20 days was used.

In Figure 4, the analytical- and numerical-model predicted concentration contours of species 1, 5 and 10 are compared at the plume centerline cross-section (x-z vertical cross-section at $y = 155$ ft). The results show good agreement between the concentration profiles predicted by the models.

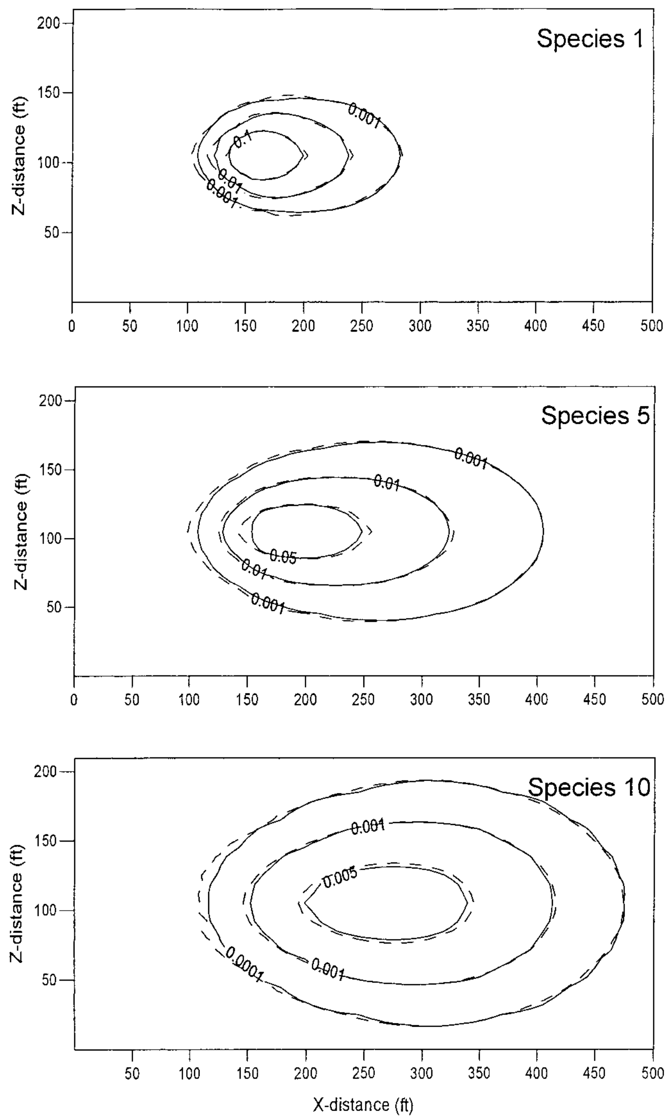


Figure 4. Comparison of species 1, 5 and 10 concentration distributions predicted by the analytical and numerical solutions in a x-z centerline cross-section for the three-dimensional example. Dashed and solid lines represent RT3D and analytical results, respectively.

3.4. NONUNIFORM INITIAL CONDITIONS

All example problems solved in the previous sections assume the initial conditions of all the reactive species to be zero. However, in field situations, it is common that the initial conditions (the time when the fieldwork was conducted) at the site may have certain contaminant mass distribution. Since it is very hard (if not impossible) to quantify the actual mass and duration of contaminant release, often it is of interest to forecast the plume evolution using the monitored field data as the initial condition. The decomposition solution methodology described in this work can be easily extended to account for any type of nonuniform initial conditions. For demonstration purposes, an application to a two-dimensional problem is described.

The initial condition for a two-dimensional single-species transport problem corresponding to an instantaneous mass release m at time $t = 0$ at the location $x = \xi$ and $y = \zeta$ is written as

$$c(x, y, 0) = m\delta(x - \xi)\delta(y - \zeta). \tag{16}$$

If the aquifer is assumed to be infinite, with $c(\pm\infty, \pm\infty, t) = 0$, then the analytical solution to this problem is given by the expression (Bear, 1979):

$$c(x, y, t) = \frac{m}{4\pi\phi v t\sqrt{\alpha_T \alpha_L}} \exp\left[-\frac{(x - \xi - vt)^2}{4\alpha_L v t} - \frac{(y - \xi)^2}{4\alpha_T v t} - \lambda t\right]. \tag{17}$$

However, if the aquifer is assumed to have some initial contaminant mass distribution given by a function $f(x, y)$ then,

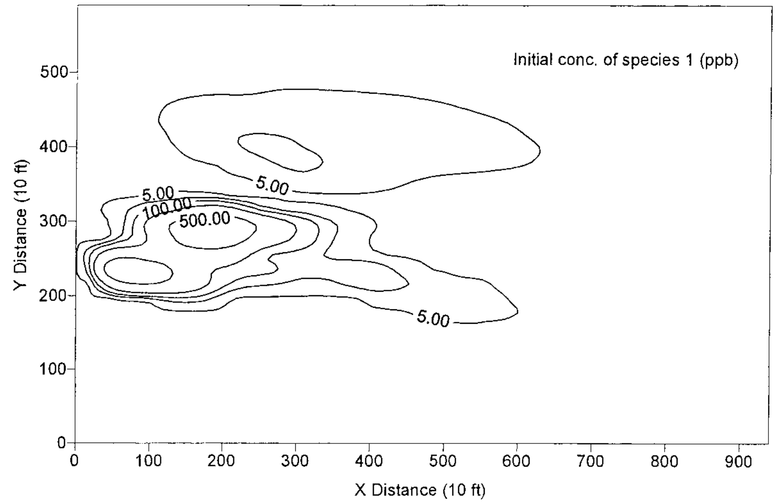
$$c(x, y, 0) = f(x, y), \tag{18}$$

where $f(x, y)$ is the function used for representing the initial concentration distribution observed. Under these nonuniform initial conditions, the superposition principle can be used to derive the following analytical solution

$$\begin{aligned} c(x, y, t) \; = \; & \frac{1}{4\pi\phi v t\sqrt{\alpha_T \alpha_L}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} c(x, y, 0) \; \times \\ & \times \; \exp\left[-\frac{(x - \xi - vt)^2}{4\alpha_L v t} - \frac{(y - \zeta)^2}{4\alpha_T v t} - \lambda t\right] \mathrm{d}\xi \, \mathrm{d}\zeta. \end{aligned} \tag{19}$$

If Equation (19) is used as the basic semi-analytical solution, then the transport of any number of reactive species with arbitrary initial condition function can be solved using the proposed decomposition method. To implement this solution for multi-species reactive transport, all initial concentration profiles should be first transformed into 'a' domain using (7):

$$\begin{bmatrix} a_1(x, y, 0) \\ a_2(x, y, 0) \\ \vdots \\ a_n(x, y, 0) \end{bmatrix} = \mathbf{P} \begin{bmatrix} c_1(x, y, 0) \\ c_2(x, y, 0) \\ \vdots \\ c_n(x, y, 0) \end{bmatrix} = \mathbf{P} \begin{bmatrix} f_1(x, y) \\ f_2(x, y) \\ \vdots \\ f_n(x, y) \end{bmatrix}, \tag{20}$$



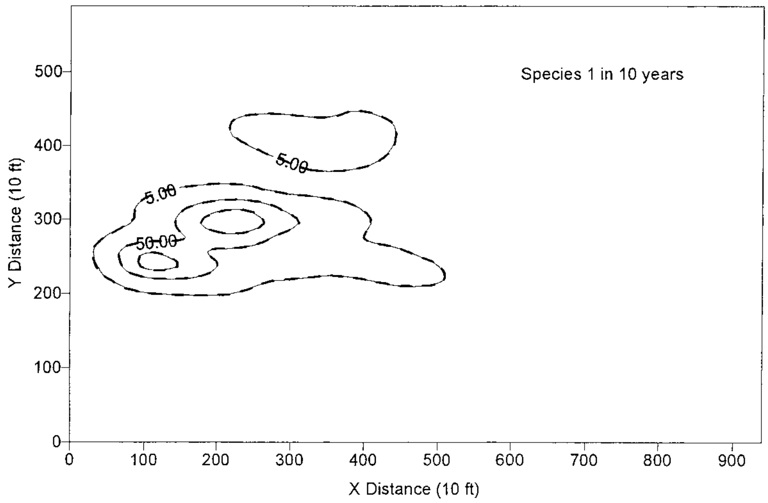


Figure 5. Concentration distribution of species 1 in a two-dimensional aquifer with nonuniform initial condition. Dashed and solid lines represent RT3D and analytical results, respectively.

where f_1, f_2, and f_n represent initial concentrations of species 1, 2 and n in the 'c' domain. In the 'a' domain, the auxiliary concentration is calculated using (19) as

$$a_i(x, y, t) = \frac{1}{4\pi\phi v t\sqrt{\alpha_T \alpha_L}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} a_i(x, y, 0) \times \times \exp\left[-\frac{(x-\xi-vt)^2}{4\alpha_L vt} - \frac{(y-\zeta)^2}{4\alpha_T vt} - \lambda t\right] \mathrm{d}\xi\, \mathrm{d}\zeta, \quad \forall i = 1, 2, \cdots, n. \tag{21}$$

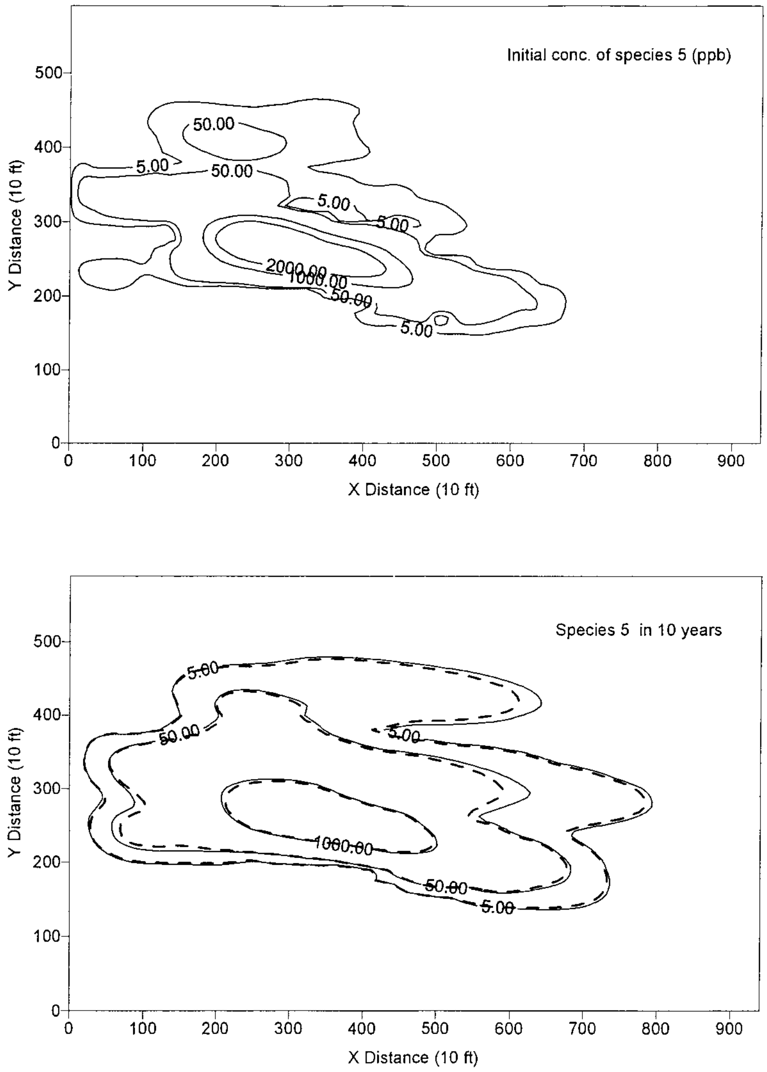


Figure 6. Concentration distribution of species 5 in a two-dimensional aquifer with nonuniform initial condition. Dashed and solid lines represent RT3D and analytical results, respectively.

Later, the real concentration profiles can be calculated using the inverse transformation Equation (15).

The solution procedure was applied to model a real field data set. The contaminated aquifer used in this example is 9500 ft long, 6000 ft wide, and 12 ft thick. The observed regional velocity is 0.1 ft/day, longitudinal and transverse dispersivities are 40 ft and 8.0 ft, respectively. First-order reaction rates for all 10 species are 5.0×10^{-4}, 1.25×10^{-3}, 1.1×10^{-3}, 1.0×10^{-4}, 1.0×10^{-4}, 5.0×10^{-5}, 5.0×10^{-5}, 3.0×10^{-5}, 4.0×10^{-5}, 5.0×10^{-6} (day^{-1}), and the yield coefficients are: 0.0, 0.79, 0.50, 0.45, 0.74, 0.64, 0.37, 0.51, 0.51, 0.45. Monitored initial concentrations were available for species 1, 2, 5 and 6 in the reaction network. Other species were not of interest and are assumed to have zero initial concentrations. The problem was also set up and solved numerically using the RT3D code. The concentrations profiles predicted by the analytical and numerical models are compared in Figures 5 and 6. The concentration profiles of the first and the fifth species (species 1 and 5) are only presented here. Good agreement between the solutions demonstrates the validity of the analytical solution strategy for nonuniform initial conditions.

Conclusions

A general transformation method has been developed to solve a system of multiple partial differential equations that are coupled by sequential or parallel first-order reaction networks. Using the proposed method, the coupled PDEs are decomposed into multiple independent subsystems corresponding to each species in the reaction network. Each decomposed subsystem is identical to the single-species first-order reactive transport equation. Therefore, after applying the decomposition strategy, all previously published analytical solutions to the single-species first-order reactive problem can be directly utilized to solve the coupled reactive transport problem. The method is an efficient strategy for solving any number of sequential or parallel reactive transport equations in multiple dimensions.

Appendix A: Detailed Derivations of the Decomposition Methodology for a One-Dimensional Two-Species Reactive Transport Problem

One-dimensional fate and transport equations for two reacting species that are coupled by a sequential first-order decay reaction can be written as

$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial x^2} - v\frac{\partial c_1}{\partial x} - k_1 c_1, \tag{22}$$

$$\frac{\partial c_2}{\partial t} = D\frac{\partial^2 c_2}{\partial x^2} - v\frac{\partial c_2}{\partial x} + yk_1 c_1 - k_2 c_2. \tag{23}$$

The transformation matrix equation for this problem can be written as

$$\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ \left(\frac{y\,k_1}{k_1 - k_2}\right) & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}. \tag{24}$$

The matrix equation can be written as the following two linear transformation equations:

$$a_1 = c_1, \tag{25}$$

$$a_2 = c_2 + \frac{yk_1}{k_1 - k_2} c_1. \tag{26}$$

Differentiating Equation (26) partially with respect to time we get

$$\frac{\partial a_2}{\partial t} = \frac{\partial c_2}{\partial t} + \frac{yk_1}{k_1 - k_2}\frac{\partial c_1}{\partial t}. \tag{27}$$

Substituting (22) and (23) in (27) we get

$$\frac{\partial a_2}{\partial t} = D\frac{\partial^2 c_2}{\partial x^2} - v\frac{\partial c_2}{\partial x} + yk_1c_1 - k_2c_2 + + \frac{yk_1}{k_1 - k_2}\left[D\frac{\partial^2 c_1}{\partial x^2} - v\frac{\partial c_1}{\partial x} - k_1c_1\right]. \tag{28}$$

Equation (28) can be rearranged as

$$\frac{\partial a_2}{\partial t} = D\frac{\partial^2}{\partial x^2}\left[c_2 + \frac{yk_1}{k_1 - k_2}c_1\right] - - v\frac{\partial}{\partial x}\left[c_2 + \frac{yk_1}{k_1 - k_2}c_1\right] + yk_1c_1 - k_2c_2 - \frac{yk_1^2c_1}{k_1 - k_2}. \tag{29}$$

Using (26), Equation (29) can be written as

$$\frac{\partial a_2}{\partial t} = D\frac{\partial^2 a_2}{\partial x^2} - v\frac{\partial a_2}{\partial x} - k_2c_2 + yk_1c_1 - \frac{yk_1^2c_1}{k_1 - k_2}. \tag{30}$$

Combining the last three terms, Equation (30) can be simplified to

$$\frac{\partial a_2}{\partial t} = D\frac{\partial^2 a_2}{\partial x^2} - v\frac{\partial a_2}{\partial x} - k_2a_2. \tag{31}$$

A standard, single-species, one-dimensional transport and decay solution (e.g. Bear, 1979) can be used in the transformed domain to solve (31) to evaluate a_2 values; then, c_2 values can be computed using the inverse transformation equation (15). The process can be repeated for any number of species by using the proposed transformation methodology.

Appendix B: Derivation of Equation (14) for Species 6

Consider species 6 in the example problem; when $i = 6$, following definition (7) we get

$$a_6 = \mathbf{P}_6\mathbf{c} = P(1,6)c_1 + P(2,6)c_2 + P(5,6)c_5 + P(6,6)c_6, \tag{32}$$

where $\mathbf{P}_6$ is the vector of the 6th row in $\mathbf{P}$ matrix and

$$P(1,6) = \frac{y_2y_5y_6k_1k_2k_5}{(k_1 - k_6)(k_2 - k_6)(k_5 - k_6)}, \quad P(2,6) = \frac{y_5y_6k_2k_5}{(k_2 - k_6)(k_5 - k_6)}, \quad P(5,6) = \frac{y_6k_5}{(k_5 - k_6)}, \quad P(6,6) = 1.0. \tag{33}$$

Differentiating (32) with respect to time, yields

$$\begin{aligned}\frac{\partial a_6}{\partial t} &= P(1,6)\frac{\partial c_1}{\partial t} + P(2,6)\frac{\partial c_2}{\partial t} + P(5,6)\frac{\partial c_5}{\partial t} + P(6,6)\frac{\partial c_6}{\partial t} \\ &= P(1,6)[L(c_1) - k_1c_1] + P(2,6)[L(c_2) - k_2c_2 + y_2k_1c_1] + \\ &\quad + P(5,6)[L(c_5) - k_5c_5 + y_5k_2c_2] + \\ &\quad + P(6,6)[L(c_6) - k_6c_6 + y_6k_5c_5].\end{aligned} \tag{34}$$

Combining the transport terms, we obtain

$$\begin{aligned}\frac{\partial a_6}{\partial t} &= P(1,6)[L(c_1)] + P(2,6)[L(c_2)] + P(5,6)[L(c_5)] + \\ &\quad + P(6,6)[L(c_6)] + P(1,6)[-k_1c_1] + P(2,6)[-k_2c_2 + y_2k_1c_1] + \\ &\quad + P(5,6)[-k_5c_5 + y_5k_5c_2] + P(6,6)[-k_6c_6 + y_6k_5c_5] \\ &= L(a_6) + R(a_6),\end{aligned} \tag{35}$$

where $R(a_6)$ represents the reaction terms in Equation (35). By introducing the definition of **P** components (33), we have

$$\begin{aligned}R(a_6) &= \frac{y_2y_5y_6k_1k_2k_5}{(k_1-k_6)(k_2-k_6)(k_5-k_6)}[-k_1c_1] + \\ &\quad + \frac{y_5y_6k_2k_5}{(k_2-k_6)(k_5-k_6)}[-k_2c_2 + y_2k_1c_1] + \\ &\quad + \frac{y_6k_5}{(k_5-k_6)}[-k_5c_5 + y_5k_2c_2] + [-k_6c_6 + y_6k_5c_5] \\ &= -\frac{y_2y_5y_6k_1k_2k_5}{(k_1-k_6)(k_2-k_6)(k_5-k_6)}k_1c_1 + \\ &\quad + \frac{y_5y_6k_2k_5}{(k_2-k_6)(k_5-k_6)}y_2k_1c_1 - \\ &\quad - \frac{y_5y_6k_2k_5}{(k_2-k_6)(k_5-k_6)}k_2c_2 + \frac{y_6k_5}{(k_5-k_6)}y_5k_2c_2 - \\ &\quad - \frac{y_6k_5}{(k_5-k_6)}k_5c_5 + y_6k_5c_5 - k_6c_6.\end{aligned} \tag{36}$$

Combining terms with common concentration factors, gives

$$\begin{aligned}R(a_6) &= -k_6\frac{y_2y_5y_6k_1k_2k_5}{(k_1-k_6)(k_2-k_6)(k_5-k_6)}c_1 - k_6\frac{y_5y_6k_2k_5}{(k_2-k_6)(k_5-k_6)}c_2 - \\ &\quad - k_6\frac{y_6k_5}{(k_5-k_6)}c_5 - k_6c_6 \\ &= -k_6[P(1,6)c_1 + P(2,6)c_2 + P(5,6)c_5 + P(6,6)c_6] = -k_6a_6.\end{aligned} \tag{37}$$

Therefore,

$$\frac{\partial a_6}{\partial t} = L(a_6) - k_6a_6. \tag{38}$$

This format is identical to the PDE of a single species transport with first-order reaction. Similarly, any other species in the reaction network can be transformed into such an independent partial differential equation, for which analytical solutions are readily available for various boundary and initial conditions.

Appendix C: Single Species Analytical Solutions

The multi-species analytical solution methodology discussed in this work, requires an analytical solution to the standard single-species transport first-order decay problem:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial x} - \lambda c, \tag{39}$$

where λ is the first-order reaction rate.

For solving one-dimensional problems, we use the analytical solution presented by Bear (1979) for predicting radioactive tracer transport in a semi-infinite column. Constant concentration inlet-boundary condition is assumed. The analytical solution is (Bear, 1979):

$$\begin{aligned} c(x,t) \;=\; & \frac{c_0}{2}\exp\left(\frac{xv}{2D_x}\right)\left[\exp(-\beta x)\operatorname{erfc}\frac{x-(v^2+4\lambda D_x)^{1/2}t}{2(D_x t)^{1/2}}+\right.\\ & \left. +\exp(\beta x)\operatorname{erfc}\frac{x+(v^2+4\lambda D_x)^{1/2}t}{2(D_x t)^{1/2}}\right], \end{aligned} \tag{40}$$

where c_0 is the concentration of the transported species at the inlet boundary and

$$\beta = \left(\frac{v^2}{4D_x^2} + \frac{\lambda}{D_x}\right)^{1/2}, \tag{41}$$

$$\operatorname{erfc}(\xi) = 1 - \operatorname{erf}(\xi) = \frac{2}{\sqrt{\pi}}\int_{\xi}^{\infty} \exp(-\tau^2)\,\mathrm{d}\tau. \tag{42}$$

For solving two-dimensional problems we use Wilson and Miller (1978) solution, which can be used for simulating a continuous point source in an infinite plane with uniform flow. The analytical solution is

$$\begin{aligned} c(x,y,t) \;=\; & \frac{c_0 Q}{4\pi\phi(D_x D_y)^{1/2}}\exp\left(\frac{xv}{2D_x}\right)\left(\frac{D_x}{vr}\right)^{1/2}\times\\ & \times\exp\left(-\frac{vr}{2D_x}\right)\operatorname{erfc}\left(\frac{2u-vr/2D_x}{2u^{1/2}}\right), \end{aligned} \tag{43}$$

where $c_0 Q$ is point-source (mass) injection rate, ϕ is the effective porosity, and

$$r = \sqrt{\left(\frac{x^2}{D_x} + \frac{D_x}{D_y}y^2\right)\gamma}, \qquad u = \frac{r^2}{4\gamma D_x t}, \tag{44}$$

$$\gamma = 1 + \frac{4D_x\lambda}{\nu^2}. \tag{45}$$

For solving three-dimensional problems, we use Kim *et al.*'s (1988) solution. For a continuous point source injecting into an infinite three-dimensional aquifer domain with uniform flow, the solution is

$$\begin{aligned} c(x, y, z, t) \;=\; & \frac{c_0 Q}{8\pi\phi(D_x D_y D_z)^{1/2} r} \exp\left(\frac{x\nu}{2D_x}\right) \times \\ & \times \left\{ \exp\left[-\sqrt{r^2\left(\lambda + \frac{\nu^2}{4D_x}\right)}\right] \times \right. \\ & \times \left[2 - \operatorname{erfc}\left(\sqrt{\left(\lambda + \frac{\nu^2}{4D_x}\right)t} - \sqrt{\frac{r^2}{4t}}\right)\right] + \\ & \left. + \exp\sqrt{r^2\left(\lambda + \frac{\nu^2}{4D_x}\right)} \operatorname{erfc}\left[\sqrt{\left(\lambda + \frac{\nu^2}{4D_x}\right)t} + \sqrt{\frac{r^2}{4t}}\right]\right\}, \end{aligned} \tag{46}$$

where $c_0 Q$ is the point source (mass) injection rate and r is the representative distance, which can be computed as

$$r = \sqrt{\frac{x^2}{D_x} + \frac{y^2}{D_y} + \frac{z^2}{D_z}}. \tag{47}$$

Acknowledgements

Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. This work was supported by the U.S. Department of Energy Office of Technology Development. The first author was supported by the Associated Western Universities, Inc., Western Division under grant DE-FG06-89ER-7522 with the U.S. Department of Energy.

References

Bear, J.: 1960, The transition zone between fresh and salt waters in coastal aquifers, PhD Thesis, University of California, Berkeley, California, U.S.A.

Bear, J.: 1979, *Hydraulics of Groundwater*, McGraw-Hill.

Beljin, M. S.: 1991, Review of three-dimensional analytical models for solute transport in ground-water system, International Ground Water Modeling Center, Holcomb Research Institute, Butler University, Indianapolis, Indiana, U.S.A.

Clement, T. P., Sun, Y., Hooker, B. S. and Petersen, J. N.: 1998, Modeling multi-species reactive transport in groundwater aquifers, *Groundwater Monitoring and Remediation* **18**(2), 79–92.

Van Genuchten, M. Th. and Alves, W. J.: 1982, Analytical solutions of the one-dimensional convective-dispersive solute transport equation, Agricultural Research Service, Department of Agriculture.

Van Genuchten, M. Th.: 1985, Convective-dispersive transport of solutes involved in sequential first-order decay reactions, *Comput. Geosci.* **11**(2), 129–147.

Kim, C. L., Chambre, P. L., Lee, W. W.-L. and Pigherd, T. H.: 1988, Contaminant transport from an array of sources, Earth Science Division, LBL-24200, UC-403, Berkeley, Lawrence Berkeley Laboratory, University of California, U.S.A. pp. 43–47.

Lunn, M., Lunn, R. J. and Mackay, R.: 1996, Determining analytic solution of multiple species contaminant transport, with sorption and decay, *J. Hydrol.* **180**, 195–210.

Ogata, A.: Dispersion in porous media, PhD Thesis, Northwestern University, Illinois, U.S.A. 1958.

Sun, Y., Petersen, J. N. and Clement, T. P.: 1997, Analytical solutions for multiple species reactive transport in multiple dimensions, *J. Contam. Hydrol.* (accepted).

Sun, Y., Petersen, J. N., Clement, T. P. and Skeen, R. S.: 1998, Development of analytical solutions for multi-species transport with serial and parallel reactions, *Water Resour. Res.* (accepted).

Toride, N., Leij, F. J. and van Genuchten, M. Th.: 1995, The CXTFIT code for estimating transport parameters from laboratory and field tracer experiments, U.S. Salinity Laboratory Report, No. 137.

Wilson, J. L. and Miller, P. J.: 1978, Two-dimensional plume in uniform groundwater flow, *J. Hydraul. Div.* **104**, 503–514.