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SEAM3D

A Numerical Model for Three-Dimensional Solute Transport Coupled to Sequential Electron Acceptor-Based Biological Reactions in Groundwater

Documentation and User's Guide

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Prepared for   US Army Corps of Engineers
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Preface

This report provides documentation of the computer code, SEAM3D, including mathematical model development and a user guide for the code. The focus of this report is two new modules to the SEAM3D code: the Chlorinated Ethene and Cometabolism Packages. Included in this report are model and code verification exercises for the new modules and an application of the code to a field problem. The work reported herein was conducted under the Cleanup Pillar of the Strategic Environmental Research and Development Program (SERDP), as part of Work Unit CU-1062, "Development of Simulators for In-Situ Remediation Evaluation, Design, and Operation." SERDP is sponsored by the U.S. Department of Defense, U.S. Environmental Protection Agency, and the U.S. Department of Energy. Work Unit CU-1062 was conducted by the U.S. Army Engineer Research and Development Center (ERDC) under the purview of the Environmental Laboratory (EL). EL involvement in SERDP was coordinated by Dr. John Cullunane, Program Manager for the EL Installation Restoration Research Program (IRRP). Mr. Charles Miller was Assistant Manager for the IRRP. Ms. Catherine Vogel was the Cleanup Program Manager for SERDP.

The Principal Investigator of Work Unit CU-1062 was Dr. Mark S. Dortch, Chief, Water Quality and Contaminant Modeling Branch (WQCMB), Environmental Processes and Effects Division (EPED), EL. The work documented in this report was conducted by Virginia Polytechnic Institute and State University (Virginia Tech) through a research contract (DACA39-95-K-0054) monitored by ERDC. The ERDC's Contracting Officer's Representative and contract monitor was Dr. Carlos E. Ruiz, of the WQCMB.

The principal investigator for this study was Dr. Mark A. Widdowson of the Charles E. Via, Jr. Department of Civil and Environmental Engineering, Virginia Tech. Model development was performed by Drs. Widdowson and Dan W. Waddill. Code development, users guide, and model applications were performed by Drs. Waddill and Widdowson. Dr. Ruiz and Dortch provided guidance during model and code development. Dr. Francis H. Chapelle of the U.S. Geological Survey (USGS) contributed to the development of the conceptual and mathematical models.

Field and laboratory measurements by the USGS were essential to the verification of SEAM3D. Chapter 4 describes the application of a site model developed using SEAM3D to the transport and biotranformation of chlorinated ethenes in groundwater at a DoD facility. This part of the research was made possible by the efforts of Drs. Chapelle and Paul M. Bradley of the USGS, Columbia, South Carolina. This work resulted from a cooperative research agreement between the USGS and Virginia Tech.

1. Introduction

1.1 Overview of SEAM3D

This report describes improvements to and verification of two new components to SEAM3D (Sequential Electron Acceptor Model, 3 Dimensional), a numerical model and code for solute transport with aerobic and sequential anaerobic biodegradation and dissolution of compounds from non-aqueous phase liquids (NAPLs). Initial versions of SEAM3D (versions 1.0 and 2.0) were developed using the solute transport codes MT3D and MT3DMS, respectively (Waddill and Widdowson, 2000). SEAM3D 3.0 (described herein) is based on MT3DMS 4.00 for use with MODFLOW-2000. SEAM3D 2.0 and 3.0 are contained in the Department of Defense Groundwater Modeling System (GMS) in GMS 3.0/3.1 and 4.0, respectively.

SEAM3D consists of a series of modules for simulating the fate and transport of multiple constituents in a three-dimensional, anisotropic, heterogeneous domain. Figure 1-1 shows the structure of SEAM3D 3.0, including the parent code (MT3DMS) for simulating physical transport, sources and sinks of mass derived from liquid sources and sinks, and basic reactions (sorption and first-order decay). SEAM3D 3.0 consists of the MT3DMS modules and four additional packages: Biodegradation, NAPL Dissolution, Reductive Dechlorination and Cometabolism. Waddill and Widdowson (2000) present model and code verification exercises for the Biodegradation and NAPL Dissolution Packages and site model application at a petroleum-contaminated site.

In SEAM3D, dissolved and solid-phase constituents are placed into structured categories by the user based on microbial processes affecting each constituent. These categories include electron donors (or substrate), electron acceptors, daughter or intermediate products, end products of electron acceptor reduction, non-reactive tracers, mineral nutrients, chlorinated ethenes and recalcitrant compounds. Using the Reductive Dechlorination Package, SEAM3D can simulate the 3D transport of a parent chlorinated solvent compound (tetrachloroethene, PCE or trichloroethene, TCE) and daughter products of reductive dehalogenation (TCE, cis, 1-2-dichloroethene, DCE and vinyl chloride, VC) coupled to relevant biological processes in aquifers: direct oxidation, reductive dehalogenation, and cometabolism. The applicability and rate of each process impacting each compound is dependent on the model-simulated redox condition in each model cell of the finite-difference grid. In the Cometabolism Package, designated recalcitrant compounds are subject to aerobic cometabolism.

In the Biodegradation Package, compounds are simulated as electron donors (i.e., hydrocarbon substrates) for microbial growth, with available electron acceptors (EAs) utilized in the following sequence: O_2, NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, and CO_2. SEAM3D can account for Mn(II), Fe(II), H_2S, CH_4, and a user defined nitrogenous compound as products of biodegradation. In addition, each substrate can produce a single daughter product. Biodegradation of each substrate follows Monod kinetics, modified to include the effects of EA and nutrient availability. Inhibition functions allow any EA to inhibit utilization of all other EAs that provide less energy to the microbes. Microbial biomass is simulated as scattered microcolonies attached to the porous medium.

The NAPL Dissolution Package allows simulation of the dissolution of electron donors (e.g., hydrocarbon contaminants) and chlorinated ethenes (PCE, TCE and/or DCE) from light and dense NAPLs into the aqueous phase. SEAM3D does not simulate multi-phase flow; however, time-dependent accumulation and addition of a NAPL and/or removal of a NAPL source at specified times may be included in simulations.

1.2 Biodegradation of Chlorinated Ethenes

At many sites, biological processes are an important component of the natural attenuation of chlorinated ethenes (Weidemeier et al. 1998). Chlorinated ethenes are subject to a range of microbial degradation processes that include reductive dechlorination (Vogel and McCarty 1985; Barrio-Lage et al. 1987, 1990; Bouwer 1994; Vogel 1994; Odum et al. 1995), aerobic oxidation (Hartmans et al. 1985; Davis and Carpenter 1990; Phelps et al. 1991; Bradley and Chapelle 1996, 1998a, 1998b; Bradley et al. 1998b), anaerobic oxidation (Bradley and Chapelle 1996; Bradley and Chapelle 1998b; Bradley et al. 1998b), and aerobic cometabolism (Wilson and Wilson 1985; McCarty and Semprini 1994; Semprini 1995; Semprini et al. 1990, 1991). Environmental conditions under which these processes occur are known; however, it is often difficult to determine the contribution of each process based purely on field data.

1.2.1 Reductive Dechlorination

The most critical attenuation process, reductive dechlorination, in which tetrachloroethene (PCE) and trichloroethene (TCE) and chlorinated daughter products (cis-dichloroethene, cisDCE, and vinyl chloride, VC) are reduced to form ethene and ethane, has been studied extensively in both the field and laboratory. Microbial reductive dechlorination has been observed at numerous anaerobic chloroethene-contaminated aquifers, but the extent of dechlorination is highly variable from site to site (Bouwer 1994; Vogel 1994; McCarty and Semprini 1994; Chapelle 1996; Gossett and Zinder 1996; McCarty 1996). In reductive dechlorination, chloroethene serve as electron acceptors and molecular hydrogen (H_2) reacts to replace a chlorine on a chlorinated ethene molecule (Vogel et al. 1987). PCE readily undergoes reductive dechlorination to TCE except in aerobic aquifers. Reductive dechlorination of TCE to cisDCE occurs under Fe(III)-reducing conditions and in more strongly reducing environments. Reductive dechlorination of cisDCE to yield VC apparently requires at least sulfate-reducing conditions (Vogel et al. 1987; Chapelle 1996) but proceeds more readily in methanogenic environments. Reductive dechlorination of VC to ethene is often slow and is significant only under highly reducing, methanogenic conditions (Vogel and McCarty 1985; Barrio-Lage et al. 1987, 1990; Freedman and Gossett 1989; DiStefano et al. 1991; De Bruin et al. 1992; Bouwer 1994; Ballapragada et al. 1995; Fennell et al. 1995; Maymo-Gatell et al. 1995; Odum et al. 1995; Wu et al. 1995). As a result of this decreasing potential, reductive dechlorination of chlorinated ethenes is often incomplete and often leads to the accumulation of cisDCE and VC in groundwater (Major et al. 1991; Kitanidis et al. 1993; McCarty and Reinhard 1993; Haston et al. 1994; Weaver et al. 1995; Wilson et al. 1995). Complete reductive dechlorination to ethene is rare due to low electron donor availability and a sparse microbial community capable of this complete transformation (Chapelle 2001). Although halorespirers capable of reducing PCE to TCE to DCE are relatively common (Holliger et al. 1993 Sharma et al. 1996; Maymo-Gatell et al. 1997), to

date only one *Dehalococcus ethenogenes*, has been shown to completely degrade PCE to ethene (Maymo-Gatell et al. 1997).

1.2.2   Aerobic Oxidation

Rapid microbial degradation of VC, including mineralization, has been observed in laboratory cultures and aquifer samples under aerobic conditions (Hartmans et al. 1985; Davis and Carpenter 1990; Phelps et al. 1991; Bradley and Chapelle 1996, 1998a, 1998b; Bradley et al. 1998b). In the presence of oxygen, VC can serve as a sole carbon source for growth and metabolism (Hartmans et al. 1985; Hartmans and de Bont 1992). In liquid cultures, DCE has been shown to oxidize under aerobic conditions, but apparently without supporting growth (Bradley and Chapelle 1999). The oxidation of cisDCE and VC will be limited at anaerobic sites where reductive dechlorination is efficient (Chapelle 2001). However, at sites where the redox condition progresses from highly reducing to aerobic conditions, aerobic degradation of cisDCE and VC may be significant when these compounds are produced in anoxic zones and transported to a downgradient zone of oxic groundwater or at the interface of groundwater and surface water systems (Bradley and Chapelle 1998a, 1998b).

1.2.3   Anaerobic Oxidation

Anaerobic oxidation of cisDCE and VC is a process that has only been recognized recently (Bradley and Chapelle 1996). In a series of papers, it was shown that VC, and to a lesser extent DCE, could oxidize to CO_2 under Fe(III)-reducing conditions (Bradley and Chapelle 1996, 1997; Bradley et al. 1998b). The implications of these findings to the natural attenuation of chlorinated ethenes may be profound at sites where PCE/TCE can be readily transformed to cisDCE and VC. Given a sufficient flow path, anaerobic oxidation provides a possible microbial pathway for complete degradation of chlorinated ethenes in aquifers (e.g., Plattsburg AFB, NY; see Bradley et al. 1998b). However, the occurrence and overall contribution of anaerobic oxidation at chloroethene-contaminated sites is controversial and site-specific factors that control complete transformation of cisDCE and VC is the subject of current research (e.g., SERDP projects CU-1167, CU-1168, CU-1169).

1.2.4   Aerobic Cometabolism

Another process that leads to microbial degradation of chlorinated ethenes is cometabolic oxidation. It is known that a wide variety of aerobic microorganisms utilizing methane (Wilson and Wilson 1985) and other substrates (see McCarty and Semprini 1994) are able to oxidize TCE, DCE, and VC to CO_2 without the accumulation of toxic intermediates (Chapelle 2001). Aerobic cometabolism of chlorinated ethene requires oxygen and a primary substrate to initiate and sustain the process. In the case of natural attenuation, this situation is not likely to exist because oxygen and methane do not typically co-occur in aquifers. Likewise, in plumes containing chlorinated solvents where petroleum hydrocarbon compounds are also present, oxygen depletion would be expected. Consequently, significant aerobic cometabolic oxidation of chlorinated ethenes in such systems would be limited to transient events (Chapelle 2001) such as reaeration around the edges of the plume.

1.3   Biodegradation Modeling

As described in Section 1.2, the fate and transport of chloroethenes and other recalcitrant compounds is dependent on the prevailing terminal electron accepting processes (TEAPs) in an aquifer. The most critical attenuation process, reductive dechlorination, has been studied extensively in both the field and laboratory. Because reductive dechlorination of chloroethene contaminants will only occur in anoxic groundwater, this process will be sustained as long as reducing conditions and an ample supply of electron donor are maintained and dehalogenating organisms are present. Organic carbon, which is fermented to produce hydrogen, is either supplied naturally or is derived from contaminant sources (e.g., petroleum hydrocarbons). If the groundwater system is not fully reducing, reducing agents (e.g., vegetable oil) may be supplied to the aquifer to increase the rate of reductive dechlorination.   Numerical (e.g., RT3D, Clement 1997) and analytical models (e.g., BIOCHLOR, Aziz et al. 2000) have been developed to simulate the fate and transport of chlorinated ethenes in groundwater. Site models developed using RT3D and BIOCHLOR are limited to two zones (anaerobic and aerobic). The zones do not change with time and are not based on a simulated redox condition. Furthermore, NAPL dissolution is not considered in RT3D.

1.4   Purpose of this Report

The purpose of this report is 1) to describe two new modules for SEAM3D, the Reductive Dechlorination Package (RDP) and the Cometabolism Package; 2) to present scenarios for verification of the new SEAM3D modules; 3) to present results of a field scale application of SEAM3D to an unconfined aquifer contaminated by TCE, and 4) to provide detailed information on model input, output, and execution.

1.5   Acknowledgement
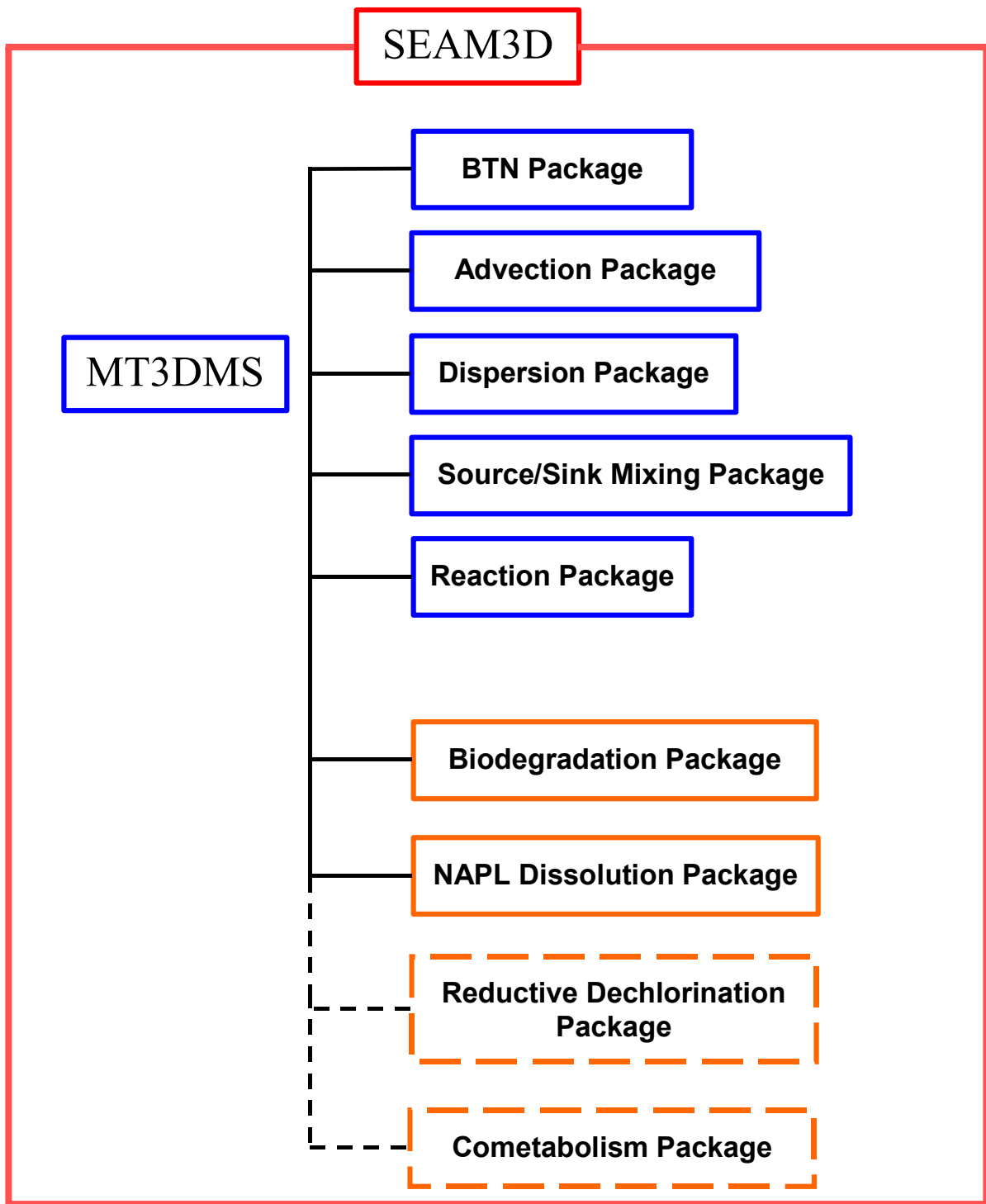
Figure 1.1. Overview of SEAM3D (red) including MT3DMS packages (blue), the Biodegradation and NAPL Dissolution Packages (solid orange, developed in the initial version of the code), and the Reductive Dechlorination and Cometabolism Packages (dashed orange).

2. Model Development

2.1 Conceptual Model

In the subsurface environmental, chlorinated ethenes are known to biodegrade by any one of three biological degradation mechanisms:

1. Direct Oxidation
2. Reductive Dechlorination
3. Cometabolism

Degradation mechanisms are summarized in Table 2.1 for the four chlorinated ethenes included in the SEAM3D Reductive Dechlorination Package (SEAM3D-RDP).

The SEAM3D-RDP is designed to simulate both reductive dechlorination and direct oxidation of chloroethenes. Recent experimental studies have demonstrated aerobic and anaerobic oxidation of VC and cis-DCE, but direct oxidation appears limited to higher energy-yielding terminal electron accepting processes (TEAPs). All simulated chlorinated ethenes may undergo reductive dechlorination with the rate of transformation dependent on the prevailing TEAP simulated in any given model cell. Just as the prevailing TEAP in an aquifer exhibits a temporal and spatial dependence, SEAM3D is designed to simulate the same observed trend. Only cis-DCE and VC may be undergo transformation due to direct oxidation. Cometabolism is assumed to have only a limited impact on the biodegradation of chlorinated ethenes under intrinsic conditions in the absence of oxygen.

The SEAM3D Cometabolism Package is designed to simulate aerobic cometabolism of user-designated recalcitrant compounds (recalcitrants). Cometabolism of recalcitrants is assumed to result from aerobic oxidation of methane or petroleum-derived compounds (e.g., toluene). Recalcitrants may be three of the four chloroethenes (PCE is not included as a possible recalcitrant compound) or any user-defined compound (e.g., MTBE).

2.1.1 Electron Donor for Simulating Reductive Dechlorination

Molecular hydrogen is the electron donor for reductive dechlorination of PCE, TCE, cis-DCE, and VC. However, SEAM3D-RDP does not explicitly simulate the concentration of hydrogen with a model variable. It is known that the level of hydrogen in groundwater under intrinsic conditions is a function of the TEAP, increasing when more reducing conditions exist in a ground-water system. Because chloroethenes serve as electron acceptors for halorespiring microbes, higher energy-yielding electron acceptors are assumed to inhibit the reductive dechlorination rate. In the SEAM3D-RDP, the influence of the hydrogen concentration is indirectly factored into the biodegradation sink terms for the chlorinated ethenes through the TEAP inhibition functions. Input parameters for the maximum rate of reaction for reductive dechlorination are also compound dependent.

2.1.2 Hydrocarbon Transport and Biodegradation

The sequential electron acceptor model depicts transport of multiple hydrocarbon substrates or other electron donors coupled to aerobic and sequential anaerobic biodegradation

in groundwater. Mass removal and concentration changes are calculated in the SEAM3D Biodegradation Package. Biodegradation follows Monod kinetics, modified to include the effect of electron acceptor (EA) availability and a rate inhibition term (Waddill and Widdowson 1988). However, the model is designed to operate under either growth (time-dependent microbial population) or no-growth (steady-state biomass concentration) option. Hydrocarbon compounds may be designated as growth substrates that serve as electron donors in which the rate of direct oxidation is dependent on the terminal electron accepting process. Microbial populations simulated in the model may utilize multiple hydrocarbon substrates simultaneously, but not all hydrocarbons are designated as substrates. Other biologically-based reactions and generation of end products and intermediate reactants are also included. VC and cis-DCE may serve as electron donors in the SEAM3D-RDP when conditions in a model cell favor direct oxidation. Mathematical representation of reductive dechlorination is discussed below.

2.1.3   Electron Acceptor-Based Utilization

When multiple EAs are available, it is assumed microbes tend to utilize them in sequence, starting with the one that provides the highest Gibbs free energy. In the model, EAs are used in the following order: oxygen (O_2), nitrate (NO_3^-), manganese (Mn^{4+}), ferric iron (Fe^{3+}), sulfate (SO_4^{2-}), and carbon dioxide (CO_2). However, the model user has some flexibility in allowing all or several anaerobic processes to occur simultaneously but at different rates. Ferric iron and Mn (IV) are assumed to occur as a solid phase ion, while the other EAs are dissolved in the aqueous phase. Carbon dioxide concentration is not modeled. Utilization of the aqueous phase EAs is assumed to follow modified Monod kinetics, while utilization of Fe(III) and Mn(IV) is zero order, which is based on the assumption that solid phase EAs are utilized by direct contact with the microorganism. If the concentration of Fe(III) falls below a minimum value, then Fe(III) utilization ceases. Likewise, if the concentration of Mn(IV) falls below a minimum value, then Mn(IV) utilization ceases. Chlorinated ethenes serve as EAs under anaerobic conditions at a rate dependent on the predominant EA in the model cell.

2.1.4   Microbial Populations

The microbial phase is assumed to be comprised of as many as nine different bacterial populations that exist as scattered microcolonies attached to the porous medium. Predetermined microcolony configurations or user-specified dimensions are not required as input parameters. The model assumes that mobile organisms have a negligible effect compared to the attached microbes. The SEAM3D Biodegradation Package includes aerobes, facultative nitrate reducers, anaerobic manganese reducers, anaerobic iron reducers, anaerobic sulfate reducers, methanogens, and aerobic methanotrophs (Table 2.2). Simulation of aerobic methanotrophs is a new feature in the Biodegradation Package.

Two biomass concentration variables are simulated in the current version of SEAM3D-RDP, both responsible for the reduction of chlorinated ethenes. One population utilizes only PCE and TCE as EAs, preferentially using PCE, but inhibited by higher energy-

yielding EAs. The second population utilizes only cis-DCE and VC as EAs, preferentially using cis-DCE, but potentially inhibited in the presence of PCE and TCE.

Microbial growth, if modeled, is assumed to depend on the availability of electron donors (typically hydrocarbon substrates) and suitable EAs. Limitation of mineral nutrients is considered but does not need to be explicitly modeled. For example, biodegradation rates under intrinsic conditions may reflect nutrient-limited conditions.

2.1.5 Reductive Dechlorination

In the simulation of reductive dechlorination using the SEAM3D-RDP chlorinated ethenes (PCE, TCE, cis-DCE, and VC) may serve as EAs. These compounds are reduced under anaerobic conditions in which H_2 is the assumed electron donor (though not explicitly simulated). Chlorinated ethenes are utilized as EAs in the absence of oxygen and nitrate. Recent experimental evidence suggests that each chlorinated ethene will biodegrade under all anaerobic TEAPs. Table 2-3 shows the recommended TEAPs underwhich reductive dechlorination will take place and the relative rate of reaction based on studies published in the literature. Chloride is produced as an end product to each successive step in the reductive dechlorination process. Ethene is produced as a result of the biodegradation of VC. First-order biodegradation of ethene may be simulated using the Reaction Package, but the production of ethane is not an option.

As designated EAs in the SEAM3D-RDP, chlorinated ethenes are subject to the same energy yield sequence simulated in the SEAM3D Biodegradation Package. Reductive dechlorination will proceed at a maximum rate under methanogenesis and will be inhibited to some extent in model cells where higher-energy yielding TEAPs are dominant, beginning with sulfate reduction. In the case of methanogenesis, competition for hydrogen between dechlorinating microbes and methanogens is not simulated. Among the four chlorinated ethenes, the yield of energy decreases with the number of chloride atoms so that the parent compound (PCE or TCE) will be preferentially used over daughter products (cis-DCE and VC or TCE, if PCE is the parent compound).

2.1.6 Aerobic Cometabolism

The conceptual and mathematical models used in developing the SEAM3D Cometabolism Package are based on the previously published work (Semprini et al 1990), validated at a chlorinated ethene site. The equations were modified to incorporate up to three recalcitrant compounds subject to aerobic cometabolism. The cometabolism rate is a function of the concentration of a electron donor, either a user-designated hydrocarbon compound or methane, and the dissolved oxygen concentration. Cometabolism is accomplished by either the aerobic or methanotrophic populations.

2.2 Mathematical Model

Model variables and governing equations are presented in this section. The complete system of governing equations consists of coupled partial and ordinary differential equations describing solute transport, biodegradation, biogeneration, microbial growth and decay, and sorption. Boundary and initial conditions are user-specified and are required to develop a complete mathematical model.

2.2.1 Model variables

Macroscopic concentration variables fall into the categories specified below. Some named constituents are built into the code (e.g., electron acceptors). Other constituents are user-specified.

1. Aqueous-phase biodegradable hydrocarbon compounds:

   a) User-specified growth substrate(s)
   b) Non-growth, biodegradable hydrocarbons

2. Aqueous-phase terminal electron acceptors:

   a) oxygen
   b) nitrate
   c) sulfate
   d) methanogenesis (no electron acceptor concentration variable required)

3. Solid-phase terminal electron acceptors:

   a) manganese: Mn(IV)
   b) ferric iron: Fe(III)

4. Aqueous-phase mineral nutrient for microbial growth (not required)

5. Aqueous-phase conservative (non-biodegradable) solute (not required)

6. Aqueous-phase intermediate or end product solute:

   a) single daughter product for each biodegradable contaminant (1a and 1b)
   b) N_2
   c) Mn(II)
   d) Fe(II)
   e) H_2S
   f) CH_4
   g) chloride[1]
   h) ethene[1]

7. Aqueous-phase recalcitrant compounds:

   a) User-specified (Note that the order of the recalcitrant variables is not important unless the model is setup to include the SEAM3D-RDP, in which case the same order, shown below, should be followed)

8. Aqueous-phase chlorinated ethenes (terminal electron acceptors):

   a) perchloroethene (PCE)[1] - not required
   b) trichloroethene (TCE)[1]
   c) dichloroethene (DCE)[1,2]
   d) vinyl chloride (VC)[1,2]

---

[1] Variable in SEAM3D-RDP only
[2] May also serve as a substrate

9. Microbial biomass (SEAM3D Biodegradation Package):

    a) strict aerobes
    b) facultative, nitrate-reducing anaerobes
    c) Mn-reducing anaerobes
    d) Fe-reducing anaerobes
    e) sulfate-reducing anaerobes
    f) methanogens
    g) methanotrophs

10. Microbial biomass (SEAM3D-RDP):

    a) PCE/TCE reducers
    b) cis-DCE/VC reducers

2.2.2 Transport equations

Aqueous phase transport is described by the advection-dispersion equation for each biodegradable substrate, EA, end product, mineral nutrient and nonbiodegradable solute. These equations are coupled through source/sink terms for biodegradation. For each non-chlorinated hydrocarbon contaminant (substrate or non-growth substrate, S_{ls}) the transport equation is:

$$-\frac{\partial}{\partial x_i}(v_i S_{ls}) + \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial S_{ls}}{\partial x_j}\right) + \frac{q_s}{\theta}S_{ls}^* - R_{\sin k,ls}^{bio} + R_{source,ls}^{NAPL} = R_{ls}\frac{\partial S_{ls}}{\partial t} \tag{2.1}$$

where S_{ls} is the aqueous phase hydrocarbon concentration [M_{ls} L^{-3}] for ls=1,2,...,NS (number of hydrocarbon substrates); S_{ls}^* is the hydrocarbon point source concentration [M_{ls} L^{-3}]; v_i is the average pore water velocity [L T^{-1}]; x_i is distance [L]; D_{ij} is the tensor for the hydrodynamic dispersion coefficient [L^2 T^{-1}]; $R_{\sin k,ls}^{bio}$ is a biodegradation sink term dependent on the mode of respiration [M_{ls} L^{-3} T^{-1}]; $R_{source,ls}^{NAPL}$ is a hydrocarbon source term due to non-aqueous phase liquid (NAPL) dissolution [M_{ls} L^{-3} T^{-1}]; R_{ls} is the retardation factor for hydrocarbon ls [L^o]; and t is time [T]; θ is aquifer porosity [L^o]; and q_s is the volumetric flux of water per unit volume of aquifer [T^{-1}] with $q_s > 0$ for sources and $q_s < 0$ for sinks. In the case of a point sink, the concentration is generally not specified, and the model uses $S_{ls}^* = S_{ls}$. Conservative and reactive solutes (NAPL derived or otherwise) are simulated using Equation (2.1) in which a first order decay term replacing the biodegradation sink term for the latter case.

Transport of each non-chlorinated aqueous phase EA (E_{le}) is:

$$-\frac{\partial}{\partial x_i}(v_i E_{le}) + \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial E_{le}}{\partial x_j}\right) + \frac{q_s}{\theta}E_{le}^* - R_{\sin k,le}^{bio} = \frac{\partial E_{le}}{\partial t} \tag{2.2}$$

where E_{le} is the EA concentration [M_{le} L^{-3}] for le=1,2,...,NE (number of EAs); E_{le}^* is the EA point source concentration [M_{le} L^{-3}]; and $R_{sink,le}^{bio}$ is the EA biodegradation sink term [M_{le} L^{-3} T^{-1}]. A retardation factor does not appear in Equation (2.2) since O$_2$, NO$_3^-$, and SO$_4^{2-}$ are not typically adsorbed to aquifer solids. Equation (2.2) does not apply when le = 3 or 4 since both Mn(IV) and Fe(III) are bound to the solid phase (the change in Mn(IV) and Fe(III) concentrations over time will be described below).

Transport of biodegradation products (P_{lp}), including daughter products, is:

$$-\frac{\partial}{\partial x_i}\left(v_i P_{lp}\right)+\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial P_{lp}}{\partial x_j}\right)+\frac{q_s}{\theta}P_{lp}^*-\lambda P_{lp}+R_{source,lp}^{bio}=R_{lp}\frac{\partial P_{lp}}{\partial t} \qquad (2.3)$$

where P_{lp} is the aqueous phase end product concentration [M_{lp} L^{-3}] for lp=1,2,...,NP (number of end products); P_{lp}^* is the product point source concentration [M_{lp} L^{-3}]; λ_{lp} is the product first order decay coefficient [T^{-1}]; $R_{source,lp}^{bio}$ is a biodegradation source term dependent on the mode of biogeneration [M_{lp} L^{-3} T^{-1}]; and R_{lp} is the end product retardation factor [L^o].

Transport of mineral nutrients (N_{ln}) is:

$$-\frac{\partial}{\partial x_i}\left(v_i N_{ln}\right)+\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial N_{ln}}{\partial x_j}\right)+\frac{q_s}{\theta}N_{ln}^*-R_{sink,ln}^{bio}=R_{ln}\frac{\partial N_{ln}}{\partial t} \qquad (2.4)$$

where N_{ln} is the aqueous phase nutrient concentration [M_{ln} L^{-3}] for ln=1,2,...,NN (number of nutrients); N_{ln}^* is the nutrient point source concentration [M_{ln} L^{-3}]; $R_{sink,ln}^{bio}$ is the nutrient biodegradation sink term [M_{ln} L^{-3} T^{-1}]; and R_{ln} is the nutrient retardation factor [L^o].

The general equation of transport of chlorinated ethenes (C_{lc}) is:

$$-\frac{\partial}{\partial x_i}\left(v_i C_{lc}\right)+\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C_{lc}}{\partial x_j}\right)+\frac{q_s}{\theta}C_{lc}^*+\sum R_{source/sink,lc}=R_{lc}\frac{\partial C_{lc}}{\partial t} \qquad (2.5)$$

where C_{lc} is the chlorinated ethene concentration [M_{lc} L^{-3}] for lc=1,2,...,NC (number of compounds = 4 if PCE is the parent compound; =3 if TCE is the parent compound); C_{lc}^* is the point source concentration for a chlorinated ethene [M_{lc} L^{-3}]; R_{lc} is the retardation factor for a chlorinated ethene [L^o]; and $\sum R_{source/sink,lc}$ is the sum of all sources and sinks:

$$\sum R_{source/sink,lc}=-R_{sink,lc}^{bio,EA}-R_{sink,lc}^{bio,ED}+R_{source,lc}^{bio}+R_{source,lc}^{DNAPL} \qquad (2.5a)$$

where $R_{sink,lc}^{bio,EA}$ is a biodegradation sink term to account for the reduction of a chlorinated ethene [M_{lc} L^{-3} T^{-1}]; $R_{sink,lc}^{bio,ED}$ is a biodegradation sink term to account for the oxidation of a chlorinated ethene [M_{lc} L^{-3} T^{-1}]; $R_{source,lc}^{DNAPL}$ is a source term of a chlorinated ethene dissolving from a dense non-aqueous phase liquid (DNAPL) [M_{lc} L^{-3} T^{-1}]; and $R_{source,lc}^{bio}$ is a

biodegradation source term to account for the production of a lower molecular weight chlorinated ethene due to reductive dechlorination [M_{lc} L^{-3} T^{-1}].

The general equation of transport of recalcitrant compounds (C_{lr}) is:

$$-\frac{\partial}{\partial x_i}(v_i C_{lr}) + \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C_{lr}}{\partial x_j}\right) + \frac{q_s}{\theta}C_{lr}^* + -R_{sink,lr}^{com} + R_{source,lr}^{NAPL} = R_{lr}\frac{\partial C_{lr}}{\partial t} \qquad (2.6a)$$

where C_{lr} is the recalcitrant compound concentration [M_{lc} L^{-3}] for lr=1,2,...,NR (number of recalcitrants); C_{lc}^* is the point source concentration for a recalcitrant [M_{lr} L^{-3}]; R_{lr} is the retardation factor for a recalcitrant [L^o]; and $R_{sink,lr}^{com}$ is the cometabolic biodegradation sink term [M_{lr} L^{-3} T^{-1}].

For the growth substrate (S_1 only) associated with aerobic cometabolism, the transport equation is modified to include two biodegradation sink terms:

$$-\frac{\partial}{\partial x_i}(v_i S_1) + \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial S_1}{\partial x_j}\right) + \frac{q_s}{\theta}S_1^* - R_{sink,1}^{bio} - R_{sink,1}^{com} + R_{source,1}^{NAPL} = R_1\frac{\partial S_1}{\partial t} \qquad (2.6b)$$

where $R_{sink,1}^{com}$ is the cometabolic biodegradation sink term [M_{ls} L^{-3} T^{-1}].

Similarly, when the Cometabolism Package is active, the oxygen transport equation is modified, giving:

$$-\frac{\partial}{\partial x_i}(v_i E_1) + \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial E_1}{\partial x_j}\right) + \frac{q_s}{\theta}E_1^* - R_{sink,le=1}^{bio} - R_{sink,le}^{com} = \frac{\partial E_1}{\partial t} \qquad (2.6c)$$

where $R_{sink,le=1}^{bio}$ is an oxygen sink term resulting from aerobic biodegradation of $S_2, S_3, ... S_{NS}$ [M_{le} L^{-3} T^{-1}]; and R_{sink}^{com} a sink term resulting from aerobic biodegradation of S_1 [M_{le} L^{-3} T^{-1}].

2.2.3   Source/Sink terms – SEAM3D Biodegradation Package

The biodegradation source/sink term is evaluated by summing the effect of each microcolony on the substrates, EAs, nutrients, and products of biodegradation. The x subscripts for the six microcolonies and the le subscripts for the valid EAs within a microcolony are given in Table 2-2. Currently, SEAM3D allows microcolony 2 to utilize both O_2 and NO_3^-, while the other microcolonies utilize only one EA. For each substrate degraded by microcolony x, the sink term is

$$R_{sink,ls}^{bio} = \sum_x \frac{M_x}{\theta} r_{x,ls} \qquad (2.7)$$

where M_x is the microbial biomass concentration [M_b L_{pm}^{-3}] for x = 1,2,...,NM (number of microcolonies); and $r_{x,ls}$ is the utilization rate of substrate ls in microcolony x [M_{ls} M_b^{-1} T^{-1}]. For each EA, the sink term is

$$R_{\sin k, le}^{bio} = \sum_x \frac{M_x}{\theta} r_{x,le} \qquad (2.8)$$

where $r_{x,le}$ is the utilization rate of EA le in microcolony x [$M_{le} M_b^{-1} T^{-1}$]. For each nutrient, the sink term is

$$R_{\sin k, ln}^{bio} = \sum_x \frac{M_x}{\theta} r_{x,ln} \qquad (2.9)$$

where $r_{x,ln}$ is the utilization rate of nutrient ln in microcolony x [$M_{ln} M_b^{-1} T^{-1}$]. For the product CH_4, the source term is

$$R_{source,CH4}^{bio} = \sum_{ls} \zeta_{x,ls} \frac{M_x}{\theta} r_{x,ls} \qquad (2.10)$$

where $\zeta_{x,ls}$ is the product generation coefficient [$M_{lp} M_{ls}^{-1}$], with $x = 6$ for CH_4 production. For the daughter products of the substrates, the source term is

$$R_{source,lp}^{bio} = \zeta_{x,ls}^{dau} \frac{M_x}{\theta} r_{x,ls} \qquad (2.11)$$

where $\zeta_{x,ls}^{dau}$ is the daughter product generation coefficient [$M_{ld} M_{ls}^{-1}$]. For the EA products, the source term is

$$R_{source,lp}^{bio} = \zeta_{x,le} \frac{M_x}{\theta} r_{x,le} \qquad (2.12)$$

where $\zeta_{x,le}$ is the product generation coefficient [$M_{lp} M_{le}^{-1}$], with $x = le = 2$ for N_{user}, $x = le = 3$ for Mn(II), $x = le = 4$ for Fe(II), and $x = le = 5$ for H_2S.

2.2.4   Utilization equations – SEAM3D Biodegradation Package

Utilization of each substrate within microcolony x follows

$$r_{x,ls} = \sum_{le} v_{x,ls,le} \qquad (2.13)$$

where $v_{x,ls,le}$ is the specific rate of substrate utilization (see Equation 2.17) for microcolony x growing on substrate ls and EA le [$M_{ls} M_b^{-1} T^{-1}$], and the summation over le includes only the valid EAs for microcolony x (Table 2.2). Utilization of each EA follows

$$r_{x,le} = \sum_{ls} \gamma_{x,ls,le} v_{x,ls,le} \qquad (2.14)$$

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where $\gamma_{x,ls,le}$ is the EA use coefficient [M_{le} M_{ls}^{-1}], representing the mass of EA le used per unit mass of substrate ls. Since Mn(IV) and Fe(III) are assumed to be attached to the solid phase, transport is not considered and utilization follows

$$-\frac{M_x}{\rho_b} r_{x,le} = \frac{dE_{le}}{dt}$$

(2.15)

where $x = le = 3$ for Mn(IV) and $x = le = 4$ for Fe(III); and E_{le} is the solid phase concentration [M_{le} M_{solid}^{-1}]. Utilization of each nutrient follows

$$r_{x,ln} = \sum_{le} \sum_{ls} \psi_{x,ls,le} v_{x,ls,le}$$

(2.16)

where $\psi_{x,ls,le}$ is the nutrient use coefficient [M_{ln} M_{ls}^{-1}] representing the mass of nutrient ln used per unit mass of substrate ls.

Using Monod kinetics modified for nutrient and EA availability, $v_{x,ls,le}$ may be written

$$v_{x,ls,le} = v_{x,ls,le}^{max} \left[\frac{\overline{S}_{ls}}{\overline{K}_{x,ls,le}^{s} + \overline{S}_{ls}} \right] \left[\frac{\overline{E}_{le}}{\overline{K}_{x,le}^{e} + \overline{E}_{le}} \right] N_x I_{le,li}$$

(2.17)

where $v_{x,ls,le}^{max}$ is the maximum specific rate of substrate utilization for microcolony x growing on substrate ls and EA le [M_{ls} M_b^{-1} T^{-1}]; $\overline{K}_{x,ls,le}^{s}$ is the effective half saturation constant for substrate ls utilizing EA le [M_{ls} L^{-3}]; $\overline{K}_{x,le}^{e}$ is the effective half saturation constant for EA le [M_{le} L^{-3}]; $\overline{S}_{ls}$ is the effective concentration of substrate ls [M_{ls} L^{-3}]; $\overline{E}_{le}$ is the effective concentration of EA le [M_{le} L^{-3}]; and N_x is a Monod function describing nutrient limitations. $I_{le,li}$ is an inhibition function (Widdowson et al. 1988) defined by

$$I_{le,li} = 1 \qquad\qquad \text{for } le = 1 \qquad\qquad (2.17a)$$

and $$I_{le,li} = \prod_{li=1}^{le-1} \left[\frac{\kappa_{le,li}}{\kappa_{le,li} + \overline{E}_{li}} \right] \qquad\qquad \text{for } le = 2, 3, 4, 5 \text{ or } 6 \qquad\qquad (2.18b)$$

where $\kappa_{le,li}$ is the EA inhibition coefficient [M_{le} L^{-3}] representing inhibition of the use of EA le by EA li. If an EA is not specified in a particular simulation, then it is not included in Equation (2.18b). The inhibition function represents the concept that the availability of any EA may inhibit utilization of other EAs that provide less Gibbs free energy to the microbes. As $\kappa_{le,li}$ is assigned a larger value or $\overline{E}_{li}$ decreases, then the inhibitory effect decreases. In analogous fashion, the presence of methane is allowed to inhibit methanogenesis. In this case, the inhibition coefficient κ represents the methane concentration that causes the rate of methanogenesis to be reduced by one half.

N_x may be defined (Widdowson et al. 1988) as

$$N_x = \prod_{ln} \left[\frac{\overline{N}_{ln}}{\overline{K}^n_{x,ln} + \overline{N}_{ln}} \right] \tag{2.19}$$

where $\overline{K}^n_{x,ln}$ is the effective half saturation constant for nutrient ln [M_{ln} L^{-3}]; and $\overline{N}_{ln}$ is the effective concentration of nutrient ln [M_{ln} L^{-3}]. Since Equation (2.19) uses the product of each nutrient Monod term, all nutrients are allowed to limit microbial growth simultaneously. Alternatively, a user option permits only the minimum nutrient to limit growth as follows:

$$N_x = \min_{ln} \left[\frac{\overline{N}_{ln}}{\overline{K}^n_{x,ln} + \overline{N}_{ln}} \right] \tag{2.20}$$

where the minimum is taken over the range of specified nutrients.

Effective concentrations are used in Equations (2.17) through (2.20) to account for threshold concentrations below which the cells cannot grow (Button 1985; Bosma et al. 1996). $\overline{S}_{ls}$ is defined as

$$\overline{S}_{ls} = max(S_{ls} - S^t_{ls}, 0) \tag{2.21}$$

where S^t_{ls} is the threshold concentration of substrate ls. Likewise, $\overline{K}^s_{x,ls,le}$ is defined as

$$\overline{K}^s_{x,ls,le} = max(K^s_{x,ls,le} - S^t_{ls}, 0) \tag{2.22}$$

where $K^s_{x,ls,le}$ is the half saturation constant for substrate ls utilizing EA le [M_{ls} L^{-3}]. In analogous fashion, $\overline{E}_{le}$, $\overline{N}_{ln}$, $\overline{K}^e_{x,le}$, and $\overline{K}^n_{x,ln}$ are defined using E^t_{le} and N^t_{ln} as the threshold concentrations. When actual concentrations are below threshold, lack of growth is generally attributed to endogenous requirements for cell maintenance (Button 1985). Another explanation is that low concentrations of substrate, EAs, or nutrients may fail to induce enzymes for carrier proteins that transport these components into the cell (Bosma et al. 1996).

For the Mn(IV) and Fe(III) reducing populations, the substrate utilization rate is assumed to be independent of the EA concentration (E_{le}) over a range of values. Therefore, when E_{le} exceeds E^t_{le}, the expression is zero order with respect to the EA, and Equation (2.17) becomes

$$v_{x,ls,le} = v^{max}_{x,ls,le} \left[\frac{\overline{S}_{ls}}{\overline{K}^s_{x,ls,le} + \overline{S}_{ls}} \right] N_x I_{le,li} \tag{2.23}$$

Conversely, when E_{le} falls below E_{le}^t, $v_{x,ls,le}^{max}$ is set to zero in Equation (2.23) and substrate utilization due to that population ceases. This approach, suggested by Chapelle (1996, personal communication) is designed to simulate bioavailability of solid phase constituents; i.e. when $E_{le} < E_{le}^t$ the microbes no longer have direct access to EA on the solid phase.

SEAM3D also assumes that methanogenesis is not limited by EA availability, since CO_2 is typically produced during oxidation of substrates under all other TEAP's modeled. These TEAP's precede methanogenesis and tend to occur at higher rates. Thus, CO_2 is assumed to be abundant, and the rate of substrate utilization follows Equation (2.23) under methanogenesis. This simplification allows SEAM3D to avoid simulating the complexities of the carbon cycle in the subsurface environment. To fully describe the fate and transport of CO_2, an existing geochemical model could be coupled with the biodegradation model.

2.2.5   Microbial growth equations – SEAM3D Biodegradation Package

In deriving the microbial growth equations, we distinguish between background substrates, which are not modeled explicitly, and the hydrocarbon (HC) substrates being modeled. Background substrates are the carbon sources that microbes utilize prior to aquifer contamination by HC substrates. When the aquifer is uncontaminated, the background substrate, EA, nutrient, and biomass concentrations are assumed to be at steady state. Thus the background death rate ($k_{d_x}^{bk}$) is equal to the growth rate at time zero ($G_x^{bk,0}$), just prior to HC contamination. SEAM3D calculates $G_x^{bk,0}$ as

$$G_x^{bk,0} = Y_x^{bk} v_x^{max,bk} \left[\frac{\overline{E}_{le}}{\overline{K}_{x,le}^e + \overline{E}_{le}} \right] N_x \tag{2.24}$$

where $Y_x^{bk} = \frac{1}{NS} \sum_{ls} Y_{x,ls,le}$ and $v_x^{max,bk} = \frac{1}{NS} \sum_{ls} v_{x,ls,le}^{max}$ for le representing the final EA utilized by population x. The use of averaged values for Y_x^{bk} and $v_x^{max,bk}$ ensures that $k_{d_x}^{bk}$ will be of the same order of magnitude as the growth rates ($G_{x,ls,le}$) due to HC substrates (see Equation 2.26). Initial values for $\overline{E}_{le}$ and N_x are obtained as the spatial average of the initial concentrations, thus requiring the user to input initial concentrations that represent pristine conditions. In Equation (2.24), the substrate Monod term has been set to one, under the assumption that the half saturation constant for background substrate is quite small, as is often the case in oligotrophic systems. The inhibition term does not appear in Equation (2.24) since we assume that each population has reached steady state in the presence of inhibitory EAs.

When contamination occurs, steady state no longer applies, as HC substrates cause biomass growth accompanied by depletion of EAs and nutrients. As a result, periods of rapid microbial growth may be followed by rapid death. The mass balance Equation for growth and death of microbial population x is written

$$\frac{1}{M_x}\frac{dM_x}{dt} = -k_{d_x} + G_{x,ls,le} \tag{2.25}$$

where k_{d_x} is the "effective" death rate [T^{-1}], and $G_{x,ls,le}$ is the growth rate due to the HC substrates, defined as

$$G_{x,ls,le} = \sum_{le} \sum_{ls} Y_{x,ls,le} \nu_{x,ls,le} \tag{2.26}$$

where $Y_{x,ls,le}$ is the biomass yield coefficient [$M_b\ M_{ls}^{-1}$], representing the mass of microcolony x produced per unit mass of substrate ls while utilizing EA le. The effective death rate (k_{d_x}) is computed as the difference between $k_{d_x}^{bk}$ (assumed constant over time) and the current growth rate as follows:

$$k_{d_x} = max\left[0, k_{d_x}^{bk} - \left(G_x^{bk} + G_{x,ls,le}\right)\right] \tag{2.27}$$

where G_x^{bk} is given by Equation (2.24) with $\overline{E}_{le}$ and N_x computed from current concentrations at each block in the model domain. In regions having no HC substrate, EAs and nutrients remain at background levels; thus $k_{d_x} = 0$, and biomass concentrations also remain at background levels. When HC substrates cause sufficient microbial utilization of EA and nutrient, G_x^{bk} and $G_{x,ls,le}$ decrease such that $k_{d_x} > 0$. The value of k_{d_x} will return to zero if HC subtrates are transported out of a zone, and EA and nutrient concentrations return to backgound levels.

If necessary, biomass size is limited by switching to Monod, no growth kinetics (Simkins and Alexander 1984) when substrate concentrations are insufficient to allow the microbes to double. Thus, G_x^{bk} and $G_{x,ls,le}$ are set to zero when

$$M_x \geq \phi\sum_{ls}\left(Y_{x,ls,le} S_{ls}\right) \tag{2.28}$$

where le is the index of the predominant TEAP for population x. Overall, Equations (2.24) to (2.28) link biomass concentrations to the available substrates, EAs, and nutrients, thereby preventing excessive growth or death. Simulation of biomass may not be desireable in all situations, perhaps due to lack of data. Thus, microbial death and growth can be eliminated from the model by setting the input values of $k_{d_x}^{bk}$ and $Y_{x,ls,le}$ to zero.

2.2.6 *Biological source/sink terms – SEAM3D Reductive Dechlorination Package*

The biodegradation sink term for the reductive dechlorination process is expressed by

$$R_{sink,lc}^{bio,EA} = \frac{M_y}{\theta} v_{lc}^{max,EA} \left[\frac{\overline{C}_{lc}}{\overline{K}_{lc}^e + \overline{C}_{lc}} \right] I_{lc,li} \tag{2.29}$$

where M_y is the microbial biomass concentration of chlorinated ethene reducers [M_b L_{pm}^{-3}] for $x = 1$ or 2; $v_{lc}^{max,EA}$ is the maximum rate of reductive dechlorination for a chlorinated ethene lc [M_{lc} M_b^{-3} T^{-1}]; $\overline{K}_{lc}^e$ is the effective half saturation constant for a chlorinated ethene (serving as an EA) lc [M_{lc} L^{-3}]; $\overline{C}_{lc}$ is the effective concentration of a chlorinated ethene lc [M_{lc} L^{-3}]; and $I_{lc,li}$ is an inhibition function defined by

$$I_{lc,li} = \prod_{li=1}^{5} \left[\frac{\kappa_{lc,li}}{\kappa_{lc,li} + \overline{E}_{li}} \right] I_{lc,lj} \tag{2.30a}$$

where $\qquad I_{lc,lj} = 1 \qquad\qquad$ for $lc = 1$ (or 2, PCE absent) $\qquad$ (2.30b)

and $\qquad I_{lc,lj} = \prod_{lj=1}^{lc-1} \left[\frac{\kappa_{lc,lj}}{\kappa_{lc,lj} + \overline{C}_{lj}} \right] \qquad$ for $lc = 2, 3,$ or 4 $\qquad$ (2.30c)

where $\kappa_{lc,li}$ is the EA inhibition coefficient [M_{le} L^{-3}] representing inhibition of the use of a chlorinated ethene lc (as an EA) by EA li (where $li = 1, 2, 3, 4,$ or 5 only); $\kappa_{lc,lj}$ is the EA inhibition coefficient [M_{le} L^{-3}] representing inhibition of the use of a chlorinated ethene lc (as an EA) by a higher molecular weight chlorinated ethene lj. If an EA is not specified for a particular simulation using the SEAM3D Biodegradation Package, then it is not included in Equation (2.30a).

It is now known that the prevailing TEAP influences the efficiency of transformation of cis-DCE and VC to CO_2 and the rate of reductive dechlorination of all chlorinated ethenes. In Equation (2.30a) the overall rate of reaction is dependent on the compounds undergoing reduction and the prevailing TEAP. The maximum rate of reaction ($v_{lc}^{max,EA}$) is compound dependent but is independent of the prevailing TEAP. The inhibition function in Equation (2.30a) will mathematically control the rate of reaction for reductive dechlorination based on the availability and concentration of higher energy-yielding EAs.

The biodegradation sink term for direct oxidation is similar to Equation (2.17) and is expressed as

$$R_{sink,lc}^{bio,ED} = \sum_{x} \frac{M_x}{\theta} v_{x,lc,le}^{max} \left[\frac{\overline{C}_{lc}}{\overline{K}_{x,lc,le}^{ed} + \overline{C}_{lc}} \right] \left[\frac{\overline{E}_{le}}{\overline{K}_{x,le}^e + \overline{E}_{le}} \right] I_{le,li} \tag{2.31}$$

where $v_{x,lc,le}^{max}$ is the maximum rate of direct oxidation for a chlorinated ethene lc by microcolony x utilizing EA le [M_{lc} M_b^{-3} T^{-1}]; $\overline{K}_{x,lc,le}^{ed}$ is the effective half saturation constant for a chlorinated ethene lc (serving as an electron donor) utilizing EA le [M_{lc} L^{-3}]; and $\overline{K}_{x,le}^{e}$ is the effective half saturation constant for EA le [M_{le} L^{-3}].

Production of a chlorinated daughter product is expressed in terms of the rate of reduction of the parent compound

$$R_{source,lc}^{bio} = \zeta_{lc,lc-1}^{dau} R_{sink,lc-1}^{bio,EA}$$
(2.32)

where $\zeta_{lc,lc-1}^{dau}$ is the daughter product generation coefficient [M_{lc} M_{lc-1}^{-1}].

2.2.7 Biological sink terms – Cometabolism Package

The cometabolic biodegradation sink term for the growth substrate ($ls = 1$, S_1) and $x = 1$ ($le = 1$, E_1) is:

$$R_{sink,ls=1}^{com} = \frac{M_x}{\theta} r_{x,1}^{com}$$
(2.33)

$$r_{x,1}^{com} = v_{x,1,1}^{max} \left[\frac{\overline{S}_1}{\overline{K}_{x,1,1}^{s} + \overline{S}_1 + \frac{\overline{S}_1^2}{K_H} + \overline{C}_1 \frac{K_m}{\overline{K}_{I1}} + \overline{C}_2 \frac{K_m}{\overline{K}_{I2}} + \overline{C}_3 \frac{K_m}{\overline{K}_{I3}}} \right] \left[\frac{\overline{E}_1}{\overline{K}_{x,1}^{e} + \overline{E}_1} \right] N_x.$$
(2.34)

where $\overline{C}_{lr}$ is the effective concentration of the recalcitrant compounds [M_{lr}/L^3], in which $\overline{C}_{lr} = C_{lr} - C_{min}$ when $C_{lr} > C_{min}$ or $\overline{C}_{lr} = 0$ when $C_{lr} \leq C_{min}$; C_{min} is the minimum concentration of the recalcitrant compounds below which cometabolism ceases [M_{lr}/L^3]; $\overline{K}_{I,lr}$ is the effective half-saturation constants for the recalcitrant compounds [M_{lr}/L^3], in which $\overline{K}_{I,lr} = K_{lr} - C_{min}$; K_m is the enzyme half-saturation constant for growth substrate [M_{ls}/L^3]; and K_{HAL} is the Haldine constant for growth substrate [M_{ls}/L^3].

The cometabolic biodegradation sink term for oxygen and $x = 1$ ($ls = 1$, S_1) is:

$$R_{sink,le=1}^{com} = \frac{M_x}{\theta} \gamma_{x,1,1} r_{x,1}^{com}.$$
(2.35)

For the first recalcitrant variable ($lr = 1$) with $x = 1$ ($ls = 1$, S_1 and $le = 1$, E_1), the cometabolic biodegradation sink term is:

$$R_{sink,lr=1}^{com} = \frac{F_A M_x}{\theta} k_{lr=1}^{max} \left[\frac{\overline{C}_1}{\overline{K}_{I1} + \overline{C}_1 + \overline{S}_1 \frac{\overline{K}_{I1}}{K_m} + \overline{C}_2 \frac{\overline{K}_{I1}}{\overline{K}_{I2}} + \overline{C}_3 \frac{\overline{K}_{I1}}{\overline{K}_{I3}}} \right] \left[\frac{\overline{E}_1}{\overline{K}_{x,1}^e + \overline{E}_1} \right] N_x \quad (2.36)$$

where k_{lr}^{max} is the maximum specific utilization rate for of the recalcitrant compounds [T^{-1}]; and F_A is the fraction of the aerobic microbial population active towards cometabolism [M/M].

For the second recalcitrant variable ($lr = 2$) with $x = 1$ ($ls = 1$, S_1 and $le = 1$, E_1), the cometabolic biodegradation sink term:

$$R_{sink,lr=2}^{com} = \frac{F_A M_x}{\theta} k_{lr=2}^{max} \left[\frac{\overline{C}_2}{\overline{K}_{I2} + \overline{C}_2 + \overline{S}_1 \frac{\overline{K}_{I2}}{K_m} + \overline{C}_1 \frac{\overline{K}_{I2}}{\overline{K}_{I1}} + \overline{C}_3 \frac{\overline{K}_{I2}}{\overline{K}_{I3}}} \right] \left[\frac{\overline{E}_1}{\overline{K}_{x,1}^e + \overline{E}_1} \right] N_x \quad (2.37)$$

For the third recalcitrant variable ($lr = 3$) with $x = 1$ ($ls = 1$, S_1 and $le = 1$, E_1), the cometabolic biodegradation sink term:

$$R_{sink,lr=3}^{com} = \frac{F_A M_x}{\theta} k_{lr=3}^{max} \left[\frac{\overline{C}_3}{\overline{K}_{I3} + \overline{C}_3 + \overline{S}_1 \frac{\overline{K}_{I3}}{K_m} + \overline{C}_1 \frac{\overline{K}_{I3}}{\overline{K}_{I1}} + \overline{C}_2 \frac{\overline{K}_{I3}}{\overline{K}_{I2}}} \right] \left[\frac{\overline{E}_1}{\overline{K}_{x,1}^e + \overline{E}_1} \right] N_x \quad (2.38)$$

Recalcitrant concentration variables may specified and cross-linked by the user within the Reductive Dechlorination Package (e.g., TCE and *cis*-DCE, but not PCE). In this case, Equation (2.5a) for those compounds is:

$$\sum R_{source/sink,lc} = -R_{sink,lc}^{bio,EA} - R_{sink,lc}^{bio,ED} + R_{source,lc}^{bio} + R_{source,lc}^{DNAPL} - R_{sink,lc}^{com} \quad (2.39)$$

2.2.8   *Microbial growth equations – Cometabolism Package*

The initial condition of the aerobic population that performs cometabolism is specified in the Biodegradation Package. A fraction of the aerobic population is assumed responsible for cometabolism. This fraction ($0 \le F_A \le 1$) is specified in the Cometabolism Package, so that if M_1 is the concentration of the aerobic microbial population, then $F_A M_1$ is the concentration of the aerobic microbial population active towards cometabolism.

The microbial growth equation for $x = 1$ in the Biodegradation Package includes two additional terms that are only included when the Cometabolism Package is active:

$$\frac{dM_x}{dt} = M_x\left(-k_{d_x} + G_{x,ls,le}\right) + T_{R_1}\theta R_{sink,lr=1}^{com} + T_{R_2}\theta R_{sink,lr=2}^{com} + T_{R_3}\theta R_{sink,lr=3}^{com} \quad (2.40)$$

where $T_{R_{lr}}$ is the transformation capacity for the recalcitrant compounds [M_b M_{ls}^{-1} T^{-1}].

The fraction of the aerobic microbial population active towards cometabolism is based on the sign of the LHS of Equation (2.40) so that

$$\frac{1}{F_A}\frac{dF_A}{dt} = -b_d \text{ when } \frac{dM_x}{dt} < 0 \tag{2.41}$$

where b_d is the death rate of the aerobic microbial population active towards cometabolism [T^{-1}]. Otherwise,

$$F_A = 1 \text{ when } \frac{dM_x}{dt} \geq 0 \tag{2.42}$$

2.2.9 DNAPL dissolution source term – SEAM3D NAPL Dissolution Package

When groundwater contacts a non-aqueous phase liquid (NAPL), components of the NAPL will dissolve into the aqueous phase until equilibrium is reached or NAPL mass is depleted. Since model handling of the dissolution of nonbiodegradable tracers is identical to biodegradable compounds, the following description will focus on chlorinated ethenes only. For each chlorinated ethenes *lc*, the driving force for dissolution is the difference between the actual aqueous phase concentration (C_{lc}), and the equilibrium concentration (C_{lc}^{eq}). In general, the rate of dissolution of C_{lc} into groundwater depends on the interfacial area between the NAPL and water, (Imhoff et al. 1993), aquifer heterogeneity (Mayer and Miller 1996), the size and shape of the NAPL blobs (Powers et al. 1994) and the groundwater velocity (Pfannkuch 1984). Thus, if transport processes occur at a high rate relative to the NAPL dissolution rate, C_{lc} may remain lower than C_{lc}^{eq}. This effect can be described mathematically (Imhoff et al. 1993; Parker et al. 1991) by a mass transfer rate coefficient (k^{NAPL}), such that the NAPL dissolution term (Equation 2.5a) for chlorinated ethenes *lc* becomes

$$R_{source,lc}^{NAPL} = max\left[0, k^{NAPL}\left(C_{lc}^{eq} - C_{lc}\right)\right]. \tag{2.43}$$

Using Raoult's Law, C_{lc}^{eq} is calculated (Corapcioglu and Baehr 1987; Parker et al. 1991) as

$$C_{lc}^{eq} = f_{lc}C_{lc}^{sol} \tag{2.44}$$

where f_{lc} is the mole fraction of chlorinated ethene *lc* in the NAPL [mol_{lc} mol_{NAPL}^{-1}]; and C_{lc}^{sol} is the solubility of pure chlorinated ethene *lc* in water. During each time step, f_{lc} is computed as

$$f_{lc} = \frac{C_{lc}^{NAPL}/\omega_{lc}}{I^{NAPL}/\omega_I + \sum_{ls=1}^{NS} C_{lc}^{NAPL}/\omega_{lc} + \sum_{lt=1}^{NT} T_{lt}^{NAPL}/\omega_{lt}} \tag{2.45}$$

where C_{lc}^{NAPL} is the NAPL mass of chlorinated ethene lc per unit mass dry soil [M_{lc} M_{solid}^{-1}]; I^{NAPL} is the NAPL concentration of inert (i.e., relatively insoluble constituents) [M_I M_{solid}^{-1}]; T_{lt}^{NAPL} is the NAPL concentration of nonbiodegradable tracer lt [M_{lt} M_{solid}^{-1}], and ω_j is the molecular weight of NAPL constituent j. Equations (2.44) and (2.45) represent the concept that the effective solubility of any NAPL constituent is reduced when other constituents are simultaneously dissolving into the aqueous phase. With each time step, C_{lc}^{NAPL} is updated as

$$\frac{dC_{lc}^{NAPL}}{dt} = -\frac{\theta}{\rho_b} R_{source,lc}^{NAPL} \tag{2.46}$$

where ρ_b is the bulk density of the porous medium [M_{solid} L_{pm}^{-3}]. Thus, dissolution causes the NAPL concentration of chlorinated ethene lc to decrease as the aqueous phase concentration increases.

2.3   Model Implementation

The sequential electron acceptor model (SEAM3D) is implemented as a numerical, block-centered, finite difference computer algorithm (Waddill and Widdowson 2000). SEAM3D, 2.0 and higher, are based on the code MT3DMS (Zheng and Wang 1999). MT3DMS is capable of simulating a single solute in groundwater under the influence of advection, dispersion, source/sink mixing, adsorption, and first order decay. SEAM3D extends the modular structure of MT3DMS such that computer memory is not reserved for unused options. For example, if the user chooses to model aerobic biodecay only, then memory is not reserved for the anaerobic processes. SEAM3D 3.0 interfaces with the groundwater flow model MODFLOW-2000; thus it supports a variety of aquifer configurations, boundary conditions, and groundwater sources and sinks.

In solving the advection term in the transport equations, SEAM3D supports only the standard finite difference method and the TVD (ULTIMATE) scheme. SEAM3D does not support the implicit GCG Package. In contrast to the particle tracking algorithms (e.g., MOC), the finite difference option ensures that mass will be conserved as constituents are utilized or produced during biodegradation. Numerical dispersion error can be minimized by setting the grid spacing on the order of the dispersivity values (Zheng and Bennett 1995). During each transport time step, concentration changes due to advection, dispersion, and source/sink mixing and calculated using the MT3DMS modules. The SEAM3D Biodegradation Package calculates values for $\overline{S}_{ls}$, $\overline{E}_{le}$, and $\overline{N}_{ln}$ which are used in Equation (2.17) to obtain $v_{x,ls,le}$, from which the utilization rates are calculated in Equations (2.13), (2.14), and (2.16), and to obtain the biomass concentrations (Equation 2.24). SEAM3D allows the transport time step to be subdivided into smaller increments for the biodegradation calculations.

SEAM3D can only be executed with the Biodegradation Package active. Both the Reductive Dechlorination and Cometabolism Packages use electron donor and electron acceptor concentration values calculated in the Biodegradation Package. Models may be developed using the Reductive Dechlorination and Cometabolism Packages separately or in combination.

	Microbial Mechanism		
Compound	*Direct Oxidation*	*Reductive Dechlorination*	*Aerobic Cometabolism*
PCE	No	Yes	*NS*
TCE	No	Yes	User Defined
DCE	Yes	Yes	User Defined
VC	Yes	Yes	User Defined

Table 2.1   Biodegradation mechanisms considered in the SEAM3D Reductive Dechlorination and Cometabolism Packages for perchloroethene (PCE), trichloroethene (TCE), cis, 1-2 dichloroethene (DCE), and vinyl chloride (VC). *NS* = not simulated in the Cometabolism Package.

x, y[1]	Microbial Population	Ie[2]	EA	Utilization Possibly Inhibited by	End Products[3]
x=1	Strict aerobes	1	O_2	--	H_2O, CO_2
x=2	Facultative NO_3 reducers	1	O_2	--	H_2O, CO_2
		2	NO_3	O_2	NO_x
x=3	Anaerobic Mn(IV) reducers	3	Mn(IV)	O_2, NO_3	Mn(II)
x=4	Anaerobic Fe(III) reducers	4	Fe(III)	O_2, NO_3, Mn(IV)	Fe(II)
x=5	Anaerobic SO_4 reducers	5	SO_4	O_2, NO_3, Mn(IV), Fe(III)	HS^-
x=6	Anaerobic methanogens	6	CO_2	O_2, NO_3, Mn(IV), Fe(III), SO_4	CH_4
x=7	Aerobic methanotrophs	1	O_2	--	H_2O, CO_2
y=1	PCE/TCE reducers		PCE/TCE	O_2, NO_3, Mn(IV), Fe(III), SO_4	Cl
y=2	cis-DCE/vC reducers		DCE/VC	O_2, NO_3, Mn(IV), Fe(III), SO_4	Cl, C_2H_4[4]

Note: The EAs are listed in order of highest (1, oxygen) to lowest Gibbs free energy provided. Use of each EA is inhibited by the presence of an EA that provides higher energy.

[1] Subscript for microbial group (*x = SEAM3D Biodegradation Package, y = SEAM3D RDP*)

[2] Subscript for valid EA within a microbial group

[3] H_2O, CO_2 are not simulated in SEAM3D

[4] Ethene (C_2H_4) is an end product of vinyl chloride reduction.

Table 2.2. Electron acceptors used by the microbial populations for biodegradation of hydrocarbon substrates. Electron acceptors are listed in order of highest to lowest Gibbs free energy per half reaction. Utilization of each electron acceptor is inhibited by the presence of an electron acceptor that provides higher energy.

Chlorinated ethene	Anaerobic TEAP			
	Mn(IV) reduction	Fe(II) reduction	SO$_4$ reduction	Methanogenesis
PCE	+	+	++	+++
TCE	+	+	++	+++
DCE	+	+	+	+++
VC	+	+	+	+++

Table 2.3. Anaerobic terminal electron acceptor processes (TEAPs) underwhich reductive dechlorination can be simulated with the SEAM3D Reductive Dechlorination Package. Symbols +, ++, and +++ indicate the relative rate of reaction from low to high.

3. SEAM3D Code Demonstration

For the new SEAM3D packages, simulations are presented to demonstrate model capabilities and the nature of the microbial reactions. Simulations include closed system-models where concentration versus time is simulated to demonstrate biodegradation processes in the SEAM3D Reductive Dechlorination (SEAM3D-RDP) and Cometabolism Packages. Transport simulations are also presented.

3.1 Demonstration of Biodegradation Processes

Time-dependent test cases were devised, in which advection, dispersion, and source/sink terms were negligible, so concentration changes depended solely on biodegradation. In each case, the model domain represented a 16 x 16 x 1 m confined aquifer, divided into 16 blocks using 4 x 4 x 1 m spacing. In generating the groundwater flow field, the piezometric surface was maintained horizontal, so all values of $\bar{v}_i$ and q_s were zero in the transport simulations. Transport and biodegradation parameters were identical at all nodes, forcing the concentration gradients to be zero.

In the demonstration of the SEAM3D-RDP, anaerobic conditions were assumed to exist in the closed system with iron-reduction and methanogenesis as the only active microbial processes. Aerobic microbial process was negligible in the absence of dissolved oxygen. In the demonstration of the SEAM3D Cometabolism Package, aerobic conditions were specified in the closed system at time zero and anaerobic biodegradation of hydrocarbon and recalcitrant compounds were assumed to be negligible in the presence of dissolved oxygen and within the time frame of the simulated period.

3.1.1 Reductive Dechlorination of Chloroethenes

Figure 3.1 is a plot of simulation results in which PCE (starting concentration = 5.8 mg/L) is biodegraded via reductive dechlorination, resulting in the production of TCE. The simulated biodegradation of TCE was controlled in the presence of PCE using an inhibition function that increased to 1.0 as the PCE concentration decreased. The relatively low value of the inhibition coefficient $(\kappa_{le,li} = 0.01$ mg/L; i.e., inhibition of the use of TCE in the presence of PCE) resulted in the sharp growth of the TCE curve and rapid transition over to a high rate of TCE biodegradation when the PCE concentration decreased below 0.01 mg/L. Similarly, the transformation of TCE to cis-DCE was noted, followed by the production and reductive dechlorination of VC.

The biotransformation of VC to ethene is shown in Figure 3.2. Ethene production did not commence until 40 days, which corresponded with the biodegradation of cis-DCE and hence, VC production and subsequently, the final step of reductive dechlorination. Ethene production accelerated as time approached 90 days, corresponding with the near removal of cis-DCE. The production of chloride was also demonstrated in Figure 3.2, beginning with the biodegradation of PCE and continuing with time. The breaks in slope corresponded with the sharp changes in the various reductive dechlorination steps, beginning at time = 20 days when

TCE transformation was prevalent and then again at times of 40 and 90 days when cis-DCE and VC transformation, respectively, dominated the system.

3.1.2 Direct Oxidation of Chloroethenes

In the previous example, direct oxidation of VC or cis-DCE by the iron-reducing population was not simulated. Figure 3.3 is a plot of simulation results for the chloroethenes in which direct anaerobic oxidation of VC is added to the simulation shown in Figure 3.1. All model input parameters were the same as the previous demonstration except that $v_{x,ls,le}^{max}$ was 0.04 day^{-1} and $K_{x,ls,le}^s$ was 1.0 mg/L for the direct oxidation of VC under iron-reducing conditions. In this example, relative to the previous results, the inclusion of direct anaerobic oxidation only impacted the concentration of VC. In the previous example (Figure 3.1), the maximum concentration of VC was 1.38 mg/L, occurring at time = 86 d. With the addition of direct oxidation, the peak concentration of VC was less (1.097 mg/L) and occurred earlier, at time = 83 d. At the end of simulation (time = 100 d), direct anaerobic oxidation and reductive dechlorination combined to drop the concentration of VC to 1.2 µg/L. In the reductive dechlorination-only simulation, the VC concentration was 332 µg/L after 100 days.

Figure 3.4 shows that the production of ethene is approximately equal to that shown in the reductive dechlorination-only case and that the peak concentration is 0.80 mg/L compared to 0.83 mg/L in Figure 3.2. (Note that the transformation of ethene to ethane was not simulated in this example.) This result was expected and demonstrated that the inclusion of direct anaerobic oxidation had only a slight impact on the rate and extent of reductive dechlorination of VC in this example. The production of ferrous iron is also plotted in Figure 3.4, resulting from the direct oxidation of VC by the iron-reducing population. For the first 40 days of the simulation, the production of Fe(II) was due to naturally-occurring organic carbon, but at time = 40days, a sharp increase in the rate of Fe(II) production was noted as VC was produced. This rate dropped off near the end of simulation as the concentration of VC approached zero.

3.1.3 Aerobic Cometabolism of a Single Recalcitrant Compound

To demonstrate the kinetics of aerobic cometabolism on a basic level, a simulation was devised in which a growth substrate and a single recalcitrant compound were both present at an initial concentration of 1.0 mg/L. Dissolved oxygen was present at 5.0 mg/L. Initially, the fraction of the aerobic population capable of cometabolism was 0.30. As the aerobic microbial population increased with time, an increasing rate of hydrocarbon degradation and cometabolic biodegradation of the recalcitrant compound was apparent (Figure 3.5). From approximately 10 to 80 days, the recalcitrant compound continued to undergo degradation in the presence of aerobic biodegradation of the growth substrate and at a rate less than that of the hydrocarbon. At approximately 80 days, the buildup of the aerobic population combined with the lowering of the concentration of the growth substrate was such that the rate of cometabolic biodegradation of the recalcitrant compound substantially increased, resulting in complete removal of the recalcitrant compound by 90 days.

3.1.4 Aerobic Cometabolism of Multiple Recalcitrant Compounds

In this example, aerobic cometabolism of two recalcitrant compounds was simulated. A growth substrate was present at an initial concentration of 2.0 mg/L. The initial

concentrations of the first and second recalcitrant compounds were 5.0 and 1.0 mg/L, respectively. Dissolved oxygen was present at 5.0 mg/L. Figure 3.6 shows that the simulated response of the growth substrate, oxygen and the first recalcitrant compound is similar to the trend for the same constituents shown in Figure 3.5. Relative to the second recalcitrant compound, the first recalcitrant was preferentially cometabolized. By 43 days the concentration of the first recalcitrant was zero, at which point the rate of cometabolism of the second recalcitrant increased, resulting in complete degradation of the compound over the last 10 days for the simulation.

3.2 SEAM3D-RDP Transport Simulation

Selected capabilities of the SEAM3D-RDP were demonstrated in a hypothetical fully three-dimensional domain. SEAM3D was applied to a hypothetical, three-dimensional domain (Figures 3.7 and 3.8), whose dimensions were selected as 1000 m in the longitudinal x-direction, by 400 m in the transverse y-direction, by 15 m in the vertical z-direction. The domain was divided into 40 rows, 100 columns, and 5 layers using 10 by 10 by 3 m blocks.

The model was designed to demonstrate simulation of 3D transport of contaminants derived from a mixed chlorinated solvent/petroleum hydrocarbon source. In this example, reductive dechlorination of chloroethenes (PCE and chlorinated progeny) was included in the simulation along with the biodegradation of a single hydrocarbon (BTEX) using oxygen, Fe^{3+}, and CO_2 (for methanogenesis) as electron acceptors.

3.2.1 Flow parameters

MODFLOW was used to generate the steady state flow field for contaminant transport. The uppermost aquifer was unconfined with a hydraulic conductivity of 6 m day^{-1} (Figure 3.7). The lower layers were given a transmissivity of 18 m day^{-1}, and the vertical leakance between layers was 6 m day^{-1}. Each of the five model layers was homogeneous. Boundary conditions were no flow along $y = 0$ and $y = 400$, and a constant head of 53 m at $x = 0$ and 48 m at $x = 1000$. Thus without recharge, the hydraulic gradient was a uniform 0.005. The bottom of the unconfined aquifer was given the same slope as the water table, so its thickness was uniform.

3.2.2 Transport parameters

Longitudinal dispersivity (α_x) was chosen as 15 m, transverse dispersivity (α_y) was 4.5 m, and vertical dispersivity (α_z) was 0.12 m. The effective porosity for transport was 0.25. The retardation factor for the endproduct Fe(II) was chosen to be 4.5, while all other solutes were not retarded.

A constant source of contaminants (BTEX and PCE) was located near $x = 200$ and $y = 200$ (Figure 3.7) and were introduced only in the uppermost layer of the domain (Figure 3.8). Initial concentrations at all nodes were 4.1 g m^{-3} for dissolved oxygen (DO), 0.02 g m^{-3} for dissolved Fe(II), 0.001 g m^{-3} for methane (CH$_4$), and 100 μg g^{-1} for solid phase Fe(III). Initial concentrations for BTEX and PCE were 45 g m^{-3} in the source area and zero elsewhere. Minimum concentrations (below which biodegradation will not occur) were set at 10 μg g^{-1} for Fe(III) and 0.3 g m^{-3} for aqueous electron acceptors (EAs). Separate simulations showing

the influence of redox on reductive dechlorination by changing the source strength of BTEX and by decreasing the background level of DO were also demonstrated.

Boundary conditions were specified as constant concentration equal to the initial condition at the upgradient boundary ($x = 0$) for all source contaminants, aqueous phase EAs, daughter products and endproducts. For all species, nodes not specified as constant concentration were allowed to be active, and solute flowed out of the domain under zero dispersion if necessary. All simulations ran for 4000 days.

3.2.3 Results and Discussion

The final areal distributions of BTEX and PCE are shown in Figure 3.9. Although both contaminants have an identical source concentration and sorption parameters, the BTEX plume was attenuated to a greater degree relative to the PCE plume (i.e., a shorter BTEX plume with lower concentrations). In this case, BTEX was readily biodegraded, serving as a hydrocarbon substrate for aerobic and anaerobic microbial populations. The effect of the BTEX on the redox conditions in the ground-water system is shown in Figure 3.10. Dissolved oxygen was removed from the groundwater after passing through the BTEX source area (left column, middle plot). The formation of a Fe(II) plume downgradient of the source (right column, middle plot) indicated that iron-reduction is active downgradient of the source. This observation was reinforced by the formation of a methane plume (right column, top plot) originating from the source area, indicating that Fe(III) was utilized and methanogenic conditions were present in the source zone. The presence of strongly reducing conditions in the source zone resulted in reductive chlorination of PCE and potentially, chlorinated progeny. This was confirmed by the presence of chloride (right column, bottom plot) originating from the source.

Figure 3.11 shows the final areal distributions of the chlorinated ethenes – TCE, cis-DCE, and VC (top, middle and bottom plots, respectively) – at 4000 days. A comparison of the three plots showed that the peak concentration of three chlorinated daughter products was successively located further downgradient of the PCE source . Furthermore, the peak concentration in each plume was less than the source compound. These observations were consistent with data trends noted at many chlorinated solvent sites where strongly reducing conditions are known to exist.

3.2.4 Impact of Dissolved Oxygen on Reductive Dechlorination

In the previous simulation, BTEX served as an effective reducing agent for removing DO and Fe(III) in the source zone, allowing reductive dechlorination of PCE and chlorinated progeny. The influence of background dissolved oxygen was shown in a simulation in which the initial and upgradient boundary concentration of DO is lowered to 2.0 mg/L (Figure 3.12). The positive effect of this decrease on the rate and extent of reductive dechlorination was demonstrated through comparison of DO and chloroethene concentration distributions between the previous simulation (high DO) and the low DO simulation. For an identical BTEX source, even less oxygen was present downgradient of the BTEX/PCE source zone and more strongly reducing conditions would be expected. The result was a smaller PCE plume and slight larger and more concentrated TCE, cis-DCE and VC plumes relative to the high DO case.

3.2.5 *Impact of BTEX Source on Reductive Dechlorination*

In this simulation, the effect of the BTEX source on the rate and extent of reductive dechlorination was investigated. For the low DO case, the concentration of BTEX in the source zone was reduced by a factor of 100. Figure 3.13 showed that the reduced BTEX source had little impact on the DO distribution, indicating that the redox conditions would not be favorable for reductive dechlorination. Relative to the PCE plume of the previous simulation (high BTEX/low DO) the PCE plume in the low BTEX/low DO simulation was larger and more concentrated. Most noticeable was the lack of TCE production and subsequent production of cis-DCE and VC in the oxidized aquifer system.

3.3 Conclusions

The new SEAM3D modules (Reductive Dechlorination and Cometabolism Packages) demonstrated close agreement with the conceptual model for these biodegradation processes and with laboratory and field observations. Model demonstrations for the SEAM3D-RDP indicated that the use of inhibition functions was effective in simulating sequential utilization of chlorinated ethenes. Similarly, the transport simulation demonstrated that the SEAM3D Biodegradation Package was capable of simulating variable redox conditions in an aquifer system and when combined with the SEAM3D-RDP, SEAM3D produced realistic results showing redox conditions controlling the rate of reductive dechlorination.
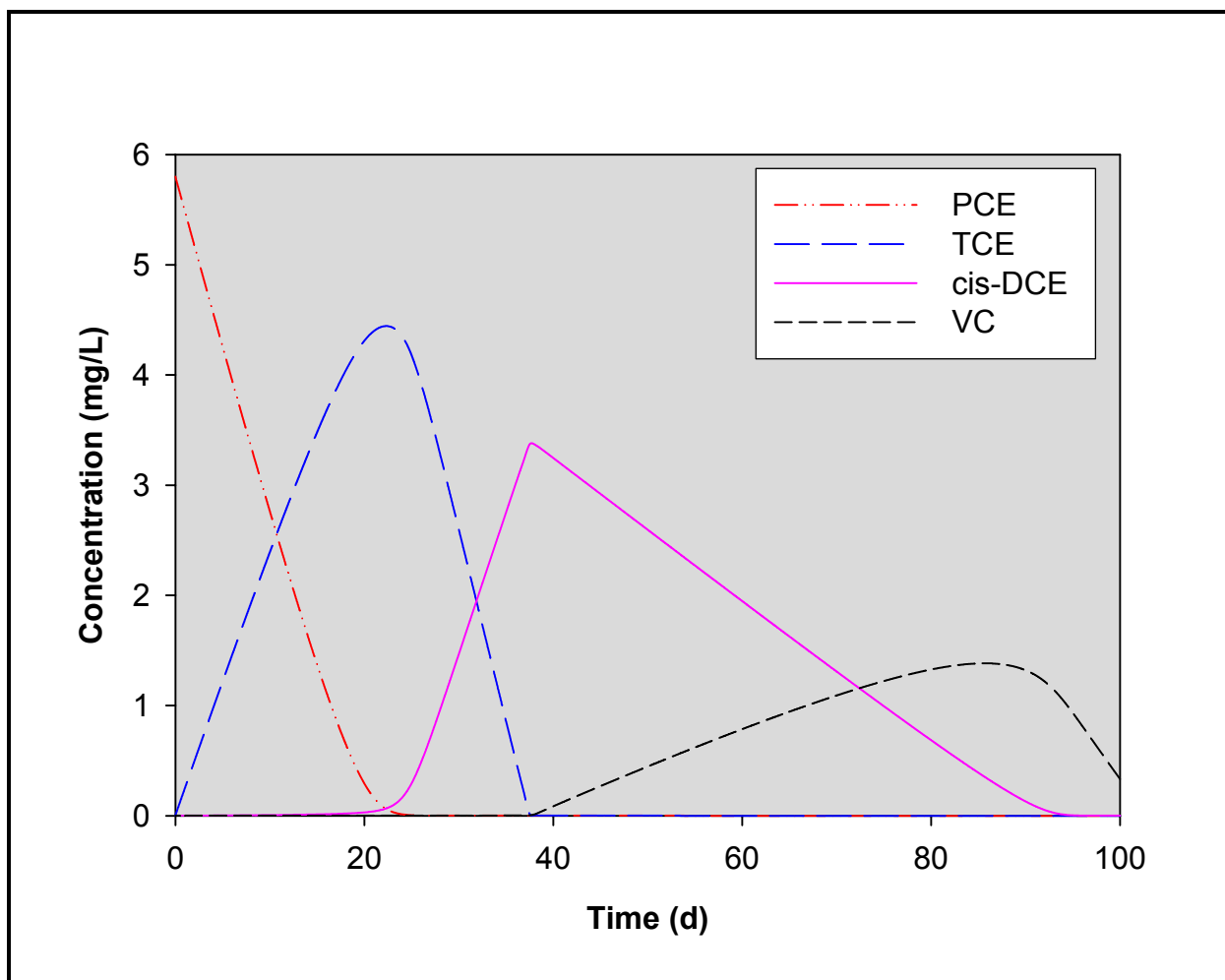
Figure 3.1. Simulated concentration of chloroethenes in a closed system with reductive chlorination only using the SEAM3D-RDP.
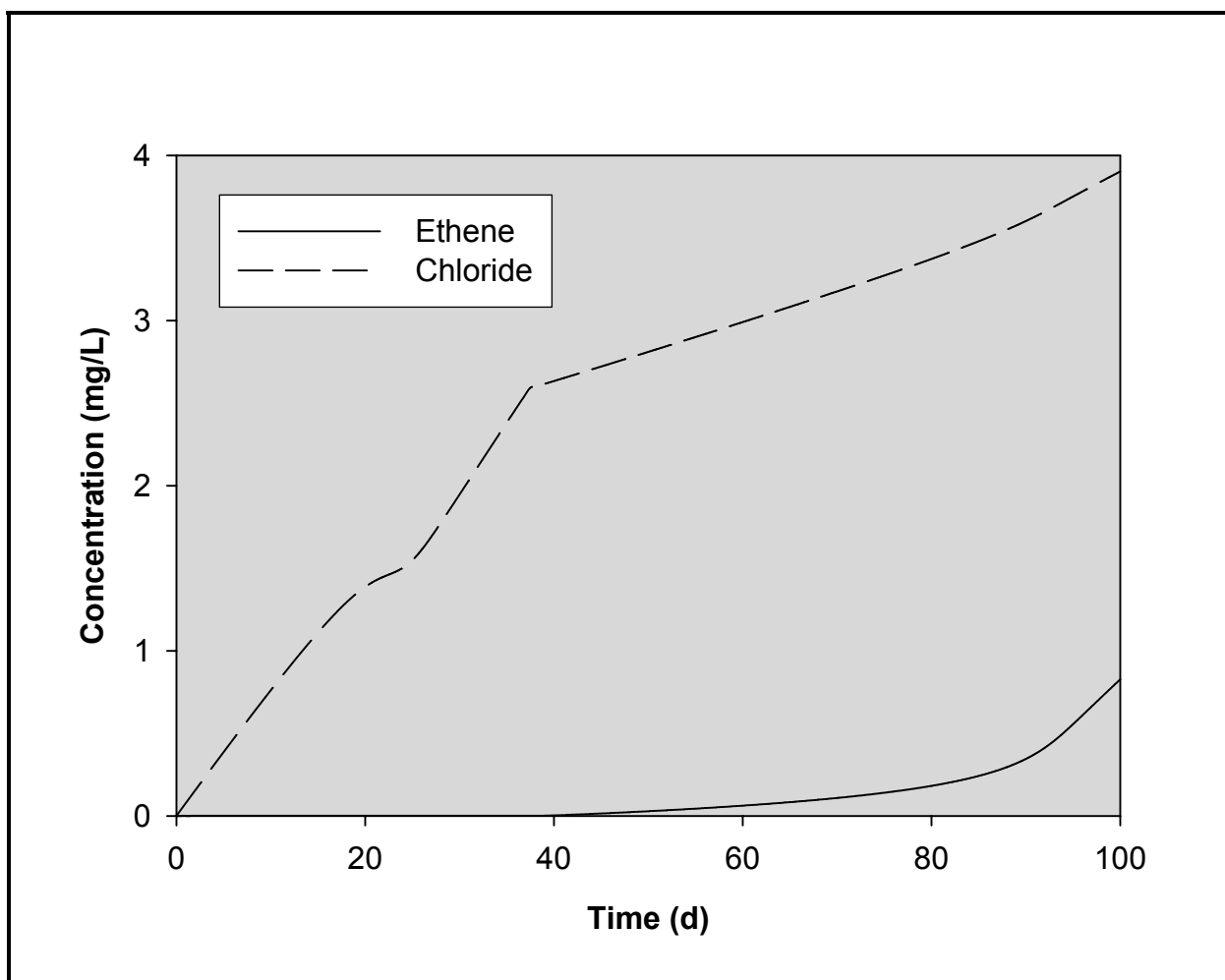
Figure 3.2. Simulated production of ethene and chloride in conjunction with the closed-system SEAM3D-RDP model shown in Figure 3.1.
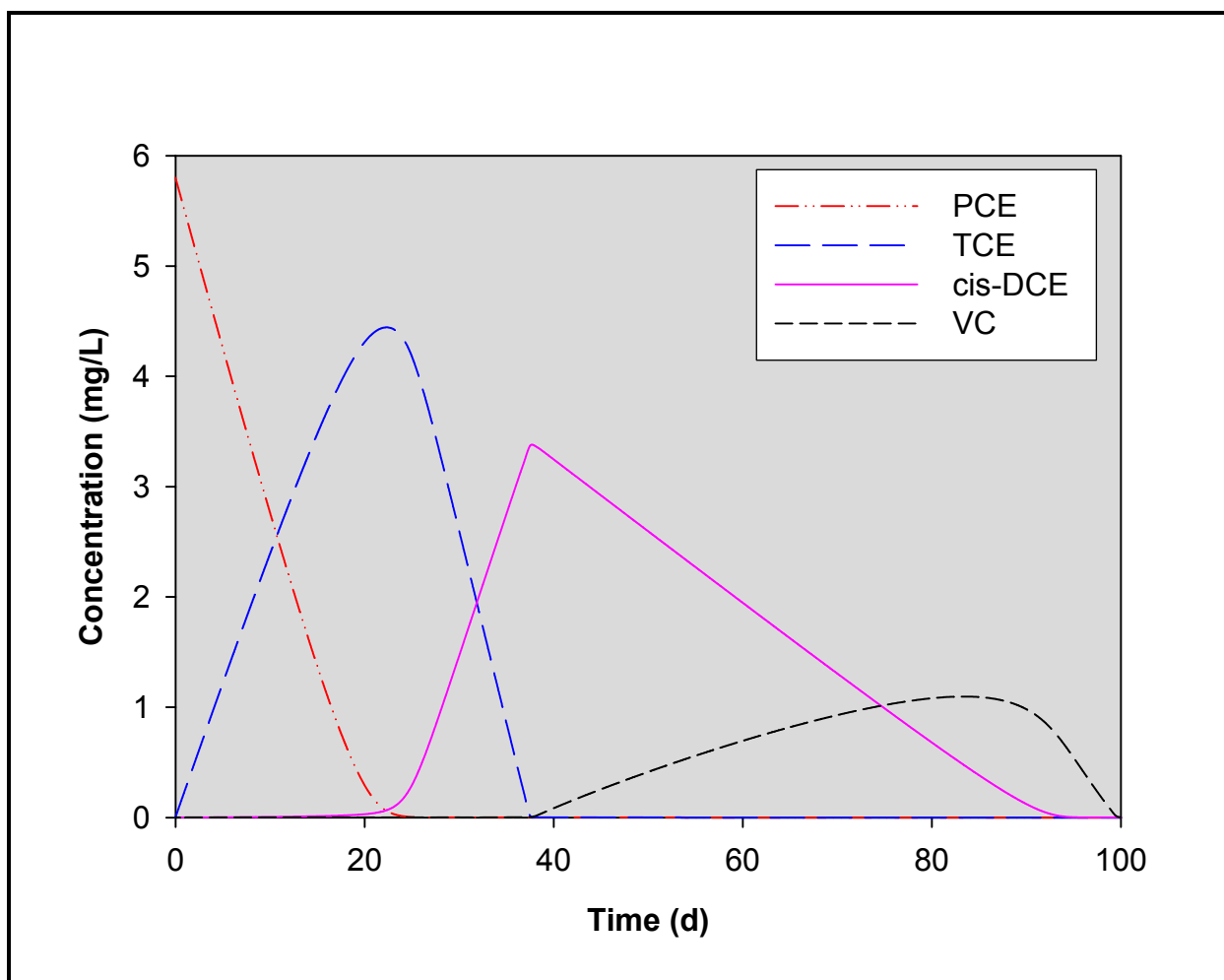
Figure 3.3   Simulated concentration of chloroethenes in a closed system with reductive chlorination of all compounds and direct anaerobic (iron-reducing) oxidation of VC using the SEAM3D-RDP.
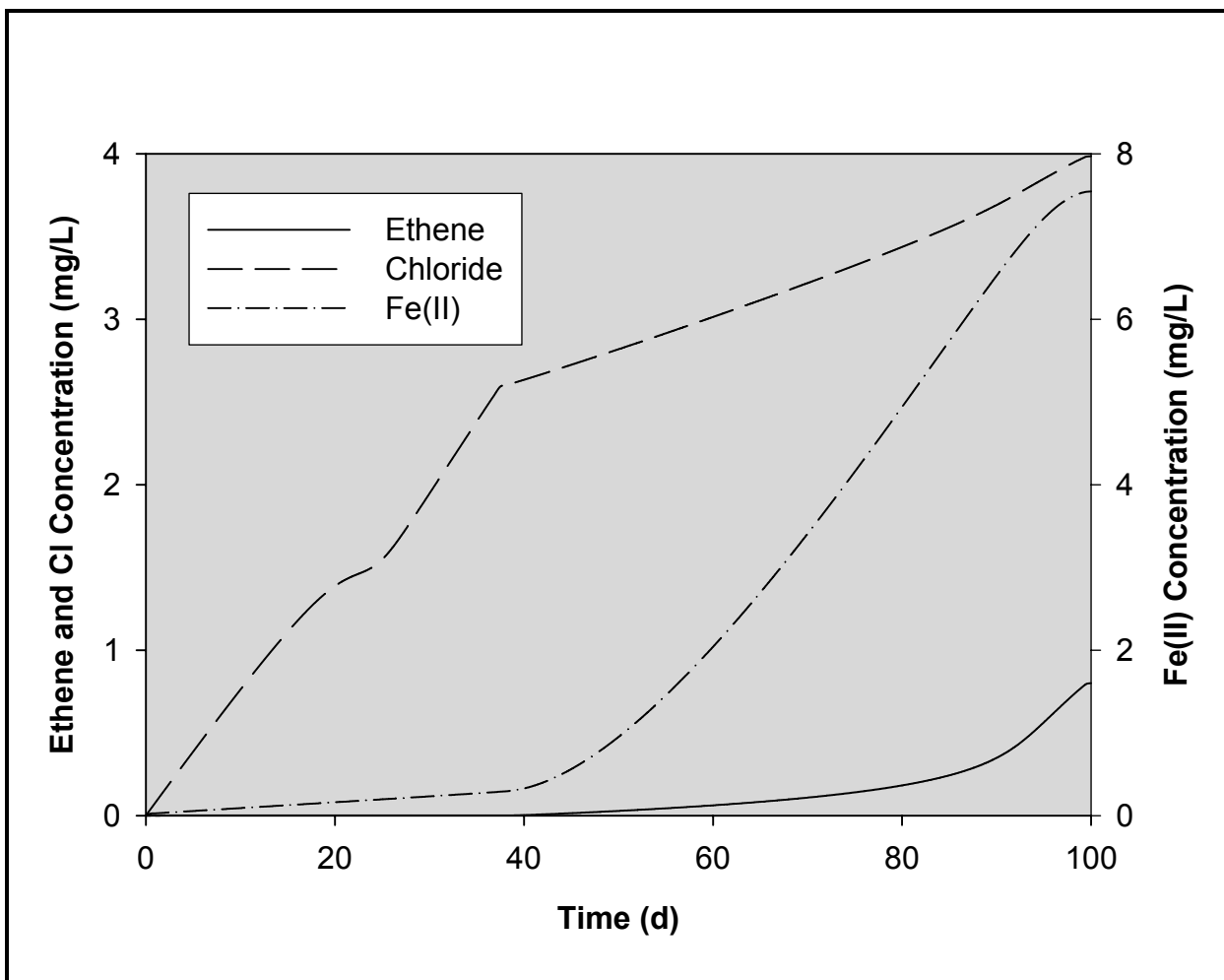
Figure 3.4. Simulated production of ethene and chloride resulting from reductive dechlorination and production of Fe(II) resulting from direct anaerobic oxidation in a closed-system model shown in Figure 3.3.
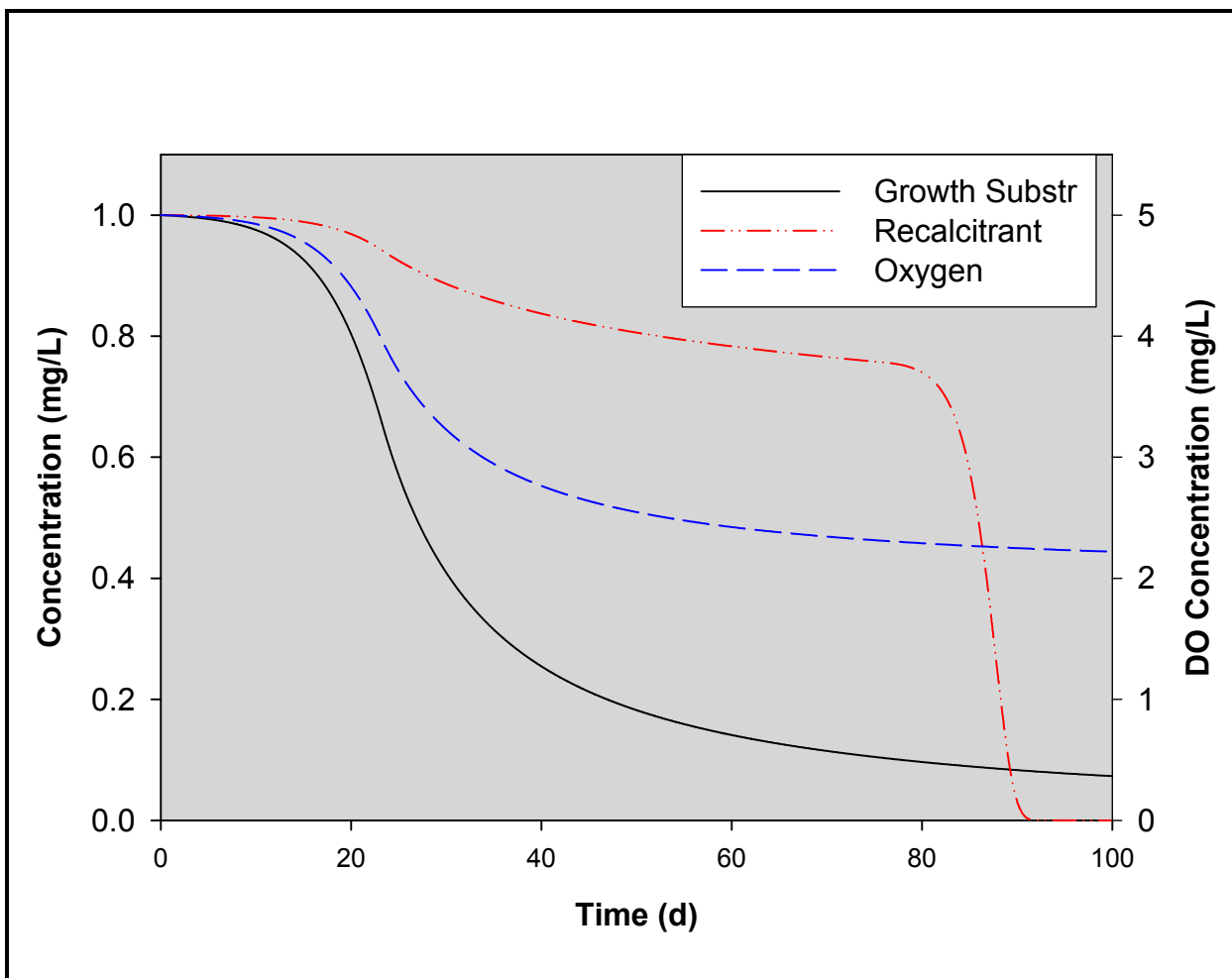
Figure 3.5.   Aerobic biodegradation of a growth substrate and oxygen, and cometabolism of a single recalcitrant compound in a closed system using the SEAM3D Biodegradation and Cometabolism Packages.
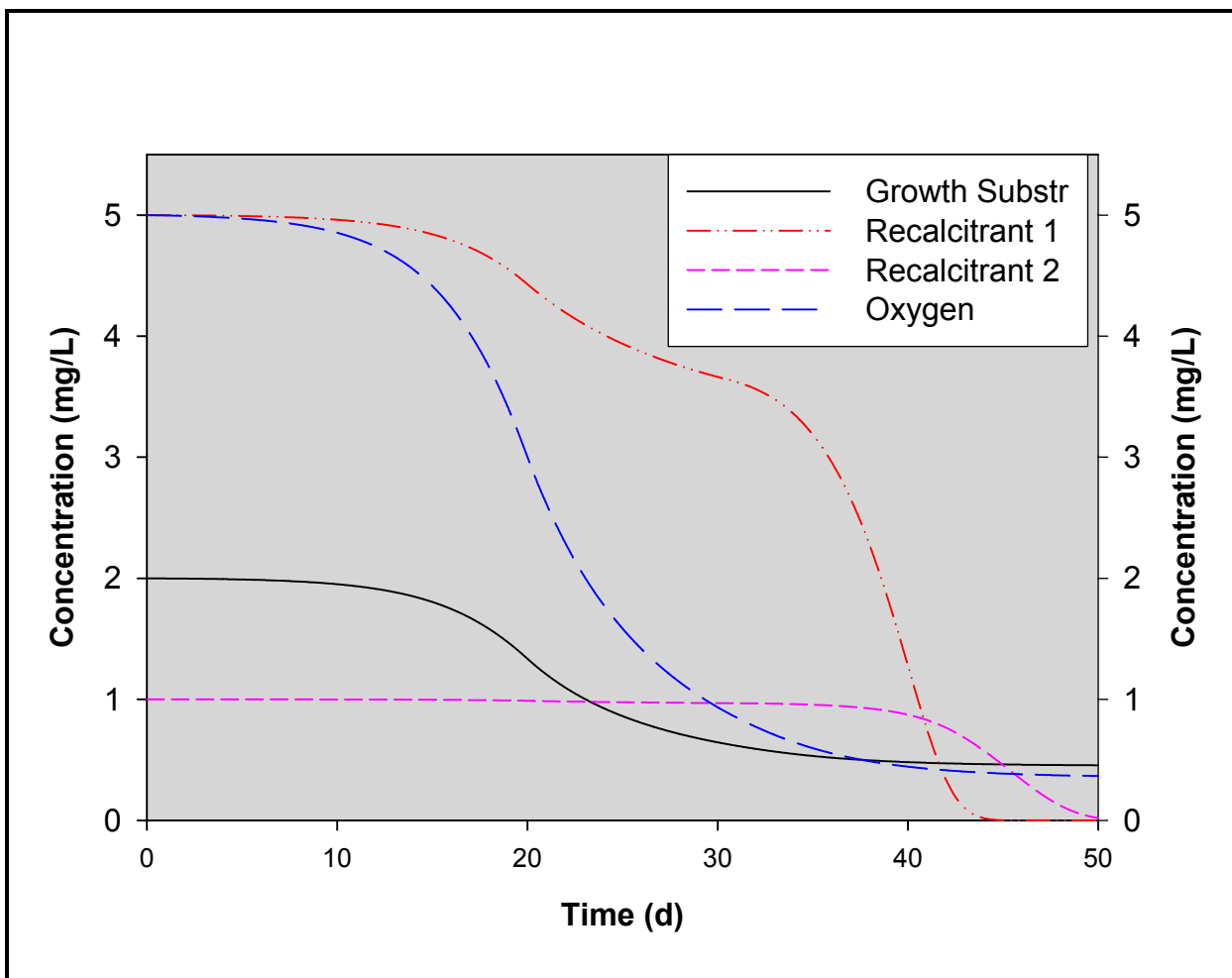
Figure 3.6. Aerobic cometabolic biodegradation of two recalcitrant compounds in a closed system with a single growth substrate and oxygen, using the SEAM3D Biodegradation and Cometabolism Packages.
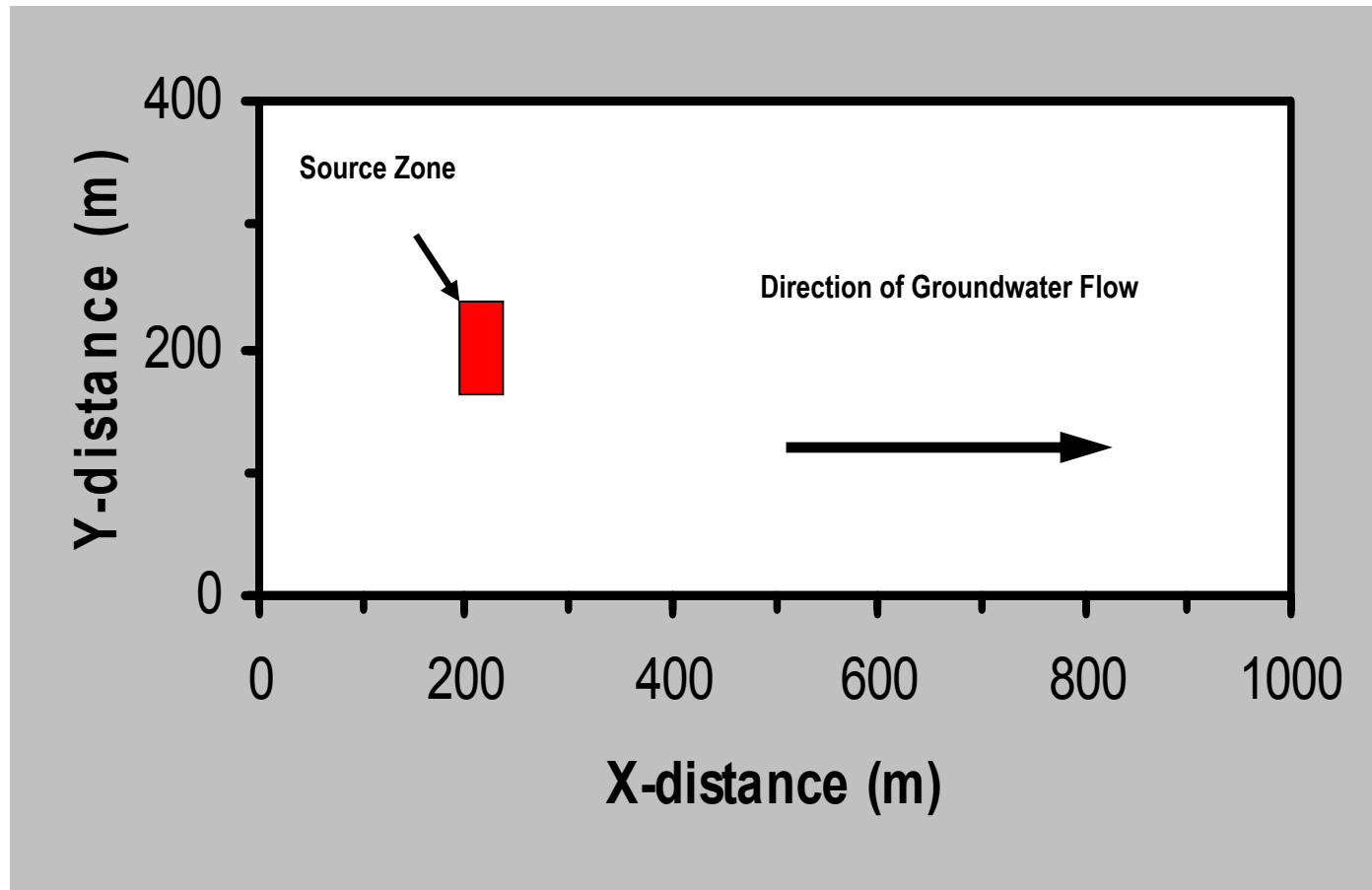
Figure 3.7. Areal view of the three-dimensional model domain with BTEX/PCE source.
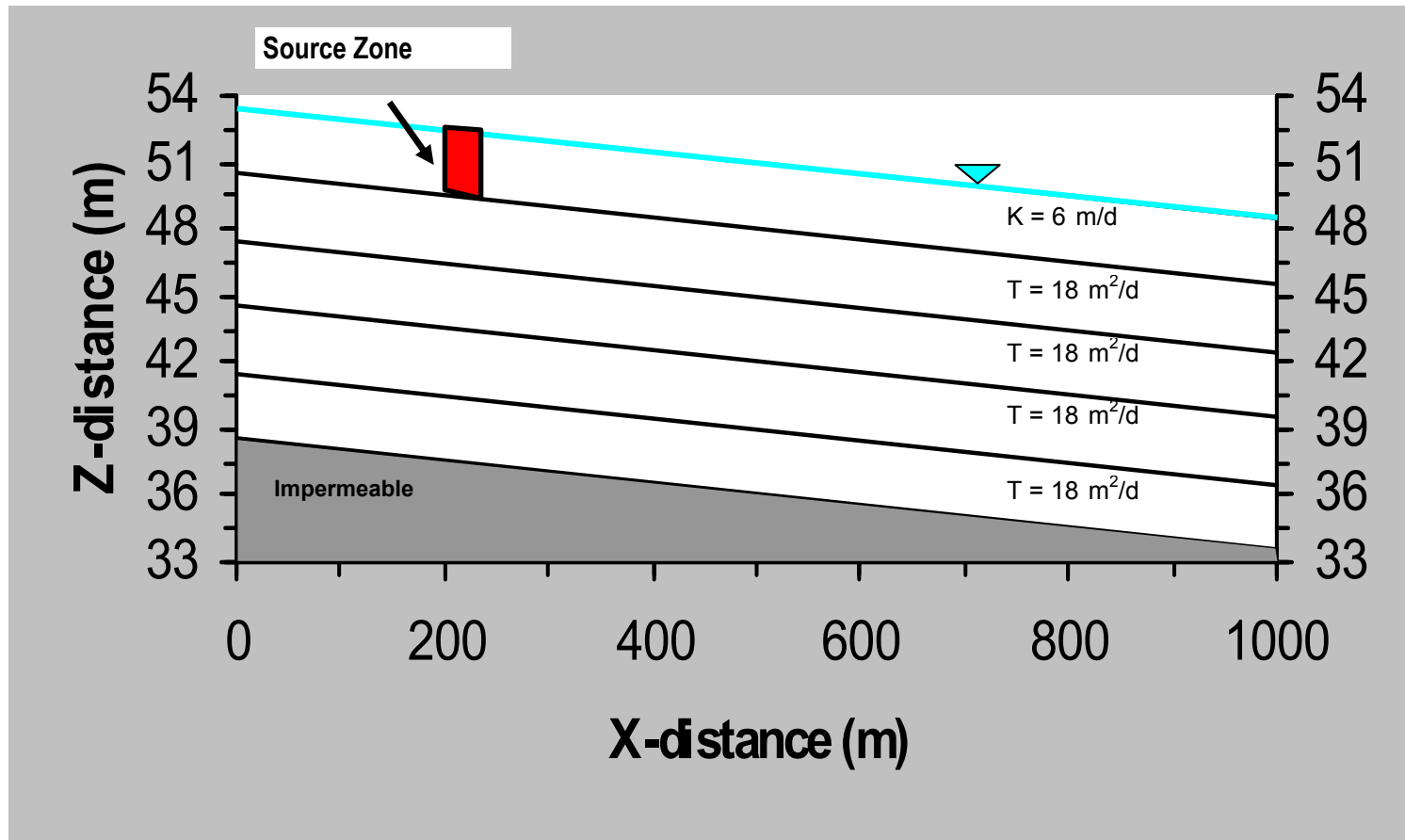
Figure 3.8. Vertical cross section through the 3D model domain, showing the location of the BTEX/PCE source zone, elevations of water table, model layers, and aquifer base and model layer properties.
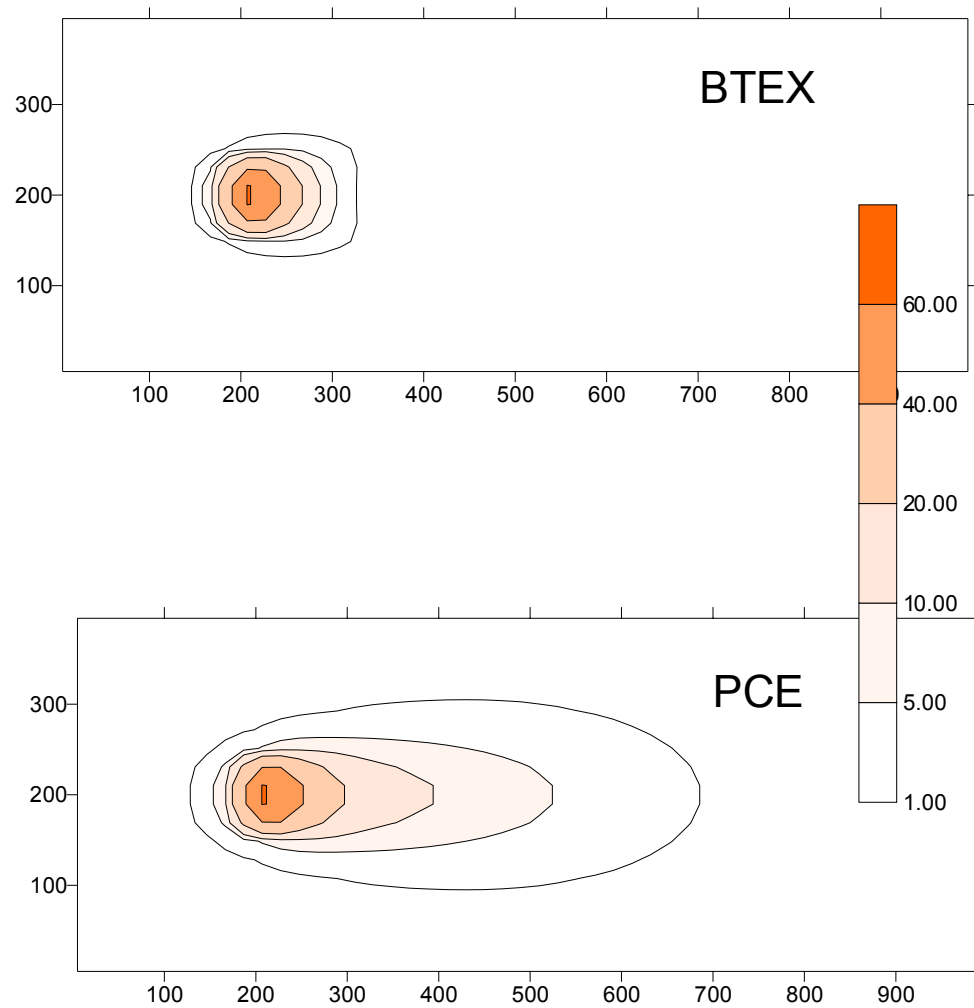
Figure 3.9. Concentrations of hydrocarbon (top figure – BTEX) and chlorinated solvent hydrocarbon (bottom figure – PCE) in layer 1 at 4000 days. Hydrocarbon biodegradation was simulated with DO, Fe(III), and CO_2 as sequential electron acceptors. Reductive dechlorination accounted for PCE biodegradation.
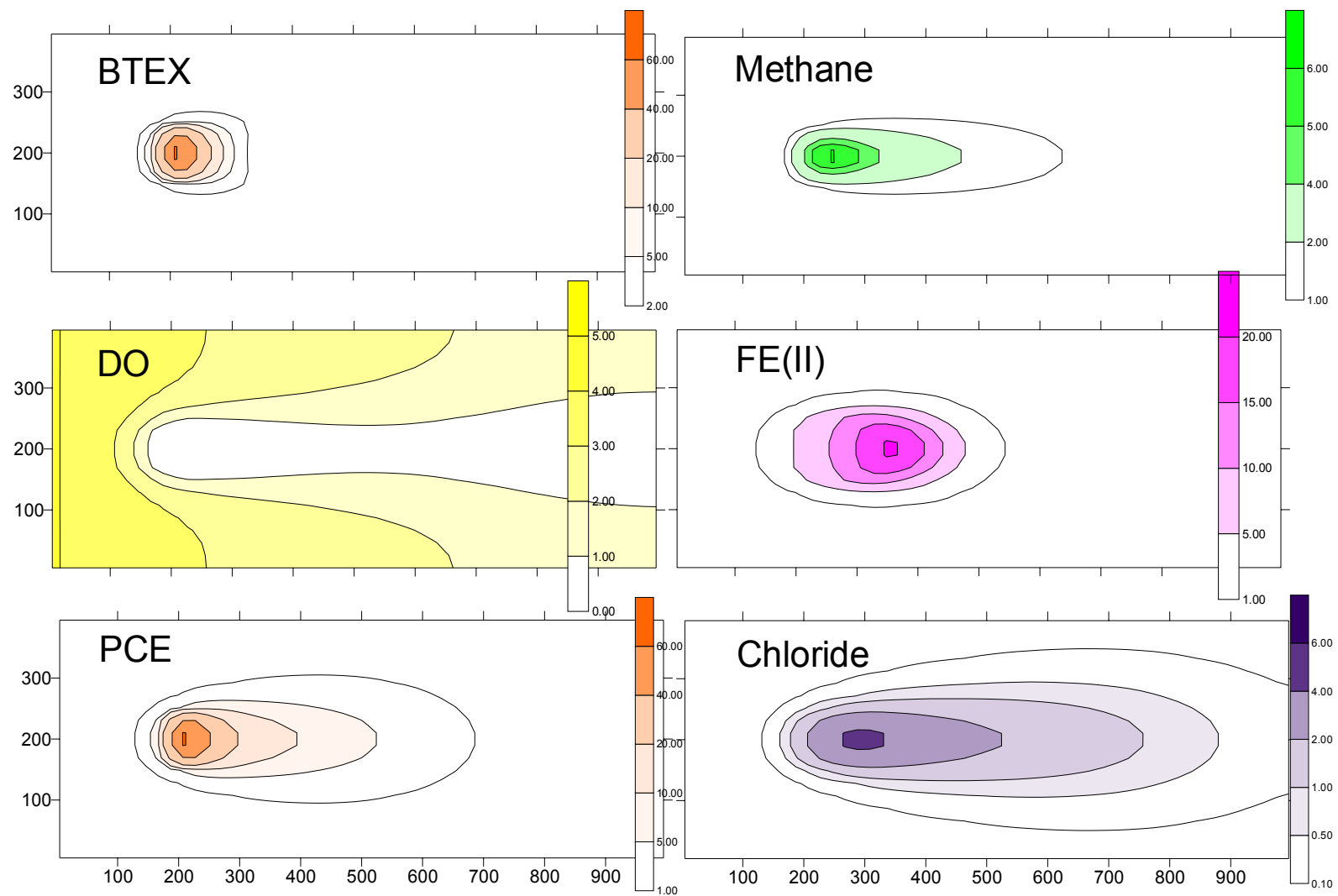
Figure 3.10. Concentration distribution at 4000 days in model layer 1 for BTEX, DO, and PCE (left column) and for endproducts (right column) from methanogenesis (CH_4) and iron-reduction ($Fe2^+$) and reductive chlorination (Cl).
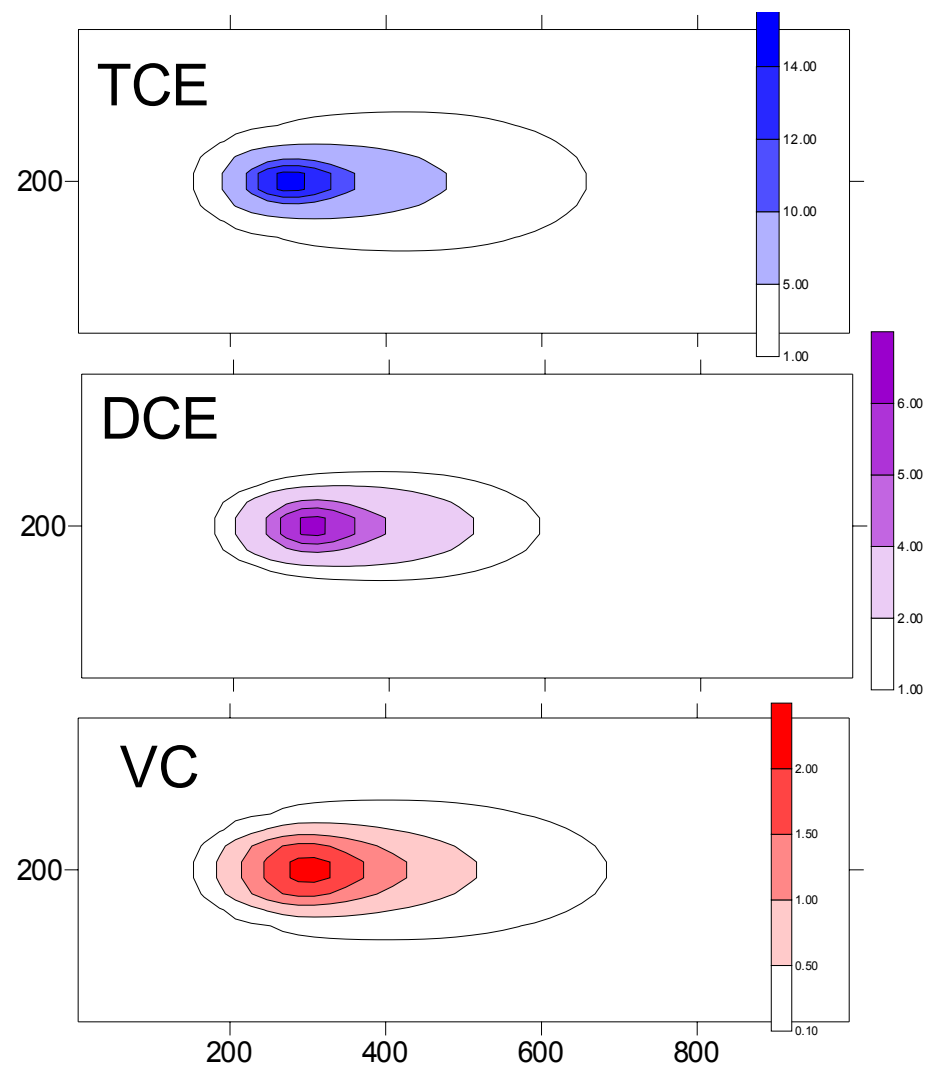
Figure 3.11. Concentrations of TCE (top), cis-DCE (middle) and VC (bottom) in model layer 1 at 4000 days.
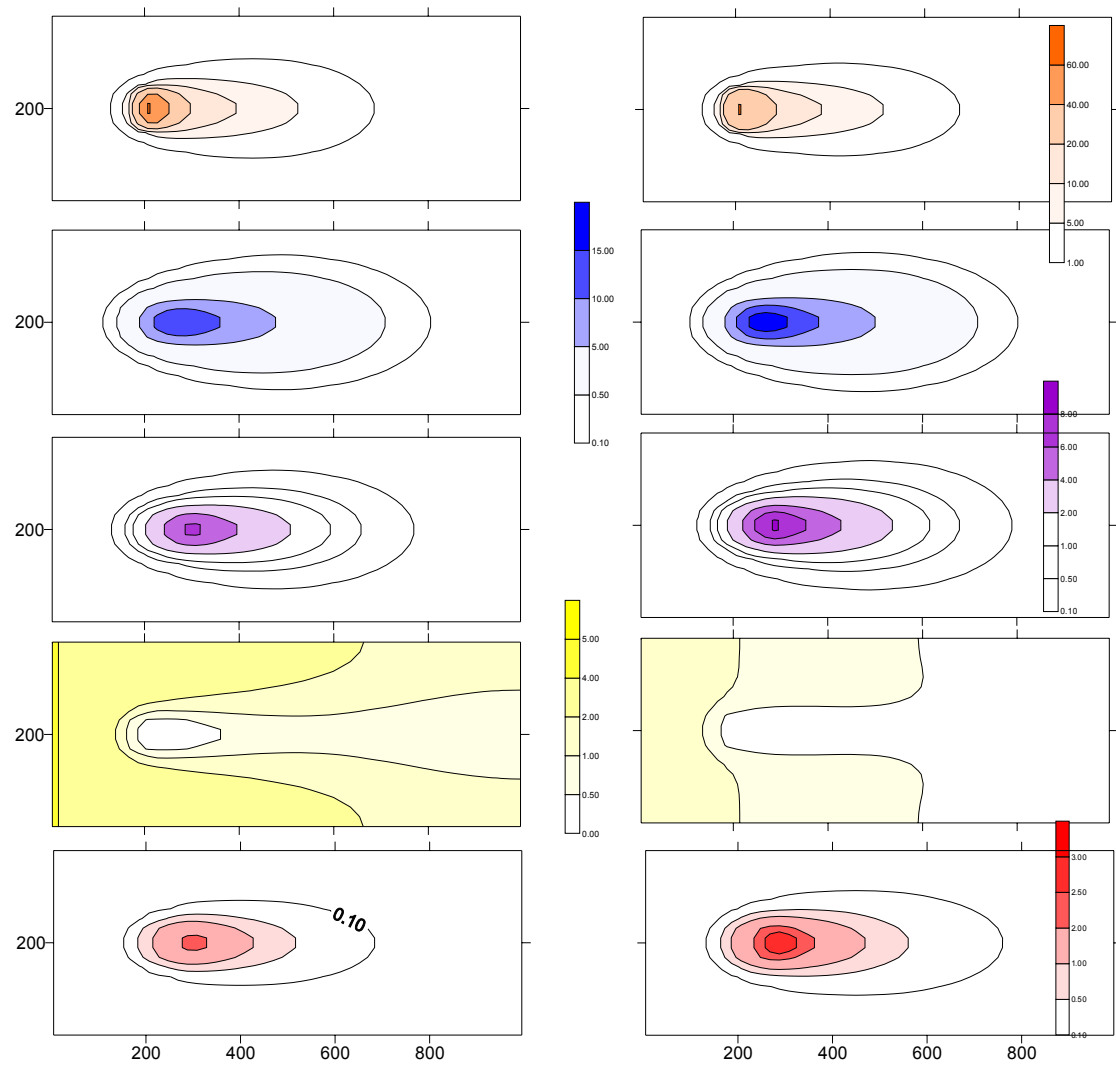
Figure 3.12. Concentrations in model layer 1 at 4000 days (in order, top to bottom) of PCE, TCE, cis-DCE, DO and VC for the previous model simulation (High DO – left column) and the low DO case (right column).
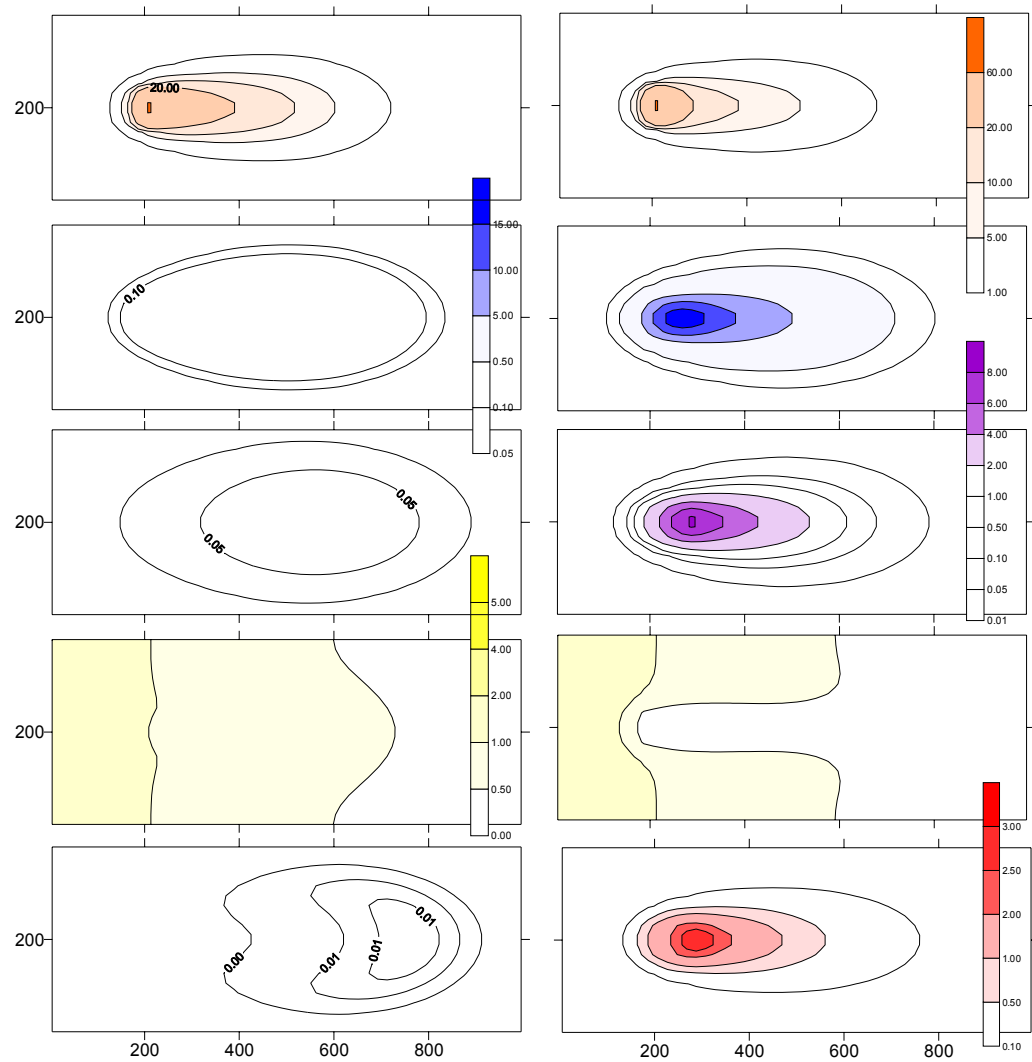
Figure 3.13. Concentrations in model layer 1 at 4000 days (in order, top to bottom) of PCE, TCE, cis-DCE, DO and VC
for the previous model simulation (High BTEX/Low DO – right column) and the low BTEX/low DO case (left).

5.   SEAM3D MODEL INPUT

5.1   General Information

Since SEAM3D is based on MT3DMS 4.0 (Zheng and Wang, 1999), much of the input is identical for the two models, and a basic understanding of MT3DMS is the first step toward mastering SEAM3D. Users who are unfamiliar with MT3DMS will benefit from reading the MT3DMS technical documentation (Zheng and Wang, 1999). The following sections paraphrase and condense information from the MT3DMS technical documentation, while information relevant to the additional subroutines in SEAM3D is provided in greater detail. SEAM3D will not require detailed input or reserve computer memory for model options that are not specified by the user. For example, if dissolution of contaminants from a non-aqueous phase liquid (NAPL) is not simulated, then the user does not create the NAPL dissolution input file (see Section 5.2.7).

Estimation of model parameters for biodegradation may be based on laboratory measurements, published values, and theoretical estimates. To produce maximum flexibility, SEAM3D allows parameters to vary across the aquifer layers and among the various substrates and electron acceptors for biodegradation. However, in the absence of detailed information, the user is advised to enter identical parameter values to describe the layers and certain biodegradation processes. Thus, parameter estimation can be simplified when available data do not support a more detailed analysis. Further information on parameter estimation is included in the detailed input instructions (Sections 5.2.1 to 5.2.6).

5.1.1   Types of Input

Like MT3DMS, input for SEAM3D may be formatted, list-directed, or unformatted.

Formatted

Input variables may be formatted as integer, real, character, or logical. In the detailed input instructions (Sections 4.2.1 to 4.2.6), the format column uses I to specify an integer, F for a real number, A for a character variable, and L for a logical variable. Input conventions follow the standards of the FORTRAN 77 language.

List Directed

List directed, or free format, input involves a sequence of values separated by blanks or commas. The list directed record terminates when a slash (/) is encountered, repeat counters are permitted, and each new record should begin on a new line of the input file.

Unformatted

Unformatted files contain binary characters and must be written and read by the computer. Relative to formatted files, unformatted files are smaller and can be processed more readily.

5.1.2   Array Readers

Most of the input data for SEAM3D is handled by the subroutines IARRAY and RARRAY in the utility module of the program. IARRAY reads one or two dimensional integer arrays, and RARRAY reads one or two dimensional real arrays. Three dimensional arrays are handled by reading a two dimensional areal array for each model layer. Each time an array reader is called, it initially reads an array control record, which occupies a single line of the input filed and is formatted as follows:

Record:	IREAD	CNSTNT (real) or ICONST (integer)	FMTIN	IPRN
Format:	I10	F10.0 (real) or I10 (integer)	A20	I10

If IREAD = 0, then RARRAY sets all elements of the array equal to CNSTNT, or IARRAY sets all elements equal to ICONST.

If IREAD = 100, then array values (entered on the lines following the array control record) are read in the format specified by FMTIN.

If IREAD = 101, then array values are read as blocks, which are entered on the lines following the array control record. The first line contains only the record NBLOCK, which is an integer specifying the number of blocks to follow. Each block occupies a single line, consisting of I1, I2, J1, J2, VALUE; where I1 is the index of the first row of the block, I2 is the index of the last row, J1 is the index of the first column of the block, J2 is the index of the last column, and VALUE is the value assigned to array elements within the block.

If IREAD = 102, then array values are read as zones.

If IREAD = 103, then array values are read in list directed format.

If IREAD is equal to a nonzero value other than 100, 101, 102, or 103, then array values are read from a separate file. If IREAD is positive, then IREAD is the unit number for the separate file, which is formatted according to FMTIN. If IREAD is negative, then the separate file is unformatted, and the absolute value of IREAD is its unit number.

If IREAD $\neq$ 0 and CNSTNT or ICONST $\neq$ 0, then all elements in the array are multiplied by CNSTNT or ICONST.

The format specifier FMTIN must be enclosed in parentheses.

If IREAD $\neq$ 0, then IPRN acts as a flag to indicate whether the array will be printed for checking. The array will not be printed in IPRN is negative.

5.1.3   Units

Like MT3DMS, SEAM3D requires the user to specify units and use consistent units for all input and output variables. In addition, the time unit must be consistent with that used in the flow model. The single exception to this rule involves the concentrations of solid phase

electron acceptors, which are entered as mass of electron acceptor per 1 x 10^6 mass of soil solids (e.g. micrograms per gram). Units of METERS for length and GRAMS for mass are convenient because they produce concentration units of grams per cubic meter, which is equivalent to milligrams per liter.

5.2   Input Instructions

Many of the input lines are identical in both SEAM3D and MT3DMS. In the following sections, these lines will be given the same numbering style as in the MT3DMS user guide (e.g., A1 for the first line of the Basic Transport File). Many input lines in SEAM3D are required only if certain model options are switched on. For example, if no inorganic nutrients are simulated, then nutrient parameters such as initial concentrations are not entered. In addition, six terminal electron accepting processes (TEAPs) are built into the model: oxygen-, nitrate-, manganese-, iron-, and sulfate-reduction and methanogenesis. TEAPs are model options which may be switched on or off.

In the detailed input instructions, certain input lines are grouped underneath the conditional statement that indicates whether the lines should be included in the file. Often these groups are preceded by a line of descriptive text that helps the user locate the lines in the file for editing. In order to illustrate input structure, example input files are included with the SEAM3D source code and executable files. It is highly recommended that the user prepare input files by modifying existing files.

The terms "outer loop" and "inner loop" are used throughout the detailed input instructions to indicate the order for entering lines describing arrays of more than two dimensions. For example, in line E14 of the Biodegradation Package, the subroutine RARRAY must be called repeatedly to read the four dimensional array XMOLD(ncol, nrow, nlay, nclny). Each time RARRAY is called, it reads a two dimensional array XMOLD(ncol, nrow) for specified values of nlay and nclny. Thus the model must loop through values for nlay and nclny, going through the inner loop first. In other words, for the first microbial population, (nclny = 1), RARRAY is called for each model layer before moving to the second microbial population (nclny = 2).

5.2.1 *Input Instructions for the Basic Transport Package*

This input file contains information describing the model configuration, initial conditions, and output options. It must be created for all simulations and is read on unit 1.

Initial concentrations of hydrocarbon substrates, electron acceptors, inorganic nutrients, products, daughters, and nonbiodegradable tracers should be based on concentrations measured in the field. If a certain process is not included in the simulation, then the corresponding parameters are not entered and need not be estimated. For example, if nitrate reduction is not simulated, then initial and minimum concentrations of nitrate are not entered in the basic transport package.

The Basic Transport Package is identical for SEAM3D and MT3DMS, with TRNOPT(6), TRNOPT(7), TRNOPT(8), and TRNOPT(9) defined as shown in line A5 of the table below. Note that the biodegradation package must be simulated in order to simulate cometabolism, NAPL dissolution, or chlorinated ethenes; i.e., TRNOPT(6) must be set equal to "true" if the user wishes to set TRNOPT(7) or TRNOPT(8) or TRNOPT(9) equal to "true."

In line A3, the total number of mobile components (MCOMP) is the sum of the number of nonbiodegradable tracers, hydrocarbon substrates, aqueous phase electron acceptors, inorganic nutrients, products, daughters, recalcitrant compounds subject to cometabolism, and chlorinated ethene compounds subject to reductive dechlorination. The number of solid phase electron acceptors are not included in this total since they will be entered in the Biodegradation Package. In SEAM3D, MCOMP should be set equal to NCOMP. The initial concentrations of components must be entered in the following order:

1. Nonbiodegradable tracers
2. Hydrocarbon substrates
3. Aqueous phase electron acceptors
4. Inorganic nutrients
5. Products
6. Daughters
7. Recalcitrant (cometabolized) compounds*
8. Components related to Reductive Dechlorination (in the following order)
    - PCE (if included in the simulation)
    - TCE
    - DCE
    - VC
    - Ethene
    - Chloride

* If both the Cometabolism Package and the Reductive Dechlorination Package are active, some or all of the recalcitrant compounds may be identical to the components listed in the Reductive Dechlorination Package. In this case, mobile components should only be entered once (i.e., do not double-count recalcitrant compounds).

Line	Variable	Format	Description
A3	NLAY	I10	Total number of layers
	NROW	I10	Total number of rows
	NCOL	I10	Total number of columns
	NPER	I10	Total number of stress periods
	NCOMP	I10	Total number of components
	MCOMP	I10	Total number of mobile components
A5	TRNOPT(10) TRNOPT(6) for biodegradation TRNOPT(7) for NAPL dissolution TRNOPT(8) for Cometabolism TRNOPT(9) for Reductive Dechlorination	10L2	Flags for major transport options: advection, dispersion, source/sink mixing, chemical reactions, solver technique, biodegradation, NAPL dissolution, cometabolism, and reductive dechlorination. Enter T to include the option in the simulation; enter F to omit the option.

5.2.2 *Input Instructions for the Advection Package*

This input file must be created only if the Advection Package is specified in the Basic Transport Package; i.e., TRNOPT(1) is set to "T". Input for advection is read on unit 2, and advection is normally included in all simulations. SEAM3D only supports either the standard finite difference solution or the third-order TVD solution for advection. Because SEAM3D does not support other advection solution methods, parameters for particle tracking are not required.

Line	Variable	Format	Description
B1	MIXELM	I10	Flag indicating advection solution method MIXELM = 0 for upstream finite difference method MIXELM = -1 for third-order TVD
	PERCEL	F10.0	Courant number (generally, PERCEL ≤ 0.2)
	MXPART	I10	Not used by SEAM3D, so any integer may be entered

5.2.3 *Input Instructions for the Dispersion Package*

This input file must be created only if the Dispersion Package is specified in the Basic Transport Package; i.e., TRNOPT(2) is set to "T". Input for dispersion is read on unit 3, and dispersion is normally included in all simulations. The Dispersion Package is identical for SEAM3D and MT3DMS.

5.2.4   Input Instructions for the Source/Sink Mixing Package

This input file must be created if source/sink options (including constant head or general-head-dependent boundary conditions) are specified in the flow model. It is also necessary to specify the Source/Sink Mixing Package in the Basic Transport Package; i.e., TRNOPT(3) is set to T. Input for source/sink mixing is read on unit 4. The location and rates for the fluxes (due to wells, drains, recharge, evapotranspiration, rivers, and general-head-dependent boundary conditions) are obtained from the flow solution through the unformatted head and flow file. If a flux is positive, then it acts as a source, and concentrations must be specified. If a flux is negative, then it acts as a sink, and concentrations are set equal to the current concentrations within the block. The Source/Sink Mixing Package is identical for SEAM3D and MT3DMS.

5.2.5   Input Instructions for the Reaction Package

This input file must be created only if the Reaction Package is specified in the Basic Transport Package; i.e., TRNOPT(4) is set to "T". Input is read on unit 9, and the Reaction Package is identical for SEAM3D and MT3DMS.

5.2.6   Input Instructions for the Biodegradation Package

This input file must be created only if the Biodegradation Package is specified in the Basic Transport Package; i.e., TRNOPT(6) is set to "T". Input is read on unit 11.

Due to the difficulty in quantifying aquifer microbes, data on the initial microbial biomass (M_x) may not be available, and only a rough estimate of M_x may be obtained. Under pristine conditions, when the groundwater contains significant O_2, it can be assumed that aerobic biomass predominates. Anaerobic microbes would exist only in anaerobic microsites that develop within soil aggregates. Thus, the value of M_x for each anaerobic biomass can be estimated as an order of magnitude lower than the aerobic biomass. In general, if M_x for the anaerobes is on the order of 0.01 g m^{-3}, then the anaerobic biomass must undergo significant growth before the population exerts a significant impact on biodegradation. For the aerobes, M_x equal to 0.3 g m^{-3} corresponds to 1 x 10^6 cells cm^{-3}, assuming a cell volume of 1 μm^3, cell density of 1.0 g cm^{-3}, and aquifer porosity of 0.3. This number of cells usually allows significant aerobic utilization of substrates to occur without additional microbial growth. The minimum concentrations of substrates, electron acceptors, and nutrients may be set to zero unless measured data indicate otherwise.

In order to reflect the high rate and energy yield of aerobic metabolism, parameters controlling aerobic utilization, growth, and death should generally be much higher than those of the anaerobic processes. The maximum specific rate of substrate utilization ($v_{x,ls,le}^{max}$) may be based on laboratory or field estimates. Certain substrates, such as those in the alkane group, are resistant to anaerobic biodecay, so $v_{x,ls,le}^{max}$ for alkanes may be set to zero for each anaerobic process. Alkanes would still biodegrade using oxygen. For aerobic biodegradation of hydrocarbons, laboratory estimates of $v_{x,ls,le}^{max}$ have been reported as 1.0 day^{-1} (Kindred and Celia, 1989), 1.7 day^{-1} (Borden and Bedient, 1986), 3.5 to 8.0 day^{-1} (Arcangeli and Arvin,

1992), and 8.3 to 9.9 day^{-1} (Chen et al., 1992). Biodegradation rates in the field may be much lower than observed in the laboratory. A field study by MacIntyre et al. (1993) found that aerobic biodecay of benzene could be approximated by a pseudo-first order rate constant of 0.0070 day^{-1}. Chapelle and Lovley (1990) reported that microbial metabolic rates based on laboratory incubations may overpredict in situ rates by two orders of magnitude.

Values of the half saturation coefficients for substrates ($K_{x,ls,le}^s$) and electron acceptors ($K_{x,le}^e$) may be based on literature values if no measurements are available. For hydrocarbons, $K_{x,ls,le}^s$ has been reported in the range of 0.1 g m^{-3} (Kindred and Celia, 1989), 0.13 g m^{-3} (Borden and Bedient, 1986), 0.6 g m^{-3} (Arcangeli and Arvin, 1992), 1.88 to 4.55 g m^{-3} (Chang et al., 1993), 12.2 to 17.4 g m^{-3} (Chen et al., 1992). For oxygen, $K_{x,le}^e$ has been reported as 0.10 g m^{-3} (Borden and Bedient, 1986; Kindred and Celia, 1989; Chen et al., 1992). For nitrate, $K_{x,le}^e$ has been reported as 0.1 g m^{-3} (Kindred and Celia, 1989), and 2.6 g m^{-3} (Chen et al., 1992). With the exception of oxygen, values for half saturation coefficients are reported over a wide range, but SEAM3D model results are generally much more sensitive to biomass concentration and $v_{x,ls,le}^{max}$ than to the half saturation coefficients.

The yield coefficient ($Y_{x,ls,le}$) for aerobes is often estimated as 0.5 g g^{-1} (Arcangeli and Arvin, 1992; Borden and Bedient, 1986; Chen et al., 1992; Wodzinski and Johnson, 1968), although values as low as 0.25 have been used (Kindred and Celia, 1989). For anaerobes, $Y_{x,ls,le}$ is usually lower than for aerobes, with 0.2 g g^{-1} being the theoretical maximum yield under sulfate reducing conditions (Edwards et al., 1992). It is recommended that the user allow SEAM3D to calculate values for the effective death terms ($k_{d_x}^{bk}$) internally, using the method described in Section 2.1.4.

When an inhibition coefficient ($\kappa_{le,li}$) is assigned a small value relative to its corresponding electron acceptor (EA), the EA must be essentially depleted before utilization of the next EA begins. In contrast, the inhibition process becomes insignificant if $\kappa_{le,li}$ is assigned a large value. Numerous values for inhibition coefficients have been reported. For inhibition by oxygen, $\kappa_{le,li}$ values vary between 0.01 and 0.1 g m^{-3} (Kindred and Celia, 1989; Chen et al., 1992). Research has shown that methanogenesis may predominate over SO_4^{2-} reduction when the SO_4^{2-} concentration falls between 0.6 to 1.4 g m^{-3} (Vroblesky et al., 1996). Thus the value of $\kappa_{le,li}$ for SO_4^{2-} inhibition of methanogenesis should be within a similar range. In general, values of $\kappa_{le,li}$ for a particular inhibitor need not vary among the EA processes that are inhibited. For example, a value of $\kappa_{le,li} = 0.1$ g m^{-3} could be used to describe oxygen inhibition of all of the anaerobic processes. Values of $\kappa_{le,li}$ may be adjusted during calibration to match measured concentrations of products.

EA use coefficients ($\gamma_{x,ls,le}$) can be estimated from the stoichiometric relationship between each EA and the corresponding substrate. For aromatic hydrocarbons, there is little variation in the stoichiometry, and toluene may be used as a representative compound. Thus values for $\gamma_{x,ls,le}$ should be approximately equal to 3.1 g g^{-1} for O_2, 4.8 g g^{-1} for NO_3^-, 42.0 g g^{-1} for Fe(III), 4.5 g g^{-1} for SO_4^{2-} (Borden et al., 1995), and 18.0 g g^{-1} for Mn(IV) (Baedecker et al., 1993). The actual value of $\gamma_{x,ls,le}$ will depend somewhat on the specific hydrocarbon, and

the amount of microbial assimilation of substrate into cell material. The generation term for methane ($\zeta_{x,ls}$) can be estimated as 0.8 g g^{-1}, based on the stoichiometric relationship between toluene and methane (Borden et al., 1995). The EA generation terms ($\zeta_{x,le}$) can also be based on stoichiometric relationships. If N_2 is the final product of nitrate reduction, then $\zeta_{x,le}$ should be close to 0.5 g g^{-1}. For sulfide production, $\zeta_{x,le}$ should be close to 1.0 g g^{-1} (Edwards et al., 1992). During calibration, the generation term for Fe(II) will often need to be reduced from its theoretical value to match the measured concentrations of Fe(II). This reduction is necessary because Fe(II) can react chemically with compounds such as SO_4^{2-}; thus, only a fraction of the Fe(II) produced by microbes may be measured in the groundwater (Lovley et al., 1994).

Line	Variable	Format	Description
F1	NTRAC	I10	Total number of non-biodegradable tracers $0 \leq NTRAC \leq 5$
	NHCAR	I10	Total number of biodegradable substrates $1 \leq NHCAR \leq 8$
	NNUTR	I10	Total number of inorganic nutrients $0 \leq NNUTR \leq 5$
	NDAUT	I10	Total number of daughter products $0 \leq NDAUT \leq NHCAR$
F2	STOCHOPT	L2	Flag for spatial variability option for maximum specific rate of substrate utilization. Enter T to allow the parameter to vary in space; enter F for constant value.
F3	CLNOPT(7)	7L2	Flags for TEAP options: aerobes, NO_3 reducers, Mn(IV) reducers, Fe(III) reducers, SO_4 reducers, methanogens, methanotrophs. Enter T to include the TEAP in the simulation; enter F to omit.
F4	ENDOPT(4)	4L2	Flags for product options: N_xO_y, Mn(II), Fe(II), H_2S. Enter T to include the product in the simulation; enter F to omit. Note that ENDOPT(5) for CH_4 is not entered here since it is automatically set from CLNOPT(6) for methanogens.
F5	Descriptive text	None	"Hydrocarbon Minimum Concentrations"
F6	AHMIN(nhcar)	F10.0	Minimum concentrations: Enter AHMIN on a separate line F6 for each hydrocarbon

F7	Descriptive text	None	"EA Starting and Minimum Concentrations"

(Enter lines F8 and F9 if the number of solid phase electron acceptors > 0)

F8	SEOLD(ncol, nrow, nlay, nslid)	RARRAY	Starting concentrations: Enter SEOLD(ncol, nrow) on a separate line F8 for each layer (inner loop) and for each solid phase electron acceptor (outer loop). The solid phase electron acceptors are read in the following order: Fe(III), Mn(IV). NSLID is the total number of solid phase electron acceptors (calculated automatically from the TEAP options)
F9	SEMIN(nslid)	F10.0	Minimum concentrations: Enter SEMIN after SEOLD(ncol, nrow) for each solid phase electron acceptor
F10	AEMIN(nelec)	F10.0	Minimum concentrations: Enter AEMIN on a separate line F10 for each electron acceptor
F11	Descriptive text	None	"Nutrient Minimum Concentrations"

(Enter line F12 if the number of nutrients > 0)

F12	ANMIN(nnutr)	F10.0	Minimum concentrations: Enter ANMIN on a separate line F12 for each nutrient
F13	Descriptive text	None	"Biomass Starting Concentrations"
F14	XMOLD(ncol, nrow, nlay, nclny)	RARRAY	Starting concentrations: Enter XMOLD(ncol, nrow) on a separate line F14 for each layer (inner loop) and for each microbial population (outer loop). NCLNY is the total number of microbial populations in the simulation
F15	XMMIN	F10.0	Minimum conc. For all microbial populations: Enter XMMIN after the last entry of XMOLD(ncol, nrow) for the final microbial population Note: only one value for XMMIN is entered, and it applies to all microbial populations
F16	NITER	I10	Number of biodegradation time steps per transport time step
F17	KSCR, ISCR,JSCR	3I10	Layer, row, and column indices for screen output

| F18 | Descriptive text | None | "Electron Acceptor Inhibition Terms" |

(Enter lines F19 and F20 if the total number of EA processes (including methanogenesis) > 1)

| F19 | Descriptive text | None | "Inhibition of [inhibitee]" Enter this line prior to each inhibitor process. |

| F20 | AKINH(ninh, ninh) | F10.0 | Electron acceptor inhibition coefficient: Enter AKINH(*lj, lk*) for each inhibitor *lk* (inner loop) of electron acceptor process *lj* (outer loop) Note that electron acceptor process *lj* will require entry of (*lj* - 1) inhibitors NINH = the total number of electron acceptor processes minus one |

Example 1:   Simulate aerobes and NO_3 reducers (NINH = 1)

Line 1:   "Inhibition of NO_3"
Line 2:   AKINH(1,1) -- coef. of O_2 inhibition of NO_3

Example 2:   Simulate aerobes, Fe(III), SO_4 reducers, and methanogens (NINH = 3)

Line 1:   "Inhibition of Fe(III)"
Line 2:   AKINH(1,1) -- coef. of O_2 inhibition of Fe(III)

Line 3:   "Inhibition of SO_4 "
Line 4:   AKINH(2,1) -- coef. of O_2 inhibition of SO_4
Line 5:   AKINH(2,2) -- coef. of Fe(III) inhibition of SO_4

Line 6:   "Inhibition of methanogenesis"
Line 7:   AKINH(3,1) -- coef. of O_2 inhib. of methanogenesis
Line 8:   AKINH(3,2) -- coef. of Fe(III) inhib. of methanogenesis
Line 9:   AKINH(3,3) -- coef. of SO_4 inhib. of methanogenesis

| F21 | Descriptive text | None | "Elec. Acc. Product Generation Coefs." |

(Enter line F22 if NENDE > 0)

| F22 | ENDE(nende) | F10.0 | Electron acceptor product generation coefficient: Enter ENDE on a separate line E22 NENDE times NENDE is the number of products from the electron acceptors (specified in ENDOPT of the basic transport package), excluding methanogenesis. |

| F23 | Descriptive text | None | "Methane Generation Coefficients" |

(Enter line F24 if methanogenesis is simulated)

| F24 | ENDH(nhcar) | F10.0 | Methane generation coefficients: Enter ENDH on a separate line E24 for each hydrocarbon |

| F25 | Descriptive text | None | "Daughter Generation Coefficients" |

(Enter line F26 if NDAUT >0)

| F26 | ENDD(ndaut) | F10.0 | Daughter generation coefficients: Enter ENDD on a separate line F26 for each daughter product |

| F27 | Descriptive text | None | "Electron Acceptor Use Coefficients" |

(Enter lines F28 and F29 for each electron acceptor process, excluding methanogenesis)

| F28 | Descriptive text | None | "Use of [Electron Acceptor, .e.g. O_2]" Enter this line prior to each electron acceptor process. |

| F29 | AGAM(nhcar, neatot) | F10.0 | Use coefficients: Enter AGAM on a separate line F29 for each hydrocarbon (inner loop) and for electron acceptor (outer loop) |

Electron acceptor loop is read in the following order: O_2, NO_3, Fe(III), Mn(IV), SO_4 (i.e. from highest to lowest energy).

NEATOT is the total number of electron acceptors simulated. Lines are not read for electron acceptors that are not included in the simulation

| F30 | Descriptive text | None | "Nutrient Use Coefficients" |

(Enter line F31 if NNUTR > 0)

| F31 | APSI(nhcar, nnutr) | F10.0 | Nutrient use coefficients: Enter APSI on a separate line F31 for each hydrocarbon (inner loop) and for each nutrient (outer loop) |

(Enter lines F32 through F43 for each microbial population (i.e. NCLNY times):
microbial populations are read in the order of highest to lowest energy)

For CLNOPT(1-6) = T

F32	Descriptive text	None	Microbial Population Name, e.g. "Aerobes"
F33	Descriptive text	None	"Death Rate"
F34	XKD(nclny)	F10.0	First order decay rate for the microbial population

XKD < 0 death rate calculated by model (recommended)

XKD = 0 no microbial death

XKD > 0 death rate is constant at the specified value

F35	Descriptive text	None	"Half Saturation Constants"
F36	AKHALFH(nhcar, nli, nclny)	F10.0	Hydrocarbon half saturation constant: Enter AKHALFH on a separate line F36 for each electron acceptor utilized by the current microbial population (inner loop) and for each hydrocarbon (outer loop)
			NLI is the number of electron acceptors utilized by the current microbial population: NLI = 2 for NO_3 reducers NLI = 1 for all other populations

(Do not enter line F37 for Fe(III) or Mn(IV) reducers)

F37	AKHALFE(nli, nclny)	F10.0	Electron acceptor half saturation constant: Enter AKHALFE on a separate line F37 for each electron acceptor utilized by the current microbial population

(Enter line F38 if NNUTR > 0)

F38	AKHALFN(nnutr, nli, nclny)	F10.0	Nutrient half saturation constant: Enter AKHALFN on a separate line F38 for each electron acceptor utilized by the current microbial population (inner loop) and for each nutrient (outer loop)

F39	Descriptive text	None	"Maximum Specific Utilization Rate"

(Enter line F40 if STOCHOPT(1) is".true." -- see line F2)

F40	VSPMAX(ncol, nrow, nlay, nhcar, nli, nclny)	RARRAY	Maximum specific rate of substrate utilization: Enter VSPMAX(ncol, nrow) on a separate line F40 for each layer (inner loop), each electron acceptor utilized by the current microbial population (middle loop), and for each hydrocarbon (outer loop)

(Enter line F41 if STOCHOPT(1) is".false." -- see line F2)

F41	VSPMAX(nhcar, nli, nclny)	F10.0	Maximum specific rate of substrate utilization: Enter VSPMAX on a separate line F41 for each electron acceptor utilized by the current microbial population (inner loop) and for each hydrocarbon (outer loop)

F42	Descriptive text	None	"Yield Coefficients"
F43	YIELD(nhcar, nli, nclny)	F10.0	Yield coefficients: Enter YIELD on a separate line F43 for each electron acceptor utilized by the

current microbial population (inner loop) and for each hydrocarbon (outer loop)

For CLNOPT(7) = T

F44	Descriptive text	None	"Methanotrophs"
F45	Descriptive text	None	"Death Rate"
F46	XKD(nclny)	F10.0	First order decay rate for the methanotrophic population
			XKD < 0 death rate calculated by model (recommended)
			XKD = 0 no microbial death
			XKD > 0 death rate is constant at the specified value
F47	Descriptive text	None	"Half Saturation Constants"
F48	AKHALFM	F10.0	Methane half saturation constant
F49	AKHALFE(nli, nclny)	F10.0	Electron acceptor half saturation constant: Note: NLI = 1

(Enter line F38 if NNUTR > 0)

F50	AKHALFN(nnutr, nli, nclny)	F10.0	Nutrient half saturation constant: Enter AKHALFN on a separate line F50 for each nutrient. Note: NLI = 1.
F51	Descriptive text	None	"Maximum Specific Utilization Rate"

(Enter line F40 if STOCHOPT(1) is".true." -- see line F2)

F52	VSPMAXM(ncol, nrow, nlay)	RARRAY	Maximum specific rate of methane utilization: Enter VSPMAXM(ncol, nrow) on a separate line F52 for each layer

(Enter line F41 if STOCHOPT(1) is".false." -- see line F2)

F53	VSPMAXM	F10.0	Maximum specific rate of methane utilization:
F54	Descriptive text	None	"Yield Coefficient"
F55	YIELDM	F10.0	Yield coefficient for methanotrophic population
F56	Descriptive text	None	"Minimum Concentration for Methane as a Growth Substrate"
F57	AHMINM	F10.0	Minimum methane concentration

5.2.7   Input Instructions for the NAPL Dissolution Package

This input file must be created only if the NAPL Dissolution Package is specified in the Basic Transport Package; i.e., TRNOPT(7) is set to "T". In order to simulate NAPL dissolution, the Biodegradation Package must also be simulated; i.e. TRNOPT(6) is set to "T". Input is read on unit 12.

Normally, the number of hydrocarbon substrates in the NAPL (NHDIS) will correspond to the number in the overall simulation (NHCAR). It is possible to have NHCAR > NHDIS, since contaminants may derive from sources other than the NAPL; however, NHDIS cannot be greater than NHCAR. The same concept holds true for the nondegradable tracers.

For chlorinated ethenes, only PCE, TCE, and DCE are allowed to exist in the NAPL. Thus, the number of chlorinated ethenes in the NAPL (NCDIS) cannot exceed 3 if PCE is simulated or 2 if PCE is not simulated. When required, NCDIS is specified in the Reductive Dechlorination Package. When both the Cometabolism Package and the Reductive Dechlorination Package are activated, the number of chlorinated ethene compounds in the NAPL is specified in the Reductive Dechlorination Package using NCDIS.

For compounds that are not specified in the Reductive Dechlorination Package, the number of recalcitrant compounds in the NAPL (NRDIS) is specified in the Cometabolism Package. The total number of compounds subject to cometabolism and present in the NAPL may never exceed 3. In some cases, both the Cometabolism and Reductive Dechlorination Packages are required to specify the total . For example, if both TCE and MTBE are present in the NAPL, NCDIS =1 and NRDIS = 1. In this case, another compound (e.g., *cis*-DCE) could be subject to cometabolism but not present in the NAPL.

Estimates of the initial mass fractions within the NAPL may be obtained from laboratory analysis or from the literature. For example, if the NAPL is gasoline, mass fractions of benzene, toluene, ethylbenzene, and xylenes have been reported (e.g. Sigsby et al., 1987). Values for solubility and molecular weight are readily available from chemical handbooks.

Line	Variable	Format	Description
G1	MXDIS	I10	Number of nodes where NAPL conc. is specified
	IMLOAD	I10	Flag for mass loading to NAPL: = 0 No time dependent mass loading is simulated = 1 Time dependent mass loading is simulated
	NHDIS	I10	Number of hydrocarbons in the NAPL ($0 \leq$ NHDIS $\leq$ NHCAR)
	NTDIS	I10	Number of tracers in the NAPL ($0 \leq$ NTDIS $\leq$ NTRAC)

G2	NSCH	I10	Number of schedules for simulation of mass loading
	MAXSUB	I10	Maximum number of subschedules per schedule
G3	Descriptive text	None	"Initial Mass Fractions in NAPL"
G4	FRAH(nhdis)	F10.0	Initial mass fraction of hydrocarbons in NAPL: Enter FRAH on a separate line G4 for each hydrocarbon in the NAPL NHDIS is the number of hydrocarbons in the NAPL
G5	FRAT(ntdis)	F10.0	Initial mass fraction of tracers in NAPL: Enter FRAT on a separate line G5 for each tracer in the NAPL NTDIS is the number of tracers in the NAPL
G6	FRAC(ncdis)	F10.0	Initial mass fraction of chlorinated ethenes in NAPL: Enter FRAC on a separate line G6 for each chlorinated ethene in the NAPL NCDIS is the number of chlorinated ethenes in the NAPL
G7	FRAR(nrdis)	F10.0	Initial mass fraction of recalcitrant compounds in NAPL: Enter FRAR on a separate line G7 for each recalcitrant in the NAPL NRDIS is the number of recalcitrants in the NAPL and not specificed in G6
G8	Descriptive text	None	"Solubility"
G9	SOLUBH(nhdis)	F10.0	Hydrocarbon solubility: Enter SOLUBH on a separate line G9 NHDIS times
G10	SOLUBT(ntdis)	F10.0	Tracer solubility: Enter SOLUBT on a separate line G10 NTDIS times
G11	SOLUBC(ncdis)	F10.0	Chlorinate ethene solubility: Enter SOLUBC on a separate line G11 NCDIS times
G12	SOLUBR(nrdis)	F10.0	Recalcitrant compound solubility: Enter SOLUBR on a separate line G12 NRDIS times
G13	Descriptive text	None	"Molecular Weight"

G14	WTMOLH(nhdis)	F10.0	Hydrocarbon molecular weight: Enter WTMOLH on a separate line G14 NHDIS times
G15	WTMOLT(ntdis)	F10.0	Tracer molecular weight: Enter WTMOLT on a separate line G15 NTDIS times
G16	WTMOLC(ncdis)	F10.0	Chlorinated ethene molecular weight: Enter WTMOLC on a separate line G16 NCDIS times
G17	WTMOLR(nrdis)	F10.0	Recalcitrant compound molecular weight: Enter WTMOLR on a separate line G17 NRDIS times
G18	WTMOLI	F10.0	Inert fraction molecular weight Enter WTMOLI one time on line G18
G19	Descriptive text	None	"NAPL Parameters"

(Enter line G20 MXDIS times)

G20	KK	I10	Layer # of block containing NAPL mass
	II	I10	Row # of block containing NAPL mass
	JJ	I10	Column # of block containing NAPL mass
	ISCH	I10	Schedule # for mass loading: Enter any value if IMLOAD = 0
	SINERT	F10.0	Initial soil concentration of NAPL [M M^{-1}]
	DIFALP	F10.0	Dissolution rate [T^{-1}]
	TIMEEX	F10.0	Time when NAPL mass is removed from the block (i.e., excavation). Enter a number larger than the total simulation time to prevent excavation

(Enter the remaining lines only if IMLOAD =1)

G21	Descriptive text	None	"NAPL Mass Loading"

(Enter lines G22 and G23 NSCH times; i.e., for isch = 1 to NSCH)

G22	NSUB(isch)	I10	Number of subschedules in schedule ISCH: 1≤ NSUB(isch) ≤ MAXSUB
	SCHTIME(isch, 1)	F10.0	Starting time for NAPL loading according to subschedule 1
	SCHVAL(isch, 1)	F10.0	Mass rate of NAPL loading according to subschedule 1 [M T^{-1}].

(Enter line G23 for isub = 2 to NSUB(isch)

G23	SCHTIME(isch, isub)	F10.0	Starting time for NAPL loading according to subschedule ISUB SCHTIME(isch, nsub(isch)) must be greater than the total simulation time
	SCHVAL(isch, isub)	F10.0	Mass rate of NAPL loading according to subschedule ISUB [M T^{-1}].

5.2.8 Input Instructions for the Cometabolism Package

This input file must be created only if the Cometabolism Package is specified in the Basic Transport Package; i.e., TRNOPT(8) is set to "T". Input is read on unit 13.

Line	Variable	Format	Description
H1	RDPOPT(3) RDPOPT(1) for TCE RDPOPT(2) for cisDCE RDPOPT(3) for VC	3L2	Flag to indicate if any recalcitrant compounds are specified in the RDP. Enter T to indicate that recalcitrant is included in the RDP; enter F if not.
H2	NRCOM	I10	Number of total simulated recalcitrant compounds subject to cometabolism
	NRCOMNC	I10	Number of recalcitrants not specified using the RDP Note that NRCOMNC = NCCOM if all RDPOPT(1-3) = F; NRCOMNC < NCCOM if any RDPOPT(1-3) = T
	NRDIS	I10	Number of recalcitrants in the NAPL Enter the number of recalcitrants in the NAPL that are not specified using NCDIS
H3	Descriptive text	None	"Recalcitrant Compound Minimum Concs."
H4	ARMIN(nrcom)	F10.0	Minimum concentrations: Enter ARMIN on a separate line H3 for each recalcitrant compound
H5	Descriptive text	None	"Enzyme half saturation constants for recalcitrant compound"
H6	AKHALFR(nrcom)	F10.0	Recalcitrant compound enzyme half saturation constant: Enter AKHALFR on a separate line H5 for each recalcitrant compound
H7	Descriptive text	None	"Maximum specific rate of cometabolism"
H8	VSPMAXR(nrcom)	F10.0	Maximum specific rate of cometabolism: Enter VSPMAXR on a separate line H7 for each recalcitrant compound
H9	Descriptive text	None	"Enzyme half saturation constants for growth substrate"
H10	AKENZS	F10.0	Enzyme half saturation constants for growth substrate

H11	Descriptive text	None	"Haldine constant for growth substrate"
H12	AKHALS	F10.0	Haldine constant for growth substrate
H13	Descriptive text	None	"Death Rate"
H14	RKD	F10.0	First order decay rate for the cometabolizing aerobic population
H15	Descriptive text	None	"Fraction of aerobic population active towards cometabolism"
H16	RFA	F10.0	Initial fraction of aerobic population active towards cometabolism
H17	Descriptive text	None	"Transformation capacity for growth"
H18	TRCAP(nrcom)	F10.0	Transformation capacity: Enter TRCAP on a separate line H17 for each recalcitrant compound

5.2.9 Input Instructions for the Reductive Dechlorination Package

This input file must be created only if the Reductive Dechlorination Package is specified in the Basic Transport Package; i.e., TRNOPT(9) is set to "T". Input is read on unit 14.

Line	Variable	Format	Description
I1	PCEOPT	L2	Flag for PCE option. Enter T to include PCE in the simulation; enter F to omit PCE. Note: SEAM3D uses PCEOPT to calculate the number of chlorinated constituents in the simulation (NCHLO) NCHLO = 6 if PCEOPT = T NCHLO = 5 if PCEOPT = F
	NCDIS	I10	Number of chlorinated ethenes in the NAPL Only PCE, TCE, and DCE are allowed to exist in the NAPL, thus $(0 \leq NCDIS \leq 3$ if PCEOPT = T) $(0 \leq NCDIS \leq 2$ if PCEOPT = F)
I2	Descriptive text	None	"Chlorinated Compound Minimum Concs."
I3	ACMIN(nchlo)	F10.0	Minimum concentrations: Enter ACMIN on a separate line I3 for each chlorinated constituent
I4	Descriptive text	None	"Biomass Starting Concentrations"
I5	YMOLD(ncol, nrow, nlay, nclnc)	RARRAY	Starting concentrations: Enter YMOLD(ncol, nrow) on a separate line I5 for each layer (inner loop) and for each microbial population (outer loop). NCLNC is the total number of microbial populations for reductive dechlorination, and SEAM3D sets NCLNC = 2.
I6	YMMIN	F10	Minimum conc. for both microbial populations: Enter YMMIN after the last entry of YMOLD(ncol, nrow) for the final microbial population Note: only one value for YMMIN is entered, and it applies to both microbial populations
I7	Descriptive text	None	"Yield coefficients"
I8	YIELDC(nchlo-2)	F10.0	Yield coefficients: Enter YIELDC on a separate line I8 for

			the chlorinated ethenes PCE (only if PCEOPT = T), TCE, DCE, and VC. Note: there is no yield coefficient for Ethene or Chloride
I9	Descriptive text	None	"Chlorinated Ethene Inhibition Terms"
I10	Descriptive text	None	"Inhibition of [inhibitee]" Enter this line prior to each chlorinated ethene that is inhibited.
I11	AKINHC(nchlo-2, nchinh)	F10.0	Chlorinated ethene inhibition coefficient: Enter AKINHC(lc, lk) on a separate line I11 for each inhibitor *lk* (inner loop) of chlorinated ethene *lc* (outer loop) Note that chlorinated ethene *lc* will require entry of NCHINH inhibitors NCHINH = NTEAP+NCHLO-3, where NTEAP equals the total number of electron acceptor processes, excluding methanogenesis.

Ex. 1: Simulate aerobes, NO$_3$ and Fe(III) reducers, and methanogens with PCEOPT = F; therefore, (NTEAP=3, NCHLO=5, NCHINH = 5)

Line 1:   "Inhibition of TCE"
Line 2:   AKINHC(1,1) – coef. of O$_2$ inhibition of TCE
Line 3:   AKINHC(1,2) – coef. of NO$_3$ inhibition of TCE
Line 4:   AKINHC(1,3) – coef. of Fe(III) inhibition of TCE

Line 5:   "Inhibition of DCE"
Line 6:   AKINHC(2,1) – coef. of O$_2$ inhibition of DCE
Line 7:   AKINHC(2,2) – coef. of NO$_3$ inhibition of DCE
Line 8:   AKINHC(2,3) – coef. of Fe(III) inhibition of DCE
Line 9:   AKINHC(2,4) – coef. of TCE inhibition of DCE

Line 10:   "Inhibition of VC"
Line 11:   AKINHC(3,1) – coef. of O$_2$ inhibition of VC
Line 12:   AKINHC(3,2) – coef. of NO$_3$ inhibition of VC
Line 13:   AKINHC(3,3) – coef. of Fe(III) inhibition of VC
Line 14:   AKINHC(3,4) – coef. of TCE inhibition of VC
Line 15:   AKINHC(3,5) – coef. of DCE inhibition of VC

I12	Descriptive text	None	"Chlorinated Ethene Stoichiometric Factors"
I13	STOICH(nchlo-2, 3)	F10.0	Stoichiometric factor relating degradation of chlorinated ethenes to daughter products Enter STOICH(lc, ld) on a separate line I13 for each daughter product *ld* (inner loop) of chlorinated ethene *lc* (outer loop) as follows:

Example 2: For PCEOPT = T, (note: omit lines 2 and 3 if PCEOPT = F)

Line 1:   "Stoichiometric Factors"
Line 2:   STOICH(1,1) – coef. for PCE → TCE
Line 3:   STOICH(1,2) – coef. for PCE → Chloride
Line 4:   STOICH(2,1) – coef. for TCE → DCE
Line 5:   STOICH(2,2) – coef. for TCE → Chloride
Line 6:   STOICH(3,1) – coef. for DCE → VC
Line 7:   STOICH(3,2) – coef. for DCE → Chloride
Line 8:   STOICH(3,3) – coef. for DCE → Ethene
Line 9:   STOICH(4,1) – coef. for VC → Ethene
Line 10:   STOICH(4,2) – coef. for VC → Chloride

I14	Descriptive text	None	"Half saturation constants for reductive dechlorination"
I15	AKHALFC(nchlo-2)	F10.0	Chlorinated ethene half saturation constant: Enter AKHALFC on a separate line I15 for the chlorinated ethenes PCE (only if PCEOPT = T), TCE, DCE, and VC. Note: there is no half saturation constant for Ethene or Chloride
I16	Descriptive text	None	"Maximum specific rate of reductive dechlorination"
I17	VSPMXA(nchlo-2)	F10.0	Maximum specific rate of reductive dechlorination: Enter VSPMXA on a separate line I17 for the chlorinated ethenes PCE (only if PCEOPT = T), TCE, DCE, and VC. Note: there is no maximum specific rate constant for Ethene or Chloride

| I18 | Descriptive text | None | "Death Rate" |
| I19 | YKD(nclnc) | F10.0 | First order decay rate for the chorinated ethene microbial populations |

Enter YKD on a separate line I19 for each microbial population.

NCLNC is the total number of microbial populations for reductive dechlorination, and SEAM3D sets NCLNC = 2.

Note:
YKD < 0 death rate calculated by model (recommended)
YKD = 0 no microbial death
YKD > 0 death rate is constant at the specified value

(Enter lines I20 to I29 for each microbial population specified in the BIO package:
NCLNY microbial populations will be read in the order of highest to lowest energy)

| I20 | Descriptive text | None | Microbial Population Name, e.g. "Aerobes" |

| I21 | Descriptive text | None | "Half Saturation Constants" |
| I22 | AKHALFD(ndox) | F10.0 | Half saturation constant for direct oxidation: |

Enter AKHALFD on a separate line I22 for each chlorinated ethene (i.e. DCE and VC) that can undergo direct oxidation

NDOX is the number of chlorinated ethenes that can undergo direct oxidation, and NDOX = 2

| I23 | Descriptive text | None | "Maximum specific rate of direct oxidation" |
| I24 | VSPMXD(ndox) | F10.0 | Maximum specific rate of direct oxidation: |

Enter VSPMXD on a separate line I24 for each chlorinated ethene (i.e. DCE and VC) that can undergo direct oxidation

(Enter lines I25 and I26 under the methanogenic population if methanogenesis is simulated)
| I25 | Descriptive text | None | "Methane generation coefficients" |
| I26 | ENDC(ndox) | F10.0 | Methane generation coefficients: |

Enter ENDC on a separate line I26 for each chlorinated ethene (i.e. DCE and VC) that can undergo direct oxidation

I27   Descriptive text   None   "Electron Acceptor Use Coefficients"

(Enter lines I28 and I29 for each electron acceptor process, excluding methanogenesis)
    I28   Descriptive text   None   "Use of [Electron Acceptor, .e.g. O_2]"
                                                                          Enter this line prior to each electron acceptor process.

    I29   AGAMC(ndox, neatot)   F10.0   Use coefficients:
                                                                          Enter AGAMC on a separate line I29 for each chlorinated ethene (i.e. DCE and VC) that can undergo direct oxidation (inner loop) and for electron acceptor (outer loop)
                                                  Electron acceptor loop is read in the following order: O_2, NO_3, Fe(III), Mn(IV), SO_4 (i.e. from highest to lowest energy).
                                                  NEATOT is the total number of electron acceptors simulated. Lines are not read for electron acceptors that are not included in the simulation

6. SEAM3D MODEL OUTPUT & POST-PROCESSING

6.1   General Information

The basic output structure for SEAM3D is similar to that of MT3DMS (Zheng and Wang, 1999), and SEAM3D writes output information for all hydrocarbon substrates, electron acceptors, and other constituents in the simulation. The following sections paraphrase and condense information from the MT3DMS technical documentation (Zheng and Wang, 1999), while information relevant to the additional output of SEAM3D is provided in greater detail.

6.2   Output Files

Each time SEAM3D is run, the program generates a standard output file, plus optional output files as requested by the user in the Basic Transport Package (see Section 5.2.1). Options within the Basic Transport Package allow the user to control the frequency and type of information written to the output files. The output files are described below.

6.2.1   Standard Output File:

This file echoes the input data to allow the user to verify the accuracy of the specified parameters, flags, and options. The standard output filename (for example SEAM3D.OUT) is specified by the user at the beginning of the simulation. Each line of input is written to the standard output file immediately after being read. If an input error causes the program to stop, the user can find the location of the error by examining the standard output file with any text editor. The input error will almost always involve the line that follows the last line successfully written to the standard output file. For the times selected by the user, the standard output file will contain mass balance information and concentrations of hydrocarbon substrates, electron acceptors (EAs), nutrients, products, daughters, and tracers specified in the simulation.

6.2.2   *Unformatted Concentration Files:*

For each user specified time, these files contain concentrations that can be read by the post-processing programs or used for continuation of a run. Each aqueous phase constituent will have an unformatted concentration file named MT3D*nnn*.UCN, where *nnn* is the constituent index number. The following naming system is used:

Model Constituent	File Name		Notes
Tracers	MT3D*nnn*.UCN	*nnn* = 001, NT	NT = no. of tracers
Hydrocarbon substrates	MT3D*nnn*.UCN	*nnn* = NT+1, NH	NH = NT+ no. of hydrocarbons
Aqueous phase EAs	MT3D*nnn*.UCN	*nnn* = NH+1, NE	NE = NH+ no. of aqueous EAs
Nutrients	MT3D*nnn*.UCN	*nnn* = NE+1, NN	NN = NE + no. of nutrients
Endproducts	MT3D*nnn*.UCN	*nnn* = NN+1, NP	NP = NN + no. of products
Daughters	MT3D*nnn*.UCN	*nnn* = NP+1, ND	ND = NP + no. of daughters
Solid phase EAs	SMSEA*nn*.UCN	*nn* = 01, nslid	nslid = no. of solid phase EAs
Microbial population	SMXM*nn*.UCN	*nn* = 01, nclny	nclny = no. of microbial popluations

For example, if one tracer, one hydrocarbon substrate, and one aqueous phase electron acceptor were simulated, then concentrations of the tracer would be written to MT3D001.UCN, concentrations of the hydrocarbon would be written to MT3D002.UCN, concentrations of the aqueous phase electron acceptor would be written to MT3D003.UCN, and concentrations of the microbial population would be written to SMXM01.UCN.

6.2.3   *Observation Point Files:*

For each user specified observation point, these files contain concentrations versus time in a format that can be read by any text editor. Each aqueous phase constituent will have an observation file named MT3D*nnn*.OBS, where *nnn* is the constituent index number. In addition, each solid phase electron acceptor will have an observation file named SMSEA*nn*.OBS, where *nn* is the index number for the solid phase electron acceptor. Finally, each microbial population will have an observation file named SMXM*nn*.OBS, where *nn* is the index number for the microbial population.

6.2.4   Total Mass File:

This file, named SMMASS.DAT, contains a time series of the total mass of each constituent in the aqueous, sorbed, and NAPL phases. Total mass is calculated for the entire model domain by summing the mass within each block over the total number of blocks. For the aqueous phase, the mass within each block is the aqueous concentration divided by porosity times the block volume. For the sorbed phase, the mass within each block is the solid phase concentration times bulk density times the block volume. For the NAPL, the mass within each block is the NAPL concentration times bulk density times the block volume. The first line of SMMASS.DAT contains a descriptive header that uses the following naming convention:

HCi	ith hydrocarbon substrate
aEAi	ith aqueous phase electron acceptor
sEAi	ith solid phase electron acceptor
Nui	ith nutrient
Pri	ith product
Tri	ith tracer
Mic$i$	ith microbial population

In addition, suffixes are used on the header terms, with "Aqu" indicating aqueous phase mass, "Ads" indicating adsorbed mass, "NAPL" indicating NAPL mass, and "Tot" indicating the total of the aqueous, adsorbed, and NAPL masses.

6.2.5   Mass Balance Summary File:

Each aqueous phase constituent will have a mass balance summary file named MT3D*nnn*.MAS, where *nnn* is the constituent index number. This file contains a summary of the mass budget for each constituent simulated.

6.2.6   Model Grid Configuration File:

This file, named MT3D.CNF, contains information on the spatial discretization to be used by the post processing program.

6.3   Post-Processing

The post-processing programs included with SEAM3D are identical to those of MT3DMS. The program PM.EXE uses the unformatted concentrations files (*.UCN) and the model grid configuration file (MT3D.CNF) to produce data files for plotting. To run PM.EXE, type the name of the executable file (i.e., "PM") at the command prompt, and follow the instructions. Note that PM transforms the SEAM3D coordinate system from the upper, top, left corner of block (1, 1, 1) to the lower, bottom, right corner of block 1, NROW, NLAY). Thus the x-axis remains the same, while the y and z-axes are reversed in order to correspond to the coordinate system of most graphical programs.

The program SAVELAST.EXE extracts the last concentrations saved in the *.UCN files for use as the starting concentrations for a continuation run (see Appendix A). To run SAVELAST.EXE, type the name of the executable file (i.e., "SAVELAST") at the command prompt. The program will prompt for the name of the unformatted concentration file to be read as input and the name of the output file for output.

Since the structure of unformatted files is compiler specific, the user will need to compile PM.EXE and SAVELAST.EXE with same compiler that was used for SEAM3D and MODFLOW. Thus it may be necessary to recompile the source codes PM.FOR and SAVELAST.FOR. Additional information on the post-processing programs may be found in the MT3DMS technical documentation.

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