

RECOVERY-RD: The Development of a Biotransformation Model for Sediment Systems
Contaminated with PCBs

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VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

RECOVERY

*The Development of a Biotransformation Model for Sediment Systems
Contaminated with PCBs*

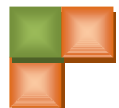
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ABSTRACT

This thesis describes the creation of RECOVERY-RD, a numerical model capable of representing the biotransformation processes associated with Polychlorinated Biphenyl (PCB) compounds in contaminated sediments for a variety of aquatic environments, including rivers and marine systems. RECOVERY-RD is intended as a screening tool for evaluating the impact of engineered sediment caps on contaminant remediation. The two key components that provided the framework for RECOVERY-RD are RECOVERY, a model for contaminant transport in stratified sediment, and SEAM3D, a numerical transport model for contaminated groundwater systems. The predictions made by RECOVERY-RD are verified using a series of test cases organized to test each phase of the modification process individually. The results show that the processes simulated by RECOVERY-RD are reasonably represented when compared to alternative calculation methods that have been previously verified. A hypothetical application of the initial version of the model provides evidence of the usefulness as a screening-level tool for the assessment of remedial efficacy.



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1 Introduction:

1.1 Background

Over the nearly fifty year period during which PCBs were produced, an estimated 175 million kilograms found their way into the environment. Of that total, more than 80% of the contamination is believed to have been released, either directly or indirectly, to oceans and rivers (Huntzinger and Veerkamp 1981). This combined with the hydrophobic nature of PCB compounds has led to a significant sediment contamination issue.

The majority of the concern associated with PCBs in sediment relates to the fact that these relatively-persistent compounds tend to bioaccumulate in the environment. This is significant when considering the fact that many PCB congeners have been identified as, among other things, carcinogens, endocrine disruptors, and general toxins (Schwarzbauer 2006). With this in mind, it is obvious that exposure prevention and environmental remediation are important to the preservation of health and the environment.

While several remedial alternatives exist, common applications often involve the installation of a subaqueous cap. This generally refers to a soil mixture that is distributed directly to the sediment-water interface for an area that has been identified as contaminated. In many cases, the sediment material may be dredged prior to capping to provide direct mass removal with the capping process designed to address any residual contamination. The properties of the capping material are designed to provide containment of the contamination within the sediment and to prevent transport of the contamination into the overlying water body. In addition, the sediment cap may create a contained



system that is more conducive to biological processes and natural recovery in general (Adriaens, Li et al. 2006).

Expanding this subject, this thesis describes the creation of a model that provides an innovative approach to simulating the behavior of polychlorinated biphenyl (PCB) compounds in stratified sediment environments. Elements of RECOVERY (Boyer, Chapra et al. 1994; Ruiz, Schroeder et al. 2000), a contaminated sediment model originally designed through a cooperative project headed by the United States Army Corps of Engineers (USACE), were used as the foundation of the new model. In addition, portions of the groundwater solute transport model SEAM3D (Sequential Electron Acceptor Model, 3D transport) were reformulated and integrated into the new model to provide a mechanism for the representation of a specific set of biological processes. The result is RECOVERY-RD, a hybrid model that is designed to specifically address biotransformation of PCB congeners as they exist in contaminated sediment systems.

While SEAM3D is typically applied to groundwater transport simulations (Widdowson, Waddill et al. 1997; Widdowson 2002), the components of the model responsible for calculating the impact of biodegradation have an analogous relationship to the processes observed in contaminated sediment systems. In addition, SEAM3D's Reductive Dechlorination Package (RDP) is capable of simulating the biotransformation processes that may take place under appropriate system conditions. While the theoretical constraints differ, this package can be used to simulate the reductive processes that apply to PCBs.

The primary objectives of this research are to 1) present equations describing the transport, biodegradation, and biotransformation of nutrients and contaminants in sediments, 2) describe the



solution technique developed for the numerical solution, and 3) validate the predictions made by the model. This is accomplished first by providing an overview of the components that have been combined to create the new model. This includes a detailed description of the original RECOVERY model and an overview of SEAM3D specifically focused on the Biodegradation Package and RDP portions of the transport code. The discussion of these components is combined with a thorough review of the numerical solution methods employed by RECOVERY as they play an important part in the connection process. Next, the progression from RECOVERY to RECOVERY-RD is covered on a step-by-step basis. Finally, the predictive capability of RECOVERY-RD is examined through the use of several test cases and a hypothetical application that exercises the functionality of the new model.

1.2 Overview of RECOVERY

The original form of RECOVERY may be used as a screening tool to examine the efficacy of sediment remediation options; most notably the system response to the implementation of a sediment cap. The model is capable of simulating a transient, one-dimensional concentration profile for a single constituent that extends vertically through three regimes: an overlying water column, a single completely-mixed, saturated sediment layer, and a saturated deep sediment layer consisting of user-defined sub-layers. In the most recent version, the modeler is able to specify the initial contaminant concentration in each of the three regimes, and the concentration of lateral flow entering the water column. System sinks include lateral outflow from the overlying water column, microbial decay, diffusive flux, and volatilization to the atmosphere, as well as mass loss/gain through particulate exchange between layers. The calculation of microbial decay is limited to the use of first order kinetics



constrained by a user-defined rate parameter. Internal processes allow for contaminant flux calculations between each regime as well as mass transfer between the aqueous and solid phases through sorption and desorption. The rate of these processes is controlled by respective mass fractions which are calculated using a linear partition isotherm between the two phases.

The most recent version of RECOVERY, version 4.3.1, exists as two cooperative pieces. The first is a graphical user interface (GUI) -based pre- and post-processor that simplifies the input generation tasks associated with the model and provides a method of output visualization. The second piece is the model executable, which is a Fortran-based program. It should be noted that some portions of the code make use of allocatable arrays, a method that provides dynamic memory allocation for variable arrays and other size-dependent variables that was first introduced as part of Fortran 90 (Chapman 1998). Some software may be unable to address this particular portion of the code, so care should be taken when choosing a compiler. Microsoft Visual Studio 2005 with an integrated Intel® compiler was used for this study, and no problems were found with respect to the dynamic memory allocation feature.

1.3 Research Objectives

The main purpose of this research was to develop a computational tool that, under the same general theme as RECOVERY, would provide an assessment of the mass transfer of contaminants between sediments contaminated with PCB compounds and an overlying body of water. The intention is that this model would serve as a preliminary or screening-level step in the process of remedial design. In addition, it would provide a mechanism for the evaluation and comparison of several remedial alternatives including natural recovery capacity as it relates to biodegradation. To achieve this goal, it



was important to modify RECOVERY to handle more complexity, particularly with respect to the representation of biotransformation as it pertains to PCBs. It is important to note that the increase in flexibility has not changed the focus of the model. The modified version of RECOVERY, or RECOVERY-RD, retains its applicability as a screening tool, but contains an improved ability to address dynamic system processes such as biotransformation. The modifications also provide the user with the ability to perform a more scrupulous sensitivity analysis for a specific application due to the variety of process representations.

As stated, the primary goal of this study was to provide a tool that could specifically focus on the biotransformation processes associated with the transport of PCBs. Enhancements made to the methods used to represent partitioning between phases were specifically designed to be relevant to PCB congeners. The decay of these compounds was also carefully addressed through the creation of a specific package of subroutines. Aptly named the PCB Package, or PCB-P, this set of subroutines directly addresses PCB decay as well as product congener generation through biotransformation. The microbial and geochemical characteristics of the system are important elements of the model that are tied directly to the decay calculation.

A final goal was to ensure the flexibility of the model by providing the user with the alternative to revert to the original methods used in RECOVERY. In the case of decay calculation, the user may choose to simulate the full biodegradation routine as calculated by the SEAM3D subroutines, or to revert to a pseudo-first order calculation that mimics the original RECOVERY calculation. For partitioning calculations, the user has the choice to use the simple linear isotherm that was carried over from RECOVERY, or a choice of two more parameterized isotherms.



2 RECOVERY

2.1 RECOVERY Processes

2.1.1 Introduction

The name RECOVERY-RD references the capability to simulate reductive dechlorination of polychlorinated biphenyl (PCB) compounds. The specificity to PCB compounds is the result of the connection to a modified version of the Reductive Dechlorination Package (RDP) from SEAM3D. This modified representation also includes biotransformations and daughter product formation with rate dependence related to electron acceptor, substrate, and microbial population availability. RECOVERY-RD operates in the same fashion as SEAM3D, in that the functionality of the modified Reductive Dechlorination Package (PCB Package, or PCBP) depends on the parameters calculated by the Biodegradation Package. RECOVERY-RD has also been expanded to include multiple, non-linear partition isotherms used to calculate solid and aqueous phase mass fractions. This is especially important when simulating PCB compounds due to the non-linear nature of their sorption character (Peloquin 2008).

This section provides a detailed description of specific portions of the original version of RECOVERY, as well as a review of the numerical methods applied by the model. The parts of RECOVERY that have not been modified are mentioned briefly within RECOVERY-RD. SEAM3D is also discussed, which provides background information on the specific portions that were used in this project. This discussion serves as a prelude to the description of the modifications that have led to the creation of RECOVERY-RD in Chapter 3. This provides a conceptual basis for the mathematical representations used



in the modified model. It is important to note that although the conceptual systems differ only slightly between the two models, the mass balance expressions vary significantly due to the specific nature of RECOVERY-RD with respect to modeled constituents. In addition, the modifications made to the calculation of constituent decay and generation have completely replaced the original decay mass balance term. This should be taken into consideration when comparing the mass balanced expressions from RECOVERY to those from RECOVERY-RD.

RECOVERY was first published in 1994 as a model capable of simulating the influence of a contaminated sediment system on the chemistry of an overlying aqueous body (Boyer, Chapra et al. 1994). Previous works by Reckhow, Chapra and others were used as the basis for RECOVERY, providing the structure for the representation of contaminant transport processes (Chapra 1982; Reckhow 1983). The 1994 model designed by Boyer, Chapra and their colleagues at the Army Corps of Engineers was novel in that it provided a testing medium for remedial design. The authors were especially interested in applying the model as a method of determining the remedial efficacy of sediment capping designs prior to implementation (Boyer, Chapra et al. 1994).

As previously stated, a contaminated column of sediment is discretized into three stratigraphic units, or regimes. Figure 1 from Ruiz et al. defines each regime and provides a conceptual diagram of the processes represented within each layer.



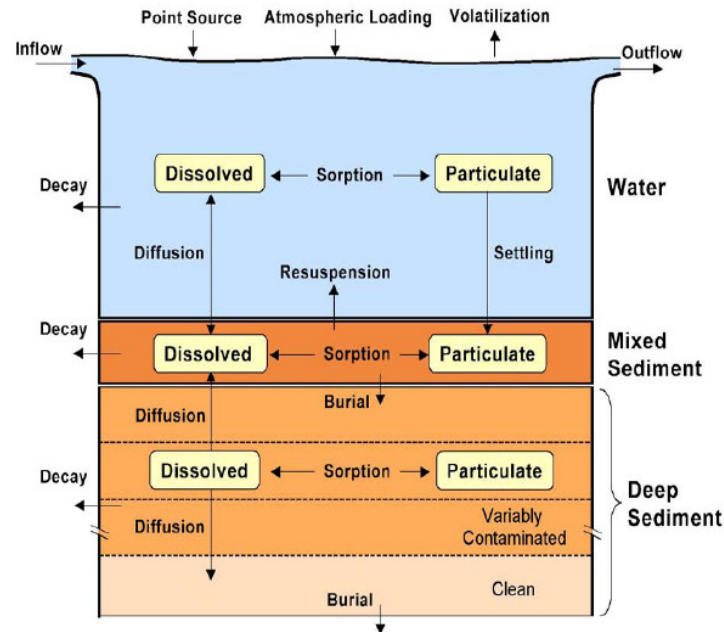


Figure 1: Schematic of Processes, RECOVERY (Adaptation from Ruiz, Schroeder et al. 2000)

The uppermost unit represents the overlying water layer, which may also be referred to as the water column. This corresponds to a river, stream, or water body that is underlain by a bed of sediment and is assumed to be completely mixed with respect to contaminant concentration and suspended sediment. The mixed sediment layer acts as the intermediate model layer and is also represented as a completely mixed unit with respect to contaminant concentration. This provides a mechanism for representing a thickness of unconsolidated material that typically exists at the water-sediment interface (Ruiz, Schroeder et al. 2000). Finally, the deep sediment unit is partitioned into a shallow, contaminated section and a deep, contaminant-free zone. These areas are further discretized into sub-layers for the purpose of numerical simulation. The discretization within the deep sediment layer also provides flexibility with respect to the representation of pollutant concentrations that vary with depth (Ruiz, Schroeder et al. 2000).



To expand on the conceptual model depicted in Figure 1, a list of the primary assumptions on which RECOVERY operates is included below:

- Single constituent simulation, no concentration dependence on other compounds
- Complete mixing horizontally, one-dimensional representation within model area
- Water and mixed layers assumed to be completely mixed vertically as well as horizontally
- Entire system assumed to be saturated
- Decay limited to first-order representation
- Partitioning limited to linear isotherm

2.1.2 Mass Balance – Ordinary Differential Equations

Concentration changes in the water column and mixed sediment layers are tracked through the use of ordinary differential equations. Each equation combines the source and sink terms that specifically apply to the appropriate regime. Since some of these terms require the contaminant concentration from an outside model layer, the equations are described as coupled. To simplify the generation of the ordinary differential equations, the deep sediment concentration value from the previous time step is used during the solution process. This allows the model to solve the ordinary differential equations before proceeding to the partial differential equations. The solution methods utilized by RECOVERY are discussed more thoroughly in section 2.2.

For the overlying water column, RECOVERY solves an ordinary differential equation that accounts for the regime-specific sources and sinks with respect to the solute in question:



$$V_w \frac{dC_w}{dt} = QC_i - QC_w - k_w V_w C_w - k_v V_w C_w - v_s A_w F_{pw} C_w + v_r A_m C_m - v_d A_m \left[F_{dpm} \left(\frac{C_m}{\phi_m} \right) - F_{dw} C_w \right] + W \quad (2.1)$$

The individual mass balance terms are defined as:

V_w = volume of water body [L^3]

C_i = constituent concentration of flow entering water column [M/L^3]

C_w = total concentration of constituent in water column [M/L^3]

C_m = total constituent concentration in mixed sediment layer [M/L^3]

Q = flushing flow rate [L^3/t]

k_w = contaminant decay rate in water column [t^{-1}]

k_v = contaminant and substrate volatilization rate (volatilization rate calculations are made as described in Ruiz et al. 2000). [t^{-1}]

v_s = settling rate, affecting only sorbed contaminant [L/t]

v_r = sediment resuspension rate, impact aqueous and solid phase solutes [L/t]

v_d = solute's water column-mixed layer mass transfer rate (further defined in Appendix A for bioturbation/diffusion- and advection-dominated mass transfer) [L/t]



F_{pw} = mass fraction of constituent adsorbed to suspended particulates in water column
[dimensionless]

F_{dpm} = mass fraction of constituent dissolved in pore water in the mixed sediment layer
[dimensionless]

F_{dw} = mass fraction of constituent dissolved in water column [dimensionless]

A_w, A_m = water surface area, mixed sediment surface area [L^2]

ϕ_m = porosity of mixed sediment layer [dimensionless]

W = external contaminant loads [M/t]

For the single mixed sediment layer, RECOVERY solves an ordinary differential equation similar to the overlying water column expression. The key difference between the two lies in the diffusion term that includes that solute concentration in the top layer of the underlying deep sediment sub-layers. The inclusion of this term couples this ordinary differential equation representation to the mass balance equations for the deep sediment. The mixed layer mass balance expression is as follows:

$$\begin{aligned}
 V_m \frac{dC_m}{dt} = & -k_m V_m C_m - v_s A_w F_{pw} C_w + v_r A_m C_m - v_b A_m C_m \\
 & + v_d A_m \left[F_{dw} C_w - F_{dpm} \left(\frac{C_m}{\phi_m} \right) \right] \\
 & + v_d A_m \left[F_{dps} \left(\frac{C_s(0)}{\phi_s} \right) - F_{dpm} \left(\frac{C_m}{\phi_m} \right) \right]
 \end{aligned} \tag{2.2}$$

where the newly introduced mass balance terms are defined below:



- $C_s(0)$ = total concentration of constituent in first deep sediment sub-layer [M/L³]
- k_m = contaminant decay rate in mixed sediment layer [t⁻¹]
- v_b = burial rate, impacting aqueous and solid phase solutes [L/t]
- F_{dps} = mass fraction of constituent dissolved in pore water in the first deep sediment sub-layer [dimensionless]
- ϕ_s = porosity of first deep sediment sub-layer [dimensionless]

The two mass balance expressions described by Equation 2.1 and Equation 2.2 are solved simultaneously using an adaptive step-size, fourth-order, Runge-Kutta Method. This is a powerful solution technique that provides an appropriate balance of approximation accuracy and computational efficiency (Press, Teukolsky et al. 1992). More information on this solution method is included in 2.2.

2.1.3 Mass Balance – Partial Differential Equations

For the deep sediment sub-layers, RECOVERY solves a series of partial differential equations that represent the sources and sinks that pertain specifically to the deep sediment regime. The equations apply to the upper series of contaminated sub-layers, as well as the deep series of initially-clean sub-layers. The contaminant mass balance of each respective sub-layer is represented as follows:

$$\frac{\partial C_s}{\partial t} = F_{dps} D_s \frac{\partial^2 C_s}{\partial z^2} - v_b \frac{\partial C_s}{\partial z} - k_s C_s \quad (2.3)$$

where the newly introduced mass balance terms are defined as:



C_s = solute concentrations in the represented deep sediment sub-layer [M/L³]

D_s = effective diffusion coefficient for solutes in the deep sediment [L²/t]

The series of partial differential equations is solved using the commonly-applied Crank-Nicolson

Technique using the following initial conditions:

For the contaminated series of sub-layers:

$$C_s = C_s^{INITIAL} @ t=0 \text{ years}$$

For the clean series of sub-layers:

$$C_s = 0 @ t=0 \text{ years}$$

This indicates that the concentration in the contaminated series of deep sediment sub-layers will be set to the user-defined initial concentration at the outset of the simulation. Furthermore, the clean series of sub-layers will initially be void of any concentration at the beginning of the simulation.

The following boundary conditions are also applied:

At the mixed sediment, uppermost deep sediment sub-layer interface:

$$J = J_{ms}$$

As total depth in the deep sediment profile approaches infinity:

$$\Delta C \rightarrow 0$$

This set of boundary conditions indicate that the system of sub-layers is bounded on the top by the rate of mass transfer between the mixed sediment layer, J_{ms} , and the uppermost deep sediment sub-layer, J .

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In addition, the system is bounded at the bottom by a concentration gradient value of zero. The solution process is described in detail in section 2.2.2.

2.1.4 Solids Budget

Within the completely mixed sediment layer, RECOVERY tracks the mass balance of particulate matter. The processes of settling, resuspension, and burial of particulate matter are internally checked using the following equation:

$$0 = v_s A_w s_w - (v_r + v_b) * A_m * (1 - \phi_s) * \rho_p \quad (2.4)$$

The input to this equation is handled by the preprocessor, which ensures that the equation is balanced. User input is required for all of the equation parameters, with the exception of one of the velocity values. The user may choose which velocity is left to be calculated.

2.1.5 Mass Fractions – Partitioning to the Solid Phase

RECOVERY calculates contaminant partitioning to the solid phase using a linear sorption isotherm. Partitioning coefficients are specified for each regime. Each value is then used to determine the dissolved and sorbed fractions of each contaminant in each model layer. This is accomplished through a parameter estimation step that calculates mass fractions representing the balance between the particulate and dissolved phases. The equations for these fractions differ depending on the model regime as follows:



For the overlying water column, the particulate mass fraction is calculated as:

Fraction in Particulate, Water Layer = F_{pw}

$$\begin{aligned}
 &= \frac{\text{Mass of Constituent (Particulate Form)}}{\text{Mass of Constituent (Dissolved Form)} + \text{Mass of Constituent (Particulate Form)}} \\
 &= \frac{K_{dw}S_w}{1 + K_{dw}S_w} \quad (2.5)
 \end{aligned}$$

where:

K_{dw} = solute partitioning coefficient in the water column [L^3/M]

S_w = concentration of suspended solids (particulate matter) in the water column [M/L^3]

The remainder is the dissolved fraction:

Fraction Dissolved, Water Layer = F_{dw}

$$\begin{aligned}
 &= \frac{\text{Mass of Constituent (Dissolved Form)}}{\text{Mass of Constituent (Dissolved Form)} + \text{Mass of Constituent (Particulate Form)}} \\
 &= \frac{1}{1 + K_{dw}S_w} \quad (2.6)
 \end{aligned}$$

For the completely-mixed sediment layer, the pore-water mass fraction is calculated as:

Fraction Dissolved in Pore Water, Mixed Sediment Layer = F_{dpm}

$$= \frac{\text{Mass of Constituent (Dissolved Form)}}{\text{Mass of Constituent (Dissolved Form)} + \text{Mass of Constituent (Particulate Form)}}$$



$$= \frac{1}{\phi_m + K_{dm}(1 - \phi_m)\rho_p} \quad (2.7)$$

where:

K_{dm} = solute partitioning coefficient in the mixed sediment layer [L^3/M]

For the individual deep sediment sub-layers, the pore-water mass fraction is calculated as:

Fraction Dissolved in Pore Water, Deep Sediment Sub – layers = F_{dps}

$$= \frac{\text{Mass of Constituent (Dissolved Form)}}{\text{Mass of Constituent (Dissolved Form) + Mass of Constituent (Particulate Form)}} \\ = \frac{1}{\phi_s + K_{ds}(1 - \phi_s)\rho_p} \quad (2.8)$$

where:

K_{ds} = solute partitioning coefficient in the each deep sediment sub-layer [L^3/M]

Since there are no concentration-dependent terms in the linear isotherm, each of the respective mass fractions requires only a single calculation. This is done at the beginning of a given simulation and the calculated values are used to identify the mass associated with each phase of the simulated system.



2.1.6 Simulation of First-Order Decay

As the mass balance expressions indicate, RECOVERY is capable of modeling first-order decay of a solute in each of the three model regimes as well as both partitioned phases. The rate of decay is controlled by user-defined kinetic parameters that are specified by unit and phase. This method of decay representation is intended to provide the user with the ability to model multiple mechanisms. In the latest version of the RECOVERY model documentation, Ruiz et al. describe the decay representation as follows: "The decay rate constants, k_w , k_m , and k_s , represent all mechanisms for decay except volatilization, which is accounted for separately. These mechanisms include photolysis, hydrolysis, and bacterial degradation." (Ruiz, Schroeder et al. 2000).

2.1.7 Additional Parameters

RECOVERY represents diffusive mass transfer between the overlying water column and the mixed sediment layer, the mixed sediment layer and the top layer of the deep sediment, and each of the individual deep sediment sub-layers. The ordinary differential equations for the water column and mixed sediment layers use a mass transfer coefficient that is defined within the latest model documentation (Ruiz, Schroeder et al. 2000).

Volatilization to the atmosphere from the overlying water column is represented within RECOVERY through the calculation of a representative rate coefficient. The value of this parameter is also discussed in the latest RECOVERY documentation (Ruiz, Schroeder et al. 2000).



Both processes discussed above are retained in their original forms within RECOVERY-RD. No modifications were made to the representation of any of the associated relationships for the respective mass balance terms.

2.2 Numerical Methods in RECOVERY

This section includes detailed descriptions of the numerical solution methods as they apply to the original form of RECOVERY. The descriptions are based on the programmatic structure of the original RECOVERY, version 4.3.1 (Ruiz, Schroeder et al. 2000). The numerical methods described here are used to determine the concentration derivatives with respect to time as represented by the mass balance expressions discussed in the previous section. This serves as an introduction for the next section, which details the modification process that transformed RECOVERY into RECOVERY-RD.

2.2.1 Ordinary Differential Equation Solution

Equation 2.1 and Equation 2.2 show the ordinary differential equations that are used to represent the transient mass balance with respect to contaminant concentration in the overlying water column and completely-mixed sediment layers, respectively. The equations are solved using an adaptive step size, fourth-order Runge-Kutta method (Ruiz, Schroeder et al. 2000). In general, Runge-Kutta methods are single point approximations of derivative terms. That is, the predicted result from a single-point method will be based solely on results from the previous step (Hoffman 2001). While several forms of the Runge-Kutta method exist, RECOVERY uses the most commonly applied, fourth-order variety (Press, Teukolsky et al. 1992). Equations 2.9 through 2.13 show the series of equations



that form the fourth-order Runge-Kutta approximation as defined by Antia, with the terms slightly modified to correspond to the RECOVERY application (Antia 2002):

$$C_{n+1} - C_n = \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \quad (2.9)$$

$$k_1 = (dC)_n = dt_n \left(\frac{dC}{dt} \right)_n = h_n f(t_n, C_n) \quad (2.10)$$

$$k_2 = (dC)_{n+1/2} = dt_{n+1/2} \left(\frac{dC}{dt} \right)_{n+1/2} = h_n f \left(t_n + \frac{1}{2} h_n, C_n + \frac{1}{2} k_1 \right) \quad (2.11)$$

$$k_3 = (dC)_{n+1/2} = dt_{n+1/2} \left(\frac{dC}{dt} \right)_{n+1/2} = h_n f \left(t_n + \frac{1}{2} h_n, C_n + \frac{1}{2} k_2 \right) \quad (2.12)$$

$$k_4 = (dC)_{n+1} = dt_{n+1} \left(\frac{dC}{dt} \right)_{n+1} = h_n f(t_n + h_n, C_n + k_3) \quad (2.13)$$

Where:

C = Concentration of modeled constituent [M/L³]

n = Counter indicating current time step [dimensionless]

h = Size of time step [t]

t = Current time [t]

As the first expression above shows, the resulting approximation of the concentration change over a particular time step will be the weighted average of four derivatives represented as k_1 through k_4 .

Figure 16.1.3 from Press et al. is an excellent example that helps visualize this approach as it corresponds to approximating the path of the ODE (Press, Teukolsky et al. 1992).



The Runge-Kutta method used by RECOVERY is modified to have an adaptive nature with respect to time stepping. This means that the time step size is modified depending on the comparison of the local truncation error produced for a trial time step and a user-defined convergence criterion. The estimate of this error is produced through “step-doubling” or taking the difference of 2 results using different approaches (Press, Teukolsky et al. 1992). The first result is produced as the resulting concentration value over a single time step. The second result is produced by using the same cumulative change in time, but divided into two individual steps. The resulting truncation error (Δ) may then be represented as:

$$\Delta = C_{1(\text{Single Step})} - C_{2(\text{Two Individual Steps})} \quad (2.14)$$

The calculated value of this truncation error may then be compared to the user-defined convergence criterion. Since RECOVERY requires the simultaneous solution of the water column and mixed sediment layer ODEs, the comparison is made between the convergence criterion and the maximum error between the two approximations (Ruiz, Schroeder et al. 2000).

Figure 2 shows the program structure associated with the ODE solution phase of RECOVERY:



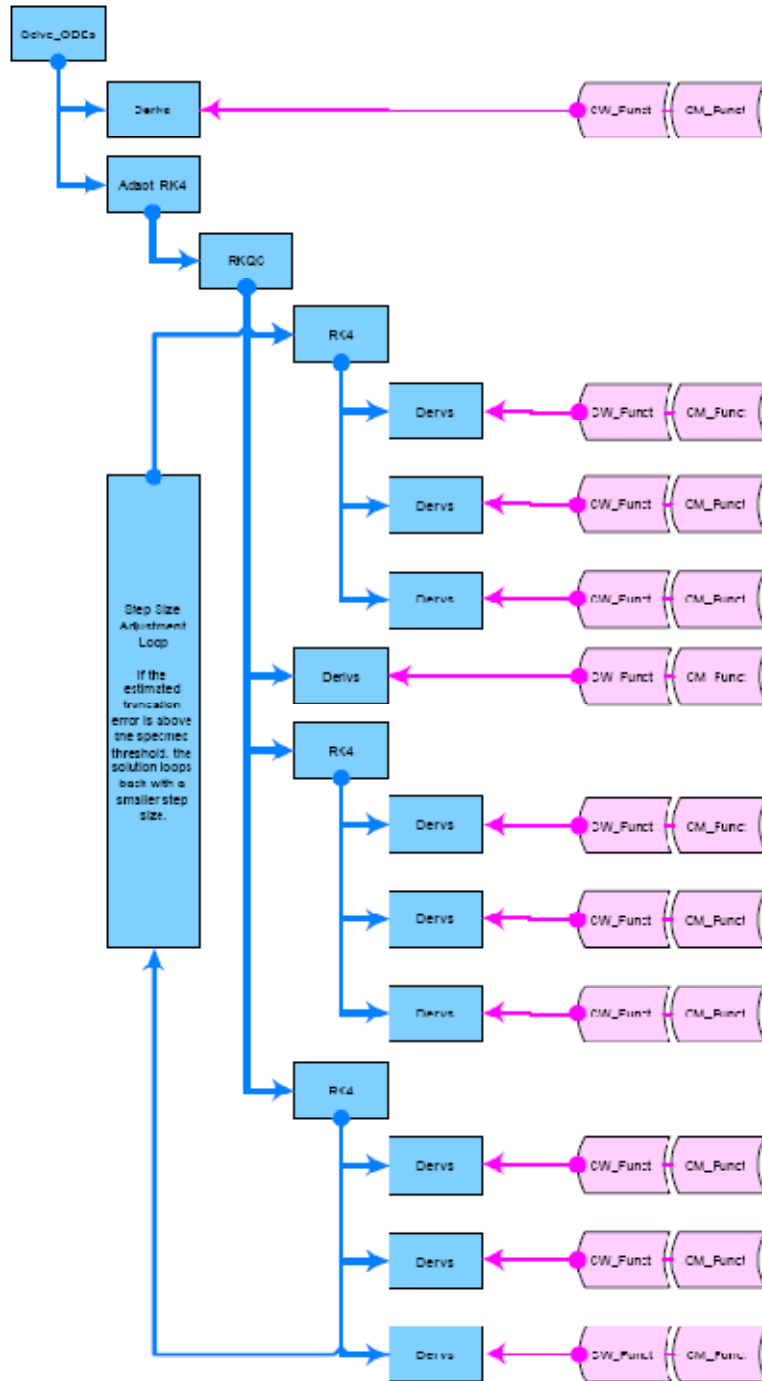


Figure 2: ODE Solution Diagram, RECOVERY. Blue shading indicates a separate subroutine. Pink shading indicates a separately defined program function.



Each call to the 'Derivs' subroutine represents an approximation of the concentration derivative associated with the terms described in Equations 2.10 through 2.13. As Figure 2 indicates, the solution method will cycle until an appropriate time step size has been determined. After each iteration, the truncation error is compared to an internally-defined tolerance. Should the value of the truncation error exceed the acceptable tolerance, the time step size is reduced and another iteration is initiated. A truncation error that satisfies the tolerance results in an increase in the step size for the next time approximation.

2.2.2 Partial Differential Equation Solution

Partial differential equations are used to represent the contaminant mass balance in each of the deep sediment sub-layers. In RECOVERY, the PDE expressions, as shown by Equation 2.3, are solved using the Crank-Nicholson technique in a separate step that immediately follows the ODE solution. It is important to note that the time step size and mixed layer concentration are determined during the ODE solution phase. Therefore, these values are exported from the ODE solution after each completed step for use by the PDE solver.

Equation 2.15 shows a general form of the Crank-Nicolson expression as it applies to the original form of RECOVERY:

$$\left(\frac{dC}{dt}\right)^n = \alpha C^{n+1} + (1 - \alpha)C^n \quad (2.15)$$

The symbol α (alpha) represents the Crank-Nicolson factor, a weighting mechanism that determines the method by which the temporal derivative is approximated. RECOVERY adheres to the common



approach, which is to use a value of 0.5 that evenly splits the approximation between the explicit and fully implicit representations (Batu 2006). Hinkelmann discusses other values of the Crank-Nicolson factor and the potential issues associated with their use (Hinkelmann 2005).

Both sides of Equation 2.15 can be expanded to show the complete Crank-Nicolson finite difference approximation of the concentration derivative with respect to time. The expanded, one-dimensional approximation is shown below:

$$\frac{C_i^{n+1} - C_i^n}{dt} = \alpha \left(\frac{C_{i+1}^{n+1} - 2C_i^{n+1} + C_{i-1}^{n+1}}{\Delta Z^2} \right) + (1 - \alpha) \left(\frac{C_{i+1}^n - 2C_i^n + C_{i-1}^n}{\Delta Z^2} \right) \quad (2.16)$$

This approximation is completed for each of the individual deep sediment sub-layers in a single phase that directly follows the ODE solution.

2.3 SEAM3D

In this study, SEAM3D (Sequential Electron Acceptor Model 3-Dimensional) provides a structure for the calculation of mass changes due to biodegradation and biotransformation. The original SEAM3D model was based on the widely-applied groundwater solute transport code MT3DMS (Zheng and Wang 1999). The main group of program packages that compose MT3DMS is expanded by the Biodegradation, Cometabolism, Reductive Dechlorination, and NAPL Dissolution Packages in SEAM3D. The additional packages that accompany SEAM3D provide an expanded model that directly addresses biological decay, cometabolic processes, biotransformation of chlorinated ethene compounds, and dissolution from NAPL sources (Widdowson 2002). The expanded capabilities with respect to the



simulation of biological conditions are advancements over previous numerical models capable of representing reductive dechlorination, such as RT3D (Clement 1997).

The Biodegradation Package provides a medium for the simulation of terminal electron acceptor processes, or TEAPs for short. A modified form of traditional Monod kinetics is applied to a variety of constituent categories to calculate their respective change in mass due to biodegradation. The represented categories are hydrocarbon substrate or electron donor compounds, electron acceptors, products of electron acceptor degradation, daughter compounds produced from the hydrocarbon substrate category, mineral nutrients, and non-reactive tracers. Along with the constituent categories, utilizing microbial populations are simulated under the assumption that they congregate on the surface of the non-porous fraction of the aquifer (Widdowson 2002).

Using the TEAP conditions defined by the Biodegradation Package, SEAM3D is capable of simulating the fate and transport of chlorinated ethene compounds and their associated daughter products through the Reductive Dechlorination Package (RDP). The parent compounds that may be simulated are PCE and TCE, which may result in the production of daughter products such as DCE and Vinyl Chloride. Ethene and chloride are also simulated as byproducts of the dehalogenation process. Similar to the Biodegradation Package, the rate of decay is controlled by Monod-form expressions that include additional controls based on the biological state of the simulated system (Widdowson 2002).



3 Modification of RECOVERY; Creation of RECOVERY-RD

3.1 Introduction

This section provides a description of the steps that were taken during the creation of RECOVERY-RD. It is important to note that the graphical user interface (GUI) associated with version 4.3 of RECOVERY handles a small amount of the input conversion that is transferred to the executable (.exe) model, as well as all of the tasks associated with input file generation. For RECOVERY-RD, the input processing tasks have been transferred to a Microsoft Excel spreadsheet.

The discussion of model modifications is organized in a chronological order that generally reflects the schedule of changes. Each phase of the modification process was considered a separate task that required testing before advancing to the next step. Some phases included multiple components which were combined prior to testing. Verification of these changes is discussed in Chapter 4. An outline of the phases associated with the modification process is shown below.

1. *Modify RECOVERY to handle several constituents per simulation.*
2. *Restructure mass balance expressions to include the proposed Monod-form decay terms*
 - a. *Modify RECOVERY to address categories of constituents as they exist in SEAM3D*
3. *Connect applicable packages from SEAM3D*
 - a. *Connect the Biodegradation Package from SEAM3D to RECOVERY-RD*
 - b. *Modify the Biodegradation Package to handle compounds simulated by RECOVERY-RD*
 - c. *Connect the Reductive Dechlorination Package from SEAM3D to RECOVERY-RD*
 - d. *Modify the Reductive Dechlorination Package to handle biotransformation of PCBs*
4. *Implement additional, non-linear partitioning options and retain the original linear model*



5. *Reformat Monod-form decay terms to include a pseudo first-order option*

3.2 Conversion to Multiple-Constituent Model

The creation of RECOVERY-RD started with the modification of the original version of RECOVERY to a model capable of simulating multiple contaminants in a single simulation. This was an important step in the modification process as it reformatted the model for inclusion of the concentration-dependent decay terms calculated by the SEAM3D packages. It is important to understand that RECOVERY could not simply be modified to loop from start to finish for each constituent. This is due to the fact that the decay and generation terms need to be recalculated for each time step; therefore the constituents must be bundled in a single transient simulation to appropriately calculate the respective mass balance terms.

Nearly every aspect of RECOVERY was adjusted to account for multiple constituents. This includes the input and output portions of the model that were originally created with singular variables in mind. The only portions of the model that remain untouched are the system variables that do not reflect a relationship to the modeled constituent, such as the physical parameters of the model (sediment specific gravity, etc.) For those parameters that do reflect this relationship, the placeholders within RECOVERY were modified from a single variable to an array of values that had available locations for each category of constituent. In addition, RECOVERY was modified to repeat every calculation for each of the active constituents in a given simulation. It should be noted that this modification step alone has drastically increased the memory requirement of the model.



The numerical methods used by RECOVERY to solve the mass balance expressions also required an initial set of adjustments to accommodate multiple constituents. The ODE solution was adjusted to loop through each of the modeled constituents. The modified Runge-Kutta formulation is described below:

$$C_{n+1}^i - C_n^i = \frac{1}{6}(k_1^i + 2k_2^i + 2k_3^i + k_4^i) \quad (3.1)$$

$$k_1^i = (dC)_n^i = dt_n \left(\frac{dC}{dt} \right)_n^i = h_n f(t_n, C_n^i) \quad (3.2)$$

$$k_2^i = (dC)_{n+1/2}^i = dt_{n+1/2} \left(\frac{dC}{dt} \right)_{n+1/2}^i = h_n f \left(t_n + \frac{1}{2}h_n, C_n^i + \frac{1}{2}k_1^i \right) \quad (3.3)$$

$$k_3^i = (dC)_{n+1/2}^i = dt_{n+1/2} \left(\frac{dC}{dt} \right)_{n+1/2}^i = h_n f \left(t_n + \frac{1}{2}h_n, C_n^i + \frac{1}{2}k_2^i \right) \quad (3.4)$$

$$k_4^i = (dC)_{n+1}^i = dt_{n+1} \left(\frac{dC}{dt} \right)_{n+1}^i = h_n f(t_n + h_n, C_n^i + k_3^i) \quad (3.5)$$

The superscript, i , in each of the expressions above reflects the fact that the solution has been modified to cycle through multiple constituents. That is, for each derivative approximation step, all of the terms in equations 3.1 through 3.5 are calculated for each modeled constituent. In addition, the solution was modified to calculate the cumulative error as the maximum value over all modeled constituents and layers. This causes the solution to compare the maximum error value over all of the modeled constituents to the user-defined tolerance. Therefore, the resulting time step size is based on the maximum rate of concentration change for all compounds.



An example calculation from the multiple-constituent modification process is provided below. The example compares the original RECOVERY calculation of the dispersion coefficient for the individual deep sediment sub-layers to the RECOVERY-RD version. In both examples, the variable 'ndss' represents the total number of deep sediment sub-layers calculated by the model. In both cases, the code is looping through each deep sediment sub-layer and filling the 'Dss' array with the appropriate calculated value. However, in the second example the 'Dss' array now has two dimensions as opposed to one in the original code. The second dimension accounts for the number of constituents that are active in the simulation. With this additional dimension introduced, the code must now perform two calculation loops: one for the active constituents (ii) and another for the total number of deep sediment sub-layers (i). While this is a very simple example of the first step in the modification process, it adequately represents the complexity of multi-constituent calculations.

Example I: Original RECOVERY Calculation of the Deep Sediment Dispersion Coefficient

```
! Calculate Dss
```

```
Do i = 1, ndss  
    Dss(i) = Dm*Pors(i)**2  
Enddo
```

Example II: RECOVERY-RD Calculation of the Deep Sediment Dispersion Coefficient

```
! Calculate Dss (For each constituent --MAM--)
```

```
Do ii=1, constituents  
    Do i = 1, ndss
```



```
Dss(ii,i) = Dm(ii)*Pors(i)**2
```

```
Enddo
```

```
End Do
```

The result of this step in the modification process was a model that could reproduce the results predicted by the original version of RECOVERY for several constituents in a single simulation. The testing process and results are discussed in Chapter 4.

3.3 Modification of Mass Balance Expressions

The second phase of the modification process involved changes to the mass balance expressions used by the original RECOVERY. Figure 3 shows the modified conceptual model that served as the basis for modifications made to the mass balance term calculation process.



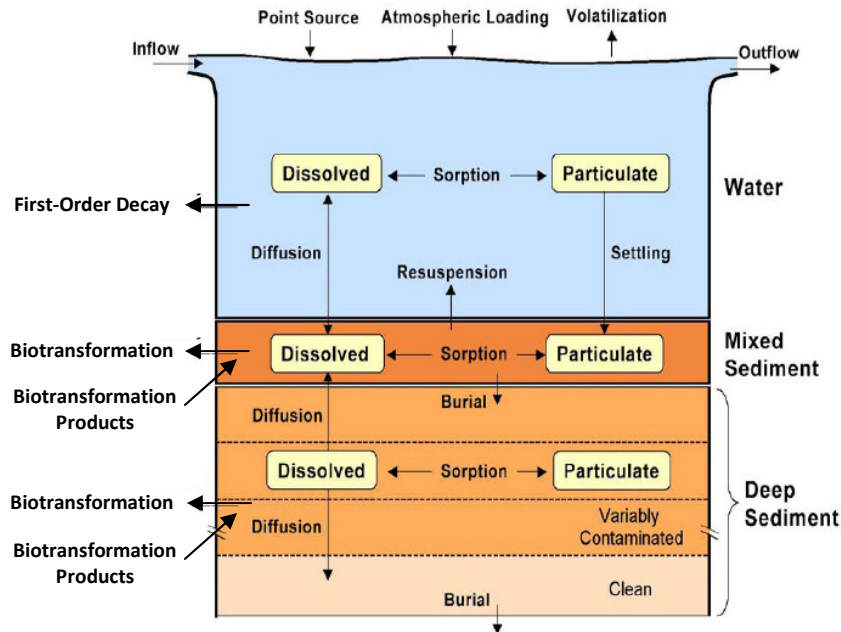


Figure 3: Schematic of Processes, RECOVERY-RD (Adaptation from Ruiz, Schroeder et al. 2000)

While the majority of the processes remain the same, a significant difference exists between the calculation of the decay term in RECOVERY and the biotransformation calculations made in RECOVERY-RD. The modified calculations associated with the Monod-form decay term are discussed in the upcoming sections. To address the future implementation of the SEAM3D subroutines, the first-order decay terms were excluded from the mass balance equations in the mixed sediment and deep sediment sub-layers. As Figure 3 indicates, the first-order decay term was retained in the water layer equation. It should be noted that although the original form of the decay term was removed from RECOVERY-RD, the simulation of first-order decay remains as an option to the user. This is described later in this chapter.

Since the focal point of RECOVERY-RD is the biological decay of PCB compounds, four categories of compounds were identified that would be required components of any simulation. Each constituent



was assigned a particular location in the array structure of RECOVERY-RD. This method was used to preserve the integrity of the concentration calculations associated with each individual constituent. The categories and array assignments are described below in Table 1.

Constituent Category	Constituent Range (Array Location)
Hydrocarbon Substrates (HCs)	1 – 3
Aqueous Phase Electron Acceptors (EAs)	4 – 6
Products of Electron Acceptor Degradation (PRs)	7 – 11
PCB Congeners and Products of PCB Decay (PCBs)	12 – 50*

Table 1: RECOVERY-RD Constituent Categories. *Note: The PCB category was arbitrarily limited to an upper bound of 50 to preserve program efficiency. Chloride (Cl⁻) is included in this category and occupies the position after the final active PCB congener.

Each category represents a specific group of constituents with some combination of transport, decay, and/or generation processes that may be modeled using RECOVERY-RD. In the case of the Electron Acceptor Product category, transport is not currently simulated. Concentration changes for this category are limited to production through the decay of an associated electron acceptor. This process is further discussed in section 3.4.1. Table 2 and Table 3 further define the Electron Acceptor and Product of Electron Acceptor Decay categories according to their respective components, each of which has a specific role with respect to biodegradation.



Electron Acceptors	Array Location
O ₂ (aq)	4
NO ₃ (aq)	5
Mn(IV) (s)	Not Tracked*
Fe(III) (s)	Not Tracked*
SO ₄ (aq)	6
CO ₂ (aq)	Not Tracked**

Table 2: RECOVERY-RD Electron Acceptor Representation. *Note: Transport processes are not tracked due to solid-phase character. Concentration reductions due to biodegradation are calculated by the Biodegradation Package. **Note: CO₂ assumed to be readily available in pore water, therefore concentration is not tracked.



Products of Electron Acceptor Decay	Array Location
User-Defined Nitrogenous Compound (N_xO_y)	7
Mn(II)	8
Fe(II)	9
H ₂ S	10
CH ₄	11

Table 3: RECOVERY-RD Electron Acceptor Product Representation.

This categorical structure provided a framework for the required modifications to the mass-balance expressions. RECOVERY develops these equations as individual terms calculated by a subroutine that is called at the outset of a simulation. The calculation statements were first adjusted to cycle through the entire set of active constituents, reflecting the different source and sink terms that apply to each category. The modified forms of the individual mass-balance expressions are shown below.

In the overlying water column, the mass-balance expressions for each of the constituent categories generally resemble the forms used in RECOVERY.

For each PCB congener, mass balance within the water column is represented as follows:



$$V_w \frac{dC_{w,lc}}{dt} = QC_{i,lc} - QC_{w,lc} - k_w^{c,lc} V_w C_{w,lc} - k_v^{c,lc} V_w C_{w,lc} - v_s A_w F_{pw} C_{w,lc} + v_r A_m C_{m,lc} + v_d^{c,lc} A_m (F_{dm} C_{m,lc} / \phi_m - F_{dw} C_{w,lc}) + W_{c,lc} \quad (3.6)$$

where

C = Concentration of PCB congener, subscript indicates regime

lc = Subscript indicates mass-balance term associated with PCB congener 'lc'

For each hydrocarbon substrate, mass balance within the water column is represented as follows:

$$V_w \frac{dS_{w,ls}}{dt} = QS_{i,ls} - QS_{w,ls} - k_w^{s,ls} V_w C_{w,lc} - k_v^{s,ls} V_w S_{w,ls} - v_s A_w F_{pw} S_{w,ls} + v_r A_m S_{m,ls} + v_d^{s,ls} A_m (F_{dm} S_{m,ls} / \phi_m - F_{dw} S_{w,ls}) + W_{s,ls} \quad (3.7)$$

where

S = Concentration of hydrocarbon substrate, subscript indicates regime

ls = Subscript indicates mass-balance term associated with hydrocarbon substrate 'ls'

For each aqueous-phase electron acceptor, mass balance within the water column is represented as follows:

$$V_w \frac{dE_{w,le}}{dt} = QE_{i,le} - QE_{w,le} + v_r A_m E_{m,le} + v_d^{e,le} A_m (F_{dm} E_{m,le} / \phi_m - F_{dw} E_{w,le}) + W_{e,le} \quad (3.8)$$



where

E = Concentration of Aqueous-Phase Electron Acceptor, subscript indicates regime

le = Subscript indicates mass-balance term associated with electron acceptor 'le'

With the exception of the electron acceptor category, the mass-balance expressions match the original form used in RECOVERY. This is to be expected, especially when considering the fact that decay is still represented within this unit as a reaction that follows first-order kinetics. The differences observed for the electron acceptor category reflects the modifications made to the mass fractions, which effectively removes any non-dissolved phase mass balance terms. Essentially, several terms have been removed that represent sources and sinks due to mass that has partitioned to the solid phase. The modifications to the mass fraction representation are discussed in more detail later in this section.

In the mixed-sediment layer equations, the first-order decay term was dropped and replaced with biodegradation mass balance terms representing mass loss or gain depending on the constituent category. The calculation of the modified decay terms is discussed in sections 3.4.1 and 3.4.2.

For each PCB congener, mass balance within the mixed sediment layer is represented as follows:

$$\begin{aligned}
 V_m \frac{dC_{m,lc}}{dt} = & v_s A_w F_{pw} C_{w,lc} - v_r A_m C_{m,lc} - v_b A_m C_{m,lc} \\
 & + v_d^{c,lc} A_m (F_{dw} C_{w,lc} - F_{dm} C_{m,lc} / \phi_m) + v_m^{c,lc} A_m (F_{ds} C_{s,lc}(0) / \phi_{s1} - F_{dm} C_{m,lc} / \phi_m) \\
 & - V_m F_{dm} R_{sink,lc}^{bio} + V_m F_{dm} R_{source,lc}^{bio}
 \end{aligned} \quad (3.9)$$

Where:



$R_{\text{sink}}^{\text{bio}}$ = Biodegradation sink term

$R_{\text{source}}^{\text{bio}}$ = Biodegradation source term

For each hydrocarbon substrate, mass balance within the mixed sediment layer is represented as

follows:

$$\begin{aligned} V_m \frac{dS_{m,ls}}{dt} &= v_s A_w F_{pw} S_{w,ls} - v_r A_m S_{m,ls} - v_b A_m S_{m,ls} \\ &+ v_d^{s,ls} A_m (F_{dw} S_{w,ls} - F_{dm} S_{m,ls} / \phi_m) \\ &+ v_m^{s,ls} A_m (F_{ds} S_{s,ls}(0) / \phi_{s1} - F_{dm} S_{m,ls} / \phi_m) - V_m F_{dm} R_{\text{sink},ls}^{\text{bio}} \end{aligned} \quad (3.10)$$

For each aqueous-phase electron acceptor, mass balance within the mixed sediment layer is

represented as follows:

$$\begin{aligned} V_m \frac{dE_{m,le}}{dt} &= -v_r A_m E_{m,le} - v_b A_m E_{m,le} \\ &+ v_d^{e,le} A_m (F_{dw} E_{w,le} - F_{dm} E_{m,le} / \phi_m) \\ &+ v_m^{e,le} A_m (F_{ds} E_{s,le}(0) / \phi_{s1} - F_{dm} E_{m,le} / \phi_m) - V_m R_{\text{sink},le}^{\text{bio}} \end{aligned} \quad (3.11)$$

For the most part, the mixed layer mass balance expressions maintain their original form with the exception of the decay term. Again, the electron acceptor category differs significantly due to the removal of terms related to partitioned mass.



Similar to the mixed layer expressions, the deep sediment sub-layer PDEs (3.12 through 3.14) were modified to include the appropriate biodegradation terms for each constituent category:

For each PCB congener, mass balance within each deep sediment sub-layer is represented as follows:

$$\frac{\partial C_{s,lc}}{\partial t} = F_{ds} D_{s,lc} \frac{\partial^2 C_{s,lc}}{\partial z^2} - v_b \frac{\partial C_{s,lc}}{\partial z} - F_{ds} R_{\text{sink},lc}^{bio} + F_{ds} R_{\text{source},lc}^{bio} \quad (3.12)$$

For each hydrocarbon substrate, mass balance within each deep sediment sub-layer is represented as follows:

$$\frac{\partial S_{s,ls}}{\partial t} = F_{ds} D_{s,ls} \frac{\partial^2 S_{s,ls}}{\partial z^2} - v_b \frac{\partial S_{s,ls}}{\partial z} - F_{ds} R_{\text{sink},ls}^{bio} \quad (3.13)$$

For each aqueous-phase electron acceptor, mass balance within each deep sediment sub-layer is represented as follows:

$$\frac{\partial E_{s,le}}{\partial t} = D_{s,le} \frac{\partial^2 E_{s,le}}{\partial z^2} - v_b \frac{\partial E_{s,le}}{\partial z} - R_{\text{sink},le}^{bio} \quad (3.14)$$

Once again, the equations retain the general form established by RECOVERY, but include the modified representation of decay and/or generation. Also of note is the fact that the electron acceptor category does not show representative mass fraction values as these variables have defaulted to values of one, indicating their entirely-aqueous nature.

To address the modified mass-balance representations shown above, the term calculation portion of RECOVERY-RD was reformatted. In the previous modification step, this portion of the model



code had been adjusted to loop through the set of active constituents. In this phase of modifications, the lines of code responsible for the calculation of the mass balance coefficients were modified to be specific to the constituent categories. That is, only the mass balance terms associated with each category are calculated and included in the cumulative terms sent to the solution routines. The only additional terms that are calculated are the appropriate biodegradation source and sink terms which are described in the following section.

The final step in this phase of modifications was the adjustment of the mass-fraction calculations associated with the aqueous-phase portion of the electron acceptor and product of electron acceptor decay categories. Since the constituents that compose each of these categories exist only in the aqueous phase by definition, the applicable mass-fraction values must reflect this nature. This was accomplished by modifying the mass-fraction formulations for the EA and PR categories in the following manner:

For the overlying water column, the particulate mass fraction is calculated as:

Fraction in Particulate, Water Layer = Fpw

$$= \frac{\text{Mass of Constituent (Particulate Form)}}{\text{Mass of Constituent (Dissolved Form)} + \text{Mass of Constituent (Particulate Form)}}$$

$$= \frac{K_{dw}S_w}{1 + K_{dw}S_w} = 0 \quad (3.15)$$

The remainder is the dissolved fraction:

Fraction Dissolved, Water Layer = Fdw



$$\begin{aligned}
 &= \frac{\text{Mass of Constituent (Dissolved Form)}}{\text{Mass of Constituent (Dissolved Form)} + \text{Mass of Constituent (Particulate Form)}} \\
 &= \frac{1}{1 + K_{dw}S_w} = 1.0
 \end{aligned} \tag{3.16}$$

For the completely-mixed sediment layer, the pore-water mass fraction is calculated as:

Fraction Dissolved in Pore Water, Mixed Sediment Layer = Fdpm

$$\begin{aligned}
 &= \frac{\text{Mass of Constituent (Dissolved Form)}}{\text{Mass of Constituent (Dissolved Form)} + \text{Mass of Constituent (Particulate Form)}} \\
 &= \frac{1}{\phi_m + K_{dm}(1 - \phi_m)\rho_p} = \frac{1}{\phi_m}
 \end{aligned} \tag{3.17}$$

For the individual deep sediment sub-layers, the pore-water mass fraction is calculated as:

Fraction Dissolved in Pore Water, Deep Sediment Sub – layers = Fdps

$$\begin{aligned}
 &= \frac{\text{Mass of Constituent (Dissolved Form)}}{\text{Mass of Constituent (Dissolved Form)} + \text{Mass of Constituent (Particulate Form)}} \\
 &= \frac{1}{\phi_s + K_{ds}(1 - \phi_s)\rho_p} = \frac{1}{\phi_s}
 \end{aligned} \tag{3.18}$$



3.4 Addition of SEAM3D Packages (General Implementation)

The original form of the RECOVERY model provides a reasonable estimate of decay through the use of a first-order calculation as defined in Chapter 2. This is a conservative approach that represents several potential decay processes with a single, user-defined rate parameter. While first-order decay provides a reasonable estimate under specific conditions, it does not account for the limitations imposed by the microbial and geochemical populations that may or may not be present in the sediment. More specifically, the first-order approximation does not functionally relate the concentrations of controlling compounds or microbial populations to the calculated rate of decay. This shortcoming can result in significant errors in the calculation of decay rates for systems with rate-limiting characteristics. The inherent variability associated with this condition requires a more parameterized kinetic model coupled with a more rigorous simulation method. Additional discussion of the inappropriateness of the first-order decay representation with respect to PCB compounds is provided by Stow and Jackson (Stow, Jackson et al. 1999).

Once RECOVERY was modified to handle multiple constituents and to address each constituent category individually, the decay representation was adjusted to better represent the biotransformation of PCB compounds. The original, first-order decay term was replaced with a single variable, R_{BIO} , which is calculated through a series of subroutines that compose the Biodegradation (BIO) and Reductive Dechlorination (RDP) Packages from SEAM3D. For each mass balance equation, the R_{BIO} variable represents the rate of change due to biodegradation or biotransformation. For the ODE solution phase, each value of the R_{BIO} variable is subtracted from the additional mass balance terms for the mixed sediment layer. For the PDE solution, the R_{BIO} variable is multiplied by the previously-determined time step size and subtracted from the right-hand side array.



Figure 4 is a general depiction of the connection between the mass balance formulations from the original RECOVERY and the SEAM3D packages:

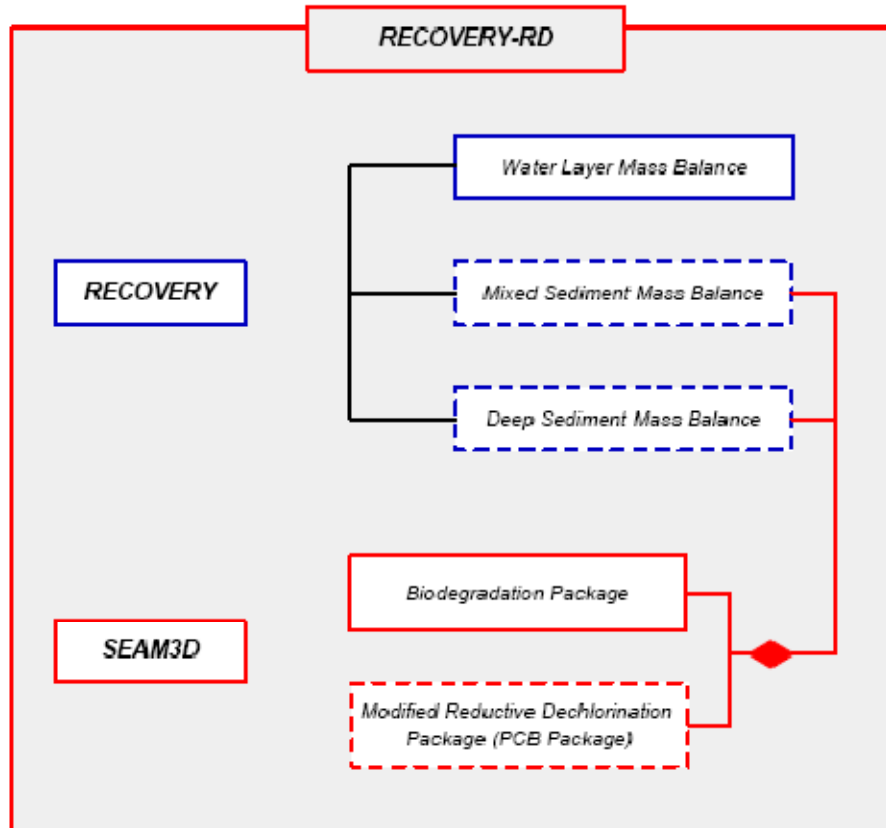


Figure 4: Overview of SEAM3D / RECOVERY Interaction. Dashed lines indicate modification from original version with respect to the calculation of decay.

Both of the SEAM3D packages were heavily modified to appropriately connect to the programmatic structure used in RECOVERY. The specific modifications to each package are individually discussed in the next two sections.



Modifications were also made to the structure of RECOVERY-RD to provide the appropriate set of input to the SEAM3D packages. Since SEAM3D addresses only the decay associated with pore-water solutes, the RECOVERY-RD concentrations required translation before being used in the SEAM3D calculations. This process is shown in Figure 5.



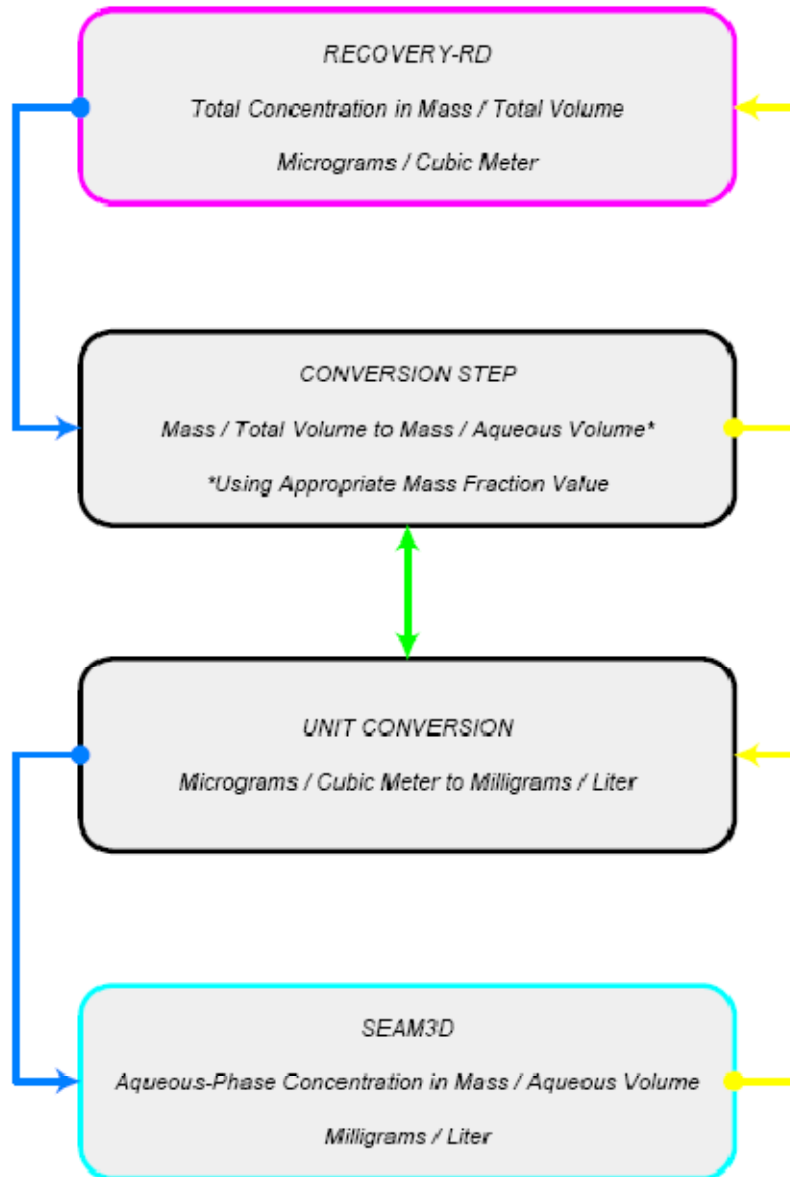
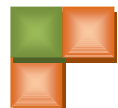


Figure 5: Conversion between RECOVERY-RD and SEAM3D Subroutines

The conversion process works in both directions, and is completed upon entering and exiting both of the SEAM3D packages, which are described in the following sections.



3.4.1 Biodegradation (BIO) Package

This section provides a brief explanation of the calculations performed within the Biodegradation package, as well as a detailed description of the modifications associated with the assimilation of the package with RECOVERY-RD. As discussed in Chapter 2, the Biodegradation (BIO) package from SEAM3D is a series of subroutines that models the biodegradation processes associated with the typical geochemical components of a contaminated saturated system. The rate of decay or generation is calculated using Monod-form expressions that utilize additional system constraints such as inhibition by more energetic compounds (Widdowson 2002). By integrating RECOVERY and the Biodegradation package, RECOVERY-RD becomes a model that is capable of not only simulating more complexity with respect to decay processes, but also has more potential for verification using field observations. In addition, the Biodegradation package provides RECOVERY-RD with the appropriate basis for the simulation of biotransformation of PCBs. The interaction between PCB congeners and the Biodegradation package is discussed in the next section.

The integration of RECOVERY and the Biodegradation package was initialized by combining the preliminary version of RECOVERY-RD with a subset of the subroutines that comprise the original Biodegradation package. The subset consisted of the following subroutines:



Subroutine	Function
BIO2DF	Organizes initial information for Biodegradation package
BIO2RP	Reads biodegradation input file
BIO2AL	Allocation of variable arrays with respect to the Biodegradation Package
BIO2AD	Updates solid-phase electron acceptor concentrations after each time step
BIO2SV	Calculates change in concentration for each category associated with the Biodegradation Package

Table 4: Biodegradation Package Subroutines Used by RECOVERY-RD

The remaining subroutines were determined to be unnecessary for the purpose of this study since they were associated with structured output related to more spatially complex SEAM3D simulations. This set of subroutines was then simplified through the removal of the non-reactive tracer, nutrient, and daughter product categories since they are not included as part of the structure of RECOVERY-RD and do not influence the rates associated with the remaining components. Finally, the influence of retardation



was removed from the main calculation subroutine, BIO2SV. This is due to the fact that RECOVERY-RD handles the impact of retardation through the use of mass fractions; therefore including this parameter would have been redundant and not accurate with respect to the mass balance expressions.

The resulting modified Biodegradation package was then connected to RECOVERY-RD as part of the ordinary differential equation solution phase. The existing Runge-Kutta solution was modified to include calls to the Biodegradation package subroutines during each derivative determination. Figure 6 shows the modified structure of the ODE solution:



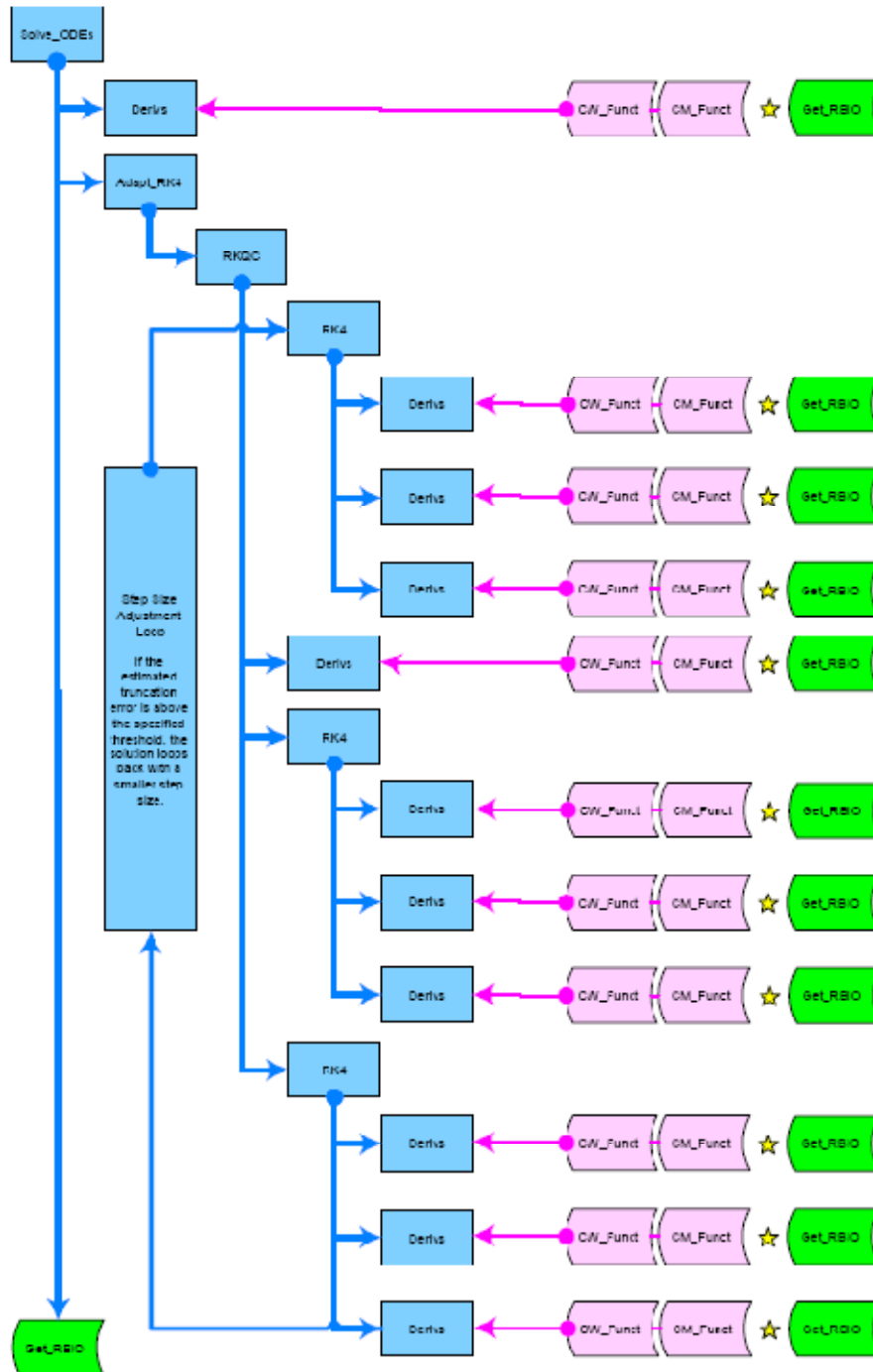


Figure 6: Modified ODE Solution Diagram, RECOVERY-RD. Blue shading indicates a separate subroutine. Pink shading indicates a separately defined program function.



As the figure indicates, each derivative approximation has two sources of input that combine within the 'Derivs' subroutine to form each respective mass balance equation. The first is the set of combined coefficients that were calculated as part of the initialization phase of the model. Each of these combined coefficients is multiplied by the appropriate regime concentration within the 'Cw_funct' and 'Cm_funct' functions. The second source of input is the set of resulting concentration changes attributed to biodegradation for each simulated constituent, which is represented by an array of variables " R_{BIO} ". The Biodegradation package calculates these values given the concentration of each constituent at the beginning of the time step and the appropriate interval, or time step size, over which decay and/or generation occurs. Due to the adaptive nature of the Runge-Kutta method, the interval size may change significantly over a single iteration. To appropriately address this characteristic, the calculations within the Biodegradation package must be repeated each time the concentration derivative with respect to time is re-approximated. An additional call to the Biodegradation package was also added as a final step in the ODE solution phase. This was done to ensure that the R_{BIO} values associated with the deep sediment sub-layers were calculated over the appropriate time interval, using the appropriate initial concentrations. The resulting discrepancy between the decay term formulations in the mixed and deep sediment regimes is discussed in Chapter 4.

For most compounds, the values of the R_{BIO} variable array represent a concentration decrease due to the biodegradation / biotransformation process. In the case of some constituents, such as PCB congeners or products of electron acceptor decay, they may also represent an increase in concentration, or production, due to the decay of a related constituent. The R_{BIO} term is calculated for each sediment layer and for each active constituent included in a given simulation. The value of this term is then added or subtracted from the mass balance equation for the appropriate layer and constituent, and finally



multiplied by the time step size to provide the cumulative change in concentration over the appropriate time interval.

In RECOVERY-RD, the calculation of the R_{BIO} variable follows modified versions of the Monod-form decay expressions used by SEAM3D. Each mass loss, or sink equation was modified to neglect the influence of nutrient limitations as shown below.

For each hydrocarbon substrate, ls :

$$R_{\text{sink},ls}^{\text{bio}} = \sum_x \frac{M_x}{\theta} \left(\sum_{le} \hat{q}_{x,ls,le} \left[\frac{\bar{S}_{ls}}{\bar{K}_{x,ls,le}^s + \bar{S}_{ls}} \right] \left[\frac{\bar{E}_{le}}{\bar{K}_{x,le}^e + \bar{E}_{le}} \right] I_{le,li} \right) \quad (3.19)$$

where:

M_x = Concentration of reducing microbial biomass population x [M/L^3]

θ = Porosity of sediment [dimensionless]

$\hat{q}_{x,ls,le}$ = Maximum rate utilization by Microcolony x for the use of hydrocarbon substrate ls and electron acceptor le [1/T]

\bar{S}_{ls} = Effective concentration of hydrocarbon substrate ls [M/L^3] defined as the difference between the current concentration, S_{ls}^i , and minimum concentration, S_{ls}^{min} .

$\bar{K}_{x,ls,le}^s$ = Effective half saturation constant for hydrocarbon substrate ls utilizing electron acceptor le [M/L^3] defined as the difference between the specified half saturation value, $K_{x,ls,le}^s$, and minimum concentration, S_{ls}^{min} .



\bar{E}_{le} = Effective concentration of electron acceptor le [M/L^3] defined as the difference between the current concentration, E_{le}^i , and minimum concentration, E_{le}^{\min} .

$\bar{K}_{x,le}^e$ = Effective half saturation constant for electron acceptor le [M/L^3] defined as the difference between the specified half saturation value, $K_{x,le}^e$, and minimum concentration, E_{le}^{\min} .

$I_{le,li}$ = Electron acceptor inhibition function representing inhibited use of electron acceptor le by more-energetic electron acceptor li [dimensionless]

It is important to note that the minimum, or threshold concentrations used in the expressions above are user-defined parameters that may be used to represent a concentration below which decay and/or generation processes become negligible. While the typical approach is to specify a minimum concentration of zero, some cases where supporting laboratory data exists may call for greater values. In such instances, the concentration may represent a threshold value below which extracellular processes become insignificant with respect to internal requirements such as cell maintenance (Widdowson 2002).

For each aqueous-phase electron acceptor, le :

$$R_{\sin k,le}^{bio} = \sum_x \frac{M_x}{\theta} \left(\sum_{ls} \gamma_{x,ls,le} \hat{q}_{x,ls,le} \left[\frac{\bar{S}_{ls}}{\bar{K}_{x,ls,le}^s + \bar{S}_{ls}} \right] \left[\frac{\bar{E}_{le}}{\bar{K}_{x,le}^e + \bar{E}_{le}} \right] I_{le,li} \right) \quad (3.20)$$



where:

$\gamma_{x,ls,le}$ = Use coefficient for mass unit of electron acceptor le required per mass unit of hydrocarbon substrate ls [dimensionless]

For each solid-phase electron acceptor, $le = 3,4$, corresponding to iron and manganese:

$$R_{sink,le}^{bio} = \sum_x \frac{M_x}{\rho_b} \left(\sum_{ls} \gamma_{x,ls,le} \hat{q}_{x,ls,le} \left[\frac{\bar{S}_{ls}}{\bar{K}_{x,ls,le}^s + \bar{S}_{ls}} \right] I_{le,li} \right) \quad (3.21)$$

Where electron acceptor inhibition is represented as:

$$I_{le,li} = 1 \quad \text{for } le = 1, \text{ oxygen} \quad (3.22)$$

$$I_{le,li} = \prod_{li=1}^{le-1} \left[\frac{K_{le,li}}{K_{le,li} + \bar{E}_{li}} \right] \quad \text{for } le = 2, 3, 4, 5, \text{ or } 6 \quad (3.23)$$

Source terms associated with products of electron acceptor decay were also adjusted to neglect the influence of nutrient limitation. For methane, the product generation term is represented as:

$$R_{source,CH_4}^{bio} = \sum_{ls} \zeta_{x,ls} \frac{M_x}{\theta} \left(\sum_{le} \hat{q}_{x,ls,le} \left[\frac{\bar{S}_{ls}}{\bar{K}_{x,ls,le}^s + \bar{S}_{ls}} \right] \left[\frac{\bar{E}_{le}}{\bar{K}_{x,le}^e + \bar{E}_{le}} \right] I_{le,li} \right) \quad (3.24)$$

where:

$\zeta_{x,ls}$ = Generation coefficient associated with methane production [dimensionless]



And for the remaining products of electron acceptor decay, the generation term is represented as:

$$R_{source,le}^{bio} = \zeta_{x,le} \frac{M_x}{\theta} \sum_{ls} \gamma_{x,ls,le} \hat{q}_{x,ls,le} \left[\frac{\bar{S}_{ls}}{\bar{K}_{x,ls,le}^s + \bar{S}_{ls}} \right] \left[\frac{\bar{E}_{le}}{\bar{K}_{x,le}^e + \bar{E}_{le}} \right] I_{le,li} \quad (3.25)$$

Where:

$\zeta_{x,ls}$ = Generation coefficient associated with products of electron acceptor decay
[dimensionless]

The calculations described above are part of the “bio2sv” subroutine portion of the Biodegradation Package. The other subroutines are used only during the first step through the ODE solution, with the exception of ‘bio2ad’. This subroutine is called during the final step through the ODE solution for each time step.

3.4.2 Modified Reductive Dechlorination Package / PCB Package

This section describes the modifications that were made to RECOVERY-RD that enabled the connection of the Reductive Dechlorination Package from SEAM3D. The section also describes the modifications made to the Reductive Dechlorination Package that led to the creation of the PCB Package. It is important to note that each component of the RDP from SEAM3D was immediately renamed once it was added to RECOVERY-RD. The naming convention was changed from ‘CHL’, indicating that the original package was associated with chlorinated ethenes, to ‘PCB’, which indicates



the focus of the new package on PCB compounds. Therefore, future references to the PCB package are referring to the modified set of calculations. While the modification process associated calculation structure was complex, the conceptual framework of the RDP served as the perfect basis for creating a PCB-specific biotransformation package.

The Reductive Dechlorination Package (RDP) is a series of subroutines that is included as an optional part of SEAM3D. The RDP is specifically formulated to address the biotransformation processes associated with the chlorinated ethene (PCE-TCE-DCE-VC, etc.) degradation chain. The calculated rates of decay and generation are functionally related to the system parameters as calculated by the Biodegradation package. Therefore, a simulation that utilizes the Reductive Dechlorination Package must also include the terms generated as part of the Biodegradation Package. As was the case with the Biodegradation Package integration, not all of the RDP subroutines were required within RECOVERY-RD.

Table 5 provides a description of the Reductive Dechlorination Package subroutines that were added to RECOVERY-RD:



<u>Subroutine</u>	<u>Function</u>
CHL2RP/PCB2RP	Reads reductive dechlorination/PCB dechlorination input file
CHL2AL/PCB2AL	Allocation of variable arrays with respect to the Reductive Dechlorination/PCB Package
CHL2SV/PCB2SV	Calculates change in concentration for each category associated with the Reductive Dechlorination/PCB Package

Table 5: Reductive Dechlorination/PCB Package Subroutines Used by RECOVERY-RD. Note that the naming convention was modified to reflect the focus of RECOVERY-RD.

Once the newly-renamed PCB Package had been connected to RECOVERY-RD, modifications were made to the entire model to address the biotransformation of PCB congeners. The following modifications were made to coincide with PCB-specific decay characteristics (Peloquin 2008):



Organization:

The organization of the input file associated with a particular simulation must reflect the generation of PCB congeners due to biotransformation. This being the case, the main RECOVERY-RD input file (.REC) must include a method to identify the potential product associated with each congener. To address this connection, the main input file was adjusted to include an identification number associated with the current PCB congener, as well as an identification of the potential product. The identification number was based on the BZ congener numbering system as defined by Ballschmiter (Ballschmiter and Zell 1980). Should a congener have no potential product, this number is set to a value of 0 (zero). This task is handled by the Excel-based preprocessor which also generates the entire series of congener products depending on a user-defined selection of decay processes. The factors that control the product generation associated with the biotransformation of a particular parent PCB congener were identified by Peloquin (Peloquin 2008). In addition, the PCB category of the main input file was sequentially ordered from highest BZ number to lowest BZ number. This was done to reflect the order in which the congeners would be expected to decay.

Inhibition:

The Reductive Dechlorination Package recognizes the potential for inhibited decay due to the presence of a more-chlorinated compound. This is accomplished through the use of an inhibition term that is based on the existing concentrations of the more chlorinated compound or compounds, as well as a user-defined inhibition factor (Widdowson 2002). In the case of PCB compounds, decay is completely inhibited by the presence of more chlorinated congeners. With this in mind, the calculation structure of the RDP was completely reformatted. The calculation of a congener-specific inhibition term



was replaced with a test that corresponds to each layer of the model excluding the water column. For each time step, the current concentration of the actively-decaying congener in each sediment layer is compared to the user-defined threshold concentration for PCB congeners. No additional decay occurs below the threshold value for any simulated PCB congener. The comparison ensures that the most-chlorinated PCB congener present in each layer will be the first to decay. Figure 7 shows the process associated with the test:



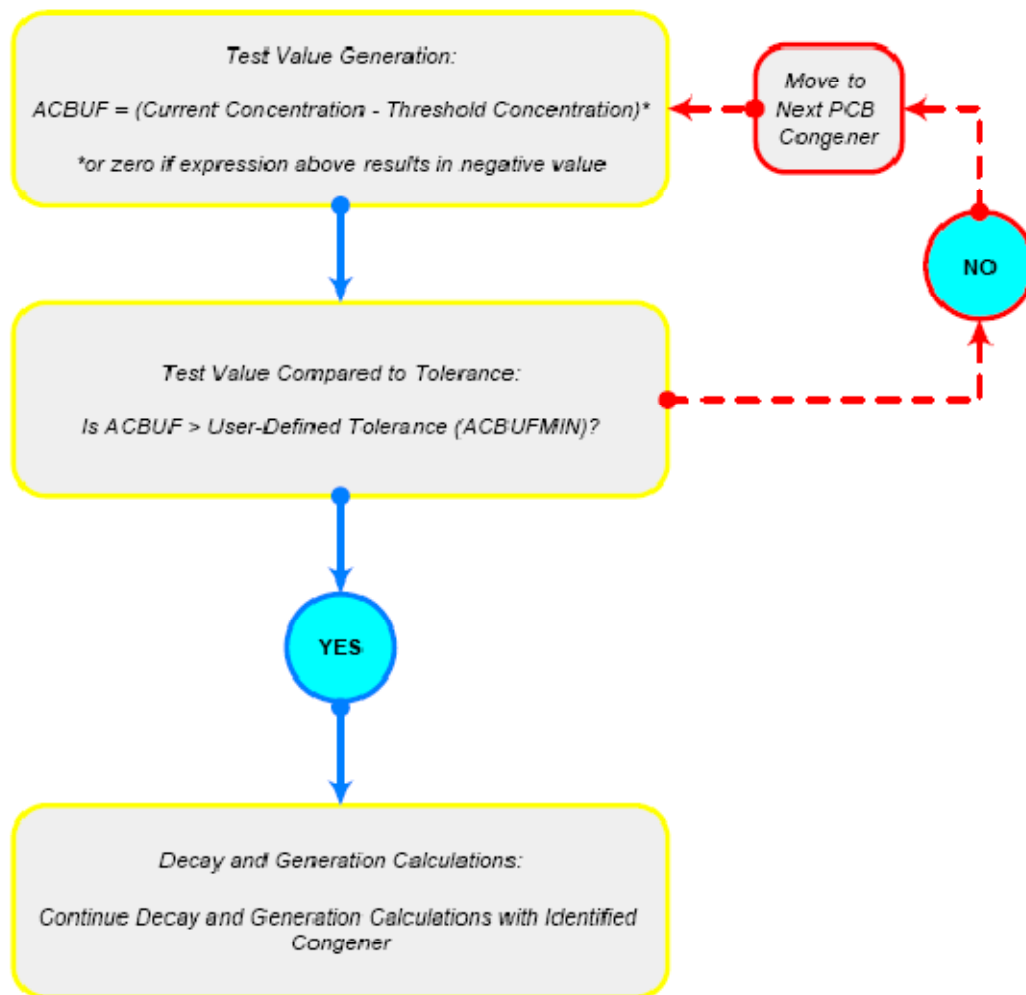


Figure 7: Identification of Currently-Decaying PCB Congener

During the initial phase of testing, the comparison described above was made directly between the current and threshold concentrations. The results showed that when compared to an appropriately-defined SEAM3D proxy, the model was not appropriately transitioning the decay calculations to the next congener in line when the original parent reached the threshold value. This was determined to be the result of the difference between using a direct comparison to the threshold concentration as opposed to the use of an inhibition function, as is the case with the Reductive Dechlorination Package. The

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inhibition function used by the RDP generally follows the form shown in Equation 3.23 with the exception of the fact that inhibition factors are required for each of the simulated chlorinated ethene compounds. The resulting value of this function controls the rate of decay associated with each of the less-chlorinated compounds. When using low inhibition factors, the model is simulating significant inhibition with respect to more-chlorinated compounds, and the decay rates associated with each of the less-chlorinated compounds will be essentially zero. This condition will persist until the concentration of the most-chlorinated congener becomes small, at which time decay will transition to the next constituent. While this condition essentially mimics what is done within the PCB package, the use of the inhibition function helps to overcome the condition where the concentration of the most-chlorinated compound approaches the threshold value, but never exactly reaches it. This becomes problematic when considering the PCB package since the representation of inhibition by more chlorinated congeners was completely removed.

To address this issue, an additional parameter was added to accelerate the transition process within the PCB package as compounds approach the defined threshold value. This parameter, which is referred to in Figure 7 as the “User-Defined Tolerance” and within the program as “ACMINBUF”, represents the difference between the current and minimum concentrations that cannot be reasonably defined. That is, the tolerance value provides a small buffer for the threshold concentration that protects the numerical precision of the concentration calculations as they are compared to the specified minimum. More specifically, the tolerance value is intended to help the PCB package appropriately simulate the transition points between decay and generation for PCB congeners as they are temporally identified by the Reductive Dechlorination Package.



The testing process associated with the PCB Package also indicated that the appropriate tolerance or buffer value for a particular simulation varied depending on the rate of congener decay, which is relatively constant for all PCB congeners. This rate can be generally estimated from the controlling parameters, which are the maximum rate of substrate utilization and effective half saturation constant for PCBs. The relationship between the generalized rate of congener decay and the tolerance value was developed using a series of simulations described below in Table 8:

Each row in the table above describes the rate parameters for a pair of simulations organized in the same manner as Test Case II, which is described in Chapter 4. The point of the paired structure was to match results from a MODFLOW/SEAM3D simulation through manual manipulation of the tolerance value within a corresponding RECOVERY-RD model. The generalized rate parameters were assigned in a manner that represents the range of possibility for both values. Essentially, the point was to represent the range of potential PCB decay rates and by doing so, determine a relationship that can be used within the model to define the appropriate tolerance value for a given application. The simulations described in Table 6 provided the series of data points shown below.



SEAM3D Run ID	V_{max}	K	PCE Initial Concentration	V_{max}/K	Best Fit Tolerance Value
1	10	10	10	1	2.00E-05
2	10	10	1	1	3.00E-05
3	10	10	0.1	1	3.00E-05
4	10	1	10	10	1.00E-04
5	10	1	1	10	5.00E-05
6	10	1	0.1	10	2.00E-05
7	10	0.1	10	100	1.00E-45
8	10	0.1	1	100	1.00E-40
9	10	0.1	0.1	100	1.00E-33
10	1	10	10	0.1	2.00E-05
11	1	10	1	0.1	2.00E-05
12	1	10	0.1	0.1	2.00E-05
13	1	1	10	1	2.00E-05
14	1	1	1	1	2.00E-05
15	1	1	0.1	1	2.00E-05
16	1	0.1	10	10	1.00E-04
17	1	0.1	1	10	1.00E-04
18	1	0.1	0.1	10	5.00E-05
19	5	10	10	0.5	2.00E-05
20	5	10	1	0.5	2.00E-05
21	5	10	0.1	0.5	2.00E-05
22	5	1	10	5	3.00E-05
23	5	1	1	5	3.00E-05
24	5	1	0.1	5	2.00E-04
25	5	0.1	10	50	1.00E-20
26	5	0.1	1	50	1.00E-20
27	0.1	0.1	0.1	1	2.00E-05

Table 6: Simulation Parameters for Tolerance Value Determination



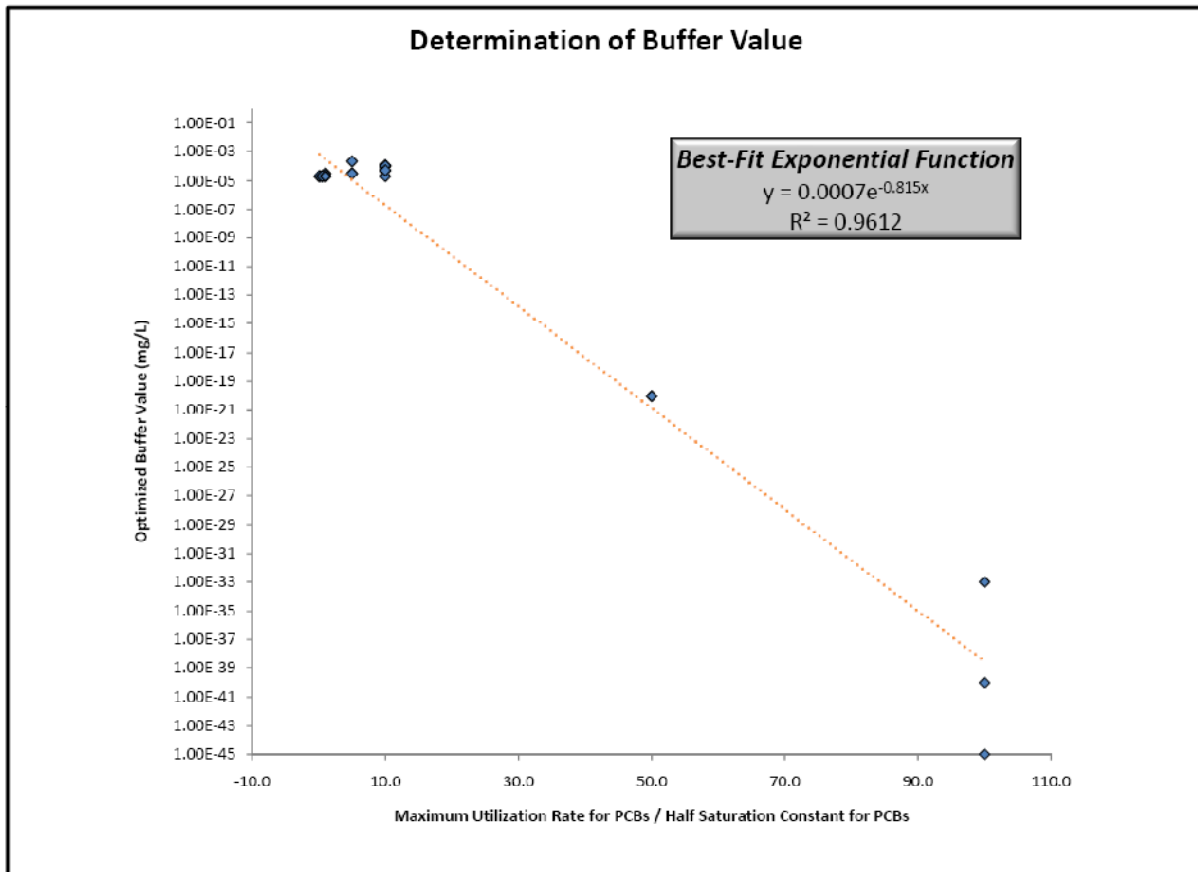


Figure 8: Determination of Buffer Value

The comparison shown in Figure 8 was made between the manually-calibrated buffer value and a ratio representing the relationship between the two controlling rate parameters for each simulation. While this dataset is highly skewed toward the smaller ratio values, this method of comparison provided the best opportunity for the definition of a functional relationship that spanned the gambit of simulated parameters. The regression results showed that an exponential function provided the best fit to the entire set of data, which was the desired goal of this portion of the creation process.



The resulting exponential function was then slightly modified to include the influence of non-zero threshold concentrations as follows:

$$y = 0.0007 * e^{-0.815*X} + ACMIN \quad (3.26)$$

Note: *ACMIN represents the threshold, or minimum concentration for all PCB congeners.*

Equation 3.26 was inserted into the PCB package as an internal mechanism for the calculation of the tolerance value. For each simulation, the model uses the user-defined rate parameters along with Equation 3.26 to determine the appropriate buffer value. The functionality of this portion of the model is displayed as part of test cases II and III in Chapter 4.

Microbial Populations:

The RDP allows the user to define several microbial populations that specifically reduce a particular set of chlorinated ethene compounds. In the case of PCB congeners, a single population is adequate (Peloquin 2008). Therefore, the calculation structure of the PCB package was limited to the use of a single microbial population for all potential congeners in a given simulation.

Product Generation:

The generation of product congeners was modified to follow the parent-product structure defined in the modified main input file. That is, for a given decaying parent compound, generation is assigned to the congener identified as the potential product. This appropriately addresses standard reduction as well as the situation where multiple parent congeners produce the same product congener. As is the case with the decay of chlorinated ethene compounds, chloride is produced as a byproduct of each parent-daughter pair. To adequately represent chloride production, a specific set of input

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parameters was defined at the end of the PCB congener category. This set of input corresponds to chloride, which provides a tracking mechanism within RECOVERY-RD.

Direct Oxidation:

Along with the reductive dechlorination process, the RDP has the capability of simulating mass loss due to direct oxidation for 1-2 dichloroethene (DCE) and vinyl chloride (VC). This was applied to the PCB package for PCB congeners with BZ identifications between 1 and 39.

Time Stepping:

The original time step modification process of the ODE solution had the potential to be problematic with respect to the representation of biotransformation of PCB congeners. The issue lies in the congener-product relationship, and how the decay process transitions between each pair of compounds. As the concentration of a particular parent congener approaches the threshold, the associated decay rate decreases due to the form of the Monod expression. If this condition exists in the mixed sediment layer, the ODE solution may respond by increasing the time step size. This has the potential to be problematic since the increase in time step size may adversely affect the point at which the decay calculation transitions to the product or the congener with the next-highest BZ number.

To prevent this from occurring, the ODE solution was modified to limit the time step size to a maximum of one month. The solution is still allowed to vary the step size, but in the event that the step exceeds one month, the step is reduced back to the initial size of 0.001 years. While this may not be the optimal solution, it does provide the model with the flexibility that is gained from the adaptive nature as well as the precision to accurately simulate the sequential decay of PCB congeners.



3.5 Addition of Non-Linear Partition Isotherm Option

This portion of the modification process involved alterations associated with the partitioning characteristics discussed in Chapter 2. As previously discussed, the original RECOVERY represents solute partitioning in each of the three model regimes using a linear isotherm. The fraction of solute associated with the aqueous and solid phases is based on a user-defined partitioning coefficient, k_d . To more-precisely model the sorption processes typically associated with PCB compounds, RECOVERY-RD has been expanded to include the ability to represent more complex isotherms. The partitioning characteristics of PCB compounds were identified by Peloquin (Peloquin 2008).

Two additional sorption isotherms were added to RECOVERY-RD by modifying the calculation of the partitioning coefficient using the following expression:

$$K_d = \left[f_1 K_{f1} (A_d)^{N_1-1} + f_2 K_{f2} (A_d)^{N_2-1} + f_3 K_{f3} (A_d)^{N_3-1} \right] \quad (3.27)$$

Where the parameters in Equation 3.27 are defined as follows:

N_1 = Freundlich exponent for fraction 1 [dimensionless]

N_2 = Freundlich exponent for fraction 2 [dimensionless]

N_3 = Freundlich exponent for fraction 3 [dimensionless]

K_{f1} = Partitioning Coefficient for fraction 1 [m^3/g]

K_{f2} = Partitioning Coefficient for fraction 2 [m^3/g]

K_{f3} = Partitioning Coefficient for fraction 3 [m^3/g]



- f_{1w} = Fraction 1 in water [dimensionless]
- f_{1m} = Fraction 1 in mixed sediment [dimensionless]
- f_{1d} = Fraction 1 in deep sediment [dimensionless]
- f_{2w} = Fraction 2 in water [dimensionless]
- f_{2m} = Fraction 2 in mixed sediment [dimensionless]
- f_{2d} = Fraction 2 in deep sediment [dimensionless]
- f_{3w} = Fraction 3 in water [dimensionless]
- f_{3m} = Fraction 3 in mixed sediment [dimensionless]
- f_{3d} = Fraction 3 in deep sediment [dimensionless]

As Equation 3.28 indicates, the expression for the modified partitioning coefficient is based on three fraction values that are determined from the following relationships:

$$f_2 = \text{TOC}/F_2 \quad \text{Note: when } F_2 = 0, f_2=0$$

$$f_3 = \text{TOC}/F_3 \quad \text{Note: when } F_2 = 0, f_2=0 \quad (3.28)$$

$$f_1 = \text{TOC} - f_2 - f_3 = f_{oc}$$

RECOVERY-RD was modified to address non-linear partitioning through the implementation of the equations described above. The parameters required for the calculation of the modified partitioning coefficient are included in a specific non-linear partitioning file that is created by the preprocessor. The file is only created and included as part of a simulation when input is provided that is consistent with a



non-linear isotherm. If the file is not created, and is therefore not present in the working directory, RECOVERY-RD defaults to the standard linear isotherm.

In addition, RECOVERY-RD was modified to recognize total organic carbon (TOC) instead of the fraction of organic carbon (FOC) when non-linear partitioning is in use. The specification of TOC completely replaces FOC when non-linear partitioning is active, which allows for the calculation of the fraction values described by Equation 3.28. The TOC value may vary with depth in the deep sediment system using the user layers option provided for FOC.

Although the non-linear partitioning option was part of the creation of RECOVERY-RD, it is not included as part of the testing process associated with this thesis. The complexity of the required tests exceeded the scope of this study. However, verification of the non-linear partitioning representation within RECOVERY-RD is expected to be included in a future publication by Peloquin (Peloquin 2008).

3.6 Retention of First-Order Decay Kinetics (Pseudo-First-Order)

While the inclusion of the SEAM3D packages created a model with more detail, it was also important to retain a more generic decay representation. In many cases, data availability may hinder the ability to apply a complicated representation of decay. In such instances, the first-order decay representation may be more appropriate. Therefore, the user is provided the opportunity to decide between the full decay solution, and a pseudo-first-order representation that is based on a linearized version of the fully decay representation. To address this issue, the PCB decay expressions within RECOVERY-RD were modified to include an additional parameter, ϵ , which has a value of either 1 or 0



depending on the user's choice of decay representation as defined during preprocessing. Equation 3.29 shows the modified expression:

$$\begin{aligned}
 R_{\text{sink},lc}^{\text{bio}} &= R_{\text{sink},lc}^{\text{bio},rd} + R_{\text{sink},lc}^{\text{bio},ox} \\
 &= \left(\frac{M_x}{\theta} \right)^{(\varepsilon)} \left(\hat{q}_{x,lc,le}^{rd} \left[\frac{\bar{C}_{lc}}{\bar{K}_{x,lc,le}^e + (\varepsilon) * \bar{C}_{lc}} \right] I_{lc,li} \right) \\
 &\quad + (\varepsilon) * \sum_x \frac{M_x}{\theta} \left(\hat{q}_{x,lc,le}^{ox} \left[\frac{\bar{C}_{lc}}{\bar{K}_{x,lc,le}^{ed} + \bar{C}_{lc}} \right] \left[\frac{\bar{E}_{le}}{\bar{K}_{x,le}^e + \bar{E}_{le}} \right] I_{le,ox} \right)
 \end{aligned} \tag{3.29}$$

Should the user choose to revert to the original first-order representation, ε is given a value of 0.

Otherwise, ε is equal to 1.0, and the PCB decay calculation follows the full Monod-form expression. A comparison of the results provided by this method to the original first-order representation is included in Chapter 4.



4 Results and Discussion

4.1 Introduction

RECOVERY-RD was verified using a series of test cases designed to probe the modifications made to the original RECOVERY code. Each step in the testing process represents an increase in the complexity with respect to process representation. The results of each test case were compared to reasonable surrogates which vary in form depending on the complexity associated with the simulation. The results of Test Case I are compared to a series of simulations using version 4.3.1 of the unmodified version of RECOVERY. The results from Test Cases II and III are compared to an appropriately-simplified MODFLOW/SEAM3D simulation created using the pre- and post-processor GMS. Test Cases IV and V are compared to the results of Test Case III. In addition, an example application of the final version of the model is included after the series of test cases. The RECOVERY-RD test cases and the respective surrogates are described in detail for each test case below.

4.2 Test Case I: Multiple Constituents

4.2.1 Purpose

The purpose of the first test case was to verify that initial version of RECOVERY-RD was cycling through multiple constituents and producing results that matched the outcome of individual runs completed using RECOVERY. At this point in the modification process, changes were consistent with the descriptions provided in Sections 3.1 and 3.2. This was important as a prelude to the inclusion of



concentration-dependent, Monod-form decay terms in the mixed and deep sediment mass balance expressions.

4.2.2 Setup

The first test case was organized by simulating the transport of two generic compounds using RECOVERY and RECOVERY-RD. The RECOVERY model was created using version 4.3.1, which includes the GUI pre-processor. The two compounds were simulated independently using identical system parameters and chemical properties for both model applications. A list of the input parameters used for this simulation is included in Appendix A. The RECOVERY-RD model used the identical set of input parameters that were created using the associated Excel-based pre-processor. A copy is included in Appendix B.

The simulation was organized to have relatively high initial concentrations in the water column and mixed sediment layers. In the deep sediment, the initial concentrations for both constituents are set to zero. This allows the model to simulate the progression of contamination through an initially clean series of deep sediment sub-layers.

4.2.3 Assumptions/Simplifications

While the compounds simulated in this test case are specifically named, it is important to understand that their parameter values may not be appropriately defined due to the ambiguous nature of the test case. The parameters were specifically chosen to correspond between the two models and



to provide large mass balance terms that would highlight differences in the results, not to reflect the actual parameters associated with a particular compound. That is, the parameter values reflect the purpose of the test case and are not intended to provide an accurate transport simulation.

Due to the decay representation discrepancy between the RECOVERY and RECOVERY-RD, the decay term in the mass balance equation was eliminated from both versions. The individual terms for the three flow regimes were eliminated from RECOVERY by setting the decay constant to 0. This was reproduced within RECOVERY-RD by manually altering the biological decay term to be a constant value of zero for each time step. This ensured that RECOVERY-RD would not be calculating mass loss due to biodegradation or any other decay mechanism. An alternative testing approach using the pseudo first-order decay representation is presented in test case V.

Due to the adaptive step-size nature of the two models, it was assumed that the RECOVERY-RD results would not exactly match those produced with the original RECOVERY. This is attributed to the fact that when using RECOVERY-RD, the step size will be controlled by the constituent with the most rapidly changing concentration over a particular time interval. In the case of the original RECOVERY, the simulation has only one possible constituent that will control the time step size. With this in mind, the results were analyzed on an interval basis by the solution at particular points within the modeled time frame that correspond closely to each other. In addition, this test case was conducted before the addition of the step-size cap. At this point in the modification process, there was no need for this mechanism since the model was incapable of calculating production. Therefore, the results produced for this test case may differ slightly from those produced with the final version of RECOVERY-RD. The concentration calculations would be essentially identical, but the time step sizes would differ significantly.



4.2.4 Results

The results of Test Case I are organized according to the modeled constituent. The predicted concentrations are compared in the water column, mixed sediment layer, and each of the first ten deep sediment sub-layers. The transient predictions are provided for the first two model units, and a final profile is provided for the group of deep sediment sub-layers. Both models are compared over a 10 year simulation period. The figures below compare the simulated concentrations for the two modeled constituents in the water column and mixed sediment layers:



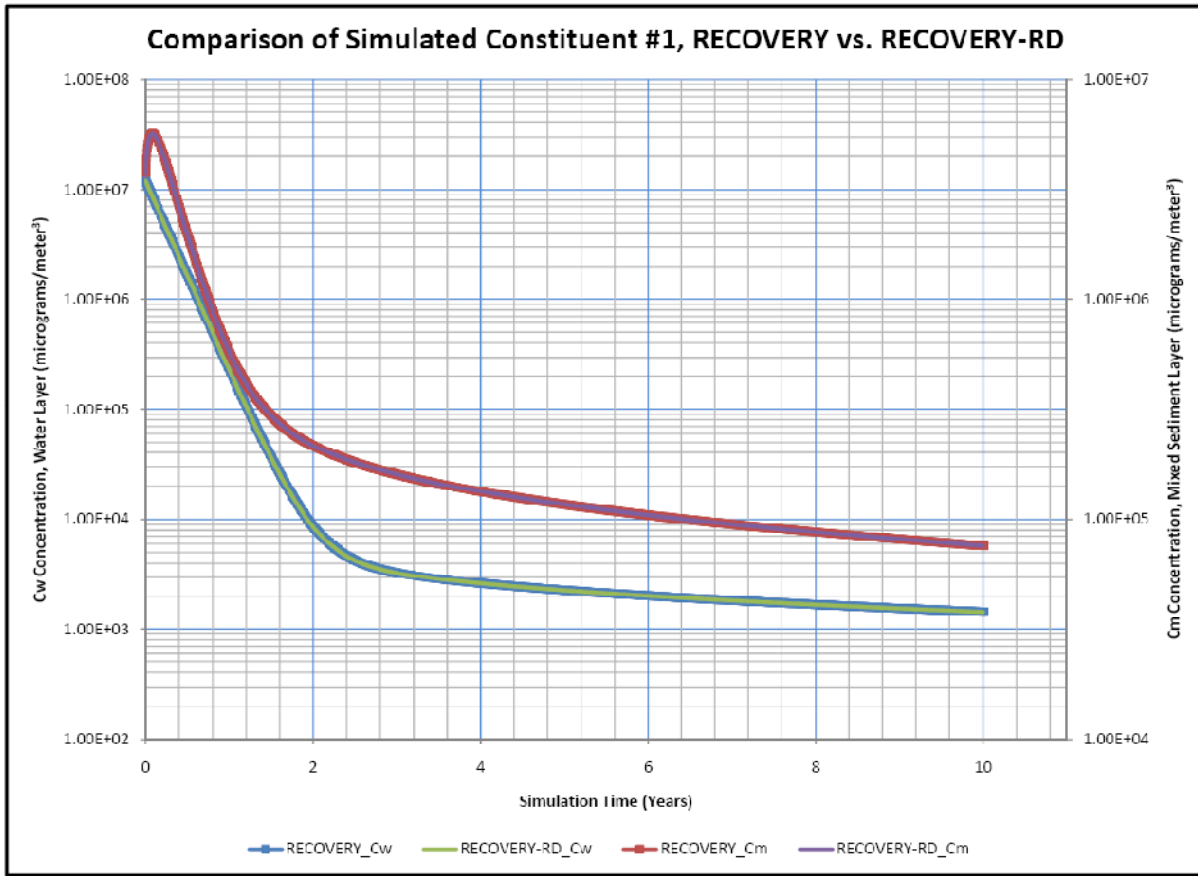
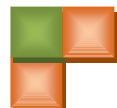


Figure 9: Test Case I, Constituent #1



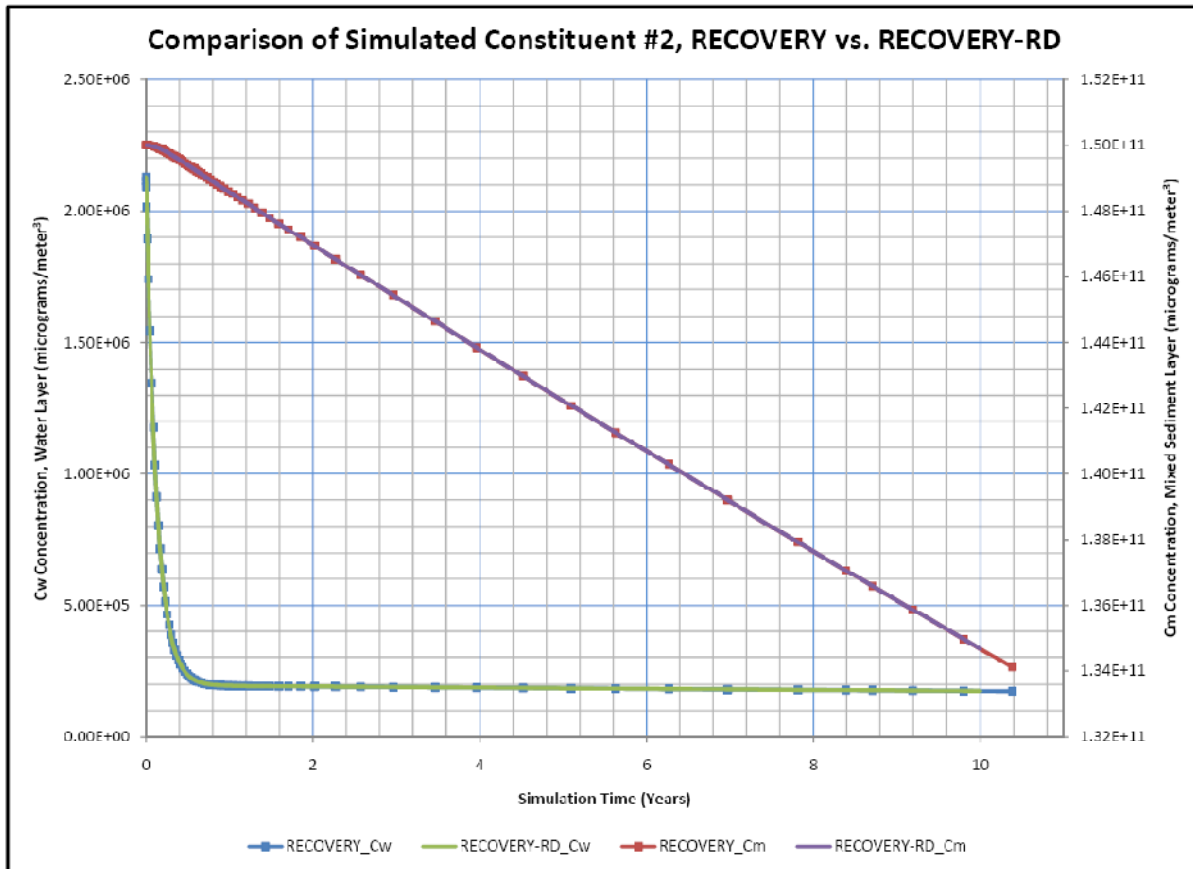


Figure 10: Test Case I, Constituent #2

Figure 9 and Figure 10 show that there is no discernable difference between the model predictions in the top two layers. This indicates that RECOVERY-RD is successfully reproducing the results obtained from individual RECOVERY simulations. In other words, the modifications made to the ODE solution have not adversely affected the accuracy of the model predictions. This is of particular importance since the ODE solution not only initializes, but more importantly drives the entire solution process associated with both models. Figure 10 shows the “overshoot” produced by the RECOVERY simulation in late time.



This is the result of the adaptive solution method recognizing a relatively small concentration gradient with respect to time. In such a case, the step size will be increased based on a code-defined threshold. This “overshoot” was expected to be associated with the constituent that had the lowest rate of concentration change in the water column and mixed sediment layers.

While the comparison of the upper units verifies the consistency of the ODE approximations, it was also important to compare the predictions in the deep sediment system. This ensures that no errors exist in the solution phase associated with the solution of the series of partial differential equations representing the deep sediment unit. Figure 11 and Figure 12 show the predicted concentration profiles for both modeled constituents:



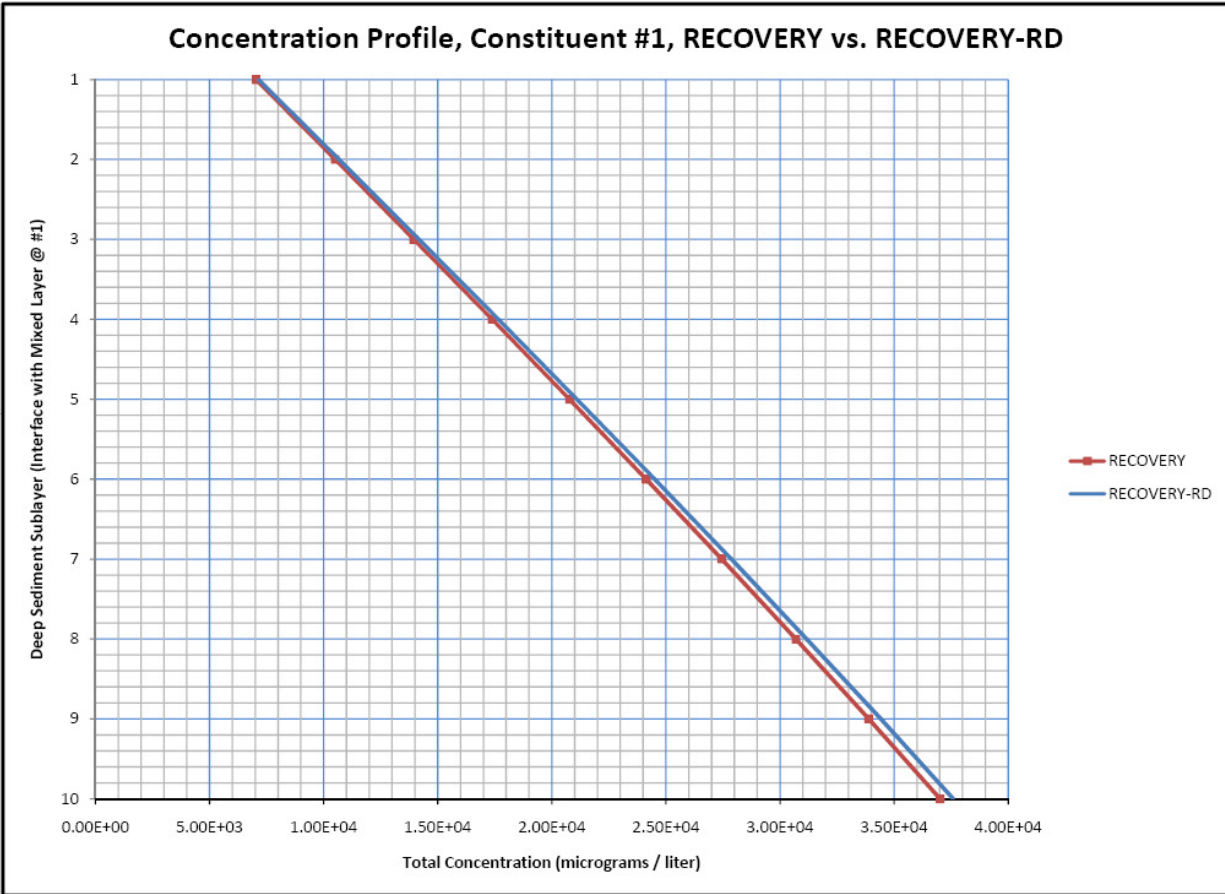


Figure 11: Test Case I, Deep Sediment Profile of Constituent #1 at End of Simulation



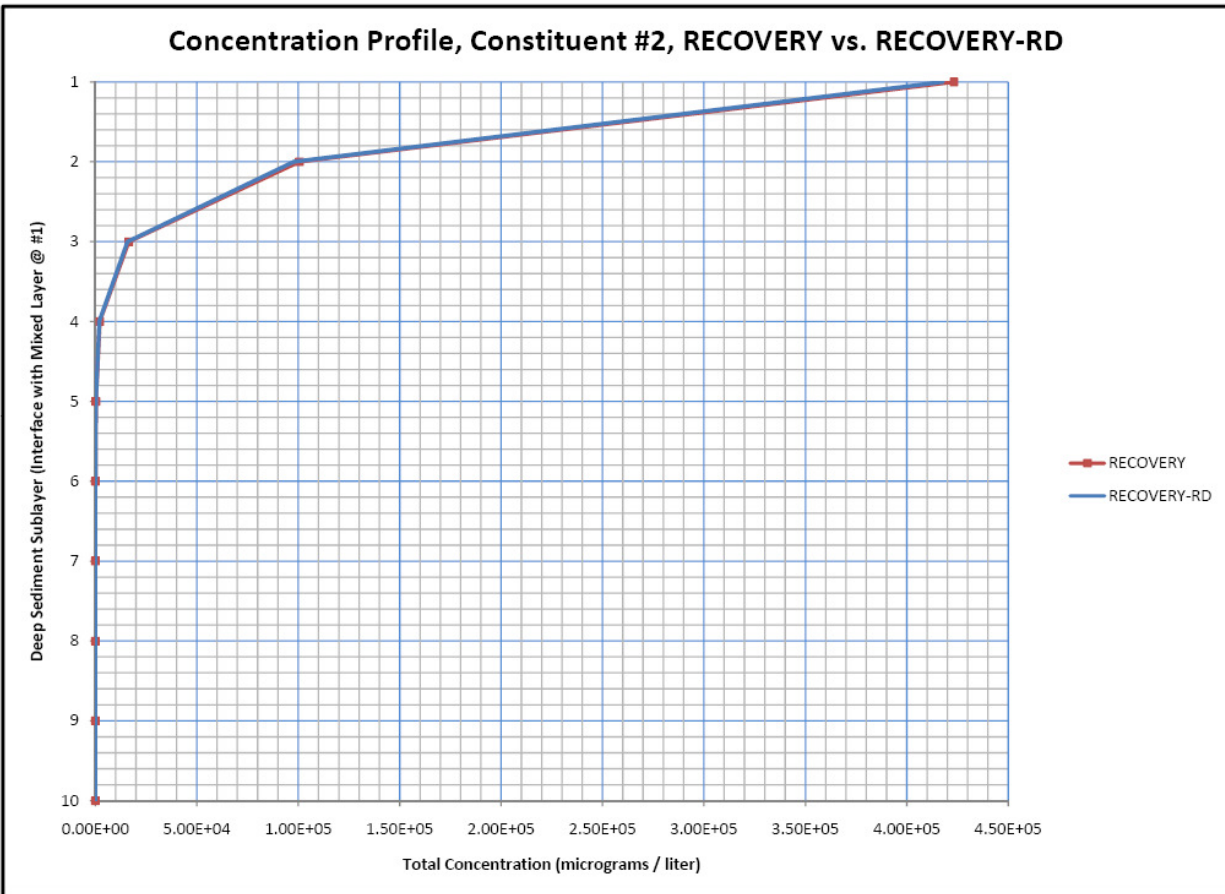


Figure 12: Test Case I, Deep Sediment Profile of Constituent #2 at End of Simulation

The close correspondence between the deep sediment concentration profiles displayed above indicates that the modifications associated with the PDE solution have maintained the consistency of the original approximation method. The slight divergences apparent in Figure 11 and Figure 12 are due to small differences between the times at which the two models are compared. Each profile was based on the final time step for each model, and in the case of both constituents, the final time values did not exactly match. The result is an imperfect comparison, but one that provides a general idea of model performance.



The results of Test Case I indicate that RECOVERY-RD is accurately reproducing the results that would be expected from individual simulations using the original version of RECOVERY. The cumulative simulation time differences are explained by the modifications made to the time step calculation portion of the ODE solution. This set of results indicated that the initial version of RECOVERY-RD was suitable for the second set of modifications.



4.3 Test Case II: BIO and PCB Packages

4.3.1 Purpose

The purpose of this test case was to examine the connection between RECOVERY-RD and the modified set of subroutines that represent the Biodegradation and Reductive Dechlorination Packages from SEAM3D. The connection process associated with each package was accomplished independently including the modifications involved with converting the Reductive Dechlorination Package to the PCB Package.

4.3.2 Setup

Test Case II was organized to represent the biotransformation process initialized by PCB congener 125, as identified by the BZ numbering system. To maintain a relatively simple simulation, a single hydrocarbon substrate was simulated under aerobic and methanogenic conditions. The initial concentration distribution of oxygen was limited to very low concentrations in each of the modeled units. Table 7 provides a list of the simulated constituents:



Substrate	Electron Acceptor	Product of Electron Acceptor Decay	PCB Congener (BZ #)	Products of PCB Decay
<i>Hydrocarbon #1</i>	$O_2(aq)$	--	125	$Cl^-(aq)$
--	$CO_2(aq)$	$CH_4(aq)$	71	--
--	--	--	32	--

Table 7: Simulated Constituents for Test Case II

As the table indicates, PCB-125 creates two additional congeners when reduced under the specified conditions. Chloride is also produced as a byproduct of the reduction process. The final congener, PCB-32, is also subject to mass loss due to direct oxidation since it's associated BZ identification is below the threshold value of 39. Figure 13 shows the decay and generation associated with each congener. The



rate of product generation associated with each parent congener is controlled by specified stoichiometric relationships.

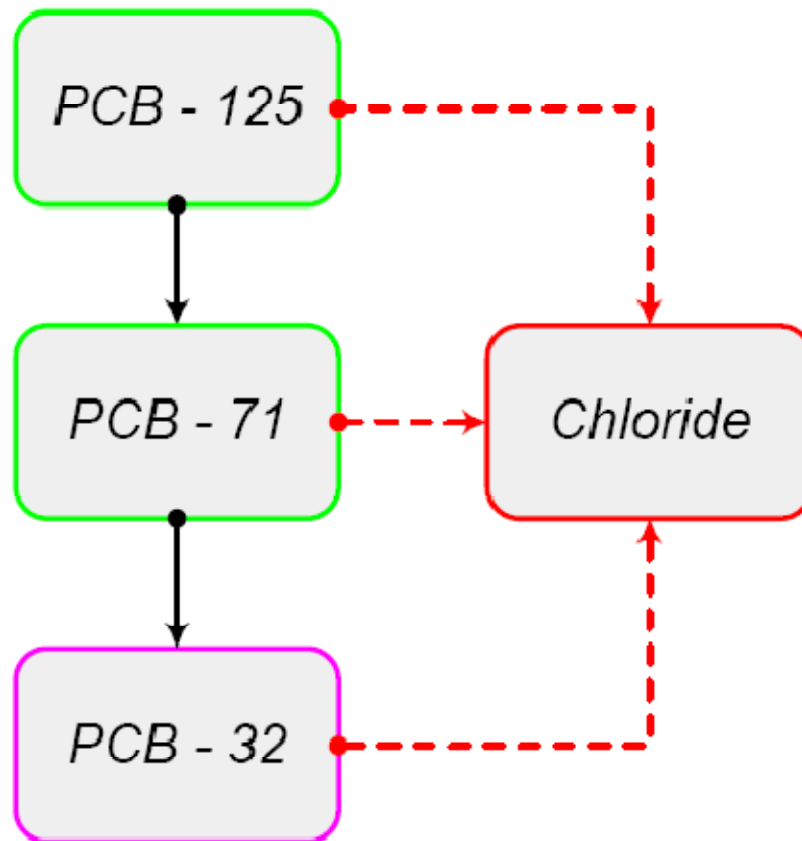


Figure 13: Biotransformation Process in Test Case II. Note: Pink outline indicates congener subject to direct oxidation.



A comparable MODFLOW/SEAM3D simulation was organized to reflect an identical system to that being modeled with RECOVERY-RD. Figure 14 provides a general depiction of the MODFLOW grid associated with this test case:

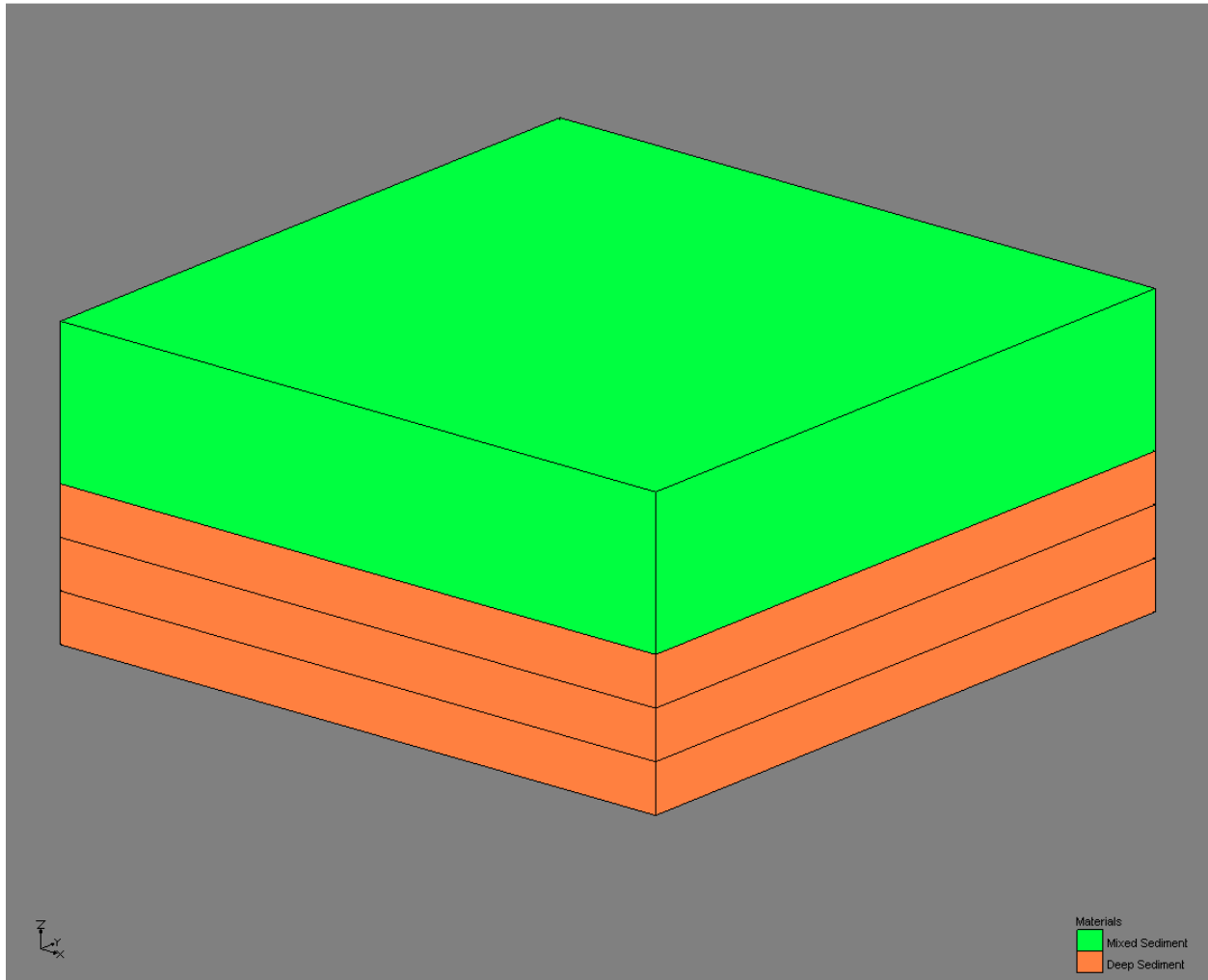
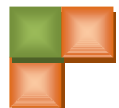


Figure 14: MODFLOW/SEAM3D Model Grid

The physical specifications and boundary conditions were applied in a manner that eliminated cell to cell flux, therefore removing physical transport due to advection, dispersion, and diffusion. In addition, the

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specifications associated with biodegradation and reductive dechlorination were adjusted to create an appropriate comparison between the two simulation methods. The input to the Biodegradation and Reductive Dechlorination Packages is included in Appendices C and D. Applying the RDP as a proxy for the PCB Package, three chlorinated ethene compounds were used to represent the series of PCB congeners simulated with RECOVERY-RD. Table 8 shows the correspondence between compounds for the two representations:

PCB Package		RDP
<i>PCB-125</i>	↔	<i>PCE</i>
<i>PCB-71</i>	↔	<i>TCE</i>
<i>PCB-32</i>	↔	<i>DCE</i>
<i>Chloride</i>	↔	<i>Chloride</i>

Table 8: Reductive Dechlorination and PCB Package Comparison, Test Case II



4.3.3 Assumptions/Simplifications

Both models were simplified to eliminate all potential discrepancies between the mass balance representations. This was accomplished within RECOVERY-RD by manually altering the internal mass balance expressions to only account for the biological decay and generation terms. All other terms in each of the mass balance expressions (with respect to the modeled constituents) were set to 0 by default. Partitioning between phases was also essentially eliminated from the RECOVERY-RD simulation by manually setting the Octanol-water partitioning coefficients for the hydrocarbon substrate and PCB congeners to very low values. This basically results in the simulation of entirely aqueous-phase solutes.

The simplification of the SEAM3D simulation was slightly more complicated due to the two-step process associated with flow and transport modeling under the MODFLOW construct. First, the influence of advection was eliminated by creating a MODFLOW simulation with no flow gradient. This was easily accomplished using identical boundary condition definitions. Essentially, this reduced the cell-by-cell flow terms calculated by MODFLOW to zero values. Second, the influence of dispersion was eliminated by defining a zero value for the dispersivity of each model layer. Finally, diffusive effects were eliminated by setting the diffusion coefficient to zero. In both cases, the result is a model that only represents the loss and generation of mass due to biotransformation.

Under the conditions described above, contaminant transport between model layers is completely eliminated. With this in mind, model results were only compared between the two models for the mixed sediment layer and the first three deep sediment sub-layers. This simplified the production of the MODFLOW/SEAM3D model since only four total model layers were required. In SEAM3D, the input to the Reductive Dechlorination Package was carefully adjusted to provide the best possible match between the chlorinated ethene compounds and the PCB congeners being simulated by



RECOVERY-RD. The most significant simplification was related to the terms representing inhibition by more-chlorinated compounds. To match the RECOVERY-RD representation, these inhibition terms were given extremely large values. Although this brings the biotransformation representations supplied by the RDP and PCB-P closer together, it was assumed that the results would not exactly match. This is mainly due to the different methods used by the two packages with respect to decaying compounds. In SEAM3D, the inhibition terms control the decay rates associated with each of the chlorinated ethene compounds. In RECOVERY-RD, a single PCB congener decays until it reaches the specified threshold, then the code identifies the congener to which the decay calculation should transfer.

4.3.4 Results

The results of Test Case III are summarized in two parts. The first is a comparison of the substrate, electron acceptor, and product categories for the two models. The concentration changes associated with this set of constituents is handled by the Biodegradation Package for both models. Figure 15 shows the concentration in layer 1 of the SEAM3D model, which corresponds to the mixed sediment layer in the RECOVERY-RD representation, as it changes with time:



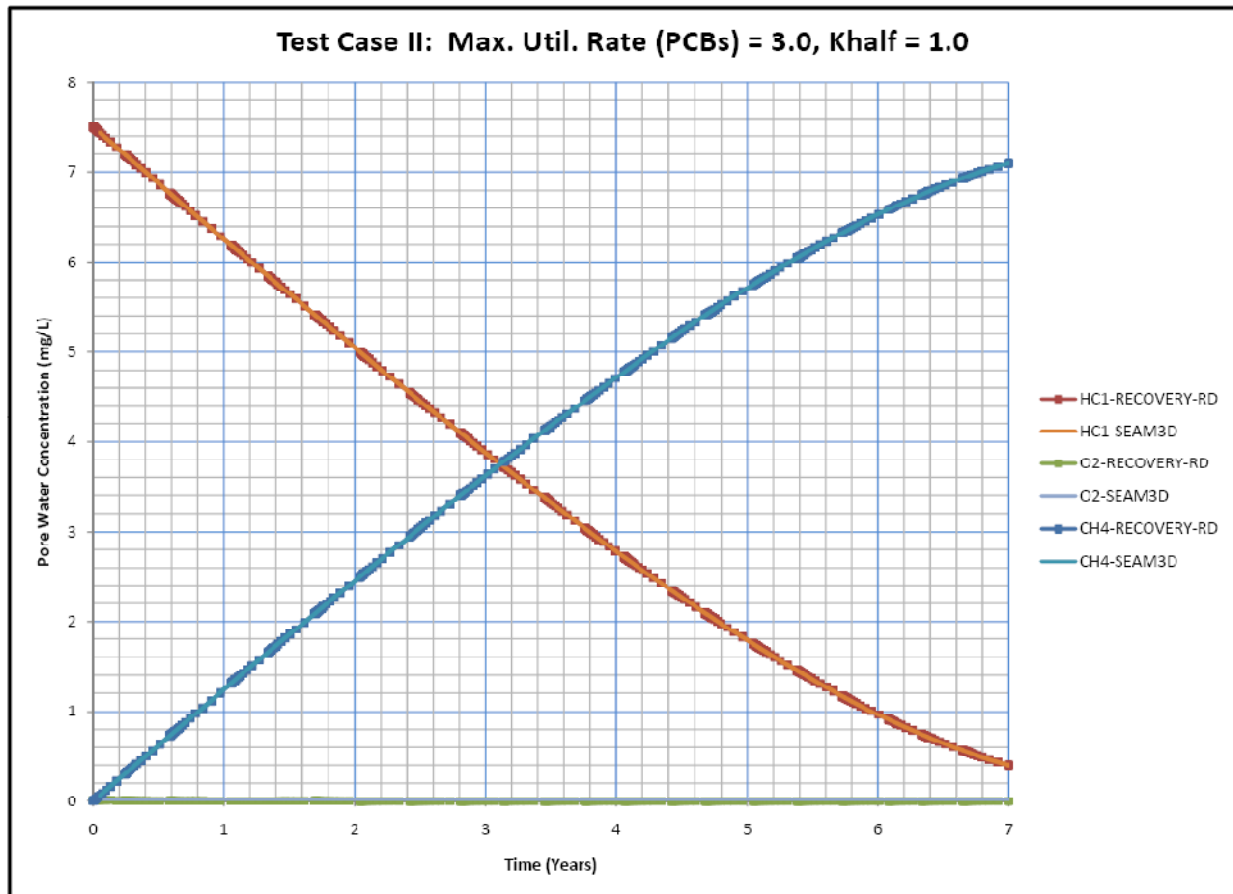


Figure 15: Test Case II, Electron Acceptors and Product Compounds in Mixed Sediment Layer

The figure above shows the activity in the mixed layer associated with methanogenesis. The fact that there is no discernable difference between the two models indicates that the connection between the Biodegradation Package and RECOVERY-RD has been successfully completed.

The second comparison is made between the series of simulated chlorinated ethene compounds in SEAM3D and the PCB congener group headed by PCB-125 in RECOVERY-RD. Again, this comparison is made between layer 1 of the SEAM3D model and the mixed sediment layer in RECOVERY-RD:



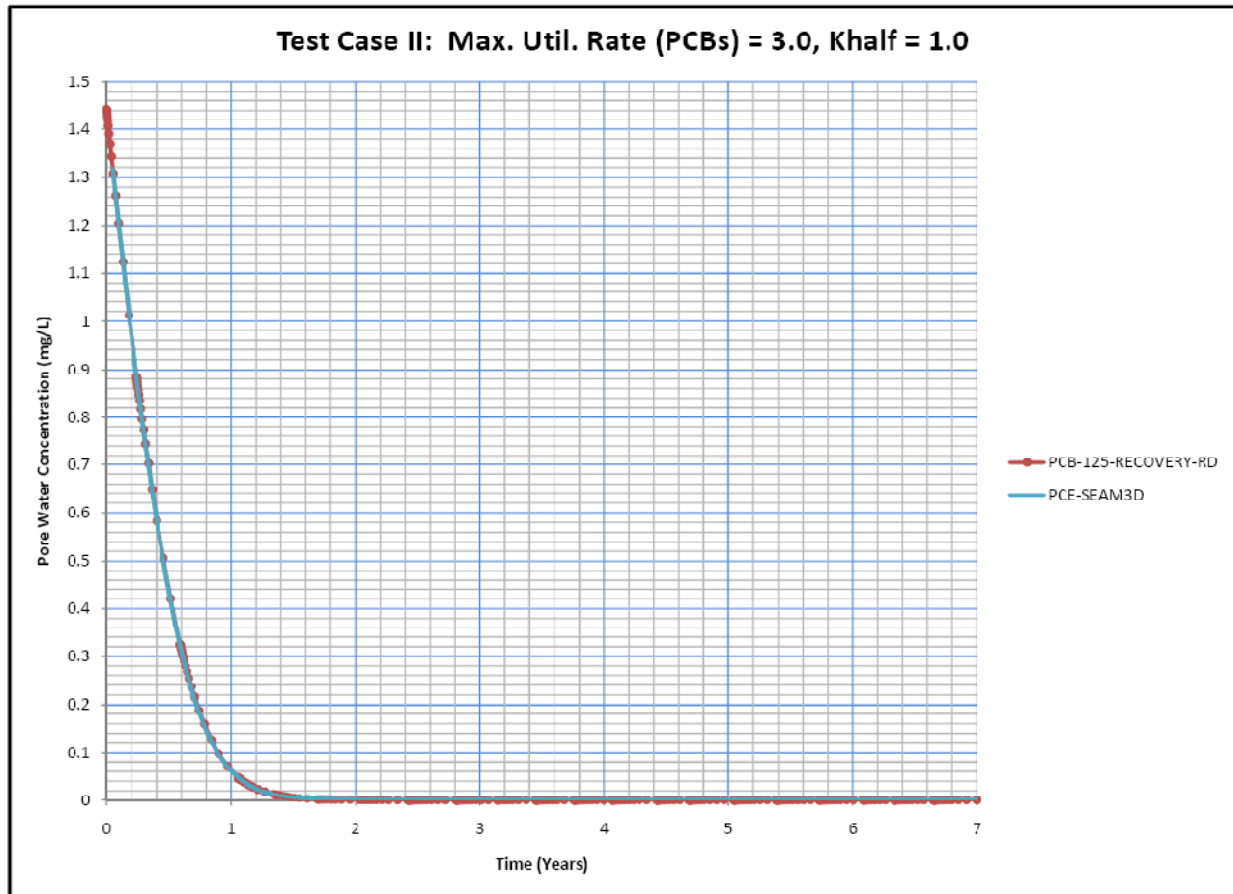


Figure 16: Test Case II, First Tier of RDP/PCB Compounds in Mixed Sediment Layer

Figure 16 shows that RECOVERY-RD is producing results that are consistent with the decay calculations made by the original Reductive Dechlorination Package. It is important to note that this figure is only indicative of the “sink” portion of the mass balance term associated with reductive dechlorination. This is due to the fact that PCB-125 and PCE are the ultimate parent compounds in each respective simulation, and there will be no modeled process that will result in production for either item. The product compounds associated with the degradation PCB-125 and PCE are PCB-71 and TCE, respectively. The simulated concentrations of the second tier of modeled constituents are compared in Figure 17:

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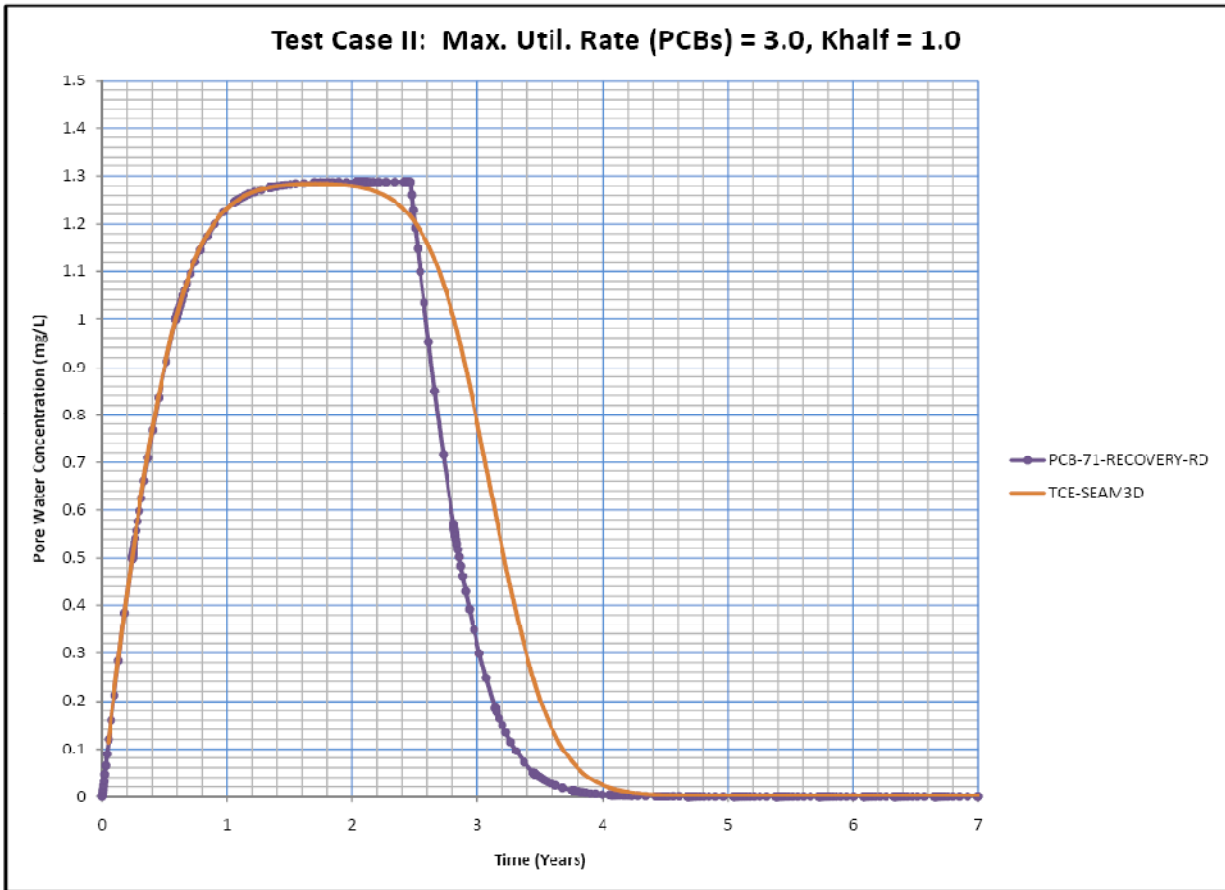


Figure 17: Test Case II, Second Tier of RDP/PCB Compounds in Mixed Sediment Layer

While the production side of both compounds matches perfectly, divergence is observed on the reduction side. This is due to the different representations used by the two models to transition between decay and production as discussed in chapter 3. Figure 18 and Figure 19 show further evidence of this difference:



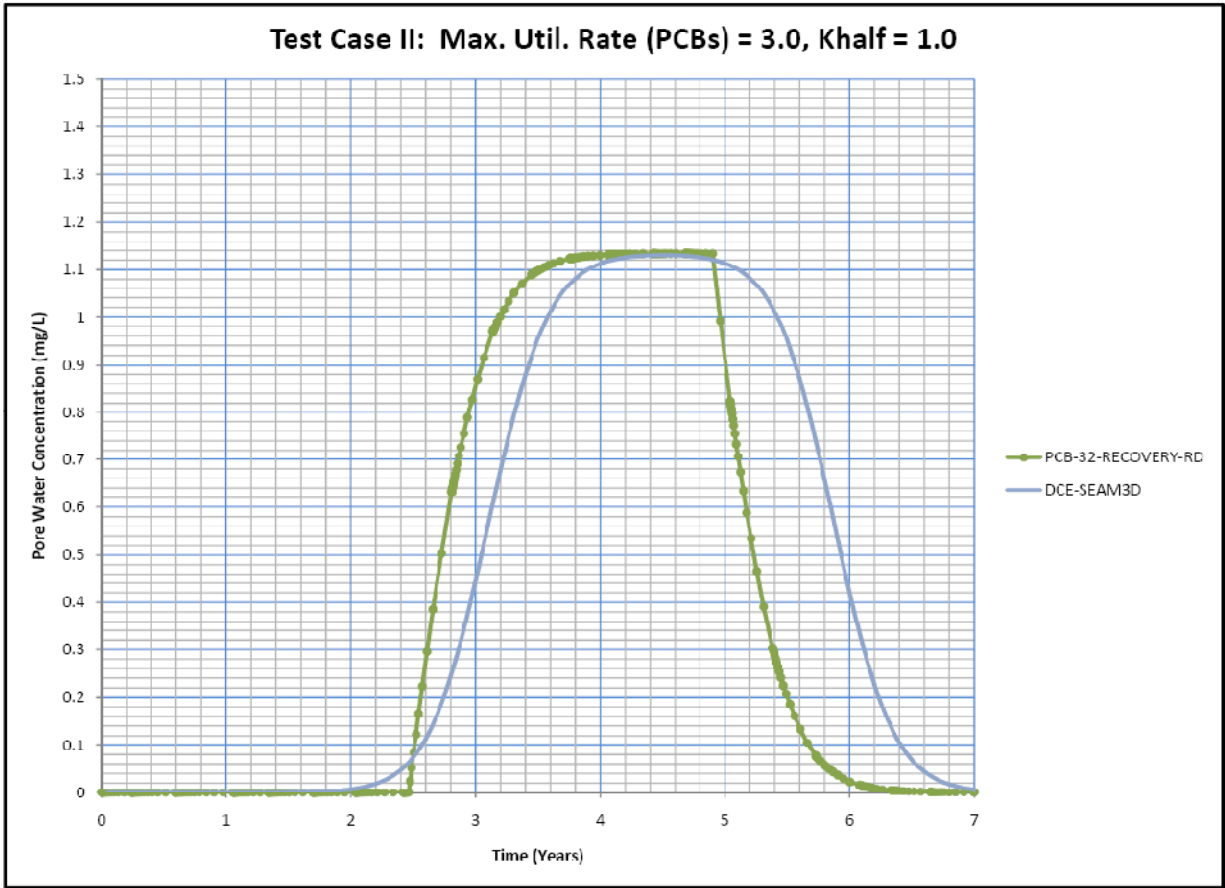


Figure 18: Test Case II, Third Tier of RDP/PCB Compounds in Mixed Sediment Layer



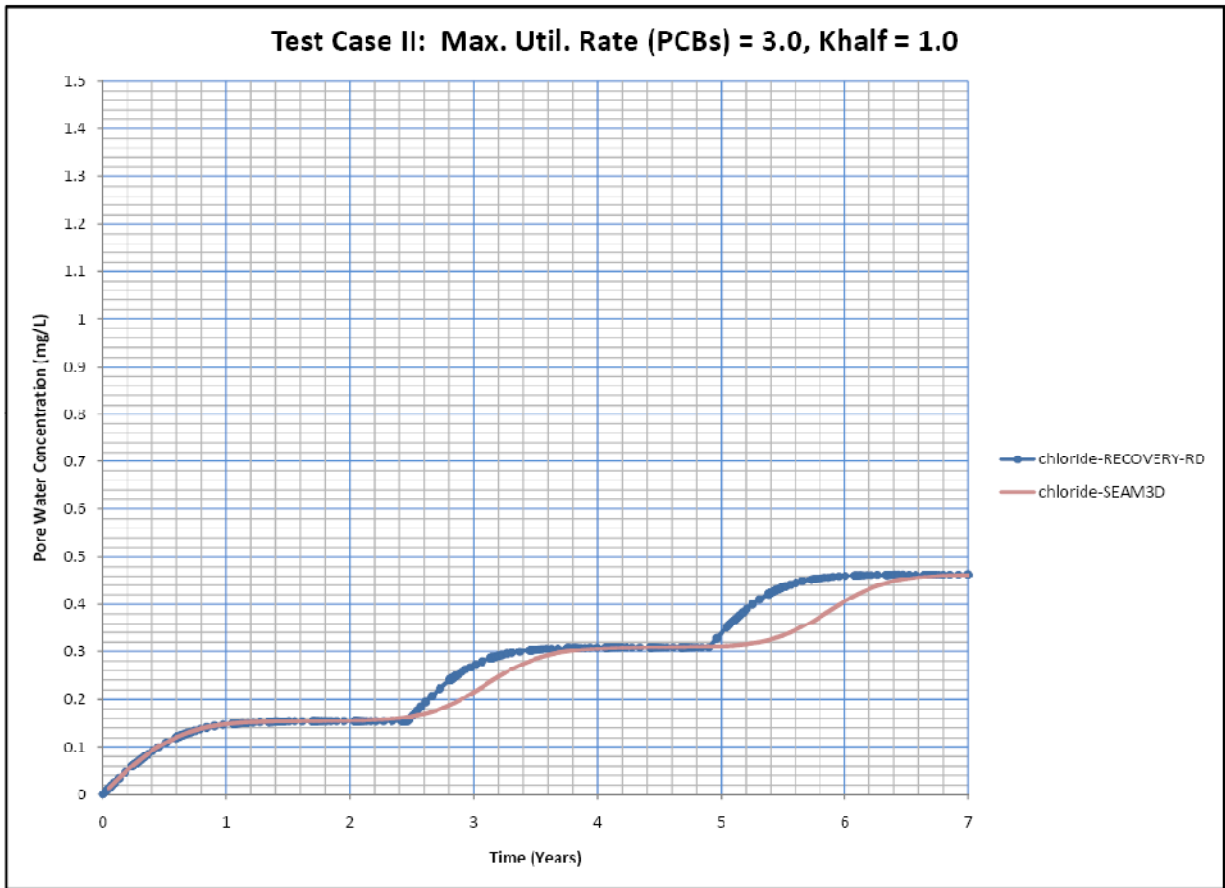


Figure 19: Test Case II, Chloride Byproduct in Mixed Sediment Layer

Again, the divergence due to the transition identification method is obvious. Although the predictions differ, the use of the buffer value significantly decreases the magnitude of the inconsistency. The most reasonable approach was to determine the value of the buffer using the linear regression that has been discussed. The imperfect nature of the linear regression method influences the observable difference.



The results provided by Test Case II indicate that the connections made to the Biodegradation and PCB Packages have been completed to the point that RECOVERY-RD is producing reasonable results. In addition, the results show that the PCB package reasonably predicts the biotransformation process as it relates to PCB congeners. While differences exist between the SEAM3D and RECOVERY-RD simulations, the predictions are consistent with the general pattern of reduction and production of congeners.



4.4 Test Case III: Pseudo-First-Order Decay

4.4.1 Purpose

Test Case III was designed to assess the first-order decay option within RECOVERY-RD. The implementation of this option involved the addition of a user-defined parameter to the Monod-form expressions developed by the PCB package. The modifications associated with this option are described in Chapter 3. The results obtained from the RECOVERY-RD portion of Test Case II are used to validate the results introduced in this section.

4.4.2 Setup

Test Case III consists of an exact replication of Test Case II with the exception of the decay option. The input to RECOVERY-RD was modified to use flag values of zero for the mixed and deep sediment units, which causes the decay terms calculated by the PCB Package to revert to quasi-first-order expressions. All additional input to both RECOVERY-RD simulations remains exactly as it is in Test Case II.

4.4.3 Assumptions/Simplifications

The set of assumptions and simplifications that pertain to the RECOVERY-RD portion of Test Case II correspond to this set of simulations as well. It is also important to understand that the use of the first-order decay option negates the ability to represent mass loss of PCB congeners due to direct oxidation. This is evident when looking at the final form of the direct oxidation sink term, which is

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multiplied by the decay flag value. When the user chooses the first-order option, the flag is assigned a value of zero. The result is a complete removal of the direct oxidation term, effectively removing the potential impact of this process completely.

It is also important to understand that this test case simply compares the Monod-form decay and production formulations to an unmodified first-order representation. That is, to accurately represent first-order decay with a single rate parameter, the user must adjust the maximum utilization rate and half saturation constants. The combination of these parameters is used to represent the desired rate parameter related to the decay and production of PCB congeners. In this case, no adjustment was made to these values. Therefore, the comparison is made between simulations with identical maximum utilization rates and half saturation constants.

4.4.4 Results

The first-order option only applies to the calculations made by the PCB Package; therefore the results obtained from the Biodegradation Package are identical to each other. Figure 20 shows this result:



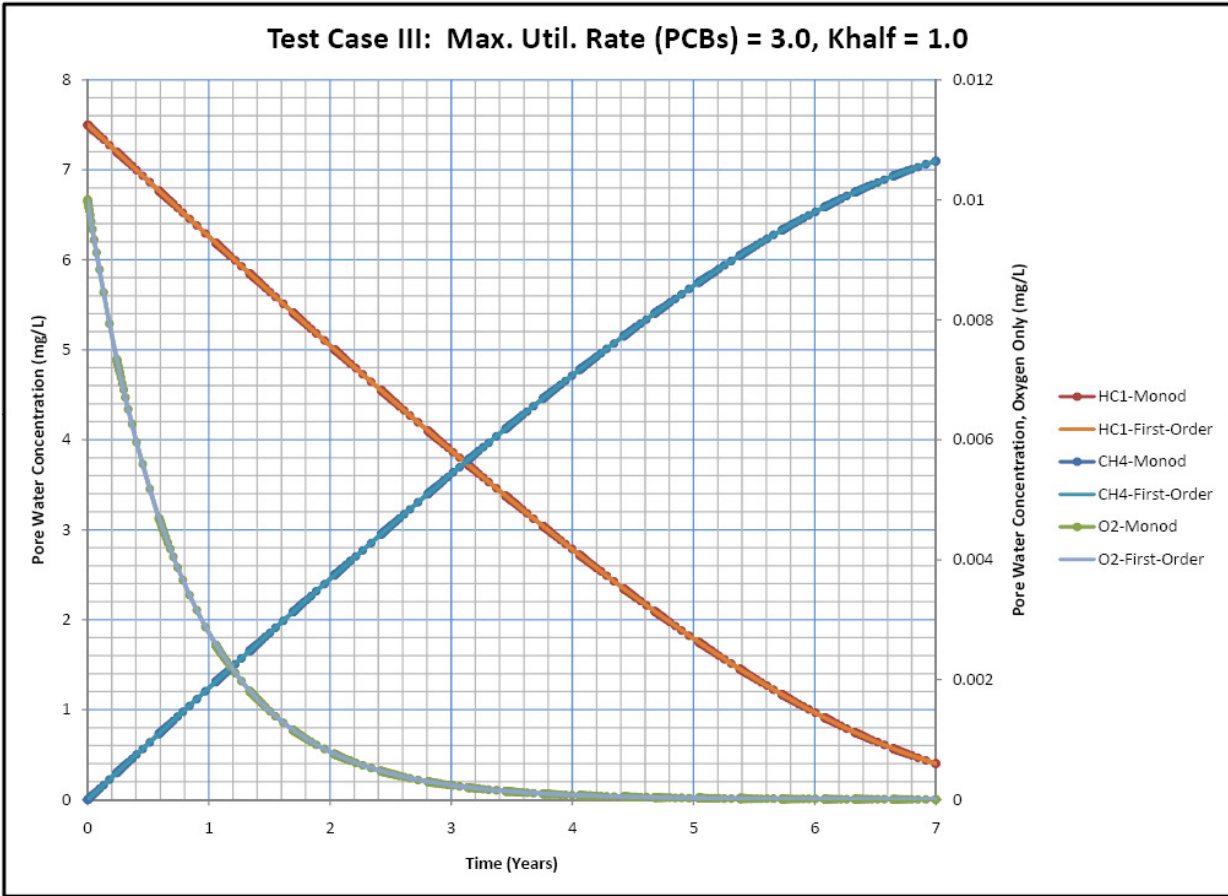


Figure 20: Test Case III, Electron Acceptors and Product Compounds in Mixed Sediment Layer

The same set of PCB congeners used in Test Case II was used for this simulation. The degradation chain begins with PCB-125, as indicated in Figure 21:



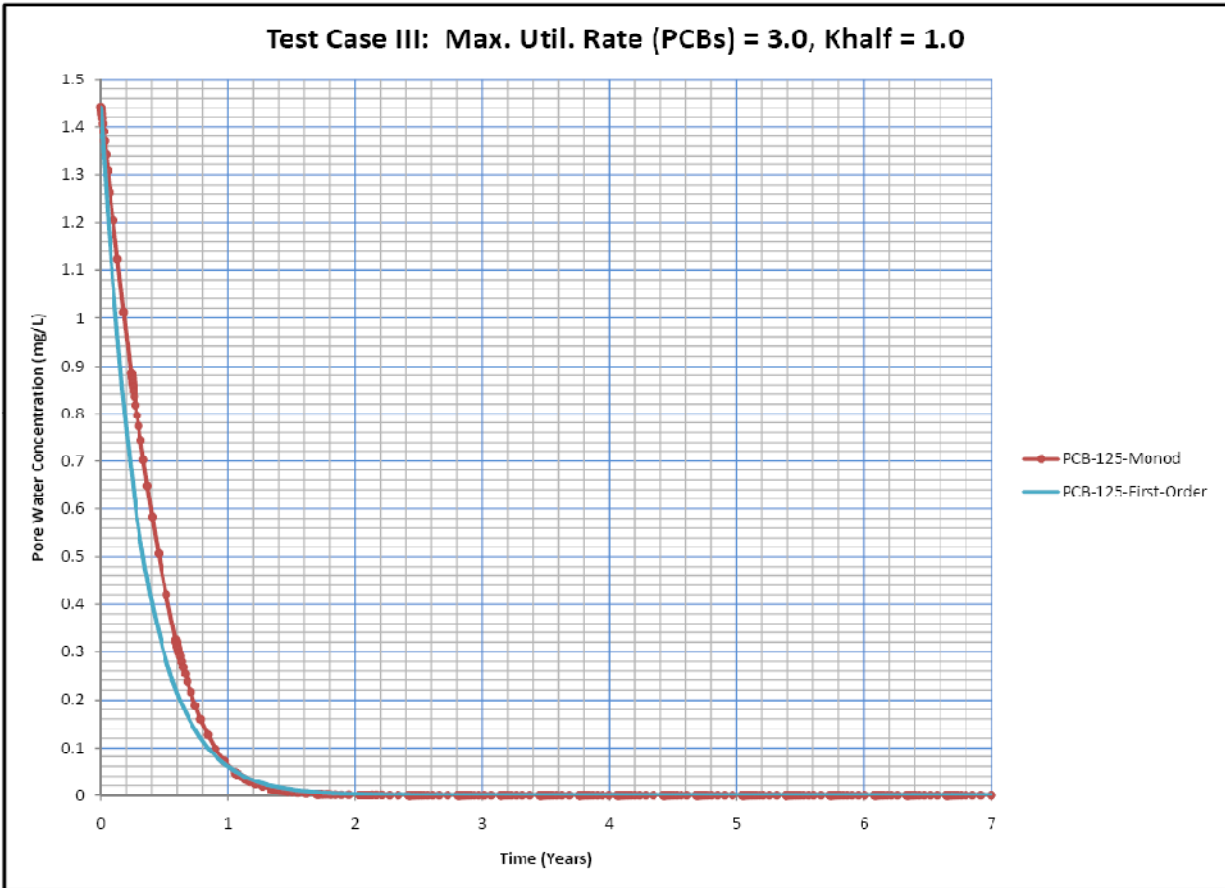


Figure 21: Test Case III, First Tier of RDP/PCB Compounds in Mixed Sediment Layer

The figure above shows that the first-order option causes PCB-125 to decay more rapidly than the Monod-form version of the model. This reflects the influence of the concentration variable located in the denominator of the Monod-form expression. The removal of this value by the first-order decay flag creates a smaller denominator value, which translates to a greater decay rate for points at which the concentration is significant. As the concentration is lowered, this effect is lessened, and the Monod-form rate overtakes the first-order option. This is observed after approximately one year of simulation.



The second tier of PCB congeners shows the influence of the concentration buffer value on simulations that use the first-order decay option:

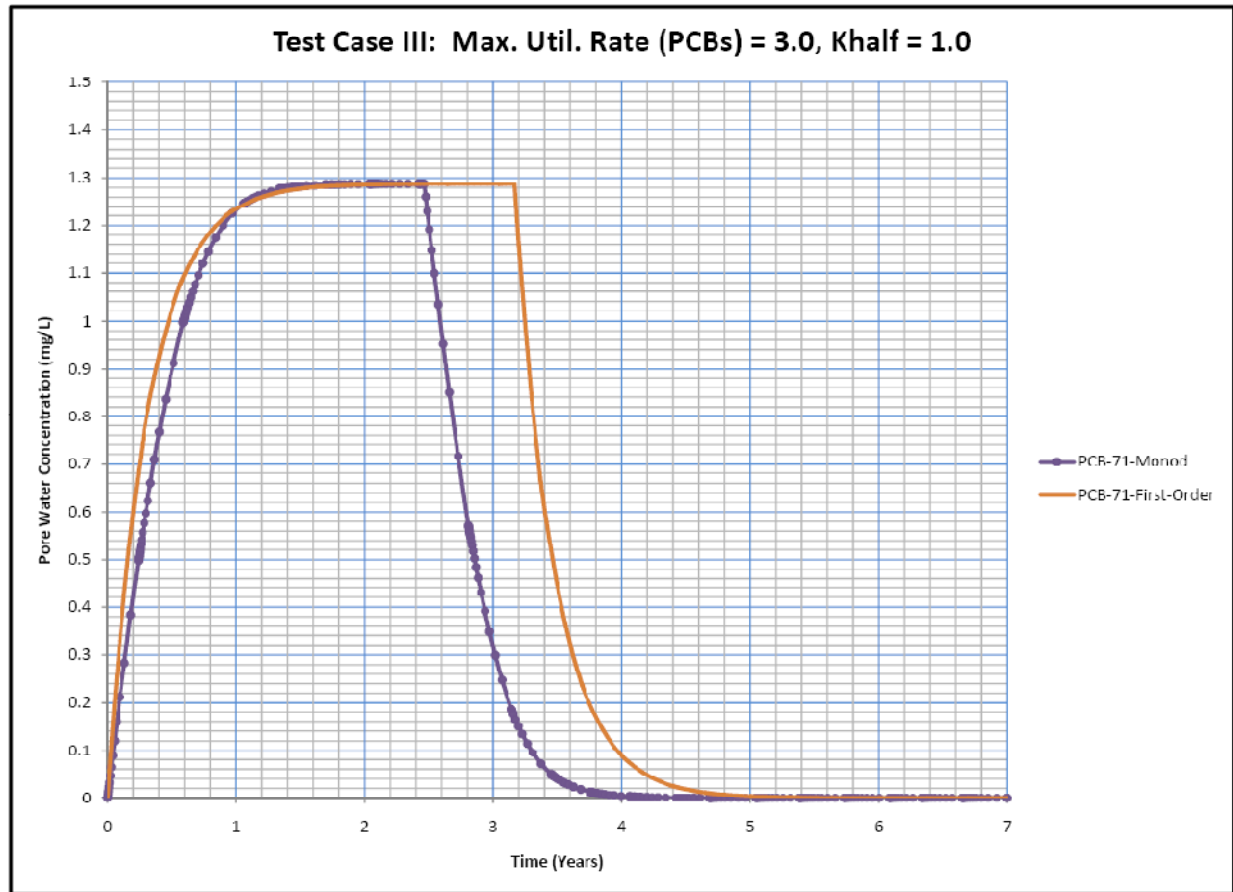


Figure 22: Test Case III, Second Tier of RDP/PCB Compounds in Mixed Sediment Layer

As discussed in Chapter 3, the concentration buffer value is determined from a regression analysis based on the rate parameters associated with the simulated PCB congeners. The value of the concentration buffer does not change if the first-order option is implemented despite the potential for different decay



and production rates. Although this is a potential discrepancy, Figure 23 shows that the two different methods both provide reasonable rate estimates when compared to the SEAM3D surrogate:

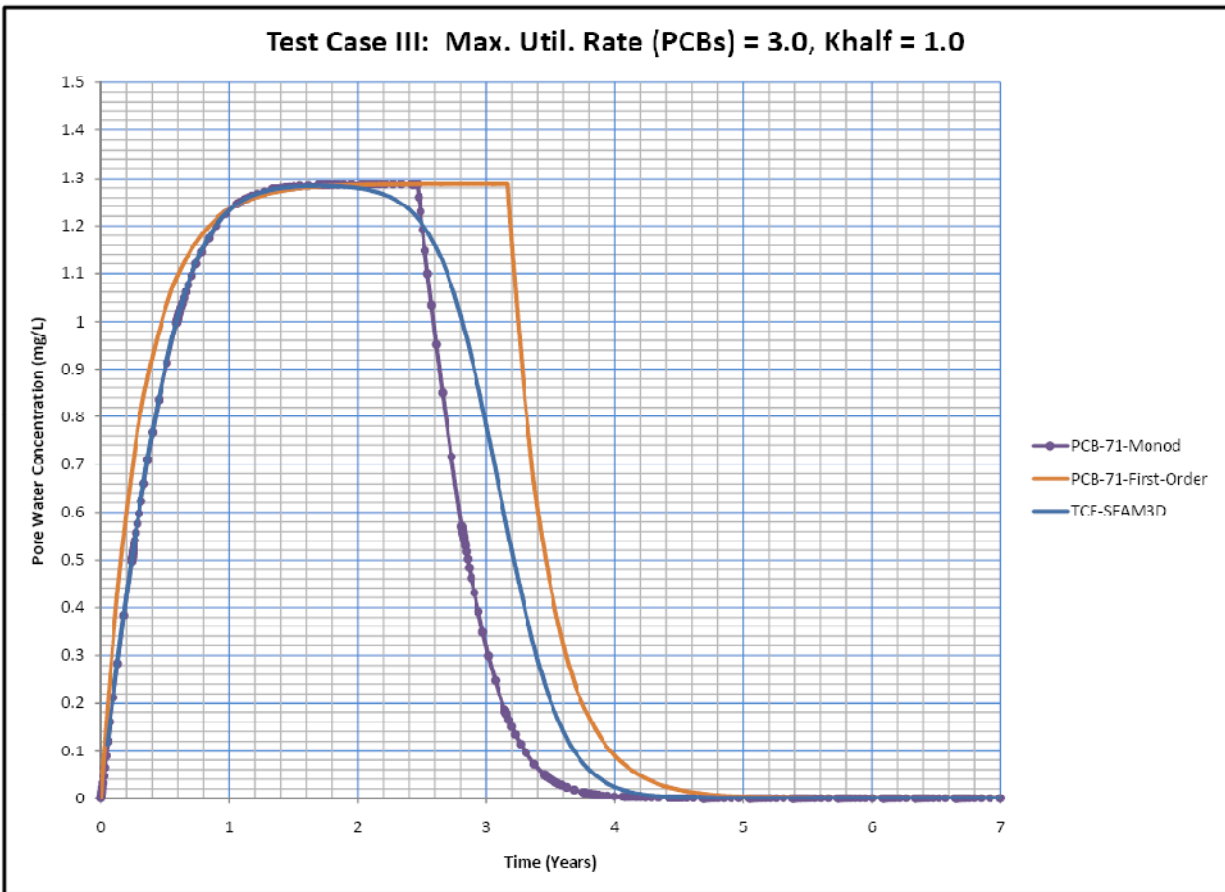


Figure 23: Test Case III, Second Tier of RDP/PCB Compounds in Mixed Sediment Layer Including SEAM3D Comparison

The figure above indicates that the first order and Monod options may be used to predict conservative and liberal rates of decay and production, respectively. This is a promising result with respect to the general applicability of RECOVERY-RD, especially when considering the screening-level intentions associated with a typical simulation.



An additional issue is highlighted by Figure 24:

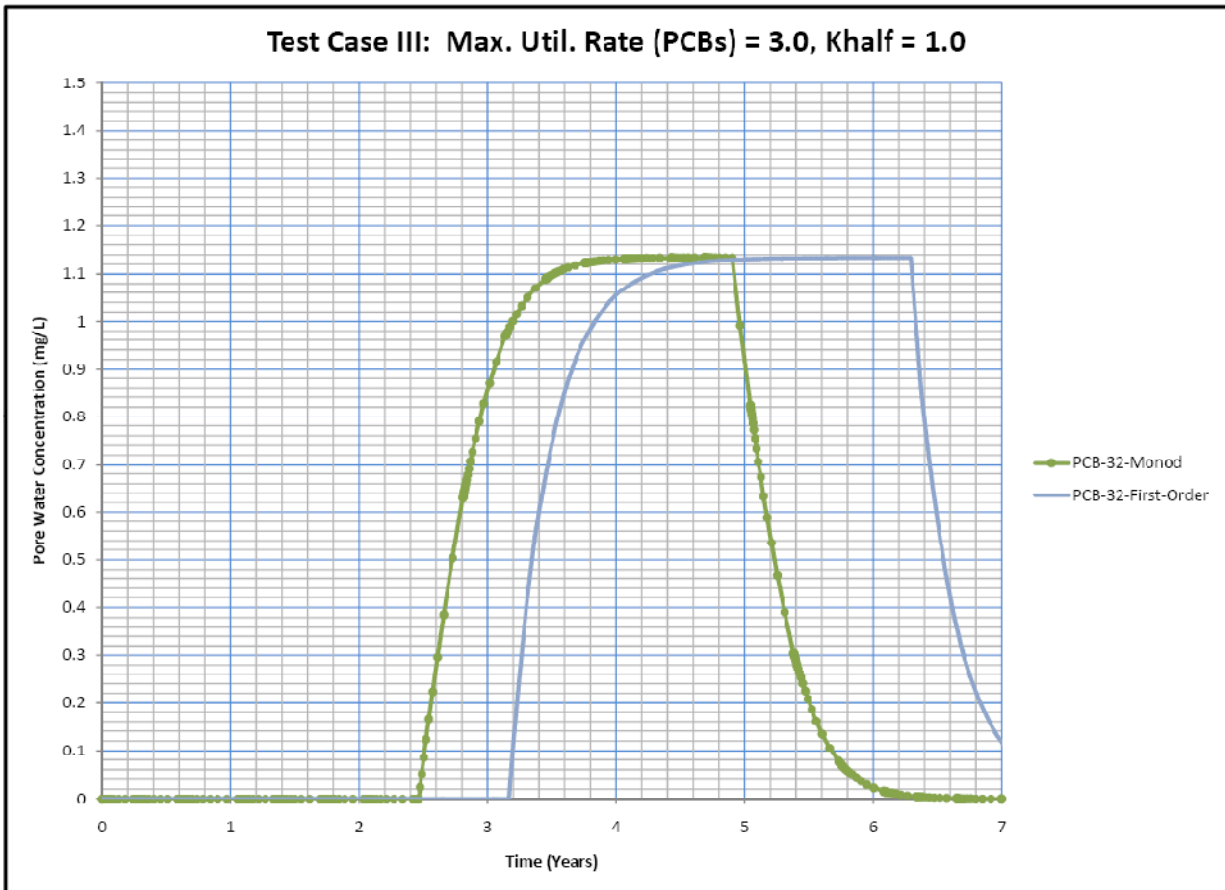


Figure 24: Test Case III, Third Tier of RDP/PCB Compounds in Mixed Sediment Layer

As a simulation progresses through a parent-product congener chain, the rate discrepancy associated with the transition identification increases. This being the case, results born from simulations with a large number of parent and product congeners must be qualified. Again, as Figure 25 indicates, the first-order option may provide the user with an opportunity to investigate a more conservative result:



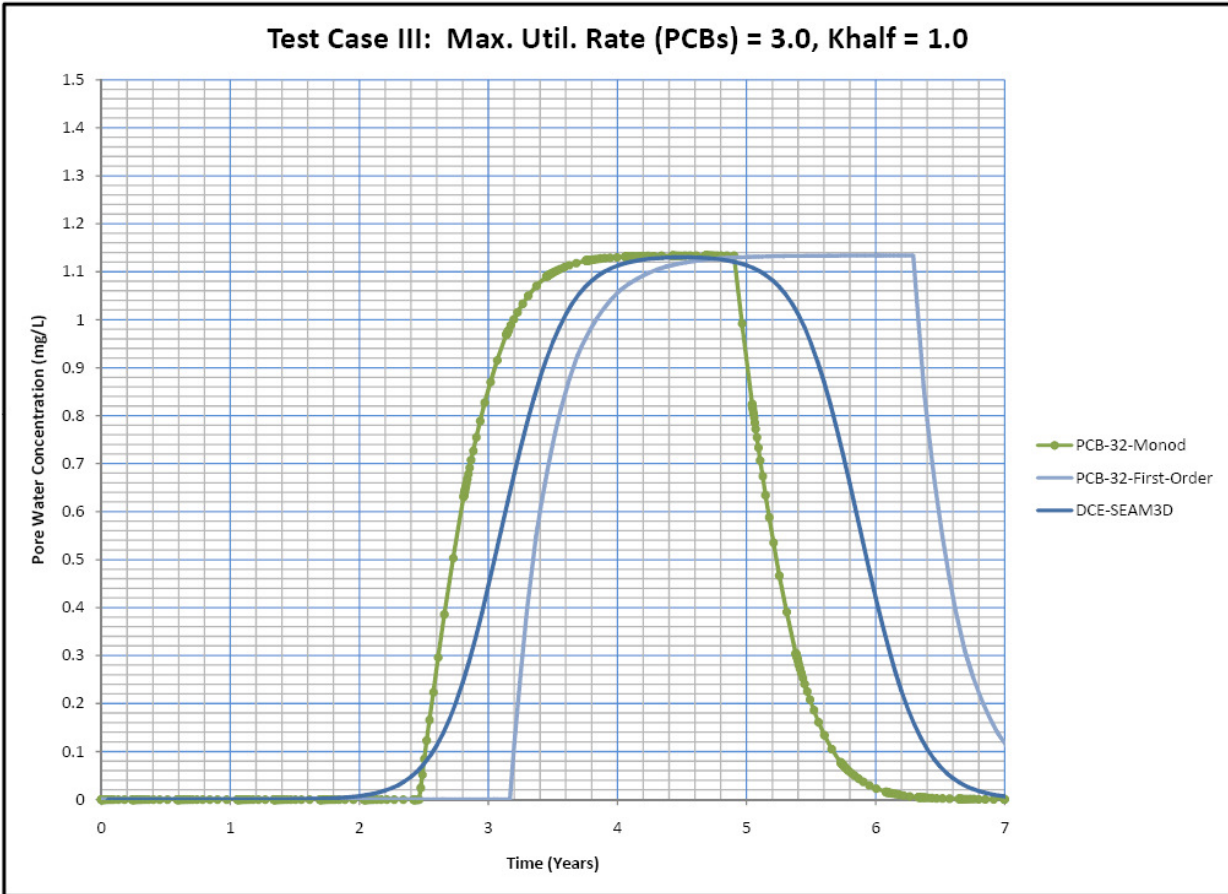


Figure 25: Test Case III, Third Tier of RDP/PCB Compounds in Mixed Sediment Layer Including SEAM3D Comparison

The cumulative effect of the rate discrepancy between the two models is better represented by the comparison of the chloride byproduct results:



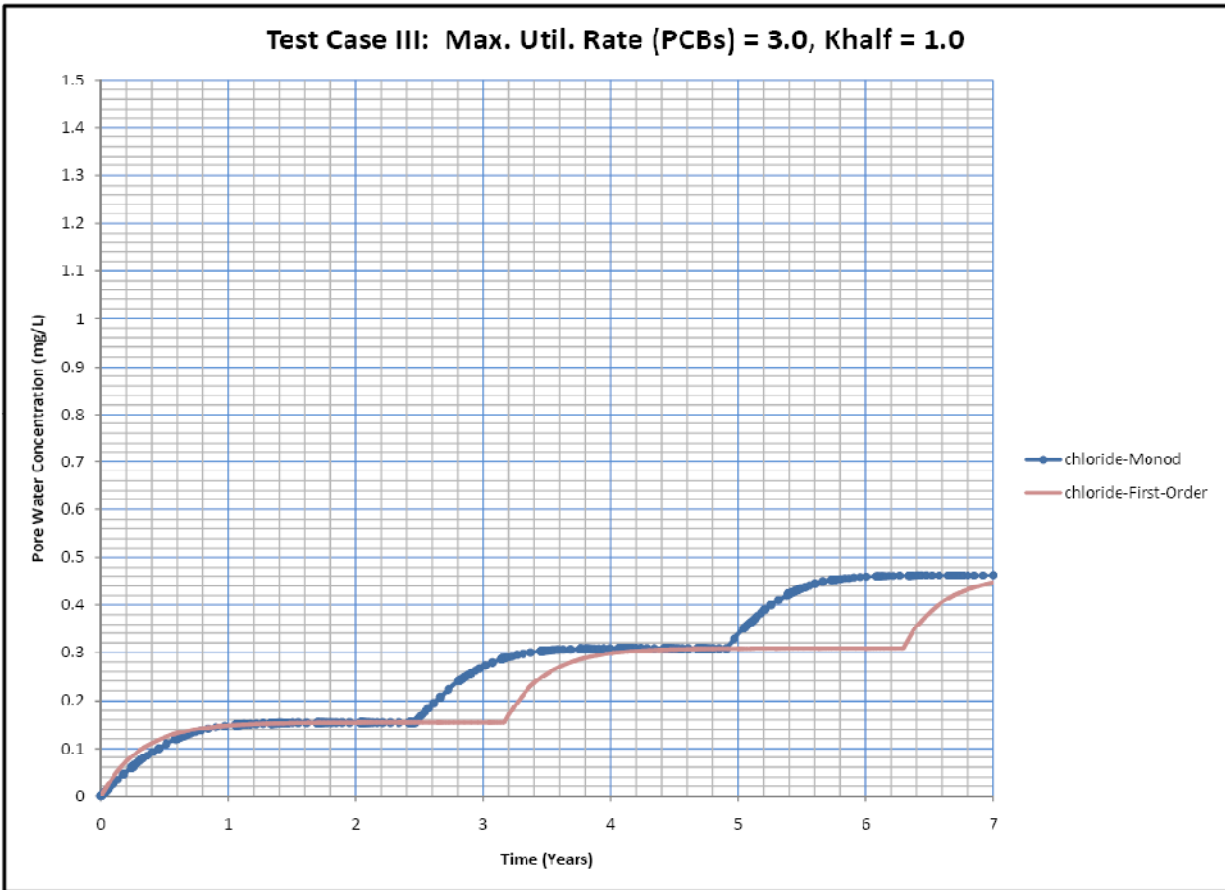


Figure 26: Test Case III, Chloride Byproduct in Mixed Sediment Layer

As this test case indicates, the error associated with the use of the buffer/tolerance value compared to the results obtained from the Reductive Dechlorination Package may be quantified through the use of the first-order decay option in RECOVERY-RD. For a given model application, a sensitivity analysis comparing both decay options would provide the user with conservative and liberal estimates of the overall rate of congener transformation. While the magnitude of this error seems relatively large, it is important to remember the significant amount of simplifications associated with this test case. A



more realistic application would include additional mass balance terms that would combine to mitigate the differences observed here. Again, the simplifications were necessary due to the conceptual differences between RECOVERY-RD and SEAM3D.



4.5 Hypothetical Application of RECOVERY-RD

4.5.1 Purpose

The purpose of this section was to provide an example application of the final version of RECOVERY-RD. A semi-realistic, albeit relatively simple, hypothetical problem is proposed that provides an example of how RECOVERY-RD would be implemented in practice. It is important to keep in mind that RECOVERY-RD was created as a screening-level model.

4.5.2 Setup

The entire three-regime system, with the exception of the clean set of deep sediment sub-layers, is specified to have an initially-constant contaminant concentration profile. The purpose of this specification is to provide a constant initial condition, which provides the best starting point for a comparison between model regimes at the end of the simulation. That is, the difference between the uniform starting condition and the final concentration profile provides the best depiction of transport between units.

The hypothetical system is represented as an overlying water unit with a steady rate of uncontaminated inflow. This acts as a flushing mechanism through the import of clean water and the export of contaminated flow, both of which occur only in the first model layer. The water column is underlain by a deep sediment system that is a combination of clean and contaminated deep sediment sub-layers and a completely-mixed sediment layer. The mixed sediment layer is used as a



representation of a clean material cap used to prevent contamination of the overlying water body. Biologically, the system is dominated by methanogenesis.

Transport associated with the movement of particulate matter between layers is relatively limited due to small burial, resuspension, and settling velocities combined with a simplified representation of partitioning. The properties associated with the PCB congeners represented within this simulation, particularly the octanol-water partitioning coefficients, were simplified to limit partitioning to the solid phase. This was done to provide a better case for the representation of the biotransformation processes within the modified model.

4.5.3 Results

The following series of figures indicates the simulated response within the model system. Since the water column mass balance does not include terms calculated by the biodegradation and PCB packages, methane generation is not observed. In addition, products of electron acceptor decay are not actively transported; therefore no observable increase in methane concentration is possible within the overlying water column. In addition, the electron donor compound, simulated as a general hydrocarbon substrate, is subject to relatively steady reduction throughout the simulation. For these reasons, only the simulated PCB congeners and byproduct chloride results are presented in this section.

The results are presented by model regime, starting with the first deep sediment sub-layer and working up to the water column. The constituents are ordered according to the PCB congener production pattern, with the chloride byproduct located at the end of each regime group. This organization structure provides a method for observing the biotransformation process as it is simulated



within the sediment layers. It also provides evidence of additional processes as they pertain to the overlying water column. A brief discussion is included at the end of the set of transient concentration figures.

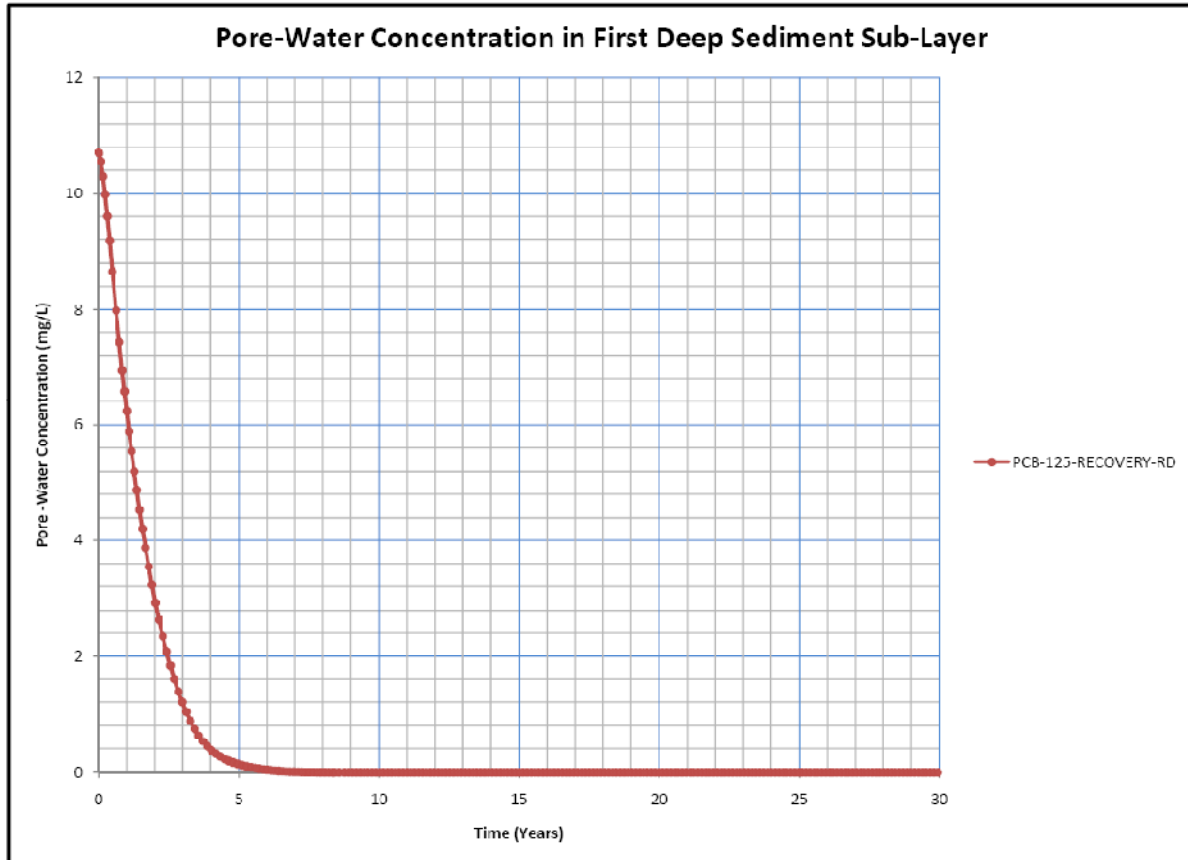


Figure 27: Hypothetical Application, PCB-125 in First Deep Sediment Sub-layer



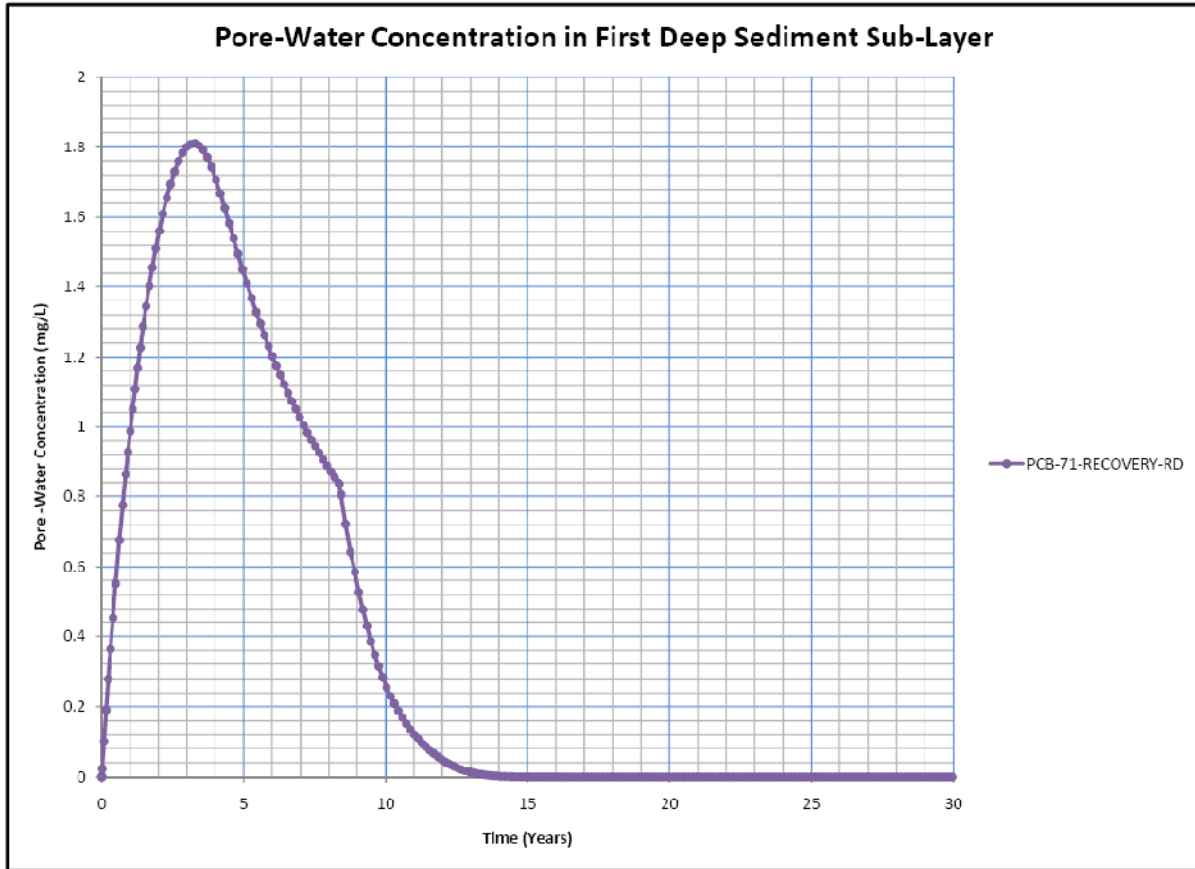
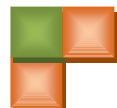


Figure 28: Hypothetical Application, PCB-71 in First Deep Sediment Sub-layer



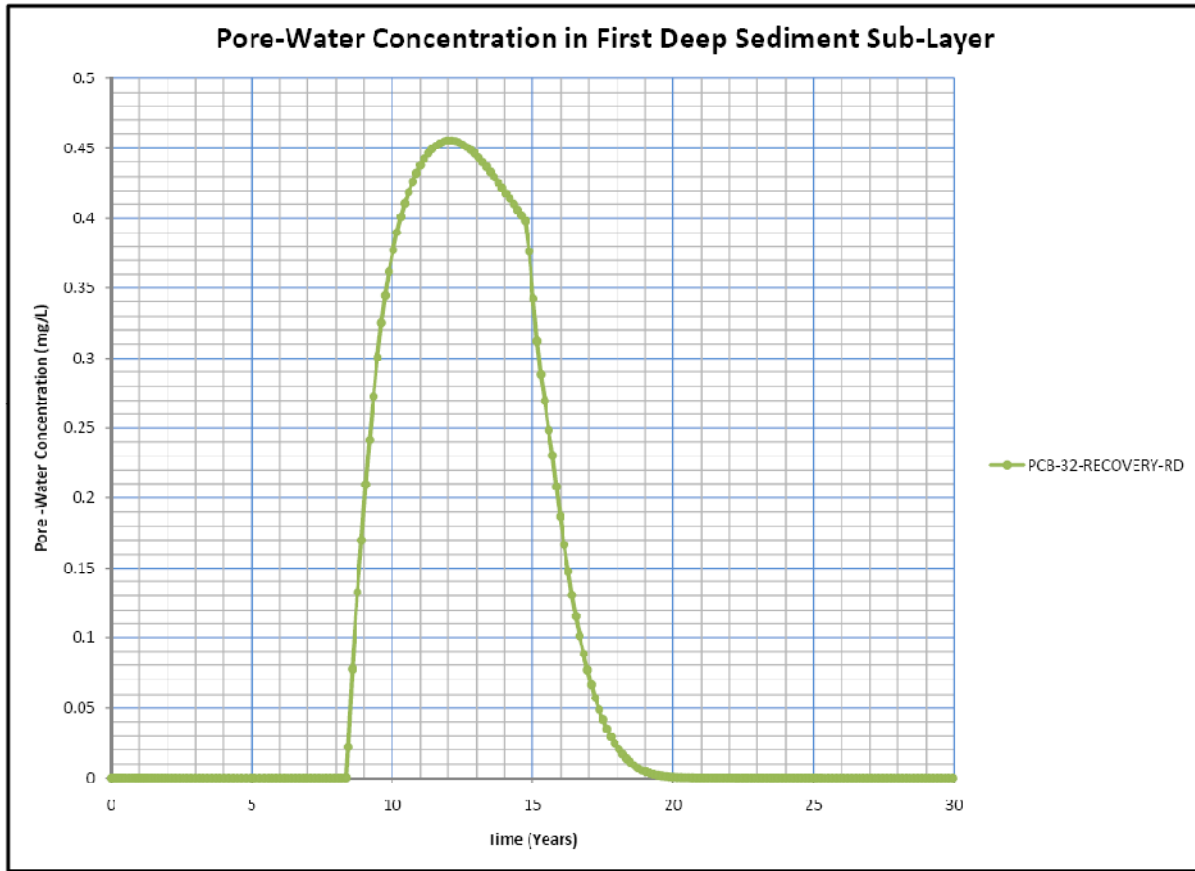


Figure 29: Hypothetical Application, PCB-32 in First Deep Sediment Sub-layer



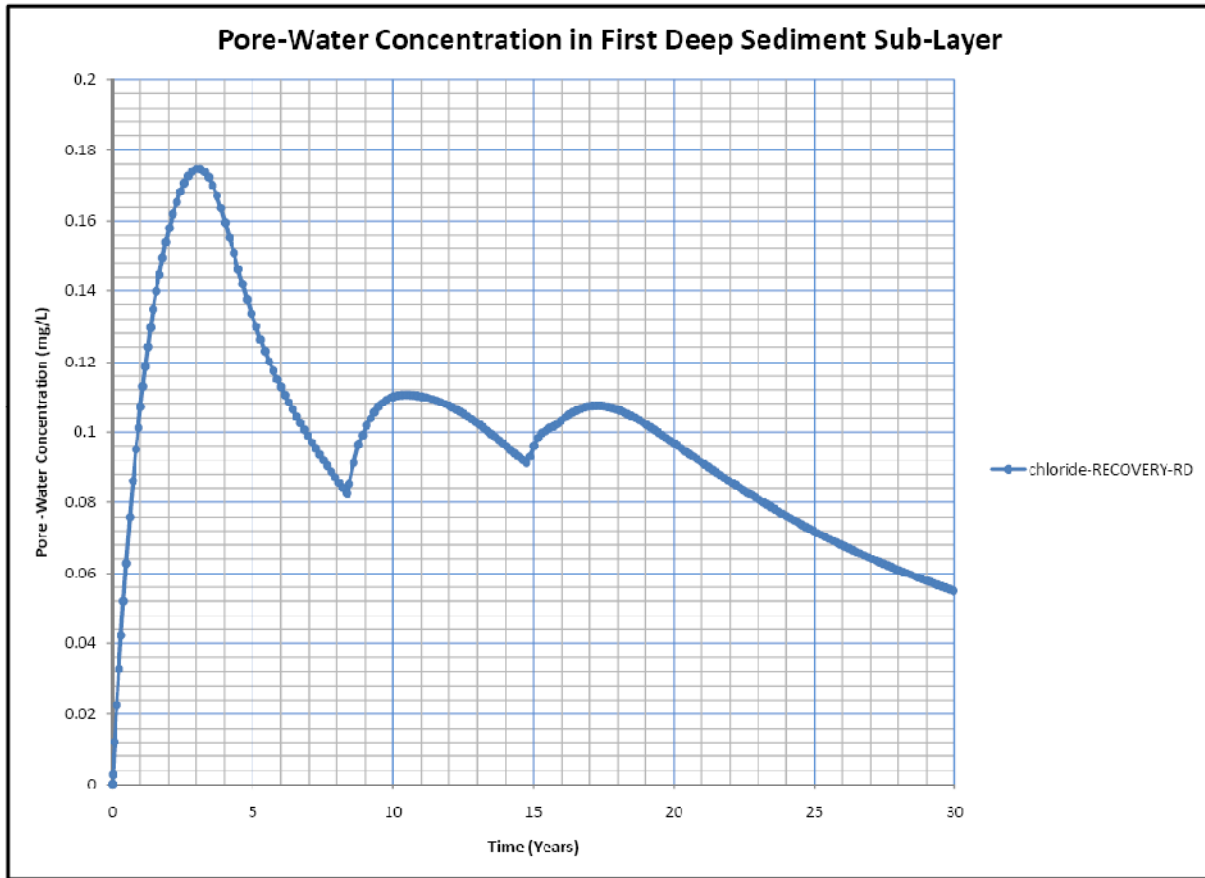


Figure 30: Hypothetical Application, Chloride Byproduct in First Deep Sediment Sub-layer



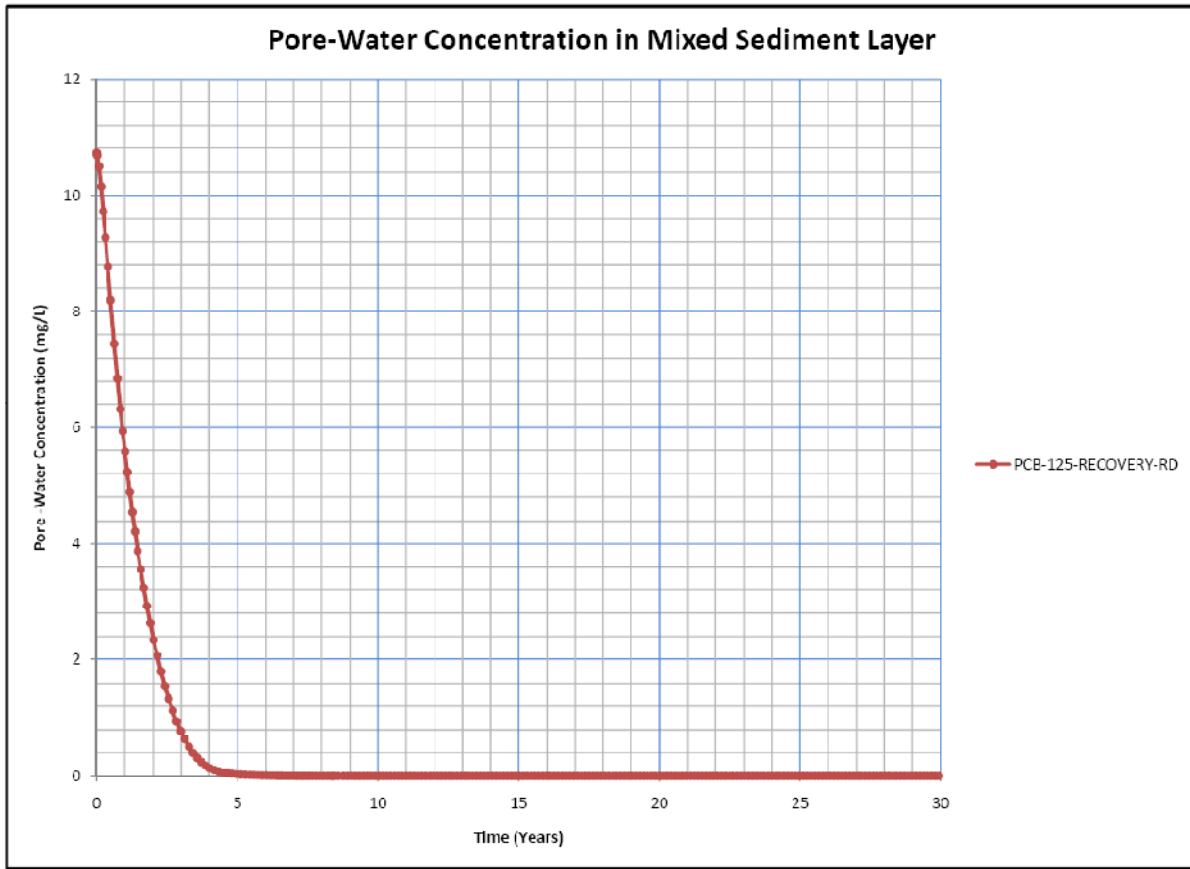


Figure 31: Hypothetical Application, PCB-125 in Mixed Sediment Layer



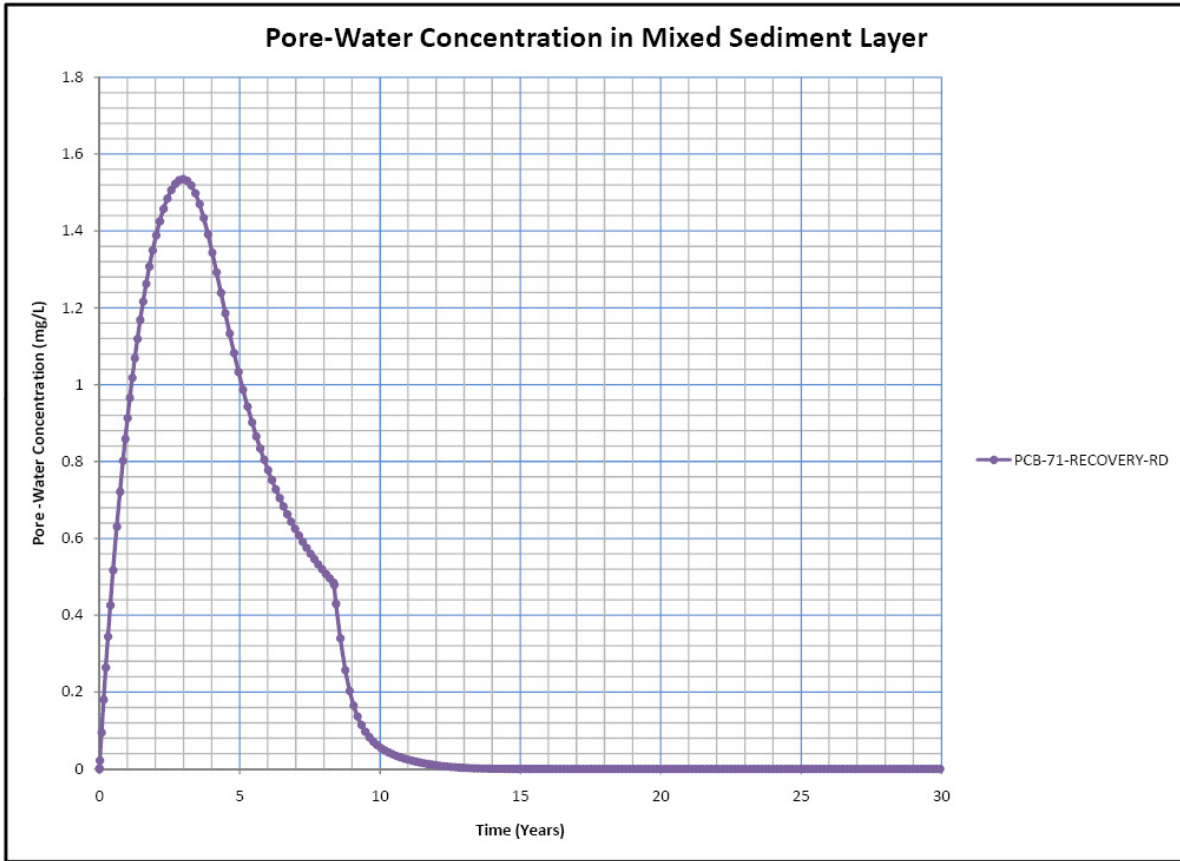


Figure 32: Hypothetical Application, PCB-71 in Mixed Sediment Layer



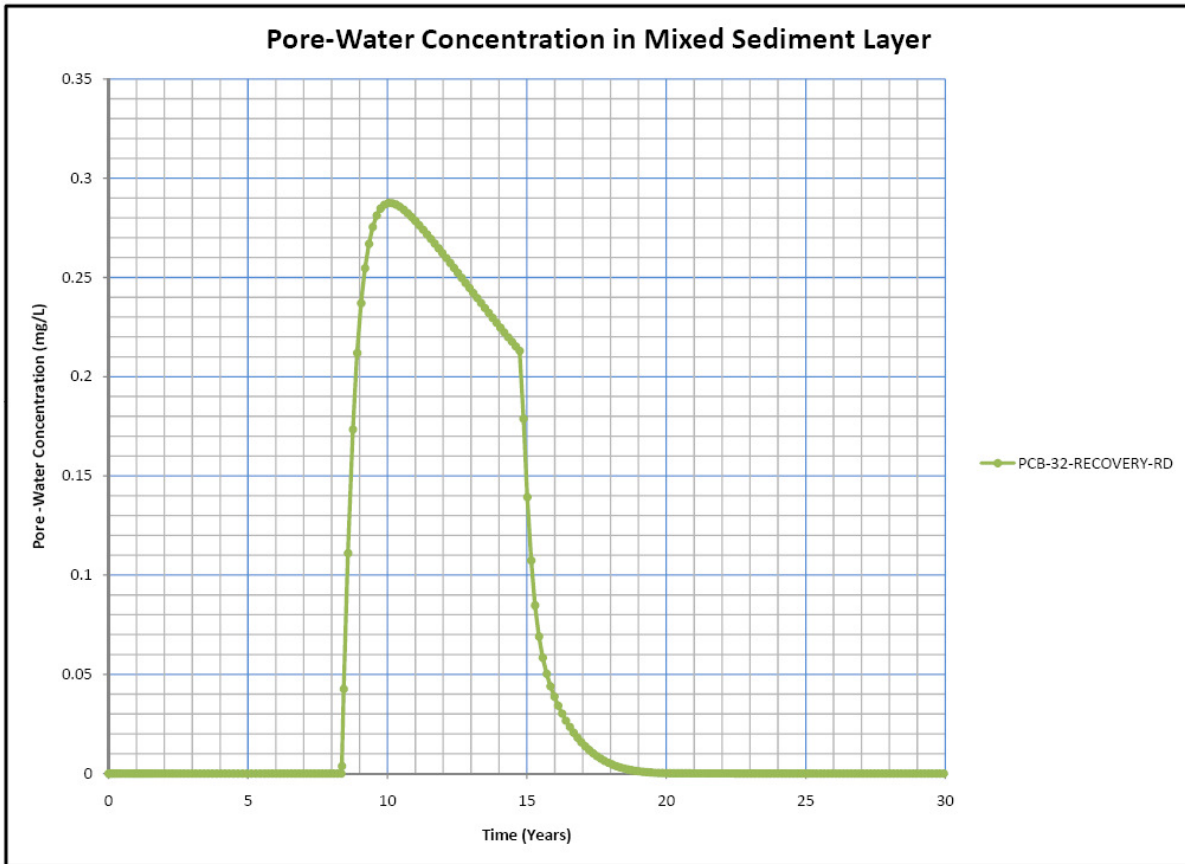


Figure 33: Hypothetical Application, PCB-32 in Mixed Sediment Layer



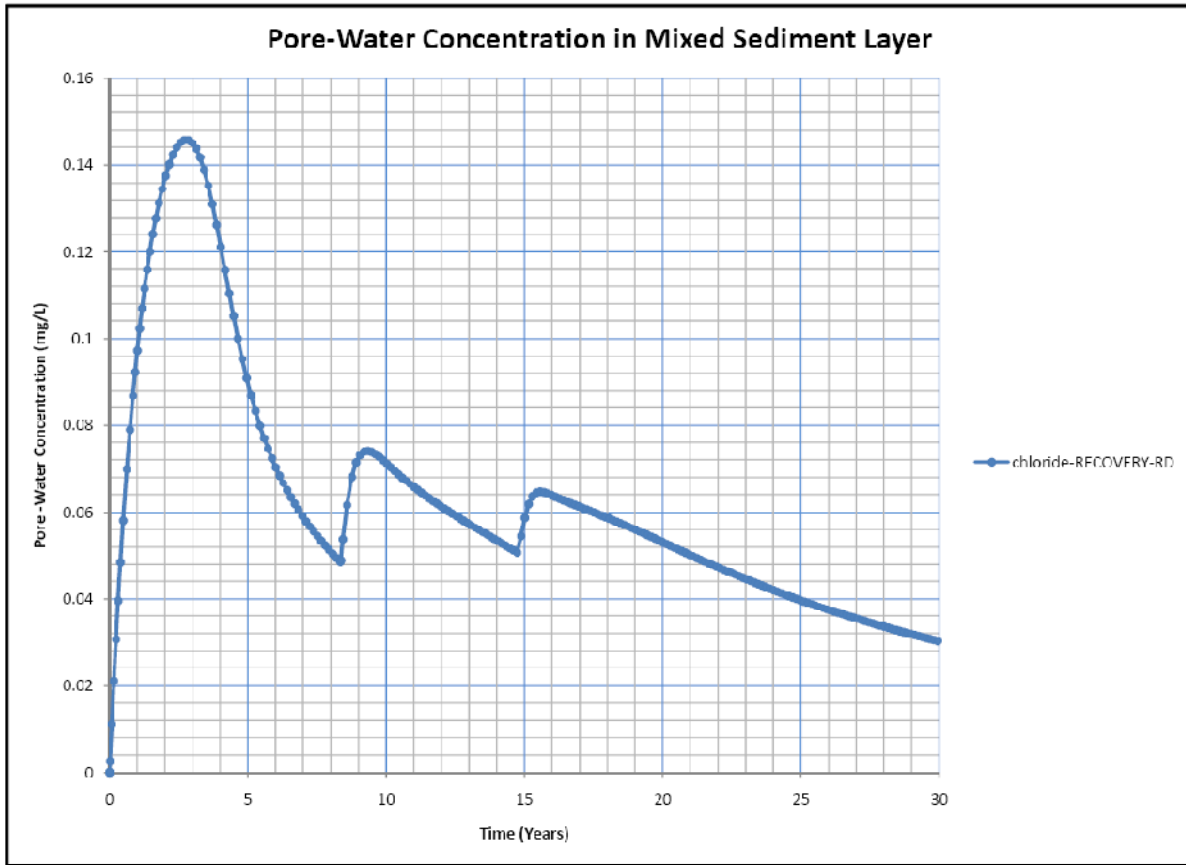


Figure 34: Hypothetical Application, Chloride in Mixed Sediment Layer



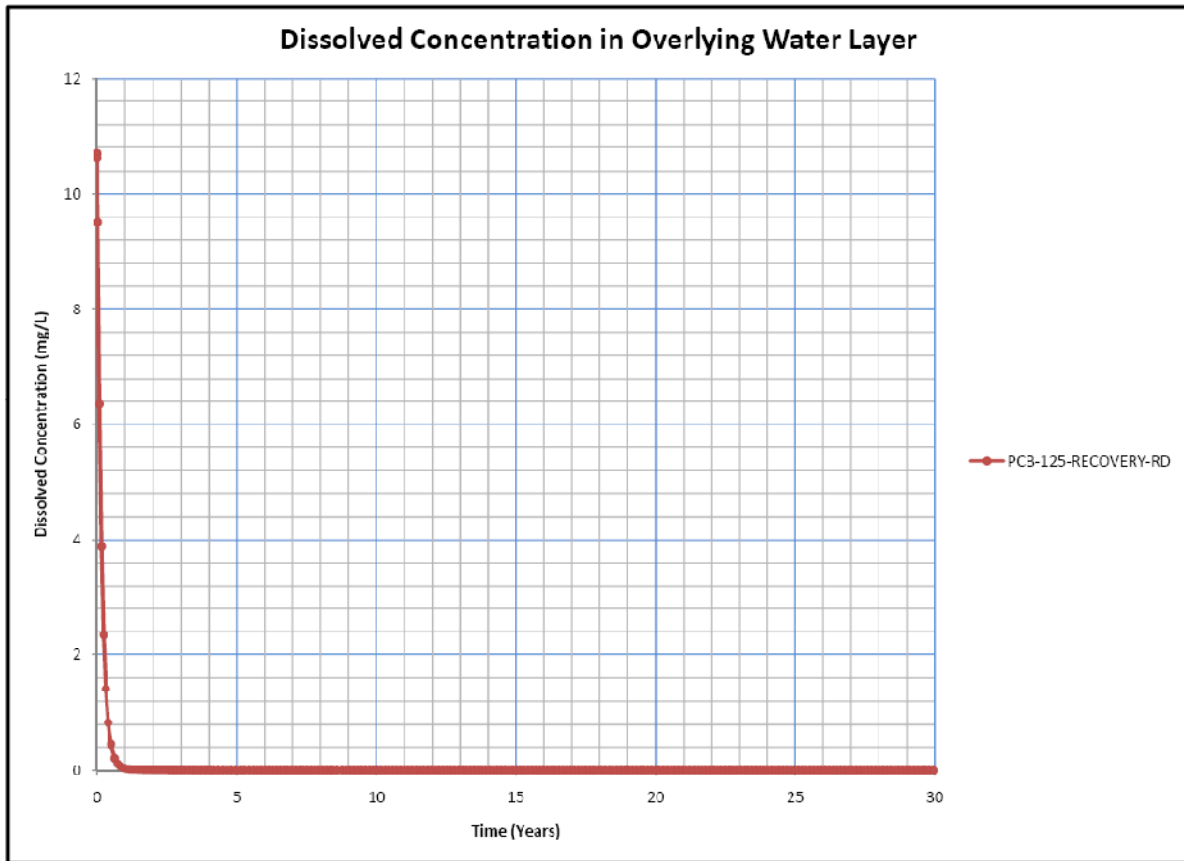


Figure 35: Hypothetical Application, PCB-125 in Water Column



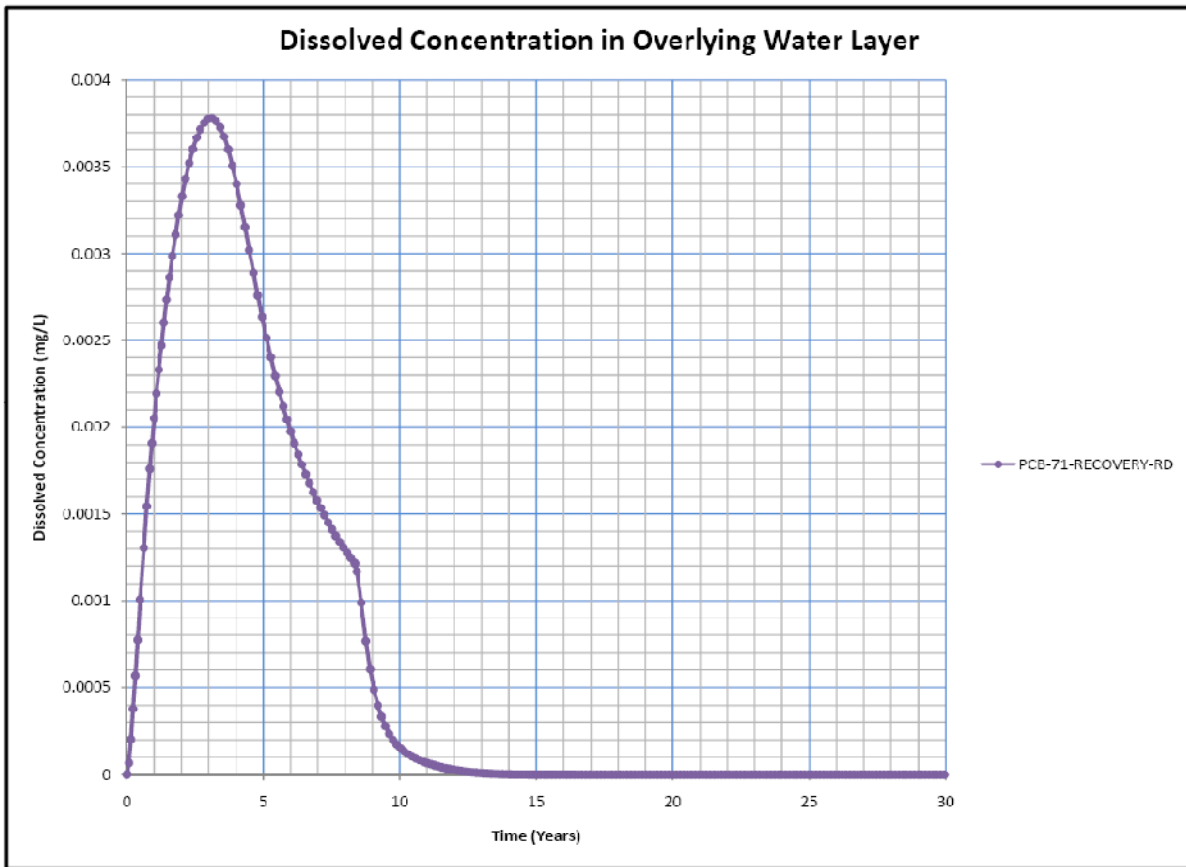
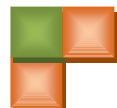


Figure 36: Hypothetical Application, PCB-71 in Water Column



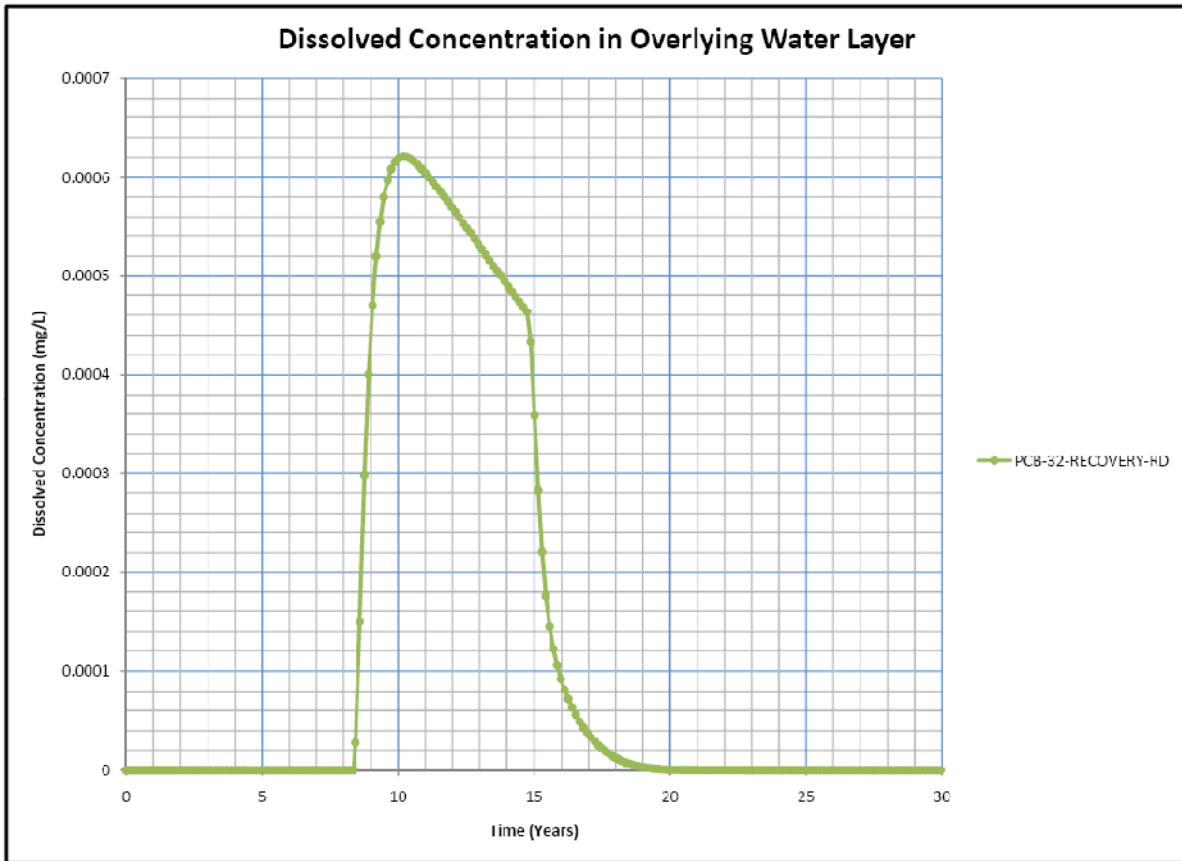


Figure 37: Hypothetical Application, PCB-32 in Water Column



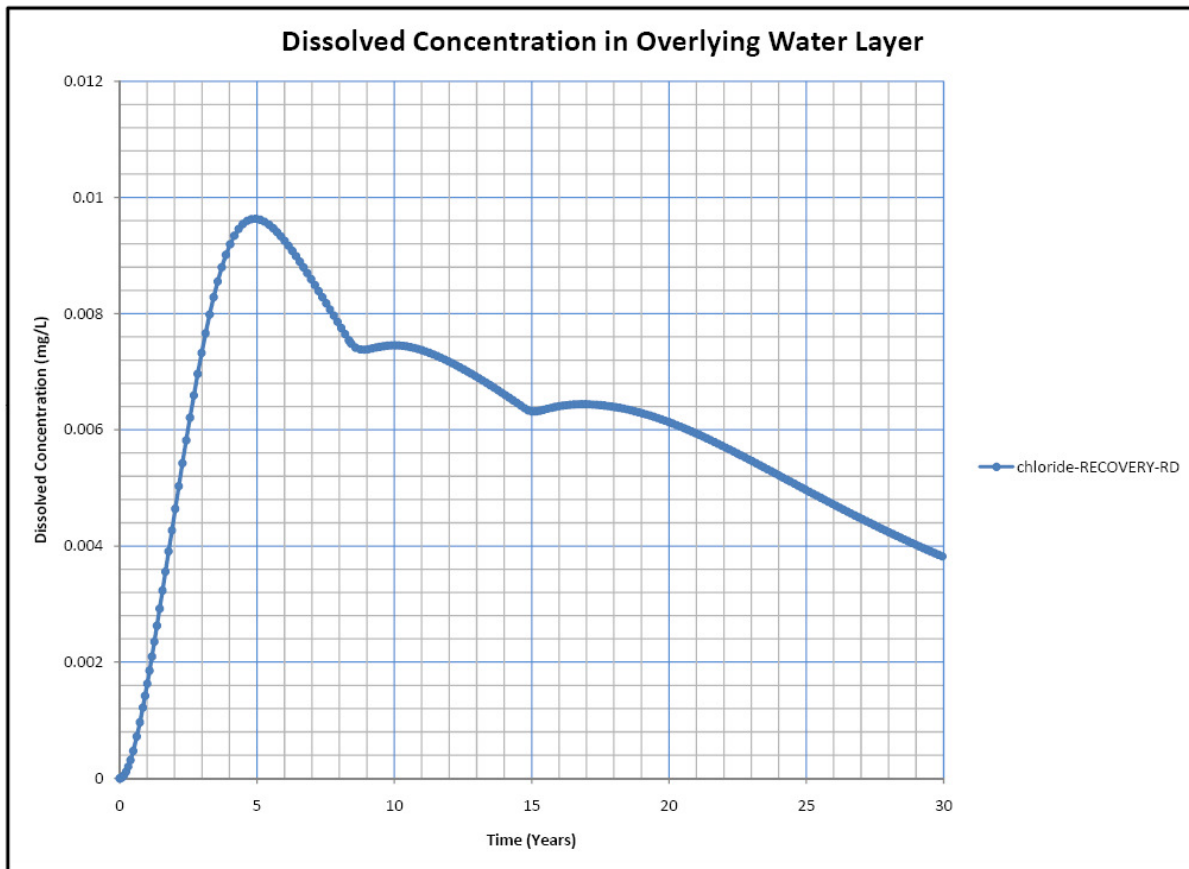


Figure 38: Hypothetical Application, Chloride Byproduct in Water Column

The key point that may be gleaned from this set of results is the significant difference that exists between the water layer and the sediment system. A comparison between the decay rates for the ultimate product, PCB-125, shows a much more rapid decline with respect to dissolved concentration in the overlying water column. This can be attributed to the flushing mechanisms in the water column that have been previously discussed. Essentially, the water column is being flushed while biotransformation



occurs at a lesser rate within the sediment layers. The product congeners, PCB-71 and PCB-32, are then transported to the water column by diffusive flux from the mixed sediment layer.

The last part of Test Case III is a set of concentration profiles for the first five model layers representing each of the simulated PCB congeners as well as chloride. Each profile compares the starting condition to the final result at the end of the 30 year simulation period. This set of figures provides evidence of the separation provided by a sediment cap between the water layer and deep sediment system.



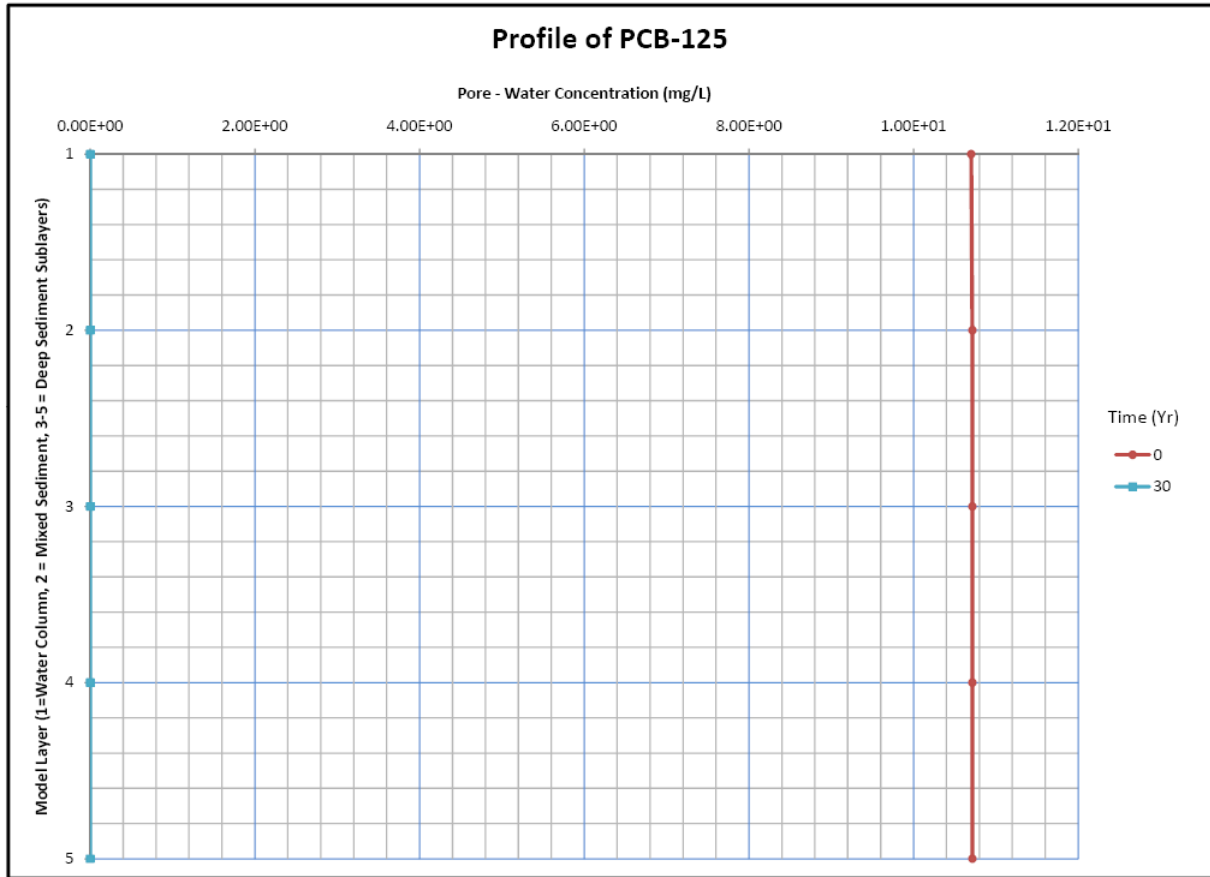


Figure 39: Hypothetical Application, Initial and Final Concentration Profiles of PCB-125



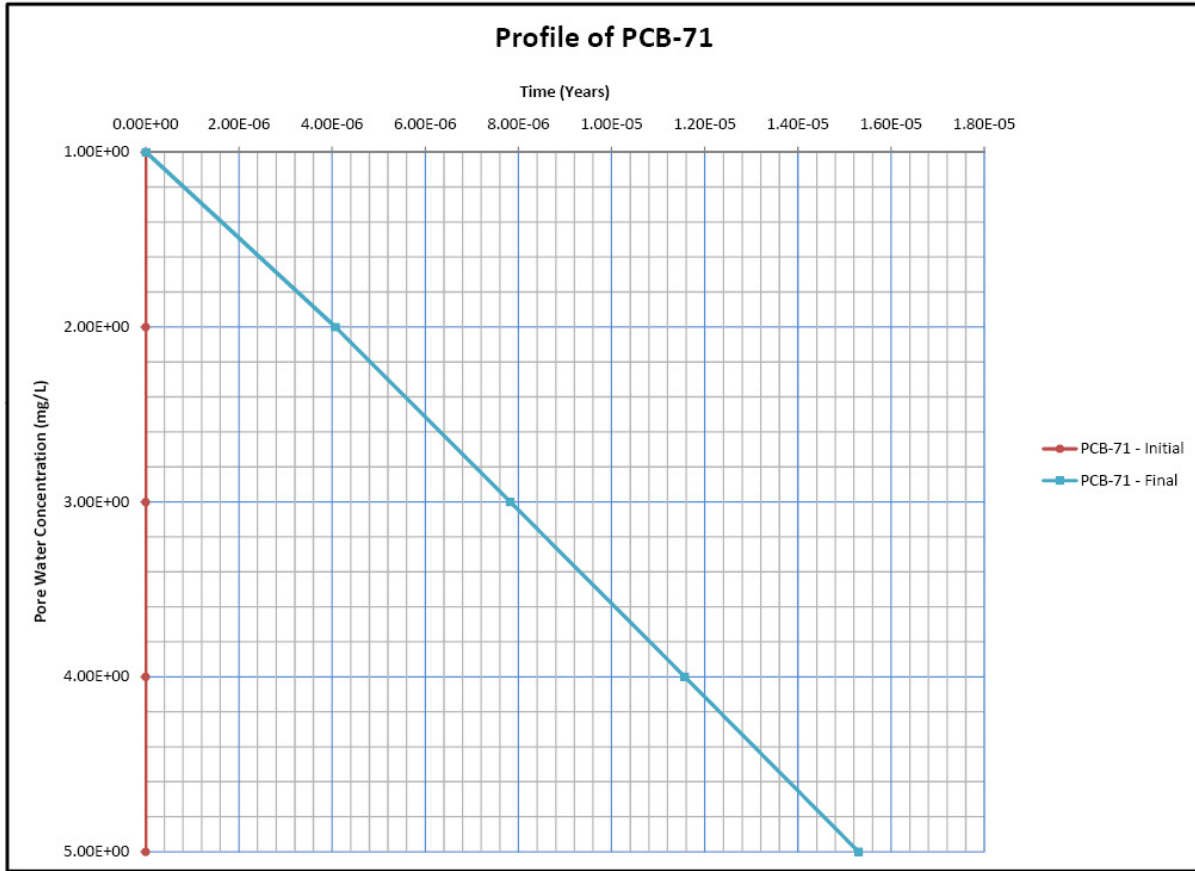


Figure 40: Hypothetical Application, Initial and Final Concentration Profiles of PCB-71



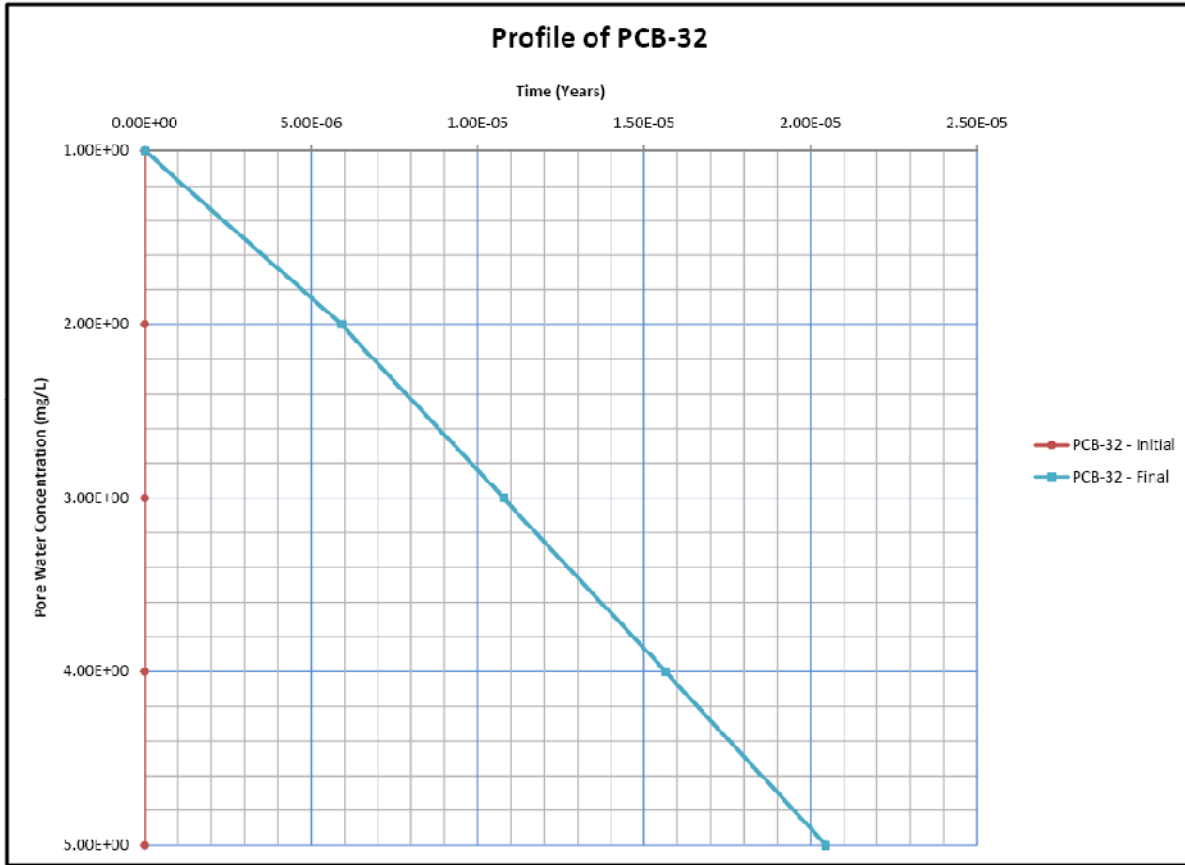


Figure 41: Hypothetical Application, Initial and Final Concentration Profiles of PCB-32



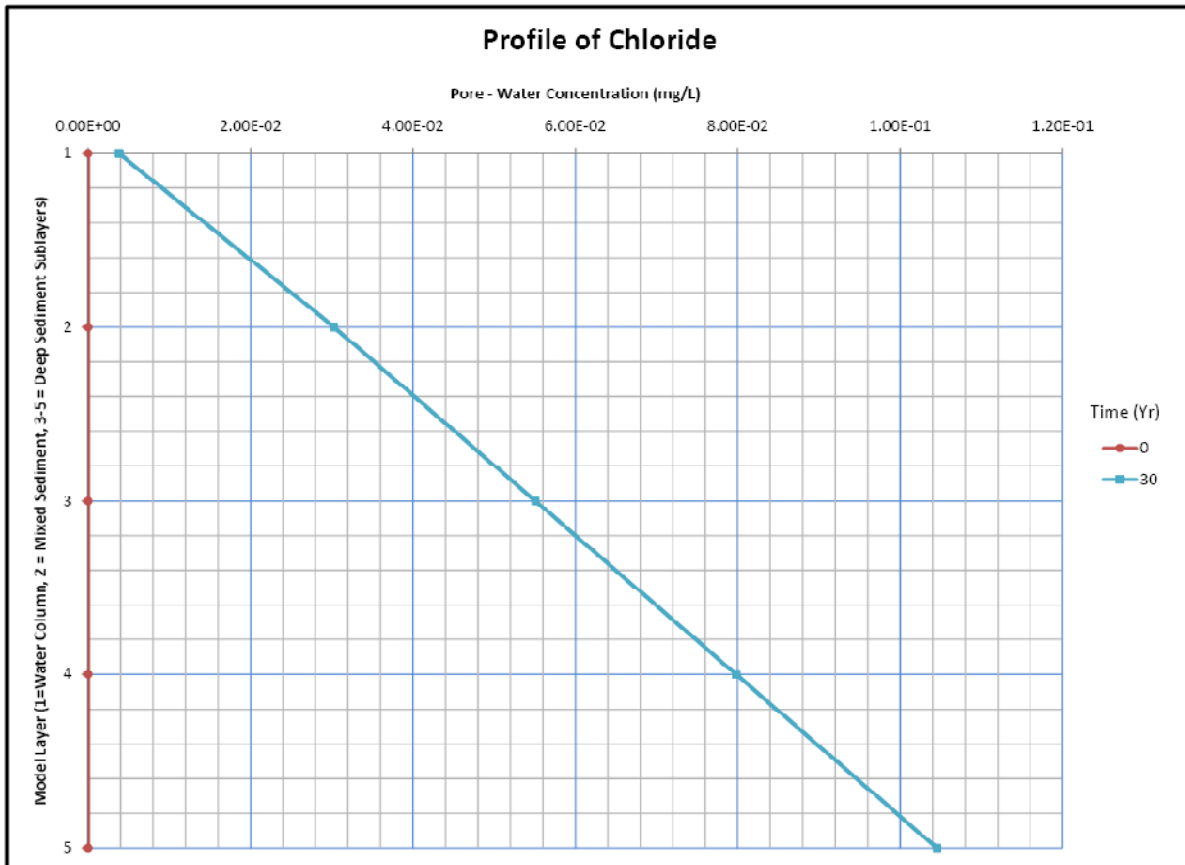


Figure 42: Hypothetical Application, Initial and Final Concentration Profiles of Chloride

The pore-water concentration profiles provide support for the conclusions made from the first set of figures. As the overlying water column or layer number 1 is mostly influenced by flushing and diffusion from the mixed sediment layer, the sediment system is mostly controlled by biological decay and generation. In addition, mass transport within the deep sediment system is also observed as the concentration of the product congeners increases with depth.



While a more realistic application may be significantly different with respect to the initial conditions and partitioning parameters, this test case provides a simplified representation of the effectiveness of a subaqueous cap. In addition, this test is evidence of the effectiveness of in-situ natural recovery through biotransformation. Essentially, this shows that RECOVERY-RD is capable of serving as a testing mechanism for a remedial design that combines two approaches.



5 Conclusions

The research findings described in this thesis have resulted in a validated model for the simulation of the transport and biotransformation of PCBs in stratified sediment systems. Referring back to the introductory section, RECOVERY-RD represents a significant step forward due to the representation of PCB-specific processes. This includes the creation of a package of model code specifically formulated to address the convoluted biological processes associated with PCB congeners. This is particularly important due to the potentially-significant interest in natural recovery through biodegradation.

In general, the design of RECOVERY-RD has created a useful tool for the design of effective remedial techniques for systems contaminated with PCB compounds, particularly sub-aqueous sediment caps. The evaluation of a remedial technique such as capping requires careful testing prior to implementation. RECOVERY-RD provides a tool that can accomplish this task in a relatively straightforward manner. In addition, RECOVERY-RD retains most of the functionality of the original RECOVERY. This provides the user with significant flexibility with respect to the simulation of transport and decay processes, which is important when considering the intentions associated with the model. In screening-level applications, the ability to represent variety and perform sensitivity analyses is of utmost importance.

The test cases discussed in the Chapter 4 show that RECOVERY-RD provides reasonable results when compared to established surrogates. In each case, the modifications were validated and qualified based on the assumptions associated with each test. While some of the modifications resulted in divergence from the results obtained from SEAM3D, the magnitude of this difference can be quantified



through a traditional sensitivity analysis. In addition, the test cases were generated in a way that highlights this difference. More realistic applications will still be subject to the discrepancy, but to a lesser degree than observed in test cases II and III. Finally, the hypothetical application provides a good example of a relatively simple examination that could be accomplished with RECOVERY-RD.



6 Recommendations for Further Research

This section provides a brief discussion of areas where RECOVERY-RD may be improved by future work. The suggestions relate to particular areas of RECOVERY-RD that were identified during the testing process.

Program Efficiency

An effort to improve solution efficiency would require a significant amount of changes with respect to the format of the two models. A secondary goal of this study was to minimize the modifications for both RECOVERY and the SEAM3D packages that were used. This being the case, a knowledgeable programmer could drastically improve both the required calculation time and the memory requirement for a given simulation.

Generalization of PCB Package to Include General Reductive Processes

Although the Reductive Dechlorination Package was modified to be specific to the biotransformation characteristics of PCB compounds, it may be reasonable to use a more generalized approach that could apply to a wider range of contaminants. This would involve reformatting the inhibition terms associated with more chlorinated compounds, as they exist in the original RDP.

Integration of Nutrient Availability

The original form of the Biodegradation Package, as it exists within SEAM3D, has the capability to consider decay rate limitations imposed by nutrient availability. This has been disabled within the RECOVERY-RD version of the package due to the minor role associated with PCB biotransformation.



Significant reformatting of the programming structure would be required to consider this process within RECOVERY-RD.

Safeguards within Program (Time Stepping, Rapid PCB decay, etc.)

As described earlier, a safeguard was added to the step-size increase portion of the ODE solution that prevents time step values from becoming too large. This safeguard was generically defined and could easily be revised. Similarly, the tolerance value that protects the threshold concentration for PCB decay could be determined in a more accurate manner. A more accurate method would involve a more parameterized regression that includes the inhibition function representing the electron acceptor category.

GUI-Base Input Dialog

The GUI-based pre- and post-processor associated with version 4.3.1 of RECOVERY provides an elegant method of input creation. While the Microsoft Excel-based input dialog associated with RECOVERY-RD is certainly more powerful, it lacks the aesthetic appeal of a GUI.



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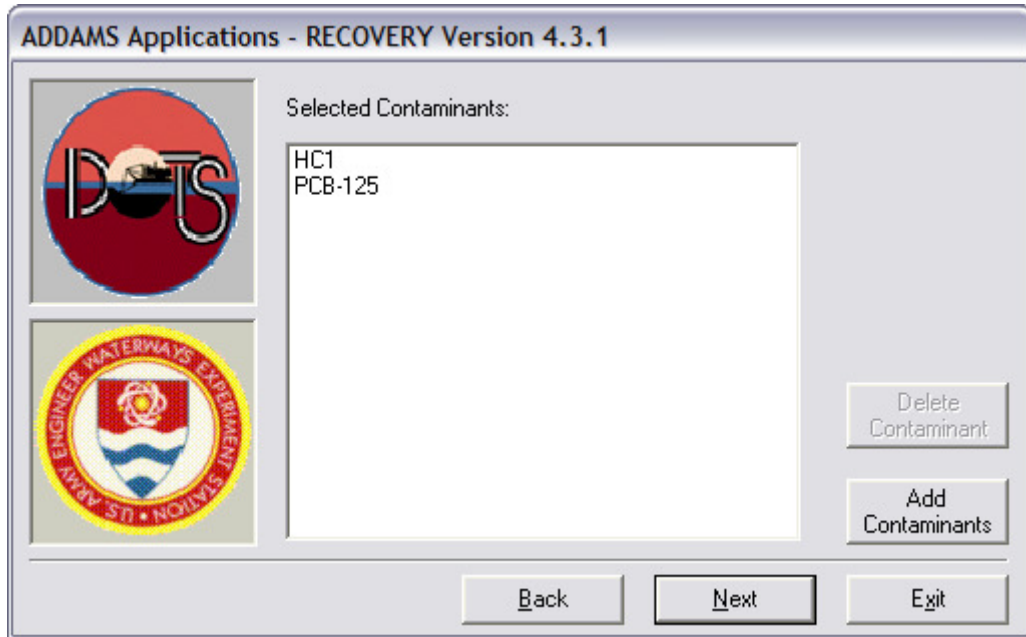
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Appendix A: RECOVERY Input for Test Case I





Test Case I, RECOVERY, Identification of Constituents



ADDAMS Applications - RECOVERY Version 4.3.1

MORPHOMETRY AND HYDROLOGY

Import data from an existing RECOVERY data file for use under ARAMS/FAMES:

Water

Mixed Sediments

Deep Contaminated Sediments

Clean Sediments

WATER

Choose one of the external loading options below.

Steady State Time Varying

Suspended Solids Concentration (mg/L) Ref: 0

Weight Fraction Carbon in Solid Ref: 0

Enter 3 of the following values and press Recalculate Button to calculate the 4th value

Water Surface Area (m²) Ref: 0

Water Depth (m) Ref: 0

Flow Through (m³/yr) Ref: 0

Residence Time (years) Ref: 0

Calculated Residence Time (years)

Test Case I, RECOVERY, Morphometry and Hydrology of Water Column



ADDAMS Applications - RECOVERY Version 4.3.1

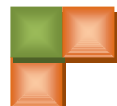
MORPHOMETRY AND HYDROLOGY

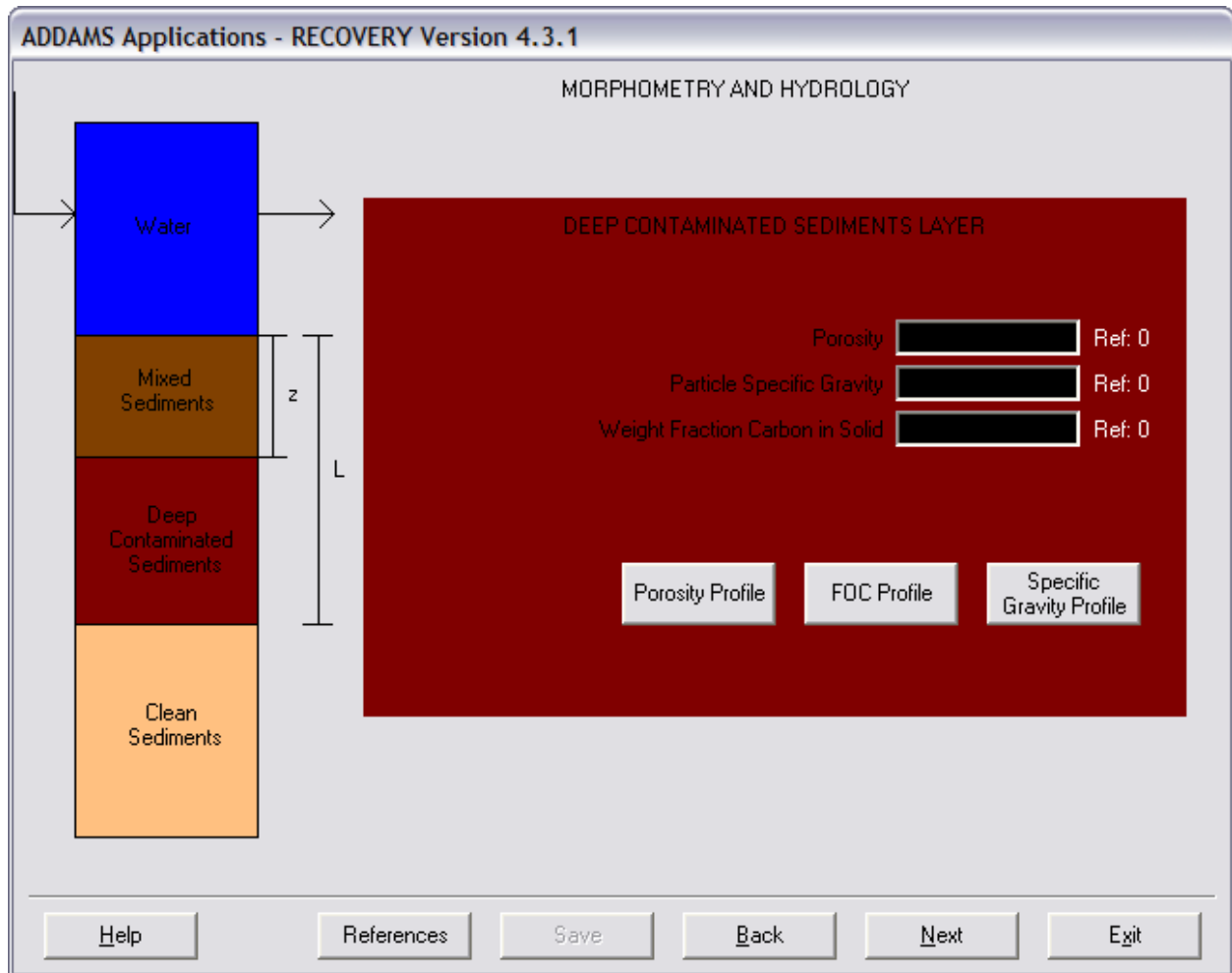
L = Contaminated Sediments Depth (m) Ref: 0
 z = Depth of Mixed Sediments Layer (m) Ref: 0

MIXED SEDIMENTS LAYER

Mixed Sediments Layer Surface Area (m²) Ref: 0
 Porosity Ref: 0
 Particle Specific Gravity Ref: 0
 Weight Fraction Carbon in Solid Ref: 0

Test Case I, RECOVERY, Morphometry and Hydrology of Mixed Sediment Layer





Test Case I, RECOVERY, Morphometry and Hydrology of Deep Sediment System



ADDAMS Applications - RECOVERY Version 4.3.1

SYSTEM PROPERTIES

Wind Speed (m/sec)	<input type="text" value="2.0000"/>	Ref: 0
Enhanced Diffusion (cm ² /sec)	<input type="text" value="0.00000000E+00"/>	Ref: 0
Enhanced Mixing Depth (cm)	<input type="text" value="0"/>	Ref: 0

Input two of the following velocities and the third will be calculated:

Resuspension Velocity (m/yr)	<input type="text" value="0"/>	Ref: 0
Burial Velocity (m/yr)	<input type="text" value=".0005"/>	Ref: 0
Settling Velocity (m/yr)	<input type="text" value="90"/>	Ref: 0

Calculated Resuspension Velocity (m/yr)

Test Case I, RECOVERY, System Properties



ADDAMS Applications - RECOVERY Version 4.3.1

Previous Compound HC1 Properties Next Compound

Initial Concentration in Water (micrograms/L) Ref: 0
 Inflow Concentration (micrograms/L) Ref: 0
 Additional Constant External Loadings (kg/year) Ref: 0
 Initial Concentration in Mixed Sediments (mg/kg) Ref: 0
 Initial Concentration in Deep Sediments (mg/kg) Ref: 0

Molecular Difussivity (cm²/sec) Ref: 0
 Henry's Constant (atm·m³/gmole) Ref: 0
 Molecular Weight Ref: 0
 Octanol-Water Partition Coeff. (mg/m³ Octanol)/(mg/m³ Water) Ref: 0

For contaminants with an Octanol-Water partition coefficient of zero, partition coefficients can be specified by clicking on the "View Calculated Data" button.

DECAY COEFFICIENTS (1/yr)

Dissolved Contaminant:				Particulate Contaminant:			
In Water	<input type="text" value="0"/>	Ref: 0		In Water	<input type="text" value="0"/>	Ref: 0	
In Mixed Layer	<input type="text" value="0"/>	Ref: 0		In Mixed Layer	<input type="text" value="0"/>	Ref: 0	
In Deep Sediments	<input type="text" value="0"/>	Ref: 0		In Deep Sediments	<input type="text" value="0"/>	Ref: 0	

Test Case I, RECOVERY, Constituent 1 (HC1) Properties



ADDAMS Applications - RECOVERY Version 4.3.1

Previous Compound PCB-125 Properties Next Compound

Initial Concentration in Water (micrograms/L) 2130.0000 Ref: 0
 Inflow Concentration (micrograms/L) 0.0000 Ref: 0
 Additional Constant External Loadings (kg/year) 0.0000 Ref: 0
 Initial Concentration in Mixed Sediments (mg/kg) 2.00000000E+05 Ref: 0
 Initial Concentration in Deep Sediments (mg/kg) 0.00000000E+00 Ref: 0

Deep Sediments Concentration Profile

Molecular Difussivity (cm²/sec) 2.0000E-06 Ref: 0
 Henry's Constant (atm·m³/gmole) 5.9200E-05 Ref: 0
 Molecular Weight 326.4600 Ref: 0
 Octanol-Water Partition Coeff. (mg/m³ Octanol)/(mg/m³ Water) 5750000.0000 Ref: 0

For contaminants with an Octanol-Water partition coefficient of zero, partition coefficients can be specified by clicking on the "View Calculated Data" button.

View Calculated Data

DECAY COEFFICIENTS (1/yr)

Dissolved Contaminant:			Particulate Contaminant:		
In Water	<input type="text" value="0"/>	Ref: 0	In Water	<input type="text" value="0"/>	Ref: 0
In Mixed Layer	<input type="text" value="0"/>	Ref: 0	In Mixed Layer	<input type="text" value="0"/>	Ref: 0
In Deep Sediments	<input type="text" value="0"/>	Ref: 0	In Deep Sediments	<input type="text" value="0"/>	Ref: 0

Help References Save Back Next Exit

Test Case 1, RECOVERY, Constituent 3 (PCB-125) Properties



ADDAMS Applications - RECOVERY Version 4.3.1

MODEL PARAMETERS

Total Period of Simulation (years)	<input type="text" value="10.00"/>
Number of Time Steps Between Print Intervals for Output File	<input type="text" value="1"/>
Number of Time Steps Between Print Intervals for Sediment Layers	<input type="text" value="10"/>
Number of Layers to Print	<input type="text" value="50"/>

Using small values (such as 1) for the time steps between print intervals (especially with long simulation periods) can cause large amounts of data to be output by the model. If the deep sediments profile does not animate properly or the application crashes, increase these numbers and run the model again.

Test Case I, RECOVERY, Model Parameters



Appendix B: RECOVERY-RD Input for Test Case I



Instructions: Complete Sections 1-3 on this sheet and then Steps 1-8 on the Input (A), (B), and (C) worksheets. Enter values into white cells only.

1. System morphometry and hydrology

WATER

External loading options (type "x" in only one): steady state time varying

Enter 3 of the following values and Excel will calculate the 4th value.

Water surface area, A_w (m^2)	<input type="text" value="1.00E+07"/>	Suspended solids concentration (mg/L)	<input type="text" value="5"/>
Water depth (m)	<input type="text" value="10"/>	Weight fraction carbon in solid	<input type="text" value="0.05"/>
Flow through, Q (m^3/yr)	<input type="text" value="2.00E+07"/>		
Residence time (yrs)	<input type="text" value="5"/>		

MIXED SEDIMENTS LAYER

L = contaminated sediments depth (m)	<input type="text" value="1"/> (max L = 50 m)	Porosity	<input type="text" value="0.7"/>
z = depth of mixed sediments layer (m)	<input type="text" value="0.05"/>	Particle specific gravity	<input type="text" value="2.5"/>
Mixed sediments surface area, A_m (m^2)	<input type="text" value="1.00E+07"/>	Weight fraction carbon in solid	<input type="text" value="0.05"/>

DEEP CONTAMINATED SEDIMENTS LAYER

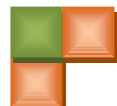
Porosity	<input type="text" value="0.7"/>
Particle specific gravity	<input type="text" value="2.5"/>
Weight fraction carbon in solid	<input type="text" value="0.05"/>

Porosity, FOC and Specific Gravity Profiles (optional):

Maximum depth (meters) = 0.95	Porosity		FOC		Specific Gravity	
Depth (m)	Depth (m)	Porosity	Depth (m)	FOC	Depth (m)	Specific Gravity
<input type="text" value="0.05"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>

Depth entries specify the cumulative depth to which the corresponding parameter value will extend. Depth is relative to the mixed-deep sediments interface. NOTE, the cumulative depth cannot exceed the maximum specified above.

Test Case I, RECOVERY-RD, System Morphometry and Hydrology



2. System Properties

Wind speed (m/sec)	2
Enhanced diffusion (cm ² /sec)	0
Enhanced mixing depth (cm)	0

Enter 2 of the following velocities and Excel will calculate the 3rd value.

Resuspension velocity, v_r (m/yr)		1E-04
Burial velocity, v_b (m/yr)	0.0005	
Settling velocity, v_s (m/yr)	90	

Test Case I, RECOVERY-RD, System Properties**3. Model Parameters**

Time period of simulation (years)	10
Number of time steps between print intervals for output file	1
Number of time steps between print intervals for sediment layers	10
Number of layers to print	50

Using small values (such as 1) for the time steps between print intervals (especially with long simulation periods) can cause the model to output large amounts of data. If the deep sediments profile does not animate properly or the application crashes, increase these numbers and run the model again.

Test Case I, RECOVERY-RD, Model Parameters

INPUT (A): PCB congeners and dechlorination processes
 Instructions: complete the START worksheet and then Steps 1-3 on this and the Input (D) and (O) worksheets.

STEP 1. Enter BZ # of each congener at time = 0
 Enter BZ #s separated by a comma and space then press enter. (Up to 20 BZ #s may be entered.)
 125

STEP 2. Identify the simulated dechlorination process(es):
 Type an "x" in the box for processes you want to simulate, delete the "x" from processes you don't want to simulate, and click the Update button to the right.

M	G	C	H	P	N	LM & ortho
x						

Values in this table fill automatically based on the input above.

M	G	C	H	P	N	LM & ortho
x						

Table 1 (results in red are the terminal products)

BZ #	Structure	Stepwise Dechlorination Product (BZ #) by Process result if only this process was used (e.g.)							Result of Multiple Processes
		M	G	C	H	P	N	LM & ortho	
125	2,3,4,5,6	71	79	71	79	79	71	76	71
71	2,3,4,6	32	32	32	27	27	32	33	32
32	2,4,6	32	32	10	32	32	32	8	32

GENERAL INFORMATION ON PCBs

Predicted Stepwise Dechlorination. This input dialogue is tied to an algorithm that predicts each successive product of repeated dechlorination steps ("stepwise dechlorination"). Based on the dechlorination process(es) specified, the most susceptible chlorine is removed from each initial PCB congener. Products are then subjected to another dechlorination step. This continues until no further dechlorination is possible under the given process(es). The results are reported in Table 1. For a single process, chlorines are attacked in the order shown in the first table below. When multiple processes are selected, the algorithm prioritizes dechlorination based on Williams's sediment ranking, which can be written in the following order:
 DFM, DFP, SFP, SFM, UFM, UFP, LP, LM, SFC, UFO, LO

BZ Numbers. The 209 congeners are identified herein using the system developed by Ballschmiter & Zell (1980). These "BZ Numbers" have been universally adopted despite their departure from IUPAC number in the case of 11 congeners (numbers 33, 34, 76, 98, 122, 123, 124, 125, 177, 196, 201).

Structure. There are 10 possible positions for chlorine substitution (replacing the hydrogens in the original biphenyl), as denoted by numbers assigned to each of the carbon atoms. See the diagram below.

Polychlorinated Biphenyl (PCB)

Dechlorination Processes. The algorithm uses the seven processes (M, G, C, H, P, N, & LM) described by Bedard and Quensen (1995) and adds a process to allow the removal of both meta (M) and ortho-substituted chlorines (ortho). These processes attack chlorines in specific positions as shown in the following table.

Key	Positions Attacked by Dechlorination Process						
	M	G	C	H	P	N	LM & ortho
DF = double-linked							
DFM = double-linked meta	DFM	DFP	DFM	DFM	DFM	DFM	DFM
DFP = double-linked para	DFM	DFP	DFM	SFP	DFP	DFP	DFM
DFH = double-linked ortho	DFM	SFP	DFM	SFP	SFP	DFP	DFM
DFN = double-linked ortho	DFM	SFP	DFM	SFP	SFP	SFP	DFM
DFL = double-linked ortho	DFM	SFP	DFM	SFP	SFP	SFP	DFM
DFO = double-linked ortho	DFM	SFP	DFM	SFP	SFP	SFP	DFM
DFM = meta-substituted							
DFP = para-substituted							
DFH = ortho-substituted							
DFN = ortho-substituted							
DFL = ortho-substituted							
DFO = ortho-substituted							

Using Hudson River, Silver Lake, and Wood Pond sediments, Williams (1974) developed an approximate ranking for the susceptibility of chlorine positions on PCBs to undergo dechlorination.

Ranking based on acclimation times observed in laboratory experiments and dechlorination patterns observed in laboratory and environmental samples:

Order: Position of chlorine on chlorinated ring

1. doubly-flanked meta chlorine (2,3,4- to 2,4-; 2,3,4,6- to 2,4,6-)
2. doubly-flanked para chlorine (3,4,5- to 3,5-; 2,3,4,5- to 2,3,5-)
3. singly-flanked para chlorine (3,4- to 3-; 2,4,5- to 2,5-)
4. singly-flanked meta chlorine (2,3,5- to 2,5-; 2,4,5- to 2,4-)
5. unflanked meta or para ortho or meta-substituted ring (2,5- to 2-; 2,4- to 2-; 2,4,6- to 2,6-)
6. isolated meta or para chlorine (3- or 4- to biphenyl; opposite a substituted ring)
7. singly-flanked ortho chlorine (2,3,5,6- to 2,3,5-)
8. unflanked ortho chlorine on di- or tri-substituted ring (2,4,6- to 2,4- to 4-)
9. isolated ortho chlorine (5- to biphenyl)

Test Case I, RECOVERY-RD, PCB Congeners and Dechlorination Processes



STEP 6: Substrate Concentrations and Properties (enter values in the white cells)

Hydrocarbon #	Initial Water Conc.	Initial Mixed Conc.	Initial Deep Conc.*	Inflow Conc.	External Load	K _w diss. water	K _w part. water	K _w diss. mixed	K _w part. mixed	K _w diss. deep	K _w part. deep	Molecular diffusivity	Henry's Constant	Molecular Weight
(HC #)	(µg/L)	(mg/kg _{max})	(mg/kg _{max})	(µg/L)	(kg/yr)	(yr ⁻¹)	(yr ⁻¹)	(yr ⁻¹)	(yr ⁻¹)	(yr ⁻¹)	(yr ⁻¹)	(cm ² /sec)	(atm·m ³ /mole)	(g/mole)
1	12000	5	5	0	0	0.01	0	0.08	0	0.08	0	0.000005	0.0000121	46.1
2				0	0	0.005	0	0.03	0	0.03	0	0.000005	0.000183	88.1
3				0	0	0.001	0	0.005	0	0.005	0	0.000005	0.0000013	94.1

* You may enter starting concentrations that vary with depth using the Input (D) worksheet

Test Case I, RECOVERY-RD, Substrate Concentrations and Properties

K _{ow}	K _D water	K _D mixed	K _D deep	K _s , Half-Sat. Constant	Threshold conc.	E _{meth} , Methane Gen. Coefs.	η _{o,ls} , EA Use Coeff. (of O ₂)	η _{n,ls} , EA Use Coeff. (of NO ₃)	η _{s,ls} , EA Use Coeff. (of Fe(III))	η _{m,ls} , EA Use Coeff. (of Mn(IV))	η _{s,ls} , EA Use Coeff. (of SO ₄)
(mg/g[octanol]/mg/g[H ₂ O])	(m ² /g)	(m ² /g)	(m ² /g)	(mg/L _{water})	(mg/L _{water})	(g[met]/g[HC])	(g[EA]/g[HC])	(g[EA]/g[HC])	(g[EA]/g[HC])	(g[EA]/g[HC])	(g[EA]/g[HC])
0.49	1.51E-08	1.51E-08	1.51E-08	See table in Step 8 below	0	0.1	0	0	0	0	0
5.37	1.66E-07	1.66E-07	1.66E-07		0	0.1	0	0	0	0	0
29.8	8.88E-07	8.88E-07	8.88E-07		0	0.1	0	0	0	0	0

Test Case I, RECOVERY-RD, Substrate Concentrations and Properties (Continued)



STEP 7: Electron Acceptor and EA Product Concentrations and Properties

Electron Acceptor	Initial Water Conc. (mg/L)	Initial Mixed Conc. (mg/L)	Initial Deep Conc.* (mg/L)	Inflow Conc. (mg/L)	Mineral Load (kg/d)	Molecular Weight (g/mol)	Heavy's Constant (kg-mol/mole)	Molecular Weight (g/mol)	Half-Sat. Constant (mg/L)	Threshold conc. (mg/L)	R _{max} Inhib. Coeff. (by CS) (mg/L)	R _{max} Inhib. Coeff. (by HS) (mg/L)	R _{max} Inhib. Coeff. (by NH ₄) (mg/L)	R _{max} Inhib. Coeff. (by Fe(II)) (mg/L)	R _{max} Inhib. Coeff. (by SO ₄) (mg/L)	R _{max} Inhib. Coeff. (by SO ₃) (mg/L)	EA Product Coeff. (kg-mol/kg)	EA Use Coeff. (of EA) (kg/kg)	EA Coeff. (of PCBs) (mg/mg)	EA Inhib. Coeff. (of PCBs) (mg/mg)	
O ₂	0	0	0	0	0	32	1.00E-06	32	0	0	100	0	0	0	0	0	0	0	0	100	
NO ₃	0	0	0	0	0	62	1.00E-06	62	0	0	100	0	0	0	0	0	0	0	0	0	100
Mn(IV) (as Mn)	0	0	0	0	0	55	1.00E-06	55	0	0	100	0	0	0	0	0	0	0	0	0	100
Fe(II) (as Fe)	0	0	0	0	0	55	1.00E-06	55	0	0	100	0	0	0	0	0	0	0	0	0	100
SO ₄	0	0	0	0	0	98	1.00E-07	1.00E-10	0	0	100	0	0	0	1000	0	0	0	0	0	100
CO ₂	0	0	0	0	0	44	1.00E-06	44	0	0	100	0	0	0	1000	0	0	0	0	0	100

* You may enter starting concentrations directly with depth using the Input (I) worksheet

STEP 8: EA Product Concentrations and Properties

EA Product	Initial Water Conc. (mg/L)	Initial Mixed Conc. (mg/L)	Initial Deep Conc.* (mg/L)	Inflow Conc. (mg/L)	Mineral Load (kg/d)	Molecular Weight (g/mol)	Heavy's Constant (kg-mol/mole)	Molecular Weight (g/mol)
N ₂	0	0	0	0	0	28	1.00E-06	28
NH ₄	0	0	0	0	0	18	1.00E-06	18
HS	0	0	0	0	0	34	1.00E-06	34
SO ₃	0	0	0	0	0	81	1.00E-06	81

* You may enter starting concentrations directly with depth using the Input (I) worksheet

Create input files for RECOVERY-RD?
CREATE

Test Case I, RECOVERY-RD, EA and EA Product Concentrations and Properties

STEP 9: Revised Electron Acceptor Process (TEAP) Microbiology data

Microbiology	Active TEAPs Enter (reactive), Exit (inertive)	Initial Mixed Conc. (mg/L)	Initial Deep Conc.* (mg/L)	Threshold Conc. (mg/L)	K _d Death Rate (1/d)	K _d Half Sat. Constant Using HC:			K _d Max Specific Rate of HC Use Using HC:			Y _{max} Maximal Yield Coeff. Using HC:			
						HC(1) (mg/L)	HC(2) (mg/L)	HC(3) (mg/L)	HC(1) (d ⁻¹)	HC(2) (d ⁻¹)	HC(3) (d ⁻¹)	HC(1) (mg/mg)	HC(2) (mg/mg)	HC(3) (mg/mg)	
direct oxidizers	T	0.01	0	0	0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
NO ₃ reducers (using O ₂)	F	0	0	0	0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
NO ₃ reducers (using NO ₃)	F	0	0	0	0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
Mn-reducers	F	0	0	0	0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
Fe-reducers	F	0	0	0	0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
SO ₄ -reducers	F	0	0	0	0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
Methanogens	T	0.1	0.1	0	0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
PCP-dechlorinators	T	1000	1000	0	0	0	0	0	0	0	0	0	0	0	0

* You may enter starting concentrations directly with depth using the Input (I) worksheet

Create biodegradation and RD input files?
CREATE

Test Case I, RECOVERY-RD, TEAP Parameters



Appendix C: SEAM3D Biodegradation Package Input for Test Case II



Biodegradation Package ✕

Gen. Coeff.	Use Coeff.	Sat. Const.	Rates
Min. Conc.	Start. Conc.		Elec. Acc.

Number of bio steps per transport step:

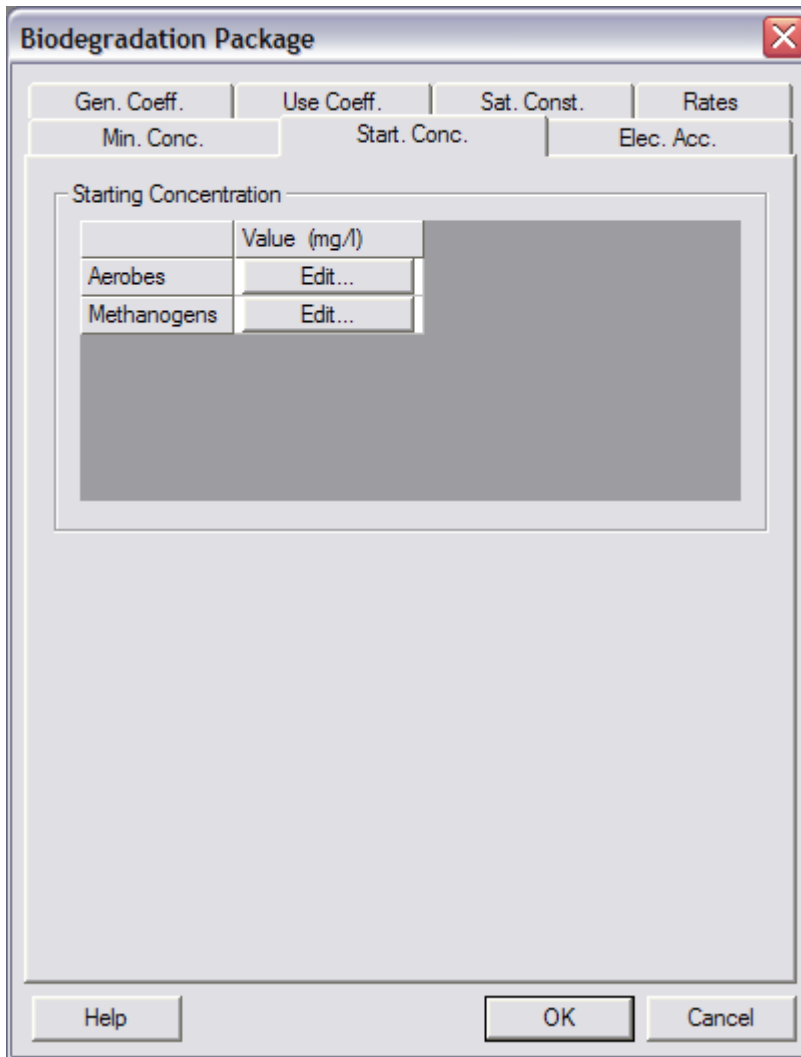
Screen output cell I: J: K:

Microcolony minimum concentration: (mg/m³)

Minimum Concentration

	Value (mg/m ³)
Substrate	0.0
O2	0.0

Test Case II, SEAM3D, Biodegradation Package Input Window #1



Test Case II, SEAM3D, Biodegradation Package Input Window #2*

*Note: Aerobe and Methanogen Starting Concentrations = 0.1 mg/L



Biodegradation Package [X]

Gen. Coeff.	Use Coeff.	Sat. Const.	Rates
Min. Conc.	Start. Conc.	Elec. Acc.	

Inhibition Coefficient

	Value
Methane-O2	1.0

Yield Coefficient

	Value
O2-Substrate	0.0
Methane-Substrate	0.0

Help OK Cancel

Test Case II, SEAM3D, Biodegradation Package Input Window #3



Biodegradation Package

Min. Conc. Start. Conc. Elec. Acc.
Gen. Coeff. Use Coeff. Sat. Const. Rates

Product Coefficient

Methane Coefficient

	Value
Substrate	1.0

Daughter Coefficient

Help OK Cancel

Test Case II, SEAM3D, Biodegradation Package Input Window #4



Value	
O2-Substrate	10.0

Test Case II, SEAM3D, Biodegradation Package Input Window #5



Biodegradation Package [X]

Min. Conc.	Start. Conc.	Elec. Acc.
Gen. Coeff.	Use Coeff.	Sat. Const.
		Rates

Hydro. Half Saturation Constant

	Value
O2-Substrate	1.0
Methane-Substrate	1.0

Electron Acceptor Half Saturation Constant

	Value
O2	10.0

Nutrient Half Saturation Constant

Use all nutrients to limit growth Use min. nutrient to limit growth

Help OK Cancel

Test Case II, SEAM3D, Biodegradation Package Input Window #6

Biodegradation Package [X]

Min. Conc.	Start. Conc.	Elec. Acc.
Gen. Coeff.	Use Coeff.	Sat. Const.
Rates		

Death Rate

	Value
Aerobes	0.0
Methanogens	0.0

Calculated by model
 No death
 Constant

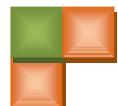
Max. Specific Rate of Substrate Utilization

	Value
O2-Substrate	10.0
Methane-Substrate	10.0

Vary spatially

Help OK Cancel

Test Case II, SEAM3D, Biodegradation Package Input Window #7



Appendix D: SEAM3D Reductive Dechlorination Package Input for Test Case II



Reductive Dechlorination Package

Coefficients | Reductive Dechlorination Factors

Concentrations | Saturation Constants | Rates

Min. concentration for microbe populations: 0.0

Chlorinated Compound Minimum Concentration

	Value
PCE	0.0
TCE	0.0
DCE	0.0
VC	0.0
Ethene	0.0
Chloride	0.0

Starting Concentration

	Value
PCE/TCE Reducers	Edit...
DCE/VC Reducers	Edit...

Help | OK | Cancel

Test Case II, SEAM3D, Reductive Dechlorination Package Input Window #1*

*Note: PCE/TCE and DCE/VC Reducer Starting Concentrations = 1 mg/L



Reductive Dechlorination Package [X]

Coefficients Reductive Dechlorination Factors
Concentrations Saturation Constants Rates

Half Sat. Constant for Reductive Dechlorination

	Value
PCE	1.0
TCE	1.0
DCE	1.0
VC	1.0

Half Sat. Constant for Direct Oxidation

	Value
Aerobes-DCE	0.0
Aerobes-VC	0.0
Methanogens-DCE	0.0
Methanogens-VC	0.0

Help OK Cancel

Test Case II, SEAM3D, Reductive Dechlorination Package Input Window #2



Reductive Dechlorination Package

Coefficients Reductive Dechlorination Factors
Concentrations Saturation Constants Rates

Death Rate

	Value	
PCE/TCE Reducers	0.0	
DCE/VC Reducers	-1.0	

Calculated by model No death Constant

Max. Specific Rate of Reductive Dechlorination

	Value	
PCE	3.0	
TCE	3.0	
DCE	3.0	
VC	3.0	

Max. Rate of Direct Oxidation

	Value	
Aerobes-DCE	0.0	
Aerobes-VC	0.0	
Methanogens-DCE	0.0	

Help OK Cancel

Test Case II, SEAM3D, Reductive Dechlorination Package Input Window #3*

Note: All Maximum Rates of Direct Oxidation = 0



Reductive Dechlorination Package [X]

Concentrations Saturation Constants Rates

Coefficients Reductive Dechlorination Factors

Yield Coefficient

	Value	
PCE	0.0	
TCE	0.0	
DCE	0.0	
VC	0.0	

Use Coefficient

	Value	
O2-DCE	0.0	
O2-VC	0.0	

Methane Generation Coefficient

	Value	
Methanogens-DCE	0.0	
Methanogens-VC	0.0	

Help OK Cancel

Test Case II, SEAM3D, Reductive Dechlorination Package Input Window #4



Reductive Dechlorination Package

Concentrations | Saturation Constants | Rates
Coefficients | **Reductive Dechlorination Factors**

Chlorinated Ethene Inhibition Terms

	Value
PCE - O2	100.0
TCE - O2	100.0
TCE - PCE	0.00001
DCE - O2	100.0
DCE - PCE	10000.0
DCE - TCE	0.00001

Chlorinated Ethene Stoichiometric Factors

	Value
PCE->TCE	0.89278932
PCE->Chloride	0.10721068
TCE->DCE	0.88014109
TCE->Chloride	0.11985891
DCE->VC	0.86410933
DCE->Chloride	0.13589067

Help OK Cancel

Test Case II, SEAM3D, Reductive Dechlorination Package Input Window #5, Part A*

*Note: Tables continued in **Error! Reference source not found.**



Reductive Dechlorination Package

Concentrations Saturation Constants Rates
Coefficients Reductive Dechlorination Factors

Chlorinated Ethene Inhibition Terms

	Value
DCE - PCE	10000.0
DCE - TCE	0.00001
VC - O2	100.0
VC - PCE	10000.0
VC - TCE	10000.0
VC - DCE	0.00001

Chlorinated Ethene Stoichiometric Factors

	Value
TCE->Chloride	0.11985891
DCE->VC	0.86410933
DCE->Chloride	0.13589067
DCE->Ethene	0.0
VC->Ethene	0.5
VC->Chloride	0.5

Help OK Cancel

Test Case II, SEAM3D, Reductive Dechlorination Package Input Window #5, Part B



Appendix E: RECOVERY-RD Input for Test Case II



Instructions: Complete Sections 1-3 on this sheet and then Steps 1-8 on the Input (A), (B), and (C) worksheets. Enter values into white cells only.

1. System morphometry and hydrology

WATER

External loading options (type "x" in only one): steady state time varying

Enter 3 of the following values and Excel will calculate the 4th value.

Water surface area, A_w (m^2)	3.60E+03	Suspended solids concentration (mg/L)	5
Water depth (m)	2	Weight fraction carbon in solid	0.05
Flow through, Q (m^3/yr)	2.00E+07		
Residence time (yrs)	0.00036		

MIXED SEDIMENTS LAYER

L = contaminated sediments depth (m)	1 (max L = 50 m)	Porosity	0.7
z = depth of mixed sediments layer (m)	0.01	Particle specific gravity	2.5
Mixed sediments surface area, A_m (m^2)	3.60E+03	Weight fraction carbon in solid	0.05

DEEP CONTAMINATED SEDIMENTS LAYER

Porosity	0.7	Particle specific gravity	2.5
Weight fraction carbon in solid	0.05		

Porosity, FOC and Specific Gravity Profiles (optional):

Maximum depth (meters)	Depth (m)		Depth (m)		Depth (m)	
= 0.99	Porosity	FOC	FOC	Specific Gravity	Specific Gravity	Specific Gravity
Depth entries specify the cumulative depth to which the corresponding parameter value will extend. Depth is relative to the mixed-deep sediments interface. NOTE, the cumulative depth cannot exceed the maximum specified above.						

Test Case II, RECOVERY-RD, System Morphometry and Hydrology



2. System Properties

Wind speed (m/sec)	2
Enhanced diffusion (cm ² /sec)	0
Enhanced mixing depth (cm)	0

Enter 2 of the following velocities and Excel will calculate the 3rd value.

Resuspension velocity, v_r (m/yr)		1E-04
Burial velocity, v_b (m/yr)	0.0005	
Settling velocity, v_s (m/yr)	90	

Test Case II, RECOVERY-RD, System Properties**3. Model Parameters**

Time period of simulation (years)	10
Number of time steps between print intervals for output file	1
Number of time steps between print intervals for sediment layers	1
Number of layers to print	1

Using small values (such as 1) for the time steps between print intervals (especially with long simulation periods) can cause the model to output large amounts of data. If the deep sediments profile does not animate properly or the application crashes, increase these numbers and run the model again.

Test Case II, RECOVERY-RD, Model Parameters

INPUT (A): PCB congeners and dechlorination processes
 Instructions: complete the START worksheet and then Steps 1 & 2 on this and the input (B) and (C) worksheets.

STEP 1. Enter BZ # of each congener at time = 0
 Enter BZ #s separated by a comma and space then press enter. (Up to 20 BZ #s may be entered)
 125

STEP 2. Identify the simulated dechlorination process(es):
 Type an "x" in the box for processes you want to simulate, delete the "x" from processes you don't want to simulate, and click the Update button to the right.

M	Q	C	H'	H	P	N	LM & ortho
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Update

Values in this table fill automatically based on the input above.

M	Q	C	H'	H	P	N	LM & ortho
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Table 1 (results in red are the terminal products)

BZ #	Structure	Stepwise Dechlorination Product (BZ #) by Process result if only this process was used							Result of Multiple Processes
		M	Q	C	H'	H	P	N	
125	2',3,4,5,6	71	73	71	73	73	71	76	71
71	2,3,4,5	0E	0E	0E	27	27	0E	00	0E
32	2,4,6	32	32	10	32	32	32	8	32

GENERAL INFORMATION ON PCBs

Predicted Stepwise Dechlorination. This input dialog is tied to an algorithm that predicts each successive product of repeated dechlorination steps ("stepwise dechlorination"). Based on the dechlorination process(es) specified, the most susceptible chlorine is removed from each initial PCB congener. Products are then subjected to another dechlorination step. This continues until no further dechlorination is possible under the given process(es). The results are reported in Table 1. For a single process, chlorines are attacked in the order shown in the first table below. When multiple processes are selected, the algorithm prioritizes dechlorination based on Willam's estimates below, which can be written in the following order: DFM, DFP, SFP, 3FM, UFM, UFP, LP, LM, SFO, UFO, LO.

BZ Numbers. The 209 congeners are identified herein using the system developed by Ballschmied & Zell (1980). These "BZ Numbers" have been universally adopted despite their slight departure from IUPAC number in the case of 11 congeners (numbers 33, 34, 76, 03, 123, 123, 124, 125, 177, 186, 201).

Structure. These are 10 possible positions for chlorine substitution (replacing the hydrogens in the original Biphenyl), as denoted by numbers assigned to each of the carbon atoms. See the diagram below.

Polychlorinated Biphenyl (PCB)

Dechlorination Processes. The algorithm uses the seven processes (M, Q, C, H', H, P, N) described by Bedard and Quensen (1995) and adds a process to allow the removal of lone meta (LM) and ortho-substituted chlorines (ortho). These processes attack chlorines in specific positions as shown in the following table.

Key	Positions Attacked by Dechlorination Process						
	M	Q	C	H'	H	P	N
DF = substituted							LM & ortho
SF = single-substituted	DFM	DFP	DFM	SFM	DFM	SFP	DFM
UF = un-substituted	SFM	SFP	SFM	UFP	UFP	SFP	SFM
L = lone	UFM	SFM	UFM	SFP	SFP	SFP	SFM
M = meta-substituted	UF	UFP	SFM				LO
P = para-substituted			UF				
O = ortho-substituted							

Using Hudson River, Great Lakes, and Woods Pond sediments, Williams (1994) developed an approximate ranking for the susceptibility of chlorine positions on PCBs to undergo dechlorination.

Ranking based on acclimation times observed in laboratory experiments and dechlorination patterns observed in laboratory and environmental samples!

Order: Position of chlorine on chlorinated ring

- 1 double-flanked meta chlorine (2,3,4- to 2,4-, 2,3,4,6- to 2,4,6)
- 2 double-flanked para chlorine (3,4,5- to 3,5; 2,3,4,5- to 2,3,5)
- 3 singly flanked para chlorine (3,4- to 3-, 2,4,5- to 2,5)
- 4 singly flanked meta chlorine (2,3,5- to 2,5-, 2,4,5- to 2,4)
- 5 unflanked meta or para on 4- or 6-substituted ring (2,5- to 2-, 2,4-, to 2-, 2,4,6- to 2,6)
- 6 isolated meta or para chlorine (5- or 4- to biphenyl) opposite a substituent ring
- 7 singly flanked ortho chlorine (2,3,6,6'- to 2,3,6)
- 8 unflanked ortho chlorine on 4- or 6-substituted ring (2,4,6- to 2,4- to 4-)
- 9 isolated ortho chlorine (2- to biphenyl)

Test Case II, RECOVERY-RD, PCB Congeners and Dechlorination Processes



STEP 6: Substrate Concentrations and Properties (enter values in the white cells)

Hydrocarbon #	Initial Water Conc.	Initial Mixed Conc.	Initial Deep Conc.*	Inflow Conc.	External Load	K _w water column	Molecular diffusivity	Henry's Constant	Molecular Weight	K _{ow} (mg/g[octanol])	K _D water (calculated)
(HC #)	(µg/L)	(mg/kg _{sediment})	(mg/kg _{sediment})	(µg/L)	(kg/yr)	(yr ⁻¹)	(cm ² /sec)	(atm·m ³ /mole)	(g/mole)	/mg/g[H ₂ O]	(m ² /g)
1	0	7	7	0	0	0.01	0.000005	0.0000121	46.1	1.00E-10	3.09E-18
2				0	0	0.01	0.000005	0.0000121	46.1	1.00E-10	3.09E-18
3				0	0	0.01	0.000005	0.0000121	46.1	1.00E-10	3.09E-18

* You may enter starting concentrations that vary with depth using the Input (D) worksheet

Test Case II, RECOVERY-RD, Substrate Concentrations and Properties

K _D mixed (calculated)	K _D deep (calculated)	K ^s , Half-Sat. Constant	Threshold conc.	ξ _{w,lo} , Methane Gen. Coefs.	γ _{o,lo} , EA Use Coeff. (of O ₂)	γ _{h,lo} , EA Use Coeff. (of NO ₃)	γ _{Fe,lo} , EA Use Coeff. (of Fe(III))	γ _{Mn,lo} , EA Use Coeff. (of Mn(IV))	γ _{SO₄,lo} , EA Use Coeff. (of SO ₄)
(m ² /g)	(m ² /g)	(mg/L _{water})	(mg/L _{water})	(g/meth)/g[HC]	(g[-A])/g[HC]	(g[-A])/g[HC]	(g[-A])/g[HC]	(g[-A])/g[HC]	(g[-A])/g[HC]
3.09E-18	3.09E-18	See table in Step 8 below	0	1	10	0	0	0	0
3.09E-18	3.09E-18		0	0	0	0	0	0	0
3.09E-18	3.09E-18		0	0	0	0	0	0	0

Test Case II, RECOVERY-RD, Substrate Concentrations and Properties (Continued)



STEP 7a: Electron Acceptor and EA Product Concentrations and Properties

Electron Acceptor	Initial Water Conc. (µg/L)	Initial Mixed Conc. (mg/kg _{sediment})	Initial Deep Conc. (mg/kg _{sediment})	Inflow Conc. (µg/L)	External Load (kg/yr)	Molecular Diffusivity (cm ² /sec)	Henry's Constant (atm·m ³ /mole)	Molecular Weight (g/mole)	Half-Sat. Constant (mg/L)	Threshold conc. (mg/L)	K ₁₀ Inhib. Coeff. (by O ₂) (mg/L _{sediment})	K ₁₀ Inhib. Coeff. (by NO ₃) (mg/L _{sediment})	K ₁₀ Inhib. Coeff. (by Mn(IV)) (mg/L _{sediment})	K ₁₀ Inhib. Coeff. (by Fe(III)) (mg/L _{sediment})	K ₁₀ Inhib. Coeff. (by SO ₄) (mg/L _{sediment})	Product Gen. Coeff. (g/product/g EA)	EA Use Coeff. (of PCBs) (g(gEA)/gPCB)	K ₁₀ Coeff. (of PCBs) (mg/L _{sediment})	ERBC Coeff. (of PCBs) (mg/L _{sediment})
O ₂	0	0.00933	0.00933	0	0	2.00E-05	0.7692	32	See table in Gap 6	0	100	200	300	1620	540	0	1.00E-02	100	100
NO ₃	0	0	0	0	0	2.00E-06	1.00E-05	62	0	100	200	300	1620	540	0	0.5	100	100	100
Mn(IV) solid	0	0	0	0	0	2.00E-06	1.00E-05	56	0	100	200	300	1620	540	0	0.5	100	100	100
Fe(III) solid	0	0	0	0	0	2.00E-06	1.00E-05	56	0	100	200	300	1620	540	0	0.5	100	100	100
SO ₄	0	0	0	0	0	8.00E-07	1.00E-10	96	0	100	200	300	1620	540	0	0.5	100	100	100
CO ₂	0	0	0	0	0	1.00E-05	0.677	44	0	100	200	300	1620	540	0	0.5	100	100	100

* You may enter starting concentrations that vary with depth using the Input (b) worksheet

STEP 7b: EA Product Concentrations and Properties

EA Product	Conc. (µg/L)	Conc. (mg/kg _{sediment})	Conc. (mg/kg _{sediment})	Conc. (µg/L)	Load (kg/yr)	diffusivity (cm ² /sec)	Constant (atm·m ³ /mole)	Weight (g/mole)
HC ₁	0	0	0	0	0	2.00E-06	1.639	28
HC ₂	0	0	0	0	0	2.00E-05	0.01	58
HC ₃	0	0	0	0	0	2.80E-05	0.01	18
CH ₄	0	0	0	0	0	1.50E-05	0.677	16

* You may enter starting concentrations that vary with depth using the Input (b) worksheet

Create RECOVERY-RD input files?
CREATE

Test Case II, RECOVERY-RD, EA and EA Product Concentrations and Properties

STEP 8: Terminal Electron Acceptor Process (TEAP) / Microcolony data

Microcolony	Active TEAPs Enter for x=0,7 (Te-active, F=inactive)	Initial Mixed Conc. (mg/L)	Initial Deep Conc. (mg/L)	Threshold Conc. (mg/L)	K _d Death Rate	K ₁₀ HC Half-Sat. Constant Using HC:			K ₁₀ EA Half-Sat. Constant	q ^{max} Max Specific Rate of HC Util. Using HC:			Y _{biom} Biomass Yield Coeff. Using HC:		
						HC(1) (mg/L _{sediment})	HC(2) (mg/L _{sediment})	HC(3) (mg/L _{sediment})		HC(1) (yr ⁻¹)	HC(2) (yr ⁻¹)	HC(3) (yr ⁻¹)	HC(1) (mg/L _{sediment})	HC(2) (mg/L _{sediment})	HC(3) (mg/L _{sediment})
strict aerobes	T	0.1	0.1	0	0	1	0	0	10	10	0	0	0	0	0
NO ₃ reducers (using O ₂)					The value below also applies for direct oxidation	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
NO ₃ reducers (using NO ₃)	F	0	0	The same value applies to all micro-colonies	0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
Mn-reducers	F	0	0		0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
Fe-reducers	F	0	0		0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
SO ₄ reducers	F	0	0		0	0.01	0.01	0.01	10	0.5	0.25	0.125	0	0	0
Methanogens	T	0.1	0.1		0	1	0	0	10	10	0	0	0	0	0
dechlorinators	T	1	1		0										

* You may enter starting concentrations that vary with depth using the Input (b) worksheet

Create biodegradation & RD input files?
CREATE

Test Case II, RECOVERY-RD, TEAP Properties



Appendix F: RECOVERY-RD Input for Test Case III



STEP 5: Biotransformation Parameters**a. SEDIMENT. Reaction kinetics can be modeled using linear or Monod expressions.**

(Enter 0 for linear or 1 for Monod then enter the appropriate parameters below)

mixed sed. = deep sed = *The values entered below will be the same for all congeners. To vary these parameters between congeners, manually enter different values in the PCB Properties worksheet.***Monod Parameters**Half-saturation concentration for PCB utilization for: RD (mg/L) =
direct oxid (mg/L) = Maximum utilization rate for: reductive dechlorination (yr^{-1}) =
oxidation (yr^{-1}) = Threshold concentration for: reductive dechlorination (mg/L) =
oxidation (mg/L) = Yield coefficient for PCBs (g[bio]/g[PCB]) = **b. WATER COLUMN. First-order decay occurs in the regime. Enter the decay rate:**Decay rate in water column (yr^{-1}) =

Test Case III, RECOVERY-RD, First-Order Decay Input



Appendix G: RECOVERY-RD Input for Model Application



Instructions: Complete Sections 1-3 on this sheet and then Steps 1-8 on the Input (A), (B), and (C) worksheets. Enter values into white cells only.

1. System morphometry and hydrology

WATER

External loading options (type "x" in only one): steady state time varying

Enter 3 of the following values and Excel will calculate the 4th value.

Water surface area, A_w (m^2)	3.60E+03	Suspended solids concentration (mg/L)	5
Water depth (m)	10	Weight fraction carbon in solid	0.05
Flow through, Q (m^3/yr)	1.00E+04		
Residence time (yrs)	3.6		

MIXED SEDIMENTS LAYER

L – contaminated sediments depth (m)	1 (max L = 50 m)	Porosity	0.7
z = depth of mixed sediments layer (m)	0.5	Particle specific gravity	2.5
Mixed sediments surface area, A_m (m^2)	3.60E+03	Weight fraction carbon in solid	0.05

DEEP CONTAMINATED SEDIMENTS LAYER

Porosity	0.7
Particle specific gravity	2.5
Weight fraction carbon in solid	0.05

Porosity, FOC and Specific Gravity Profiles (optional):

Maximum depth (meters) = 0.5	Depth (m)	Porosity	Depth (m)	FOC	Depth (m)	Specific Gravity
Depth entries specify the cumulative depth to which the corresponding parameter value will extend. Depth is relative to the mixed-deep sediments interface. NOTE: the cumulative depth cannot exceed the maximum specified above.						

Scroll Down

2. System Properties

Wind speed (m/sec)	2
Enhanced diffusion (cm^2/sec)	0
Enhanced mixing depth (cm)	0

Enter 2 of the following velocities and Excel will calculate the 3rd value.

Resuspension velocity, v_r (myr)	0.000001	
Burial velocity, v_b (myr)	0.000001	
Settling velocity, v_s (myr)		0.3

3. Model Parameters

Time period of simulation (years)	30
Number of time steps between print intervals for output file	10
Number of time steps between print intervals for sediment layers	10
Number of layers to print	10

Using small values (such as 1) for the time steps between print intervals (especially with long simulation periods) can cause the model to output large amounts of data. If the deep sediments profile does not animate properly or the application crashes, increase these numbers and run the model again.

Example Application of RECOVERY-RD, System Morphometry and Hydrology



INPUT (A): PCB congeners and dechlorination processes
 Instructions: complete the START worksheet and then Steps 1-8 on this and the Input (B) and (C) worksheets

STEP 1. Enter BZ # of each congener at time = 0
 Enter BZ #s separated by a comma and space then press enter. (Up to 20 BZ #s may be entered.)
 125

STEP 2. Identify the simulated dechlorination process(es):
 Type an 'x' in the box for processes you want to simulate, delete the 'x' from processes you don't want to simulate, and click the Update button to the right.

M	O	C	H'	H	P	N	LM & ortho
x							

Values in this table fill automatically based on the input above.

M	O	C	H'	H	P	N	LM & ortho
x							

Table 1 (results in red are the terminal products)

BZ #	Structure	Stepwise Dechlorination Product (BZ # by Process (if only this process was used))							Result of Multiple Processes
		M	O	C	H'	H	P	N	
125	2',3,4,5,6'	71	73	71	73	73	71	76	71
71	2,3',4,6'	32	32	32	27	27	27	32	33
32	2,4',6	32	32	10	32	32	32	32	8

GENERAL INFORMATION ON PCBs

Predicted Stepwise Dechlorination. This is not a dialogue, it is an algorithm that predicts each successive product of repeated dechlorination steps ("stepwise dechlorination"). Based on the dechlorination process(es) specified, the most susceptible chlorine is removed from each initial PCB congener. Products are then subjected to another dechlorination step. This continues until no further dechlorination is possible under the given process(es). The results are reported in Table 1. For a single process, chlorines are attacked in the order shown in the first table below. When multiple processes are selected, the algorithm prioritizes dechlorination based on Williams's estimates below, which can be written in the following order: DFM, DFP, SFP, SFM, UFM, UFP, LP, LM, SFO, JFO, LO.

BZ Numbers. The 205 congeners are identified herein using the system developed by Dalschmiller & Zell (1980). These "BZ Numbers" have been universally adopted despite their slight departure from IUPAC number in the case of 11 congeners (numbers 33, 34, 76, 93, 122, 125, 124, 125, 177, 195, 201).

Structure. There are 10 possible positions for chlorine substitution (replacing the hydrogens in the original biphenyl), as denoted by numbers assigned to each of the carbon atoms. See the diagram below.

Polychlorinated Biphenyl (PCB)

Dechlorination Processes. An algorithm uses the seven processes (M, O, C, H, P, & N) described by Bodard and Quinson (1966) and adds a process to allow the removal of leno meta (LM) and ortho-substituted chlorines (ortho). These processes attack chlorines in specific positions as shown in the following table.

Key	M	O	C	H	H'	P	N	LM & ortho
DF = dechlorinated								
DF = single-flanked	SFM	SFP	SFM	SFM	DFM	DFP	SFM	LM
UF = unflanked	SFM	SFP	SFM	DFP	SFP	SFP	SFM	SFO
L = one	UFM	SFM	JFM	SFP	SFP	SFP	SFP	UFO
N = meta-substituted		UFP	JFP	SFM				LO
D = para-substituted		LF	LP	SFM				
O = ortho-substituted								

Using Hudson River, Silver Lake, and Woods Hole sediments, Williams (1994) developed an approximate ranking for the susceptibility of chlorine positions on PCBs to undergo dechlorination.

Ranking based on acclimation times observed in laboratory experiments and dechlorination patterns observed in laboratory and environmental samples!

Order:

- double-flanked meta chlorine (2,3,4- to 2,4-; 2,3,4,6- to 2,4,6)
- double-flanked para chlorine (3,4,5- to 3,5-; 2,3,4,5- to 2,3,5)
- single-flanked para chlorine (3,4- to 3-; 2,4,5- to 1,5-)
- single-flanked meta chlorine (2,3,5- to 1,5-; 2,4,5- to 1,4-)
- unflanked meta or para on di- or tri-substituted ring (2,5- to 1-; 2,4- to 2-; 2,4,6- to 2,6)
- isolated meta or para chlorine (3- or 4- to biphenyl) opposite a substituted ring
- single-flanked ortho chlorine (2,3,5,6- to 2,3,5)
- unflanked ortho chlorine on di- or tri-substituted ring (2,4,6- to 2,4- to 4-)
- isolated ortho chlorine (6- to biphenyl)

Example Application of RECOVERY-RD, PCB Congeners and Dechlorination Processes



STEP 3: System properties. Enter values in the white boxes. Values in the colored boxes are from the START worksheet.

suspended solids concentration in water (g/m³): 5

particle density (g/m³): mixed sediment 2.50E+06, deep sediment 2.50E+06

porosity: 0.7

fraction organic carbon (foc): water (foc_w) 0.05, mixed (foc_m) 0.05, deep (foc_d) 0.05

Type of sorption process:

- Linear. To simulate linear sorption, set $n = 1$ below and enter zero in the eight boxes under multiple fractions.
- Freundlich. $n_1 = 1$ Freundlich exponent (dimensionless)
- Multiple fractions. f_1 and f_2 represent additional carbon fractions (e.g. slack carbon, pitch). Input values, F_1 & F_2 (below), are defined: $F_i = TDC/f_i$

$F_{2w} = 0$ fraction 2 in the water column
 $F_{2m} = 0$ fraction 2 in the mixed sediment
 $F_{2d} = 0$ fraction 2 in the deep sediment
 $n_2 = 0$ Freundlich exponent (dimensionless)
 $K_{i2} = 0.5$ partitioning coefficient for fraction 2 (m³/g)

$F_{3w} = 0$ fraction 3 in the water column
 $F_{3m} = 0$ fraction 3 in the mixed sediment
 $F_{3d} = 0$ fraction 3 in the deep sediment
 $n_3 = 0$ Freundlich exponent (dimensionless)
 $K_{i3} = 0.1$ partitioning coefficient for fraction 3 (m³/g)

STEP 4: Initial Congener Concentrations (enter values in the white boxes):

Table 2 (Dissolved concentration & solubility provided as a reference.)

EZ #	Initial TOTAL Concentration (µg/L)			Initial Dissolved Concentration			Solubility (µg/L)	Inflow conc. (µg/L)	External Load (µg/y)
	Water	Mixed	Deep	Water	Mixed	Deep			
125	1.07E+04	1.00E+07	1.00E+01	1.07E+04	1.07E+07	1.07E+07		3.00E+10	3.00E+00

* You may enter starting concentrations that vary with depth using worksheet input (D)

STEP 5: Biotransformation Parameters

a. SEDIMENT. Reaction kinetics can be modeled using linear or Monod expressions. (Enter 0 for linear or 1 for Monod then enter the appropriate parameters below)

mixed sed. = 1, deep sed. = 1

The values entered below will be the same for all congeners. To vary these parameters between congeners, manually enter different values in the PCB Properties worksheet.

Monod Parameters

Half-saturation concentration for PCB utilization for: reductive (mg/L) = 5.00E+01, oxidative (mg/L) = 0.00E+00

Maximum utilization rate for: reductive dechlorination (yr⁻¹) = 1.00E+00, oxidation (yr⁻¹) = 0.00E+00

Threshold concentration for: reductive dechlorination (mg/L) = 0.00E+00, oxidation (mg/L) = 0.00E+00

Yield coefficient for PCBs (g(bio)/g(PCB)) = 0.00E+00

b. WATER COLUMN. First-order decay occurs in the regime. Enter the decay rate.

Decay rate in water column (yr⁻¹) = 0.0000

Scroll Down

Values in this table fill automatically.

Table 3: PCB Output Data

EZ #	Initial Water Concentration (µg/L)	Inflow Conc. (µg/L)	External Load (µg/yr)	Initial Mixed Concentration (mg/kg _{sediment})	Initial Deep Concentration (mg/kg _{sediment})	Molecular diffusivity (cm ² /sec)	Henry's Constant (atm-m ³ /mole)	Molecular Weight (g/mole)	K _{ow} (mg/g[octanol])	K ₀ water (calculated) (m ³ /g)	K ₀ mixed (calculated) (m ³ /g)	K ₀ deep (calculated) (m ³ /g)	K _w diss., water (yr ⁻¹)	K _w part., water (yr ⁻¹)	K _w diss., mixed (yr ⁻¹)
125	10700	0	0	10	10	2.00E-16	5.92E-05	326.46	1.00E+10	3.09E-18	3.09E-18	3.09E-18	0.00E+00	0.00E+00	0.00E+00
71	0	0	0	0	0	2.00E-16	1.31E-04	292.01	1.00E+10	3.09E-18	3.09E-18	3.09E-18	0.00E+00	0.00E+00	0.00E+00
25	0	0	0	0	0	2.00E-16	2.14E-04	297.35	1.00E+10	3.09E-18	3.09E-18	3.09E-18	0.00E+00	0.00E+00	0.00E+00

Example Application of RECOVERY-RD, Properties and Starting Contaminant Concentrations



STEP 6: Substrate Concentrations and Properties (enter values in the white cells)

Hydrocarbon # (HC #)	Initial Water Conc. ($\mu\text{g/L}$)	Initial Mixed Conc. ($\text{mg/kg}_{\text{sediment}}$)	Initial Deep Conc.* ($\text{mg/kg}_{\text{sediment}}$)	Inflow Conc. ($\mu\text{g/L}$)	External Load (kg/yr)	K_w water column (yr^{-1})	Molecular diffusivity (cm^2/sec)	Henry's Constant ($\text{atm}\cdot\text{m}^3/\text{mole}$)	Molecular Weight (g/mole)	K_{ow} ($\text{mg/g}[\text{octanol}]/\text{mg/g}[\text{H}_2\text{O}]$)	K_D water (calculated) (m^2/g)	K_D mixed (calculated) (m^2/g)
1	0	1	1	0	0	0.01	0.000005	0.0000121	46.1	1.00E-10	3.09E-18	3.09E-18
2				0	0	0.01	0.000005	0.0000121	46.1	1.00E-10	3.09E-18	3.09E-18
3				0	0	0.01	0.000005	0.0000121	46.1	1.00E-10	3.09E-18	3.09E-18

* You may enter starting concentrations that vary with depth using the Input (D) worksheet

Example Application of RECOVERY-RD, Substrate Concentrations and Properties

K_D deep (calculated) (m^2/g)	K^s , Half-Sat. Constant ($\text{mg/L}_{\text{water}}$)	Threshold conc. ($\text{mg/L}_{\text{water}}$)	$\xi_{x,1s}$, Methane Gen. Coefs. ($\text{g}[\text{meth}]/\text{g}[\text{HC}]$)	$\gamma_{1s,1e}$, EA Use Coeff. (of O_2) ($\text{g}[\text{EA}]/\text{g}[\text{HC}]$)	$\gamma_{1s,1e}$, EA Use Coeff. (of NO_2) ($\text{g}[\text{EA}]/\text{g}[\text{HC}]$)	$\gamma_{1s,1e}$, EA Use Coeff. (of Fe(III)) ($\text{g}[\text{EA}]/\text{g}[\text{HC}]$)	$\gamma_{1s,1e}$, EA Use Coeff. (of Mn(IV)) ($\text{g}[\text{EA}]/\text{g}[\text{HC}]$)	$\gamma_{1s,1e}$, EA Use Coeff. (of SO_4) ($\text{g}[\text{EA}]/\text{g}[\text{HC}]$)
3.09E-18	See table in Step 8 below	0	1	10	0	0	0	0
3.09E-18		0	0	0	0	0	0	0
3.09E-18		0	0	0	0	0	0	0

Example Application of RECOVERY-RD, Substrate Concentrations and Properties (Continued)



