Natural attenuation of chlorinated ethene compounds: model development and field-scale application at the Dover site

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Abstract

A multi-dimensional and multi-species reactive transport model was developed to aid in the analysis of natural attenuation design at chlorinated solvent sites. The model can simulate several simultaneously occurring attenuation processes including aerobic and anaerobic biological degradation processes. The developed model was applied to analyze field-scale transport and biodegradation processes occurring at the Area-6 site in Dover Air Force Base, Delaware. The model was calibrated to field data collected at this site. The calibrated model reproduced the general groundwater flow patterns, and also, it successfully recreated the observed distribution of tetrachloroethene (PCE), trichloroethene (TCE), dichloroethylene (DCE), vinyl chloride (VC) and chloride plumes. Field-scale decay rates of these contaminant plumes were also estimated. The decay rates are within the range of values that were previously estimated based on lab-scale microcosm and field-scale transect analyses. Model simulation results indicated that the anaerobic degradation rate of TCE, source loading rate, and groundwater transport rate are the important model parameters. Sensitivity analysis of the model indicated that the shape and extent of the predicted TCE plume is most sensitive to transmissivity values. The total mass of the predicted TCE plume is most sensitive to TCE anaerobic degradation rates. The numerical model developed in this study is a useful engineering tool for integrating field-scale natural attenuation data within a rational modeling framework. The model results can be used for quantifying the relative
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### 1. Introduction

Past operations in support of various military operations have resulted in chemical contamination of the subsurface soil and associated groundwater at the Area-6 site in Dover Air Force Base, Delaware. The contaminants of concern include fuel-hydrocarbons and chlorinated solvents, including tetrachloroethene (PCE) and trichloroethene (TCE). A TCE groundwater plume present in the center of the Area-6 west management unit is the largest plume detected on this site. The plume originates from multiple contaminant sources that were created by the past spills and waste disposal activities associated with various aircraft maintenance operations. A PCE plume, much smaller in size relative to the TCE plume, also originates from these contaminant sources.

In 1994, a consortium of industrial and government agencies, known as the Remediation Technology Development Forum (RTDF) chlorinated solvent bioremediation work group initiated a research program to evaluate the feasibility of monitored natural attenuation technology for remediating the chlorinated solvent contamination at the Dover Area-6 site. The term "monitored natural attenuation" refers to the reliance on natural processes to achieve site-specific cleanup objectives within a reasonable time frame (USEPA, 1997). The attenuation processes that are at work in such a remediation approach include a variety of in situ physical, chemical, and biological processes that, under favorable conditions, act without human intervention to reduce mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater. The in situ processes may include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization, transformation or destruction of contaminants (USEPA, 1997).

Decisions to employ monitored natural attenuation as the remediation alternative should be adequately supported by detailed site characterization. In addition, demonstrating the efficacy of this remediation approach at a field site would likely require analytical or numerical simulation of complex attenuation processes (USEPA, 1997). Since most site contamination problems involve multiple contaminants, models that can simulate reactive transport of multiple species are typically more useful for natural attenuation analysis.

Rifai et al. (1987) developed a two-species bioremediation model, known as BIOPLUME-II, to predict the fate and transport of hydrocarbon contaminants that degrade via aerobic reactions. The model was used to study aerobic bioremediation and other attenuation mechanisms occurring at several fuel-hydrocarbon sites (Rifai et al., 1988; Chiang et al., 1989). The BIOPLUME-II model was recently updated to describe other anaerobic reaction mechanisms for modeling hydrocarbon decay processes (Rifai et al., 1995). Essaid et al. (1995) developed a detailed multi-species reactive transport model, known as BIOMOC, for modeling intrinsic bioremediation at a crude oil spill site.
BIOMOC can be used to simulate the degradation of volatile and nonvolatile fractions of dissolved organics by aerobic processes, manganese reduction, iron reduction, and methanogenesis. The model was used to study the field-scale transport and degradation processes occurring at the Bemidji crude oil spill site in Minnesota. Clement (1997) and Clement et al. (1998) developed a multi-species reactive transport code for simulating bioremediation scenarios in subsurface environments. Unlike other bioremediation simulation codes, which are usually setup to solve a specific type of contaminant transport problem, RT3D is a general-purpose reactive transport solver that can be used for solving any number of transport equations that are coupled with any type of biochemical kinetics. For example, Lu et al. (1999) used RT3D to solve a set of reactive transport equations that describe hydrocarbon decay and transport under aerobic and sequential-anaerobic environments. Sun et al. (1998) used RT3D to solve a multi-species model that describe hydrocarbon decay coupled with bacterial growth and transport. Clement et al. (1998) used RT3D to solve a four-species, sequential degradation reaction model for predicting anaerobic degradation of chlorinated solvent chemicals such as PCE and TCE. Details of further application of RT3D code to several other types of reaction systems are discussed in Clement (1997).

Review of published literature suggests that most of the previous natural attenuation modeling efforts have primarily focused on analyzing the degradation potential of hydrocarbon plumes (Rifai et al., 1988; Chiang et al., 1989; Essaid et al., 1995). Semprini et al. (1995) completed a field study in a sandy aquifer near St. Joseph, Michigan, which demonstrated the natural anaerobic transformation potential of the aquifer to degrade chlorinated solvent-related chemicals. The study concluded that dechlorination of TCE, dichloroethylene (DCE) and vinyl chloride (VC) are associated with sulfate reduction and methanogenic conditions of the aquifer. However, no modeling work was performed to correlate the observed concentration data with the site hydrogeology.

The objective of this study was to develop a natural attenuation model for predicting the fate and transport of chlorinated solvents and their degradation products in saturated groundwater systems. A mathematical modeling framework for chlorinated solvent degradation was formulated based on the field data collected at a Remediation Technologies Development Forum’s study site in Dover Air Force Base, Delaware. The modeling goal was to develop a cause–effect framework to correlate the observed contaminant concentration distribution with the physical, chemical, and source characterization data collected at the site. The developed model was calibrated to recreate the degradation conditions and contaminant distribution patterns currently observed at the site. It should be noted that the proposed modeling framework is a preliminary attempt to describe a complex field problem; therefore, no effort was made to extend the model for predictive analysis.

2. Conceptual models

Analyzing site data using a mathematical model is often an integral part of a natural attenuation evaluation study. Models can be used to analyze and estimate contaminant
mass balances, remediation time periods, travel times, and exposure levels at sensitive receptor locations. Such modeling analyses, which are useful for demonstrating the ability of various in situ natural processes to meet remedial objectives, initially require formulation of site-specific conceptual models. A conceptual model is a qualitative representation of a transport system that conveys what is known or suspected about contaminant sources, release mechanisms, and the fate and transport of those contaminants. Conceptual models usually provide the basis for systematically assessing the extent of potential natural attenuation processes that are occurring at a site. The quality of the output from computer models will be directly related to the quality of the conceptual models. Therefore, in any groundwater modeling exercise, the most important step is the conceptual model development step (Bear et al., 1992). Mathematically, a conceptual model is nothing more than a set of assumptions that relate to items such as boundary conditions, initial conditions, geological description, flow regime, source/sink distribution, hydraulic conductivity distribution, transport parameters, and other flow and transport parameters. For modeling natural attenuation, one has to first develop a set of conceptual models to describe the following three distinct processes: (1) groundwater flow, (2) contaminant transport, and (3) biogeochemical reactions. In the following sections, the steps involved in developing conceptual models for these three processes are illustrated using the hydrogeological and contaminant data collected at the Dover site.

2.1. Site description

Dover Air Force Base is located near the city of Dover, DE, USA. The base is spread over about 78 km²; and within the base, the Area-6 site is approximately 9000 ft (≈ 3 km) long in the north–south direction and 6000 ft (≈ 2 km) wide in the east–west direction. Fig. 1 shows the surface features of Area-6 site. The reference coordinates used in Fig. 1 (and in all subsequent figures) are the State Plane coordinates (NAD-83) measured in feet. The figure shows the location of all known or suspected sources. Numerous wells are located throughout the site to monitor the contaminant concentration and groundwater levels. The groundwater flow at this site is predominately from the north toward the St. Jones river loops in the southern and western boundaries.

2.2. Conceptual model for groundwater hydrology

The subsurface below the Area-6 site has a contaminated water-table aquifer, which is bounded by an impermeable formation (Dames and Moore, 1994; DERS, 1997). A conceptual model for the geological cross-section of the aquifer is shown in Fig. 2. As depicted in the figure, the aquifer is located in a permeable zone consisting of a mixture of silty, sandy, and/or gravelly material. A low-permeability clay layer, known as the Calvert formation, forms the lower boundary of the aquifer. Based on site characterization data, two distinct zones, designated as shallow and deep zones, are identified within the permeable aquifer region (Dames and Moore, 1994; DERS, 1997). The shallow zone consists of low-permeability, silty–sandy material with thickness ranging from 5 to 10 ft. The deep zone consists of sandy–gravelly deposit of about 10–15 ft thickness. The location of the upper boundary of the deep zone (an upward fining sequence) and the
lower boundary of the deep zone (the Calvert formation) were discernible in most of the drilling logs. Based on slug and pump test studies, average hydraulic conductivity of the shallow and deep zones were estimated to be 35 and 85 ft/ day, respectively (Dames and Moore, 1994; DERS, 1997).

The measured groundwater elevations across the site range from 14 to 3 ft above the mean sea level. A contour map of groundwater levels observed during the spring 1997 sampling survey is presented in Fig. 3. The contours show that the groundwater gradient is fairly low in the northern region (near the source areas) and becomes steeper near the river.

2.3. Conceptual model for contaminant hydrology

The contaminant concentration data collected at the site show that the majority of contaminant mass is present in the deep permeable zone (Dames and Moore, 1994; Klier et al., 1998). In addition, most of the contamination at this site is associated with the chlorinated solvent chemicals PCE and TCE. Groundwater monitoring data also indicate that TCE is the predominant dissolved contaminant (Klier et al., 1998). Contaminant distribution measured in the soil core samples collected at this site shows that TCE is the most dominant contaminant with maximum soil-phase TCE concentration values ranging almost 40 times greater than PCE (Ball et al., 1997).
Review of past records suggests that the Area-6 site must have received contaminants from a variety of sources over multiple time periods. The locations of a few known sources have been identified, but others have been only speculated on (Klier et al., 1998). Presently, there is no evidence for the presence of continuous free-phase Dense
Non-Aqueous Phase Liquid (DNAPL) at this site. The likely sources for continuing release of contaminants are the DNAPL ganglia that are trapped in the pore spaces or the residual sorbed or diffused contaminants that are trapped in the low-permeability clay lenses. Based on groundwater and site characterization data, the following conceptual model was proposed to explain the contaminant pattern currently observed at the site. The primary contaminants (waste PCE and TCE solvents) must have been introduced in the past as DNAPLs into the upper zone of the Columbia formation. The DNAPLs appear to have preferentially migrated downward through the aquifer into the deep zone. The driving force for the downward movement was likely the density difference. Once in the deep zone, further downward migration appears to have been prevented by the Calvert formation (acting as an impermeable lower boundary) or the DNAPL might have essentially attained non-mobile, residual saturation levels when it reached this depth. Modeling of contaminant diffusion characteristics of soil core samples taken from the Calvert formation, at a location down gradient from the source region, suggests that the DNAPL might have reached the bottom of the deep zone about 10–15 years prior to a 1995 field soil sampling event (Ball et al., 1997). After reaching the deep zone, the contaminants would have been subjected to the horizontal flow regime that operates more actively in this zone. Due to the high permeability of the deep zone (and low permeability of the upper zone), the contaminants emanating from the DNAPL are primarily trapped in the deep layer. To reflect these hydrogeological transport conditions, in our numerical model, we described the high-permeability deep zone as a separate layer, which is bounded by the relatively low-permeability sandy–silty layer at the top and the impermeable clayey layer (the Calvert formation) at the bottom.

2.4. Conceptual model for biodegradation reactions

PCE and TCE are the primary solvent contaminants that were originally disposed at the Dover AFB field site. However, high concentrations of chlorinated solvent degradation products such as cis-DCE and VC, traces of ethene (ETH), and elevated levels (above background) of chloride ions were observed in the monitoring wells located downstream from the suspected source locations (Klier et al., 1998). The observed concentration distributions of various degradation byproducts are shown in Fig. 4. The presence of high levels of cis-DCE, VC, and ETH suggests that the indigenous microbes present at the site are actively degrading the original contaminants PCE and TCE.

A conceptual biochemical reaction model was formulated to mathematically describe the biodegradation processes expected to occur at the Dover site. Previous studies conducted at other sites have indicated that anaerobic reductive dechlorination is the predominant biochemical process responsible for the biotransformation of highly chlorinated solvents (Wiedemeier et al., 1996; Wu et al., 1998). Reductive dehalogenation is an oxidative–reductive reaction in which electrons are transferred from donor (e.g., reduced organic substrates) to a chlorinated hydrocarbon acceptor resulting in the replacement of a chlorine substituent on the molecule with hydrogen (Vogel and McCarty, 1985). Biotransformation of the chlorinated ethenes occurs via sequential dechlorination of PCE to TCE, TCE to DCE, DCE to VC, and finally VC to ETH. However, under favorable environmental conditions, other biochemical processes may
Fig. 4. Field measured DCE, VC, and chloride plume contours.
also degrade the chlorinated organics. For example, Alvarez-Cohen and McCarty (1991) discussed the pathways for aerobic TCE cometabolism by a mixed methanotrophic culture. McCarty and Semprini (1994) suggested that DCE and VC have a potential to degrade via both direct and cometabolic aerobic pathways. Based on microcosm studies conducted with radio-labeled test chemicals, Klier et al. (1999) recently provided evidence for aerobic DCE biodegradation in subsurface soils. Bradley and Chapelle (1998) provided field evidences for aerobic microbial degradation of DCE and VC in stream-bed sediments. Bradley et al. (1998) provided data for DCE degradation under Mn(IV)-reducing conditions. For comparative purposes, the later investigators also performed radioactive-carbon labeled studies to demonstrate DCE degradation under aerobic conditions.

Based on the above literature information and the observed site geochemistry (Klier et al., 1998, 1999), a coupled aerobic–anaerobic reaction model was formulated to simulate the degradation patterns of PCE/TCE and their daughter products. The degradation reaction pathways assumed in the model are illustrated in Fig. 5. In the model, PCE is assumed to degrade only via the anaerobic pathway; other solvent compounds including TCE, DCE, and VC are assumed to degrade via both aerobic and anaerobic pathways. The degradation kinetics of all these biological reactions are complex and might depend on several biochemical and environmental factors. Moreover, the rate of degradation will depend on the type and amount of dechlorinating bacteria present in the aquifer and the availability of electron donors such as hydrogen (Maymo-Gatell et al., 1995). However, for practical field-scale applications, chlorinated solvent degradation reactions are often hypothesized as lumped first-order decay reactions. For example, Wiedemeier et al. (1996) assumed this hypothesis and completed an extensive literature survey to compile first-order rate constants for different chlorinated solvent chemicals. In the present work, the kinetics of all the degradation reactions described in Fig. 5 are assumed as first-order with respect to the respective contaminant concentration. Processes not simulated in the model are growth and decay of bacteria, and the availability limitations of carbon, oxygen, and other biochemical intermediates.

The use of first-order kinetics is appropriate when the biodegradation rate is primarily a function of the concentration of the contaminant, and when the microbial mass is not increasing or decreasing over time within the region of interest. Therefore, if an active...
bioremediation technique is used at a site to increase the mass of the subsurface bacteria (either by injecting growth nutrients or by injecting cultured bacterial cells), then the assumptions associated with first-order kinetics may not be valid. For most natural attenuation modeling applications, the first-order assumption can be considered as a reasonable approximation (Wiedemeier et al., 1996). Moreover, the assumption of first-order kinetics is often acceptable for biodegradation at low-pollutant concentration levels (Schmidt et al., 1985).

In the numerical model, the first-order degradation rates of all the biological reactions are allowed to spatially vary on a node-by-node basis. To delineate the spatially changing anaerobic and aerobic patterns present at the site, a reaction-zone model was developed based on the observed groundwater geochemistry data (Klier et al., 1998). This conceptual reaction-zone model was used as the basis for assigning the values of rate constants in different regions. The extent of each reaction zone was established from the observed distribution of degradation by-products such as DCE, VC, and chloride (see Fig. 4), and other chemical parameters such as oxygen and methane, shown in Fig. 6. The field data presented in Fig. 6 indicates the presence of active anaerobic regions near the source area. The presence of the anaerobic zone is likely due to the oxygen demand posed by the fuel hydrocarbon and other biodegradable organic compounds that were co-disposed at or near the source areas. In addition, natural carbon present in the sediment material might also be serving as a potential carbon source. However, the origin and the total quantity of different carbon sources present at this site are yet to be identified.

Fig. 7 shows the spatial extent of different reaction zones assumed in the conceptual reaction-zone model. Using this model, appropriate reaction rates were assigned for the numerical simulations. The assigned rate parameters were allowed to vary from zone to zone. However, within a given zone, the parameters were assumed to remain both spatially and temporally constant over the entire simulation period. As described in Fig. 7, the site was assumed to have four distinct reaction zones: two anaerobic zones of different characteristics, a transition zone, and an aerobic zone. In the anaerobic zones, anaerobic reactions are assumed to be the predominant degradation reactions, and in the oxidized zone, aerobic reactions are assumed to be the predominant reactions.

The approach used in this study for delineating the spatial extent of the reaction zones is a subjective procedure which is based on large amounts of site-specific data. This approach has several limitations. For example, by imposing the field data directly into the model, we have tightly constrained the problem to a specific field condition, and hence, the model may not be applicable at other sites where such intensity of data may not be available. Moreover, we have hypothesized that the reaction zones must have been formed by the co-disposed hydrocarbons (or other electron donors) rather instantaneously (compared to chlorinated solvent degradation rates), and remained stable during the entire simulation period. However, the field data collected within the finite amount of project time is insufficient to validate this stable reaction-zone hypothesis. Like any other field projects, this work is an outcome of a study completed with limited resources. Under these constraints, the stable reaction-zone hypothesis seems to be a "pragmatic" engineering approximation for modeling this problem. Clearly, much work needs to be done to develop procedures to automatically generate transient reaction
zones based on geochemical considerations. McNab and Narasimhan (1994) proposed a partial redox disequilibrium approach to model sequential chemical transformation in natural groundwater systems. They solved a hypothetical test problem to demonstrate the use of their model. However, direct application of such research models to field-scale bioremediation problems may be somewhat problematic because there is very little information available about the complex chemical interactions that may take place between inorganic chemicals as a result of the progress of the degradation reactions. In addition, such complex models will add a long list of additional unknown model parameters, which will be difficult to quantify under field conditions. Therefore, before adding additional complexities to the bio/geochemical reaction framework, careful
consideration must be given to the feasibility of parameter estimation process under practical field conditions.

3. Mathematical model

The RT3D computer code (Clement, 1997; Clement et al., 1998) was used to solve the bioreactive transport model developed in this study. RT3D was originally developed from the DoD_1.5, 1997-version of the EPA-transport code MT3D (Zheng, 1990). RT3D is a general-purpose reactive transport solver that has been previously verified against several analytical and numerical solutions (Clement et al., 1998; Sun and Clement, 1999; Sun et al., 1998, 1999).

In RT3D, the general macroscopic equations describing the fate and transport of aqueous- and solid-phase species, respectively, in multi-dimensional saturated porous media are represented as (Clement, 1997):

\[
\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C_k}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left( v_i C_k \right) + \frac{q_i}{\phi} C_{k_{1,2}} \pm r_k, \quad k = 1,2 \ldots m \tag{1}
\]

\[
\frac{d \tilde{C}_{im}}{dt} = \pm \bar{r}_{im}, \quad im = 1,2, \ldots (n-m) \tag{2}
\]

where \( n \) is the total number of species, \( m \) is the total number of aqueous-phase (mobile) species (thus, \( n - m \) is the total number of solid-phase or immobile species), \( C_k \) is the
aqueous-phase concentration of the $k$th species [ML$^{-3}$], $C_{i,k}$ is the solid-phase concentration of the $m$th species [MM$^{-1}$], $D_{ij}$ is the hydrodynamic dispersion coefficient [L$^2$T$^{-1}$], $v_i$ is the pore velocity [LT$^{-1}$], $q_i$ is the volumetric flux of water per unit volume of aquifer that represents sources and sinks [T$^{-1}$], $C_s$ is the concentration of source/sink [ML$^{-3}$], $r$ represents all aqueous-phase reaction rate terms that describe the mass of the species removed or produced per unit volume per unit time [ML$^{-3}$T$^{-1}$], and $\bar{r}$ represents all solid-phase reaction rate terms [MM$^{-1}$T$^{-1}$]. Saturated groundwater flow velocities are calculated from predicted groundwater head values. Groundwater heads are computed by solving the three-dimensional saturated groundwater flow equation using the groundwater flow code MODFLOW (McDonald and Harbaugh, 1988).

The fate and transport of different chlorinated ethene species mediated by the dechlorination reactions described in Fig. 5 can be mathematically represented by a set of transport equations. Assuming first-order biodegradation kinetics, transport and transformation of PCE, TCE, DCE, VC, ETH, and Cl can be simulated by solving the following set of partial differential equations:

$$R_e \frac{\partial [PCE]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [PCE]}{\partial x_j} \right) \frac{\partial (v_i [PCE])}{\partial x_i} + \frac{q_i}{\phi} [PCE]_s - K_r [PCE]$$

(3)

$$R_t \frac{\partial [TCE]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [TCE]}{\partial x_j} \right) \frac{\partial (v_i [TCE])}{\partial x_i} + \frac{q_i}{\phi} [TCE]_s + Y_{T/\nu} K_r [PCE] - K_{T1} [TCE] - K_{T2} [TCE]$$

(4)

$$R_D \frac{\partial [DCE]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [DCE]}{\partial x_j} \right) \frac{\partial (v_i [DCE])}{\partial x_i} + \frac{q_i}{\phi} [DCE]_s + Y_{D/\nu} K_{T1} [TCE] - K_{D1} [DCE] - K_{D2} [DCE]$$

(5)

$$R_V \frac{\partial [VC]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [VC]}{\partial x_j} \right) \frac{\partial (v_i [VC])}{\partial x_i} + \frac{q_i}{\phi} [VC]_s + Y_{V/\nu} K_{D1} [DCE] - K_{V1} [VC] - K_{V2} [VC]$$

(6)

$$R_E \frac{\partial [ETH]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [ETH]}{\partial x_j} \right) \frac{\partial (v_i [ETH])}{\partial x_i} + \frac{q_i}{\phi} [ETH]_s + Y_{E/\nu} K_{V1} [VC] - K_{E1} [ETH] - K_{E2} [ETH]$$

(7)

$$R_C \frac{\partial [Cl]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [Cl]}{\partial x_j} \right) \frac{\partial (v_i [Cl])}{\partial x_i} + \frac{q_i}{\phi} [Cl]_s + Y_{C/\nu} K_{P1} [PCE] + Y_{1C/T} K_{T1} [TCE] + Y_{1C/D} K_{D1} [DCE] + Y_{1C/V} K_{V1} [VC] + Y_{2C/T} K_{T2} [TCE] + Y_{2C/D} K_{D2} [DCE] + Y_{2C/V} K_{V2} [VC]$$

(8)
where [PCE], [TCE], [DCE], [VC], [ETH], and [Cl] represent contaminant concentrations of various species [mg/l]; $K_p$, $K_{T1}$, $K_{D1}$, and $K_{V1}$, and $K_{E1}$ are first-order anaerobic degradation rate constants [day$^{-1}$]; $K_{T2}$, $K_{D2}$, and $K_{V2}$ are first-order aerobic degradation rate constants [day$^{-1}$]; and $R_p$, $R_T$, $R_D$, $R_V$, $R_E$, and $R_C$ are retardation factors. Stoichiometric yield values, $Y$, can be calculated from the reaction stoichiometry and molecular weights. For example, anaerobic degradation of one mole of PCE would yield one mole of TCE, therefore $Y_{P/T} = \frac{\text{molecular weight of TCE}}{\text{molecular weight of PCE}} = \frac{165.8}{131.4} = 0.79$. Based on similar calculations, values of $Y_{D/T}$, $Y_{V/D}$, and $Y_{E/V}$ (which are chlorinated compound yields under anaerobic reductive dechlorination conditions) were calculated to be: 0.79, 0.74, 0.64 and 0.45, respectively; values of $Y_{1C/P}$, $Y_{1C/T}$, $Y_{1C/D}$, and $Y_{1C/V}$ (which are yield values for chloride under anaerobic conditions) were calculated to be: 0.21, 0.27, 0.37, and 0.57, respectively; and finally values of $Y_{2C/T}$, $Y_{2C/D}$, and $Y_{2C/V}$ (yield values for chloride under aerobic conditions) were calculated to be: 0.81, 0.74, and 0.57, respectively. Note that the reaction models used assume that the biological degradation reactions only occur in the aqueous phase, which is a conservative assumption.

The RT3D code uses the operator-split strategy which allows definition of different reaction models through a plug-in user-defined reaction module Clement, 1997. Using this strategy, the biological reaction kinetics included in the transport Eqs. (3)-(8) can be separated and assembled together as a set of ordinary differential equations:

\[
\begin{align*}
\frac{d[PCE]}{dt} &= \frac{K_P[TCE]}{R_P} \\
\frac{d[TCE]}{dt} &= \frac{Y_{P/T} K_P[PCE] - K_{T1}[TCE] - K_{T2}[TCE]}{R_D} \\
\frac{d[DCE]}{dt} &= \frac{Y_{D/T} K_T[TCE] - K_{D1}[DCE] - K_{D2}[DCE]}{R_D} \\
\frac{d[VC]}{dt} &= \frac{Y_{V/D} K_V[DCE] - K_{V1}[VC] - K_{V2}[VC]}{R_V} \\
\frac{d[ETH]}{dt} &= \frac{Y_{E/V} K_V[VC] - K_{E1}[ETH] - K_{E2}[ETH]}{R_E} \\
\frac{d[Cl]}{dt} &= \left\{ Y_{1C/P} K_{P1}[PCE] + Y_{1C/T} K_{T1}[TCE] + Y_{1C/D} K_{D1}[DCE] + Y_{1C/V} K_{V1}[VC] + Y_{2C/T} K_{T2}[TCE] + Y_{2C/D} K_{D2}[DCE] + Y_{2C/V} K_{V2}[VC] \right\} / R_C
\end{align*}
\]

To simulate the chlorinated solvent reactive transport system, the kinetic model developed above needs to be coded into a RT3D reaction module. In this study, we developed a six-component reaction module by coding Eqs. (9)-(14) in an RT3D-specified format as described in Clement (1997). In addition, the conceptual models for flow and
transport developed in previous sections were directly implemented in the flow and tracer-transport modeling frameworks of the MODFLOW and RT3D codes.

4. Groundwater flow simulations

For numerical modeling purposes, we described the contaminated deep zone as a single, continuous, confined unit with spatially variable transmissivity values. The different transmissivity zones used in the model were based on observed geological data (DERS, 1997). Flow conditions are assumed to be at steady state. Leakage of water from the upper low-permeability unit into the deep zone was described by setting a recharge boundary condition on the top of the grid. Initial transmissivity values were assigned based on the site characterization data (DERS, 1997). The groundwater head values at the model boundary and at the St. Jones River were set based on the measured groundwater head values (Klier et al., 1998). Using a flow model with fixed head boundaries all the way around the edge of the model posed a potential danger of incorrectly reflecting the overall groundwater flow budget. Since no field data was available for estimating the groundwater budget, additional constraints were imposed during the calibration process to verify that the hydraulic conductivity and recharge-rates used in the model are within the range of measured/estimated values.

The groundwater flow code MODFLOW was used to simulate the steady-state groundwater head distribution. A finite difference grid with a uniform cell size of 100 × 100 ft was used in all simulations. An anisotropy factor of 0.75 was used in the flow model to reflect the observed preferential migration pattern of the plume towards the southerly direction (Klier et al., 1998). The effective average recharge to the deep

Fig. 8. Groundwater contours based on model-predicted data (ft above MSL).
zone was estimated to be 0.0006 ft/day, which is within the range of values measured at this site (Ei et al., 1999). A trial-and-error procedure was used to adjust the transmissivity, within a range of measured values, to fit the observed groundwater head distribution. The groundwater head contours predicted by the model are presented in Fig. 8. It can be observed from the figure that the model-predicted groundwater contour patterns are close to the observed groundwater pattern previously presented in Fig. 3. The transmissivity values for the site range from 300 to 1200 ft²/day (or assuming an average thickness of 12 ft, the conductivity values range from 25 to 100 ft/day), which are within the range estimated during site characterization studies.

5. Contaminant transport simulations

5.1. Tracer transport simulations

To understand the contaminant transport behavior at the site, multiple tracer transport simulations were completed. An average layer thickness of 12 ft was used in all transport simulations. Based on laboratory and field data, the retardation factor of PCE, TCE, and DCE were calculated to be 1.3, 1.2, and 1.1, respectively (Ei et al., 1999; West et al., 1999), and the average porosity value for the site was estimated to be 0.38 (DERS, 1997). Dispersivity values were estimated based on the literature data (Gelhar et al., 1992) and were later verified through test tracer simulations. Estimation of macroscopic dispersivity for any field-scale transport problem is a difficult task. In general, dispersivity values are expected to be a function of the observation scale, however, the nature of this dependence and its interrelation to hydraulic conductivity variations is not so obvious and has been the subject of some controversy (Neuman, 1990; Gelhar et al., 1992; Molz and Bowman, 1993). In this study, we used the guidelines presented in Gelhar et al. (1992) and estimated the field-scale dispersivity value for our problem as 40 ft. The horizontal to transverse dispersivity ratio is assumed to be 0.2. To check the validity of these values, preliminary tracer simulations (results not shown) were completed and the shape of the model-predicted tracer plume was compared against the observed contaminant plume patterns. The tracer simulations indicated that the assumed dispersivity values are reasonable because further increase in dispersivity values predicted unrealistically wide plumes (smeared in the east–west direction), and smaller dispersivity values predicted much narrower plumes.

5.2. Reactive transport simulations

Multi-species reactive transport simulations were performed to predict the contaminant plumes observed during the 1997 March–April monitoring efforts completed at the Dover site. To define initial conditions, we assumed the presence of a pristine aquifer before the contamination period. Based on previous site investigation studies, the contaminant plumes at Area-6 are estimated to be about 40 years old (Dames and Moore, 1994), which was assumed to be the total duration of all transport simulations. The 40-year simulation period was divided into four equal stress periods to reflect the
temporal changes in contaminant mass release rates (i.e., temporal changes in mass release from the DNAPL ganglia or changes in mass release rate due to source control or depletion). Within each stress period, the contaminant mass release rates were maintained the same. Hypothetical wells, which discharged the primary contaminants PCE and TCE, were used to simulate the sources. The locations of the wells correspond to the source locations shown in Fig. 1. The injection flow rates at all the source grids were maintained at relatively low levels so that the added flow did not affect the groundwater head contours.

Like many other field sites, the total amount of contaminant mass discharged into the groundwater system is an unknown quantity. This is a common impediment that usually limits the use of transport models at any realistic field site. It is important to note that even if one knows the total mass of released DNAPL, the information may not be of much use. The mass that is of relevance in a natural attenuation modeling study is the amount that has effectively dissolved (and is currently dissolving) from the DNAPL phase into the groundwater. To quantify this value, detailed characterization efforts would be required to account for the amount of DNAPL trapped in the vadose zone, mass removed from various remedial actions such as soil-vapor extraction, DNAPL mass trapped as ganglia or pools within the saturated zone, and the time-variant mass-transfer characteristics of the ganglia or pools. Unfortunately, it is impossible to quantify all these processes under natural field conditions with any amount of certainty.

To circumvent the limitations associated with source uncertainties, in this study, the contaminant sources were quantified through a model calibration process, which are in turn, constrained by measured field-scale mass balance estimates of various contaminant species. The mass-balance constraints were developed based on the observed distribution plume concentration levels. Firstly, the monitored plume data for PCE, TCE, DCE, and VC were used to estimate the current amount of solvent mass present as dissolved plumes in the deep zone. The dissolved mass of solvent plumes currently present at the site are: 162 kg of PCE, 834 kg of TCE, 692 kg of DCE, and 36 kg of VC, and 24,271 kg of excess chloride above 10 mg/l background level. Since the retardation factors for PCE, TCE, and DCE are estimated to be 1.3, 1.2, and 1.1, respectively, the contaminant mass in the soil phase can be estimated as: 48 kg of PCE, 166 kg of TCE, and 69 kg of DCE. These field-scale mass balance estimates served as useful values during the calibration process to constrain the source estimation problem.

The reaction rate constants assumed in the model were bounded by the literature values given in Wiedemeier et al. (1996). Multiple model simulations were completed by varying the reaction parameters and source strengths to calibrate the model to fit the PCE, TCE, DCE, VC, ETH, and chloride concentration profiles observed in 1997. The calibrated degradation rates for various anaerobic and aerobic reactions are tabulated in Table 1, and the calibrated mass release rates from the assumed sources are tabulated in Table 2. The model calibrated reaction rate constants, summarized in Table 1, are within the range of values measured for the site based on independent lab-scale microcosm and field-scale transect studies (Ei et al., 1999; West et al., 1999). The field estimated apparent reaction rates ranged from 3.5 to 7.0 \times 10^{-4} \text{ day}^{-1} for PCE, from 1.5 to 5.4 \times 10^{-4} \text{ day}^{-1} for TCE, from 4.4 to 6.1 \times 10^{-4} \text{ day}^{-1} for cis-DCE, and was 8.2 \times 10^{-4} \text{ day}^{-1} for VC (Ei et al., 1999). It is interesting to note that the lowest
reaction rate, that of TCE (1.5 × 10⁻⁴ day⁻¹), was calculated for the down gradient portion of the plume, in the area designated as the transition zone in the numerical model. The lab-scale microcosm rate for anaerobic degradation of PCE was 3.1(±2.6) × 10⁻⁴ day⁻¹, and other decay rates ranged from 1.2(±2.4) to 6.7(±8.0) × 10⁻⁵ day⁻¹ for TCE, from 1.4(±0.6) to 6.2(±5.2) × 10⁻⁶ day⁻¹ for DCE, from 0.37(±0.01) to 1.1(±1.5) × 10⁻² day⁻¹ for VC; aerobic rates range from 0.8(±2.5) to 1.1(±2.2) × 10⁻³ day⁻¹ for DCE, and from 3.1(±1.9) to 3.7(±7.4) × 10⁻⁴ day⁻¹ for VC (West et al., 1999). While most model-estimated rate constants are within the range of values reported above, the anaerobic DCE degradation rate estimated by the model and by the field transect study is notably higher than the laboratory value. No specific reasons could be identified to resolve this anomaly except to hypothesize that the lab conditions used in the microcosm study might not have reflected the field condition.

Table 1
Calibrated degradation rate constants (day⁻¹)

<table>
<thead>
<tr>
<th>First-order rate constant</th>
<th>Associated contaminant</th>
<th>Anaerobic zone-1</th>
<th>Anaerobic zone-2</th>
<th>Transition zone</th>
<th>Aerobic zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>KPF (anaerobic)</td>
<td>PCE</td>
<td>3.2 × 10⁻⁴</td>
<td>4.0 × 10⁻⁴</td>
<td>1.0 × 10⁻⁴</td>
<td>0.0</td>
</tr>
<tr>
<td>KPT (anaerobic)</td>
<td>TCE</td>
<td>9.0 × 10⁻⁴</td>
<td>4.5 × 10⁻⁴</td>
<td>1.125 × 10⁻⁴</td>
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<tr>
<td>KTD (aerobic)</td>
<td>DCE</td>
<td>8.45 × 10⁻⁴</td>
<td>6.5 × 10⁻⁴</td>
<td>1.625 × 10⁻⁴</td>
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<tr>
<td>KVD (aerobic)</td>
<td>VC</td>
<td>8.0 × 10⁻³</td>
<td>4.0 × 10⁻³</td>
<td>1.0 × 10⁻³</td>
<td>0.0</td>
</tr>
<tr>
<td>KED (aerobic)</td>
<td>ETH</td>
<td>2.4 × 10⁻²</td>
<td>1.2 × 10⁻²</td>
<td>0.3 × 10⁻²</td>
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Table 2
Estimated contaminant source mass release rates, m (kg/yr)

<table>
<thead>
<tr>
<th>Source number</th>
<th>Stress period #1 PCE</th>
<th>Stress period #1 TCE</th>
<th>Stress period #2 PCE</th>
<th>Stress period #2 TCE</th>
<th>Stress period #3 PCE</th>
<th>Stress period #3 TCE</th>
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<td>0</td>
<td>0</td>
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<td></td>
</tr>
</tbody>
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Table 3 shows a comparison of model-calculated dissolved plume mass for each contaminant vs. the mass estimates made based on the field data. The table shows good agreement between model and field data. The total amount of contaminant mass discharged over the 40-year period was estimated to be 1433 kg for PCE and 19,250 kg for TCE. From the model-predicted chloride data, we estimated that about 19,500 kg of "TCE-equivalent" solvent mass has been degraded at this site over the 40-year period. Note that when estimating the biodegraded solvent mass, we have lumped the chloride produced from the partial degradation of PCE or TCE into DCE and VC, and the chloride produced from the total degradation of PCE, into an equivalent TCE mass unit. The TCE-equivalent mass was computed by multiplying the cumulative excess chloride mass by the TCE-to-chloride yield factor (131.5/106.5).

The model-predicted concentration contours for PCE and TCE are compared against the observed contaminant concentration contours in Figs. 9 and 10. The model-predicted DCE, VC, ETH, and chloride concentration contours are presented in Figs. 11 and 12 (compare these figures against field-data shown in Fig. 4). The results show that the model successfully recreated the general features of field-measured groundwater plume patterns. It is important to realize that, due to the nonlinear nature of the calibration problem, the model results discussed in this study may not be the unique solution. However, the calibrated values could be considered as reasonable field-scale estimates because: (a) the model reproduced the general behavior of multiple contaminant plumes; (b) the reaction parameters were constrained within literature limits during model calibration; (c) the calibration process was constrained by the field estimates of plume masses; and finally (d) the estimated reaction rates were close to the field and/or lab-measured rates.

6. Sensitivity analysis

Several types of sensitivity analysis methods are available for assessing the behavior of a model to changes in its input parameters. In our investigation, we used a perturbation method to assess the sensitivity of the natural attenuation model. Multiple sensitivity simulations were performed to quantify the model sensitivity with respect to
different parameters. However, detailed analyses of sensitivity simulation results were restricted to the TCE plume because it is the largest plume (in terms of size and mass) at this site, and hence, it controls the fate and transport of all byproduct plumes. Based on preliminary simulation studies, we identified the three most important parameters that control the fate and transport of the TCE plume. These are: (1) the TCE anaerobic first-order reaction rate, $K_{fa}$; (2) the source release rate, $m_i$; and (3) the transmissivity values, $T$. We used two plume descriptors, the total plume mass and the plume extent, to examine the sensitivity results. The total plume mass was numerically computed by
integrating the TCE concentration distribution over the entire simulation area. The plume extent was assessed by visually comparing the predicted TCE plume sizes predicted under the different conditions. A contour level of 10 µg/l was used to delineate the TCE plume. The calibrated model parameters were used as the baseline values in all sensitivity analyses. Simulations were completed by perturbing one of the three selected parameters by 50% above or below its baseline value while maintaining all other parameters at the baseline value. To perturb the TCE anaerobic decay rate or
transmissivity values, the values of one of these parameters were either increased or decreased (by ±50%) at every nodal point throughout the entire simulation domain. To perturb source strengths, the contaminant mass release rates at all source locations were either increased or decreased by ±50%. Results of the sensitivity simulations were examined after a 32-year simulation time period. This shorter simulation time was selected for all sensitivity simulations to ensure that the simulated TCE plumes
particularly the plume simulated with higher transmissivity values) were contained within the study domain; this helped us compare visually the sensitivity results of predicted plume boundaries.

The sensitivity of the TCE plume extent to changes in different model parameters is illustrated in Fig. 13. It can be observed from this figure that the plume extent is most sensitive to changes in transmissivity values and least sensitive to source release rates. The observed high sensitivity to transmissivity values is, to some extent, due to the
Fig. 13. Sensitivity of the TCE plume extent to changes in model parameters.
Table 4
Sensitivity of TCE plume mass to changes in model parameters

<table>
<thead>
<tr>
<th></th>
<th>Mass at 50% of baseline value (kg)</th>
<th>Mass at the baseline value (kg)</th>
<th>Mass at 150% of baseline value (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First-order TCE decay rate, $K_T$</td>
<td>4222</td>
<td>1689</td>
<td>796</td>
</tr>
<tr>
<td>Source mass release rate, $m$</td>
<td>804</td>
<td>2472</td>
<td></td>
</tr>
<tr>
<td>Transmissivity, $T$</td>
<td>1710</td>
<td></td>
<td>1773</td>
</tr>
</tbody>
</table>

assumed fixed head boundary conditions used in the flow model. By forcing the flow model to have constant head boundaries, we have constrained the hydraulic gradient, and hence, any changes in transmissivity would have automatically changed the net groundwater flux through the system. Therefore, the transmissivity sensitivity simulations may be considered as sensitivity simulations to changes in the overall groundwater budget.

Table 4 shows the values of model-computed TCE mass for all sensitivity simulations. The mass-balance results shown in the table indicate that the integrated TCE plume mass is most sensitive to changes in $K_T$ values and least sensitive to changes in transmissivity values. It is interesting to note that when considering sensitivity with respect to the plume extent, transmissivity is the most sensitive parameter; whereas, when considering sensitivity with respect to the plume mass, $K_T$ is the most sensitive parameter, and transmissivity is the least sensitive parameter. These sensitivity results demonstrate the importance of constraining the calibration problem to simultaneously fit the mass-balance estimates and observed plume shapes.

7. Discussion

A comprehensive, multi-species, biodegradation reaction model was developed for modeling the natural attenuation processes occurring at a chlorinated solvent release site. The model was integrated within the numerical framework of the reactive transport code RT3D. The integrated model is a useful tool for simulating the fate and transport of chlorinated solvent chemicals in saturated groundwater systems. The numerical model allows for the simulation of simultaneously occurring aerobic and anaerobic biological degradation processes. The model was designed to be general enough to describe spatial variations in reaction patterns to describe aerobic and anaerobic reaction zones.

The computer model was applied at a chlorinated solvent natural attenuation study site in Dover Air Force Base, Delaware. The flow and transport models were calibrated to reflect the field conditions observed at the site. The model successfully recreated the flow conditions observed at the site. In addition, the concentration distribution of PCE, TCE, DCE, VC, and chloride plumes predicted by the model matched the observed data
reasonably well. The field-scale degradation parameters estimated via the model calibration process were within the range of values measured by other laboratory and field methods. Since the calibration exercise was restricted to simultaneously satisfy several constraints, which were based on the measured site data, the estimated biodegradation rates can be considered as reasonable values for the Dover AFB site.

Sensitivity analysis was completed to understand the sensitivity of the model parameters. Detailed analyses were restricted to the TCE plume, the largest plume present at the site and also controls the fate and transport of other byproduct plumes. Preliminary screening simulations indicated that the degradation rate of TCE, source loading rate, and transmissivity values were the three most critical model parameters that affect TCE plume migration patterns. Further analysis of the model results indicated that the size of the TCE plume is most sensitive to transmissivity and least sensitive to source loading rates, whereas the total mass of the TCE plume is most sensitive to the decay rates and least sensitive to transmissivity values.

The numerical model constructed for this study is a simplified mathematical approximation of a complex bio/geo-chemically mediated reactive transport system. The purpose of the present study has been limited to the development and application of a simple reactive transport model for the chlorinated solvent natural attenuation problem. Considering the complexity of the problem, the proposed model should be considered as a preliminary effort to simulate a complex multi-species transport system. No effort was made to apply the model for predictive purposes; and this study has been restricted to predicting the observed plume conditions. The purpose of this “historical-data matching effort” was to explore the ability of the proposed methodology to establish a cause-effect connection between the historical sources and hydrogeochemical site conditions. Clearly, much work needs to be done to further improve the predictive capability of the reactive transport model. Nevertheless, the model description developed in this study has been shown as a useful rational framework for integrating various types of natural attenuation data collected at a chlorinated solvent release site. The results of the model simulations can be used for understanding the efficacy of natural attenuation and for studying the relative importance of various simultaneously occurring field-scale attenuation processes.

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