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RT3D Reaction Modules for Natural and Enhanced Attenuation of Chloroethanes, Chloroethenes, Chloromethanes, and Daughter Products

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Summary

This document describes a suite of Monitored Natural Attenuation/Enhanced Attenuation (MNA/EA) reaction modules that were developed for addressing complex chlorinated solvent reactions using the RT3D numerical solute transport code. As an introduction, an overview of these MNA/EA reaction modules is presented, including discussions of similarities between reaction modules, the purpose of key reaction parameters, and important considerations for using the reaction modules. Subsequent sections provide the details of the reaction kinetics (conceptual model and equations), data input requirements, and example (batch reactor) results for each reaction module. This document does not discuss reaction module implementation or validation; such information will accompany the software in the form of release notes or a supplement to the RT3D manual.

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1.0   Introduction

Monitored Natural Attenuation (MNA) is an environmental management strategy that relies on a variety of attenuation processes to destroy, transform, or immobilize contaminants and is implemented at appropriate sites by demonstrating that contaminant plumes have low risk and are either stable or shrinking. Numerical modelling can be one component of an assessment of MNA or Enhanced Attenuation (EA) (i.e., if MNA is not a viable single remedy). Numerical reactive transport modelling provides a tool with which to quantify the relative stability of a contaminant plume, particularly in cases where simpler evaluations are not suitable because of complex hydrology, past activity at the site, multiple contaminant sources, and/or complex reaction of multiple species. Selection of an appropriate model configuration to represent spatial and temporal variations in site-specific attenuation processes can facilitate assessment of the contaminant loading and attenuation capacity (i.e., mass balance) at the site.

RT3D is a numerical code for simulating three-dimensional multi-species reactive transport in groundwater for a user-configured site model [Clement, 1997; Clement et al., 1998; Clement and Johnson, 2002; Johnson et al., 2006]. RT3D can provide information to help analyze the relative importance of different fate and transport processes at an individual site and assess the plume in terms of a mass balance approach. A RT3D model can also be used to estimate the future fate and transport of contaminants. These predictions can be valuable input, along with other site information, in making timely decisions regarding implementation of remedial actions or for planning monitoring activities. A key function of the predictive capability of models is to estimate whether the remedy will meet the remediation goals when this determination cannot be made directly with field data.

The RT3D code solves a system of reactive transport equations for the tracked chemical species using an operator-split strategy to uncouple the advection, dispersion, source/sink mixing, and reaction terms of the governing transport equations [Johnson and Truex, 2006]. These separate terms are encapsulated in so-called "Packages," which delineate portions of the code as well as the required data input. RT3D improved on the publicly available MT3D code (whose more recent versions go by the name MT3DMS [Zheng and Wang, 1999]) by entirely replacing the Reaction Package code. The Reaction Package for RT3D is structured such that the reaction terms split off from the transport equations can be assembled into a reaction module comprised of a set of coupled ordinary differential equations (ODEs). Multiple reaction modules are defined within the RT3D code, with each reaction module encapsulating a set of kinetic equations that describe reaction of specific contaminants. Different approaches for describing contaminant degradation or transformation may be implemented for the same contaminants in different reaction modules.

RT3D versions 1.0 and 2.5 [Clement, 1997; Clement and Johnson, 2002] included a set of general-purpose reaction modules, including BTEX degradation (kinetic and instantaneous), rate-limited sorption, double Monod kinetics, and two simple chlorinated ethene reaction

modules. Additionally, RT3D has the ability to apply any user-defined reaction kinetics. While this user-defined option provides a means to employ more complex chlorinated solvent reaction kinetics, practitioners may not take advantage of this approach for two primary reasons. Users that configure an RT3D model through the graphical interface of a groundwater modelling software package may overlook the potential of the user-defined reaction module option if that option is absent in the graphical interface. Secondly, even when practitioners are aware of the user-defined reaction module option, they may view it as intimidating because it involves writing and compiling Fortran code.

This document describes a suite of MNA/EA reaction modules that were developed for addressing complex chlorinated solvent reactions using RT3D. As an introduction, an overview of these MNA/EA reaction modules is presented, including discussions of similarities between reaction modules, the purpose of key reaction parameters, and important considerations for using the reaction modules. Subsequent sections provide the details of the reaction kinetics (conceptual model and equations), data input requirements, and example (batch reactor) results for each reaction module. This document does not discuss reaction module implementation or validation; such information will accompany the software in the form of release notes or a supplement to the RT3D manual [Clement, 1997].

1.1   Overview of MNA/EA Reaction Modules

Eight RT3D reaction modules were developed for modelling complex chlorinated solvent reaction kinetics as part of evaluating MNA or EA. These eight modules are applicable for simulation of reactive transport of the chlorinated solvent chemicals listed in Table 1. Figure 1 shows the basic decision process for selecting one of these reaction modules for use in assessing MNA applications at a specific site, depending on the contaminant group or groups that are present. In the case where only chloroethenes are of concern, the selection also depends on whether there is enough information and a desire to explicitly model a link between geochemical oxidation/reduction conditions and dechlorination. For MNA/EA sites, chloroethene reductive dechlorination using substrate/biomass-dependent reaction rates or cometabolic aerobic dechlorination can be selected to model the impact of biostimulation on dechlorination. Table 2 summarizes the purpose of the RT3D reaction modules (both the existing ones and those described in this document). Table 2 also lists the total number of chemical species that are tracked, the number of constituents that are in the mobile aqueous phase (versus attached to the immobile soil phase), and the number of reaction parameters required for each reaction module.

Table 1. *Chlorinated Contaminant Species Grouped by Contaminant Type*

	Abbreviation	Contaminant Name (Synonyms)	Chemical Formula	CAS RN [a]	Molecular Weight [b] (g/mol)
Chloroethenes	PCE	Tetrachloroethene (Tetrachloroethylene, Perchloroethene)	$CCl_2=CCl_2$	127-18-4	165.8334
	TCE	Trichloroethene (Trichloroethylene)	$CHCl=CCl_2$	79-01-6	131.38834
	1,2-cis-DCE	cis-1,2-Dichloroethene (cis-1,2- Dichloroethylene, cis-DCE, c-DCE)	$CHCl=CHCl$	156-59-2	96.94328
	1,2-trans-DCE	trans-1,2-Dichloroethene (trans-1,2-Dichloroethylene, trans-DCE, t-DCE)	$CHCl=CHCl$	156-60-5	96.94328
	1,1-DCE	1,1-Dichloroethene (1,1-Dichloroethylene)	$CCl_2=CH_2$	75-35-4	96.94328
	VC	Chloroethene (Vinyl Chloride, Chloroethylene)	$CH_2=CHCl$	75-01-4	62.49822
Chloroethanes	1,1,2,2-TeCA	1,1,2,2-Tetrachloroethane	$CHCl_2-CHCl_2$	79-34-5	167.84928
	1,1,2-TCA	1,1,2-Trichloroethane (Vinyl Trichloride)	$CH_2Cl-CHCl_2$	79-00-5	133.40422
	1,2-DCA	1,2-Dichloroethane (Ethane Dichloride)	CH_2Cl-CH_2Cl	107-06-2	98.95916
	1,1,1,2-TeCA	1,1,1,2-Tetrachloroethane	$CHCl-CCl_3$	630-20-6	167.84928
	1,1,1-TCA	1,1,1-Trichloroethane	CH_3-CCl_3	71-55-6	133.40422
	1,1-DCA	1,1-Dichloroethane	CH_3-CHCl_2	75-34-3	98.95916
	CA	Chloroethane (Ethyl Chloride)	CH_3-CH_2Cl	75-00-3	64.5141
Chloromethanes	CT	Tetrachloromethane (Carbon Tetrachloride)	CCl_4	56-23-5	153.8227
	CF	Trichloromethane (Chloroform)	$CHCl_3$	67-66-3	119.3776
	DCM	Dichloromethane (Methylene Dichloride, Methylene Chloride)	CH_2Cl_2	75-09-2	84.93258
	CM	Chloromethane (Methyl Chloride)	CH_3Cl	74-87-3	50.48752

[a]   CAS = Chemical Abstracts Service (see http://www.cas.org/EO/regsys.html)
[b]   Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

Contaminants of Concern

Mixture of chloroethanes, chloroethenes, and/or chloromethanes

Chloromethanes Only

Chloroethanes (with or without chloroethenes)

Chloroethenes Only

Mixed Chlorinated Solvent Dechlorination
first-order reaction rates

Chloromethane Dechlorination
first-order reaction rates

1,1,2,2-TeCA Isomer?

Yes

No

Have detailed geochemical information? — Yes →

Redox-Linked Dechlorination of Chloroethenes
first-order reaction rates linked to geochemical indicator species

No

Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes
first-order reaction rates

Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes
first-order reaction rates

*Added substrate to enhance **anaerobic** bioactivity?* — Yes →

Substrate-Linked Reductive Dechlorination of Chloroethenes
dechlorination rates linked to substrate metabolism

No

Chloroethene Dechlorination
first-order reaction rates

← No —

*Added substrate to enhance **aerobic** bioactivity?* — Yes →

Cometabolic Aerobic Dechlorination of Chloroethenes
dechlorination rates linked to methanotroph activity

Figure 1. *Flowchart Depicting the Logic for Selection of RT3D MNA/EA Reaction Modules Based on the Contaminant(s) Present, What Data is Available, and the MNA/EA Scenario under Consideration*

Table 2. *Summary of RT3D Reaction Modules (Existing and New)*

Existing [a]	RT3D Reaction Module	Brief Description / Purpose	NCOMP (MCOMP) [b]	Number of Reaction Parameters [c]
♦	**No Reaction**	Simulation of non-reactive tracer.	user specified	0
♦	**Two-Species Instantaneous Reactions**	Instantaneous stoichiometric consumption of electron donor (e.g. hydrocarbon) and electron acceptor (e.g., oxygen) in each transport time step. BIOPLUME-II type reactions.	2 (2)	1
♦	**Six Species, First-Order, Rate-Limited, BTEX Degradation using Sequential Electron Acceptors**	First-order degradation of electron donor (e.g., BTEX) under up to six electron acceptor regimes, each with it's own reaction rate. Electron acceptors are utilized in a sequential manner in the order of O_2, NO_3^-, Fe^{2+}, SO_4^{2-}, and CO_2 (i.e., oxygen is the preferred electron acceptor until it is consumed, then the nitrate regime controls, and so on).	6 (6)	21

Table 2. (contd)

Existing [a]	RT3D Reaction Module	Brief Description / Purpose	NCOMP (MCOMP) [b]	Number of Reaction Parameters [c]
♦	**Rate-Limited Sorption**	Sorption is represented as a mass transfer-limited process that is a function of a mass transfer rate and the concentration driving force between aqueous and adsorbed phases. Equilibrium adsorption should not be used concurrently with this reaction module. No degradation is included in this reaction module, only the rate-limited sorption.	2 (1)	2
♦	**Double Monod Model**	Reaction between an electron donor and an electron acceptor that is mediated by actively growing and decaying bacteria. Bacteria are present in both aqueous and soil phases, where transfer between phases is based on first-order kinetic expressions. No specific microscopic biomass structure is assumed, and diffusional limitations across any soil phase biofilm are neglected. Permeability and porosity changes caused by bacterial growth are not accounted for in this reaction module.	4 (3)	8
♦	**Sequential First-Order Decay**	Sequential degradation reactions for up to 4 chemical species using first-order reaction kinetics (e.g., PCE → TCE → DCE → VC).	4 (4)	7
♦	**Aerobic/Anaerobic PCE/TCE Dechlorination**	Degradation of chlorinated ethenes (PCE, TCE, DCE, and VC) via both aerobic and anaerobic pathways, which are described with first-order reaction kinetics.	6 (6)	9
♦	**User-Defined Kinetics**	User-specified reaction kinetics. Any suitable/appropriate reaction kinetics may be described and implemented with this reaction module using the approach described in the RT3D manual [Clement, 1997].	user specified; limited to 100 species	user specified; limited to 100 parameters
	Mixed Chloroethene/ Chloroethane/ Chloromethane Dechlorination	Dechlorination of a mixture of chloroethene, chloroethane, and chloromethane compounds using first-order rate expressions. This reaction module includes aerobic, anoxic/anaerobic, and abiotic reactions.	18 (18)	53
	Chloromethane Dechlorination	Dechlorination of chloromethane compounds using first-order rate expressions. This reaction module includes aerobic, anoxic/anaerobic, and abiotic reactions.	5 (5)	9
	Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes	Dechlorination of 1,1,2,2-tetrachloroethane and chloroethenes using first-order rate expressions. Includes 1,1,2-TCA and 1,2-DCA. This reaction module includes aerobic, anoxic/anaerobic, and abiotic reactions.	11 (11)	35

Table 2. *(contd)*

Existing[a]	RT3D Reaction Module	Brief Description / Purpose	NCOMP (MCOMP)[b]	Number of Reaction Parameters[c]
	Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes	Dechlorination of 1,1,1,2-tetrachloroethane and chloro-ethenes using first-order rate expressions. Includes 1,1,1-TCA and 1,1-DCA. This reaction module includes aerobic, anoxic/anaerobic, and abiotic reactions.	11 (11)	28
	Chloroethene Dechlorination	Dechlorination of chloroethene compounds using first-order rate expressions. All DCE isomers are included and additional pathways are represented (as compared to the Aerobic/Anaerobic PCE/TCE Dechlorination reaction module). This module includes aerobic and anoxic/anaerobic reactions (abiotic reactions are negligible for chlorinated ethenes).	7 (7)	16
	Redox-Linked Dechlorination of Chloroethenes	Dechlorination of chloroethene compounds using first-order rate expressions. This module includes aerobic and anoxic/anaerobic reactions, where the rate of these reactions is controlled by the oxidation/reduction conditions in the aquifer. Oxygen, nitrate, iron, sulfate/sulfide, and methane are used as indicator compounds to define the geochemical conditions. The user may choose to fix the spatial distribution of the geochemical indicator concentrations or allow the geochemical indicator compounds to undergo oxidation/reduction to give a time-varying spatial distribution of geochemical conditions.	15 (14)	39
	Substrate-Linked Reductive Dechlorination of Chloroethenes	Reductive dechlorination of chloroethene compounds using substrate/biomass-dependent reaction rates. The rates of dechlorination reactions are dependent on substrate (lactate) consumption and microbial growth.	15 (12)	44
	Cometabolic Aerobic Dechlorination of Chloroethenes	Cometabolic dechlorination of TCE, DCE isomers, and VC by methanotrophic bacteria. The rate of dechlorination is dependent on the rate of methane consumption and microbial growth.	8 (6)	18

[a] These reaction modules (marked with a ♦) were available beginning with RT3D version 1.0 [Clement, 1997].
[b] NCOMP is the total number of chemical compounds that are tracked and MCOMP is the number of chemical compounds that are mobile (aqueous phase species).
[c] Reaction parameters must all be of the same type, with either a constant value for all spatial locations or with a variable distribution through the spatial domain.

Five of the RT3D MNA/EA reaction modules represent the dechlorination reaction pathways for various mixtures of chlorinated ethenes, chlorinated ethanes, and chlorinated methanes. The complex network of biological and abiotic reaction pathways that are represented in these modules are depicted in Figure 2. The five reaction modules represent (1) the full reaction pathway network, (2) the chlorinated methanes only, (3) the 1,1,2,2-TeCA/PCE contaminant families, (4) the 1,1,1,2-TeCA/PCE contaminant families, and (5) the chlorinated ethenes only. The reaction network does not include heterogeneous abiotic reactions or abiotic reactions with half-lives of more than 200 years. Because these reaction modules target MNA conditions, cometabolism pathways (aerobic or anaerobic) are also not included.
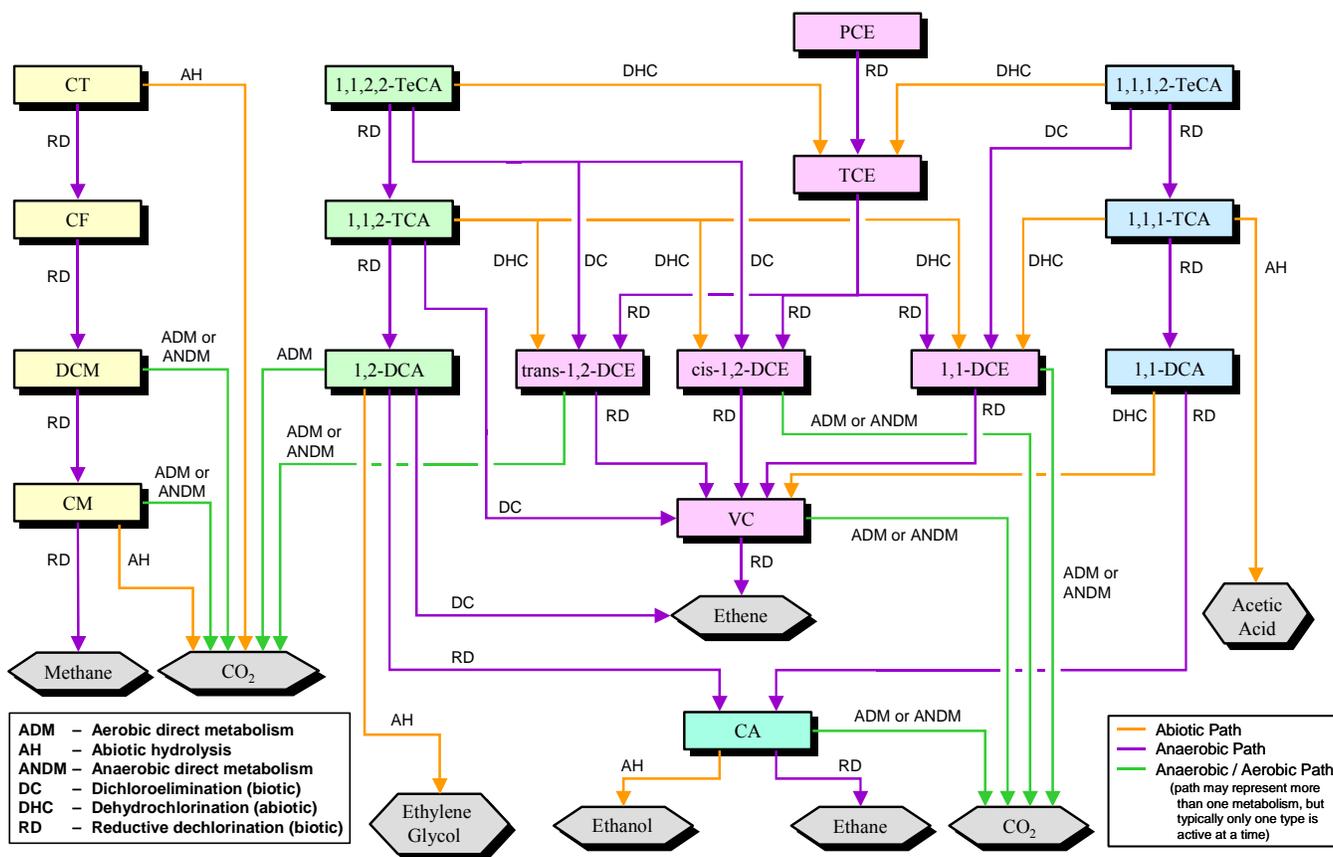
Figure 2. *Reaction Pathway Network for Chlorinated Ethenes, Ethanes, and Methanes — Heterogeneous abiotic reactions, abiotic pathways with a half-life greater than 200 years, and cometabolic reaction pathways are not included.*

Aerobic, anoxic, and anaerobic biological reaction pathways/conditions are all represented using first-order rate expressions. Table 3 describes the types of reaction processes that are noted for the pathways in Figure 2. The spatial distribution of a degradation regime (i.e., aerobic, anoxic, anaerobic, etc.) is delineated via user-specified zones within the RT3D model [e.g., Johnson et al., 2003a; Clement et al., 2000]. Reaction rates should be defined for each zone to represent the

expected microbial activity of that zone. The relevant reactions for a specific site (as determined by the user) may include all or some of the reaction pathways available in a reaction module. In zones where a reaction pathway is inactive, the spatially variable rate coefficient (and/or stoichiometric yield) is set to zero. For instance, an aerobic zone may have aerobic rate coefficients set to some appropriate value, while in the same zone the rate coefficients for anaerobic reactions would be zero. These five reaction modules also include first-order rate expressions for the abiotic degradation reactions shown in Figure 2.

Table 3. *Descriptions of Biological and Abiotic Dechlorination Reactions*

Reaction	Abbreviation	Description of Reaction
Aerobic Direct Metabolism	ADM	Use of the chlorinated compound as an electron donor for aerobic metabolism.
Anaerobic Direct Metabolism	ANDM	Use of the chlorinated compound as an electron donor for anaerobic respiration – typically coupled to iron reduction.
Abiotic Hydrolysis	AH	Homogeneous abiotic dechlorination as an initial reaction step – no specific reaction for this classification. The primary end product of this pathway is shown, omitting intermediate reaction steps.
Dichloroelimination (vicinal reduction)	DC	Dechlorination of a compound where the compound is used as an electron acceptor, the bacteria may or may not gain energy by reduction of the compound. This reaction removes two chloride atoms in an elimination reaction. The more general term for this reaction is dihaloelimination.
Dehydrochlorination	DHC	This reaction removes one chloride atom and one proton in an elimination reaction. This reaction is usually referred to as abiotic, but studies indicate that the reaction can be enhanced/catalyzed by bacteria [e.g., Maymó-Gatell et al., 1999] and/or minerals (e.g., clay) [e.g., Cervini-Silva et al., 2003]. The more general term for this reaction is dehydrohalogenation. Sometimes this type of reaction is referred to as dehydrodehalogenation.
Reductive Dechlorination (hydrogenolysis)	RD	Dechlorination of a compound where the compound is used as an electron acceptor, the bacteria may or may not gain energy by reduction of the compound. This reaction removes one chloride atom from the compound and replaces it with a proton.

As an alternative to defining fixed spatial zones of activity, a reaction module is provided for first-order dechlorination of chlorinated ethenes by natural attenuation processes where the pathways and rates of transformation are dependent on the oxidation-reduction (redox) conditions. In the presence of oxygen, the reaction module allows aerobic dechlorination of DCE isomers and VC to occur. However, the presence of oxygen or nitrate inhibits the anoxic/anaerobic dechlorination pathways of the reaction module. At low oxygen concentrations, the dominant redox condition for the reaction module is determined based on the concentrations of the three key redox couples: iron (ferrous iron/amorphous ferric hydroxide),

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sulfur (sulfate/sulfide), and methane (methane/CO_2). Note that this reaction module does not perform full geochemical equilibrium calculations, but provides a simplified framework to represent the oxidation-reduction conditions in the aquifer. Tracking the redox conditions based on the oxygen, nitrate, iron, sulfur, and methane geochemical indicator species allows the user to model a continuum of reaction regimes whose spatial extent may vary over time as the redox conditions change. Alternately, this reaction module can use a fixed (temporally constant) spatial distribution of dechlorination activity that is defined based on the initial concentrations for the geochemical indicator species.

This redox-dependant reaction module is founded on the assumption that the redox conditions (determined from the key redox couples) control the dechlorination reaction rate. Based on the premise that degradation under natural attenuation conditions occurs as a result of the activity of a widely distributed and essentially constant low concentration population of indigenous bacteria, this reaction module does not track microbial growth. The bacterial species that are active, and hence the rate at which dechlorination occurs, is assumed to be dependent on the geochemical conditions. If sufficient substrate is present at a site to drive bacterial growth dynamics, other reaction modules that consider biomass growth and subsequent impacts to dechlorination rate (e.g., substrate-linked dechlorination) should be used.

Two reaction modules are provided for enhanced attenuation (or accelerated *in situ* bioremediation). Biostimulation through addition of a readily fermentable substrate is a common approach to increase the dechlorination rates. The substrate-linked reaction module provides a method for modelling the biodegradation rate of chlorinated ethenes as a function of the amount of biomass that grows on the supplied substrate. The substrate is represented by lactate, which may be fermented to propionate, acetate, and hydrogen by fermenting bacteria. Methanogenic bacteria, growing on acetate and hydrogen, drive the reductive dechlorination of the chlorinated ethenes in this reaction module.. Because the anaerobic dechlorination reaction rates are linked to the microbial population, the rates are inherently based on a spatially variable continuum. Aerobic direct metabolism of DCE and VC is represented using first-order rate expressions

The other enhanced attenuation RT3D reaction module is aerobic cometabolism of chlorinated ethenes (excluding PCE). Cometabolic chlorinated ethene degradation in this reaction module is dependent on the concentration of the chlorinated ethene compound and the concentration of methanotrophic bacteria, is inhibited by methane, requires oxygen, and deactivates biomass (i.e., the module indirectly accounts for destruction of the monooxygenase enzyme by the chlorinated ethene degradation intermediate epoxide compounds). Methanotroph biomass growth occurs in response to the availability of methane and oxygen. As with the substrate-linked reaction module, the dechlorination reaction rates are implicitly spatially variable because of the dependence on the biomass concentration.

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1.2   RT3D MNA/EA Reaction Module Commonalities

Although the MNA/EA reaction modules discussed in this document represent different reaction kinetics, they share certain common features/concepts. These common features are presented in this section.

Every MNA/EA reaction module described in this document is configured for chemical species concentrations in units of mg/L, although the actual kinetic equations are typically based on moles instead of mass. Reaction parameters are requested in convenient units and are internally converted to a molar basis where required.

All of these MNA/EA reaction modules include a conservative tracer as one of the tracked chemical species. This allows the user to assess non-reactive transport without completing a separate model configuration and simulation run. Information on the transport of a conservative tracer can be useful, for example, in the calibration of a model or in assessing "what if" scenarios.

Transformation/degradation reactions of the contaminants (biotic and abiotic) are assumed to occur only for the aqueous phase (dissolved) contaminant mass in all of these MNA/EA reaction modules. Thus, there is no degradation of the sorbed contaminant. This is a conservative assumption in terms of being protective of groundwater receptors. If sorbed-phase contaminant mass is actually degraded for a particular site, then these reaction modules will under predict the rate of mass loss, resulting in a longer transport distance and a longer remediation timeframe (depending on the extent of contaminant partitioning to the soil). Modifications to these reaction modules could be completed to provide a user-defined reaction module that explicitly tracks sorbed-phase contaminants and allows the sorbed phase contaminants to be degraded. Note that this assumption of reaction only for dissolved phase contaminant mass does not imply anything about the nature of the microbial population mediating the degradation (i.e., it does not imply that only aqueous phase microbes act on contaminants while attached microbes do nothing). However, the two Enhanced Attenuation reaction modules explicitly track microbial biomass as attached (immobile) constituents, ignoring the effects of any free-living (suspended) bacteria. While not included in these reaction modules, the impact of attached versus free-living bacteria is an area of ongoing research [e.g., Harvey and Barber, 1992; Holm et al., 1992; Doong et al., 1997; Lehman et al., 2001; Yolcubal et al., 2002; Painter et al., 2005] that could be explored through a user-defined reaction module.

For internal program consistency, the reaction parameters for these MNA/EA reaction modules must be specified in a model configuration as being either all spatially constant or all spatially variable. To implement spatial variability, reaction parameters are allowed to vary within the full 3D reactive transport model domain on a grid cell by grid cell basis.

These RT3D MNA/EA reaction modules provide a framework for modelling the reaction kinetics at a particular site. Site-specific knowledge from field data and/or laboratory tests should be applied to determine an appropriate model configuration for reaction parameter values. In the absence of site-specific information, generic data or ranges of values from the open literature may be acceptable, but the potential impact of such non-site-specific data on the model output should be discussed.

1.3   Discussion of Select Reaction Parameters

Stoichiometric dechlorination yields and reaction rate constants are reaction parameters that are used throughout the MNA/EA reaction modules. Other reaction parameters (such as Monod half saturation constants, inhibition constants, etc.) are more specific to the kinetic formulations of particular reaction modules. The document sections for individual reaction modules include information on all reaction parameters required for that reaction module, but the more common kinds of reaction parameters are described here to give a general sense of the purpose of the parameters.

Stoichiometric dechlorination yields are used in the reaction kinetics to represent the mole fraction of a product (daughter species) produced for every mole of reactant (parent) species transformed by a specific process (i.e., anaerobic dechlorination or abiotic degradation). Stoichiometric yields are constrained to sum up to 1.0 for reaction of a given parent species by a particular type of process. Note however, that some stoichiometric yield values may not be included as a user-specified reaction parameter because the daughter species (e.g., CO_2) is not explicitly tracked. While all pathways in Figure 2 are possible, some may not occur at a particular site, in which case the stoichiometric dechlorination yield is assigned a value of zero for the inactive pathway. Truex et al. [2002a] provide an example (in a user-defined reaction module) where reductive dechlorination pathways for 1,1,2,2-TeCA and 1,1,2-TCA were not included because those pathways were not observed in microcosm tests with site sediment and groundwater. In cases where there is only one reaction pathway (e.g., reductive dechlorination of PCE to TCE), the stoichiometric dechlorination yield is fixed internal to the reaction module at a value of 1.0 (i.e., the value cannot be altered by the user in the model configuration).

As an example of stoichiometric dechlorination yields, consider dechlorination of 1,1,2-TCA, which may be dechlorinated by both anaerobic and abiotic processes. Table 4 shows the calculated stoichiometric dechlorination yields for a scenario in which a total of 1.5 moles of 1,1,2-TCA are transformed to daughter products in the stated amounts (columns 1 and 2). This type of data (used to determine the stoichiometric dechlorination yield) is typically collected from site-specific microcosms or from literature data. For a microcosm test, the stoichiometric dechlorination yields would be determined along with the site-specific reaction rates by adjusting parameters to fit microcosm data from multiple experiments (i.e., differing conditions, not just replicates).

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Table 4. *Example of Stoichiometric Dechlorination Yield Resulting From Transformation of 1.5 Moles of 1,1,2-TCA*

Daughter Species	Moles Produced [a]	Reaction Type [b]	Calculated Stoichiometric Dechlorination Yield (mol/mol)	Comments
cis-DCE	0.36	abiotic (AE)	$Fab_{cDCE/112TCA} = 0.6$	Sum of Yields equals 100%
trans-DCE	0.24	abiotic (AE)	$Fab_{tDCE/112TCA} = 0.4$	
1,1-DCE	0.0	abiotic (AE)	$Fab_{11DCE/112TCA} = 0.0$	
1,2-DCA	0.18	anaerobic (RD)	$Fan_{11DCA/112TCA} = 0.2$	Sum of Yields equals 100%
VC	0.72	anaerobic (DC)	$Fan_{VC/112TCA} = 0.8$	
Total Moles:	1.5			

[a] These are purely arbitrary numbers for use in this example.
[b] See Table 3 for a list of reaction types and abbreviations.

As with the stoichiometric dechlorination yields, the reaction rates are generally site specific, although abiotic reaction rates may tend to be more consistent from site to site. Abiotic reaction rates are primarily dependent on the temperature and pH of the groundwater, while biotic reaction rates are a function of the microbial population and geochemical setting. Many of the reactions in these reaction modules assume that the biological (and abiotic) dechlorination rates can be modeled as first-order processes, implying that the biomass concentration stays constant and electron donor concentration is low (both reasonable assumptions for a MNA site). See the section on the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module for further discussion of first-order reaction kinetics.

Dechlorination rates for reactant species are determined from the overall rate at which the compound is decaying under defined conditions, coupled with the amounts of product species that are produced. Field data may be used to determine reaction rates, depending on the history of site activities and how well the subsurface is understood in terms of groundwater flow, dispersion, and adsorption. Laboratory microcosm data from multiple experiments with differing initial conditions can be used to fit the reaction rate parameters and the stoichiometric dechlorination yields. Laboratory microcosm experiments with site sediment and groundwater are useful to examine the reaction kinetics without the convoluting influences of contaminant transport processes (e.g., advection and dispersion). Typically the resultant set of reaction rate parameter values from this calibration against microcosm data will be higher than the rates seen in the field because of differences in the soil/water ratio, temperature, and the disturbed/undisturbed nature of the sediment. However, it may be reasonable to assume that the relative rates of different reaction processes (e.g., the rate of CT transformation relative to the

rate of CF transformation) consistent between the laboratory and the field. It is then necessary as part of the calibration process for the full three-dimensional reactive transport model to estimate if and what magnitude of a correction factor between the laboratory-derived rates and the rates in the field is required.

Several reaction modules use Monod half saturation constants (e.g., K_s) and/or inhibition coefficients (e.g., k_{is}) in the functional forms shown in Equations 1 and 2 for Monod and inhibition terms, respectively. The constants represent the point in a hyperbolic curve where the ordinate has a value of 0.5. Figure 3 shows example curves (with arbitrary data) for a Monod term and an inhibition term, both with constants of 5.0. These terms are used as multipliers on the kinetic equations regarding bacterial growth rate or dechlorination rate. The Monod term is typically used to account for nutrient limitations – as the concentration of a nutrient decreases, the rate of reaction will decrease. Conversely, the inhibition term restricts the rate of reaction as the concentration of an inhibiting species increases. Lu et al. [1999] provide an example usage of these types of terms for modelling BTEX biodegradation.

$$Monod\ Term \Rightarrow \frac{[Species]}{K_s + [Species]} \qquad (1)$$

$$Inhibition\ Term \Rightarrow \frac{k_{is}}{k_{is} + [Species]} \qquad (2)$$
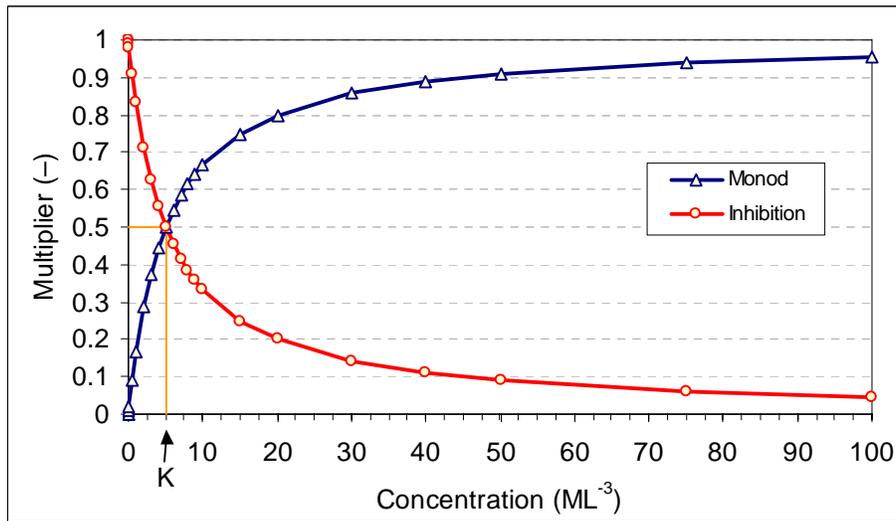
Figure 3. *Arbitrary Examples of the Curves Obtained for Monod and Inhibition Terms — These terms are typically used as multipliers on the reaction rate to account for nutrient limitations and inhibition effects, respectively.*

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Reaction parameters may be defined as spatially constant or spatially variable, depending on site conditions and the available information. For instance, if multiple geochemical settings (as discussed in Johnson et al. [2006]) are identified within the model domain, the parameters in one area can be set to different values than for another area. Reaction parameter values can vary spatially because of differences in geochemistry (e.g., concentrations/types of electron acceptors, anaerobic/anoxic/aerobic setting), temperature, substrate availability, and microbial population (in terms of both numbers of bacteria and types of bacteria). Field-scale geochemical data can be used to assign spatially variable reaction rates to account for variations in biological activity resulting from differences in, for example, substrate or electron acceptor concentrations. Alternately, laboratory microcosm data from different areas of a site may suggest different reaction rates/processes.

Where a reaction pathway is inappropriate for a given spatial location, the dechlorination rate and/or the stoichiometric dechlorination yield for that pathway can be set to zero. Alternately, a specific location may exhibit the reaction pathway, but at a slower rate than another location. Figure 4 shows an example of a reactive transport model having four different reaction zones. In this example, the "Anaerobic Zone-1" has a high anaerobic dechlorination rate and no aerobic reactions occur, "Anaerobic Zone-2" has a lower anaerobic dechlorination rate and no aerobic reactions occur, the "Transition Zone" has a low rates for both anaerobic and aerobic processes, and in the "Aerobic Zone" there is a high rate of aerobic dechlorination and zero anaerobic dechlorination. See Clement et al. [2000] and Johnson et al. [2003a] for examples of applying this zonal approach to specifying reaction parameter values for reactive transport models of actual field sites.
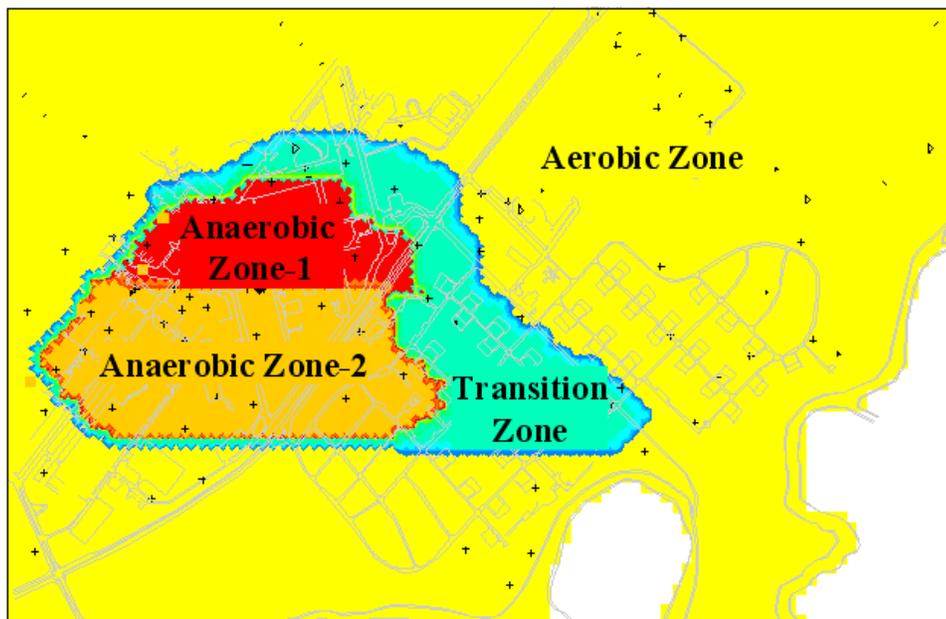
Figure 4. *Example of a Reactive Transport Model Having Multiple Reaction Zones, Each with Differing Reaction Parameter Values — Figure adapted from Clement et al. [2000].*

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1.4 Important Considerations for Using the RT3D MNA/EA Reaction Modules

The RT3D MNA/EA reaction modules described in this document were developed to provide ready access to more complex reaction scenarios that may be of interest for monitored natural attenuation or enhanced attenuation modelling evaluations. Each of these reaction modules has a clearly stated set of kinetic expressions and associated reaction parameters that incorporate certain assumptions and define one specific approach to representing the stated scenario. In some ways, these reaction modules were designed to provide flexibility in modelling potential complex reaction kinetics. For example, the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes reaction module includes many reaction pathways, but some number of those pathways may not be needed for a particular site while they are at yet another site. In other ways, the reaction modules represent specific conceptual models, such as the assumption of first-order kinetics (e.g., Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination) or the linkage of dechlorination rates to the rate of methanogenesis (Substrate-Linked Reductive Dechlorination of Chloroethenes). The user should read this document and fully understand the scope of a given reaction module, including the assumptions and limitations corresponding to the conceptual model/approach. The approach taken here for a given reaction module is only one way of addressing a reaction scenario and may or may not be appropriate for any specific site. *It is incumbent on the practitioner to assess the suitability of any RT3D reaction module for a particular application. Additionally, testing and validation of the reaction modules is not included in this report and is the responsibility of the module user.*

The descriptions of the MNA/EA reaction modules are written to explain the kinetic expressions that are used in the modules and are in no way intended to imply or assert that these approaches are the "right" or "best" way to represent the reaction kinetics. However, the authors propose that these reaction modules may be useful for MNA/EA at some sites. Indeed, the authors have successfully used prototypes of several of these reaction modules at field sites. A prototype of the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes reaction module was used to evaluate MNA for a multicomponent dissolved-phase contaminant plume at a National Priorities List site in Louisiana [Truex et al., 2002; Spencer et al., 2002]. Design of an anaerobic accelerated *in situ* bioremediation system at a U.S. Navy facility in California [Johnson et al., 1999; Leigh et al., 2000] was completed with a prototype of the Substrate-Linked Reductive Dechlorination of Chloroethenes reaction module. The rate of vinyl chloride degradation by anaerobic processes at this U.S. Navy facility was determined to be too slow for the site objectives, thus a prototype of the Cometabolic Aerobic Dechlorination of Chloroethenes reaction module was used to design an aerobic accelerated *in situ* bioremediation system [Truex et al., 2002b; Johnson et al., 2003b] for sequential anaerobic/aerobic treatment of the site.

In addition to prototype kinetic formulations, the basis of the MNA/EA reaction modules also included literature information and simplified conceptual models to describe the impact of complex processes such as geochemistry on dechlorination. The five RT3D MNA/EA reaction

modules using first-order reaction kinetic expressions to model dechlorination were configured based on a review of literature to define potential dechlorination reaction mechanisms [Johnson et al., 2006]. The literature review was not intended to be exhaustive, but provides examples of laboratory information that is available to describe the reaction pathways. In the Redox-Linked Dechlorination of Chloroethenes reaction module, the rate of dechlorination is adjusted based on a simplified framework to represent the oxidation-reduction conditions in the aquifer. This module enables the user to link dechlorination rate to the concentration of geochemical indicator species. The module is not a full geochemical model, but provides one potential means for the user to model dechlorination at sites where the oxidation-reduction conditions in the aquifer are spatially or temporally variable. While there are multiple ways to model substrate-linked reductive dechlorination, the Substrate-Linked Reductive Dechlorination of Chloroethenes reaction module specifically links the dechlorination rate to the activity of methanogenic bacteria, similar to Skeen et al. [1995]. The activity of methanogenic bacteria in this reaction module is dependent on the availability of acetate and hydrogen produced from the fermentation of lactate and propionate by other bacteria. The Cometabolic Aerobic Dechlorination of Chloroethenes reaction module uses kinetic expressions from the scientific literature [e.g., Semprini et al., 1991; Alvarez-Cohen and McCarty, 1991; Chang and Alvarez-Cohen, 1996] that describe the cometabolic degradation process with inhibition by methane and with the toxicity effect of the intermediate degradation product on the methanotrophic bacteria.

Example results representing reaction in a batch reactor are provided in this document for all of the MNA/EA reaction modules. These examples demonstrate that the expected behavior is observed under selected conditions. However, it was beyond the scope of the development effort to rigorously test these MNA/EA reaction modules and benchmark them against other numerical codes, analytical solutions, or existing field data. This exercise is left to the practitioner as part of the assessment whether these reaction modules are appropriate for a particular site. The authors intend that future efforts will address these testing and validation issues.

If the conceptual model and/or kinetic expressions of an RT3D reaction module are deemed insufficient or unsuitable for application at a given site, then the user has the option of writing a user-defined reaction module to provide the desired configuration of the kinetic expressions. The user may find that an existing reaction module can serve as a convenient starting point for making modifications. For example, additional reaction mechanisms/pathways that are not currently included in the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module may be identified in the future as valid degradation routes, and the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module could be supplemented with the new pathway(s) to form a user-defined reaction module. The RT3D manual [Clement, 1997] and version 2.5 update document [Clement and Johnson, 2002] provide information on assembling a user-defined reaction module. Alternately, the authors can be contacted for assistance in developing a new reaction module.

2.0 Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination

2.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of chloroethanes, chloroethenes, chloromethanes, and related daughter products using first-order rate expressions. The module includes abiotic, aerobic, and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 5 lists the chemical species included in this reaction module. Figure 5 shows the conceptual model describing the potential biotic and abiotic degradation pathways of both chlorinated ethene and chlorinated ethane contaminants.

The reaction pathways included in this reaction module are based on a review of literature on dechlorination reaction mechanisms for the chlorinated solvents of interest [Johnson et al., 2006]. The literature review was not intended to be exhaustive, but provides examples of laboratory information that is available to describe the reaction pathways. For convenience, a select set of references that discuss abiotic and biotic reaction pathways for chlorinated solvents are noted in this document [Mabey and Mill, 1978; Vogel et al., 1987; Jeffers et al., 1989; Washington, 1995; Chen et al., 1996; Jeffers et al., 1996; Jeffers and Wolfe, 1996; Lorah and Olsen, 1999; Truex et al., 2001; De Wildeman and Verstraete, 2003; Lorah and Voytek, 2004; Hunkeler et al., 2005]. To make this reaction module more flexible and general, several pathways that were not directly supported by laboratory data in the open literature are included (Table 6). The reaction network does not include heterogeneous abiotic reactions or abiotic reactions with half-lives of more than 200 years. Because this reaction module targets MNA conditions, non-contaminant substrate concentrations are assumed to be low enough that cometabolism pathways (aerobic or anaerobic) should not be included. If reaction mechanisms/pathways that are not currently included in this reaction module are identified as valid or important degradation routes, then such pathways could be included in a user-defined reaction module based on the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module.

Table 5. *Chemical Species Included in the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module*

No.	Abbreviation [a]	Chemical Name	Selected Alternate Name	CAS [b] Registry Number	Molecular Weight [c] (g/mol)	Chemical Formula
1	1122TeCA	1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	79-34-5	167.84928	$C_2H_2Cl_4$
2	112TCA	1,1,2-Trichloroethane	Vinyl Trichloride; 1,1,2-TCA	79-00-5	133.40422	$C_2H_3Cl_3$
3	12DCA	1,2-Dichloroethane	Ethane Dichloride; 1,2-DCA	107-06-2	98.95916	$C_2H_4Cl_2$
4	CA	Chloroethane	Ethyl Chloride	75-00-3	64.5141	C_2H_5Cl
5	1112TeCA	1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA	630-20-6	167.84928	$C_2H_2Cl_4$
6	111TCA	1,1,1-Trichloroethane	1,1,1-TCA	71-55-6	133.40422	$C_2H_3Cl_3$
7	11DCA	1,1-Dichloroethane	1,1-DCA	75-34-3	98.95916	$C_2H_4Cl_2$
8	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.8334	C_2Cl_4
9	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C_2HCl_3
10	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	$C_2H_2Cl_2$
11	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	$C_2H_2Cl_2$
12	11DCE	1,1-Dichloroethene	1,1-Dichloroethylene; Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	$C_2H_2Cl_2$
13	VC	Chloroethene	Vinyl Chloride; Chloroethylene	75-01-4	62.49822	C_2H_3Cl
14	CT	Tetrachloromethane	Carbon Tetrachloride	56-23-5	153.82270	CCl_4
15	CF	Trichloromethane	Chloroform	67-66-3	119.37764	$CHCl_3$
16	DCM	Dichloromethane	Methylene Dichloride, Methylene Chloride	75-09-2	84.93258	CH_2Cl_2
17	CM	Chloromethane	Methyl Chloride	74-87-3	50.48752	CH_3Cl
18	Tracer	Conservative Tracer	—	N/A	N/A	N/A

[a] These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.
[b] CAS = Chemical Abstracts Service (see http://www.cas.org/EO/regsys.html)
[c] Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].
N/A – Not Applicable

Figure 5. *Conceptual Model for Dechlorination Reactions in the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.*

Table 6. *Reaction Pathways Without Laboratory Data in the Open Literature, but Which Are Included in the RT3D MNA/EA First-Order Reaction Modules*

Reaction Pathway	Reaction Process	Comments
1,1-DCE → CO_2	ANDM	Potential pathway because ANDM occurs for cis/trans-1,2-DCE.
CA → CO_2	ADM	Probable, but not documented pathway based on ADM of VC.
CA → CO_2	ANDM	Probable, but not documented pathway based on ANDM of VC.
1,1,12,2-TeCA → 1,1,1-TCA	RD	This pathway is listed as a presumptive degradation route in the literature review figures [Johnson et al., 2006] despite the lack of laboratory data in the open literature.
CM → CH_4	RD	This pathway is listed as a presumptive degradation route in the literature review figures [Johnson et al., 2006] despite the lack of laboratory data in the open literature.

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The kinetic relations for the reactions in this reaction module were developed by assuming that the dechlorination kinetics can be approximated as first-order reactions. Some previous studies have shown that first-order kinetics can be reasonable for modeling dechlorination mechanisms at field scales [e.g., U.S. EPA, 1998; Clement et al., 2000] and at low concentrations [Schmidt et al., 1985]. Yet other studies [e.g., Scow et al., 1986] have determined that first-order kinetics were not appropriate. A number of factors (substrate concentration, microbial population density, etc.) can impact the type of model (first-order, Monod, logistic, etc.) that best represents biodegradation of a chemical [Simkins and Alexander, 1984; Alexander, 1985; Schmidt et al., 1985]. The first-order assumption should be assessed [e.g., Bekins et al., 1998] as part of the determination of whether the reaction module is suitable for the intended application.

First-order kinetics express the biodegradation rates as being primarily a function of the concentration of the contaminant. Implicit to the assumption of first-order kinetics is that the microbial population is nongrowing, i.e., the substrate concentration is much less than the Monod half saturation constant. First-order kinetics do not have an explicit dependence on the type or concentration of electron donor, the type or quantity of bacteria present, nutrient limitations, or the geochemical conditions. All of these factors should be evaluated prior to selecting a first-order model to represent biodegradation. Additionally, this reaction module does not include a provision for inhibition by the contaminants; the contaminants are assumed to be present at less than inhibitory concentrations.

If a biostimulation or bioaugmentation technique is used at a site (increasing the quantity of subsurface bacteria) then the assumptions associated with first-order kinetics may not be valid and the user should apply something along the lines of one of the EA reaction modules.

2.2 Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 3 to 20. These ODEs describe the reaction kinetics for the 18 chemical species in Table 5. See Table 7 for a detailed itemization of all reaction parameters used in this reaction module.

$$
\frac{dC_{1122TeCA}}{dt} = \left(-kan_{1122TeCA} \cdot C_{1122TeCA} - kab_{1122TeCA} \cdot C_{1122TeCA} \right) \tag{3}
$$

$$
\frac{dC_{1112TeCA}}{dt} = \left(-kan_{1112TeCA} \cdot C_{1112TeCA} - kab_{1112TeCA} \cdot C_{1112TeCA} \right) \tag{4}
$$

$$
\frac{dC_{112TCA}}{dt} = \left(Y_{\frac{112TCA}{1122TeCA}} \cdot Fan_{\frac{112TCA}{1122TeCA}} \cdot kan_{1122TeCA} \cdot C_{1122TeCA} - kan_{112TCA} \cdot C_{112TCA} - kab_{112TCA} \cdot C_{112TCA} \right) \tag{5}
$$

$$\frac{dC_{111TCA}}{dt} = \left(Y_{\frac{111TCA}{1112TeCA}} \cdot Fan_{\frac{111TCA}{1112TeCA}} \cdot kan_{1112TeCA} \cdot C_{1112TeCA} \ - \ kan_{111TCA} \cdot C_{111TCA} \ - \ kab_{111TCA} \cdot C_{111TCA} \right) \quad (6)$$

$$\frac{dC_{12DCA}}{dt} = \left(\begin{array}{l} Y_{\frac{12DCA}{112TCA}} \cdot Fan_{\frac{12DCA}{112TCA}} \cdot kan_{112TCA} \cdot C_{112TCA} \\[2ex] - \ kan_{12DCA} \cdot C_{12DCA} \ - \ kab_{12DCA} \cdot C_{12DCA} \ - \ kae_{12DCA} \cdot C_{12DCA} \end{array} \right) \quad (7)$$

$$\frac{dC_{11DCA}}{dt} = \left(\begin{array}{l} Y_{\frac{11DCA}{111TCA}} \cdot kan_{111TCA} \cdot C_{111TCA} \\[2ex] - \ kan_{11DCA} \cdot C_{11DCA} \ - \ kab_{11DCA} \cdot C_{11DCA} \end{array} \right) \quad (8)$$

$$\frac{dC_{CA}}{dt} = \left(\begin{array}{l} Y_{\frac{CA}{12DCA}} \cdot Fan_{\frac{CA}{12DCA}} \cdot kan_{12DCA} \cdot C_{12DCA} + Y_{\frac{CA}{11DCA}} \cdot kan_{11DCA} \cdot C_{11DCA} \\[2ex] - \ kan_{CA} \cdot C_{CA} \ - \ kab_{CA} \cdot C_{CA} \ - \ kae_{CA} \cdot C_{CA} \end{array} \right) \quad (9)$$

$$\frac{dC_{PCE}}{dt} = \left(\ - kan_{PCE} \cdot C_{PCE} \right) \quad (10)$$

$$\frac{dC_{TCE}}{dt} = \left(\begin{array}{l} Y_{\frac{TCE}{PCE}} \cdot kan_{PCE} \cdot C_{PCE} \ + \ Y_{\frac{TCE}{1122TeCA}} \cdot kab_{1122TeCA} \cdot C_{1122TeCA} \\[2ex] + \ Y_{\frac{TCE}{1112TeCA}} \cdot kab_{1112TeCA} \cdot C_{1112TeCA} \\[2ex] - \ kan_{TCE} \cdot C_{TCE} \end{array} \right) \quad (11)$$

$$\frac{dC_{cDCE}}{dt} = \left(\begin{array}{l} Y_{\frac{DCE}{1122TeCA}} \cdot Fan_{\frac{cDCE}{1122TeCA}} \cdot kan_{1122TeCA} \cdot C_{1122TeCA} \ + \ Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{cDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\[2ex] + \ Y_{\frac{DCE}{112TCA}} \cdot Fab_{\frac{cDCE}{112TCA}} \cdot kab_{112TCA} \cdot C_{112TCA} \\[2ex] - \ kan_{cDCE} \cdot C_{cDCE} \ - \ kae_{cDCE} \cdot C_{cDCE} \end{array} \right) \quad (12)$$

$$\frac{dC_{tDCE}}{dt} = \begin{pmatrix} Y_{\frac{DCE}{1122TeCA}} \cdot Fan_{\frac{tDCE}{1122TeCA}} \cdot kan_{1122TeCA} \cdot C_{1122TeCA} \;+\; Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{tDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\[4mm] +\; Y_{\frac{DCE}{112TCA}} \cdot Fab_{\frac{tDCE}{112TCA}} \cdot kab_{112TCA} \cdot C_{112TCA} \\[4mm] -\; kan_{tDCE} \cdot C_{tDCE} \;-\; kae_{tDCE} \cdot C_{tDCE} \end{pmatrix} \qquad (13)$$

$$\frac{dC_{11DCE}}{dt} = \begin{pmatrix} Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{11DCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \;+\; Y_{\frac{DCE}{112TCA}} \cdot Fan_{\frac{11DCE}{112TCA}} \cdot kan_{112TCA} \cdot C_{112TCA} \\[4mm] +\; Y_{\frac{DCE}{111TCA}} \cdot Fab_{\frac{11DCE}{111TCA}} \cdot kab_{111TCA} \cdot C_{111TCA} \\[4mm] +\; Y_{\frac{DCE}{1112TeCA}} \cdot Fan_{\frac{11DCE}{1112TeCA}} \cdot kan_{1112TeCA} \cdot C_{1112TeCA} \\[4mm] -\; kan_{11DCE} \cdot C_{11DCE} \;-\; kae_{11DCE} \cdot C_{11DCE} \end{pmatrix} \qquad (14)$$

$$\frac{dC_{VC}}{dt} = \begin{pmatrix} Y_{\frac{VC}{112TCA}} \cdot Fan_{\frac{VC}{112TCA}} \cdot kan_{112TCA} \cdot C_{112TCA} \;+\; Y_{\frac{VC}{111TCA}} \cdot Fan_{\frac{VC}{111TCA}} \cdot kan_{111TCA} \cdot C_{111TCA} \\[4mm] +\; Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{cDCE}} \cdot kan_{cDCE} \cdot C_{cDCE} \\[4mm] +\; Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{tDCE}} \cdot kan_{tDCE} \cdot C_{tDCE} \\[4mm] +\; Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{DCE11}} \cdot kan_{DCE11} \cdot C_{DCE11} \\[4mm] +\; Y_{\frac{VC}{11DCA}} \cdot kab_{11DCA} \cdot C_{11DCA} \\[4mm] -\; kan_{VC} \cdot C_{VC} \;-\; kae_{VC} \cdot C_{VC} \end{pmatrix} \qquad (15)$$

$$\frac{dC_{CT}}{dt} = \left(-kan_{CT} \cdot C_{CT} \;-\; kab_{CT} \cdot C_{CT} \right) \qquad (16)$$

$$\frac{dC_{CF}}{dt} = \left(Y_{\frac{CF}{CT}} \cdot kan_{CT} \cdot C_{CT} \;-\; kan_{CF} \cdot C_{CF} \right) \qquad (17)$$

$$\frac{dC_{DCM}}{dt} = \left(\begin{array}{l} \dfrac{Y_{DCM}}{CF} \cdot kan_{CF} \cdot C_{CF} \\[2em] \quad - \; kan_{DCM} \cdot C_{DCM} \quad - \; kae_{DCM} \cdot C_{DCM} \end{array} \right) \tag{18}$$

$$\frac{dC_{CM}}{dt} = \left(\begin{array}{l} \dfrac{Y_{CM}}{DCM} \cdot Fan_{\frac{CM}{DCM}} \cdot kan_{DCM} \cdot C_{DCM} \\[2em] \quad - \; kan_{CM} \cdot C_{CM} \quad - \; kab_{CM} \cdot C_{CM} \quad - \; kae_{CM} \cdot C_{CM} \end{array} \right) \tag{19}$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \qquad \text{\textit{(Conservative [non-reactive] tracer.)}} \tag{20}$$

The first-order decay rate constants $[\text{T}^{-1}]$ of the ith species are represented in the equations above by the kan_i, kae_i, and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the ith species is represented by the C_i term $[\text{ML}^{-3}]$. The R_i terms represent the retardation factor for the ith species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield $[\text{MM}^{-1}]$ and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relations in Equations 21 to 31.

$$Fan_{\frac{112TCA}{1122TeCA}} + Fan_{\frac{cDCE}{1122TeCA}} + Fan_{\frac{tDCE}{1122TeCA}} = 1.0 \tag{21}$$

$$Fan_{\frac{111TCA}{1112TeCA}} + Fan_{\frac{11DCE}{1112TeCA}} = 1.0 \tag{22}$$

$$Fan_{\frac{12DCA}{112TCA}} + Fan_{\frac{VC}{112TCA}} = 1.0 \tag{23}$$

$$Fan_{\frac{cDCE}{TCE}} + Fan_{\frac{tDCE}{TCE}} + Fan_{\frac{11DCE}{TCE}} = 1.0 \tag{24}$$

$$Fab_{\frac{cDCE}{112TCA}} + Fab_{\frac{tDCE}{112TCA}} + Fab_{\frac{11DCE}{112TCA}} = 1.0 \tag{25}$$

$$Fab_{\frac{11DCE}{111TCA}} \leq 1.0 \tag{26}$$

$$Fan_{\frac{CA}{12DCA}} \leq 1.0 \tag{27}$$

$$Fan_{\frac{VC}{cDCE}} \leq 1.0 \tag{28}$$

$$Fan_{\frac{VC}{tDCE}} \leq 1.0 \tag{29}$$

$$Fan_{\frac{VC}{11DCE}} \leq 1.0 \tag{30}$$

$$Fan_{\frac{CM}{DCM}} \leq 1.0 \tag{31}$$

2.3   Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 53 reaction parameters that must be specified for this reaction module are listed in Table 7 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 7. *Input Parameters for the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	$Fab_{\frac{cDCE}{112TCA}}$	fab_cdce_tca2	mol/mol	Moles of cis-1,2-DCE produced from abiotic decay of one mole of 1,1,2-TCA
2	$Fab_{\frac{tDCE}{112TCA}}$	fab_tdce_tca2	mol/mol	Moles of trans-1,2-DCE produced from abiotic decay of one mole of 1,1,2-TCA
3	$Fab_{\frac{11DCE}{112TCA}}$	fab_11dce_tca2	mol/mol	Moles of 1,1-DCE produced from abiotic decay of one mole of 1,1,2-TCA

Table 7. *(contd)*

ID #	Parameter	Fortran Variable	Units	Description
4	$Fab_{\frac{11DCE}{111TCA}}$	fab_11dce_tca1	mol/mol	Moles of 1,1-DCE produced from abiotic decay of one mole of 1,1,1-TCA
5	$Fan_{\frac{112TCA}{1122TeCA}}$	fan_tca2_teca2	mol/mol	Moles of 1,1,2-TCA produced from anaerobic decay of one mole of 1,1,2,2-TeCA
6	$Fan_{\frac{cDCE}{1122TeCA}}$	fan_cdce_teca2	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of 1,1,2,2-TeCA
7	$Fan_{\frac{tDCE}{1122TeCA}}$	fan_tdce_teca2	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of 1,1,2,2-TeCA
8	$Fan_{\frac{12DCA}{112TCA}}$	fan_dca2_tca2	mol/mol	Moles of 1,2-DCA produced from anaerobic decay of one mole of 1,1,2-TCA
9	$Fan_{\frac{VC}{112TCA}}$	fan_vc_tca2	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1,2-TCA
10	$Fan_{\frac{CA}{12DCA}}$	fan_ca_dca2	mol/mol	Moles of CA produced from anaerobic decay of one mole of 1,2-DCA
11	$Fan_{\frac{111TCA}{1112TeCA}}$	fan_tca1_teca1	mol/mol	Moles of 1,1,1-TCA produced from anaerobic decay of one mole of 1,1,1,2-TeCA
12	$Fan_{\frac{11DCE}{1112TeCA}}$	fan_11dce_teca1	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of 1,1,1,2-TeCA
13	$Fan_{\frac{cDCE}{TCE}}$	fan_cdce_tce	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TCE
14	$Fan_{\frac{tDCE}{TCE}}$	fan_tdce_tce	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TCE
15	$Fan_{\frac{11DCE}{TCE}}$	fan_11dce_tce	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TCE
16	$Fan_{\frac{VC}{cDCE}}$	fan_vc_cdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of cis-1,2-DCE
17	$Fan_{\frac{VC}{tDCE}}$	fan_vc_tdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of trans-1,2-DCE
18	$Fan_{\frac{VC}{11DCE}}$	fan_vc_11dce	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1-DCE
19	$Fan_{\frac{CM}{DCM}}$	fan_cm_dcm	mol/mol	Moles of CM produced from anaerobic decay of one mole of DCM
20	$kab_{1122TeCA}$	kab_teca2	1/day	First-order decay coefficient for abiotic dechlorination of 1,1,2,2-TeCA

Table 7. (contd)

ID #	Parameter	Fortran Variable	Units	Description
21	kab_{112TCA}	kab_tca2	1/day	First-order decay coefficient for abiotic dechlorination of 1,1,2-TCA
22	kab_{12DCA}	kab_dca2	1/day	First-order decay coefficient for abiotic dechlorination of 1,2-DCA
23	kab_{CA}	kab_ca	1/day	First-order decay coefficient for abiotic dechlorination of CA
24	$kab_{1112TeCA}$	kab_teca1	1/day	First-order decay coefficient for abiotic dechlorination of 1,1,1,2-TeCA
25	kab_{111TCA}	kab_tca1	1/day	First-order decay coefficient for abiotic dechlorination of 1,1,1-TCA
26	kab_{11DCA}	kab_dca1	1/day	First-order decay coefficient for abiotic dechlorination of 1,1-DCA
27	kab_{CT}	kab_ct	1/day	First-order decay coefficient for abiotic dechlorination of CT
28	kab_{CM}	kab_cm	1/day	First-order decay coefficient for abiotic dechlorination of CM
29	$kan_{1122TeCA}$	kan_teca2	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1,2,2-TeCA
30	kan_{112TCA}	kan_tca2	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1,2-TCA
31	kan_{12DCA}	kan_dca2	1/day	First-order decay coefficient for anaerobic dechlorination of 1,2-DCA
32	kan_{CA}	kan_ca	1/day	First-order decay coefficient for anaerobic dechlorination of CA
33	$kan_{1112TeCA}$	kan_teca1	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1,1,2-TeCA
34	kan_{111TCA}	kan_tca1	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1,1-TCA
35	kan_{11DCA}	kan_dca1	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCA
36	kan_{PCE}	kan_pce	1/day	First-order decay coefficient for anaerobic dechlorination of PCE
37	kan_{TCE}	kan_tce	1/day	First-order decay coefficient for anaerobic dechlorination of TCE
38	kan_{cDCE}	kan_cdce	1/day	First-order decay coefficient for anaerobic dechlorination of cis-1,2-DCE
39	kan_{tDCE}	kan_tdce	1/day	First-order decay coefficient for anaerobic dechlorination of trans-1,2-DCE
40	kan_{11DCE}	kan_11dce	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCE
41	kan_{VC}	kan_vc	1/day	First-order decay coefficient for anaerobic dechlorination of VC

Table 7. *(contd)*

ID #	Parameter	Fortran Variable	Units	Description
42	kan_{CT}	kan_ct	1/day	First-order decay coefficient for anaerobic dechlorination of CT
43	kan_{CF}	kan_cf	1/day	First-order decay coefficient for anaerobic dechlorination of CF
44	kan_{DCM}	kan_dcm	1/day	First-order decay coefficient for anaerobic dechlorination of DCM
45	kan_{CM}	kan_cm	1/day	First-order decay coefficient for anaerobic dechlorination of CM
46	kae_{12DCA}	kae_dca2	1/day	First-order decay coefficient for aerobic dechlorination of DCA
47	kae_{CA}	kae_ca	1/day	First-order decay coefficient for aerobic dechlorination of CA
48	kae_{cDCE}	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
49	kae_{tDCE}	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
50	kae_{11DCE}	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
51	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC
52	kae_{DCM}	kae_dcm	1/day	First-order decay coefficient for aerobic dechlorination of DCM
53	kae_{CM}	kae_cm	1/day	First-order decay coefficient for aerobic dechlorination of CM

2.4   Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 8 through 11. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in Figures 6 through 9, respectively.

Table 8. *Parameter Values for Example Simulation 1 – Anaerobic Conditions – with the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca2	0.2	mol/mol	28	kab_cm	0.000094	1/day
2	fab_tdce_tca2	0.7	mol/mol	29	kan_teca2	0.005	1/day
3	fab_11dce_tca2	0.1	mol/mol	30	kan_tca2	0.01	1/day
4	fab_11dce_tca1	0.2	mol/mol	31	kan_dca2	0.025	1/day
5	fan_tca2_teca2	0.2	mol/mol	32	kan_ca	0.025	1/day
6	fan_cdce_teca2	0.15	mol/mol	33	kan_teca1	0.005	1/day
7	fan_tdce_teca2	0.05	mol/mol	34	kan_tca1	0.01	1/day
8	fan_dca2_tca2	0.2	mol/mol	35	kan_dca1	0.025	1/day
9	fan_vc_tca2	0.8	mol/mol	36	kan_pce	0.025	1/day
10	fan_ca_dca2	0.2	mol/mol	37	kan_tce	0.025	1/day
11	fan_tca1_teca1	0.2	mol/mol	38	kan_cdce	0.025	1/day
12	fan_11dce_teca1	0.8	mol/mol	39	kan_tdce	0.025	1/day
13	fan_cdce_tce	0.8	mol/mol	40	kan_11dce	0.025	1/day
14	fan_tdce_tce	0.2	mol/mol	41	kan_vc	0.0025	1/day
15	fan_11dce_tce	0	mol/mol	42	kan_ct	0.005	1/day
16	fan_vc_cdce	0.8	mol/mol	43	kan_cf	0.0005	1/day
17	fan_vc_tdce	0.8	mol/mol	44	kan_dcm	0.005	1/day
18	fan_vc_11dce	0.8	mol/mol	45	kan_cm	0.005	1/day
19	fan_cm_dcm	0.5	mol/mol	46	kae_dca2	0	1/day
20	kab_teca2	0.006	1/day	47	kae_ca	0	1/day
21	kab_tca2	0.0015	1/day	48	kae_cdce	0	1/day
22	kab_dca2	0.00003	1/day	49	kae_tdce	0	1/day
23	kab_ca	0.001	1/day	50	kae_11dce	0	1/day
24	kab_teca1	0.006	1/day	51	kae_vc	0	1/day
25	kab_tca1	0.001	1/day	52	kae_dcm	0	1/day
26	kab_dca1	0.00005	1/day	53	kae_cm	0	1/day
27	kab_ct	0.000047	1/day				

Table 9. *Parameter Values for Example Simulation 2 – Aerobic Conditions – with the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca2	0.2	mol/mol	28	kab_cm	0.000094	1/day
2	fab_tdce_tca2	0.8	mol/mol	29	kan_teca2	0	1/day
3	fab_11dce_tca2	0.1	mol/mol	30	kan_tca2	0	1/day
4	fab_11dce_tca1	0.2	mol/mol	31	kan_dca2	0	1/day
5	fan_tca2_teca2	0	mol/mol	32	kan_ca	0	1/day
6	fan_cdce_teca2	0	mol/mol	33	kan_teca1	0	1/day
7	fan_tdce_teca2	0	mol/mol	34	kan_tca1	0	1/day
8	fan_dca2_tca2	0	mol/mol	35	kan_dca1	0	1/day
9	fan_vc_tca2	0	mol/mol	36	kan_pce	0	1/day
10	fan_ca_dca2	0	mol/mol	37	kan_tce	0	1/day
11	fan_tca1_teca1	0	mol/mol	38	kan_cdce	0	1/day
12	fan_11dce_teca1	0	mol/mol	39	kan_tdce	0	1/day
13	fan_cdce_tce	0	mol/mol	40	kan_11dce	0	1/day
14	fan_tdce_tce	0	mol/mol	41	kan_vc	0	1/day
15	fan_11dce_tce	0	mol/mol	42	kan_ct	0	1/day
16	fan_vc_cdce	0	mol/mol	43	kan_cf	0	1/day
17	fan_vc_tdce	0	mol/mol	44	kan_dcm	0	1/day
18	fan_vc_11dce	0	mol/mol	45	kan_cm	0	1/day
19	fan_cm_dcm	0	mol/mol	46	kae_dca2	0.005	1/day
20	kab_teca2	0.006	1/day	47	kae_ca	0.005	1/day
21	kab_tca2	0.0015	1/day	48	kae_cdce	0.005	1/day
22	kab_dca2	0.00003	1/day	49	kae_tdce	0.005	1/day
23	kab_ca	0.001	1/day	50	kae_11dce	0.005	1/day
24	kab_teca1	0.006	1/day	51	kae_vc	0.005	1/day
25	kab_tca1	0.001	1/day	52	kae_dcm	0.005	1/day
26	kab_dca1	0.00005	1/day	53	kae_cm	0.005	1/day
27	kab_ct	0.000047	1/day				

Table 10. *Parameter Values For Example Simulation 3 – Anaerobic Case Equivalent to Table 20 – With The Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca2	0.2	mol/mol	28	kab_cm	0	1/day
2	fab_tdce_tca2	0.8	mol/mol	29	kan_teca2	0.005	1/day
3	fab_11dce_tca2	0	mol/mol	30	kan_tca2	0.01	1/day
4	fab_11dce_tca1	0	mol/mol	31	kan_dca2	0.025	1/day
5	fan_tca2_teca2	0	mol/mol	32	kan_ca	0.025	1/day
6	fan_cdce_teca2	0.2	mol/mol	33	kan_teca1	0	1/day
7	fan_tdce_teca2	0	mol/mol	34	kan_tca1	0	1/day
8	fan_dca2_tca2	0.2	mol/mol	35	kan_dca1	0	1/day
9	fan_vc_tca2	0.8	mol/mol	36	kan_pce	0.025	1/day
10	fan_ca_dca2	0.2	mol/mol	37	kan_tce	0.025	1/day
11	fan_tca1_teca1	0	mol/mol	38	kan_cdce	0.025	1/day
12	fan_11dce_teca1	0	mol/mol	39	kan_tdce	0.025	1/day
13	fan_cdce_tce	0.8	mol/mol	40	kan_11dce	0.025	1/day
14	fan_tdce_tce	0.2	mol/mol	41	kan_vc	0.0025	1/day
15	fan_11dce_tce	0	mol/mol	42	kan_ct	0	1/day
16	fan_vc_cdce	0.8	mol/mol	43	kan_cf	0	1/day
17	fan_vc_tdce	0.8	mol/mol	44	kan_dcm	0	1/day
18	fan_vc_11dce	0.8	mol/mol	45	kan_cm	0	1/day
19	fan_cm_dcm	0	mol/mol	46	kae_dca2	0	1/day
20	kab_teca2	0.006	1/day	47	kae_ca	0	1/day
21	kab_tca2	0	1/day	48	kae_cdce	0	1/day
22	kab_dca2	0.00003	1/day	49	kae_tdce	0	1/day
23	kab_ca	0.001	1/day	50	kae_11dce	0	1/day
24	kab_teca1	0	1/day	51	kae_vc	0	1/day
25	kab_tca1	0	1/day	52	kae_dcm	0	1/day
26	kab_dca1	0	1/day	53	kae_cm	0	1/day
27	kab_ct	0	1/day				

Table 11. *Parameter Values for Example Simulation 4 – Aerobic Case Equivalent to Table 23 – with the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca2	0.2	mol/mol	28	kab_cm	0	1/day
2	fab_tdce_tca2	0.8	mol/mol	29	kan_teca2	0	1/day
3	fab_11dce_tca2	0	mol/mol	30	kan_tca2	0	1/day
4	fab_11dce_tca1	0	mol/mol	31	kan_dca2	0	1/day
5	fan_tca2_teca2	0	mol/mol	32	kan_ca	0	1/day
6	fan_cdce_teca2	0	mol/mol	33	kan_teca1	0	1/day
7	fan_tdce_teca2	0	mol/mol	34	kan_tca1	0	1/day
8	fan_dca2_tca2	0	mol/mol	35	kan_dca1	0	1/day
9	fan_vc_tca2	0	mol/mol	36	kan_pce	0	1/day
10	fan_ca_dca2	0	mol/mol	37	kan_tce	0	1/day
11	fan_tca1_teca1	0	mol/mol	38	kan_cdce	0	1/day
12	fan_11dce_teca1	0	mol/mol	39	kan_tdce	0	1/day
13	fan_cdce_tce	0	mol/mol	40	kan_11dce	0	1/day
14	fan_tdce_tce	0	mol/mol	41	kan_vc	0	1/day
15	fan_11dce_tce	0	mol/mol	42	kan_ct	0	1/day
16	fan_vc_cdce	0	mol/mol	43	kan_cf	0	1/day
17	fan_vc_tdce	0	mol/mol	44	kan_dcm	0	1/day
18	fan_vc_11dce	0	mol/mol	45	kan_cm	0	1/day
19	fan_cm_dcm	0	mol/mol	46	kae_dca2	0.005	1/day
20	kab_teca2	0.006	1/day	47	kae_ca	0.005	1/day
21	kab_tca2	0	1/day	48	kae_cdce	0.005	1/day
22	kab_dca2	0.00003	1/day	49	kae_tdce	0.005	1/day
23	kab_ca	0.001	1/day	50	kae_11dce	0.005	1/day
24	kab_teca1	0	1/day	51	kae_vc	0.005	1/day
25	kab_tca1	0	1/day	52	kae_dcm	0.005	1/day
26	kab_dca1	0	1/day	53	kae_cm	0.005	1/day
27	kab_ct	0	1/day				
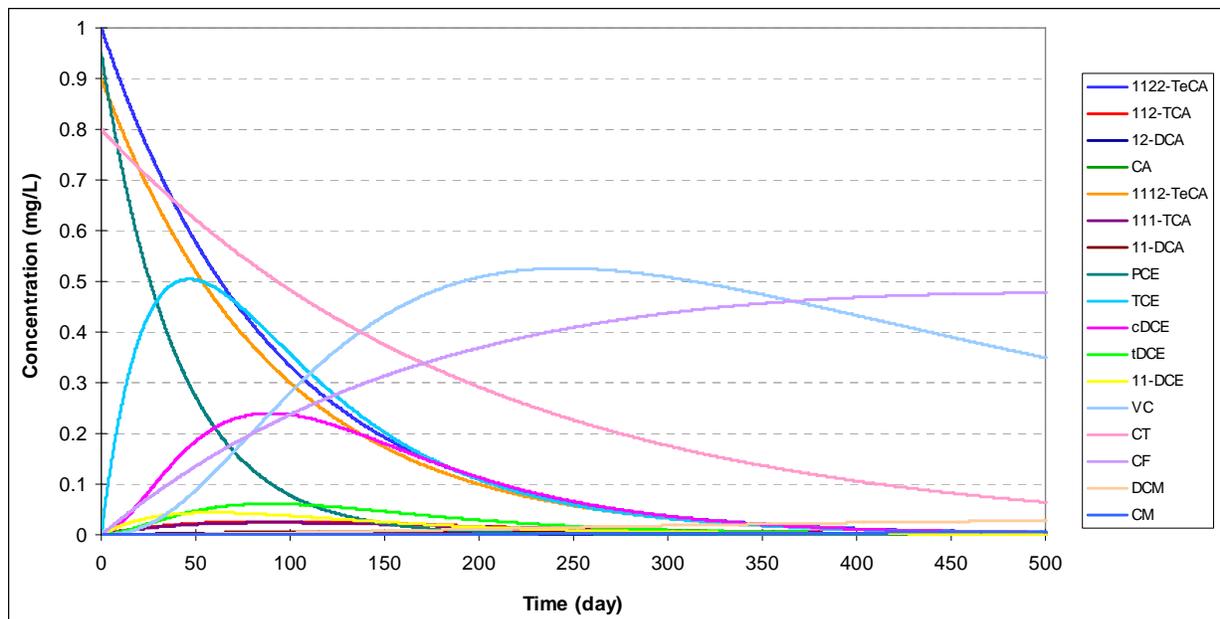
Figure 6. *Dechlorination of Mixed Chlorinated Solvents under Anaerobic Conditions Using the Parameter Values Shown in Table 8 — Initial concentrations were set to 1.0, 0.9, 0.95, and 0.8 mg/L for 1122TeCA, 1112TeCA, PCE, and CT, respectively. All other species concentrations started at zero.*
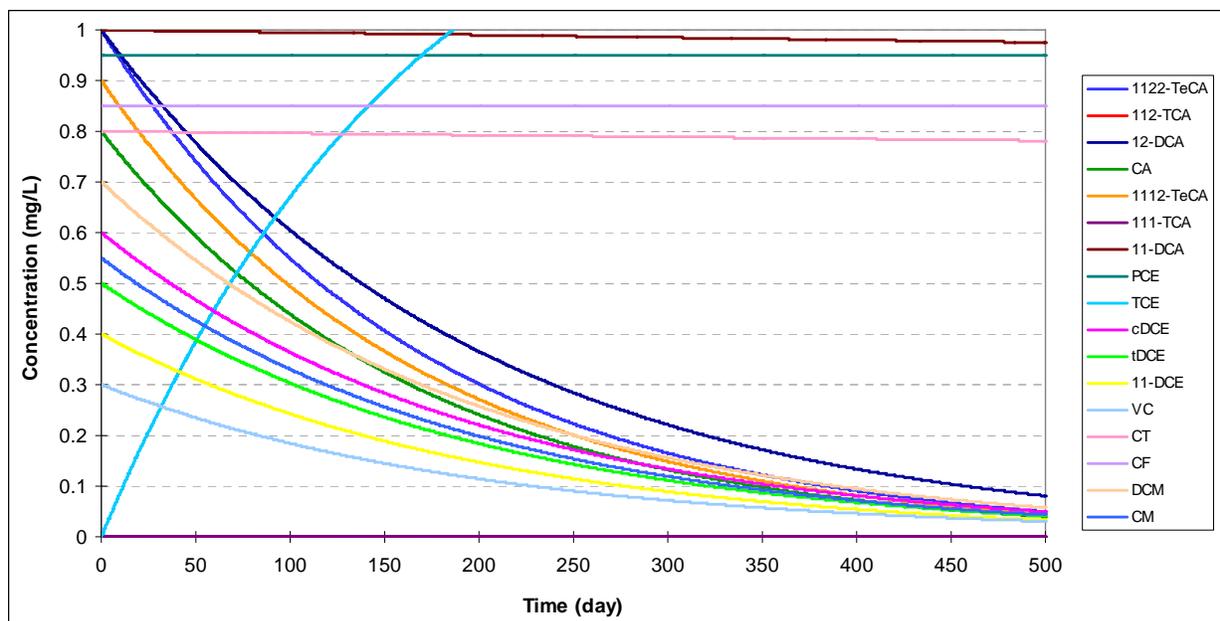
Figure 7. *Dechlorination of Mixed Chlorinated Solvents under Aerobic Conditions Using the Parameter Values Shown in Table 9 — Initial concentrations were set to 1.0 mg/L for 1122TeCA, 12DCA, and 11DCA. Initial concentrations were set to 0.9, 0.95, 0.8, 0.8, 0.6, 0.5, 0.4, 0.3, 0.85, 0.7, and 0.55 mg/L for 1112TeCA, PCE, CT, CA, cDCE, tDCE, 11DCE, VC, CF, DCM, and CM, respectively. All other species concentrations started at zero.*
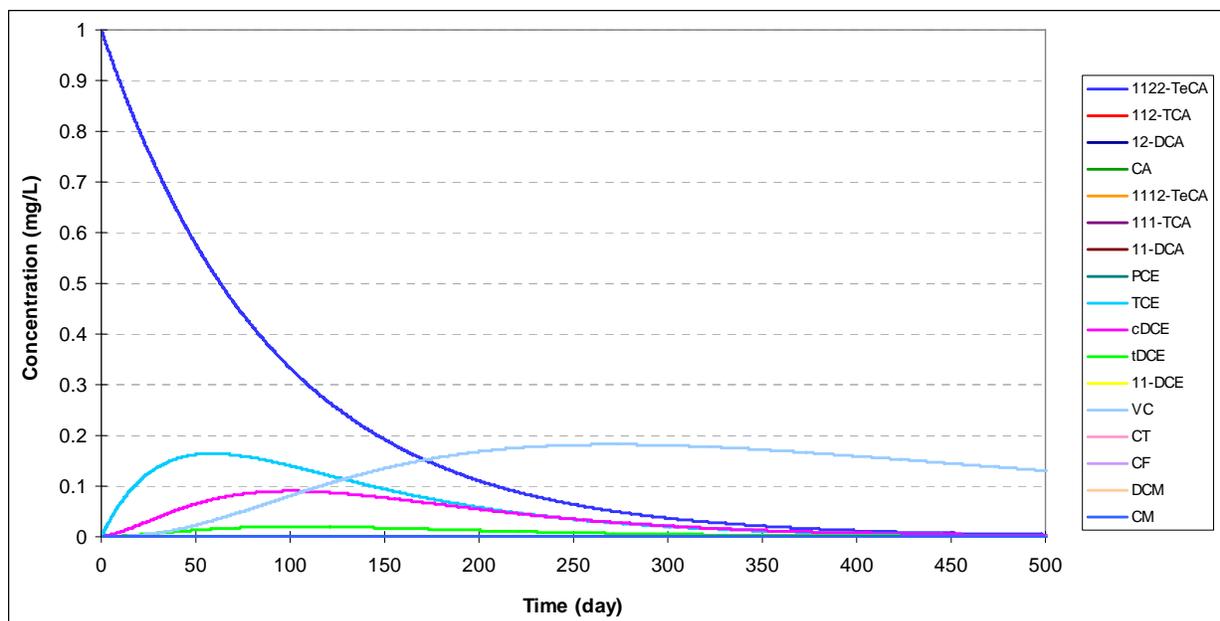
Figure 8. *Dechlorination of Mixed Chlorinated Solvents Using the Parameter Values Shown in Table 10 — The initial concentration of 1122TeCA was set to 1 mg/L. All other species concentrations started at zero. These results are the same as produced by the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes reaction module (Figure 16).*
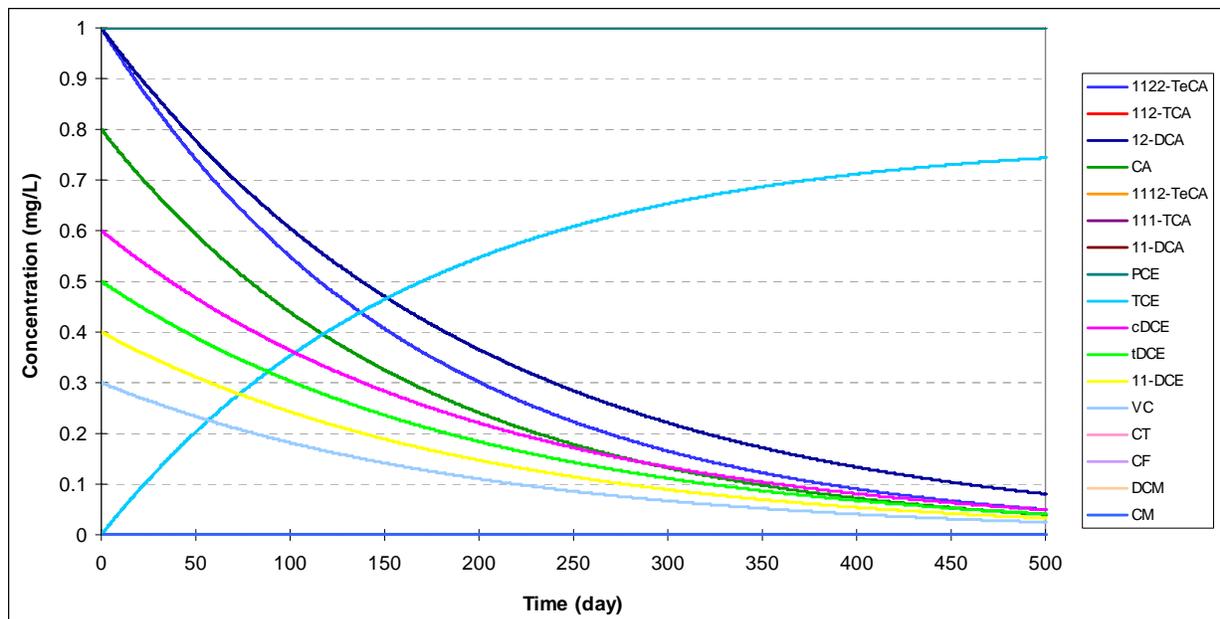
Figure 9. *Aerobic and Abiotic Degradation Using the Parameter Values Shown in Table 11 — The initial concentrations for 1122TeCA, 12DCA, and PCE were 1.0 mg/L. The initial concentrations were set to 0.8, 0.6, 0.5, 0.4, and 0.3 mg/L for CA, cDCE, tDCE, 11DCE, and VC, respectively. These results are the same as produced by the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes reaction module (Figure 19).*

3.0 Chloromethane Dechlorination

3.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of carbon tetrachloride (tetrachloromethane) and related daughter products using first-order rate expressions. The module includes abiotic, aerobic, and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 12 lists the chemical species included in this reaction module. Figure 10 shows the conceptual model describing the potential biotic and abiotic degradation pathways of chlorinated methane contaminants. See the conceptual model discussion for the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for information on the development of the reaction pathways and the assumption of first-order reaction kinetics.

Table 12. *Chemical Species Included in the Chloromethane Dechlorination Reaction Module*

No.	Abbreviation [a]	Chemical Name	Selected Alternate Name	CAS [b] Registry Number	Molecular Weight [c] (g/mol)	Chemical Formula
1	CT	Tetrachloromethane	Carbon Tetrachloride	56-23-5	153.82270	CCl_4
2	CF	Trichloromethane	Chloroform	67-66-3	119.37764	$CHCl_3$
3	DCM	Dichloromethane	Methylene Dichloride, Methylene Chloride	75-09-2	84.93258	CH_2Cl_2
4	CM	Chloromethane	Methyl Chloride	74-87-3	50.48752	CH_3Cl
5	Tracer	Conservative Tracer	—	N/A	N/A	N/A

[a] These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.
[b] CAS = Chemical Abstracts Service (see http://www.cas.org/EO/regsys.html)
[c] Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].
N/A – Not Applicable
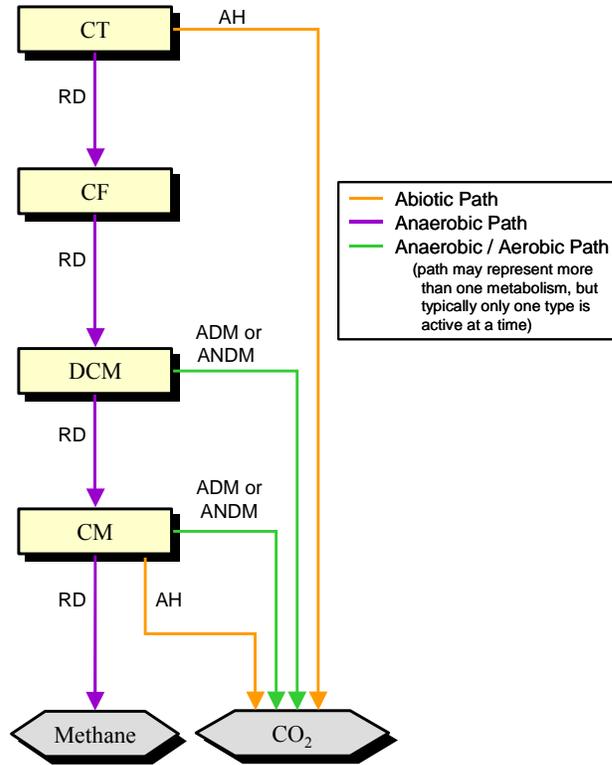
Figure 10. *Conceptual Model for Dechlorination Reactions in the Chloromethane Dechlorination Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.*

3.2   Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 32 to 36. These ODEs describe the reaction kinetics for the 5 chemical species in Table 12. See Table 13 for a detailed itemization of all reaction parameters used in this reaction module.

$$\frac{dC_{CT}}{dt} = \left(-kan_{CT} \cdot C_{CT} - kab_{CT} \cdot C_{CT} \right) \tag{32}$$

$$\frac{dC_{CF}}{dt} = \left(Y_{\frac{CF}{CT}} \cdot kan_{CT} \cdot C_{CT} - kan_{CF} \cdot C_{CF} \right) \tag{33}$$

$$\frac{dC_{DCM}}{dt} = \left(\begin{array}{l} Y_{\frac{DCM}{CF}} \cdot kan_{CF} \cdot C_{CF} \\ \\ - kan_{DCM} \cdot C_{DCM} - kae_{DCM} \cdot C_{DCM} \end{array} \right) \tag{34}$$

$$\frac{dC_{CM}}{dt} = \left(\begin{array}{c} Y_{\frac{CM}{DCM}} \cdot Fan_{\frac{CM}{DCM}} \cdot kan_{DCM} \cdot C_{DCM} \\[2ex] - \ kan_{CM} \cdot C_{CM} \ - \ kab_{CM} \cdot C_{CM} \ - \ kae_{CM} \cdot C_{CM} \end{array} \right) \qquad (35)$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \qquad \text{(Conservative [non-reactive] tracer.)} \qquad (36)$$

The first-order decay rate constants [T^{-1}] of the ith species are represented in the equations above by the kan_i, kae_i, and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the ith species is represented by the C_i term [ML^{-3}]. The R_i terms represent the retardation factor for the ith species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield [MM^{-1}] and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relation in Equation 37.

$$Fan_{\frac{CM}{DCM}} \leq 1.0 \qquad (37)$$

3.3   Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 9 reaction parameters that must be specified for this reaction module are listed in Table 13 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 13. *Input Parameters for the Chloromethane Dechlorination Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	$Fan_{\frac{CM}{DCM}}$	fan_cm_dcm	mol/mol	Moles of CM produced from anaerobic decay of one mole of DCM
2	Kab_{CT}	kab_ct	1/day	First-order decay coefficient for abiotic dechlorination of CT
3	Kab_{CM}	kab_cm	1/day	First-order decay coefficient for abiotic dechlorination of CM
4	Kan_{CT}	kan_ct	1/day	First-order decay coefficient for anaerobic dechlorination of CT
5	Kan_{CF}	kan_cf	1/day	First-order decay coefficient for anaerobic dechlorination of CF
6	Kan_{DCM}	kan_dcm	1/day	First-order decay coefficient for anaerobic dechlorination of DCM
7	Kan_{CM}	kan_cm	1/day	First-order decay coefficient for anaerobic dechlorination of CM
8	Kae_{DCM}	kae_dcm	1/day	First-order decay coefficient for aerobic dechlorination of DCM
9	Kae_{CM}	kae_cm	1/day	First-order decay coefficient for aerobic dechlorination of CM

3.4 Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 14 through 17. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 11 through 14, respectively.

Table 14. *Parameter Values for Example Simulation 1 – Base Case Anaerobic Conditions – with the Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cm_dcm	0.5	mol/mol	6	kan_dcm	0.005	1/day
2	kab_ct	0.000047	1/day	7	kan_cm	0.005	1/day
3	kab_cm	0.000094	1/day	8	kae_dcm	0	1/day
4	kan_ct	0.005	1/day	9	kae_cm	0	1/day
5	kan_cf	0.0005	1/day				

Table 15. *Parameter Values for Example Simulation 2 – Rates at 10% of Example Simulation 1 – with the Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cm_dcm	0.5	mol/mol	6	kan_dcm	0.0005	1/day
2	kab_ct	0.0000047	1/day	7	kan_cm	0.0005	1/day
3	kab_cm	0.0000094	1/day	8	kae_dcm	0	1/day
4	kan_ct	0.0005	1/day	9	kae_cm	0	1/day
5	kan_cf	0.00005	1/day				

Table 16. *Parameter Values for Example Simulation 3 – Different F Values Than Example Simulation 1 – with the Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cm_dcm	0.1	mol/mol	6	kan_dcm	0.005	1/day
2	kab_ct	0.000047	1/day	7	kan_cm	0.005	1/day
3	kab_cm	0.000094	1/day	8	kae_dcm	0	1/day
4	kan_ct	0.005	1/day	9	kae_cm	0	1/day
5	kan_cf	0.0005	1/day				

Table 17. *Parameter Values for Example Simulation 4 – Base Case Aerobic Conditions – with the Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cm_dcm	0	mol/mol	6	kan_dcm	0	1/day
2	kab_ct	0.000047	1/day	7	kan_cm	0	1/day
3	kab_cm	0.000094	1/day	8	kae_dcm	0.005	1/day
4	kan_ct	0	1/day	9	kae_cm	0.005	1/day
5	kan_cf	0	1/day				
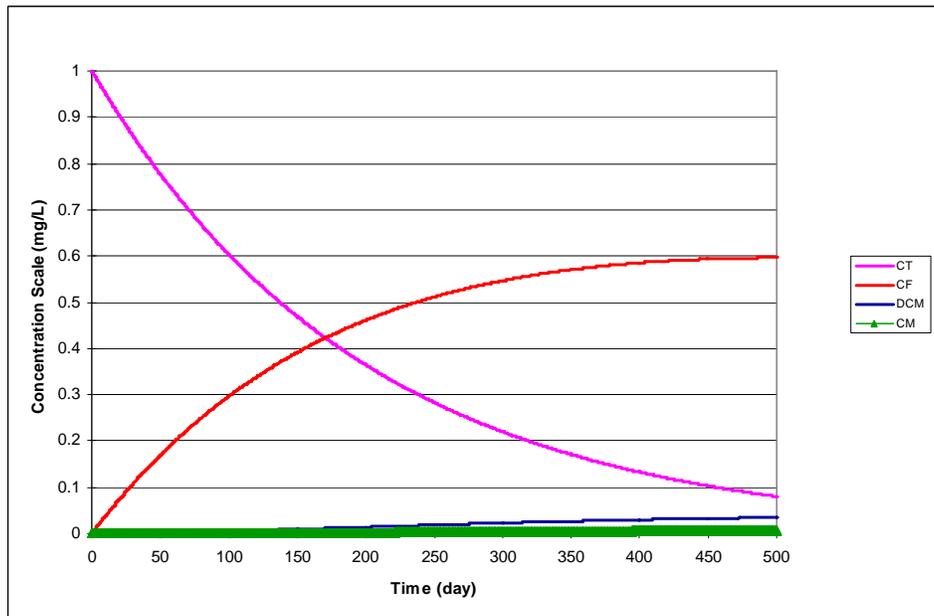
Figure 11. *Dechlorination of CT Using the Parameter Values Shown in Table 14 — The initial concentration for CT was 1 mg/L. All other species concentrations started at zero.*

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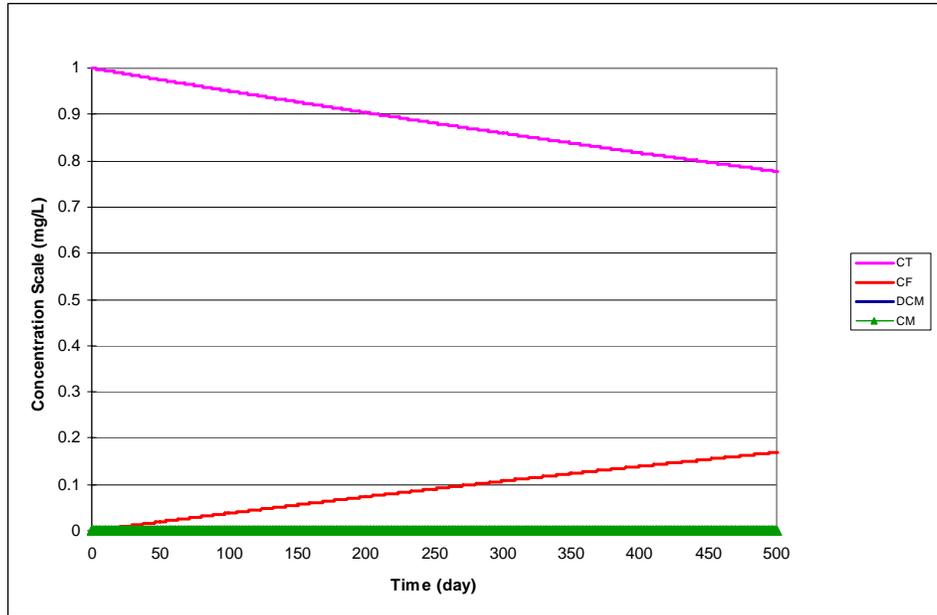
Figure 12. *Dechlorination of CT Using the Parameter Values Shown in Table 15 — The initial concentration for CT was 1 mg/L. All other species concentrations started at zero.*
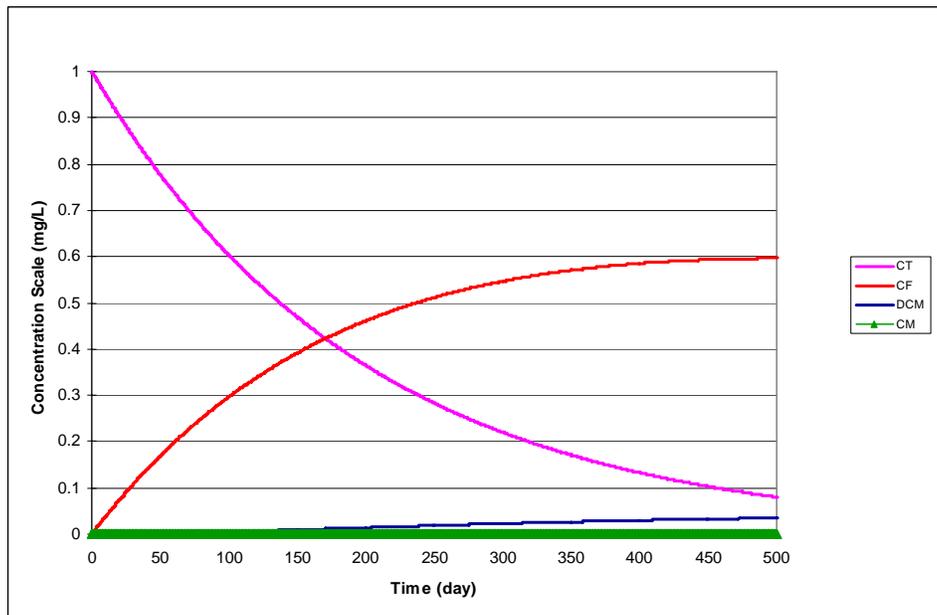
Figure 13. *Dechlorination of CT Using the Parameter Values Shown in Table 16 — The initial concentration for CT was 1 mg/L. All other species concentrations started at zero.*
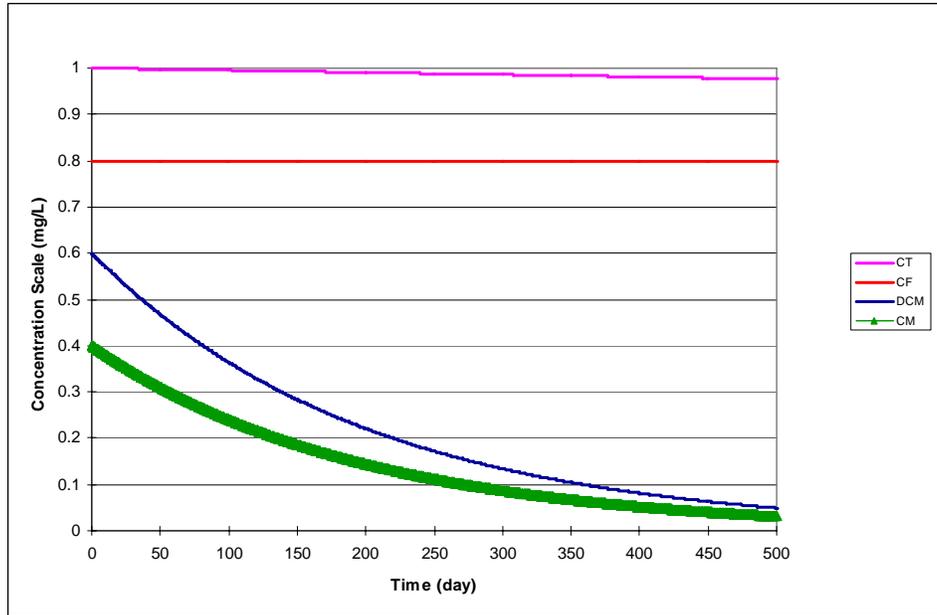
Figure 14. *Aerobic and Abiotic Degradation Using the Parameter Values Shown in Table 17 —*
The initial concentrations for CT, CF, DCM, and CM were 1, 0.8, 0.6, and 0.4 mg/L,
respectively.

4.0 Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes

4.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of 1,1,2,2-tetrachloroethane, tetrachloroethene, and related daughter products (including 1,1,2-TCA and 1,2-DCA) using first-order rate expressions. The module includes abiotic, aerobic, and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 18 lists the chemical species included in this reaction module. Dechlorination reactions for chlorinated ethane contaminants can result in formation of chlorinated ethene species, so this reaction module combines the reaction pathways for these two groups of contaminants. Figure 15 shows the conceptual model describing the potential biotic and abiotic degradation pathways of both chlorinated ethene and chlorinated ethane contaminants. See the conceptual model discussion for the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for information on the development of the reaction pathways and the assumption of first-order reaction kinetics.

Table 18. *Chemical Species Included in the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module*

No.	Abbreviation [a]	Chemical Name	Selected Alternate Name	CAS [b] Registry Number	Molecular Weight [c] (g/mol)	Chemical Formula
1	TeCA	1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	79-34-5	167.84928	$C_2H_2Cl_4$
2	TCA	1,1,2-Trichloroethane	Vinyl Trichloride; 1,1,2-TCA	79-00-5	133.40422	$C_2H_3Cl_3$
3	DCA	1,2-Dichloroethane	Ethane Dichloride; 1,2-DCA	107-06-2	98.95916	$C_2H_4Cl_2$
4	CA	Chloroethane	Ethyl Chloride	75-00-3	64.5141	C_2H_5Cl
5	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.8334	C_2Cl_4
6	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C_2HCl_3
7	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	$C_2H_2Cl_2$
8	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	$C_2H_2Cl_2$
9	11DCE	1,1-Dichloroethene	Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	$C_2H_2Cl_2$
10	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C_2H_3Cl
11	Tracer	Conservative Tracer	—	N/A	N/A	N/A

[a] These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

[b] CAS = Chemical Abstracts Service (see http://www.cas.org/EO/regsys.html)

[c] Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

Figure 15. *Conceptual Model for Dechlorination Reactions in the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.*

4.2   Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 38 to 48. These ODEs describe the reaction kinetics for the 11 chemical species in Table 18. See Table 19 for a detailed itemization of all reaction parameters used in this reaction module.

$$\frac{dC_{TeCA}}{dt} = \left(-kan_{TeCA} \cdot C_{TeCA} - kab_{TeCA} \cdot C_{TeCA} \right) \tag{38}$$

$$\frac{dC_{TCA}}{dt} = \left(Y_{\frac{TCA}{TeCA}} \cdot Fan_{\frac{TCA}{TeCA}} \cdot kan_{TeCA} \cdot C_{TeCA} - kan_{TCA} \cdot C_{TCA} - kab_{TCA} \cdot C_{TCA} \right) \tag{39}$$

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$$\frac{dC_{DCA}}{dt} = \left(\begin{array}{c} Y_{\frac{DCA}{TCA}} \cdot Fan_{\frac{DCA}{TCA}} \cdot kan_{TCA} \cdot C_{TCA} \\ \\ - \; kan_{DCA} \cdot C_{DCA} \; - \; kab_{DCA} \cdot C_{DCA} \; - \; kae_{DCA} \cdot C_{DCA} \end{array} \right) \tag{40}$$

$$\frac{dC_{CA}}{dt} = \left(\begin{array}{c} Y_{\frac{CA}{DCA}} \cdot Fan_{\frac{CA}{DCA}} \cdot kan_{DCA} \cdot C_{DCA} \\ \\ - \; kan_{CA} \cdot C_{CA} \; - \; kab_{CA} \cdot C_{CA} \; - \; kae_{CA} \cdot C_{CA} \end{array} \right) \tag{41}$$

$$\frac{dC_{PCE}}{dt} = \left(\; - \; kan_{PCE} \cdot C_{PCE} \; \right) \tag{42}$$

$$\frac{dC_{TCE}}{dt} = \left(Y_{\frac{TCE}{PCE}} \cdot kan_{PCE} \cdot C_{PCE} \; + \; Y_{\frac{TCE}{TeCA}} \cdot kab_{TeCA} \cdot C_{TeCA} \; - \; kan_{TCE} \cdot C_{TCE} \right) \tag{43}$$

$$\frac{dC_{cDCE}}{dt} = \left(\begin{array}{c} Y_{\frac{DCE}{TeCA}} \cdot Fan_{\frac{cDCE}{TeCA}} \cdot kan_{TeCA} \cdot C_{TeCA} \; + \; Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{cDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\ \\ + \; Y_{\frac{DCE}{TCA}} \cdot Fab_{\frac{cDCE}{TCA}} \cdot kab_{TCA} \cdot C_{TCA} \\ \\ - \; kan_{cDCE} \cdot C_{cDCE} \; - \; kae_{cDCE} \cdot C_{cDCE} \end{array} \right) \tag{44}$$

$$\frac{dC_{tDCE}}{dt} = \left(\begin{array}{c} Y_{\frac{DCE}{TeCA}} \cdot Fan_{\frac{tDCE}{TeCA}} \cdot kan_{TeCA} \cdot C_{TeCA} \; + \; Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{tDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\ \\ + \; Y_{\frac{DCE}{TCA}} \cdot Fab_{\frac{tDCE}{TCA}} \cdot kab_{TCA} \cdot C_{TCA} \\ \\ - \; kan_{tDCE} \cdot C_{tDCE} \; - \; kae_{tDCE} \cdot C_{tDCE} \end{array} \right) \tag{45}$$

$$\frac{dC_{11DCE}}{dt} = \left(\begin{array}{c} Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{11DCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \; + \; Y_{\frac{DCE}{TCA}} \cdot Fab_{\frac{11DCE}{TCA}} \cdot kab_{TCA} \cdot C_{TCA} \\ \\ - \; kan_{11DCE} \cdot C_{11DCE} \; - \; kae_{11DCE} \cdot C_{11DCE} \end{array} \right) \tag{46}$$

$$\frac{dC_{VC}}{dt} = \left(\begin{array}{l} Y_{\frac{VC}{TCA}} \cdot Fan_{\frac{VC}{TCA}} \cdot kan_{TCA} \cdot C_{TCA} \;+\; Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{cDCE}} \cdot kan_{cDCE} \cdot C_{cDCE} \\[2ex] \quad +\; Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{tDCE}} \cdot kan_{tDCE} \cdot C_{tDCE} \\[2ex] \quad +\; Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{11DCE}} \cdot kan_{11DCE} \cdot C_{11DCE} \\[2ex] \quad -\; kan_{VC} \cdot C_{VC} \;-\; kae_{VC} \cdot C_{VC} \end{array} \right) \tag{47}$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \qquad \textit{(Conservative [non-reactive] tracer.)} \tag{48}$$

The first-order decay rate constants $[T^{-1}]$ of the ith species are represented in the equations above by the kan_i, kae_i, and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the ith species is represented by the C_i term $[ML^{-3}]$. The R_i terms represent the retardation factor for the ith species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield $[MM^{-1}]$ and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relations in Equations 49 to 56.

$$Fan_{\frac{TCA}{TeCA}} + Fan_{\frac{cDCE}{TeCA}} + Fan_{\frac{tDCE}{TeCA}} = 1.0 \tag{49}$$

$$Fan_{\frac{DCA}{TCA}} + Fan_{\frac{VC}{TCA}} = 1.0 \tag{50}$$

$$Fan_{\frac{cDCE}{TCE}} + Fan_{\frac{tDCE}{TCE}} + Fan_{\frac{11DCE}{TCE}} = 1.0 \tag{51}$$

$$Fab_{\frac{cDCE}{TCA}} + Fab_{\frac{tDCE}{TCA}} + Fab_{\frac{11DCE}{TCA}} = 1.0 \tag{52}$$

$$Fan_{\frac{CA}{DCA}} \leq 1.0 \qquad (53)$$

$$Fan_{\frac{VC}{cDCE}} \leq 1.0 \qquad (54)$$

$$Fan_{\frac{VC}{tDCE}} \leq 1.0 \qquad (55)$$

$$Fan_{\frac{VC}{11DCE}} \leq 1.0 \qquad (56)$$

4.3   Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 35 reaction parameters that must be specified for this reaction module are listed in Table 19 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 19. *Input Parameters for the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	$Fab_{\frac{cDCE}{TCA}}$	fab_cdce_tca	mol/mol	Moles of cis-1,2-DCE produced from abiotic decay of one mole of TCA
2	$Fab_{\frac{tDCE}{TCA}}$	fab_tdce_tca	mol/mol	Moles of trans-1,2-DCE produced from abiotic decay of one mole of TCA
3	$Fab_{\frac{11DCE}{TCA}}$	fab_11dce_tca	mol/mol	Moles of 1,1-DCE produced from abiotic decay of one mole of TCA
4	$Fan_{\frac{TCA}{TeCA}}$	fan_tca_teca	mol/mol	Moles of TCA produced from anaerobic decay of one mole of TeCA
5	$Fan_{\frac{cDCE}{TeCA}}$	fan_cdce_teca	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TeCA
6	$Fan_{\frac{tDCE}{TeCA}}$	fan_tdce_teca	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TeCA
7	$Fan_{\frac{DCA}{TCA}}$	fan_dca_tca	mol/mol	Moles of DCA produced from anaerobic decay of one mole of TCA

Table 19. *(contd)*

ID #	Parameter	Fortran Variable	Units	Description
8	$Fan_{\frac{VC}{TCA}}$	fan_vc_tca	mol/mol	Moles of VC produced from anaerobic decay of one mole of TCA
9	$Fan_{\frac{CA}{DCA}}$	fan_ca_dca	mol/mol	Moles of CA produced from anaerobic decay of one mole of DCA
10	$Fan_{\frac{cDCE}{TCE}}$	fan_cdce_tce	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TCE
11	$Fan_{\frac{tDCE}{TCE}}$	fan_tdce_tce	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TCE
12	$Fan_{\frac{11DCE}{TCE}}$	fan_11dce_tce	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TCE
13	$Fan_{\frac{VC}{cDCE}}$	fan_vc_cdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of cis-1,2-DCE
14	$Fan_{\frac{VC}{tDCE}}$	fan_vc_tdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of trans-1,2-DCE
15	$Fan_{\frac{VC}{11DCE}}$	fan_vc_11dce	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1-DCE
16	kab_{TeCA}	kab_teca	1/day	First-order decay coefficient for abiotic dechlorination of TeCA
17	kab_{TCA}	kab_tca	1/day	First-order decay coefficient for abiotic dechlorination of TCA
18	kab_{DCA}	kab_dca	1/day	First-order decay coefficient for abiotic dechlorination of DCA
19	kab_{CA}	kab_ca	1/day	First-order decay coefficient for abiotic dechlorination of CA
20	kan_{TeCA}	kan_teca	1/day	First-order decay coefficient for anaerobic dechlorination of TeCA
21	kan_{TCA}	kan_tca	1/day	First-order decay coefficient for anaerobic dechlorination of TCA
22	kan_{DCA}	kan_dca	1/day	First-order decay coefficient for anaerobic dechlorination of DCA
23	kan_{CA}	kan_ca	1/day	First-order decay coefficient for anaerobic dechlorination of CA
24	kan_{PCE}	kan_pce	1/day	First-order decay coefficient for anaerobic dechlorination of PCE
25	kan_{TCE}	kan_tce	1/day	First-order decay coefficient for anaerobic dechlorination of TCE
26	kan_{cDCE}	kan_cdce	1/day	First-order decay coefficient for anaerobic dechlorination of cis-1,2-DCE
27	kan_{tDCE}	kan_tdce	1/day	First-order decay coefficient for anaerobic dechlorination of trans-1,2-DCE

Table 19. (contd)

ID #	Parameter	Fortran Variable	Units	Description
28	kan_{11DCE}	kan_11dce	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCE
29	kan_{VC}	kan_vc	1/day	First-order decay coefficient for anaerobic dechlorination of VC
30	kae_{DCA}	kae_dca	1/day	First-order decay coefficient for aerobic dechlorination of DCA
31	kae_{CA}	kae_ca	1/day	First-order decay coefficient for aerobic dechlorination of CA
32	kae_{cDCE}	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
33	kae_{tDCE}	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
34	kae_{11DCE}	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
35	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC

4.4   Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 20 through 23. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 16 through 19, respectively.

Table 20. *Parameter Values for Example Simulation 1 – Base Case Anaerobic Conditions – with the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca	0.2	mol/mol	19	kab_ca	0.001	1/day
2	fab_tdce_tca	0.8	mol/mol	20	kan_teca	0.005	1/day
3	fab_11dce_tca	0	mol/mol	21	kan_tca	0.01	1/day
4	fan_tca_teca	0	mol/mol	22	kan_dca	0.025	1/day
5	fan_cdce_teca	0.2	mol/mol	23	kan_ca	0.025	1/day
6	fan_tdce_teca	0	mol/mol	24	kan_pce	0.025	1/day
7	fan_dca_tca	0.2	mol/mol	25	kan_tce	0.025	1/day
8	fan_vc_tca	0.8	mol/mol	26	kan_cdce	0.025	1/day
9	fan_ca_dca	0.2	mol/mol	27	kan_tdce	0.025	1/day
10	fan_cdce_tce	0.8	mol/mol	28	kan_11dce	0.025	1/day
11	fan_tdce_tce	0.2	mol/mol	29	kan_vc	0.0025	1/day
12	fan_11dce_tce	0	mol/mol	30	kae_dca	0	1/day
13	fan_vc_cdce	0.8	mol/mol	31	kae_ca	0	1/day
14	fan_vc_tdce	0.8	mol/mol	32	kae_cdce	0	1/day
15	fan_vc_11dce	0.8	mol/mol	33	kae_tdce	0	1/day
16	kab_teca	0.006	1/day	34	kae_11dce	0	1/day
17	kab_tca	0	1/day	35	kae_vc	0	1/day
18	kab_dca	0.00003	1/day				

Table 21. *Parameter Values for Example Simulation 2 – Rates at 10% of Example Simulation 1 – with the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca	0.2	mol/mol	19	kab_ca	0.0001	1/day
2	fab_tdce_tca	0.8	mol/mol	20	kan_teca	0.0005	1/day
3	fab_11dce_tca	0	mol/mol	21	kan_tca	0.001	1/day
4	fan_tca_teca	0	mol/mol	22	kan_dca	0.0025	1/day
5	fan_cdce_teca	0.2	mol/mol	23	kan_ca	0.0025	1/day
6	fan_tdce_teca	0	mol/mol	24	kan_pce	0.0025	1/day
7	fan_dca_tca	0.2	mol/mol	25	kan_tce	0.0025	1/day
8	fan_vc_tca	0.8	mol/mol	26	kan_cdce	0.0025	1/day
9	fan_ca_dca	0.2	mol/mol	27	kan_tdce	0.0025	1/day
10	fan_cdce_tce	0.8	mol/mol	28	kan_11dce	0.0025	1/day
11	fan_tdce_tce	0.2	mol/mol	29	kan_vc	0.00025	1/day
12	fan_11dce_tce	0	mol/mol	30	kae_dca	0	1/day
13	fan_vc_cdce	0.8	mol/mol	31	kae_ca	0	1/day
14	fan_vc_tdce	0.8	mol/mol	32	kae_cdce	0	1/day
15	fan_vc_11dce	0.8	mol/mol	33	kae_tdce	0	1/day
16	kab_teca	0.0006	1/day	34	kae_11dce	0	1/day
17	kab_tca	0	1/day	35	kae_vc	0	1/day
18	kab_dca	0.000003	1/day				

Table 22. *Parameter Values for Example Simulation 3 – Different F Values Than Example Simulation 1 – with the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module.*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca	0.2	mol/mol	19	kab_ca	0.001	1/day
2	fab_tdce_tca	0.8	mol/mol	20	kan_teca	0.005	1/day
3	fab_11dce_tca	0	mol/mol	21	kan_tca	0.01	1/day
4	fan_tca_teca	0.8	mol/mol	22	kan_dca	0.025	1/day
5	fan_cdce_teca	0	mol/mol	23	kan_ca	0.025	1/day
6	fan_tdce_teca	0.2	mol/mol	24	kan_pce	0.025	1/day
7	fan_dca_tca	0.8	mol/mol	25	kan_tce	0.025	1/day
8	fan_vc_tca	0.2	mol/mol	26	kan_cdce	0.025	1/day
9	fan_ca_dca	0.8	mol/mol	27	kan_tdce	0.025	1/day
10	fan_cdce_tce	0.2	mol/mol	28	kan_11dce	0.025	1/day
11	fan_tdce_tce	0	mol/mol	29	kan_vc	0.0025	1/day
12	fan_11dce_tce	0.8	mol/mol	30	kae_dca	0	1/day
13	fan_vc_cdce	0.2	mol/mol	31	kae_ca	0	1/day
14	fan_vc_tdce	0.2	mol/mol	32	kae_cdce	0	1/day
15	fan_vc_11dce	0.2	mol/mol	33	kae_tdce	0	1/day
16	kab_teca	0.006	1/day	34	kae_11dce	0	1/day
17	kab_tca	0	1/day	35	kae_vc	0	1/day
18	kab_dca	0.00003	1/day				

Table 23. *Parameter Values for Example Simulation 4 – Base Case Aerobic Conditions – with the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca	0.2	mol/mol	19	kab_ca	0.001	1/day
2	fab_tdce_tca	0.8	mol/mol	20	kan_teca	0	1/day
3	fab_11dce_tca	0	mol/mol	21	kan_tca	0	1/day
4	fan_tca_teca	0	mol/mol	22	kan_dca	0	1/day
5	fan_cdce_teca	0	mol/mol	23	kan_ca	0	1/day
6	fan_tdce_teca	0	mol/mol	24	kan_pce	0	1/day
7	fan_dca_tca	0	mol/mol	25	kan_tce	0	1/day
8	fan_vc_tca	0	mol/mol	26	kan_cdce	0	1/day
9	fan_ca_dca	0	mol/mol	27	kan_tdce	0	1/day
10	fan_cdce_tce	0	mol/mol	28	kan_11dce	0	1/day
11	fan_tdce_tce	0	mol/mol	29	kan_vc	0	1/day
12	fan_11dce_tce	0	mol/mol	30	kae_dca	0.005	1/day
13	fan_vc_cdce	0	mol/mol	31	kae_ca	0.005	1/day
14	fan_vc_tdce	0	mol/mol	32	kae_cdce	0.005	1/day
15	fan_vc_11dce	0	mol/mol	33	kae_tdce	0.005	1/day
16	kab_teca	0.006	1/day	34	kae_11dce	0.005	1/day
17	kab_tca	0	1/day	35	kae_vc	0.005	1/day
18	kab_dca	0.00003	1/day				
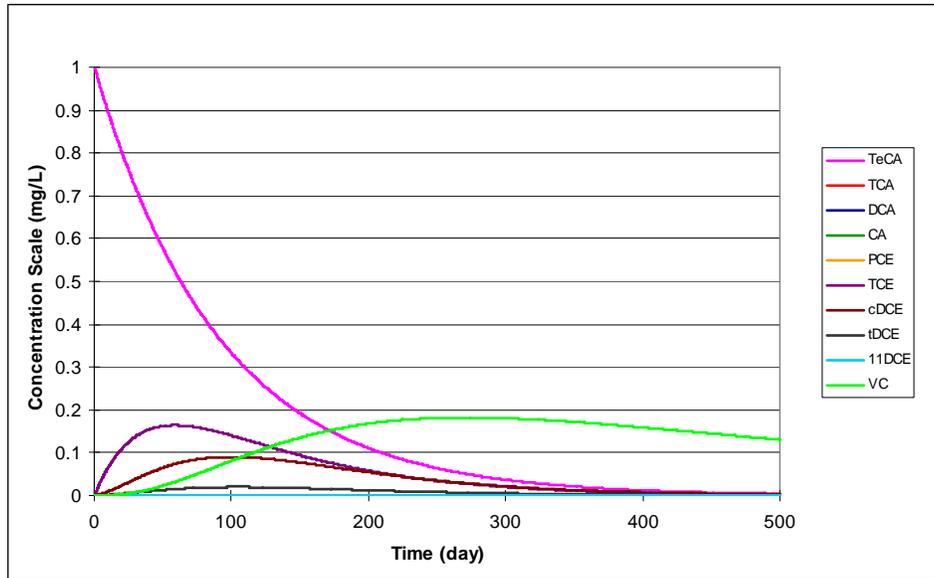
Figure 16. *Dechlorination of 1,1,2,2-TeCA Using the Parameter Values Shown in Table 20 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero. In the results, the concentrations of TCA, DCA, CA, PCE, and 11DCE are zero.*
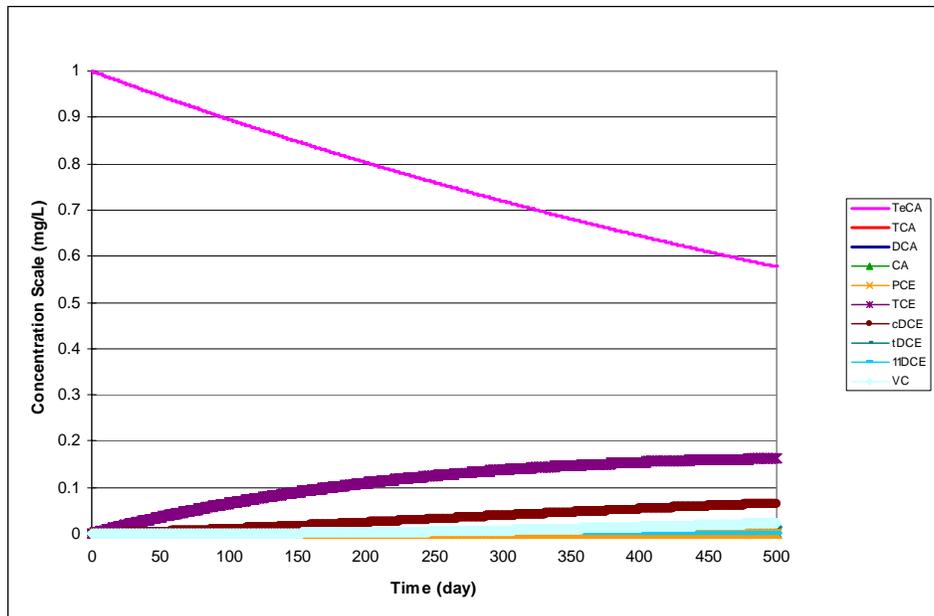
Figure 17. *Dechlorination of 1,1,2,2-TeCA Using the Parameter Values Shown in Table 21 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.*
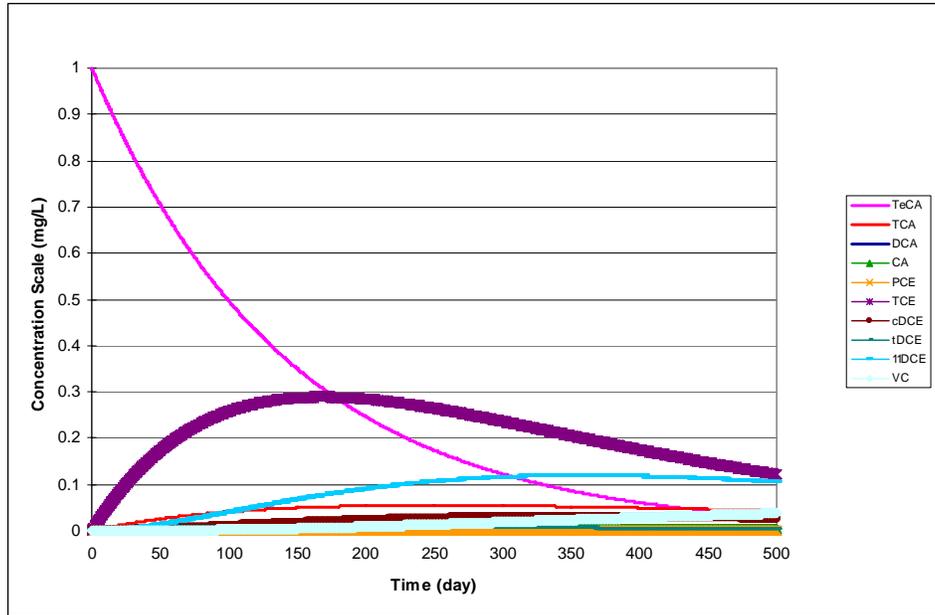
Figure 18. *Dechlorination of 1,1,2,2-TeCA Using the Parameter Values Shown in Table 22 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.*
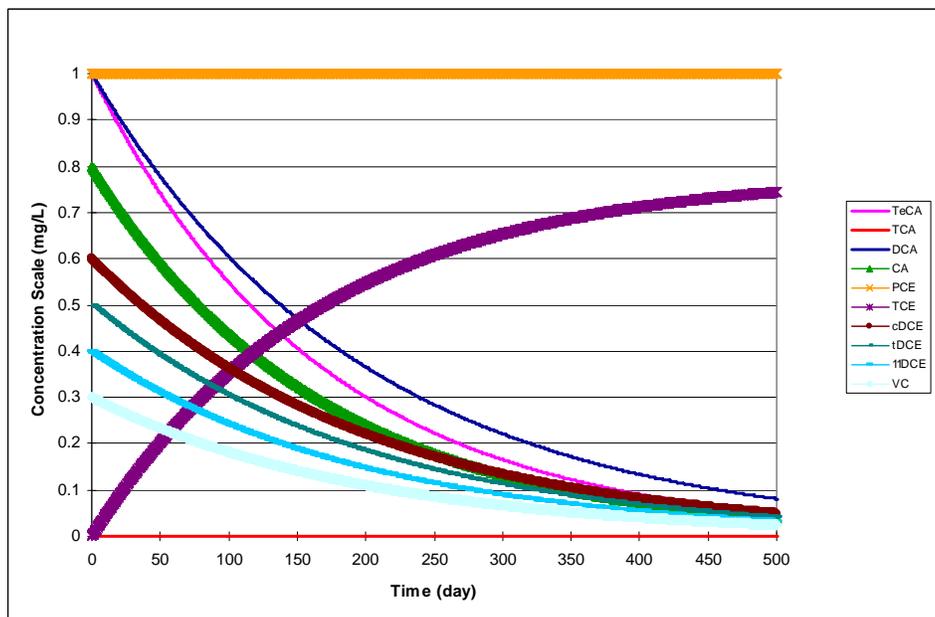
Figure 19. *Aerobic and Abiotic Degradation of Contaminants in the 1,1,2,2-TeCA and PCE Families Using the Parameter Values Shown in Table 23 — The initial concentrations for TeCA, TCA, DCA, CA, PCE, TCE, cDCE, tDCE, 11DCE, and VC were 1, 0, 1, 0.8, 1, 0, 0.6, 0.5, 0.4, and 0.3 mg/L, respectively.*

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5.0 Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes

5.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of 1,1,1,2-tetrachloroethane, tetrachloroethene, and related daughter products (including 1,1,1-TCA and 1,1-DCA) using first-order rate expressions. The module includes abiotic, aerobic, and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 24 lists the chemical species included in this reaction module. Dechlorination reactions for chlorinated ethane contaminants can result in formation of chlorinated ethene species, so this reaction module combines the reaction pathways for these two groups of contaminants. Figure 20 shows the conceptual model describing the potential biotic and abiotic degradation pathways of both chlorinated ethene and chlorinated ethane contaminants. See the conceptual model discussion for the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for information on the development of the reaction pathways and the assumption of first-order reaction kinetics.

Table 24. *Chemical Species Included in the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module*

No.	Abbreviation [a]	Chemical Name	Selected Alternate Name	CAS [b] Registry Number	Molecular Weight [c] (g/mol)	Chemical Formula
1	TeCA	1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA		167.84928	$C_2H_2Cl_4$
2	TCA	1,1,1-Trichloroethane	1,1,1-TCA		133.40422	$C_2H_3Cl_3$
3	DCA	1,1-Dichloroethane	1,1-DCA		98.95916	$C_2H_4Cl_2$
4	CA	Chloroethane	Ethyl Chloride	75-00-3	64.5141	C_2H_5Cl
5	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.8334	C_2Cl_4
6	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C_2HCl_3
7	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	$C_2H_2Cl_2$
8	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	$C_2H_2Cl_2$
9	11DCE	1,1-Dichloroethene	Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	$C_2H_2Cl_2$
10	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C_2H_3Cl
11	Tracer	Conservative Tracer	—	N/A	N/A	N/A

[a] These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

[b] CAS = Chemical Abstracts Service (see http://www.cas.org/EO/regsys.html)

[c] Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

Figure 20. *Conceptual Model for Dechlorination Reactions in the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.*

5.2 Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 57 to 67. These ODEs describe the reaction kinetics for the 11 chemical species in Table 24. See Table 25 for a detailed itemization of all reaction parameters used in this reaction module.

$$\frac{dC_{TeCA}}{dt} = \left(-kan_{TeCA} \cdot C_{TeCA} - kab_{TeCA} \cdot C_{TeCA} \right) \tag{57}$$

$$\frac{dC_{TCA}}{dt} = \left(Y_{\frac{TCA}{TeCA}} \cdot Fan_{\frac{TCA}{TeCA}} \cdot kan_{TeCA} \cdot C_{TeCA} - kan_{TCA} \cdot C_{TCA} - kab_{TCA} \cdot C_{TCA} \right) \tag{58}$$

$$\frac{dC_{DCA}}{dt} = \left(\begin{array}{l} Y_{\frac{DCA}{TCA}} \cdot kan_{TCA} \cdot C_{TCA} \\[2em] \quad - kan_{DCA} \cdot C_{DCA} \ - \ kab_{DCA} \cdot C_{DCA} \end{array} \right) \tag{59}$$

$$\frac{dC_{CA}}{dt} = \left(\begin{array}{l} Y_{\frac{CA}{DCA}} \cdot kan_{DCA} \cdot C_{DCA} \\[2em] \quad - kan_{CA} \cdot C_{CA} \ - \ kab_{CA} \cdot C_{CA} \ - \ kae_{CA} \cdot C_{CA} \end{array} \right) \tag{60}$$

$$\frac{dC_{PCE}}{dt} = \left(\ - kan_{PCE} \cdot C_{PCE} \right) \tag{61}$$

$$\frac{dC_{TCE}}{dt} = \left(\begin{array}{l} Y_{\frac{TCE}{PCE}} \cdot kan_{PCE} \cdot C_{PCE} \\[2em] \quad + \ Y_{\frac{TCE}{TeCA}} \cdot kab_{TeCA} \cdot C_{TeCA} \ - \ kan_{TCE} \cdot C_{TCE} \end{array} \right) \tag{62}$$

$$\frac{dC_{cDCE}}{dt} = \left(\begin{array}{l} Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{cDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\[2em] \quad - kan_{cDCE} \cdot C_{cDCE} \ - \ kae_{cDCE} \cdot C_{cDCE} \end{array} \right) \tag{63}$$

$$\frac{dC_{tDCE}}{dt} = \left(\begin{array}{l} Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{tDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\[2em] \quad - kan_{tDCE} \cdot C_{tDCE} \ - \ kae_{tDCE} \cdot C_{tDCE} \end{array} \right) \tag{64}$$

$$\frac{dC_{11DCE}}{dt} = \left(\begin{array}{l} Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{11DCE}{TCE}} \cdot kan_{TCE} \ \cdot C_{TCE} \ + \ Y_{\frac{DCE}{TeCA}} \cdot Fan_{\frac{11DCE}{TeCA}} \cdot kan_{TeCA} \cdot C_{TeCA} \\[2em] \quad + \ Y_{\frac{DCE}{TCA}} \cdot Fab_{\frac{11DCE}{TCA}} \cdot kab_{TCA} \cdot C_{TCA} \\[2em] \quad - kan_{11DCE} \cdot C_{11DCE} \ - \ kae_{11DCE} \cdot C_{11DCE} \end{array} \right) \tag{65}$$

$$\frac{dC_{VC}}{dt} = \begin{pmatrix} Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{cDCE}} \cdot kan_{cDCE} \cdot C_{cDCE} \\ \\ + \ Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{tDCE}} \cdot kan_{tDCE} \cdot C_{tDCE} \\ \\ + \ Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{11DCE}} \cdot kan_{11DCE} \cdot C_{11DCE} \\ \\ + \ Y_{\frac{VC}{DCA}} \cdot kab_{DCA} \cdot C_{DCA} \\ \\ - \ kan_{VC} \cdot C_{VC} \ - \ kae_{VC} \cdot C_{VC} \end{pmatrix} \tag{66}$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \qquad\qquad \text{(Conservative [non-reactive] tracer.)} \tag{67}$$

The first-order decay rate constants [T^{-1}] of the ith species are represented in the equations above by the kan_i, kae_i, and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the ith species is represented by the C_i term [ML^{-3}]. The R_i terms represent the retardation factor for the ith species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield [MM^{-1}] and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relations in Equations 68 to 73.

$$Fan_{\frac{TCA}{TeCA}} + Fan_{\frac{11DCE}{TeCA}} = 1.0 \tag{68}$$

$$Fab_{\frac{11DCE}{TCA}} \leq 1.0 \tag{69}$$

$$Fan_{\frac{cDCE}{TCE}} + Fan_{\frac{tDCE}{TCE}} + Fan_{\frac{11DCE}{TCE}} = 1.0 \tag{70}$$

$$Fan_{\frac{VC}{cDCE}} \leq 1.0 \tag{71}$$

$$Fan_{\frac{VC}{tDCE}} \leq 1.0 \tag{72}$$

$$Fan_{\frac{VC}{11DCE}} \leq 1.0 \tag{73}$$

5.3   Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 28 reaction parameters that must be specified for this reaction module are listed in Table 25 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 25. *Input Parameters for the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	$Fab_{\frac{11DCE}{TCA}}$	fab_11dce_tca	mol/mol	Moles of 1,1-DCE produced from abiotic decay of one mole of TCA
2	$Fan_{\frac{TCA}{TeCA}}$	fan_tca_teca	mol/mol	Moles of TCA produced from anaerobic decay of one mole of TeCA
3	$Fan_{\frac{11DCE}{TeCA}}$	fan_11dce_teca	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TeCA
4	$Fan_{\frac{cDCE}{TCE}}$	fan_cdce_tce	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TCE
5	$Fan_{\frac{tDCE}{TCE}}$	fan_tdce_tce	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TCE
6	$Fan_{\frac{11DCE}{TCE}}$	fan_11dce_tce	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TCE
7	$Fan_{\frac{VC}{cDCE}}$	fan_vc_cdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of cis-1,2-DCE
8	$Fan_{\frac{VC}{tDCE}}$	fan_vc_tdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of trans-1,2-DCE

Table 25. *(contd)*

ID #	Parameter	Fortran Variable	Units	Description
9	$Fan_{\frac{VC}{11DCE}}$	fan_vc_11dce	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1-DCE
10	kab_{TeCA}	kab_teca	1/day	First-order decay coefficient for abiotic dechlorination of TeCA
11	kab_{TCA}	kab_tca	1/day	First-order decay coefficient for abiotic dechlorination of TCA
12	kab_{DCA}	kab_dca	1/day	First-order decay coefficient for abiotic dechlorination of DCA
13	kab_{CA}	kab_ca	1/day	First-order decay coefficient for abiotic dechlorination of CA
14	kan_{TeCA}	kan_teca	1/day	First-order decay coefficient for anaerobic dechlorination of TeCA
15	kan_{TCA}	kan_tca	1/day	First-order decay coefficient for anaerobic dechlorination of TCA
16	kan_{DCA}	kan_dca	1/day	First-order decay coefficient for anaerobic dechlorination of DCA
17	kan_{CA}	kan_ca	1/day	First-order decay coefficient for anaerobic dechlorination of CA
18	kan_{PCE}	kan_pce	1/day	First-order decay coefficient for anaerobic dechlorination of PCE
19	kan_{TCE}	kan_tce	1/day	First-order decay coefficient for anaerobic dechlorination of TCE
20	kan_{cDCE}	kan_cdce	1/day	First-order decay coefficient for anaerobic dechlorination of cis-1,2-DCE
21	kan_{tDCE}	kan_tdce	1/day	First-order decay coefficient for anaerobic dechlorination of trans-1,2-DCE
22	kan_{11DCE}	kan_11dce	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCE
23	kan_{VC}	kan_vc	1/day	First-order decay coefficient for anaerobic dechlorination of VC
24	kae_{CA}	kae_ca	1/day	First-order decay coefficient for aerobic dechlorination of CA
25	kae_{cDCE}	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
26	kae_{tDCE}	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
27	kae_{11DCE}	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
28	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC

5.4   Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 26 through 29. These

parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 21 through 24, respectively.

Table 26. *Parameter Values for Example Simulation 1 – Base Case Anaerobic Conditions – with the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_11dce_tca	0.2	mol/mol	15	kan_tca	0.01	1/day
2	fan_tca_teca	0.2	mol/mol	16	kan_dca	0.025	1/day
3	fan_11dce_teca	0.8	mol/mol	17	kan_ca	0.025	1/day
4	fan_cdce_tce	0.8	mol/mol	18	kan_pce	0.025	1/day
5	fan_tdce_tce	0.2	mol/mol	19	kan_tce	0.025	1/day
6	fan_11dce_tce	0	mol/mol	20	kan_cdce	0.025	1/day
7	fan_vc_cdce	0.8	mol/mol	21	kan_tdce	0.025	1/day
8	fan_vc_tdce	0.8	mol/mol	22	kan_11dce	0.025	1/day
9	fan_vc_11dce	0.8	mol/mol	23	kan_vc	0.0025	1/day
10	kab_teca	0.006	1/day	24	kae_ca	0	1/day
11	kab_tca	0	1/day	25	kae_cdce	0	1/day
12	kab_dca	0.00003	1/day	26	kae_tdce	0	1/day
13	kab_ca	0.001	1/day	27	kae_11dce	0	1/day
14	kan_teca	0.005	1/day	28	kae_vc	0	1/day

Table 27. *Parameter Values for Example Simulation 2 – Rates at 10% of Example Simulation 1 – with the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_11dce_tca	0.2	mol/mol	15	kan_tca	0.001	1/day
2	fan_tca_teca	0.2	mol/mol	16	kan_dca	0.0025	1/day
3	fan_11dce_teca	0.8	mol/mol	17	kan_ca	0.0025	1/day
4	fan_cdce_tce	0.8	mol/mol	18	kan_pce	0.0025	1/day
5	fan_tdce_tce	0.2	mol/mol	19	kan_tce	0.0025	1/day
6	fan_11dce_tce	0	mol/mol	20	kan_cdce	0.0025	1/day
7	fan_vc_cdce	0.8	mol/mol	21	kan_tdce	0.0025	1/day
8	fan_vc_tdce	0.8	mol/mol	22	kan_11dce	0.0025	1/day
9	fan_vc_11dce	0.8	mol/mol	23	kan_vc	0.00025	1/day
10	kab_teca	0.0006	1/day	24	kae_ca	0	1/day
11	kab_tca	0	1/day	25	kae_cdce	0	1/day
12	kab_dca	0.000003	1/day	26	kae_tdce	0	1/day
13	kab_ca	0.0001	1/day	27	kae_11dce	0	1/day
14	kan_teca	0.0005	1/day	28	kae_vc	0	1/day

Table 28. *Parameter Values for Example Simulation 3 – Different F Values Than Example Simulation 1 – with the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_11dce_tca	0.8	mol/mol	15	kan_tca	0.01	1/day
2	fan_tca_teca	0.2	mol/mol	16	kan_dca	0.025	1/day
3	fan_11dce_teca	0.8	mol/mol	17	kan_ca	0.025	1/day
4	fan_cdce_tce	0.2	mol/mol	18	kan_pce	0.025	1/day
5	fan_tdce_tce	0	mol/mol	19	kan_tce	0.025	1/day
6	fan_11dce_tce	0.8	mol/mol	20	kan_cdce	0.025	1/day
7	fan_vc_cdce	0.2	mol/mol	21	kan_tdce	0.025	1/day
8	fan_vc_tdce	0.2	mol/mol	22	kan_11dce	0.025	1/day
9	fan_vc_11dce	0.2	mol/mol	23	kan_vc	0.0025	1/day
10	kab_teca	0.006	1/day	24	kae_ca	0	1/day
11	kab_tca	0	1/day	25	kae_cdce	0	1/day
12	kab_dca	0.00003	1/day	26	kae_tdce	0	1/day
13	kab_ca	0.001	1/day	27	kae_11dce	0	1/day
14	kan_teca	0.005	1/day	28	kae_vc	0	1/day

Table 29. *Parameter Values for Example Simulation 4 – Base Case Aerobic Conditions – with the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_11dce_tca	0.2	mol/mol	15	kan_tca	0	1/day
2	fan_tca_teca	0	mol/mol	16	kan_dca	0	1/day
3	fan_11dce_teca	0	mol/mol	17	kan_ca	0	1/day
4	fan_cdce_tce	0	mol/mol	18	kan_pce	0	1/day
5	fan_tdce_tce	0	mol/mol	19	kan_tce	0	1/day
6	fan_11dce_tce	0	mol/mol	20	kan_cdce	0	1/day
7	fan_vc_cdce	0	mol/mol	21	kan_tdce	0	1/day
8	fan_vc_tdce	0	mol/mol	22	kan_11dce	0	1/day
9	fan_vc_11dce	0	mol/mol	23	kan_vc	0	1/day
10	kab_teca	0.006	1/day	24	kae_ca	0.005	1/day
11	kab_tca	0	1/day	25	kae_cdce	0.005	1/day
12	kab_dca	0.00003	1/day	26	kae_tdce	0.005	1/day
13	kab_ca	0.001	1/day	27	kae_11dce	0.005	1/day
14	kan_teca	0	1/day	28	kae_vc	0.005	1/day
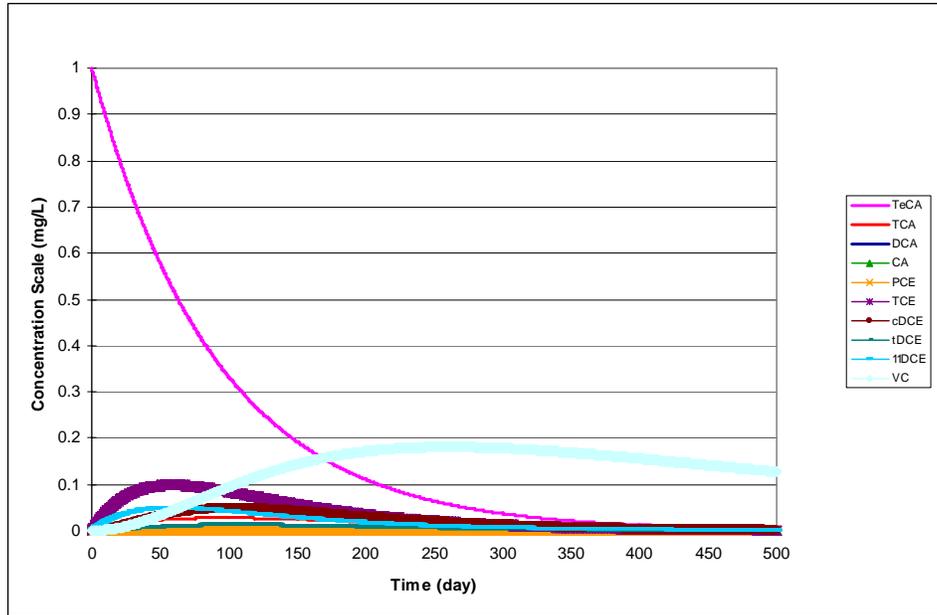
Figure 21. *Dechlorination of 1,1,1,2-TeCA Using the Parameter Values Shown in Table 26 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.*
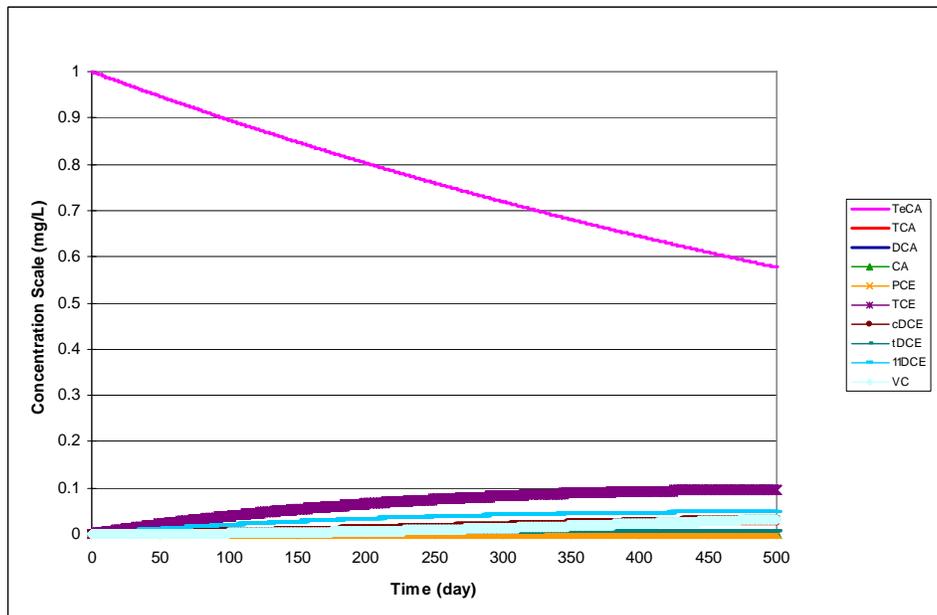
Figure 22. *Dechlorination of 1,1,1,2-TeCA Using the Parameter Values Shown in Table 27 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.*

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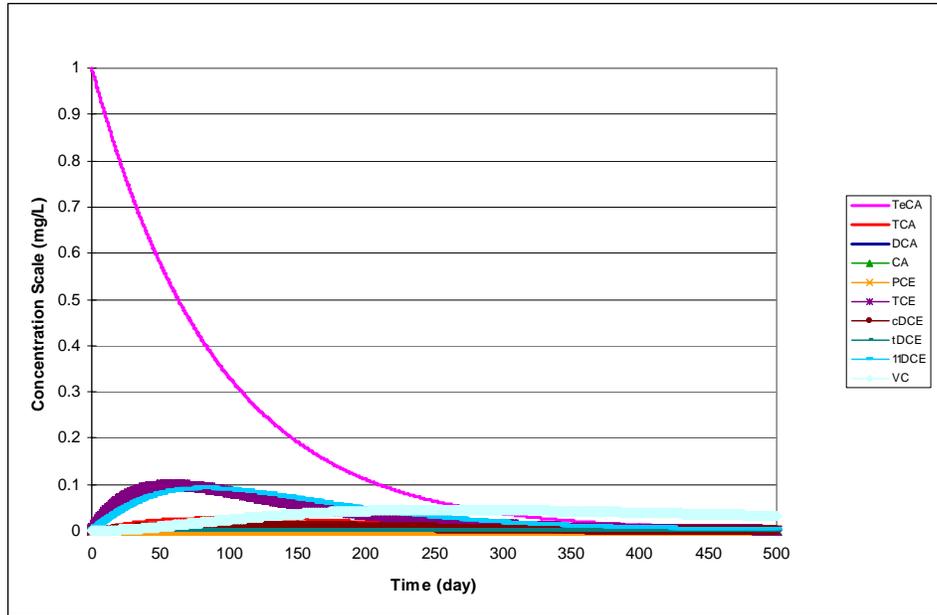
Figure 23. *Dechlorination of 1,1,1,2-TeCA Using the Parameter Values Shown in Table 28 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.*
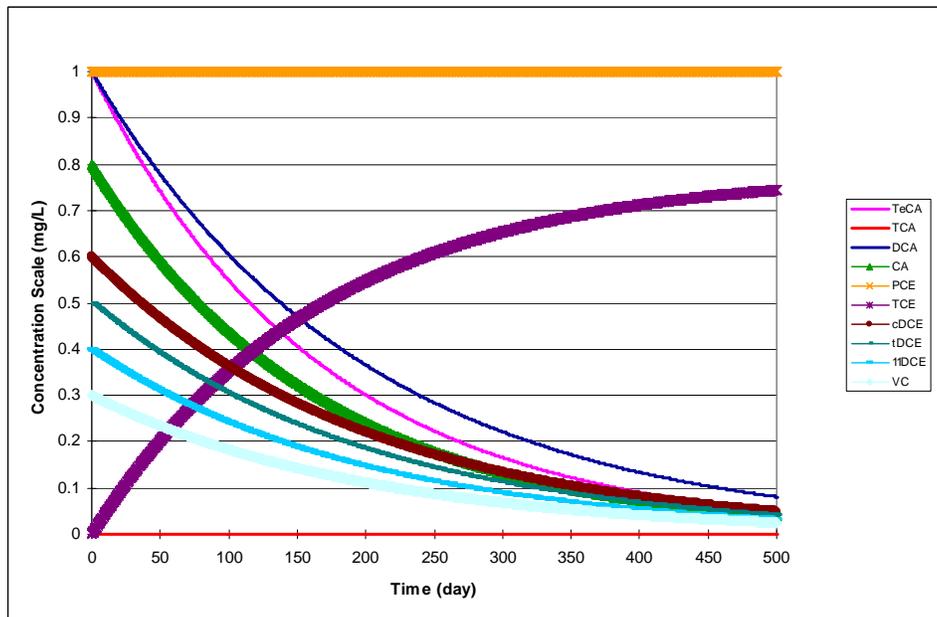
Figure 24. *Aerobic and Abiotic Degradation of Contaminants in the 1,1,1,2-TeCA and PCE Families Using the Parameter Values Shown in Table 29 — The initial concentrations for TeCA, TCA, DCA, CA, PCE, TCE, cDCE, tDCE, 11DCE, and VC were 1, 0, 1, 0.8, 1, 0, 0.6, 0.5, 0.4, and 0.3 mg/L, respectively.*

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6.0 Chloroethene Dechlorination

6.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of tetrachloroethene, and related daughter products using first-order rate expressions.   The module includes both aerobic and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 30 lists the chemical species included in this reaction module.   Figure 25 shows the conceptual model describing the potential biotic degradation pathways of both chlorinated ethene contaminants.   Note that abiotic degradation reactions for chlorinated ethene compounds are negligible, thus they are not included.   See the conceptual model discussion for the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for information on the development of the reaction pathways and the assumption of first-order reaction kinetics.

Table 30. *Chemical Species Included in the Chloroethene Dechlorination Reaction Module*

No.	Abbreviation [a]	Chemical Name	Selected Alternate Name	CAS [b] Registry Number	Molecular Weight [c] (g/mol)	Chemical Formula
1	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.8334	C_2Cl_4
2	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C_2HCl_3
3	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	$C_2H_2Cl_2$
4	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	$C_2H_2Cl_2$
5	11DCE	1,1-Dichloroethene	Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	$C_2H_2Cl_2$
6	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C_2H_3Cl
7	Tracer	Conservative Tracer	—	N/A	N/A	N/A

[a] These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

[b] CAS = Chemical Abstracts Service (see http://www.cas.org/EO/regsys.html)

[c] Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

Figure 25. *Conceptual Model for Dechlorination Reactions in the Chloroethene Dechlorination Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.*

6.2 Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 74 to 80. These ODEs describe the reaction kinetics for the 7 chemical species in Table 30. See Table 31 for a detailed itemization of all reaction parameters used in this reaction module.

$$\frac{dC_{PCE}}{dt} = \left(-kan_{PCE} \cdot C_{PCE} \right) \tag{74}$$

$$\frac{dC_{TCE}}{dt} = \left(\begin{array}{c} Y_{\frac{TCE}{PCE}} \cdot kan_{PCE} \cdot C_{PCE} \\ \\ - kan_{TCE} \cdot C_{TCE} \end{array} \right) \tag{75}$$

$$\frac{dC_{cDCE}}{dt} = \left(\begin{array}{c} Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{cDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\[2em] - kan_{cDCE} \cdot C_{cDCE} \; - \; kae_{cDCE} \cdot C_{cDCE} \end{array} \right) \tag{76}$$

$$\frac{dC_{tDCE}}{dt} = \left(\begin{array}{c} Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{tDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\[2em] - kan_{tDCE} \cdot C_{tDCE} \; - \; kae_{tDCE} \cdot C_{tDCE} \end{array} \right) \tag{77}$$

$$\frac{dC_{11DCE}}{dt} = \left(\begin{array}{c} Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{11DCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\[2em] - kan_{11DCE} \cdot C_{11DCE} \; - \; kae_{11DCE} \cdot C_{11DCE} \end{array} \right) \tag{78}$$

$$\frac{dC_{VC}}{dt} = \left(\begin{array}{c} Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{cDCE}} \cdot kan_{cDCE} \cdot C_{cDCE} \\[2em] + \; Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{tDCE}} \cdot kan_{tDCE} \cdot C_{tDCE} \\[2em] + \; Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{11DCE}} \cdot kan_{11DCE} \cdot C_{11DCE} \\[2em] - \; kan_{VC} \cdot C_{VC} \; - \; kae_{VC} \cdot C_{VC} \end{array} \right) \tag{79}$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \qquad \textit{(Conservative [non-reactive] tracer.)} \tag{80}$$

The first-order decay rate constants [T^{-1}] of the ith species are represented in the equations above by the kan_i, kae_i, and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the ith species is represented by the C_i term [ML^{-3}]. The R_i terms represent the retardation factor for the ith species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield [MM^{-1}] and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The

stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relations in Equations 81 to 84.

$$Fan_{\frac{cDCE}{TCE}} + Fan_{\frac{tDCE}{TCE}} + Fan_{\frac{DCE11}{TCE}} = 1.0 \tag{81}$$

$$Fan_{\frac{VC}{cDCE}} \leq 1.0 \tag{82}$$

$$Fan_{\frac{VC}{tDCE}} \leq 1.0 \tag{83}$$

$$Fan_{\frac{VC}{DCE11}} \leq 1.0 \tag{84}$$

6.3   Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 16 reaction parameters that must be specified for this reaction module are listed in Table 31 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 31. *Input Parameters for the Chloroethene Dechlorination Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	$Fan_{\frac{cDCE}{TCE}}$	fan_cdce_tce	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TCE
2	$Fan_{\frac{tDCE}{TCE}}$	fan_tdce_tce	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TCE
3	$Fan_{\frac{11DCE}{TCE}}$	fan_11dce_tce	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TCE
4	$Fan_{\frac{VC}{cDCE}}$	fan_vc_cdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of cis-1,2-DCE
5	$Fan_{\frac{VC}{tDCE}}$	fan_vc_tdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of trans-1,2-DCE
6	$Fan_{\frac{VC}{11DCE}}$	fan_vc_11dce	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1-DCE
7	kan_{PCE}	kan_pce	1/day	First-order decay coefficient for anaerobic dechlorination of PCE
8	kan_{TCE}	kan_tce	1/day	First-order decay coefficient for anaerobic dechlorination of TCE
9	kan_{cDCE}	kan_cdce	1/day	First-order decay coefficient for anaerobic dechlorination of cis-1,2-DCE
10	kan_{tDCE}	kan_tdce	1/day	First-order decay coefficient for anaerobic dechlorination of trans-1,2-DCE
11	kan_{11DCE}	kan_11dce	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCE
12	kan_{VC}	kan_vc	1/day	First-order decay coefficient for anaerobic dechlorination of VC
13	kae_{cDCE}	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
14	kae_{tDCE}	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
15	kae_{11DCE}	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
16	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC

6.4   Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 32 through 35. These

parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 26 through 29, respectively.

Table 32. *Parameter Values for Example Simulation 1 – Base Case Anaerobic Conditions – with the Chloroethene Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cdce_tce	0.8	mol/mol	9	kan_cdce	0.005	1/day
2	fan_tdce_tce	0.2	mol/mol	10	kan_tdce	0.005	1/day
3	fan_11dce_tce	0	mol/mol	11	kan_11dce	0.005	1/day
4	fan_vc_cdce	0.8	mol/mol	12	kan_vc	0.0025	1/day
5	fan_vc_tdce	0.8	mol/mol	13	kae_cdce	0	1/day
6	fan_vc_11dce	0.8	mol/mol	14	kae_tdce	0	1/day
7	kan_pce	0.025	1/day	15	kae_11dce	0	1/day
8	kan_tce	0.025	1/day	16	kae_vc	0	1/day

Table 33. *Parameter Values for Example Simulation 2 – Rates at 10% of Example Simulation 1 – with the Chloroethene Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cdce_tce	0.8	mol/mol	9	kan_cdce	0.0005	1/day
2	fan_tdce_tce	0.2	mol/mol	10	kan_tdce	0.0005	1/day
3	fan_11dce_tce	0	mol/mol	11	kan_11dce	0.0005	1/day
4	fan_vc_cdce	0.8	mol/mol	12	kan_vc	0.00025	1/day
5	fan_vc_tdce	0.8	mol/mol	13	kae_cdce	0	1/day
6	fan_vc_11dce	0.8	mol/mol	14	kae_tdce	0	1/day
7	kan_pce	0.0025	1/day	15	kae_11dce	0	1/day
8	kan_tce	0.0025	1/day	16	kae_vc	0	1/day

Table 34. *Parameter Values for Example Simulation 3 – Different F Values Than Example Simulation 1 – with the Chloroethene Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cdce_tce	0.2	mol/mol	9	kan_cdce	0.005	1/day
2	fan_tdce_tce	0	mol/mol	10	kan_tdce	0.005	1/day
3	fan_11dce_tce	0.8	mol/mol	11	kan_11dce	0.005	1/day
4	fan_vc_cdce	0.2	mol/mol	12	kan_vc	0.0025	1/day
5	fan_vc_tdce	0.2	mol/mol	13	kae_cdce	0	1/day
6	fan_vc_11dce	0.2	mol/mol	14	kae_tdce	0	1/day
7	kan_pce	0.025	1/day	15	kae_11dce	0	1/day
8	kan_tce	0.025	1/day	16	kae_vc	0	1/day

Table 35. *Parameter Values for Example Simulation 4 – Base Case Aerobic Conditions – with the Chloroethene Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cdce_tce	0	mol/mol	9	kan_cdce	0	1/day
2	fan_tdce_tce	0	mol/mol	10	kan_tdce	0	1/day
3	fan_11dce_tce	0	mol/mol	11	kan_11dce	0	1/day
4	fan_vc_cdce	0	mol/mol	12	kan_vc	0	1/day
5	fan_vc_tdce	0	mol/mol	13	kae_cdce	0.005	1/day
6	fan_vc_11dce	0	mol/mol	14	kae_tdce	0.005	1/day
7	kan_pce	0	1/day	15	kae_11dce	0.005	1/day
8	kan_tce	0	1/day	16	kae_vc	0.005	1/day
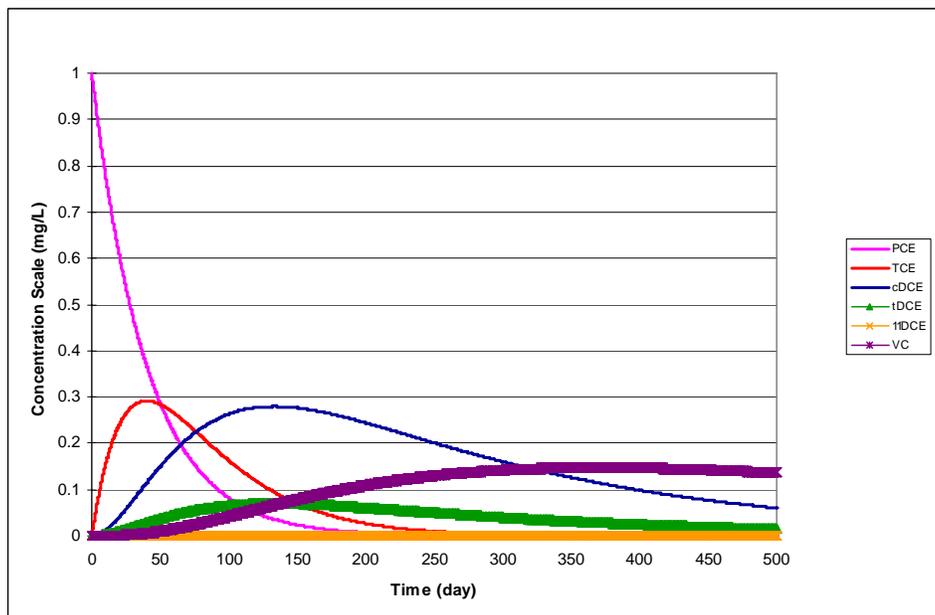
Figure 26. *Dechlorination of PCE Using the Parameter Values Shown in Table 32 — The initial concentration for PCE was 1 mg/L. All other species concentrations started at zero.*
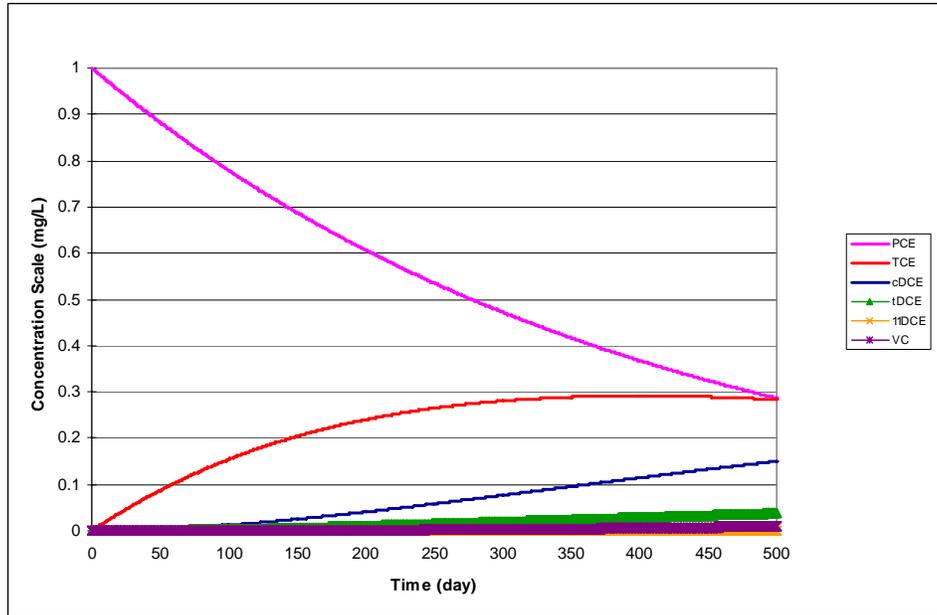
Figure 27. *Dechlorination of PCE Using the Parameter Values Shown in Table 33 — The initial concentration for PCE was 1 mg/L. All other species concentrations started at zero.*
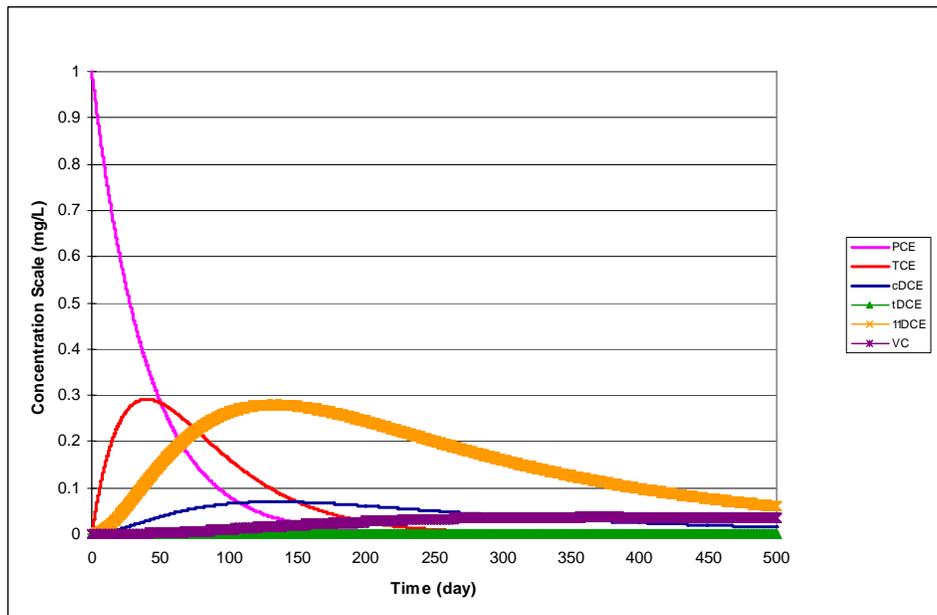
Figure 28. *Dechlorination of PCE Using the Parameter Values Shown in Table 34 — The initial concentration for PCE was 1 mg/L. All other species concentrations started at zero.*
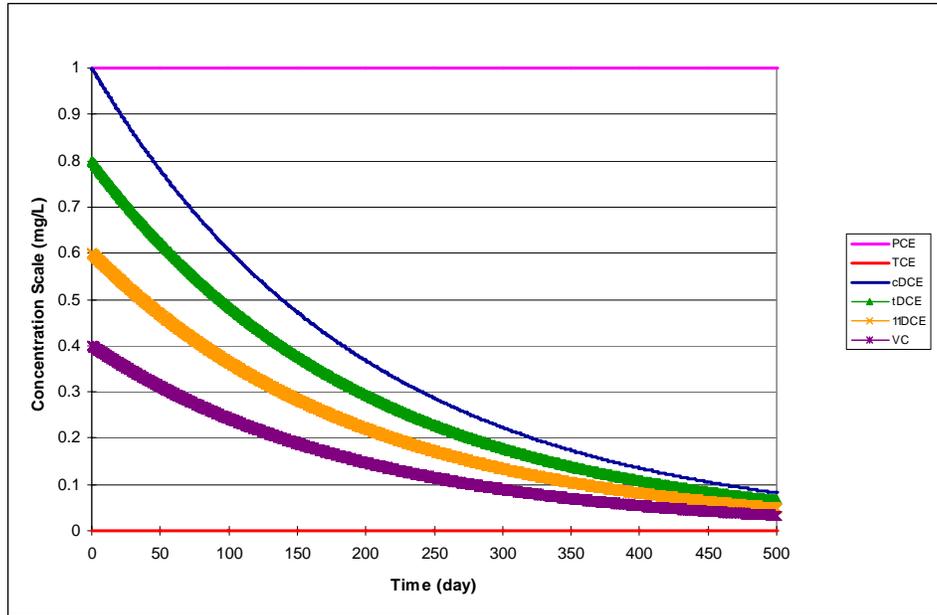
Figure 29. *Aerobic and Abiotic Degradation Using the Parameter Values Shown in Table 35 — The initial concentrations for PCE, TCE, cDCE, tDCE, 11DCE, and VC were 1, 0, 1, 0.8, 0.6, and 0.4 mg/L, respectively.*

7.0   Redox-Linked Dechlorination of Chloroethenes

7.1   Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of chlorinated ethene compounds by natural attenuation processes where the pathway and rate of transformation is dependent on the oxidation-reduction conditions. The reaction module adjusts the rate of dechlorination based on a simplified framework to represent the oxidation-reduction conditions in the aquifer. This module enables the user to link dechlorination rate to the concentration of geochemical indicator species. The module is not a full geochemical model, but provides one potential means for the user to model dechlorination at sites where the oxidation-reduction conditions in the aquifer are spatially or temporally variable. The module includes both aerobic and anoxic/anaerobic reaction pathways using first-order rate expressions (see the conceptual model description of the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for discussion on the assumption of first-order reaction kinetics). When oxygen is present, aerobic dechlorination of DCE isomers and VC can occur. If the oxygen concentration is below 0.1 mg/L, aerobic dechlorination is inhibited. At low concentrations of oxygen (dependent on a user-specified oxygen inhibition coefficient), anoxic/anaerobic dechlorination pathways are possible with rates depending on the concentration of key redox couples. Nitrate and oxygen inhibit all of the anoxic/anaerobic dechlorination pathways. The three key redox couples included in the module are iron (ferrous iron/amorphous ferric hydroxide), sulfur (sulfate/sulfide), and methane (methane/CO_2). The redox conditions, as indicated by a calculated pE value, are based on the relative concentrations of these species in each grid cell. The reaction module is based on the assumption that the redox conditions related to the key redox couples control the dechlorination reaction rate. Biological activity is not modeled explicitly under the premise that the biological activity related to natural attenuation occurs based on the low, widely distributed concentration of indigenous bacteria at a rate dependent on the geochemical conditions. The concentration of bacteria is assumed to remain constant. If sufficient substrate is present at a site to drive bacterial growth dynamics, other reaction modules that consider biomass growth and subsequent impacts to dechlorination rate should be used.

The concentrations of redox couples can be set as initial conditions with any desired spatial distribution (e.g., by interpolation of data at multiple monitoring wells). The redox species concentrations can then either 1) stay static during the simulation, or 2) vary during the simulation based on reactions of the redox species with oxygen or a user defined carbon source (modeled as a generic carbon compound). If the model is configured for varying redox couples, oxygen is also consumed by the carbon source or by oxidation of ferrous iron, sulfide, or methane. The user can enter a different first-order dechlorination rate for iron-dominated, sulfur-dominated, and methane-dominated redox conditions.

Table 36 lists the chemical species included in this reaction module. Figure 30 shows the conceptual model describing the degradation reactions modeled in this reaction module. Note that the carbon dioxide concentration is set to a constant value in the reaction module (because a buffered system is assumed). Thus, the methane-dominated redox condition is dependent only on variations in methane concentration. Ferric iron is modeled as an immobile species and all other species are mobile.

Table 36. *Chemical Species Included in the Redox-Linked Dechlorination of Chloroethenes Reaction Module*

No.	Abbreviation [a]	Chemical Name	Selected Alternate Name	CAS [b] Registry Number	Molecular Weight [c] (g/mol)	Chemical Formula
1	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.83340	C_2Cl_4
2	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C_2HCl_3
3	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	$C_2H_2Cl_2$
4	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	$C_2H_2Cl_2$
5	11DCE	1,1-Dichloroethene	Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	$C_2H_2Cl_2$
6	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C_2H_3Cl
7	OXY	Oxygen (dimer)	Dissolved Oxygen	7782-44-7	31.9988	O_2
8	NIT	Nitrate anion	—	14797-55-8	62.0049	NO_3^-
9	FE2	Ferrous Iron cation	Iron (II)	15438-31-0	55.8450	Fe^{2+}
10	SO4	Sulfate anion	Sulphate	14808-79-8	96.0626	SO_4^{2-}
11	HS	Hydrosulfide	Bisulfide	15035-72-0	33.07294	HS^-
12	CH4	Methane	—	74-82-8	16.04246	CH_4
13	DOC	Carbon Source [d]	Dissolved Organic Carbon	N/A	30.02598	CH_2O
14	Tracer	Conservative Tracer	—	N/A	N/A	N/A
15	FE3	Ferric Hydroxide (amorphous)	iron hydroxide; ferric iron; iron (III)	1309-33-7	106.86702	$Fe(OH)_3$

[a] These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.
[b] CAS = Chemical Abstracts Service (see http://www.cas.org/EO/regsys.html)
[c] Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].
[d] Dissolved organic carbon is represented by a simple hydrocarbon (based on the generic formula for an organic compound of $C_nH_{2n}O_n$ with n=1). Concentration of actual dissolved organic carbon must be converted to this basis for this reaction module.

N/A – Not Applicable

	Contaminants	Contaminant Reaction	Dominant Redox Couple or Electron Acceptor	pE Range where the redox couple controls the dechlorination rate [a]	Redox Reactions (if varying redox conditions are being modelled)
Aerobic	cDCE, tDCE, 11DCE, VC	First-Order Degradation [b]	O_2	N/A	
Anoxic / Anaerobic		NoDegradation (Inhibits Reactions Below)	NO_3^-	N/A	Presence of DOC: decrease in redox potential by reduction reactions
	PCE, TCE, cDCE, tDCE, 11DCE, VC	First-Order Dechlorination	Fe^{2+} / Fe^{3+} [c]	1.57 to - 3.42	Presence of O_2: increase in redox potential by oxidation reactions
		First-Order Dechlorination	HS^- / SO_4^{2-}	- 3.42 to - 3.89	
		First-Order Dechlorination	CH_4 / CO_2	< - 3.89	
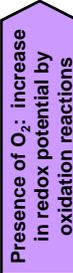
[a] Above the indicated pE range, the rates rapidly diminish to zero. The pE range was selected to represent when the reduction of the indicated electron acceptor is active.

[b] Aerobic degradation results in mineralization of the contaminants (no daughter contaminants formed).

[c] Fe^{3+} is modelled as amorphous ferric hydroxide to calculate the redox conditions.

Figure 30. *Conceptual Model for the Dechlorination Reactions of the Redox-Linked Dechlorination of Chloroethenes Reaction Module*

The conceptual model considers the rate of dechlorination or aerobic degradation as a function of the oxidation-reduction potential (at a fixed pH of 7) as controlled by key redox species that are commonly measured. These redox species also indicate the classes of microbial processes in the subsurface that are important for dechlorination or contaminant degradation reactions. The aerobic redox condition and associated degradation reactions are indicated sufficiently by the concentration of oxygen. When oxygen concentration is very low or oxygen is absent, anaerobic redox is divided into four different conditions. If nitrate is present at some location within the model domain, all other anaerobic reactions at that location are inhibited based on a user-specified inhibition coefficient. If nitrate is not present or has been depleted below the inhibitory level, anaerobic dechlorination can proceed at rates depending on the dominant electron acceptor process. The dominant electron acceptor process is defined by the relative concentrations of the redox couples shown in Figure 30. For iron, the redox potential is only a function of the ferrous iron concentration because ferric iron is only present as a solid. Ferric iron concentration are only important if the user desires to track changes in redox couples as impacted through oxidation by oxygen or through reduction by a carbon source. The sulfur redox potential is defined by the relative concentrations of sulfate and hydrosulfide (or dissolved sulfide converted to the equivalent hydrosulfide concentration based on the pH). The lowest possible redox potential occurs when methane is being produced. This redox couple uses a fixed dissolved CO_2 concentration in the reaction module such that the redox potential only varies as a function of the methane concentration. The module calculates the redox potential for each anaerobic redox

couple and the redox potential is set to the minimum value calculated for the three couples. Based on this minimum calculated redox potential, the module calculates dechlorination rates with the user-defined dechlorination rate coefficient associated with the redox range listed in Figure 30.

7.2   Reaction Equations

The basic functionality of this reaction module is described in this section for the 15 chemical species in Table 36. See Table 38 for a detailed itemization of all reaction parameters used in this reaction module.

The user must input a flag value to define the simulation as having static redox conditions or varying redox conditions. Static redox conditions may be useful if a user would like to interpolate available geochemical data and then let the module compute the distribution of related reaction rates. This rate distribution would then be used throughout the timeframe of the simulations. Use of static conditions may be suitable if it is unlikely that there will be significant changes in geochemical conditions over the duration of the simulation. By setting the flag to a value of "1" for static redox conditions, the reaction module computes the reaction rates in the first time step of the simulation based on the concentration distribution at the first time step (nominally the initial conditions). The module then holds these reaction rates constant throughout the simulation time period, though the rates will be spatially variable according to the input distribution of redox indicators. The module also sets the concentration of the redox indicators to zero after the first time step so that transport of these species is not tracked. By setting the flag to a value of "0" for varying redox conditions, the reaction module uses the full set of reactions described below at each time step to determine the dechlorination rates and associated concentration changes for each time step in the simulation.

If oxygen is present, the module first uses instantaneous (equilibrium) stoichiometric reactions (Equations 85 to 88) to deplete oxygen by sequential reaction with dissolved DOC, FE2, HS, and/or CH4 to the point where either all oxygen is consumed or all of these compounds are consumed. The initial concentrations (denoted as [Species]) for DOC, FE2, HS, CH4, and OXY are reduced to the post-oxidation concentrations $[Species]_{ox}$, which are used in the subsequent pE and dechlorination rate calculations.

$$1\,CH_2O + 1\,O_2 \rightarrow 1\,CO_2 + 1\,H_2O \tag{85}$$

$$4\,Fe^{2+} + 8\,OH^- + 2\,H_2O + 1\,O_2 \rightarrow 4\,Fe(OH)_3 \tag{86}$$

$$1\,HS^- + 1\,OH^- + 2\,O_2 \rightarrow 1\,SO_4^{2-} + 1\,H_2O \tag{87}$$

$$1\,CH_4 + 2\,O_2 \rightarrow 1\,CO_2 + 2\,H_2O \tag{88}$$
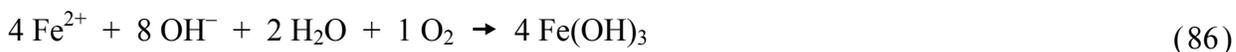
The initial oxygen concentration (prior to any oxidation reactions) inhibits anaerobic dechlorination reactions, as does the nitrate concentration (Equations 89 and 90). Oxygen must be present after the oxidation reactions for aerobic degradation of DCE isomers and VC to occur, which is enforced using the Monod term in Equation 91. However, the module does not consider consumption of oxygen during DCE isomer or VC oxidation.

$$OxyInhib = \left(\frac{k_{io}}{k_{io} + [OXY]} \right) \tag{89}$$

$$NitInhib = \left(\frac{k_{in}}{k_{in} + [NIT]} \right) \tag{90}$$

$$OxyPromo = \left(\frac{[OXY]_{ox}}{K_{O2} + [OXY]_{ox}} \right) \tag{91}$$

If the initial oxygen concentration is greater than 0.1 mg/L, then reduction of electron acceptors is not allowed in the same transport time step where they just underwent oxidization (i.e., rates of electron acceptor reduction are set to zero). If the initial oxygen concentration in a transport time step is less than 0.1 mg/L, then electron acceptors will undergo reduction at a rate depending on the electron acceptor and DOC concentration and inhibited by the initial oxygen concentration. Electron acceptors are sequentially inhibited based on 10% of the Monod half-saturation coefficient for nitrate and the Monod half-saturation coefficients for iron and sulfate. The DOC Monod half-saturation coefficient is defined as 1.0 E-4 mol/L for nitrate, iron, and sulfate and as 1.0 E-5 mol/L for methane. Equations 92 through 95 define the rates of electron acceptor reduction when the initial oxygen concentration is less than 0.1 mg/L.

$$r_{NIT} = k_{NIT} \cdot \left(\frac{[NIT]}{K_n + [NIT]} \right) \cdot \left(\frac{[DOC]_{ox}}{10^{-4} + [DOC]_{ox}} \right) \cdot OxyInhib \tag{92}$$

$$r_{FE3} = k_{FE3} \cdot \left(\frac{[FE3]_{ox}}{K_f + [FE3]_{ox}} \right) \cdot \left(\frac{[DOC]_{ox}}{10^{-4} + [DOC]_{ox}} \right) \cdot OxyInhib \cdot \left(\frac{0.1 \cdot K_n}{0.1 \cdot K_n + [NIT]} \right) \tag{93}$$

$$r_{SO4} = k_{SO4} \cdot \left(\frac{[SO4]_{ox}}{K_s + [SO4]_{ox}} \right) \cdot \left(\frac{[DOC]_{ox}}{10^{-4} + [DOC]_{ox}} \right) \cdot OxyInhib \cdot \left(\frac{0.1 \cdot K_n}{0.1 \cdot K_n + [NIT]} \right) \cdot \left(\frac{K_f}{K_f + [FE3]_{ox}} \right) \tag{94}$$

$$r_{CH4} = \mu_{CH4} \cdot \left(\frac{[DOC]_{ox}}{10^{-5} + [DOC]_{ox}} \right) \cdot OxyInhib \cdot \left(\frac{0.1 \cdot K_n}{0.1 \cdot K_n + [NIT]} \right) \cdot \left(\frac{K_f}{K_f + [FE3]_{ox}} \right) \cdot \left(\frac{K_s}{K_s + [SO4]_{ox}} \right) \tag{95}$$

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Three redox couples are represented in this reaction module:

1. Fe   iron   (ferrous iron / amorphous ferric hydroxide)
2. S   sulfur   (sulfate / hydrosulfide)
3. C   methane   (methane / CO_2)

The redox potential (pE) of a redox couple is calculated from the Nernst equation (Equation 96) using the number of electrons transferred (N_e) and the product of the reactant species concentrations to the power of the respective stoichiometric coefficients (b_i) divided by the product of the product species concentrations to the power of the respective stoichiometric coefficients (b_j) [Drever, 1988]. Assuming dilute aqueous solution, species concentrations are used in place of chemical activities. For solid species (e.g., $Fe(OH)_3$), the chemical activity is taken as 1.0. Equation 97 [Drever, 1988] is used to calculate the pE° at standard conditions (298.15 K, 1 atm, and unit activity) based on tabulated values of $\Delta G°$ (R is the gas constant, equal to 8.314472 J·K^{-1}·mol^{-1}). Free energies for the species important to the three redox couples of interest are given in Table 37. The reactions for these three redox couples are listed in Equations 98 to 100 along with calculated values for the terms of the pE° equation. The pE for each anaerobic redox couple is thus calculated for a pH of 7 (i.e., [H$^+$] = 10^{-7} mol/L) using Equations 101 to 103 (substituting in pE° values). These equations assume that the system is well buffered, thus the pH is constant and the concentration of CO_2 is constant at a value of 0.001 mol/L. At a very low concentration of a reduced species (FE2, HS, or CH4), the pE is set to an arbitrarily high value of 8.0 to prevent numerical problems. To avoid dealing with negative pE numbers in this reaction module, the pE values are shifted upwards by 10 units to obtain pE' (i.e., pE' = pE +10). The dominant redox couple is determined as the minimum of these three pE' values (Equation 104).

$$pE = pE° + \frac{1}{N_e} \cdot Log_{10}\left(\frac{\prod_{i=1}^{\#\ reactants} [reactant_i]^{b_i}}{\prod_{j=1}^{\#\ products} [product_j]^{b_j}}\right) \tag{96}$$

$$pE° = \frac{1}{N_e} \cdot Log_{10}(K_{eq}) = \frac{1}{N_e} \cdot Log_{10}\left(\frac{-\Delta G°}{R \cdot T}\right) = \frac{1}{N_e} \cdot \frac{Log_e\left(\frac{-\Delta G°}{R \cdot T}\right)}{Log_e(10)} \tag{97}$$

Table 37. *Free Energy for Chemical Species of Interest [Drever, 1988]*

Chemical Species	$\Delta G°$ (kJ)
H_2O	-237.13
$Fe(OH)_3$	-696.5
Fe^{2+}	-85.35
SO_4^{2-}	-744.53
HS^-	12.08
CO_2	-394.36
CH_4	-50.72

	$\ln(K_{eq})$	N_e	$pE°$	
$1\ Fe(OH)_3\ +\ 1\ e^-\ +\ 3\ H^+\ \rightleftarrows\ 1\ Fe^{2+}\ +\ 3\ H_2O$	40.5	1	17.57	(98)
$1\ SO_4^{2-}\ +\ 8\ e^-\ +\ 9\ H^+\ \rightleftarrows\ 1\ HS^-\ +\ 4\ H_2O$	77.5	8	4.20	(99)
$1\ CO_2\ +\ 8\ e^-\ +\ 8\ H^+\ \rightleftarrows\ 1\ CH_4\ +\ 2\ H_2O$	52.7	8	2.86	(100)
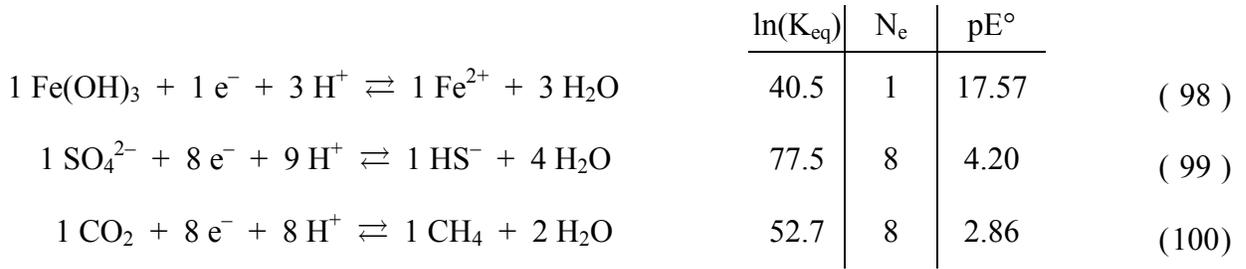
$$pE_F = 17.57 + Log_{10}\left(\frac{10^{-21}}{[FE2]_{ox}}\right) \qquad \textit{(for FE2 > 10^{-7} mol/L; pE$_F$ $\equiv$ 8.0 otherwise)} \qquad (101)$$

$$pE_S = 4.20 + \left(\frac{1}{8}\right)\cdot Log_{10}\left(\frac{[SO4]_{ox}\cdot 10^{-63}}{[HS]_{ox}}\right) \qquad \textit{(for HS > 10^{-7} mol/L; pE$_S$ $\equiv$ 8.0 otherwise)} \qquad (102)$$

$$pE_C = 2.86 + \left(\frac{1}{8}\right)\cdot Log_{10}\left(\frac{[CO2]\cdot 10^{-56}}{[CH4]_{ox}}\right) \qquad \textit{(for CH4 > 10^{-7} mol/L; pE$_C$ $\equiv$ 8.0 otherwise)} \qquad (103)$$

$$pE'_{dominant} = Minimum\left(pE'_F,\ pE'_S,\ pE'_C\right) \qquad (104)$$

As the pE' value for an aqueous solution decreases, the redox conditions are controlled by the iron, sulfur, and methane couples beginning at pE' values of 11.57, 6.58, and 6.11, respectively. Based on the dominant redox couple (i.e., pE'$_{dominant}$), fractional activities (pctFe, pctS, and pctC for iron, sulfur, and methane, respectively) are determined for each redox couple from the curves shown in Figure 31. "Fractional activities" (not to be confused with chemical activity) are assigned as values from 0.0 to 1.0 and are multipliers on the reaction rates (as discussed below). For a fractional activity of 1.0, the regime is fully active. When multiple regimes are active, only the leftmost regime on the pE' scale is allowed to impact the dechlorination rates (except in

transition zones, which are small). A sigmoidal function is used to provide a smooth (albeit steep) transition at the control points instead of using a step function (i.e., if/then logic). Sigmoidal function parameters (steepness and inflection point) were selected based on a 0.1 pE' unit change (i.e., the transition zone) where the fractional activity value changes from 0.0 to 1.0.
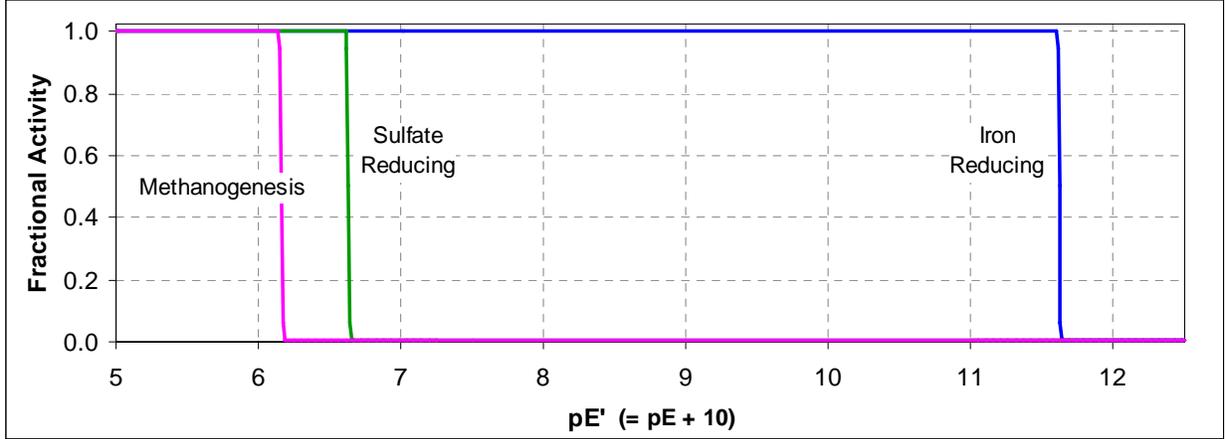
Figure 31. *pE Value (On a Shifted Scale) at Which Each Anaerobic Dechlorination Mechanism Dominates*

Anaerobic dechlorination rates are calculated based on the contaminant concentration, the inhibition from oxygen and nitrate, and the user-defined dechlorination rate coefficient associated with the dominant redox couple. Equations 105 to 110 describe the anaerobic dechlorination rates. These equations are implemented such that the dechlorination rates for only one redox regime apply (except in the small transition zone windows, where multiple regimes may apply at less than full activity). For example, at a pE'$_{dominant}$ value of 6.5, the fractional activities from Figure 31 for iron, sulfur, and methane, respectively, are 1.0, 1.0, and 0.0. The dechlorination rate in this example is that for sulfate ($kan_{Fe} + kan_S - kan_{Fe} + 0.0 = kan_S$)

$$ran_{PCE} = [PCE] \cdot OxyInhib \cdot NitInhib$$
$$\cdot \left(kan_{PCE\_Fe} \cdot pctFe + \left(kan_{PCE\_S} - kan_{PCE\_Fe} \right) \cdot pctS + \left(kan_{PCE\_C} - kan_{PCE\_S} \right) \cdot pctC \right) \quad (105)$$

$$ran_{TCE} = [TCE] \cdot OxyInhib \cdot NitInhib$$
$$\cdot \left(kan_{TCE\_Fe} \cdot pctFe + \left(kan_{TCE\_S} - kan_{TCE\_Fe} \right) \cdot pctS + \left(kan_{TCE\_C} - kan_{TCE\_S} \right) \cdot pctC \right) \quad (106)$$

$$ran_{cDCE} = [cDCE] \cdot OxyInhib \cdot NitInhib$$
$$\cdot \left(kan_{cDCE\_Fe} \cdot pctFe + \left(kan_{cDCE\_S} - kan_{cDCE\_Fe} \right) \cdot pctS + \left(kan_{cDCE\_C} - kan_{cDCE\_S} \right) \cdot pctC \right) \quad (107)$$

$$ran_{tDCE} = [tDCE] \cdot OxyInhib \cdot NitInhib$$
$$\cdot \left(kan_{tDCE\_Fe} \cdot pctFe + \left(kan_{tDCE\_S} - kan_{tDCE\_Fe} \right) \cdot pctS + \left(kan_{tDCE\_C} - kan_{tDCE\_S} \right) \cdot pctC \right) \quad (108)$$

$$ran_{11DCE} = [11DCE] \cdot OxyInhib \cdot NitInhib$$
$$\cdot \left(kan_{11DCE\_Fe} \cdot pctFe + \left(kan_{11DCE\_S} - kan_{11DCE\_Fe}\right) \cdot pctS + \left(kan_{11DCE\_C} - kan_{11DCE\_S}\right) \cdot pctC\right) \quad (109)$$

$$ran_{VC} = [VC] \cdot OxyInhib \cdot NitInhib$$
$$\cdot \left(kan_{VC\_Fe} \cdot pctFe + \left(kan_{VC\_S} - kan_{VC\_Fe}\right) \cdot pctS + \left(kan_{VC\_C} - kan_{VC\_S}\right) \cdot pctC\right) \quad (110)$$

The set of differential equations describing the reaction kinetics for all species is given in Equations 111 through 125.

$$\frac{d[PCE]}{dt} = -ran_{PCE} \quad (111)$$

$$\frac{d[TCE]}{dt} = -ran_{TCE} + ran_{PCE} \quad (112)$$

$$\frac{d[cDCE]}{dt} = -ran_{cDCE} + ran_{TCE} \cdot F_{cDCE/TCE} - kae_{cDCE} \cdot OxyPromo \cdot [cDCE] \quad (113)$$

$$\frac{d[tDCE]}{dt} = -ran_{tDCE} + ran_{TCE} \cdot F_{tDCE/TCE} - kae_{tDCE} \cdot OxyPromo \cdot [tDCE] \quad (114)$$

$$\frac{d[11DCE]}{dt} = -ran_{11DCE} + ran_{TCE} \cdot F_{11DCE/TCE} - kae_{11DCE} \cdot OxyPromo \cdot [11DCE] \quad (115)$$

$$\frac{d[VC]}{dt} = -ran_{VC} + ran_{cDCE} \cdot F_{VC/cDCE} + ran_{tDCE} \cdot F_{VC/tDCE} + ran_{11DCE} \cdot F_{VC/11DCE} - kae_{VC} \cdot OxyPromo \cdot [VC] \quad (116)$$

$$\frac{d[OXY]}{dt} = 0.0$$

(Oxygen is consumed by equilibrium oxidation reactions, but kinetic consumption of oxygen during DCE or VC biodegradation is not tracked because those are modeled as first-order processes.) $\quad (117)$

$$\frac{d[NIT]}{dt} = -r_{NIT} \cdot [NIT] \quad (118)$$

$$\frac{d[FE2]}{dt} = r_{FE3} \cdot [FE3]_{ox} \quad (119)$$

$$\frac{d[SO4]}{dt} = -r_{SO4} \cdot [SO4]_{ox} \quad (120)$$

$$\frac{d[HS]}{dt} = r_{SO4} \cdot [SO4]_{ox} \quad (121)$$

$$\frac{d[CH4]}{dt} = r_{CH4} \tag{122}$$

$$\frac{d[DOC]}{dt} = -r_{NIT} \cdot F_{DOC/NIT} \cdot [NIT]_{ox} - r_{FE3} \cdot F_{DOC/FE3} \cdot [FE3]_{ox} - r_{SO4} \cdot F_{DOC/SO4} \cdot [SO4]_{ox} \tag{123}$$

$$\frac{d[Tracer]}{dt} = 0.0 \qquad \textit{(Conservative [non-reactive] tracer.)} \tag{124}$$

$$\frac{d[FE3]}{dt} = -r_{FE3} \cdot [FE3]_{ox} \tag{125}$$

7.3   Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 39 reaction parameters that must be specified for this reaction module are listed in Table 38 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 38. *Input Parameters for the Redox-Linked Dechlorination of Chloroethenes Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	IsStatic	IsStatic	--	Value to signify whether the redox-dependant dechlorination rates are to be held constant (static) after an initial determination (1) or if the spatial distribution of redox conditions will be allowed to vary over time (0).
2	$F_{cDCE/TCE}$	f_cdce_tce	mol/mol	Molar stoichiometry of conversion from TCE to cDCE (based on site specific observation)
3	$F_{tDCE/TCE}$	f_tdce_tce	mol/mol	Molar stoichiometry of conversion from TCE to tDCE (based on site specific observation)
4	$F_{11DCE/TCE}$	f_11dce_tce	mol/mol	Molar stoichiometry of conversion from TCE to 11DCE (based on site specific observation)
5	$F_{VC/cDCE}$	f_vc_cdce	mol/mol	Molar stoichiometry of conversion from cDCE to VC (based on site specific observation)
6	$F_{VC/tDCE}$	f_vc_tdce	mol/mol	Molar stoichiometry of conversion from tDCE to VC (based on site specific observation)

Table 38. *(contd)*

ID #	Parameter	Fortran Variable	Units	Description
7	$F_{VC/11DCE}$	f_vc_11dce	mol/mol	Molar stoichiometry of conversion from 11DCE to VC (based on site specific observation)
8	K_{O2}	Ko2	mg/L	Monod half-saturation coefficient for oxygen as part of aerobic dechlorination reactions
9	K_n	Kn	mg/L	Monod half-saturation coefficient for nitrate reduction
10	K_f	Kf	mg/L	Monod half-saturation coefficient for iron reduction
11	K_s	Ks	mg/L	Monod half-saturation coefficient for sulfate reduction
12	k_{io}	kio	mg/L	Inhibition coefficient for oxygen on anaerobic activity
13	k_{in}	kin	mg/L	Inhibition coefficient for nitrate on anaerobic activity
14	kan_{PCE_Fe}	kan_pce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of PCE under iron dominated redox potential
15	kan_{PCE_S}	kan_pce_S	1/day	First-order decay coefficient for anaerobic dechlorination of PCE under sulfur dominated redox potential
16	kan_{PCE_C}	kan_pce_C	1/day	First-order decay coefficient for anaerobic dechlorination of PCE under methane dominated redox potential
17	kan_{TCE_Fe}	kan_tce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of TCE under iron dominated redox potential
18	kan_{TCE_S}	kan_tce_S	1/day	First-order decay coefficient for anaerobic dechlorination of TCE under sulfur dominated redox potential
19	kan_{TCE_C}	kan_tce_C	1/day	First-order decay coefficient for anaerobic dechlorination of TCE under methane dominated redox potential
20	kan_{cDCE_Fe}	kan_cdce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of cDCE under iron dominated redox potential
21	kan_{cDCE_S}	kan_cdce_S	1/day	First-order decay coefficient for anaerobic dechlorination of cDCE under sulfur dominated redox potential
22	kan_{cDCE_C}	kan_cdce_C	1/day	First-order decay coefficient for anaerobic dechlorination of cDCE under methane dominated redox potential
23	kan_{tDCE_Fe}	kan_tdce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of tDCE under iron dominated redox potential
24	kan_{tDCE_S}	kan_tdce_S	1/day	First-order decay coefficient for anaerobic dechlorination of tDCE under sulfur dominated redox potential
25	kan_{tDCE_C}	kan_tdce_C	1/day	First-order decay coefficient for anaerobic dechlorination of tDCE under methane dominated redox potential
26	kan_{11DCE_Fe}	kan_11dce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of 11DCE under iron dominated redox potential
27	kan_{11DCE_S}	kan_11dce_S	1/day	First-order decay coefficient for anaerobic dechlorination of 11DCE under sulfur dominated redox potential

Table 38. *(contd)*

ID #	Parameter	Fortran Variable	Units	Description
28	kan_{11DCE_C}	kan_11dce_C	1/day	First-order decay coefficient for anaerobic dechlorination of 11DCE under methane dominated redox potential
29	kan_{VC_Fe}	kan_vc_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of VC under iron dominated redox potential
30	kan_{VC_S}	kan_vc_S	1/day	First-order decay coefficient for anaerobic dechlorination of VC under sulfur dominated redox potential
31	kan_{VC_C}	kan_vc_C	1/day	First-order decay coefficient for anaerobic dechlorination of VC under methane dominated redox potential
32	kae_{cDCE}	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
33	kae_{tDCE}	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
34	kae_{11DCE}	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
35	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC
36	k_{NIT}	kNit	1/day	Maximum rate of nitrate reduction
37	k_{FE3}	kFe3	1/day	Maximum rate of iron reduction
38	k_{SO4}	kSO4	1/day	Maximum rate of sulfate reduction
39	μ_{CH4}	uCH4	mg/day	Maximum rate of methane production

7.4   Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 39 and 40. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 32 through 35, respectively.

Table 39. *Parameter Values for Example Simulations 1 and 2 with the Redox-Linked Dechlorination of Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	IsStatic	0	--	21	kan_cdce_S	0.0045	1/day
2	f_cdce_tce	1	mol/mol	22	kan_cdce_C	0.005	1/day
3	f_tdce_tce	0	mol/mol	23	kan_tdce_Fe	0	1/day
4	f_11dce_tce	0	mol/mol	24	kan_tdce_S	0	1/day
5	f_vc_cdce	1	mol/mol	25	kan_tdce_C	0	1/day
6	f_vc_tdce	1	mol/mol	26	kan_11dce_Fe	0	1/day
7	f_vc_11dce	1	mol/mol	27	kan_11dce_S	0	1/day
8	Ko2	0.5	mg/L	28	kan_11dce_C	0	1/day
9	Kn	0.5	mg/L	29	kan_vc_Fe	0.001	1/day
10	Kf	0.05	mg/L	30	kan_vc_S	0.0005	1/day
11	Ks	0.1	mg/L	31	kan_vc_C	0.0005	1/day
12	kio	0.1	mg/L	32	kae_cdce	0.01	1/day
13	kin	1	mg/L	33	kae_tdce	0	1/day
14	kan_pce_Fe	0.0005	1/day	34	kae_11dce	0	1/day
15	kan_pce_S	0.001	1/day	35	kae_vc	0.01	1/day
16	kan_pce_C	0.005	1/day	36	kNit	0	1/day
17	kan_tce_Fe	0.001	1/day	37	kFe3	0	1/day
18	kan_tce_S	0.001	1/day	38	kSO4	0	1/day
19	kan_tce_C	0.004	1/day	39	uCH4	0	mg/day
20	kan_cdce_Fe	0.004	1/day				

Table 40. *Parameter Values for Example Simulations 3 and 4 with the Redox-Linked Dechlorination of Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	IsStatic	0	--	21	kan_cdce_S	0.0045	1/day
2	f_cdce_tce	1	mol/mol	22	kan_cdce_C	0.005	1/day
3	f_tdce_tce	0	mol/mol	23	kan_tdce_Fe	0	1/day
4	f_11dce_tce	0	mol/mol	24	kan_tdce_S	0	1/day
5	f_vc_cdce	1	mol/mol	25	kan_tdce_C	0	1/day
6	f_vc_tdce	1	mol/mol	26	kan_11dce_Fe	0	1/day
7	f_vc_11dce	1	mol/mol	27	kan_11dce_S	0	1/day
8	Ko2	0.5	mg/L	28	kan_11dce_C	0	1/day
9	Kn	0.5	mg/L	29	kan_vc_Fe	0.001	1/day
10	Kf	0.05	mg/L	30	kan_vc_S	0.0005	1/day
11	Ks	0.1	mg/L	31	kan_vc_C	0.0005	1/day
12	kio	0.1	mg/L	32	kae_cdce	0.01	1/day
13	kin	1	mg/L	33	kae_tdce	0	1/day
14	kan_pce_Fe	0.0005	1/day	34	kae_11dce	0	1/day
15	kan_pce_S	0.001	1/day	35	kae_vc	0.01	1/day
16	kan_pce_C	0.005	1/day	36	kNit	0.1	1/day
17	kan_tce_Fe	0.001	1/day	37	kFe3	0.1	1/day
18	kan_tce_S	0.001	1/day	38	kSO4	0.1	1/day
19	kan_tce_C	0.004	1/day	39	uCH4	0.1	mg/day
20	kan_cdce_Fe	0.004	1/day				
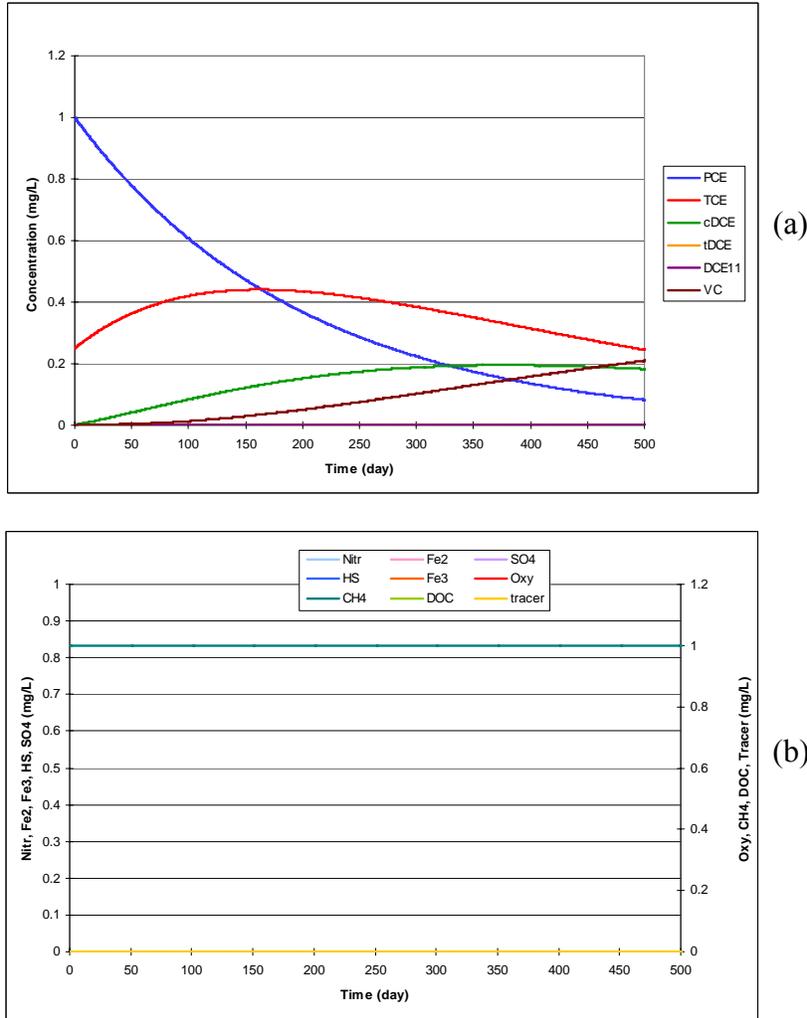
Figure 32. *Example Simulation 1: Dechlorination of PCE and TCE Using the Parameter Values Shown in Table 39 — The initial concentration for PCE, TCE, and methane were 1, 0.25, and 1 mg/L, respectively. All other species concentrations started at zero. Note that the concentrations of redox species remain constant in this simulation. Figure (a) shows chlorinated solvent concentration. Figure (b) shows the concentration of other species.*
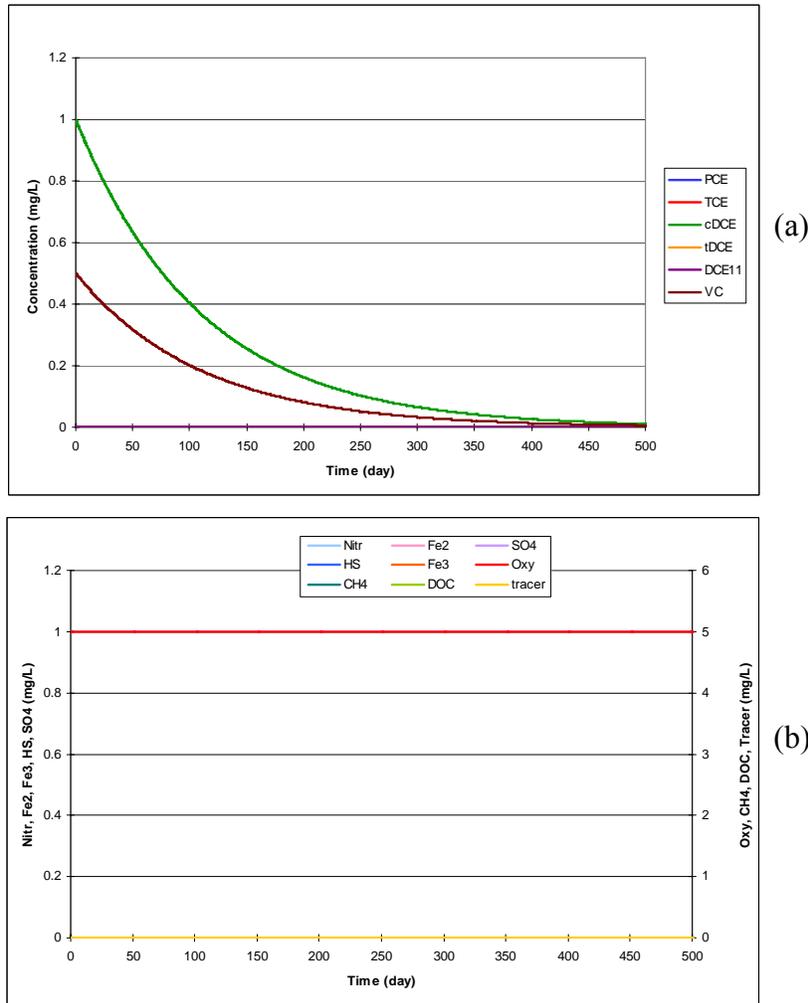
Figure 33. *Example Simulation 2: Dechlorination of cDCE and VC Using the Parameter Values Shown in Table 39 — The initial concentration for cDCE, VC, oxygen, and nitrate were 1, 0.5, 5, and 1 mg/L, respectively. All other species concentrations started at zero. Note that the concentrations of redox species remain constant in this simulation. Figure (a) shows chlorinated solvent concentration. Figure (b) shows the concentration of other species.*

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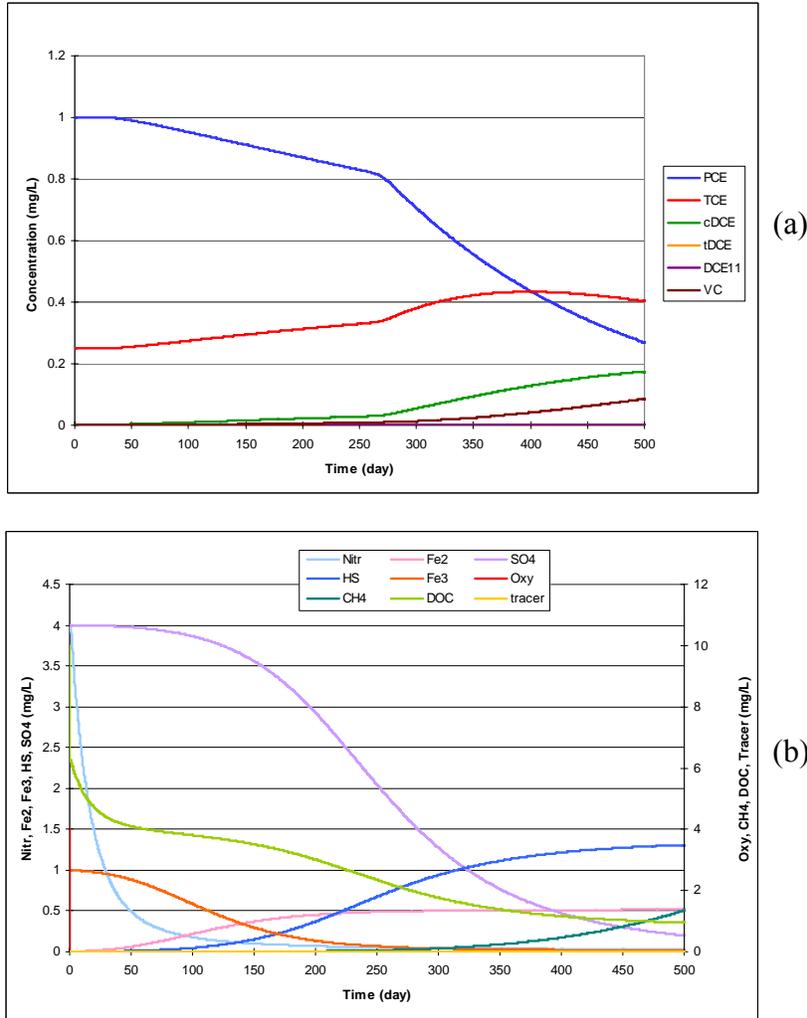
Figure 34. *Example Simulation 3: Dechlorination of PCE and TCE Using the Parameter Values Shown in Table 40 — The initial concentration for PCE, TCE, oxygen, nitrate, sulfate, dissolved organic carbon, and iron(III) were 1, 0.25, 4, 4, 4, 10, and 1 mg/L, respectively. All other species concentrations started at zero. Note that the concentrations of redox species vary in this simulation according to oxidation processes and the reduction rate input parameters. Figure (a) shows chlorinated solvent concentration. Figure (b) shows the concentration of other species.*

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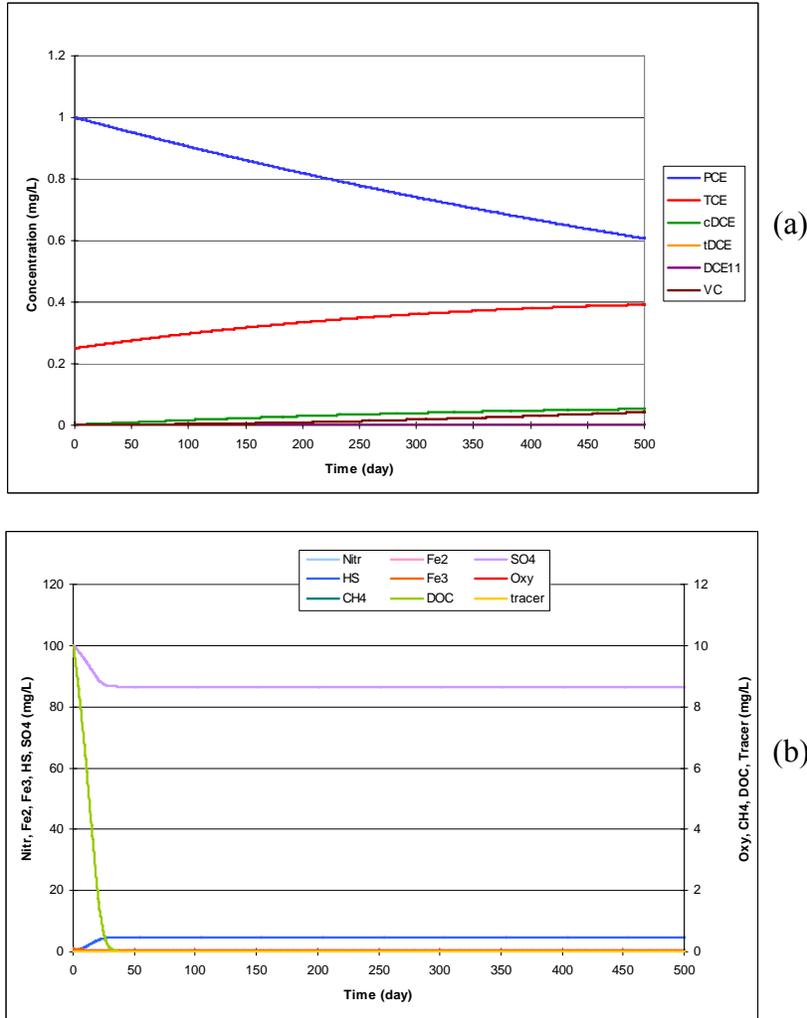
Figure 35. *Example Simulation 4: Dechlorination of PCE and TCE Using the Parameter Values Shown in Table 40 — The initial concentration for PCE, TCE, sulfate, dissolved organic carbon, and iron(III) were 1, 0.25, 100, 10, and 1 mg/L, respectively. All other species concentrations started at zero. Note that the concentrations of redox species vary in this simulation according to oxidation processes and the reduction rate input parameters. Figure (a) shows chlorinated solvent concentration. Figure (b) shows the concentration of other species.*

8.0   Substrate-Linked Reductive Dechlorination of Chloroethenes

8.1   Conceptual Model for Dechlorination Reactions

This reaction module describes reductive dechlorination of chlorinated ethene compounds linked to substrate metabolism (biostimulation) and corresponding biomass activity. The module includes an explicit description of biomass growth in response to consumption of lactate, propionate, acetate, hydrogen, and/or decaying biomass and separately models the metabolic activity of methanogens and other anaerobes able to metabolize lactate fermentation products. Both types of biomass will decay over time according to a user-specified decay rate. This reaction module does not account for changes in porosity/permeability resulting from biomass growth, although the total biomass is also tracked so that the modeler can assess the potential for biological fouling of the aquifer. If required, macroscopic models for biomass-affected porous media properties [Clement et al., 1996] could be combined with this module as a user-defined reaction module to account for changes in porosity/permeability. All anaerobic activity is inhibited by oxygen. Oxygen is depleted by lactate, propionate, or acetate through a stoichiometric reaction. Biomass growth is modeled with a Monod kinetic form, is dependent on substrate concentration, and is inhibited by high concentrations of organic acids. Reductive dechlorination of chlorinated ethene compounds is dependent on the concentration of the chlorinated ethene compound and methanogen biomass, and is inhibited by presence of higher-chlorinated ethene compounds (e.g., TCE inhibits the DCE dechlorination rate). Aerobic degradation of DCE and VC are modeled as first-order reactions (see the conceptual model description of the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for discussion on the assumption of first-order reaction kinetics).

The linkage of dechlorination to methanogenesis, similar to Skeen et al. [1995], is intended to provide a simplified conceptual model representing dechlorinating activity under methanogenic redox conditions, as an alternative to a detailed representation of all reaction mechanisms that may be involved.

Table 41 lists the chemical species included in this reaction module. Figure 36 shows the conceptual model describing the degradation reactions modeled in this reaction module.

Table 41. *Chemical Species Included in the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module*

No.	Abbreviation [a]	Chemical Name	Selected Alternate Name	CAS [b] Registry Number	Molecular Weight [c] (g/mol)	Chemical Formula
1	LAC	Lactate	2-hydroxy-propanoic acid (ion)	113-21-3 (lactic acid: 50-21-5)	89.0700	$C_3H_5O_3^-$
2	PRO	Propionate	Propanoic acid (ion)	72-03-7 (propionic acid: 79-09-4)	73.0706	$C_3H_5O_2^-$
3	ACE	Acetate	Acetic acid (ion)	71-50-1 (acetic acid: 64-19-7)	59.04402	$C_2H_3O_2^-$
4	H2	Hydrogen	—	1333-74-0	2.01588	H_2
5	MET	Methane	—	74-82-8	16.04246	CH_4
6	PCE	Tetrachloroethene	Perchloroethylene	127-18-4	165.83340	C_2Cl_4
7	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C_2HCl_3
8	DCE	Dichloroethene (all isomers)	Dichloroethylene	156-59-2	96.94328	$C_2H_2Cl_2$
9	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C_2H_3Cl
10	ETH	Ethene	ethylene	74-85-1	28.05316	C_2H_4
11	OXY	Oxygen (dimer)	dissolved oxygen	7782-44-7	31.9988	O_2
12	Tracer	Conservative Tracer	—	N/A	N/A	N/A
13	Bio1	Fermentors	—	N/A	113.11458	$C_5H_7O_2N$
14	Bio2	Methanogens	—	N/A	113.11458	$C_5H_7O_2N$
15	BioT	Total Biomass	—	N/A	113.11458	$C_5H_7O_2N$

[a] These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.
[b] CAS = Chemical Abstracts Service (see http://www.cas.org/EO/regsys.html)
[c] Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].
N/A – Not Applicable
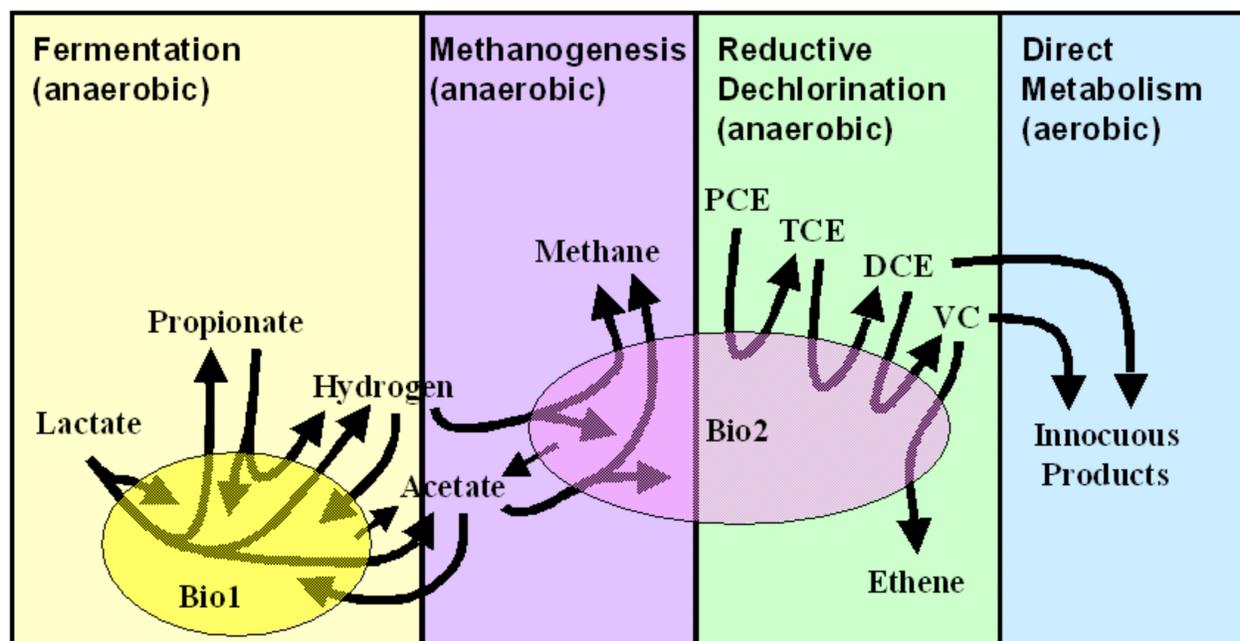
Figure 36. *Conceptual Model for the Reductive Dechlorination Reactions of the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module*

8.2 Reaction Equations

The basic functioning of this reaction module is described in this section for the 15 chemical species in Table 41. See Table 42 for a detailed itemization of all reaction parameters used in this reaction module.

If oxygen is present, the module first uses instantaneous (equilibrium) stoichiometric reactions (Equations 126 to 128) to deplete oxygen by reaction with the organic acids. The module has provisions to sequentially oxidize organic acids in the order of lactate, propionate, and acetate to the point where either all oxygen is consumed or all organic acids are consumed. The initial concentrations for lactate, propionate, acetate, and oxygen [Species] are reduced to the post-oxidation concentrations $[Species]_{ox}$, which are used in the subsequent biomass growth and dechlorination rate calculations. The sum of the residual lactate, propionate, and acetate is calculated as the organic acid concentration [OrgAcid], which is used in the determination of the organic acid inhibition term. Oxygen, $[OXY]_{ox}$, inhibits anaerobic reactions and also must be present for aerobic degradation of DCE and VC. However, the module does not consider consumption of oxygen during DCE or VC oxidation.

$$1\ C_3H_5O_3^- + 1\ H^+ + 3\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O \tag{126}$$

$$2\ C_3H_5O_2^- + 2\ H^+ + 7\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \tag{127}$$

$$1\ C_2H_3O_2^- + 1\ H^+ + 2\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O \tag{128}$$

Inhibition of biomass growth because of the presence of oxygen (InhibOxy) and organic acids (InhibOA1 and InhibOA2 for Bio1 and Bio2, respectively) is calculated based on a sigmoidal function. When the relevant concentration ($[OXY]_{ox}$ or $[OrgAcid]$) is at 90% of the inhibition coefficient value (k_{io}, k_{i1}, or k_{i2}), the inhibition term is equal to a value of 1.0. When the relevant concentration is at 110% of the inhibition coefficient value, then the fractional inhibition term has a value of 0.0. The fractional inhibition terms follow a sigmoidal functionality between those points, as shown in Figure 37. Conversely, the PromoOxy term acts in the opposite manner to allow aerobic reactions at concentrations above the value of k_{io}. The biomass decay rate is attenuated as the biomass concentration approaches the minimum in a similar manner by setting the f_{dec1} and f_{dec2} fractional terms for Bio1 and Bio2, respectively, to 0.0 at the minimum biomass concentration and to 1.0 at 120% of the minimum biomass concentration.
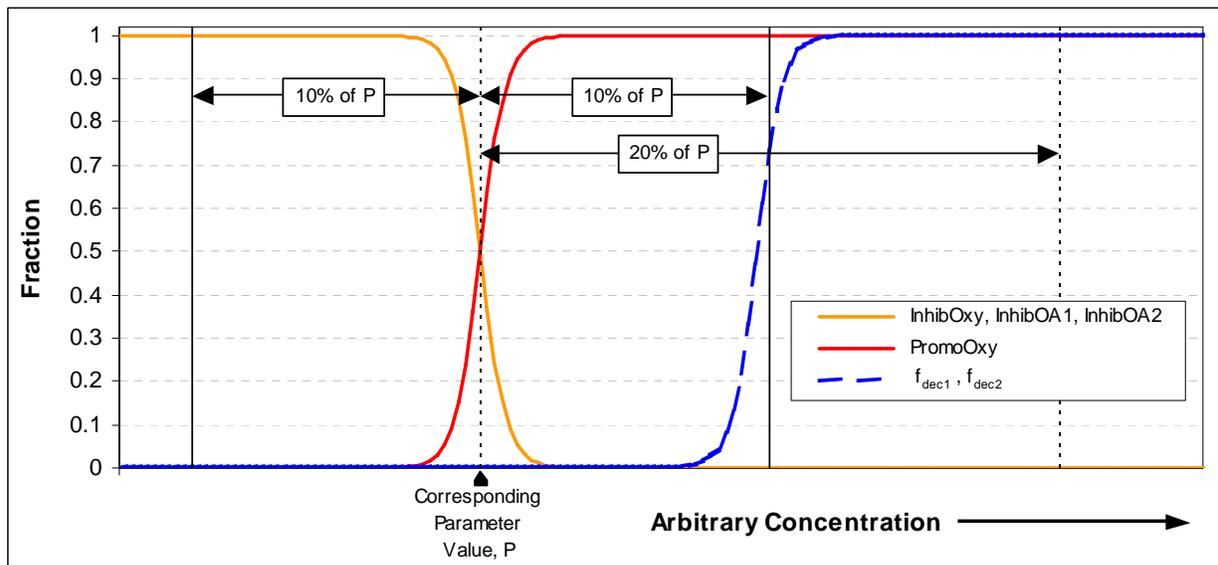
Figure 37. *Conceptual Diagram of the Behavior of the Function Representing a Change in Conditions as a Smooth Transition in the Form of a Sigmoidal Curve — This diagram depicts the trend for the various groups of parameters; the actual curves will be shifted on the X-axis based on the corresponding target concentration.*

Monod growth kinetics with inhibition by oxygen and organic acids are used to compute growth of fermentors (Bio1) and methanogens (Bio2) for the different potential substrates (Equations 129 through 134).

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$$r_1 = \mu_{l1} \cdot [Bio1] \cdot \left(\frac{[Lac]_{ox}}{K_{l1} + [Lac]_{ox}} \right) \cdot InhibOxy \cdot InhibOA1 \tag{129}$$

$$r_2 = \mu_{p1} \cdot [Bio1] \cdot \left(\frac{[Pro]_{ox}}{K_{p1} + [Pro]_{ox}} \right) \cdot InhibOxy \cdot InhibOA1 \tag{130}$$

$$r_3 = \mu_{a2} \cdot [Bio2] \cdot \left(\frac{[Ace]_{ox}}{K_{a2} + [Ace]_{ox}} \right) \cdot InhibOxy \cdot InhibOA2 \tag{131}$$

$$r_4 = \mu_{h2} \cdot [Bio2] \cdot \left(\frac{[H2]}{K_{h2} + [H2]} \right) \cdot InhibOxy \cdot InhibOA2 \tag{132}$$

$$r_5 = \mu_{a1} \cdot [Bio1] \cdot \left(\frac{[Ace]_{ox}}{K_{a1} + [Ace]_{ox}} \right) \cdot InhibOxy \cdot InhibOA1 \tag{133}$$

$$r_7 = \mu_{h1} \cdot [Bio1] \cdot \left(\frac{[H2]}{K_{h1} + [H2]} \right) \cdot InhibOxy \cdot InhibOA1 \tag{134}$$

Equations 135 through 149 describe the rate of concentration change for each chemical species. These equations include the consumption/transformation/production based on the biomass growth, oxidation of the organic acids, biomass decay, and aerobic destruction of lesser-chlorinated ethenes. Aerobic degradation of DCE and VC only occurs in the presence of oxygen (if sufficient oxygen remains after oxidation of organic acids) and is modeled as a first-order process (see the conceptual model description of the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for discussion on the assumption of first-order reaction kinetics). A fraction of the decayed biomass is assumed to be converted to acetate, which is then available to support biomass growth. Anaerobic dechlorination of TCE, DCE, and VC are inhibited by the presence of higher-chlorinated ethene species proportional to the ratio of the species to the sum of the species plus all higher-chlorinated species.

$$\frac{d[LAC]}{dt} = -r_1 \cdot \left(\frac{1}{F_{X/_{LAC}}} \right) \tag{135}$$

$$\frac{d[PRO]}{dt} = r_1 \cdot \left(\frac{F_{PRO/_{LAC}}}{F_{X/_{LAC}}} \right) - r_2 \cdot \left(\frac{1}{F_{X/_{PRO}}} \right) \tag{136}$$

$$\frac{d[ACE]}{dt} = r_1 \cdot \left(\frac{F_{ACE/LAC}}{F_{X1/LAC}} \right) + r_2 \cdot \left(\frac{F_{ACE/PRO}}{F_{X1/PRO}} \right) - r_3 \cdot \left(\frac{1}{F_{X2/ACE}} \right) - r_5 \cdot \left(\frac{1}{F_{X1/ACE}} \right)$$

$$\text{(137)}$$

$$+ F_{ACE/X} \cdot f_{dk2ace} \cdot \left(f_{dec1} \cdot k_{dec1} \cdot [Bio1] + f_{dec2} \cdot k_{dec2} \cdot [Bio2] \right)$$

$$\frac{d[H2]}{dt} = r_1 \cdot \left(\frac{F_{H2/LAC}}{F_{X1/LAC}} \right) + r_2 \cdot \left(\frac{F_{H2/PRO}}{F_{X1/PRO}} \right) - r_4 \cdot \left(\frac{1}{F_{X2/H2}} \right) - r_7 \cdot \left(\frac{1}{F_{X1/H2}} \right)$$

$$\text{(138)}$$

$$\frac{d[MET]}{dt} = qq = r_3 \cdot \left(\frac{F_{MET/ACE}}{F_{X2/ACE}} \right) + r_4 \cdot \left(\frac{F_{MET/H2}}{F_{X2/H2}} \right)$$

$$\text{(139)}$$

$$\frac{d[PCE]}{dt} = -qq \cdot F_{PCE/MET} \cdot \left(\frac{[PCE]}{K_{PCE} + [PCE]} \right)$$

$$\text{(140)}$$

$$\frac{d[TCE]}{dt} = qq \cdot \left[F_{PCE/MET} \cdot \left(\frac{[PCE]}{K_{PCE} + [PCE]} \right) - F_{TCE/MET} \cdot \left(\frac{[TCE]}{K_{TCE} + [TCE]} \right) \cdot \left(\frac{[TCE]}{[PCE] + [TCE]} \right) \right]$$

$$\text{(141)}$$

$$\frac{d[DCE]}{dt} = qq \cdot F_{TCE/MET} \cdot \left(\frac{[TCE]}{K_{TCE} + [TCE]} \right) \cdot \left(\frac{[TCE]}{[PCE] + [TCE]} \right)$$

$$- qq \cdot F_{DCE/MET} \cdot \left(\frac{[DCE]}{K_{DCE} + [DCE]} \right) \cdot \left(\frac{[DCE]}{[PCE] + [TCE] + [DCE]} \right)$$

$$\text{(142)}$$

$$- kae_{DCE} \cdot [DCE] \cdot PromoOxy$$

$$\frac{d[VC]}{dt} = qq \cdot F_{DCE/MET} \cdot \left(\frac{[DCE]}{K_{DCE} + [DCE]} \right) \cdot \left(\frac{[DCE]}{[PCE] + [TCE] + [DCE]} \right)$$

$$- qq \cdot F_{VC/MET} \cdot \left(\frac{[VC]}{K_{VC} + [VC]} \right) \cdot \left(\frac{[VC]}{[PCE] + [TCE] + [DCE] + [VC]} \right)$$

$$\text{(143)}$$

$$- kae_{VC} \cdot [VC] \cdot PromoOxy$$

$$\frac{d[ETH]}{dt} = qq \cdot F_{VC/MET} \cdot \left(\frac{[VC]}{K_{VC} + [VC]} \right) \cdot \left(\frac{[VC]}{[PCE] + [TCE] + [DCE] + [VC]} \right)$$

$$\text{(144)}$$

$$\frac{d[OXY]}{dt} = 0.0$$

(Oxygen is consumed by equilibrium oxidation reactions, but kinetic consumption of oxygen during DCE or VC biodegradation is not tracked because those are modeled as first-order processes.)

(145)

$$\frac{d[Tracer]}{dt} = 0.0$$

(Conservative [non-reactive] tracer.)

(146)

$$\frac{d[Bio1]}{dt} = r_2 + r_5 + r_1 + r_7 - f_{dec1} \cdot k_{dec1} \cdot [Bio1]$$

(147)

$$\frac{d[Bio2]}{dt} = r_3 + r_4 - f_{dec2} \cdot k_{dec2} \cdot [Bio2]$$

(148)

$$\frac{d[BioT]}{dt} = r_2 + r_5 + r_1 + r_7 + r_3 + r_4 - f_{dec1} \cdot k_{dec1} \cdot [Bio1] - f_{dec2} \cdot k_{dec2} \cdot [Bio2]$$

(149)

8.3   Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 44 reaction parameters that must be specified for this reaction module are listed in Table 42 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 42. *Input Parameters for the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	$Bio1_{min}$	minbio1	mg-DW/L	Minimum (background) biomass concentration for "fermentors"
2	$Bio2_{min}$	minbio2	mg-DW/L	Minimum (background) biomass concentration for methanogens
3	k_{dec1}	kdec1	1/day	First-order decay rate for biomass1
4	k_{dec2}	kdec2	1/day	First-order decay rate for biomass2
5	μ_{l1}	ul1	1/day	Maximum growth rate for biomass 1 on lactate
6	μ_{p1}	up1	1/day	Maximum growth rate for biomass 1 on propionate
7	μ_{a2}	ua2	1/day	Maximum growth rate for biomass 2 on acetate
8	μ_{h2}	uh2	1/day	Maximum growth rate for biomass 2 on hydrogen
9	μ_{a1}	ua1	1/day	Maximum growth rate for biomass 1 on acetate

Table 42. *(contd)*

ID #	Parameter	Fortran Variable	Units	Description
10	μ_{h1}	uh1	1/day	Maximum growth rate for biomass 1 on hydrogen
11	k_{i1}	ki1	mg/L	Inhibition coefficient for organic acids on biomass 1
12	k_{i2}	ki2	mg/L	Inhibition coefficient for organic acids on biomass 2
13	k_{io}	kio	mg/L	Inhibition coefficient for oxygen on anaerobic activity
14	K_{l1}	Kl1	mg/L	Monod half-saturation coefficient for "fermentor" growth on lactate
15	K_{p1}	Kp1	mg/L	Monod half-saturation coefficient for "fermentor" growth on propionate
16	K_{a2}	Ka2	mg/L	Monod half-saturation coefficient for methanogen growth on acetate
17	K_{h2}	Kh2	mg/L	Monod half-saturation coefficient for methanogen growth on hydrogen
18	K_{a1}	Ka1	mg/L	Monod half-saturation coefficient for "fermentor" growth on acetate
19	K_{h1}	Kh1	mg/L	Monod half-saturation coefficient for "fermentor" growth on hydrogen
20	K_{PCE}	Kpce	mg/L	Monod half-saturation coefficient for PCE dechlorination
21	K_{TCE}	Ktce	mg/L	Monod half-saturation coefficient for TCE dechlorination
22	K_{DCE}	Kdce	mg/L	Monod half-saturation coefficient for DCE dechlorination
23	K_{VC}	Kvc	mg/L	Monod half-saturation coefficient for VC dechlorination
24	f_{dk2ace}	fdk2ace	--	Fraction of biomass that can decay to produce acetate
25	$F_{ACE/X}$	f_ace_x	mol/mol	Moles of acetate formed per mole of biomass decayed
26	$F_{X1/LAC}$	f_x1_lac	mol/mol	Moles of biomass1 formed per mole of lactate
27	$F_{X1/PRO}$	f_x1_pro	mol/mol	Moles of biomass1 formed per mole of propionate
28	$F_{X1/ACE}$	f_x1_ace	mol/mol	Moles of biomass1 formed per mole of acetate
29	$F_{X1/H2}$	f_x1_h2	mol/mol	Moles of biomass1 formed per mole of hydrogen
30	$F_{X2/ACE}$	f_x2_ace	mol/mol	Moles of biomass2 formed per mole of acetate
31	$F_{X2/H2}$	f_x2_h2	mol/mol	Moles of biomass2 formed per mole of hydrogen
32	$F_{X1/LAC}$	f_ace_lac	mol/mol	Moles of acetate formed per mole of lactate
33	$F_{X1/LAC}$	f_pro_lac	mol/mol	Moles of propionate formed per mole of lactate

Table 42. *(contd)*

ID #	Parameter	Fortran Variable	Units	Description
34	$F_{XV_{LAC}}$	f_h2_lac	mol/mol	Moles of hydrogen formed per mole of lactate
35	$F_{XV_{LAC}}$	f_ace_pro	mol/mol	Moles of acetate formed per mole of propionate
36	$F_{XV_{LAC}}$	f_h2_pro	mol/mol	Moles of hydrogen formed per mole of propionate
37	$F_{XV_{LAC}}$	f_met_ace	mol/mol	Moles of methane formed per mole of acetate
38	$F_{XV_{LAC}}$	f_met_h2	mol/mol	Moles of methane formed per mole of hydrogen
39	$F_{PCE_{MET}}$	f_pce_met	mol/mol	Moles of PCE dechlorinated per mole methanogenic biomass increase
40	$F_{TCE_{MET}}$	f_tce_met	mol/mol	Moles of TCE dechlorinated per mole methanogenic biomass increase
41	$F_{DCE_{MET}}$	f_dce_met	mol/mol	Moles of DCE dechlorinated per mole methanogenic biomass increase
42	$F_{VC_{MET}}$	f_vc_met	mol/mol	Moles of VC dechlorinated per mole methanogenic biomass increase
43	kae_{DCE}	kae_dce	1/day	First-order decay coefficient for aerobic dechlorination of DCE
44	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC

8.4   Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 43 through 45. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 38 through 42, respectively.

Table 43. *Parameter Values for Example Simulation 1 with the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	minbio1	0.5	mgDW/L	23	Kvc	10	mg/L
2	minbio2	0.05	mgDW/L	24	fdk2ace	0.2	–
3	kdec1	0.023	1/day	25	f_ace_x	0.25	mol/mol
4	kdec2	0.002	1/day	26	f_x1_lac	0.05	mol/mol
5	ul1	0.1	1/day	27	f_x1_pro	0.1	mol/mol
6	up1	0.01	1/day	28	f_x1_ace	0.1	mol/mol
7	ua2	0.001	1/day	29	f_x1_h2	0.01	mol/mol
8	uh2	0.1	1/day	30	f_x2_ace	0.1	mol/mol
9	ua1	0.001	1/day	31	f_x2_h2	0.1	mol/mol
10	uh1	0.001	1/day	32	f_ace_lac	0.7	mol/mol
11	ki1	500	mg/L	33	f_pro_lac	0.4	mol/mol
12	ki2	500	mg/L	34	f_h2_lac	0.1	mol/mol
13	kio	0.1	mg/L	35	f_ace_pro	1	mol/mol
14	Kl1	15	mg/L	36	f_h2_pro	3	mol/mol
15	Kp1	15	mg/L	37	f_met_ace	1	mol/mol
16	Ka2	15	mg/L	38	f_met_h2	0.25	mol/mol
17	Kh2	0.01	mg/L	39	f_pce_met	0.4	mol/mol
18	Ka1	15	mg/L	40	f_tce_met	0.3	mol/mol
19	Kh1	0.1	mg/L	41	f_dce_met	0.2	mol/mol
20	Kpce	10	mg/L	42	f_vc_met	0.05	mol/mol
21	Ktce	10	mg/L	43	kae_dce	0.05	1/day
22	Kdce	10	mg/L	44	kae_vc	0.05	1/day

Table 44. *Parameter Values for Example Simulation 2 with the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	minbio1	0.5	mgDW/L	23	Kvc	10	mg/L
2	minbio2	0.05	mgDW/L	24	fdk2ace	0.2	–
3	kdec1	0.023	1/day	25	f_ace_x	0.25	mol/mol
4	kdec2	0.002	1/day	26	f_x1_lac	0.05	mol/mol
5	ul1	0.1	1/day	27	f_x1_pro	0.1	mol/mol
6	up1	0.01	1/day	28	f_x1_ace	0.1	mol/mol
7	ua2	0.001	1/day	29	f_x1_h2	0.01	mol/mol
8	uh2	0.1	1/day	30	f_x2_ace	0.1	mol/mol
9	ua1	0.001	1/day	31	f_x2_h2	0.1	mol/mol
10	uh1	0.001	1/day	32	f_ace_lac	0.7	mol/mol
11	ki1	500	mg/L	33	f_pro_lac	0.4	mol/mol
12	ki2	500	mg/L	34	f_h2_lac	0.1	mol/mol
13	kio	0.1	mg/L	35	f_ace_pro	1	mol/mol
14	Kl1	15	mg/L	36	f_h2_pro	3	mol/mol
15	Kp1	15	mg/L	37	f_met_ace	1	mol/mol
16	Ka2	15	mg/L	38	f_met_h2	0.25	mol/mol
17	Kh2	0.01	mg/L	39	f_pce_met	0.4	mol/mol
18	Ka1	15	mg/L	40	f_tce_met	0.3	mol/mol
19	Kh1	0.1	mg/L	41	f_dce_met	0.3	mol/mol
20	Kpce	10	mg/L	42	f_vc_met	0.3	mol/mol
21	Ktce	10	mg/L	43	kae_dce	0.05	1/day
22	Kdce	10	mg/L	44	kae_vc	0.05	1/day

Table 45. *Parameter Values for Example Simulation 3 with the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	minbio1	0.5	mgDW/L	23	Kvc	10	mg/L
2	minbio2	0.05	mgDW/L	24	fdk2ace	0.2	–
3	kdec1	0.023	1/day	25	f_ace_x	0.25	mol/mol
4	kdec2	0.002	1/day	26	f_x1_lac	0.05	mol/mol
5	ul1	0.05	1/day	27	f_x1_pro	0.1	mol/mol
6	up1	0.005	1/day	28	f_x1_ace	0.1	mol/mol
7	ua2	0.001	1/day	29	f_x1_h2	0.01	mol/mol
8	uh2	0.1	1/day	30	f_x2_ace	0.1	mol/mol
9	ua1	0.0005	1/day	31	f_x2_h2	0.1	mol/mol
10	uh1	0.0005	1/day	32	f_ace_lac	0.7	mol/mol
11	ki1	500	mg/L	33	f_pro_lac	0.4	mol/mol
12	ki2	500	mg/L	34	f_h2_lac	0.1	mol/mol
13	kio	0.1	mg/L	35	f_ace_pro	1	mol/mol
14	Kl1	15	mg/L	36	f_h2_pro	3	mol/mol
15	Kp1	15	mg/L	37	f_met_ace	1	mol/mol
16	Ka2	15	mg/L	38	f_met_h2	0.25	mol/mol
17	Kh2	0.01	mg/L	39	f_pce_met	0.4	mol/mol
18	Ka1	15	mg/L	40	f_tce_met	0.3	mol/mol
19	Kh1	0.1	mg/L	41	f_dce_met	0.2	mol/mol
20	Kpce	10	mg/L	42	f_vc_met	0.05	mol/mol
21	Ktce	10	mg/L	43	kae_dce	0.05	1/day
22	Kdce	10	mg/L	44	kae_vc	0.05	1/day

Figure 38. *Dechlorination of PCE Using the Parameter Values Shown in Table 43 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero.*
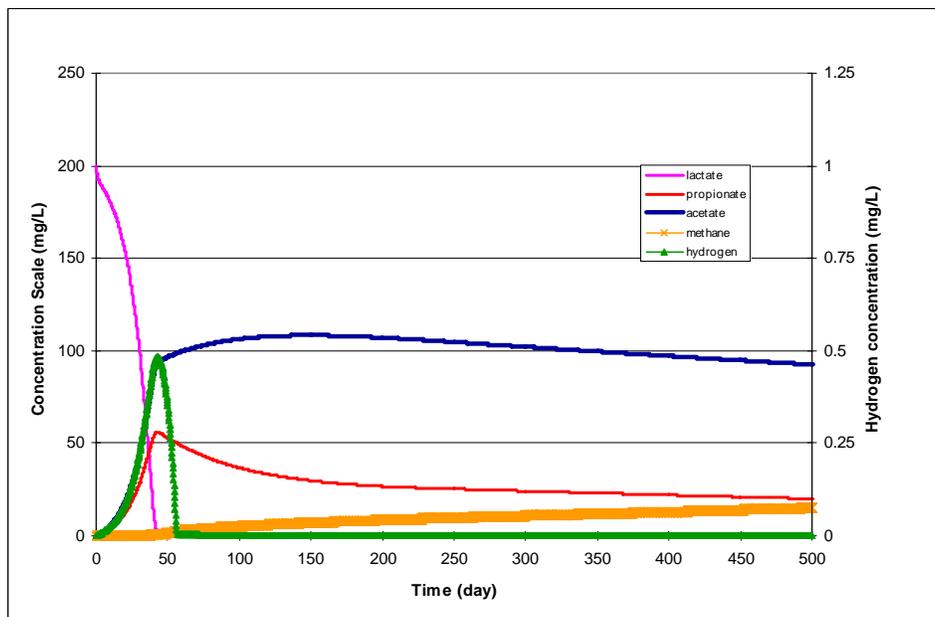
Figure 39. *Concentrations of Organic Acids, Hydrogen, and Methane During Dechlorination of PCE Using the Parameter Values Shown in Table 43 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero.*
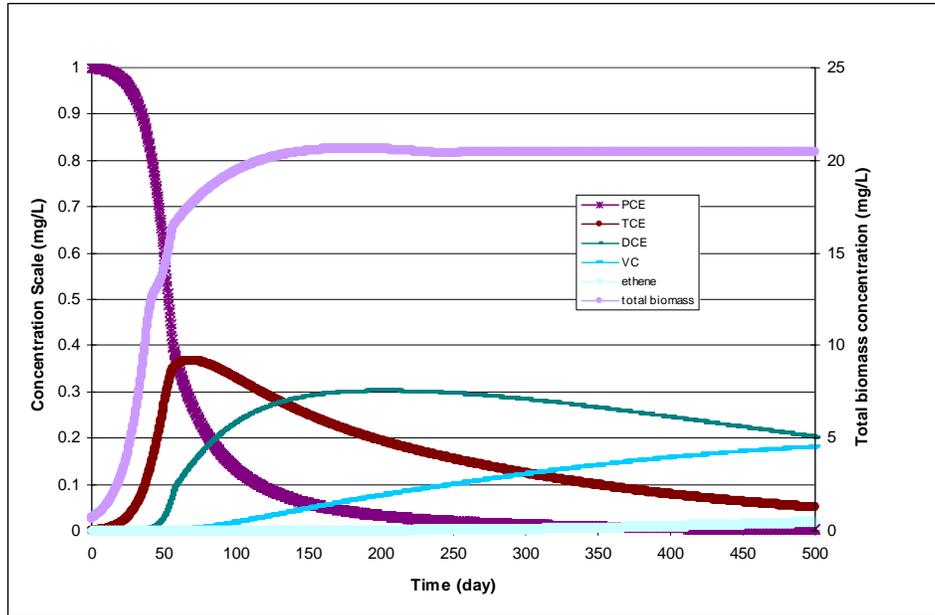
Figure 40. *Dechlorination of PCE Using the Parameter Values Shown in Table 44 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero. The organic acids, hydrogen, and methane results are the same as shown in Figure 39.*
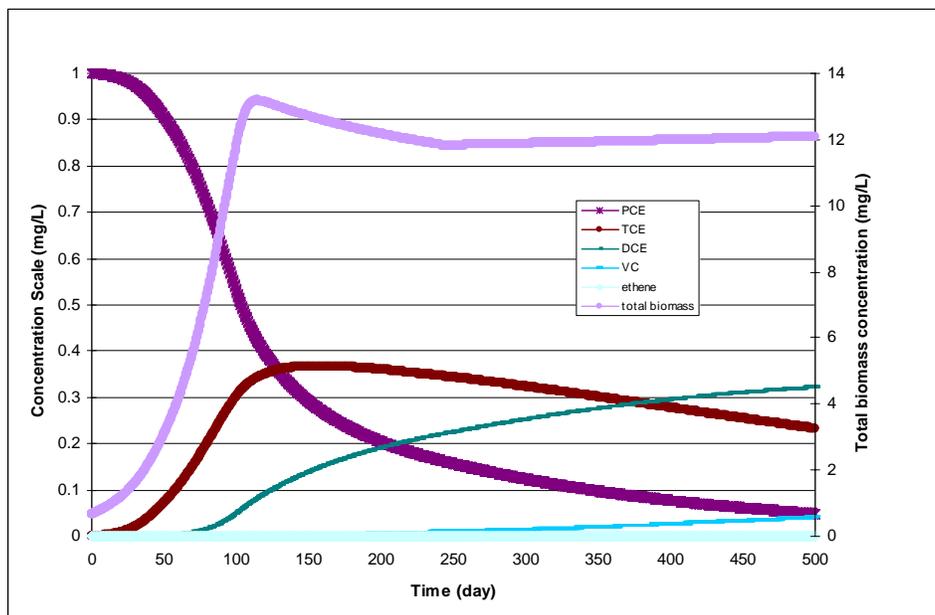
Figure 41. *Dechlorination of PCE Using the Parameter Values Shown in Table 45 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero.*

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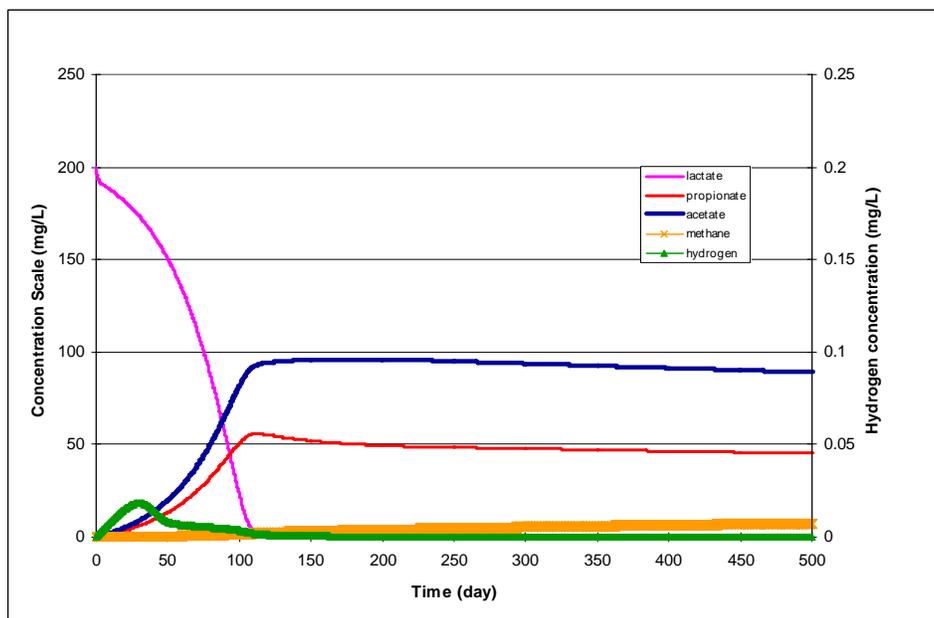
Figure 42. *Concentrations of Organic Acids, Hydrogen, and Methane During Dechlorination of PCE Using the Parameter Values Shown in Table 45 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero.*

9.0 Cometabolic Aerobic Dechlorination of Chloroethenes

9.1 Conceptual Model for Dechlorination Reactions

This reaction module describes aerobic cometabolic degradation of trichloroethene, dichloroethene isomers, and chloroethene (vinyl chloride) by methanotrophs. The module includes an explicit description of biomass growth in response to methane and oxygen and tracks both active biomass (which is able to degrade methane and chlorinated ethenes) and total biomass (a combination of active biomass and inactive biomass, the latter of which is not able to degrade methane or chlorinated ethenes). Both types of biomass decay over time according to a user-specified decay rate. This reaction module does not account for changes in porosity/permeability resulting from biomass growth, although the total biomass is also tracked so that the modeler can assess the potential for biological fouling of the aquifer. If required, macroscopic models for biomass-affected porous media properties [Clement et al., 1996] could be combined with this module as a user-defined reaction module to account for changes in porosity/permeability. The cometabolic chlorinated ethene degradation reaction is dependent on the concentration of the chlorinated ethene compound and biomass, is inhibited by methane, requires oxygen, and deactivates biomass (i.e., the module indirectly accounts for destruction of the monooxygenase enzyme by the chlorinated ethene degradation intermediate epoxide compounds). The reaction rate expressions are based on the approach of Semprini et al. [1991], who reported kinetic expressions that include methane inhibition of chlorinated ethene degradation. The rate of chlorinated ethene degradation is described with a "transformation capacity" term [Alvarez-Cohen and McCarty, 1991; Chang and Alvarez-Cohen, 1996] incorporated to represent the inactivation of enzyme as a function of the amount of chlorinated ethene degraded. The module also allows the user to input the maximum concentration of methane and oxygen in water, making it possible to model supersaturated conditions, if desired.

Table 46 lists the chemical species included in this reaction module. Figure 43 shows the conceptual model describing the degradation reactions modeled in this reaction module.

Table 46. *Chemical Species Included in the Cometabolic Aerobic Dechlorination of Chloroethenes Reaction Module*

No.	Abbreviation [a]	Chemical Name	Selected Alternate Name	CAS [b] Registry Number	Molecular Weight [c] (g/mol)	Chemical Formula
1	MET	Methane	—	74-82-8	16.04246	CH_4
2	OXY	Oxygen (dimer)	—	7782-44-7	31.9988	O_2
3	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C_2HCl_3
4	DCE	Dichloroethene (all isomers)	Dichloroethylene	156-59-2	96.94328	$C_2H_2Cl_2$
5	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C_2H_3Cl
6	Tracer	Conservative Tracer	—	N/A	N/A	N/A
7	BioA	Active Biomass	Active methanotrophs	—	113.11458	$C_5H_7O_2N$
8	BioT	Total Biomass	Active and inactive methanotrophs	—	113.11458	$C_5H_7O_2N$

[a] These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.
[b] CAS = Chemical Abstracts Service (see http://www.cas.org/EO/regsys.html)
[c] Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].
N/A – Not Applicable
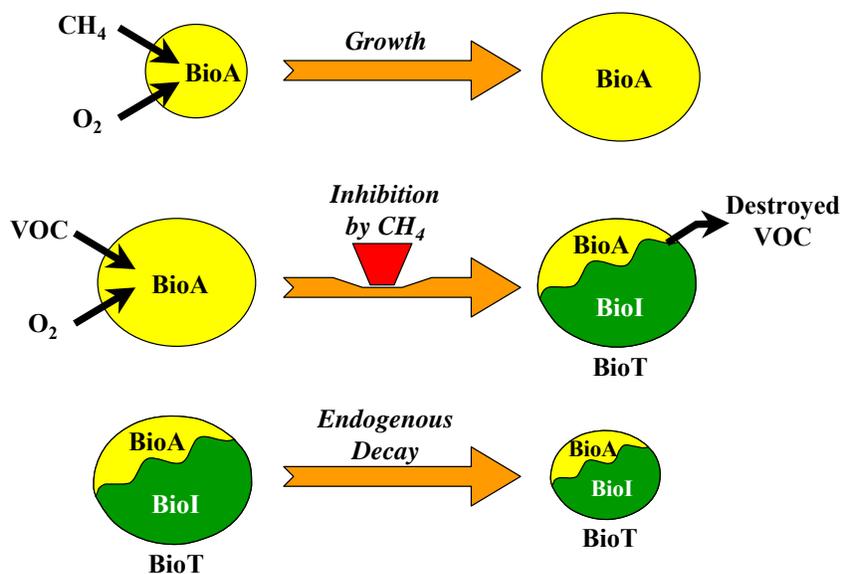
Figure 43. *Conceptual Model for Biomass Growth, Decay, and Cometabolic Degradation Reactions — Active biomass (BioA) grows, contributing to the total biomass (BioT). Active biomass can destroy VOCs (i.e., TCE, DCE, and/or VC), resulting in inactivation of a portion of the biomass (BioI). The rate of VOC destruction is inhibited by the presence of methane. Biomass will also die and decay.*

The conceptual model for biomass growth and chlorinated ethene destruction requires the presence of dissolved oxygen. Methane is metabolized by the active biomass to produce additional active biomass. TCE, DCE, and VC are destroyed by active biomass, and in the process, some of the biomass is inactivated. The TCE, DCE, VC destruction process is inhibited by methane. Active and inactive biomass both decay at a user-specified first-order decay rate.

9.2   Reaction Equations

The reaction kinetics for the conceptual model described above are presented in Equations 150 through 157. These equations represent the change in concentration over time for the 8 chemical species in Table 46. Table 47 provides a detailed itemization of all user-specified reaction parameters used in this reaction module.

Active biomass is inactivated by the chlorinated ethene destruction reactions at a ratio defined by the user-specified transformation capacity. Monod-like terms are used to implement methane inhibition of chlorinated ethene destruction. A Monod term for methane represents its importance to biomass growth. Similarly, a Monod term for oxygen is used to require the presence of oxygen for both biomass growth and chlorinated ethene destruction. The rate of chlorinated ethene destruction depends on the concentration of the chlorinated ethenes as well. The rates of all consumption/destruction/growth reactions depend on the concentration of active biomass. The active biomass and total biomass are restricted to have a concentration of at least the user-specified minimum biomass. A logistic function is used to define f_{dec1} and f_{dec2} as fractional values ranging from 0.0 to 1.0 so that as biomass decays, the biomass concentration smoothly approaches the specified minimum. Dechlorination is allowed to proceed to the point where the active biomass is reduced to the minimum biomass concentration, but additional restrictions on the inactivation of biomass (involving maxdx in Equation 156) prevent the active biomass concentration from going below the minimum biomass. The maximum concentrations of methane and oxygen are limited to the user-specified water solubilities. It is assumed that additional methane or oxygen would volatilize and leave the system. The user can accommodate super-saturation (i.e., using pure oxygen instead of air) by setting higher water solubility limits.

$$\frac{d[MET]}{dt} = -r_{MET} \tag{150}$$

$$\frac{d[OXY]}{dt} = -r_{MET} \cdot F_{\%_M} \tag{151}$$

$$\frac{d[TCE]}{dt} = -r_{TCE} = -\mu_{TCE} \cdot \left[\frac{[TCE]}{K_{TCE} \cdot \left(\frac{K_m + [MET]}{K_m} \right) + [TCE]} \right] \cdot \left(\frac{[OXY]}{K_{O_2} + [OXY]} \right) \cdot maxdx \tag{152}$$

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$$\frac{d[DCE]}{dt} = -r_{DCE} = -\mu_{DCE} \cdot \left[\frac{[DCE]}{K_{DCE} \cdot \left(\frac{K_m + [MET]}{K_m} \right) + [DCE]} \right] \cdot \left(\frac{[OXY]}{K_{O_2} + [OXY]} \right) \cdot maxdx \qquad (153)$$

$$\frac{d[VC]}{dt} = -r_{VC} = -\mu_{VC} \cdot \left[\frac{[VC]}{K_{VC} \cdot \left(\frac{K_m + [MET]}{K_m} \right) + [VC]} \right] \cdot \left(\frac{[OXY]}{K_{O_2} + [OXY]} \right) \cdot maxdx \qquad (154)$$

$$\frac{d[Tracer]}{dt} = 0.0 \qquad \text{\textit{(Conservative [non-reactive] tracer.)}} \qquad (155)$$

$$\frac{d[BioA]}{dt} = Max\left(r_{BioA}, \ -maxdx \right) \qquad (156)$$

$$\frac{d[BioT]}{dt} = F_{X/M} \cdot r_{MET} - f_{dec2} \cdot k_{decay} \cdot [BioT] \qquad (157)$$

Where r_{MET}, maxdx, and r_{BioA} are defined as in Equations 158 through 160, respectively.

$$r_{MET} = \mu_{max} \cdot [BioA] \cdot \left(\frac{[MET]}{K_m + [MET]} \right) \cdot \left(\frac{[OXY]}{K_{O_2} + [OXY]} \right) \cdot \left(\frac{1}{F_{X/M}} \right) \qquad (158)$$

$$maxdx = Max\left([BioA] - bio_0, \ 0.0 \right) \qquad (159)$$

$$r_{BioA} = F_{X/M} \cdot r_{MET} - f_{dec1} \cdot k_{decay} \cdot [BioA] - \left(\frac{r_{TCE}}{TC_{TCE}} + \frac{r_{DCE}}{TC_{DCE}} + \frac{r_{VC}}{TC_{VC}} \right) \qquad (160)$$

9.3   Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 18 reaction parameters that must be specified for this reaction module are listed in Table 47 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

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Table 47. *Input Parameters for the Cometabolic Aerobic Dechlorination of Chloroethenes Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	bio_0	bio_0	mg/L	Minimum methanotroph biomass concentration
2	k_{decay}	kdecay	1/day	Decay rate for methanotrophs
3	μ_{max}	uMax	1/day	Methanotroph maximum growth rate
4	K_m	Km	mg CH$_4$/L	Monod half-saturation coefficient for methanotroph growth for methane
5	K_{O_2}	Ko2	mg O$_2$/L	Monod half-saturation coefficient for methanotroph growth for oxygen
6	K_{TCE}	Ktce	mg TCE/L	Monod half-saturation coefficient for TCE degradation
7	K_{DCE}	Kdce	mg DCE/L	Monod half-saturation coefficient for DCE degradation
8	K_{VC}	Kvc	mg VC/L	Monod half-saturation coefficient for VC degradation
9	$F_{O/M}$	f_o_m	mol/mol	Moles of oxygen consumed per mole of methane degraded
10	$F_{X/M}$	f_x_m	mol/mol	Moles of biomass formed per mole of methane degraded
11	μ_{TCE}	utce	mg TCE / mg Biomass-day	Maximum specific TCE degradation rate coefficient per unit mass of active bacteria
12	μ_{DCE}	udce	mg DCE / mg Biomass-day	Maximum specific DCE degradation rate coefficient per unit mass of active bacteria
13	μ_{VC}	uvc	mg VC / mg Biomass-day	Maximum specific VC degradation rate coefficient per unit mass of active bacteria
14	TC_{TCE}	tctce	mol TCE / mol Biomass	Transformation capacity for TCE
15	TC_{DCE}	tcdce	mol DCE / mol Biomass	Transformation capacity for DCE
16	TC_{VC}	tcvc	mol VC / mol Biomass	Transformation capacity for VC
17	CH_{4max}	maxmet	mg/L	Maximum methane concentration in water
18	O_{2max}	maxoxy	mg/L	Maximum oxygen concentration in water

9.4   Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Table 48. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 44 and 45, respectively.

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Table 48. *Parameter Values for Example Simulations 1 and 2 with the Cometabolic Aerobic Dechlorination of Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	bio_0	0.01	mg DW/L	10	f_x_m	0.0467	mol/mol
2	kdecay	0.00018	1/day	11	utce	4.2	mg TCE/(mg BioA·day)
3	uMax	0.7	1/day	12	udce	3.1	mg DCE/(mg BioA·day)
4	Km	1.10E-03	mg/L	13	uvc	2	mg VC/(mg BioA·day)
5	Ko2	0.01	mg/L	14	tctce	0.096	mol/mol
6	Ktce	9.0E-03	mg/L	15	tcdce	0.26	mol/mol
7	Kdce	6.8E-03	mg/L	16	tcvc	0.41	mol/mol
8	Kvc	4.4E-03	mg/L	17	maxmet	23	mg/L
9	f_o_m	1.767	mol/mol	18	maxoxy	20	mg/L
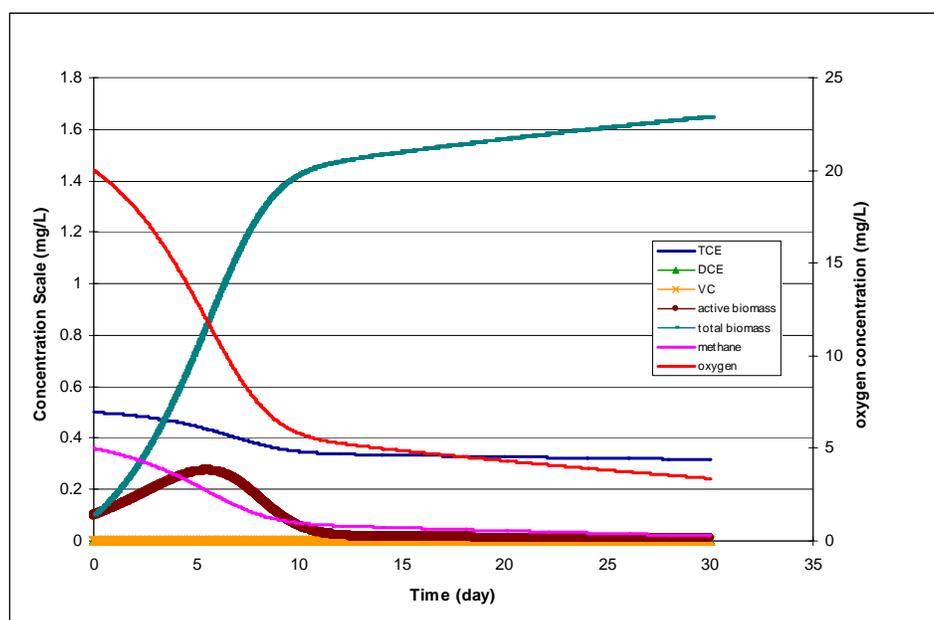
Figure 44. *Dechlorination of TCE Using the Parameter Values Shown in Table 48 — The initial concentration for TCE, DCE, VC, methane, oxygen, active biomass, and total biomass were 0.5, 5, 20, 0.1, and 0.1 mg/L, respectively.*
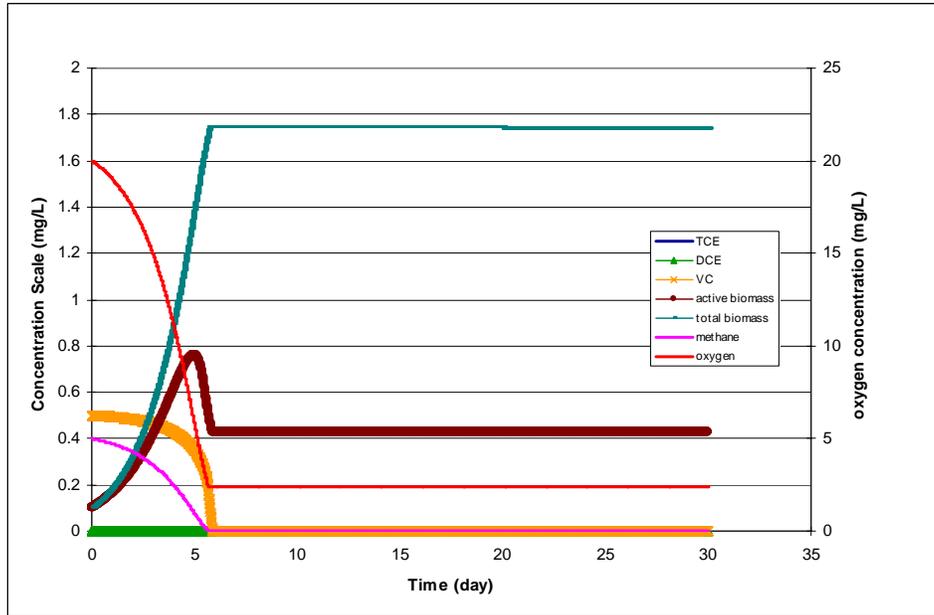
Figure 45. *Dechlorination of VC Using the Parameter Values Shown in Table 48 — The initial concentration for VC, methane, oxygen, active biomass, and total biomass were 0.5, 5, 20, 0.1, and 0.1 mg/L, respectively.*

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10.0 References

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