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DEVELOPMENT OF A ONE-DIMENSIONAL CONTAMINANT MODEL FOR STREAMS AND RIVERS

By

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DEVELOPMENT OF A ONE-DIMENSIONAL CONTAMINANT MODEL FOR STREAMS AND RIVERS

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The Contaminant Model for Streams (CMS) was developed for use in studies where both data and resources for model application are limited. CMS can be quickly and easily applied, yet it is still versatile enough to be used for a variety of conditions ranging from short term spill modeling to multi-year simulations of contaminant fate in stream water and bottom sediments.

The model can be applied for both organic and inorganic contaminants. Suspended solids can be transported or a steady-state concentration may be input. Steady-state, uniform hydraulic conditions are assumed within the modeled reach, which greatly reduces model complexity.

A model application may consist of one or more reaches connected in series or in a branched network. Possible sediment model configurations include: 1) water column only, 2) water column and mixed sediment layer, and 3) water column, mixed sediment layer, and deep sediment layer.

DEDICATION

I would like to dedicate this research to my wife and daughter. I know that my school work often kept me from spending time with them, and I plan to correct this now that I’m done.

ACKNOWLEDGMENTS

This work was supported in part by the US Army Corps of Engineers as part of my duties at the Engineer Research and Development Center (ERDC) in Vicksburg, MS.

I would like to thank Dr. Mark Dortch and the other members of the Water Quality and Contaminants Modeling Branch of the Environmental Laboratory at ERDC. I learned a great deal during my time at ERDC and hope that it is reflected in this thesis.

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INTRODUCTION

1.1 Background

The Adaptive Risk Assessment Modeling System (ARAMS) was developed for the Army by the Army Corps of Engineers Engineer Research and Development Center (ERDC) and the U.S. Army Center for Health Promotion and Preventive Medicine (US-ACHPPM) to provide a reliable platform for conducting human and ecological health risk assessment. ARAMS integrates multimedia fate/transport and multi-pathway exposure and uptake with effects assessment to characterize risk. Although many models are available in ARAMS for fate/transport in water, there were not any models for predicting fate of contaminants in streams with sediment interactions. There are many riverine water quality models available that were considered for use in ARAMS, however, none of these models met the requirements without introducing excessive complexity. An examination of existing models for such a system was conducted, but no models were found that met all of the ARAMS requirements, would integrate easily into the framework, and would be both flexible and easy-to-use. Therefore, the Contaminant Model for Streams (CMS) was planned to meet the requirements of the ARAMS modeling system while still maintaining a stand-alone mode for uses such as model calibration, testing, and comparison of numerical solution methods.

1.2 Objectives

The overall objective of this study was to develop a flexible, but easy-to-use, one-dimensional (1D), numerical contaminant model for streams and rivers. Other objectives were:

- to be able to predict time-varying contaminant concentrations in the water column and sediment bed and include the effects of sediment processes and interactions;
- to be able to simulate short-term spill concentrations, as well as long term fate;
- to provide some degree of freedom over the numerical solution settings, but still be easy to setup and run and quickly provide useful results; and
- to provide a user interface to facilitate ease of use for model set up and quickly viewing results.

This paper presents the theoretical basis for the model, the model verification results, and a description of model inputs.

CHAPTER 2

APPROACH

The fundamental law utilized in the development of the CMS is conservation of mass along the longitudinal axis (flow direction) of a surface water body, such as a stream. The stream surface water is represented by a 1D (longitudinal) discretization for mass balance, where mass concentrations are assumed to be uniform across the width and depth of the stream. Constituent mass balance is performed for the water column and sediment bed. The sediment bed is divided into a fully-mixed, active surface layer and a vertically-distributed deep layer. The sediment layers for each longitudinal segment are independent of other longitudinal bed segments, i.e., there is no longitudinal transport or transfer within the bed.

Each active sediment layer segment interacts with only the water column immediately above it and the deep layer immediately below it. The average depth of the mixed sediment layer is specified for each reach in the model. It is assumed that there will always be an active sediment layer and that the average depth of the active sediment layer will remain constant due to biological and physical processes. The solids in the active sediment layer will be affected by settling and resuspension interactions with the water column as well as burial to the deep sediment layer. However, even if the active sediment layer is scoured away due to a flood or other major event, it is assumed that sediment will be integrated from the deep sediment layer to form a new active sediment layer.

Each deep sediment layer segment is represented by a 1D (vertical) discretization for mass balance and interacts only with the active layer directly above it. Numerical solution schemes are used to provide flexibility for simulating variable inputs and a variety of processes.

2.1 Governing Equations

When using the solids transport option in the model, there are three unknowns impacting the water column mass balance: contaminant concentration in the water column, contaminant concentration in the active sediment layer and suspended solids concentration. The two unknowns for the contaminant balance require two equations: a mass balance equation for the water column and one for the active sediment layer. The deep sediment layer does not directly interact with the water column so it is not included in the water column mass balance. However, the active sediment layer is also affected by the deep sediment layer concentration. Therefore, an additional contaminant mass balance for the deep sediment layer is required. For suspended solids, a mass balance equation for the water column is required. Each of these equations are presented along with assumptions and supporting equations.

2.1.1 Water Column Contaminants

The dependent state variable for contaminants in the water column is concentration of total chemical mass (dissolved and particulate) on a total water volume basis. The governing equation becomes,

$$\begin{aligned}\frac{\partial c_w}{\partial t} + U\frac{\partial c_w}{\partial x} &= D_x\frac{\partial^2 c_w}{\partial x^2} - \left(k_{dw} + \frac{k_v}{H}\right) F_{dw}c_w - k_{pw}F_{pw}c_w \\ &\quad -\frac{V_s}{H}F_{pw}c_w - \frac{V_r}{H}c_b - \frac{V_d}{H}\left(F_{dw}c_w - F_{db}c_b\right) \qquad (2.1)\end{aligned}$$

where,

U = mean velocity (L/T)

D_x = longitudinal diffusion coefficient (L^2/T)

k_v = volatilization rate of the constituent (L/T)

x = downstream distance (L)

c_b = concentration of the constituent in the sediment bed (M/L^3), total mass on a total volume basis

k_{dw} = decay rate of dissolved constituent in the water column (T^{-1})

k_{pw} = decay rate of particulate constituent in the water column (T^{-1})

V_d = mass transfer rate across the sediment-water interface resulting from diffusion of the dissolved constituent (L/T)

V_s = suspended solids settling rate (L/T)

H = hydraulic depth of the stream (L)

F_{db} = fraction of the constituent dissolved in the active sediment layer pore water

F_{dw} = fraction of the constituent dissolved in the water column

F_{pw} = fraction of the constituent particulate in the water column

c_w = concentration of the constituent in the water column (M/L^3), total mass on a total volume basis

V_r = active sediment layer resuspension rate (L/T)

In addition to the 1D assumption, uniform velocity and dispersion are assumed along the modeled stream reach.

The processes included in the water column mass balance for contaminants are advection, diffusion, settling of particulate mass, resuspension of sediment bed mass, dissolved mass transfer across the sediment-water interface, degradation/decay, and volatilization. The mass transfer across the sediment-water interface is a diffusive flow that is dependent upon the concentration gradient of the dissolved mass between the water column and the active sediment layer. Since only dissolved constituent mass is assumed to be available for volatilization, the volatilization rate is multiplied by the fraction dissolved in the water column. Likewise, only particulate mass is assumed to settle, and the settling rate is multiplied by the fraction particulate in the water column. However, the resuspension velocity is not multiplied by either the fraction dissolved or fraction particulate because both phases are assumed to be introduced into the water column during resuspension. When the solids are resuspended into the water column, the active sediment layer pore water surrounding the solids becomes exposed and integrated into the surface water.

The terms for the fraction dissolved and fraction particulate in the water column and active sediment layer were derived using the water column and active sediment layer distribution coefficients for reversible, linear, equilibrium partitioning between dissolved and sorbed phases and are shown in Equations 2.2 - 2.5 below,

$$F_{dw} = \frac{1}{1 + K_{dw} S} \tag{2.2}$$

$$F_{pw} = \frac{K_{dw} S}{1 + K_{dw} S} \tag{2.3}$$

$$F_{db} = \frac{1}{\phi_b + K_{db} \left(1 - \phi_b\right) \rho_b} \tag{2.4}$$

$$F_{pb} = \frac{K_{db} \left(1 - \phi_b\right) \rho_b}{\phi_b + K_{db} \left(1 - \phi_b\right) \rho_b} \tag{2.5}$$

where,

K_{dw} = distribution coefficient for the constituent in the water column (L^3/M)

S = suspended solids concentration (M/L^3)

ϕ_b = porosity of the active sediment layer sediments

ρ_b = dry sediment density in the active layer (M/L^3)

K_{db} = distribution coefficient for the constituent in the active sediment layer (L^3/M)

F_{pb} = fraction of the constituent particulate in the active sediment layer

The fraction, F_{pb}, is the fraction of constituent in particulate form on a total volume basis in the active sediment layer and is used for the active layer mass balance equation.

Options are built into the model to either input the volatilization rate or to calculate it based upon Henrys Law and Whitmans two-film theory [4] as modified for the influence of water flow and wind as described in Appendix A. Mass transfer rate of dissolved constituents across the sediment-water interface is calculated based upon flow conditions, molecular diffusivity and other factors as described in Appendix B. Calculation of V_s and V_r is discussed in the section on suspended solids transport. Other independent variables in Equation 2.1 are input by the user as discussed in Appendix C.

The terms in Equation 2.1 can be grouped to form a simplified version of the advection/diffusion/reaction equation,

$$\frac{\partial c_w}{\partial t} = -U\frac{\partial c_w}{\partial x} + D_x\frac{\partial^2 c_w}{\partial x^2} - kc_w + q \tag{2.6}$$

where,

$$k = \left(k_{dw} + \frac{k_v}{H} + \frac{V_d}{H}\right) F_{dw} + \left(k_{pw} + \frac{V_s}{H}\right) F_{pw} \tag{2.7}$$

$$q = \frac{V_r}{H}c_b + \frac{V_d}{H}F_{db}c_b \tag{2.8}$$

The term k includes all of the loss terms for the constituent in the water column that depend on the water column concentration. Since the terms for resuspension and mass transfer from the sediment bed do not involve the water column concentration, they are grouped together and treated as a source term, q.

2.1.2 Active sediment Layer Contaminants

The mass balance for total (dissolved and particulate) contaminant mass in the active sediment layer for each stream segment is stated as

$$\begin{aligned}\frac{dc_b}{dt} &= -\left(k_{db}F_{db}+k_{pb}F_{pb}\right)c_b+\frac{V_d}{h}\left(F_{dw}c_w-F_{db}c_b\right)\\ &\quad -\frac{V_r}{h}c_b+\frac{V_s}{h}F_{pw}c_w-\frac{V_b}{h}c_b+\frac{V_{dd}}{h}\left(F_{dd}c_d-F_{db}c_b\right)\end{aligned} \tag{2.9}$$

where,

k_{db} = decay rate of dissolved constituent in bed pore water (T^{-1})

k_{pb} = decay rate of particulate constituent in the bed (T^{-1})

V_b = active sediment layer burial rate (L/T)

h = active sediment layer thickness (L)

V_{dd} = mass transfer rate across the active layer-deep layer interface resulting from diffusion of the dissolved constituent (L/T)

F_{dd} = fraction of the constituent dissolved at the top of the deep layer

c_d = concentration of the constituent at the top of the deep layer (M/L^3) , total mass on a total volume basis

Equation 2.9 includes the following processes for the bed: decay or degradation, mass transfer of dissolved constituents across the sediment-water interface, resuspension to the water column, settling of particulate constituents from the water column, burial to lower sediment layers, and mass transfer of dissolved constituents across the active-deep layer interface. Longitudinal exchange between adjacent bed segments, such as pore water flow or diffusion along the stream flow axis, is assumed to be negligible.

2.1.3 Deep Sediment Layer Contaminants

The deep sediment layer is modeled using an advection-diffusion equation similar to that of the water column, except that it is vertically segmented rather than longitudinally. The mass balance for total (dissolved and particulate) contaminant mass in the deep sediment layer for each stream segment is stated as

$$\frac{\partial c_d}{\partial t} + V_b \frac{\partial c_d}{\partial z} = \frac{\partial}{\partial z}\left(\phi_d F_{dd} D_s \frac{\partial c_d}{\partial z}\right) - k_{dd} F_{dd} c_d - k_{pd} F_{pd} c_d \tag{2.10}$$

where,

z = vertical distance (L)

ϕ_d = deep layer porosity

D_s = vertical diffusion coefficient (L^2/T)

k_{dd} = decay rate of dissolved constituent in deep layer pore water (T^{-1})

F_{dd} = dissolved fraction of the constituent in the deep layer

k_{pd} = decay rate of particulate constituent in deep layer pore water (T^{-1})

F_{pd} = particulate fraction of the constituent in the deep layer

The processes included in Equation 2.10 are burial, diffusion in the z-direction, and decay of dissolved and particulate contaminant mass. As in the active sediment layer, longitudinal exchange of mass within the deep layer is assumed to be negligible. Since sediment properties can vary widely depending upon the depth and type of sediment material in question, the properties of the deep sediment layer are allowed to vary with depth. This means that the porosity, fraction dissolved, and vertical diffusion coefficient must remain within the differential equation and cannot be treated as constant values as was done for the horizontal diffusion coefficient in the water column.

For the top-most segment of the deep sediment layer, Equation 2.10 is modified to include transfer of dissolved contaminant to and from the active sediment layer due to diffusion. The diffusive transfer is calculated using this method rather than being included in the vertical diffusion term of the advection-diffusion-reaction equation in order to be consistent with the diffusion term in the active sediment layer mass balance. For the top segment of the deep layer, Equation 2.10 becomes,

$$\frac{\partial c_d}{\partial t} + V_b \frac{\partial c_d}{\partial z} = \frac{\partial}{\partial z}\left(\phi_d F_{dd} D_s \frac{\partial c_d}{\partial z}\right) - k_{dd} F_{dd} c_d - k_{pd} F_{pd} c_d - \frac{V_{dd}}{d}\left(F_{dd} c_d - F_{db} c_b\right) \quad (2.11)$$

where,

d = depth of the deep sediment computational segment (L)

The terms for the fraction dissolved and fraction particulate in the deep sediment layer were derived using the deep sediment layer distribution coefficients for reversible, linear, equilibrium partitioning between dissolved and sorbed phases in the same manner as the fractions for the active sediment layer. These fractions are shown in equations 2.12 and 2.13 below,

$$F_{dd} = \frac{1}{\phi_d + K_{dd}\left(1 - \phi_d\right)\rho_d} \quad (2.12)$$

$$F_{pd} = \frac{K_{dd}\left(1 - \phi_d\right)\rho_d}{\phi_d + K_{dd}\left(1 - \phi_d\right)\rho_d} \quad (2.13)$$

where,

K_{dd} = distribution coefficient for the constituent in the deep sediment layer (L^3/M)

ρ_d = dry sediment density in the deep layer (M/L^3)

The terms in Equation 2.10 can be grouped together, similarly to the terms in Equation 2.5, to form a simplified version of the advection/diffusion/reaction equation,

$$\frac{\partial c_d}{\partial t} = -V_b\frac{\partial c_d}{\partial z} + \frac{\partial}{\partial z}\left(\phi_d F_{dd} D_s \frac{\partial c_d}{\partial z}\right) - kc_d \tag{2.14}$$

where,

$$k = k_{dd}F_{dd} + k_{pd}F_{pd} \tag{2.15}$$

The term *k* includes all of the loss terms for the constituent in the deep layer that depend on the deep layer concentration. For the top segment, Equation 2.11 can be simplified as,

$$\frac{\partial c_d}{\partial t} = -V_b\frac{\partial c_d}{\partial z} + \frac{\partial}{\partial z}\left(\phi_d F_{dd} D_s \frac{\partial c_d}{\partial z}\right) - kc_d + q_d \tag{2.16}$$

where,

$$k = k_{dd}F_{dd} + k_{pd}F_{pd} + \frac{V_{dd}}{d}F_{dd} \tag{2.17}$$

$$q_d = \frac{V_{dd}}{d}F_{db}c_b \tag{2.18}$$

The term *k* now includes the loss of contaminant mass due to diffusion to the active layer across the active-deep sediment layer interface. Since the term for the influx of dissolved contaminant mass from the active layer does not involve the deep layer concentration, it is treated as a source term, *q*.

2.1.4 Suspended Solids Transport

If suspended solids in the water column are transported, then they are treated in a similar manner to a contaminant constituent that does not decay or volatilize. The solids are advected and dispersed along the length of the stream reach in the same manner as the constituents but do not have all of the same loss mechanisms. The only loss mechanism for suspended solids in the water column is settling. There will also be an influx of solids to the water column from any sediment resuspension that occurs. The suspended solids mass balance in the water column is stated as,

$$\frac{\partial S}{\partial t} = -U\frac{\partial S}{\partial x} + D_x\frac{\partial^2 S}{\partial x^2} - \frac{V_s}{H}S + \frac{V_r}{H}S_b \tag{2.19}$$

where S_b is the concentration of solids in the active sediment layer (M/L^3), which is the same as the sediment bulk density for the active layer, $\rho_b = (1-\phi)\,\rho_d$. The remaining variables are the same as those defined previously.

CMS can also be run with a steady-state solids concentration. In this case, solids are not modeled in the water column, and the background solids concentration is held constant for the entire simulation period.

The modeled suspended solids include both inorganic and organic solids. The approach taken here is generally applicable to both types. However, total suspended solids concentration is the state variable of interest since a total solids balance is necessary to perform analyses for other water quality constituents.

The active sediment layer is assumed to have constant properties, thus, the thickness, volume, porosity, bulk density, and solids mass are constant over time (i.e., steady-state) and assumed to be uniform over the stream reach. Performing a steady-state solids balance for the sediment layer results in the following relationship,

$$V_b = \frac{V_s S}{S_b} - V_r \tag{2.20}$$

where all variables have been previously defined. With the settling and resuspension rates specified, the burial rate can be determined, which is required for the active sediment layer contaminant mass balance (Equation 2.9). Alternatively, any 2 of the 3 rates in Equation 2.20 could be specified and the unknown rate solved. The relationship of water column and bed solids and the three process rates are shown schematically in Figure 2.1. The three process rates of Equation 2.20 are applied throughout the modeled stream reach.

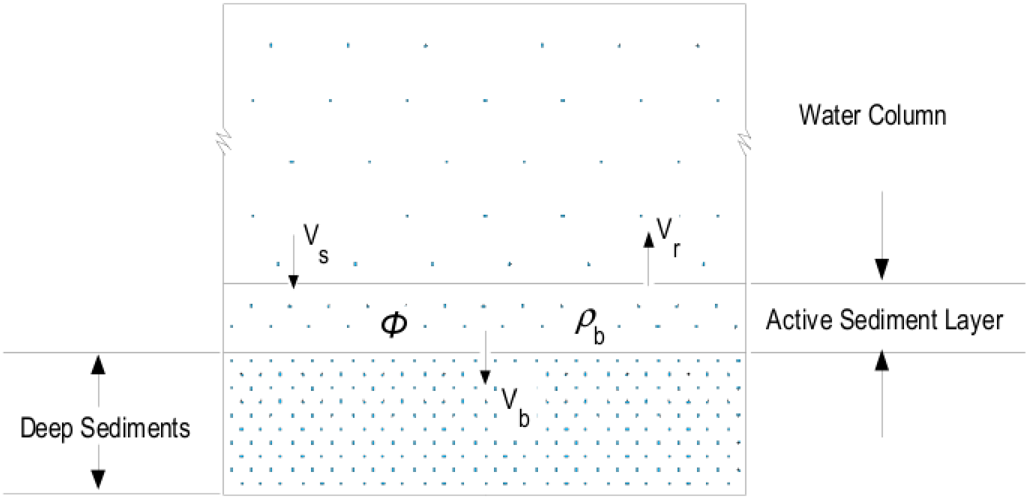

Figure 2.1: Diagram of sediment bed and water interactions for solids

2.2 Stream System Description

The stream system modeled in CMS can be as simple as a single reach or can be comprised of multiple reaches and branches. Each reach is assumed to have uniform hydraulic conditions, but the conditions may vary from reach to reach. Multiple points of interest for output can be defined for the stream system through user-entered usage locations. A usage location is a point at a given downstream distance from the beginning of the specified reach and may indicate a withdrawal point, a habitat for a species of interest, or any point where the constituent concentration is of interest. The associated distance from the beginning of the reach must be specified for each usage location. The total length of the stream reach specified in the user interface should be greater than the distance to the farthest usage location. A diagram of an example stream reach is shown in Figure 2.2.

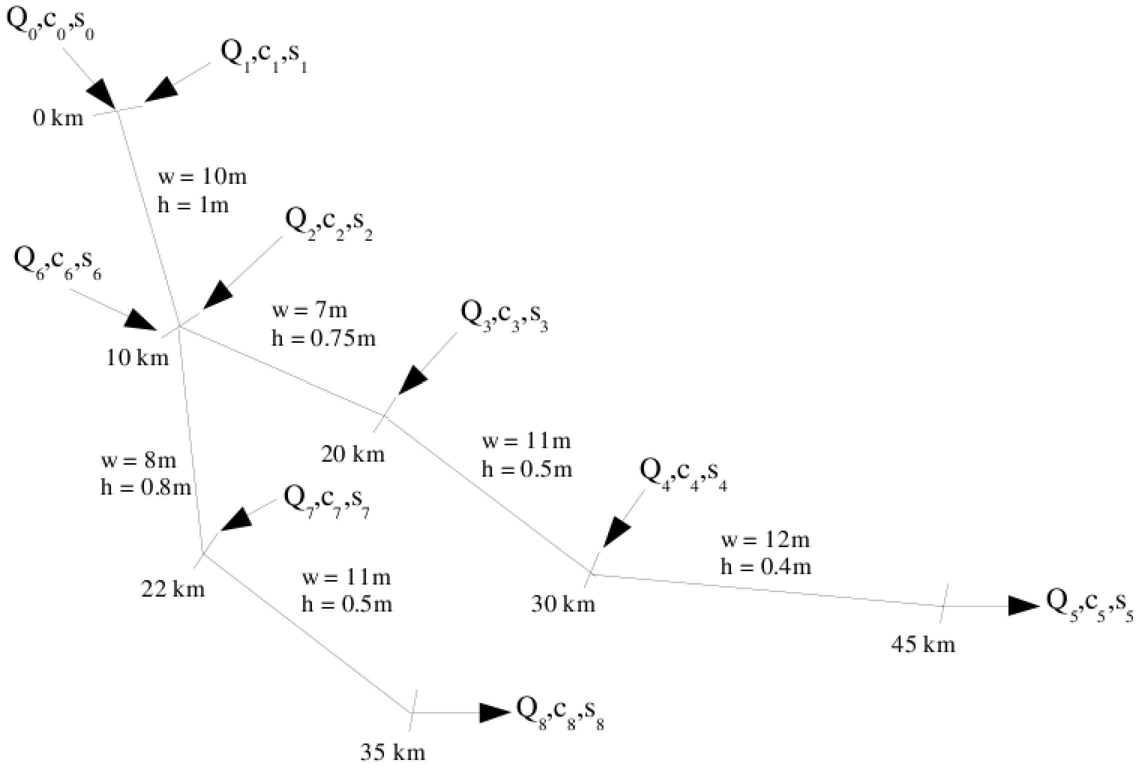

Figure 2.2: Diagram of the flows and concentrations entering and exiting the reaches. Flow, contaminant concentration, and suspended solids concentration are denoted as Q, c, and s, respectively. Average widths and depths for each stream reach are denoted as w and h.

2.2.1 Background Flow and Flux Data

Background values at the upstream boundary of the stream system can be entered for parameters such as the mean flow rate, suspended solids concentration, and constituent concentrations for the reach being modeled. Background variables are denoted with subscript *0* in Figure 2. The background values for any other stream reach in the system are simply derived from the values exiting the reach that is directly upstream. In addition to the constant, steady-state background flow and constituent loadings for the main stream reach, time-varying values can also be specified at the upstream boundary of each reach. These variables have subscripts of *1, 2, 3, 4, 6,* and *7* in Figure 2. Time-varying loading, or flux, data can be entered for water, suspended solids, and all modeled contaminant constituents. These inputs may be specified at any time point after time zero, but values for all variables must be specified for time zero, except for suspended solids, which does not need to be entered if a steady-state solids balance is selected in the project settings. In this case, the background concentration is used as the steady-state concentration for the entire stream system. The background and time-varying loading flows are added together, and a flow weighted balance is performed on the time-varying and background concentrations to set the upstream boundary flows and concentrations.

2.2.2 Hydraulic Conditions

The hydraulic conditions are not solved, but are specified. Flow conditions are assumed to be steady-state within each loading update interval and uniform over the modeled reach. Flows can change for each loading update interval due to changes in loading flow rate, but total flow rate, depth and flow area are assumed to change instantaneously over the entire reach, thus, there is no hydraulic or hydrologic routing nor any transient flow features.

Three options are currently provided for specifying hydraulic conditions:

1. specify stream width and depth as constants throughout the reach;
2. specify stream cross-sectional area and depth as a constant throughout the reach; and
3. calculate the stream cross-sectional area of flow and hydraulic depth as a function of flow in the reach.

The background flow for the stream reach is also specified as a constant. The third option, i.e., calculation of cross-sectional area and depth from flow, uses the following equations,

$$A = aQ^b \tag{2.21}$$

$$H = cA^d \tag{2.22}$$

where A is the cross-sectional area of flow, and a, b, c, and d are functional coefficients. With A, U can be calculated from U = Q/A. Most stream rating curves are in the form of Q = f (stage). Thus, there may be some effort involved in generating the relationships described by Equations 2.21 and 2.22. Cross-section channel geometry can be used to generate a relationship for A = f (stage) and coupled with the flow-stage relationship leading to development of an area-flow relationship (Equation 2.21). Also, stream top width (W) is equal to the derivative of A with respect to stage (dA / d (stage)), and H = A/W, thus, a relationship for H as a function of area can be developed (Equation 2.22).

However, Equations 2.21 and 2.22 are not appropriate for backwater flows where there is no slopoe. Therefore, the third option above would not work for instances such as a stream or river reach that flows into a reservoir behind a dam. For this reason, an option may be included in a future release of the CMS to allow importing of these parameters from a hydrodynamic model such as the Hydrologic Engineering Center River Analysis System (HEC-RAS) [13]. A linkage of this sort would be the only way to have more control over the hydraulic parameters without increasing the complexity of the CMS.

2.2.3 Water Column Boundary Conditions

Dirichlet boundary conditions are used for the upstream boundary, thus, allowing the user to specify concentrations or loading flux at the upstream boundary [4]. The upstream boundary also uses a pipe condition where advective flow is allowed into the first segment, but diffusion is not allowed across the boundary so that mass will not move backward out of the system. The concentration entering the reach is the concentration determined using the flow weighted mass balance as mentioned above. The boundary condition at the end of the reach is a Neumann condition, which is used to specify the derivative of the concentration at the downstream boundary [4]. The concentration gradient with respect to downstream distance across the boundary at segment N is assumed to be zero. Therefore, the downstream boundary concentration will be equal to the concentration of the last node, N. Advection is allowed across the boundary, but there will be no diffusion across the boundary due to the zero concentration gradient. These boundary conditions are illustrated in Figure 2.3.

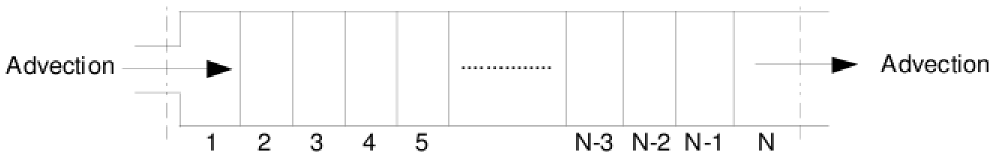

Figure 2.3: Depiction of boundary condition assumptions for the model reach

The user may specify an upstream boundary concentration or flux at any time update interval. For time steps where a boundary value is not updated, the model will perform a linear interpolation between the previous and next boundary update to determine the value that should be used for each model time step. A boundary condition must be specified for time zero and, if no other concentrations are specified, that value will be used as a steady-state condition for every time step.

2.2.4 Deep Sediment Layer Boundary Conditions

A similar set of boundary conditions are applied to the solution of the deep sediment layer. The boundary condition at the lowest modeled vertical segment, N, will be a Neumann condition and essentially the same as that at the downstream boundary in the water column solution. A zero concentration gradient is specified at the boundary so that the concentration just below the deep sediment layer will be equal to the concentration of the last vertical segment, N. Advection is allowed across the boundary, but there will be no diffusion across the boundary due to the zero concentration gradient.

The boundary between the mixed sediment and deep sediment layers is a Dirichlet condition similar to that at the upstream boundary of the water column solution. However, this boundary is specified in such a manner that both advection and diffusion are allowed across the boundary. This will allow contaminant mass to migrate upward from the deep sediment layer to the mixed sediment layer through diffusion. These boundary conditions are illustrated in Figure 2.4.

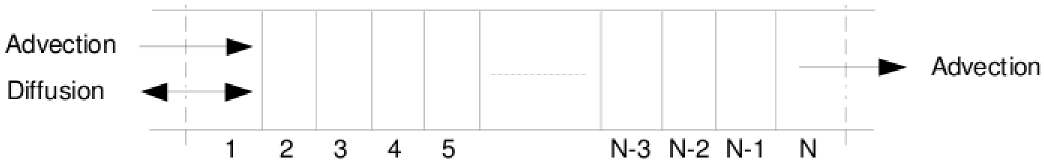

Figure 2.4: Depiction of deep sediment layer boundary condition assumptions

The boundary concentration at the active-deep layer interface will simply be the concentration of the mixed layer.

CHAPTER 3

SOLUTION METHODS

An implicit, finite difference, numerical solution scheme is used to solve the partial differential equations for surface water contaminant and suspended sediment concentrations (Equations 2.6 and 2.19). A choice between two numerical integration schemes is provided to solve the ordinary differential equation for active sediment layer contaminant mass (Equation 2.9). The deep sediment layer contaminant concentration is determined in the same manner as the water column concentration except that the integration is performed over the depth of the sediments and only a single integration scheme is available (Equation 2.14). The details of these solution methods are discussed below.

3.1 Water Column Finite Difference Scheme

A variation of the Crank-Nicolson (CR) method [4] was selected for the implicit, finite difference scheme. The CR scheme is a centered in time and centered in space approximation. This method is second-order accurate and is stable even for large time steps. The CR scheme reduces numerical dissipation by approximating the spatial derivatives at both the present and future time steps. These estimates are then averaged to obtain a spatial estimate that corresponds to the midpoint of the time step as illustrated in Figure 3.1 [4].

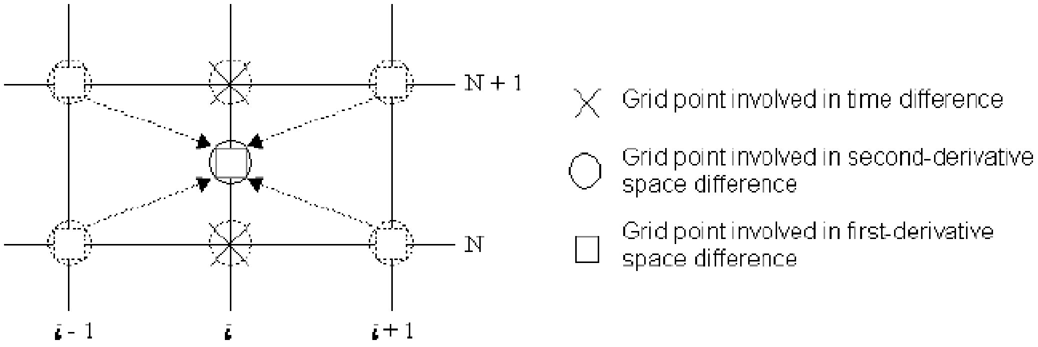

Figure 3.1: A computational molecule or stencil for the Crank-Nicolson method using a centered difference approximation for the advective term. The dashed lines are meant to show that the spatial derivative estimates at the present (N) and future (N+1) times are averaged to obtain the estimate at the intermediate time.

The time weighting in the modified CR method is performed using a coefficient of implicity (θ) as shown below for the transport-reaction equation (Equation 2.6) where a central difference for advection is used,

$$\begin{aligned} \frac{c_i^{n+1} - c_i^n}{\Delta t} &= -U\left[(1-\theta)\frac{c_{i+1}^n - c_{i-1}^n}{2\Delta x} + \theta\frac{c_{i+1}^{n+1} - c_{i-1}^{n+1}}{2\Delta x}\right] \\ &\quad +D_x\left[(1-\theta)\frac{c_{i+1}^n - 2c_i^n + c_{i-1}^n}{(\Delta x)^2} + \theta\frac{c_{i+1}^{n+1} - 2c_i^{n+1} + c_{i-1}^{n+1}}{(\Delta x)^2}\right] \\ &\quad -k\left[(1-\theta)c_i^n + \theta c_i^{n+1}\right] + q^n \end{aligned} \tag{3.1}$$

where,

c = surface water concentration for contaminant constituent or suspended sediment suspended sediment (M/L^3)

Δt = time step (T)

Δx = spatial step size (L)

n = time level

Other variables in Equation 3.1 were defined for Equations 2.1, 2.7, and 2.8. If θ is set to a value of *0.0*, the equation becomes fully explicit, and the only values included are from the current time step. If a value of *1.0* is used, the equation is fully implicit and only values from the future time step are included. The CR method is a special case where the coefficient of implicity is set to 0.5 to obtain an approximation that is centered in time as well as in space. This scheme is implemented such that the user can set the value for θ.

Collecting terms and rearranging where all of the unknown terms (values at the future time step) are on the left-hand side, and all of the known terms (values at the current time step) are on the right-hand side yields,

$$\begin{aligned} &-\left(\gamma+\lambda\right)\theta c_{i-1}^{n+1}+\left(1+2\lambda\theta+k\Delta t\theta\right)c_{i}^{n+1}+\left(\gamma-\lambda\right)\theta c_{i+1}^{n+1}\\ &=\left(\gamma+\lambda\right)\left(1-\theta\right)c_{i-1}^{n}+\left(1-2\lambda\left(1-\theta\right)-k\Delta t\left(1-\theta\right)\right)c_{i}^{n}\\ &\qquad+\left(\lambda-\gamma\right)\left(1-\theta\right)c_{i+1}^{n}+q\Delta t \end{aligned} \tag{3.2}$$

where,

$$\gamma=\frac{U\Delta t}{2\Delta x} \tag{3.3}$$

$$\lambda=\frac{D_x\Delta t}{\left(\Delta x\right)^2} \tag{3.4}$$

This results in one equation and three unknown values for c at locations $i-1$, i, and $i+1$. However, by constructing a recursive relation for nodes 1 through N, a matrix can be set up for N equations with N unknowns as shown in Equation 3.5 below, thus requiring a simultaneous solution.

$$\begin{bmatrix} \alpha_1 & (\gamma-\lambda)\theta & 0 & 0 & 0 & 0 & 0 \\ -(\gamma+\lambda)\theta & (1+2\lambda\theta+k\Delta t\theta) & (\gamma-\lambda)\theta & 0 & 0 & 0 & 0 \\ & & & \cdots\cdots\cdots & & & \\ 0 & -(\gamma+\lambda)\theta & (1+2\lambda\theta+k\Delta t\theta) & (\gamma-\lambda)\theta & 0 & 0 & 0 \\ 0 & 0 & -(\gamma+\lambda)\theta & (1+2\lambda\theta+k\Delta t\theta) & (\gamma-\lambda)\theta & 0 & 0 \\ 0 & 0 & 0 & -(\gamma+\lambda)\theta & (1+2\lambda\theta+k\Delta t\theta) & (\gamma-\lambda)\theta & 0 \\ & & & \cdots\cdots\cdots & & & \\ 0 & 0 & 0 & 0 & -(\gamma+\lambda)\theta & (1+2\lambda\theta+k\Delta t\theta) & (\gamma-\lambda)\theta \\ 0 & 0 & 0 & 0 & 0 & -(\gamma+\lambda)\theta & \alpha_2 \end{bmatrix} \begin{bmatrix} c_1^{n+1} \\ c_2^{n+1} \\ \cdots \\ c_{i-1}^{n+1} \\ c_i^{n+1} \\ c_{i+1}^{n+1} \\ \cdots \\ c_{N-1}^{n+1} \\ c_N^{n+1} \end{bmatrix} = \begin{bmatrix} d_1^n \\ d_2^n \\ \cdots \\ d_{i-1}^n \\ d_i^n \\ d_{i+1}^n \\ \cdots \\ d_{N-1}^n \\ d_N^n \end{bmatrix} \tag{3.5}$$

where d_i^n is the right side of Equation 3.2. This is defined as follows for the internal segments.

$$\begin{aligned} d_i^n &= (\gamma+\lambda)(1-\theta)\,c_{i-1}^n + (1-2\lambda(1-\theta)-k\Delta t(1-\theta))\,c_i^n \\ &\quad + (\lambda-\gamma)(1-\theta)\,c_{i+1}^n + q\Delta t \end{aligned} \tag{3.6}$$

The values of α_1, α_2, d_{1n}, and d_{Nn} depend on the numerical solution scheme that is used and the previously discussed boundary conditions that are imposed at the upstream and downstream boundaries. For the second order solution method given above, these values are given as

$$\alpha_1 = 1 + \gamma\theta + k\Delta t\theta \tag{3.7}$$

$$\alpha_2 = 1 + \gamma\theta + \lambda\theta + k\Delta t\theta \tag{3.8}$$

$$\begin{aligned} d_1^n &= (1-\lambda(1-\theta)-k\Delta t(1-\theta))\,c_1^n + (\lambda-\gamma)(1-\theta)\,c_2^n \\ &\quad + \gamma(1-\theta)\,c_b^n + \gamma\theta c_b^{n+1} + q\Delta t \end{aligned} \tag{3.9}$$

$$\begin{aligned} d_N^n &= (\gamma + \lambda)(1-\theta)\, c_{N-1}^n \\ &\quad + (1 - \lambda(1-\theta) - \gamma(1-\theta) - k\Delta t(1-\theta))\, c_N^n + q\Delta t \end{aligned} \tag{3.10}$$

where,

c_b = concentration at the upstream boundary (M/L^3)

Equation 3.5 is an NxN tridiagonal matrix, which has zero values in all positions except for the diagonal, sub-diagonal, and super-diagonal. A tridiagonal matrix can be easily solved using a form of Gaussian elimination commonly referred to in engineering disciplines as the ”Thomas Algorithm.”

Upwind differencing for the advection was added as an additional option. The coefficient of implicity was used to apply the same time weighting as was provided with the central difference scheme discussed above. The spatial derivative for advection, however, is not centered, rather only information at the current and upstream segment are used as follows,

$$advection\ term = U\left[(1-\theta)\frac{c_i^n - c_{i-1}^n}{\Delta x} + \theta\frac{c_i^{n+1} - c_{i-1}^{n+1}}{\Delta x}\right] \tag{3.11}$$

The main drawback to using the upwind differencing scheme is that it tends to introduce numerical diffusion into the solution, especially at high stream velocities or large spatial steps. However, this scheme introduces less artificial oscillation for sharp gradients than the central difference scheme and was added to the model to allow the user more flexibility and choice in solving a wider range of problems.

Equation 3.2 must be modified for upwind differencing for advection, resulting in Equations 3.12 and 3.13 below.

$$-\left(\gamma_u+\lambda\right)\theta c_{i-1}^{n+1}+\left(1+\gamma_u\theta+2\lambda\theta+k\Delta t\theta\right)c_i^{n+1}-\lambda\theta c_{i+1}^{n+1}=$$

$$\left(\gamma_u+\lambda\right)\left(1-\theta\right)c_{i-1}^{n}+\left(1-\gamma_u\left(1-\theta\right)-2\lambda\left(1-\theta\right)\right)c_i^{n}+\lambda\left(1-\theta\right)c_{i+1}^{n}+q\Delta t \quad (3.12)$$

where,

$$\gamma_u=\frac{U\Delta t}{\Delta x} \quad (3.13)$$

3.2 Active Sediment Layer Ordinary Differential Equation Solution

The option of using the Euler method or the fourth order Runga Kutta method is provided for solving for the contaminant concentration in the active sediment layer (i.e., Equation 2.9). The Euler method is easy to implement, but it is only first order accurate in time, and it is expressed as,

$$c_b^{n+1}=c_b^n+\frac{dc_b}{dt}\Delta t \quad (3.14)$$

where the term dc_b/dt is Equation 2.9 evaluated with the most recent updates for c_w and with c_b taken at time level n.

The fourth order Runge-Kutta method uses estimates of the slope at four points to calculate an improved average slope for the time interval [4]. The classical fourth order Runge-Kutta method is given by the following equation,

$$c^{n+1}=c^n+\left[\frac{1}{6}\left(k_1+2k_2+2k_3+k_4\right)\right]\Delta t \quad (3.15)$$

where the four slope estimates are defined as

$$k_1=f\left(t_i,c_i\right) \quad (3.16)$$

$$k_2 = f\left(t_i + \frac{1}{2}\Delta t, c_i + \frac{1}{2}\Delta t k_1\right) \tag{3.17}$$

$$k_3 = f\left(t_i + \frac{1}{2}\Delta t, c_i + \frac{1}{2}\Delta t k_2\right) \tag{3.18}$$

$$k_4 = f\left(t_i + \Delta t, c_i + \Delta t k_3\right) \tag{3.19}$$

When applied to the constituent mass balance given in Equation 2.9, this yields the following:

$$\begin{aligned} k_1 &= -\left(k_{db}F_{db} + k_{pb}F_{pb}\right)c_b + \frac{V_d}{h}\left(F_{dw}c_w - F_{db}c_b\right) \\ &\quad -\frac{V_r}{h}c_b + \frac{V_s}{h}F_{pw}c_w - \frac{V_b}{h}c_b + V_{dd}F_{dd}c_d - V_{dd}F_{db}c_b \end{aligned} \tag{3.20}$$

$$\begin{aligned} k_2 &= -\left(k_{db}F_{db} + k_{pb}F_{pb}\right)\left(c_b + 0.5k_1\Delta t\right) + \frac{V_d}{h}\left(F_{dw}c_w - F_{db}\left(c_b + 0.5k_1\Delta t\right)\right) \\ &\quad -\frac{V_r}{h}\left(c_b + 0.5k_1\Delta t\right) + \frac{V_s}{h}F_{pw}c_w - \frac{V_b}{h}\left(c_b + 0.5k_1\Delta t\right) \\ &\quad +V_{dd}F_{dd}c_d - V_{dd}F_{db}\left(c_b + 0.5k_1\Delta t\right) \end{aligned} \tag{3.21}$$

$$\begin{aligned} k_3 &= -\left(k_{db}F_{db} + k_{pb}F_{pb}\right)\left(c_b + 0.5k_2\Delta t\right) + \frac{V_d}{h}\left(F_{dw}c_w - F_{db}\left(c_b + 0.5k_2\Delta t\right)\right) \\ &\quad -\frac{V_r}{h}\left(c_b + 0.5k_2\Delta t\right) + \frac{V_s}{h}F_{pw}c_w - \frac{V_b}{h}\left(c_b + 0.5k_2\Delta t\right) \\ &\quad +V_{dd}F_{dd}c_d - V_{dd}F_{db}\left(c_b + 0.5k_2\Delta t\right) \end{aligned} \tag{3.22}$$

$$\begin{aligned} k_4 &= -\left(k_{db}F_{db} + k_{pb}F_{pb}\right)\left(c_b + k_3\Delta t\right) + \frac{V_d}{h}\left(F_{dw}c_w - F_{db}\left(c_b + k_3\Delta t\right)\right) \\ &\quad -\frac{V_r}{h}\left(c_b + k_3\Delta t\right) + \frac{V_s}{h}F_{pw}c_w - \frac{V_b}{h}\left(c_b + k_3\Delta t\right) \\ &\quad +V_{dd}F_{dd}c_d - V_{dd}F_{db}\left(c_b + k_3\Delta t\right) \end{aligned} \tag{3.23}$$

The final concentration in the active sediment layer at the new time step is then determined as

$$c_b^{n+1} = c_b^n + \left[\frac{1}{6}\left(k_1 + 2k_2 + 2k_3 + k_4\right)\right]\Delta t \tag{3.24}$$

Although the implicit solution for the water column is unconditionally stable, the solution for the active sediment layer is not and can generate oscillating, unrealistic concentrations. An adaptive solution option has been implemented for solving the ordinary differential equation for the bed to ensure stable results. The adaptive scheme starts with a time step, Δt, that is actually one tenth of the specified time step. This helps to insure that the initial calculations will meet the convergence criteria. For each time loop, the sediment calculations are first performed using the current time step and a value that is twice as large as the current time step. If the values from these two calculations for all segments meet the convergence criteria, the larger time step will be the new time step and the values from the calculations using this time step will be used for the current time loop. If the convergence criteria are not met, the calculations are performed using the current time step and a value that is half as large as the current time step. If the convergence criteria are met, the current time step will be unchanged. Otherwise, the routine will set the current time step to $0.5\Delta t$ and continue to iterate, lowering the time step with each iteration, until convergence is reached.

3.3 Deep Sediment Layer Finite Difference Solution

The deep sediment layer governing equation is a partial differential advection-diffusion equation similar to the governing equation of the water column. However, both the velocity and diffusion values in the vertical direction in the sediment bed are much smaller than their horizontal counterparts in the water column. The longitudinal dispersion often helps to smooth out any numerical oscillations occurring in the solution of the advection equation. In this circumstance, the diffusion rate through the pore water in the deep sediment layer is not large enough to affect a difference. To overcome this problem, the advection component is solved using the upwind differencing method while the diffusion component is solved using a fully implicit centered difference method. Applying these two solution methods to Equation 2.14 yields

$$\begin{aligned}
\frac{c_{d_i}^{n+1} - c_{d_i}^{n}}{\Delta t} &= -V_b \left[(1-\theta) \frac{c_{d_i}^{n} - c_{d^n_{i-1}}}{\Delta z} + \theta \frac{c_{d_i}^{n+1} - c_{d_{i-1}}^{n+1}}{\Delta z} \right] \\
&+ \left[\frac{(\phi_d F_{dd} D_s)_{i,i+1} \, c_{d_{i+1}}^{n+1} - (\phi_d F_{dd} D_s)_{i,i+1} \, c_{d_i}^{n+1}}{(\Delta z)^2} \right] \\
&+ \left[\frac{-(\phi_d F_{dd} D_s)_{i-1,i} \, c_{d_i}^{n+1} + (\phi_d F_{dd} D_s)_{i-1,i} \, c_{d_{i-1}}^{n+1}}{(\Delta z)^2} \right] \\
&- k_d \left[(1-\theta) \, c_{d_i}^{n} + \theta c_{d_i}^{n+1} \right] \qquad (3.25)
\end{aligned}$$

where,

Δz = spatial step size (L)

$(\phi_d F_{dd} D_s)_{i,i+1}$ = spatial derivative of deep sediment properties at $i, i+1$ interface, $\frac{(\phi_d F_{dd} D_s)_i + (\phi_d F_{dd} D_s)_{i+1}}{2}$

$(\phi_d F_{dd} D_s)_{i-1,i}$ = spatial derivative of deep sediment properties at $i-1, i$ interface, $\frac{(\phi_d F_{dd} D_s)_{i-1} + (\phi_d F_{dd} D_s)_i}{2}$

Other variables in Equation 3.25 were defined for Equations 2.10 and 2.12 - 2.15. As previously stated in section 3.1, the value of θ can be modified for Equation 3.25 such that it is fully explicit when θ is set to a value of *0.0* and fully implicit if it is set to a value of *1.0*. The current model options do not allow for the user to modify the coefficient of implicity in the deep sediment solution. The value used in the model is 0.55, which was determined to be best through model testing.

Once again, collecting terms and rearranging Equation 3.25 where all of the unknown terms (values at the future time step) are on the left-hand side, and all of the known terms (values at the current time step) are on the right-hand side yields,

$$\begin{aligned}
&-\Big(\gamma_d\theta + \left(\phi_d F_{dd} D_s\right)_{i-1,i}\gamma_d\Big)\, c_{d_{i-1}}^{n+1} \\
&+\Big(1+\gamma_d\theta + \left(\phi_d F_{dd} D_s\right)_{i-1,i}\lambda_d + \left(\phi_d F_{dd} D_s\right)_{i,i+1}\lambda_d + k_d\Delta t\theta\Big)\, c_{d_i}^{n+1} \\
&-\Big(\left(\phi_d F_{dd} D_s\right)_{i,i+1}\lambda_d\Big)\, c_{d_{i+1}}^{n+1} \\
&= \gamma_d\left(1-\theta\right) c_{d_{i-1}}^{n} + \left(1-\gamma_d\left(1-\theta\right) - k_d\Delta t\left(1-\theta\right)\right) c_{d_i}^{n}
\end{aligned} \tag{3.26}$$

where,

$$\gamma_d = \frac{V_b\Delta t}{\Delta z} \tag{3.27}$$

$$\lambda_d = \frac{\Delta t}{\left(\Delta z\right)^2} \tag{3.28}$$

This gives one equation and three unknown values for c_d at locations $i-1$, i, and $i+1$. As shown in section 3.1 for the water column, a matrix can be constructed having N equations with N unknowns. The matrix for the deep sediment solution is

$$\begin{bmatrix}
\alpha_{d1} & -(\phi_d F_{dd} D_s)_{i,i+1}\lambda_d & 0 & 0 & 0 & 0 & 0 \\
-(\gamma_d\theta+(\phi_d F_{dd} D_s)_{i-1,i}\lambda_d) & \beta & -(\phi_d F_{dd} D_s)_{i,i+1}\lambda_d & 0 & 0 & 0 & 0 \\
 & & & & \cdots\cdots & & \\
0 & -(\gamma_d\theta+(\phi_d F_{dd} D_s)_{i-1,i}\lambda_d) & \beta & -(\phi_d F_{dd} D_s)_{i,i+1}\lambda_d & 0 & 0 & 0 \\
0 & 0 & -(\gamma_d\theta+(\phi_d F_{dd} D_s)_{i-1,i}\lambda_d) & \beta & -(\phi_d F_{dd} D_s)_{i,i+1}\lambda_d & 0 & 0 \\
0 & 0 & 0 & -(\gamma_d\theta+(\phi_d F_{dd} D_s)_{i-1,i}\lambda_d) & \beta & -(\phi_d F_{dd} D_s)_{i,i+1}\lambda_d & 0 \\
 & & & & \cdots\cdots & & \\
0 & 0 & 0 & 0 & -(\gamma_d\theta+(\phi_d F_{dd} D_s)_{i-1,i}\lambda_d) & \beta & -(\phi_d F_{dd} D_s)_{i,i+1}\lambda_d \\
0 & 0 & 0 & 0 & 0 & -(\gamma_d\theta+(\phi_d F_{dd} D_s)_{i-1,i}\lambda_d) & \alpha_{d2}
\end{bmatrix}
\begin{bmatrix}
c_{d_1}^{n+1} \\ c_{d_2}^{n+1} \\ \cdots \\ c_{d_{i-1}}^{n+1} \\ c_{d_i}^{n+1} \\ c_{d_{i+1}}^{n+1} \\ \cdots \\ c_{d_{N-1}}^{n+1} \\ c_{d_N}^{n+1}
\end{bmatrix}
=
\begin{bmatrix}
d_{d_1}^{n} \\ d_{d_2}^{n} \\ \cdots \\ d_{d_{i-1}}^{n} \\ d_{d_i}^{n} \\ d_{d_{i+1}}^{n} \\ \cdots \\ d_{d_{N-1}}^{n} \\ d_{d_N}^{n}
\end{bmatrix} \tag{3.29}$$

where $d_{d_i}^n$ is the right side of Equation 3.25 and β is the diagonal matrix coefficient. For all internal segments, $d_{d_i}^n$ is defined by Equation 3.30 and β is defined by Equation 3.31.

$$d_{d_i}^n = \gamma_d (1-\theta) c_{d_{i-1}}^n + (1 - \gamma_d (1-\theta) - k_d \Delta t (1-\theta)) c_d^i \tag{3.30}$$

$$\beta = 1 + \gamma_d \theta + (\phi_d F_{dd} D_s)_{i-1,i} \lambda_d \theta + (\phi_d F_{dd} D_s)_{i,i+1} \lambda_d \theta - k_d \Delta t \tag{3.31}$$

The values of α_{d1}, α_{d2}, $d_{d_1}^n$, and $d_{d_N}^n$ depend on the numerical solution scheme that is used and the boundary conditions imposed at the top and bottom of the deep sediment layer. For the second order solution method given above, these values are given as

$$\alpha_{d_1} = 1 + \gamma_d \theta + (\phi_d F_{dd} D_s)_{i,i+1} \lambda_d \theta + k_d \Delta t \theta \tag{3.32}$$

$$\alpha_{d_2} = 1 + \gamma_d \theta + (\phi_d F_{dd} D_s)_{i-1,i} \lambda_d \theta + k_d \Delta t \theta \tag{3.33}$$

$$d_{d_1}^n = (1 - \gamma_d (1-\theta) - k_d \Delta t (1-\theta)) c_{d_1}^n + \gamma_d \theta c_b^{n+1} + \gamma_d (1-\theta) c_b^n + q_d \Delta t \tag{3.34}$$

$$d_{d_N}^n = \gamma_d (1-\theta) c_{d_{N-1}}^n + (1 - \gamma_d (1-\theta) - k_d \Delta t (1-\theta)) c_{d_N}^n \tag{3.35}$$

3.4 Operator Splitting Schemes

There are many numerical methods available for solving advection-diffusion and advection-diffusion-reaction problems, but many of these have known shortcomings under certain sets of conditions. Reactive transport is an especially difficult problem to model accurately and often requires time steps that are much smaller than those required for the advection or diffusion parts of the problem. One approach that can be used to overcome these problems is the use of an operator splitting technique. Operator splitting is a method that involves decoupling of a full model into single physics components, employing specialized numerical methods to solve each component, and coupling the resulting solutions together. This allows each part of the problem to be solved independently of the others. Therefore, different solution schemes and time steps can be employed to best capture and model each of these processes.

The transport of Nc reactive species in a one-dimensional surface water body can be described by the set of Nc reactive transport equations (Equation 3.36) with the given boundary and initial conditions:

$$\frac{\partial c_i}{\partial t} = L\left(c_i, x, t\right) + f_i\left(c_1, ..., c_i, ..., c_{Nc}\right) \;\; i = 1, ..., Nc \tag{3.36}$$

where,

L = a transport operator representing advection and diffusion of the i^{th} species along the x-axis

f_i = the chemistry influence over the i^{th} species which depends on local concentration of the other $Nc - 1$ species

c_i = the concentration of the i_{th} species at the current node

A standard operator splitting technique requires the computation of Nc independent transport systems of size Nn because the splitting technique makes the transport of the i^{th} species independent of the other species. It also requires the computation of Nn independent chemistry systems of size Nc because the splitting technique makes chemistry at one node independent of chemistry at the other nodes.

Errors introduced by the resolution of Equation 2.1 through operator splitting techniques are the combination of the errors from the transport and chemistry operators as well as the intrinsic operator splitting errors. To eliminate the errors from both the transport and chemistry operators, the global mass balance can be applied as proposed by Valocchi and Malmstead [14]. This also gives a generalization of the results independent of the transport and chemistry operator computations [3].

Operator splitting schemes generally fall into one of two classifications: iterative or non-iterative. Non-iterative schemes simply solve the transport and chemistry reactions sequentially (transport generally followed by reaction) for each time step. The iterative schemes also include some sort of iterative procedure between the time steps to insure that the values converge within a specified convergence limit.

Two operator splitting techniques have been implemented in CMS in order to completely separate the modeling of the physical and chemical processes in the water column. Advection, diffusion, and reaction components are each analyzed individually and the results are combined using the operator splitting methods. This allows for multiple solution methods for each of these processes to be added and investigated in a more developer-friendly manner. The advection process is currently the only one of these three that has multiple solution methods, but additional methods could easily be added for the other processes as well.

The CMS model first performs the transport operations, which are split using the Strang-splitting sequential non-iterative scheme. This scheme was originally proposed by Strang [12] and has been used by several authors. It is equivalent to the Alternating SNI scheme studied by Kaluarachchi and Morshed [7]. For this procedure, the advection equation is first solved over the half time step from $n\Delta t$ to $(n + 1/2)\,\Delta t$ to give the first intermediate solution. The initial condition at $n\Delta t$, as with all other schemes, is the solution of the previous time step. After solving the first advection equation, the diffusion equation is solved over the entire time step to obtain the second intermediate solution at $(n+1)\,\Delta t$. The solution of the Strang-splitting SNI scheme at $(n+1)\,\Delta t$ is then obtained after solving a second advection equation from $(n+1/2)\,\Delta t$ to $(n+1)\,\Delta t$ with the results of the diffusion equation as the initial conditions.

$$\frac{C_i^*\left[\left(n+\frac{1}{2}\right)\Delta t\right]-C_{ST_i}^n}{\frac{\Delta t}{2}}=-u\nabla C_i \tag{3.37}$$

where,

$C_{ST_i}^n$ = the initial concentration of the i^{th} species or the result from the previous time step

C_i^* = the first intermediate concentration of the i^{th} species provided by the solution of the advection operator

Application of the diffusion operator over the full time step is given by:

$$\frac{C_i^{**}\left[(n+1)\,\Delta t\right]-C_i^*\left[\left(n+\frac{1}{2}\right)\Delta t\right]}{\Delta t}=\nabla\left(D\nabla C_i\right) \tag{3.38}$$

where,

C_i^{**} = the second intermediate concentration of the i^{th} species provided by the solution of the chemistry operator

The second advection equation solved over the second half of the time step is given by:

$$C_{ST_i}^{n+1}-\frac{C_i^{**}\left[(n+1)\,\Delta t\right]}{\frac{\Delta t}{2}}=-u\nabla C_i \tag{3.39}$$

where,

$C_{ST_i}^{n+1}$ = the final concentration of the i^{th} species from the result of the second advection operator

The transport operators are split from the chemistry operator using the Standard Sequential Iterative scheme. This scheme differs from the Standard SNI scheme in several ways. For a single time step, the scheme is decomposed into a conservative transport step with a chemical source-sink term and a batch chemistry operator step. This source-sink term represents the chemistry operator, but is a constant in the transport operator. The batch chemistry operator is then solved over the time step. The solution of the chemistry operator is then used to update the source-sink term in the transport operator for the next iteration. Both steps are repeated until the convergence limit is reached.

Applying this scheme to the one-dimensional advection-diffusion-reaction equation gives the following equation for the transport operator:

$$\frac{C_{T_i}^{m}\left[(n+1)\,\Delta t\right] - C_{SS_i}^{n}}{\Delta t} = -u\nabla C_{T_i} + \nabla\left(D\nabla C_{T_i}\right) - R_{C_i}^{m-1} \tag{3.40}$$

where,

$C_{T_i}^{m}$ = the first intermediate concentration of the i^{th} species from the result of the transport operator

$R_{C_i}^{m-1}$ = the vector of the chemistry source-sink terms at each node of the domain

The solution of the chemistry operator provides the value for the chemistry source-sink term in the next iteration.

$$\frac{C_{C_i}^{m}\left[(n+1)\,\Delta t\right]-C_{T_i}^{m}\left[(n+1)\,\Delta t\right]}{\Delta t}=f_i\left(C_{C_q},...,C_{C_i},...,C_{CN_c}\right) \tag{3.41}$$

$$R_{C_i}^{m}=\frac{C_{C_i}^{m}\left[(n+1)\,\Delta t\right]-C_{T_i}^{m}\left[(n+1)\,\Delta t\right]}{\Delta t} \tag{3.42}$$

where,

$C_{C_i}^{m}$ = the second intermediate concentration of the i^{th} species from the result of the chemistry operator

$R_{C_i}^{m}$ = the new chemistry source-sink term for the next iteration

The convergence criteria must be obeyed at every node of the domain and for all species i:

$$CV_{IS_i}^{m}=max\frac{|C_{T_i}^{n+1,m}-C_{T_i}^{n+1,m-1}|}{C_{T_i}^{n+1,m}}\leq\xi \tag{3.43}$$

where,

$CV_{IS_i}^{m}$ = the convergence criterion for species i

ξ = the convergence limit

m = the index of the iteration

n = the index of the time step

Special treatment is required for the convergence criterion for nodes where $C_{T_i}^{n+1}$ is zero or negligible.

CHAPTER 4

MODEL VERIFICATION

When discussing model development and testing, the terms validation and verification are often used interchangably. However, in this paper these terms are used to define specific procedures for model testing and confirmation. Validation is referred to as the testing and authentication of a model using quality-controlled data collected from valid field measurements. The term verification is used to define a method for testing and authenticating a model using standard analytical methods or previously validated models when no appropriate field data is available for comparison. Because there was no readily available, long-term constituent concentration data to validate the CMS, the model equations have been verified using two existing contaminant models: RECOVERY [10] and PREWet [6]. Both of these models have been successfully validated as noted in their model documentation. RECOVERY is a numerical, time varying model of water column and bed contaminant mass where the water column is a single, fully mixed compartment and the bed is modeled with multiple layers over the depth. RECOVERY assumes a steady-state solids balance for the bed, and suspended solids are input and constant throughout the water column and over time. PREWet is a 1D (longitudinal), steady-state model with an analytical solution. Although PREWet calculates suspended solids concentration at the end of the reach given the concentration entering the reach and assuming a steady-state solids balance in the bed, the bed solids flux rates (burial, resuspension, deposition) are assumed uniform over the reach, and the unknown flux is computed using the entering solids concentration. Thus, the suspended solids computations are not really coupled with the contaminant computations. The steady-state solids balance in the bed of both models requires entering 2 of the 3 rates of settling, resuspension, and burial and solving for the unspecified rate assuming that bed solids mass is constant with respect to time.

One organic and one inorganic constituent were chosen for the model verification tests, and 2 test sets were run. The first test was a long-term, steady-state loading simulation run for 300 years, long enough for constituent concentrations in both the water column and sediment bed to reach steady-state values. All three models were compared for this test. This test was then repeated using the solids transport option in the CMS. A third time-varying test case with stepped constituent influx concentrations was performed over a simulation period of 100 years. The constituent flux was increased at 25 and 50 years and then decreased at 75 years. In this simulation, the constituent concentrations in the sediment bed were never allowed to reach steady-state. Only RECOVERY was compared to the CMS for this test because PREWet does not allow a variable flux input. The fourth test case is a test of the depth-varying deep sediment layer parameters for porosity and fraction organic carbon in the solids. The last test is a comparison of the CMS results from the steady-state test case with the CMS model using multiple reaches to simulate the same river reach. The input data and the results for each test set are described below.

4.1 Input Data

Three general types of data are required as input: (1) chemical-specific parameters/inputs; (2) system or water body inputs; and (3) sediment bed properties. Each of the inputs for these test are described as follows.

4.1.1 Chemical-Specific Inputs

The constituents used in the test cases were DDT and Chromium III. Both of these constituents are known water contaminants. The data required for each constituent to perform the tests with the aforementioned models is given below. Assumptions were made regarding some inputs to simplify comparisons between the models. Extremely small values were used for some input values in place of entering 0.0, such as Henrys law constant for chromium.

DDT

- Molecular weight - $354.49\ g/g-mole$
- Molecular diffusivity - $4.95x10^{-6}\ cm^2/s$
- Henrys law constant - $8.30x10^{-6}\ atm-m^3/g-mole$
- Octanol-water partition coefficient (K_{OW}) - $8.128x10^6\ mL/mL$
- Partition coefficients
    - Water column - $0\ L/kg$
    - Sediment Bed - $0\ L/kg$
- Decay rates in water column
    - Dissolved fraction - $0.00388/day$
    - Particulate fraction - $0/day$
- Decay rates in sediment bed

  - Dissolved fraction - $0.00388/day$
  - Particulate fraction - $0/day$

- Volatilization rate from the water column - 0.111 m/day (calculated)
- Mass transfer velocity between water and sediment - 0.00133 m/day (calculated)
- Initial concentration in water column - 0 mg/L
- Initial concentration in sediment bed - 0 mg/L

Chromium III

- Molecular weight - 51.996 $g/g-mole$
- Molecular diffusivity - $5.94x10^{-6}$ cm^2/s
- Henrys law constant - $9.60x10^{-40}$ $atm-m^3/g-mole$
- Octanol-water partition coefficient (K_{OW}) - 0 mL/mL
- Partition coefficients
  - Water column - $100,000$ L/kg
  - Sediment Bed - $1,000,000$ L/kg
- Decay rates in water column
  - Dissolved fraction - $0/day$
  - Particulate fraction - $0/day$
- Decay rates in sediment bed
  - Dissolved fraction - $0/day$
  - Particulate fraction - $0/day$
- Volatilization rate from the water column - 0 m/day (calculated)
- Mass transfer velocity between water and sediment - 0.00477 m/day (calculated)
- Initial concentration in water column - 0 mg/L
- Initial concentration in sediment bed - 0 mg/L

4.1.2 Water Body Parameters

Since each of the models being used are intended for different types of water bodies, the following general physical characteristics were applied to each model as appropriate to simulate the same conditions.

- Average annual depth of water body - $3\ m$
- Average annual width of water body - $50\ m$
- Length of water body - $100\ km$
- Average annual surface area of water body - $5x10^6\ m^2$
- Average annual volume of water body - $1.5x10^7\ m^3$
- Average annual flow - $1x10^9\ m^3/yr$
- Average annual temperature - $20°C$
- Average wind speed at 10m above surface - $5\ m/s$
- Incoming suspended solids concentration - $150\ mg/L$
- Fraction organic carbon in suspended solids - 0.02

4.1.3 Sediment Bed Parameters

The following parameters were applied to all models for the active sediment layer.

- Average thickness of mixed sediment layer - $10\ cm$
- Depth of deep sediment layer - $0.9\ m$
- Average porosity - 0.35
- Average dry sediment density - $2,650\ g/L$
- Fraction organic carbon in sediment bed - 0.02
- Settling velocity - $0.1\ m/day$
- Burial velocity - $4.7x10^{-6} m/day$
- Resuspension velocity - $4.467x10^{-6}\ m/day$ (calculated)

4.2 Steady-State Test Case with Constant Solids Concentration

The steady-state test case was run for each model using the information given above and a constant constituent influx of 30 mg/L for each constituent. The simulation was run for a period of 300 years allowing the water column and sediment bed concentrations for both constituents to reach steady-state. The water column and mixed sediment layer actually reach steady-state much sooner than 300 years, but the model was allowed to run longer to allow the constituents to migrate into the deep sediment layer for comparison purposes. The constituents in the deep sediment layer are acutally allowed to reach a steady-state level down to a depth near $25cm$. The following table shows the results from each of the three models. The results for CMS and PREWet are reported at the end of the modeled reach.

Table 4.1: Steady-State Test Results

Model	Contaminant	Water Conc. (mg/L)	Mixed Sediment Conc. (mg/kg)
PREWet	DDT	26.97	168,600
	Chromium III	27.34	171,400
RECOVERY	DDT	26.64	166,500
	Chromium III	27.46	171,600
CMS	DDT	26.95	168,500
	Chromium III	27.30	171,000

The results from all three models match well for both the water column and mixed sediment layer concentrations for both constituents. Concentration profiles in the deep sediment layer for the CMS and RECOVERY models are shown in Figures 4.1 and 4.2.

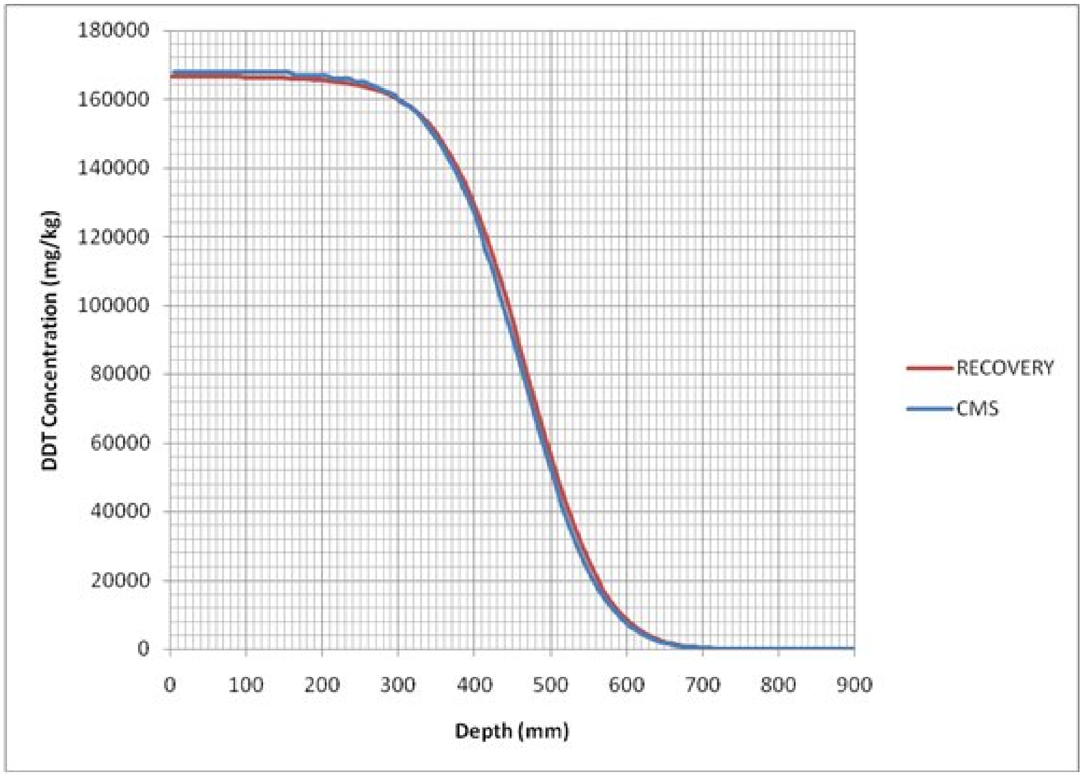

Figure 4.1: DDT concentration profile in deep sediment layer for steady-state test case

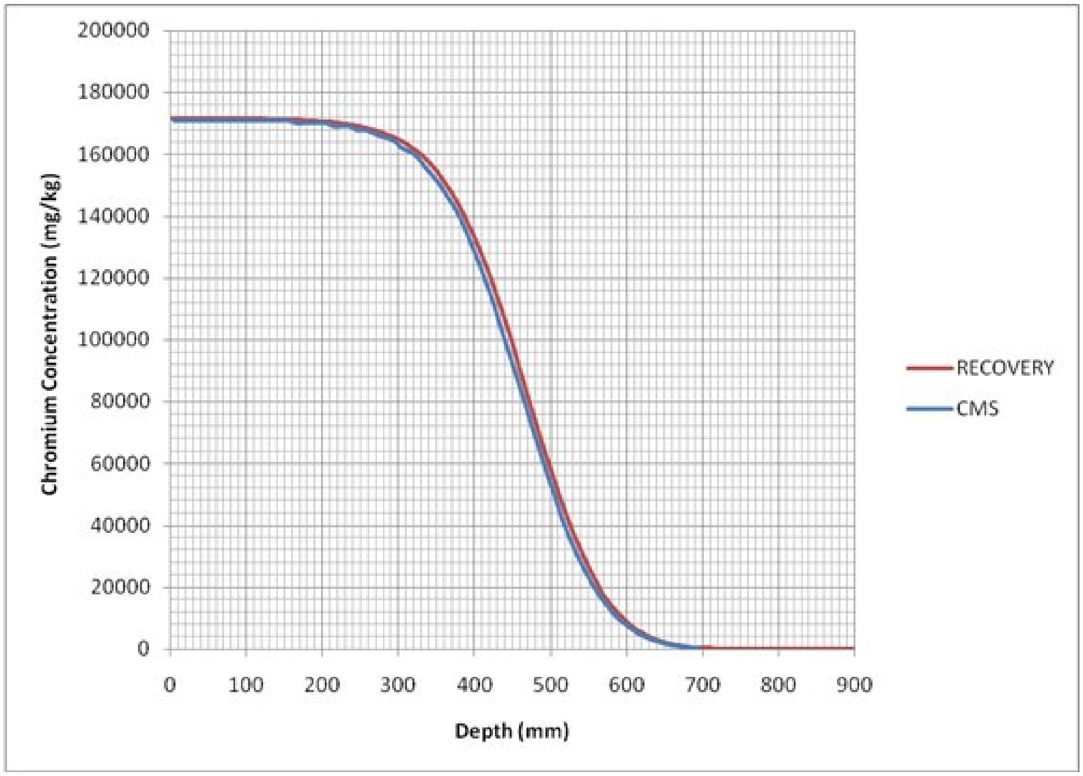

Figure 4.2: Chromium concentration profile in deep sediment layer for steady-state test case

It can be seen from the figures above that the concentration profiles in the deep sediment layer for both constituents in CMS and RECOVERY are very similar. The concentration at the top of the deep sediment layer in each model is the same as its respective mixed sediment layer concentration, and the concentrations go to zero near a depth of seven centimeters in the deep layer. This test helped to verify that the CMS is working properly at least for a steady-state loading with a steady-state solids concentration.

4.3 Steady-State Test Case with Solids Transport

The previous test was performed using a constant suspended solids concentration over the entire reach. However, this assumption may not be accurate for many streams and rivers. The suspended solids concentration can form longitudinal gradients along the length of the reach. As the solids are advected and diffused along the reach, they can be deposited to the sediment bed or joined by additional particles resuspended from the sediment bed. The solids transport option was included in the CMS in order to model cases such as this where the constituent concentrations can vary along the reach due to the suspended solids concentration gradient. The steady-state loading test case was performed again with the CMS using the solids transport option to verify that this option is working correctly. The results are shown in Table 4.2.

Table 4.2: Steady-State CMS Test Results with Solids Transport

Model	Contaminant	Water Conc. (mg/L)	Mixed Sediment Conc. (mg/kg)
CMS	DDT	26.8	185,000
	Chromium III	27.2	188,000
	Solids	135	

As seen in Table 4.2, the constituent concentrations in the mixed sediment layer for this test case are about 10% higher than in the previous test. This is due to the deposition of suspended solids along the reach as mentioned previously, which leads to a suspended solids concentration in the water column of 135 mg/L at the end of the reach. Although the PREWet model uses a steady-state solids concentration in the water column, it does have the ability to predict the solids concentration that would exist in the water column at the end of the modeled system. The exiting solids concentration predicted by PREWet for the first test case was 135.9 mg/L. This compares well with the value given by the CMS for the suspended solids concentration at the end of the reach.

A test was next performed using both the RECOVERY and PREWet models with the suspended solids concentration of 135 mg/L calculated by the CMS at the end of the stream reach. The results from this test are shown in Table 4.3.

Table 4.3: Steady-state solutions for RECOVERY and PREWet using modified suspended solids concentration of 135 mg/L

Model	Contaminant	Water Conc. (mg/L)	Mixed Sediment Conc. (mg/kg)
PREWet	DDT	26.68	184,000
	Chromium III	27.08	187,400
RECOVERY	DDT	26.39	182,000
	Chromium III	27.22	187,700

As can be seen in Table 4.3, the constituent concentrations in both the water column and mixed sediment layer computed by RECOVERY and PREWet using the modified suspended solids concentration are once again very closer to those computed by CMS when using solids transport. The concentrations predicted by the CMS in the mixed sediment layer are less than 1% higher than those given by RECOVERY and PREWet. This test helped to verify that the CMS is working properly for a steady-state loading with suspended solids transport.

4.4 Time-Varying Test Case

This test case was run for the RECOVERY model and the CMS using the same data as the steady-state case above and stepping the constituent influx at 25-year intervals for each constituent. The following table shows the inflow concentrations for the models.

Table 4.4: Constituent inflow concentrations for step function test case

Time (yr)	Influx Concentration (mg/L)
0	30
25	40
50	50
75	15

The simulation was run for a period of 100 years without allowing the sediment bed concentrations for either constituent to fully reach steady-state conditions at any point during the simulation. The inflow concentration after year 75 is assumed to remain at 15 mg/L. Table 4.5 shows the final results for both models at the end of the simulation and at the downstream end of the reach. The CMS run was made using a steady-state suspended solids concentration of 150 mg/L.

Table 4.5: Final results for RECOVERY and CMS models for the time-varying test case

Model	Contaminant	Water Conc. (mg/L)	Mixed Sediment Conc. (mg/kg)
RECOVERY	DDT	14.0	150,165
	Chromium III	14.5	154,527
CMS	DDT	14.3	152,500
	Chromium III	14.5	155,000

The comparison of CMS and RECOVERY results once again shows that both the water column and mixed sediment layer concentrations are very similar. The deep sediment concentration profiles for both models are shown in Figures 4.3 and 4.4.

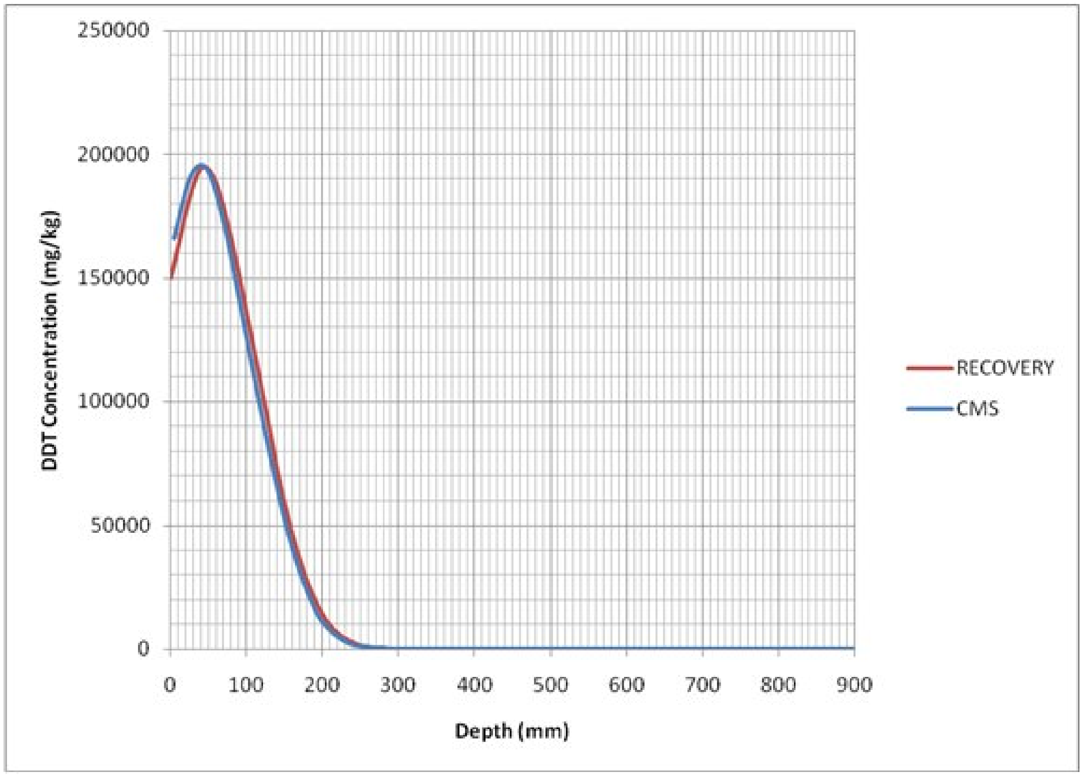

Figure 4.3: DDT concentration profile in deep sediment layer for step function test case

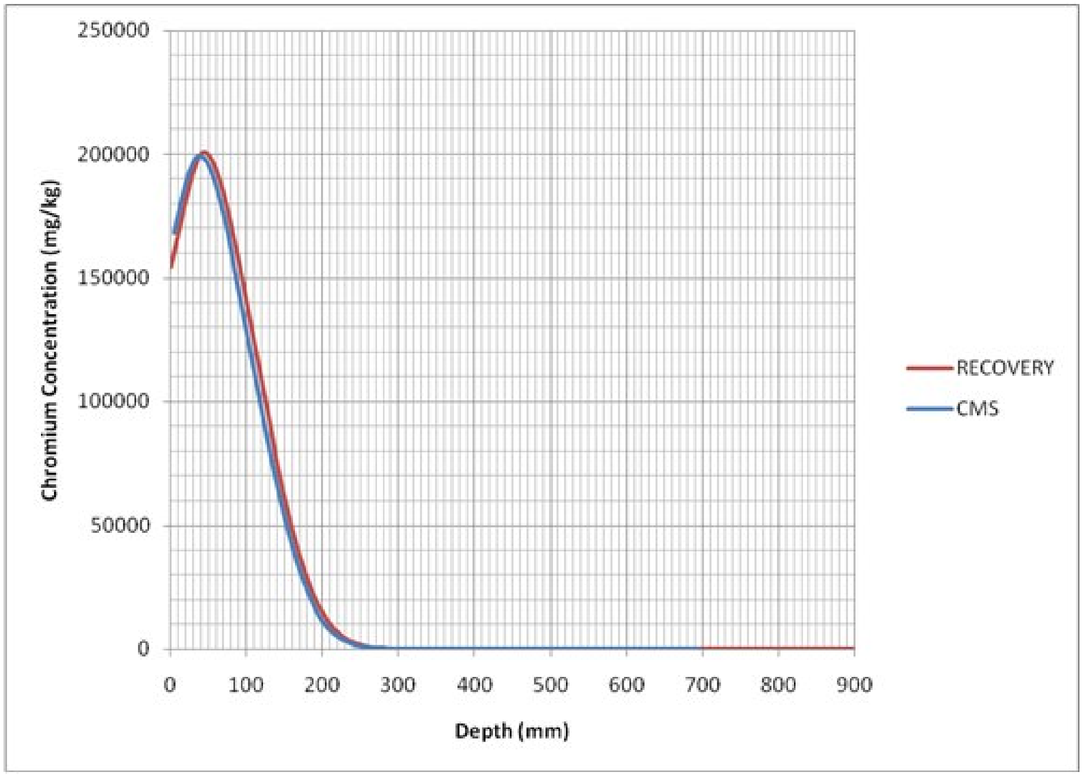

Figure 4.4: Chromium concentration profile in deep sediment layer for step function test case

There are only very minor differences in the deep sediment results between the two models, the most obvious of which appears to be a slight offset in concentration over the depth. This could be due to the fact that RECOVERY treats the entire reach as a single, fully mixed cell of homogeneous concentration, whereas, CMS computes a gradient in concentration along the reach. Due to this difference in conceptualizing the modeled reach, the water and sediment concentrations may respond to changes at slightly different rates between the two models. These changes would most likely be more evident at the mixed sediment/deep sediment interface. Thus, these differences in rates would not have been apparent in the final deep sediment profiles for the steady-state case due to the fact that the concentrations for both layers would be the same at steady-state given that the properties for the two layers are the same. Additionally, the results of the CMS are output only at the centers of the computational cells, which fall just before and just after the end of the model reach. The model results shown in Figures 4.3 and 4.4 are actually from a downstream distance of 100.5 km, which is 500 meters past the end of the model reach. Due to the longitudinal gradients produced in the CMS, both the water column and sediment bed concentrations will be different between these two longitudinal distances. Therefore, the deep sediment layer will likely respond at a different rate which could cause the offsets seen in the figures above. Understanding the differences and limits of the two models, this test helped to verify the CMS for time-varying input data.

4.5 Deep Sediment Profile Test Case

Since the deep sediment layer parameters can be specified at any depth, a test was performed to determine how well the model captures the change in concentration due to the change in sediment bed properties. The test was performed using the same parameters for the water column and mixed sediment layers that were specified in sections 4.1.2 and 4.1.3. However, the porosity and specific gravity in the deep sediment layer were allowed to vary with depth as shown in Table 4.6.

Table 4.6: Deep sediment properties

Depth (cm)	Porosity	Fraction Organic Carbon
0.0	0.35	0.02
0.1	0.20	0.02
0.2	0.35	0.02
0.4	0.35	0.10

This test case was run for a length of 500 years with the same incoming concentrations for both DDT and Chromium as used in the steady-state test case, but the loadings ceased after 200 years when the mixed sediment layer reaches steady-state. The deep sediment layer concentrations in the pore water at the end of the model run are shown in Figures 4.5 and 4.6.

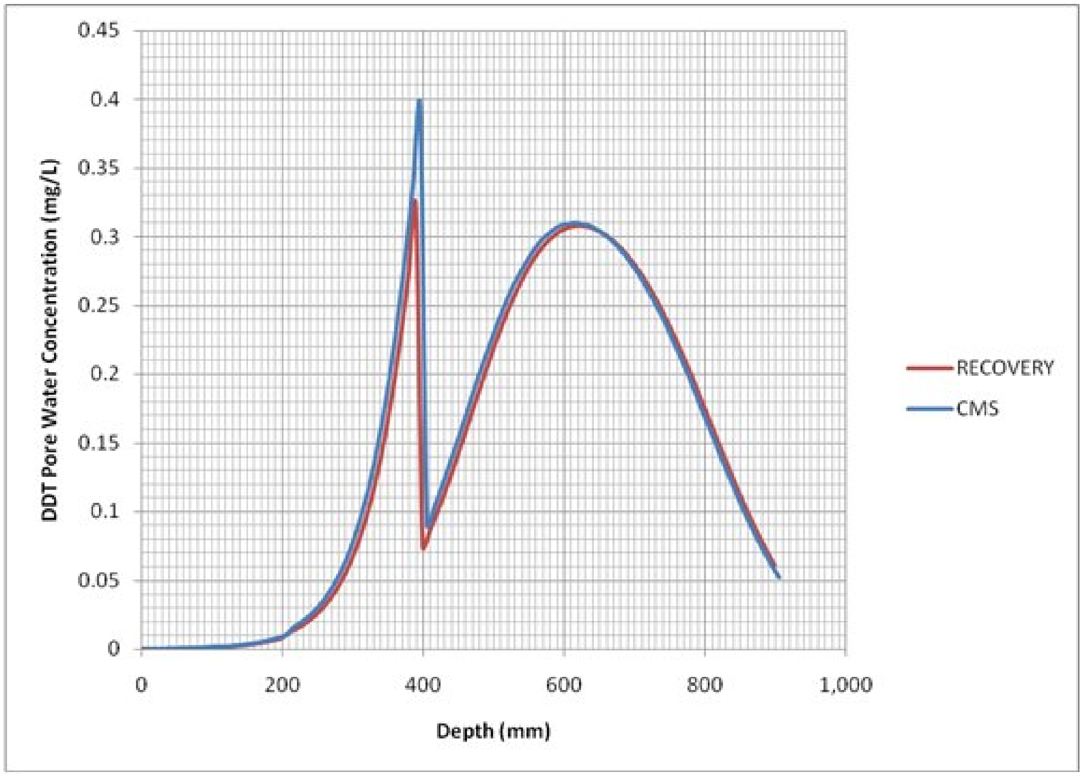

Figure 4.5: DDT pore water concentration for deep sediment layer profile test case

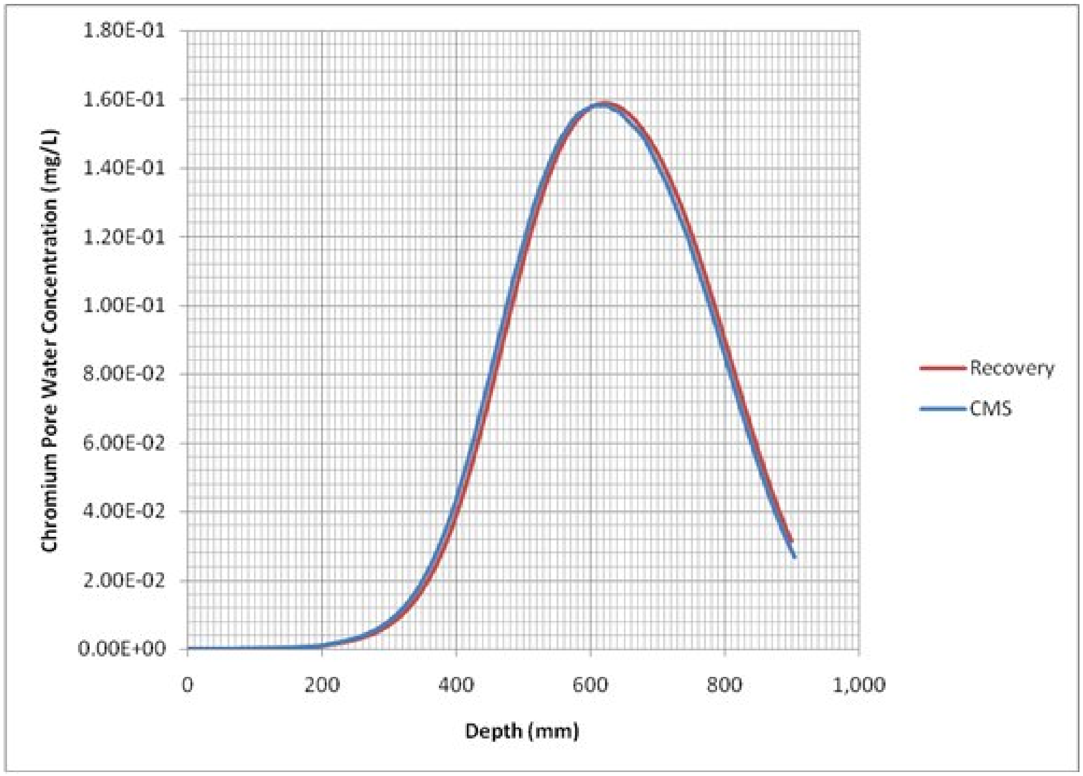

Figure 4.6: Chromium pore water concentration for deep sediment layer profile test case

As seen in the figures above, the concentrations for both constituents compare well between the two models. The only obvious distinction is the peak in Figure 4.4 near a depth of 400 mm. Minor differences such as these, however, could also be explained by the model differences stated in Section 4.5 above.

To show the effects of the sharp change in porosity between 10 and 20 cm depth, the total concentration in mg/kg for each constituent is shown in Figures 4.7 and 4.8 at year 200.

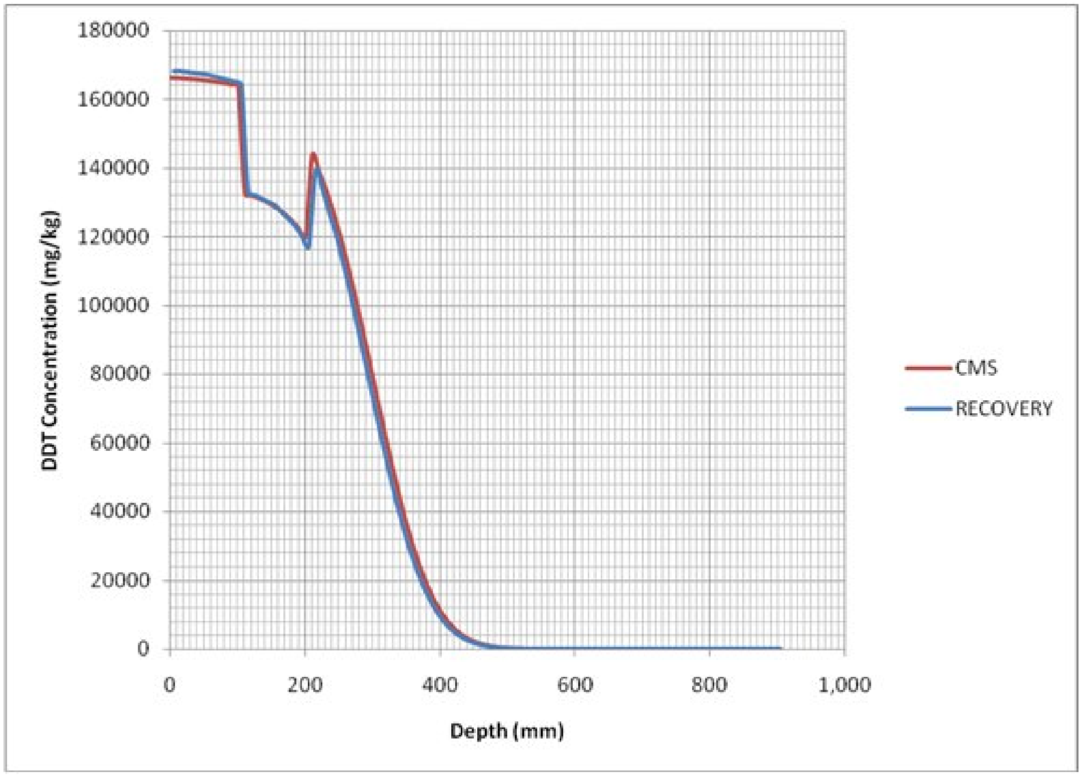

Figure 4.7: DDT concentration profile in deep sediment layer for deep sediment layer profile test case

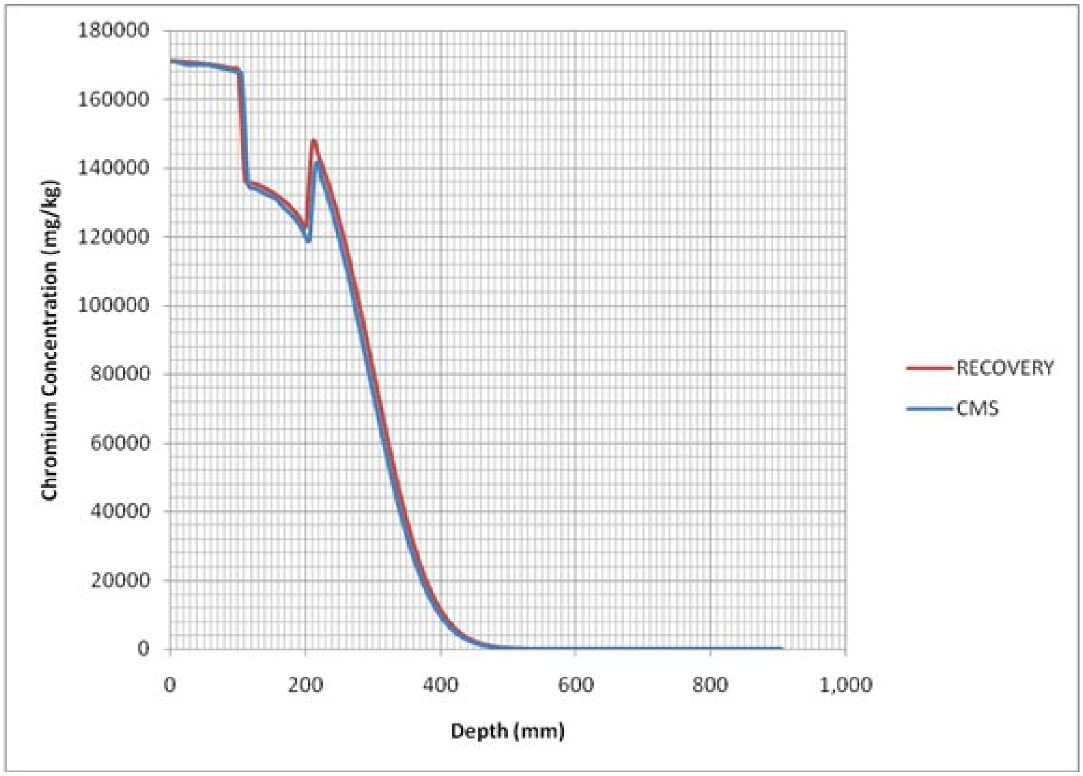

Figure 4.8: Chromium concentration profile in deep sediment layer for deep sediment layer profile test case

The concentrations in Figures 4.7 and 4.8 are again very close between the two models. This test case helped to verify that the depth-varying sediment properties were working correctly in the CMS.

4.6 Multiple Reach Test Case

In order to verify that the CMS works equally well for multiple reaches, the stead-steady-test case was run again using five 20 km reaches to simulate the single 100 kilometer reach. The reaches were modeled in series, and all parameters for each of the five reaches were identical to those used in the steady-state case with the exception of the reach length.

The constituent loadings were the same as those used in the steady-state case and entered at the beginning of the most upstream reach. The results of this test case are compared with the results from the steady-state test case in Table 4.7. The results from the multiple reach test case are given at the end of the fifth reach.

Table 4.7: Final results for multiple reach test case

Model	Contaminant	Water Conc. (mg/L)	Mixed Sediment Conc. (mg/kg)
CMS (Single Reach)	DDT	26.95	168,500
	Chromium III	27.30	171,000
RECOVERY (Multiple Reaches)	DDT	26.95	168,500
	Chromium III	27.30	171,000

As seen in Table 4.7, the water column and mixed sediment concentrations for both constituents are exactly the same for both test cases. The deep sediment layer concentration profiles at the end of the model run for both constituents are shown in Figures 4.9 and 4.10.

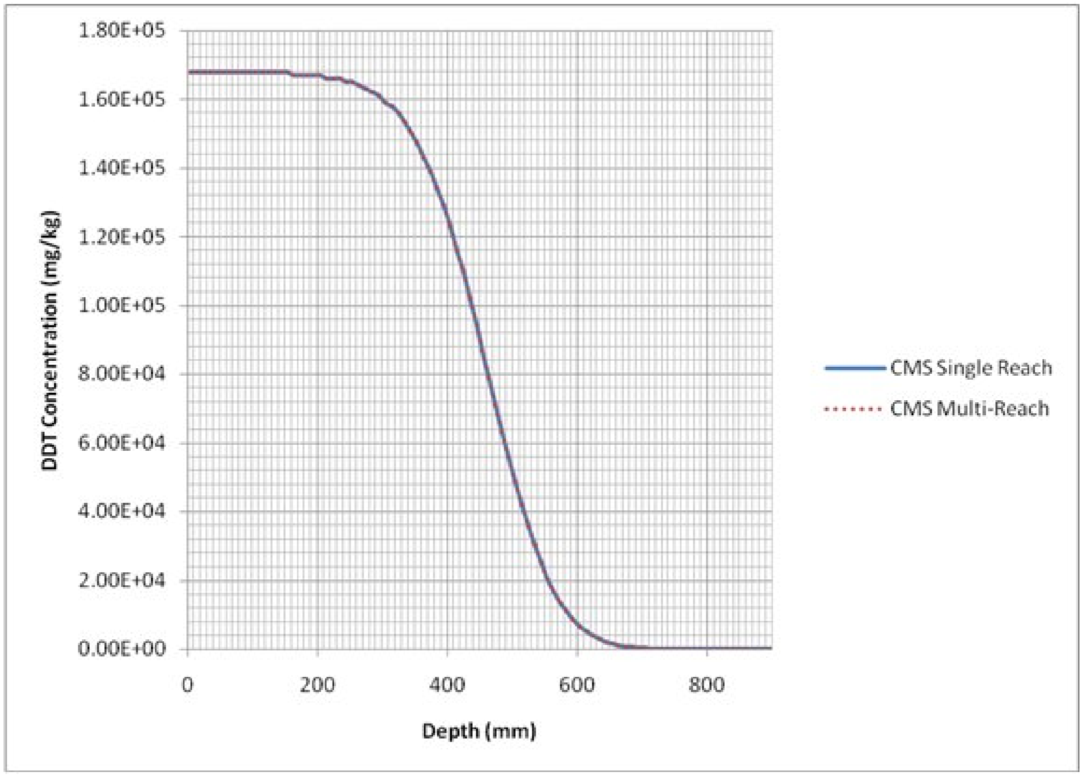

Figure 4.9: DDT concentration profile in deep sediment layer for multi-reach test case

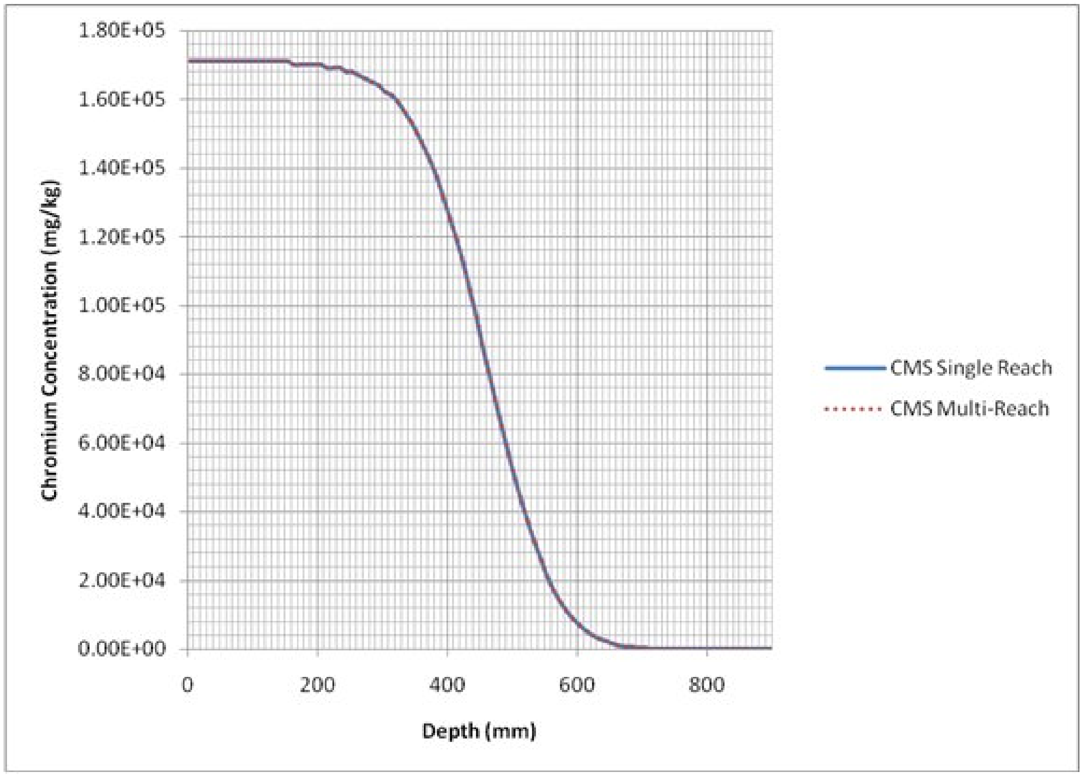

Figure 4.10: Chromium concentration profile in deep sediment layer for multi-reach test case

The deep sediment concentration profiles in Figures 4.9 and 4.10 are also identical for both constituents. This helped to verify that the CMS is functioning correctly for multiple reaches.

CHAPTER 5

CONCLUSIONS

5.1 Summary

A one-dimensional water quality model, CMS, was developed to fill a gap in the ARAMS modeling application. The scientific basis and implementation of the model have been given along with the results from the verification study. The CMS compared well to the two other models used in this study. Resulting concentrations in the surface water, mixed sediment layer, and deep sediment layer generally varied less than three percent between the models used in each test case. The CMS was verified for use with organics and heavy metals for both steady-state and time-varying inputs. The model was also verified for total and dissolved contaminant concentrations in the deep sediment layer with constant and depth-varying properties.

The test cases used in the model verification were kept simple in order to have a good comparison between the different models. However, the CMS has additional features that make it a more viable choice for many modeling scenarios. Unlike the other two models in the study, the CMS will allow the physical properties of the water body to vary with length by using multiple reaches in the model. Reaches can be connected in series or in a branching pattern to create the desired stream system. Each reach can have a unique geometry as well as incoming constituent and suspended solids concentrations or fluxes at the beginning of the reach. In addition, the ability to have time-varying flows, solids tranport, numerical solution options, and output at any point along a stream reach allows the CMS to be much more flexible and capable of being applied in many more situations than RECOVERY or PREWet. The introduction of a model with these capabilities will be an excellent addition to the set of models already present in the ARAMS project.

5.2 Model Limitations

Although the CMS has been verified as stated above, it does have limitations. The CMS is intended for use as a screening level model and does not include many options that more complex models may have. However, every model has limitations, and it's the ability to understand these limitations and apply the model as appropriate that will insure accurate results.

The range of flow rates in rivers and streams can vary greatly. Chapra [4] lists physical parameters for about a dozen rivers with widths and flow rates ranging from 16 to 200 m and 2.5 to 837 m^3/s, respectively. However, flow rates can vary even more depending on recent or current climatological and hydrologic events such as droughts and floods. CMS is applicable within the range of normal channel widths and flow rates given here but may not be applicable to extremely high flow rates such as for flood or dam-break modeling scenarios. Since CMS has no hydraulic or hydrologic routing, high flows or flows that vary greatly within a small time span may cause unrealistic results. Water bodies with widely varying depths and channel velocities may also cause problems due to the fact that the model assumes a simple channel geometry. Multiple reaches can be used to model changing channel geometries, but this approach may not work for all situations. Although the numerical solution scheme may remain stable under a wide range of conditions, the results for situations outside of these normal parameter bounds may be supsect.

The CMS requires only the total suspended solids (TSS) concentration and the fraction organic carbon (FOC) present in the solids for contaminant partitioning and solids transport. The type and size of the solids is not taken into account, although cohesive solids are generally associated with this type of partitioning and contaminant transport since they contain more organic carbon than noncohesive sediments. However, since the distinction is not made within the model, the model should be applicable to any type of solids as long as the correct values of TSS and FOC are entered and the user understands this distinction. Sediment particle size and shape are also not accounted for directly within the model. These are not required since the settling velocity is either specified or calculated using the steady-state solids balance and not based upon the geometry of the solids particles.

CMS was intially designed to model the fate and transport of military relevant compounds such as organics and heavy metals. These can be found on military bases in many forms ranging from simple diesel fuel spills to explosives residue deposited on firing ranges. CMS uses equilibrium partitioning of contaminants to solids based upon the amount of organic carbon present. This approach is applicable to both organics and heavy metals, but heavy metals can also become bound to suspended solids by other methods such as (a) physical adsorption to solid surfaces, (b) chemical sorption or binding by ligands, and (c) ion exchange [4]. Other factors such as natural background levels and chemical speciation may also affect the fate and transport of heavy metals. CMS does not handle decay products of organics or speciation of heavy metals. Despite these issues, CMS is still applicable under many situations given that the user understands the model limitations and the conditions of the system being modeled.

5.3 Recommendations

The CMS has been verified for the simulations mentioned above and the objectives of this study have been fulfilled. However, there are some additional modifications that could allow the model to function, or to improve the results, under more complex scenarios.

The CMS allows the user to choose options for the numerical solution methods. However, only the water column calculation currently has options for multiple solution methods, and this is only true for the advection operator. Since the model already includes operator-splitting methods to split the advection, diffusion, and reaction components in the solution, additional numerical methods could be added with little difficulty. Including additional numerical methods would allow for testing and determination of the circumstances under which each is more appropriate and would provide a greater applicability for the model in general.

As stated in section 2.2.2, the lack of hydraulic and hydrologic routing in the CMS limits the situations and conditions under which the model can appropriately be applied. The use of more complex channel geometries and the inclusion of flow routing would allow for greater applicability and more accurate results. However, to keep the model from becoming too complex, it is recommended to allow for this information to be imported from a one-dimensional hydraulic model when available. This data may already be present in many circumstances from previous modeling applications such as flood studies. The HEC-RAS model is widely applied for flow studies and could provide the required data while requiring only minor modifications to the CMS.

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APPENDIX A

CALCULATION OF VOLATILIZATION RATE

A modified version of the two-film theory [4] is used to calculate volatilization. Figure A.1 depicts the air-water interface and the two laminar films on either side of the interface.

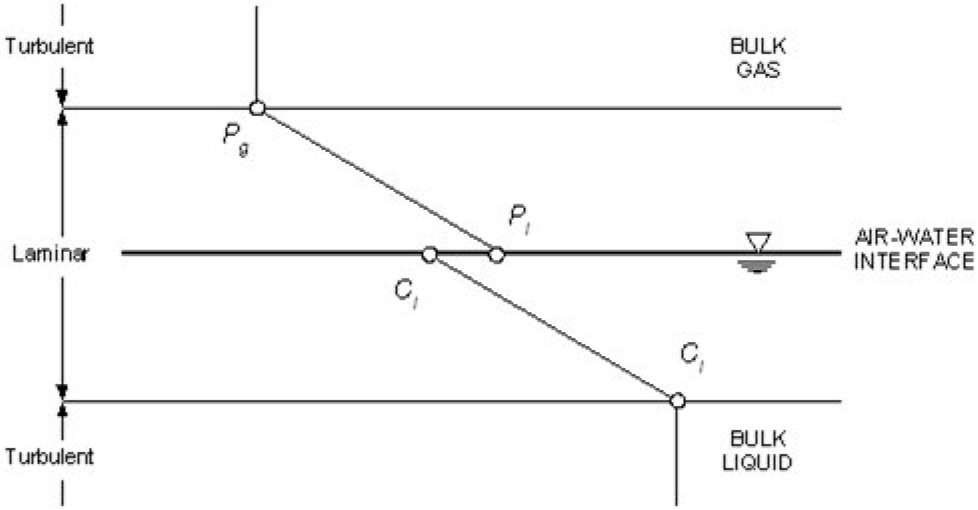


Figure A.1: Representation of Whitman's two-film theory of gas transfer

The two-film theory implies that the two laminar layers act as a series of resistors for the transfer of gas between the liquid and air. The limiting factor for the transfer rate is the film with the highest resistance or, in turn, the lowest transfer velocity. The equation for the two-film theory is given in Equation A.1.

$$\frac{1}{V_v} = \frac{1}{K_l} + \frac{RT_a}{H_c K_g} \tag{A.1}$$

where,

V_v = net transfer velocity across the air-water interface (m/day)

K_l = mass transfer velocity in the liquid laminar layer (m/day)

R = ideal Gas constant, $8.206x10^{-5}\ m^3 atm(mol\ K)^{-1}$

T_a = absolute temperature (K)

H_c = Henry's law constant $(atm\, m^3\ mol^{-1})$

K_g = mass transfer velocity in the gaseous laminar layer (m/day)

The liquid mass transfer velocity is calculated using the following formula [8] that relates the mass transfer velocity of oxygen to the current constituent using the ratio of the molecular weights.

$$K_l = K_{l,O_2}\left(\frac{32}{M}\right)^{0.25} \tag{A.2}$$

where,

K_{l,O_2} = mass transfer velocity of oxygen in the liquid laminar layer

M = molecular weight of the constituent (g/mol)

The mass transfer velocity of oxygen is determined using two formulas; the first relates the transfer velocity to the wind speed above the surface of the water (Equation A.3) [1] [2], and the other relates the transfer velocity to the stream velocity (Equation A.4) [9].

$$K_{l,O_2} = 0.728U_w^{0.5} - 0.317U_w + 0.0372U_w^2 \tag{A.3}$$

$$K_{l,O_2} = 3.93\left(\frac{U_w}{H}\right)^{0.5} \tag{A.4}$$

where,

U_w = wind speed at 10m above the surface of the water (m/s)

H = depth of the stream (m)

The largest value of the oxygen mass transfer velocity calculated with Equations A.3 and A.4 is then used in Equation A.2 since this would represent the highest possible transfer rate. The gas mass transfer velocity is calculated using another formula from Mills et al. [8], which is similar to Equation A.2 for the liquid transfer velocity. This equation relates the transfer velocity of the constituent in the gaseous phase to that of water vapor.

$$K_g = K_{g,H_2O} \left(\frac{18}{M} \right)^{0.25} \tag{A.5}$$

where,

K_{g,H_2O} = mass transfer velocity of water vapor in the gaseous laminar layer (m/s)

The mass transfer velocity for water vapor is determined as a function of wind speed using the following equation [8].

$$K_{g,H_2O} = 168 U_w \tag{A.6}$$

As can be seen from the equations above, there is no volatilization in the absence of wind with the two-film theory. However, this is not always the case for swift streams and highly volatile constituents. Therefore, the minimum value for the gas transfer coefficient, K_g, of 100 m/day will be set to prevent limiting the volatilization rate under these circumstances. This is also the approach used in both WASP [16] and ICM/TOXI [15] for fast-moving streams.

APPENDIX B

CALCULATION OF MASS TRANSFER RATE FOR SEDIMENT-WATER INTERFACE

It is assumed that the mass transfer across the sediment-water interface acts in a similar manner to the two-film model for volatilization calculations. A two-layer model does not exist for diffusion between the sediment pore water and the water column, but the transfer rate can be calculated based on the properties on each side of the boundary and will be limited by the lowest transfer velocity. The transfer rate can be limited by a low diffusion rate or flow rate in the water column or by a low diffusion rate in the sediments. To capture the influence of each of these factors, the mass transfer velocity will be calculated using formulations derived by Schink and Guinasso [11] and Di Toro et al. [5].

The formula given by Schink and Guinasso [11] is shown below in Equation B.1 and provides a rate based on water column properties such as the molecular diffusivity of the constituent in water, the viscosity of the water, and the flow shear velocity along the bed.

$$V_d = \frac{u_* \left(\frac{D_m}{v}\right)^{\frac{2}{3}}}{24} \tag{B.1}$$

where,

V_d = mass transfer velocity (cm/day)

u_* = flow shear velocity along the bed, which is approximately 10 percent of the mean velocity of flow (m/s)

D_m = molecular diffusivity of dissolved chemical (m^2/s)

v = kinematic viscosity of water at temperature T (m^2/s)

The kinematic viscosity of water can be calculated for a given temperature, T, using the following formula.

$$v = \frac{1.79x10^{-6}}{1.0 + 0.03368T + 0.000221T^2} \tag{B.2}$$

where,

T = temperature $(^{\circ}C)$

In the equation given by Di Toro et al. [5], the mass transfer is estimated as a function of the molecular weight of the constituent and the porosity of the bed sediments as shown in equation B.3 below.

$$V_d = 19\phi\,(M)^{-\frac{2}{3}} \tag{B.3}$$

where,

V_d = mass transfer velocity (cm/day)

ϕ = porosity of the bed sediments

M = molecular weight of the constituent (g/mol)

After calculation of the mass transfer velocity with each of these methods, the smaller of the two values will then be used for the mass transfer velocity since this will be the limiting rate.

APPENDIX C

MODEL INPUTS AND USER INTERFACE

A user-friendly interface has been created for entering model input data, executing the model, and examining model output.

C.1 Starting the Interface

To launch the CMS user interface in stand-alone mode, double-click the CMS icon on the desktop (Figure C.1).

Figure C.1: CMS desktop icon

The program can also be launched by clicking on the Windows ”Start” button and selecting ”Programs → CMS → CMS”. Figure C.2 shows all of the entries under the ”CMS” menu. The first entry, ”CMS”, will launch the graphical program interface. The second entry, ”CMS Help”, will launch the CMS help file. The last entry is used to remove the CMS model from the user’s computer.

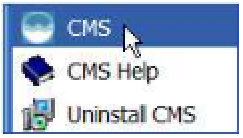
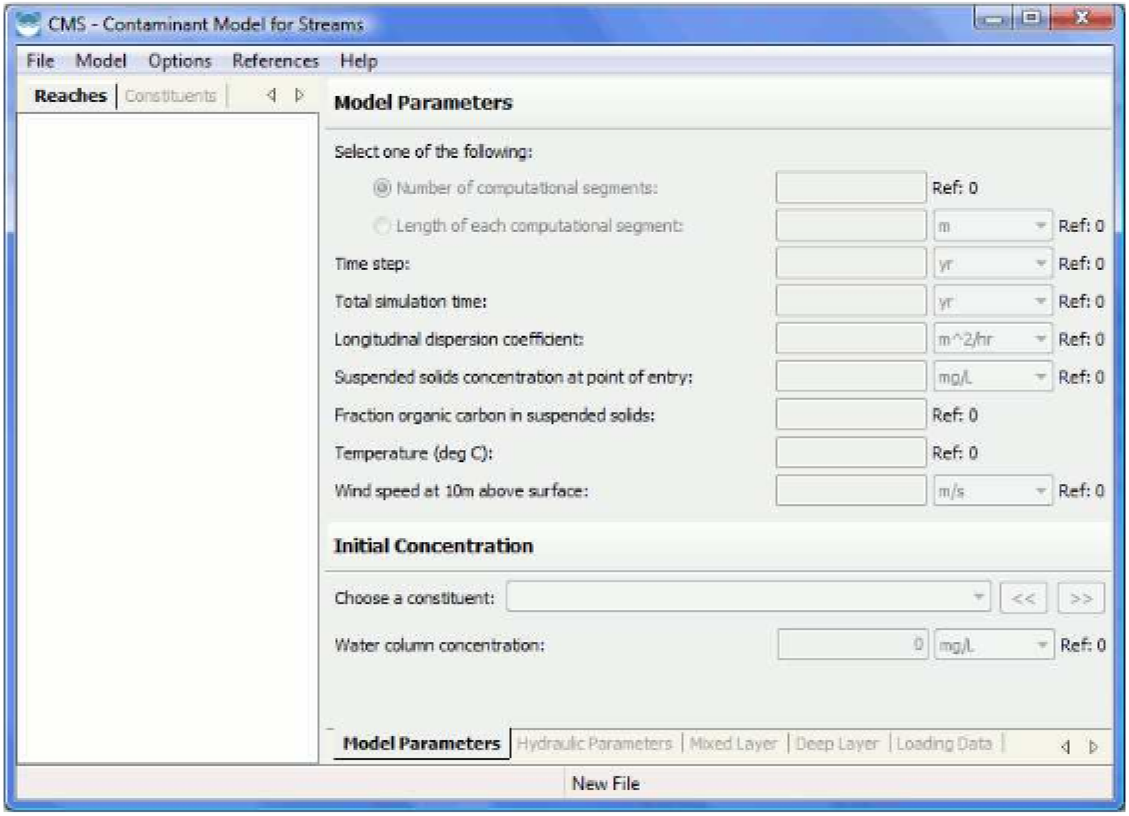


Figure C.2: CMS start menu item

When the CMS model is run from within ARAMS/FRAMES, the standard menu items are used to launch the model, run the model, and launch the results viewer.

After launching the CMS interface, the main screen will appear as shown below in Figure C.3.



Select one of the following:

- ● Number of computational segments: Ref: 0
- ○ Length of each computational segment: m Ref: 0

Time step: yr Ref: 0

Total simulation time: yr Ref: 0

Longitudinal dispersion coefficient: m^2/hr Ref: 0

Suspended solids concentration at point of entry: mg/L Ref: 0

Fraction organic carbon in suspended solids: Ref: 0

Temperature (deg C): Ref: 0

Wind speed at 10m above surface: m/s Ref: 0

Choose a constituent:

Water column concentration: 0 mg/L Ref: 0

Figure C.3: CMS main screen

When the CMS interface is first launched, the default behavior is to create a new data file. However, if at any time the user wishes to start a new project, this can be done by selecting ”File → New” from the main menu as shown in Figure C.4 below.

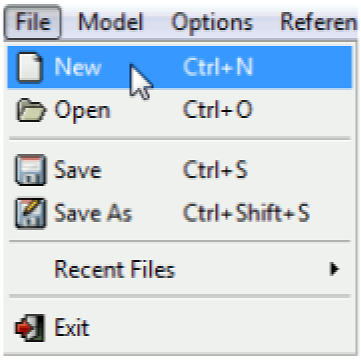


Figure C.4: New data file

To open an existing data file, select ”File → Open” from the main menu as shown in Figure C.5.

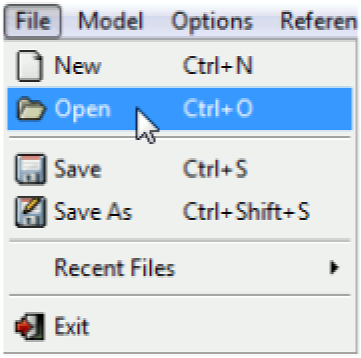
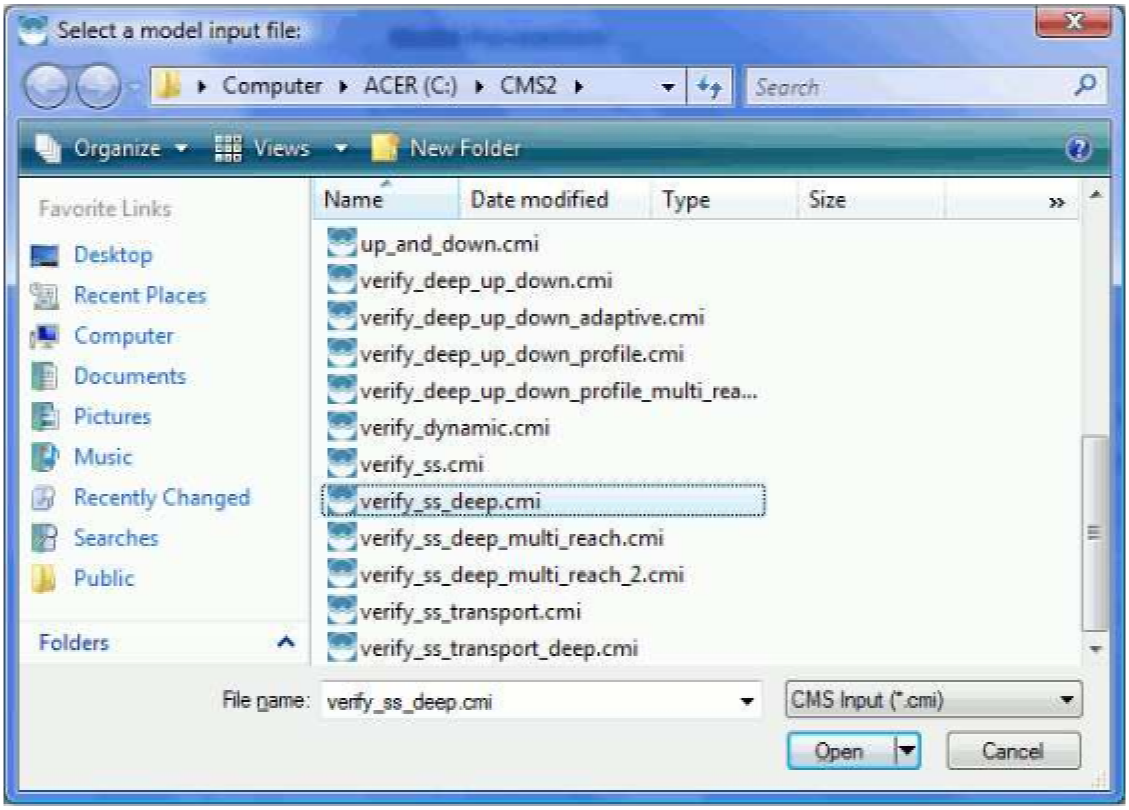


Figure C.5: Open data file

The open file dialog will then be shown as in Figure C.6. Browse to the folder where the desired file is located, select it, and click the button labeled ”Open” at the bottom of the dialog. The file can also be opened by double-clicking the left mouse button on the file from the open file dialog or from any Windows Explorer dialog. ***Note: an extension of .cmi is used for all CMS data files**.



File name: verify_ss_deep.cmi

CMS Input (*.cmi)

Figure C.6: Open file dialog

If the data file to be opened was one of the last five files to be opened, it will appear in the recent files list on the file menu. The recently used files will be numbered consecutively from one to a maximum of five and will appear under the ”Recent Files” menu item on the file menu as shown in Figure C.7. The most recently used data file will appear at the top of the list. Holding the mouse over the file name will cause the full path to the data file to be displayed on the status bar at the bottom of the main application window. To open one of these files simply select the desired item from the menu.

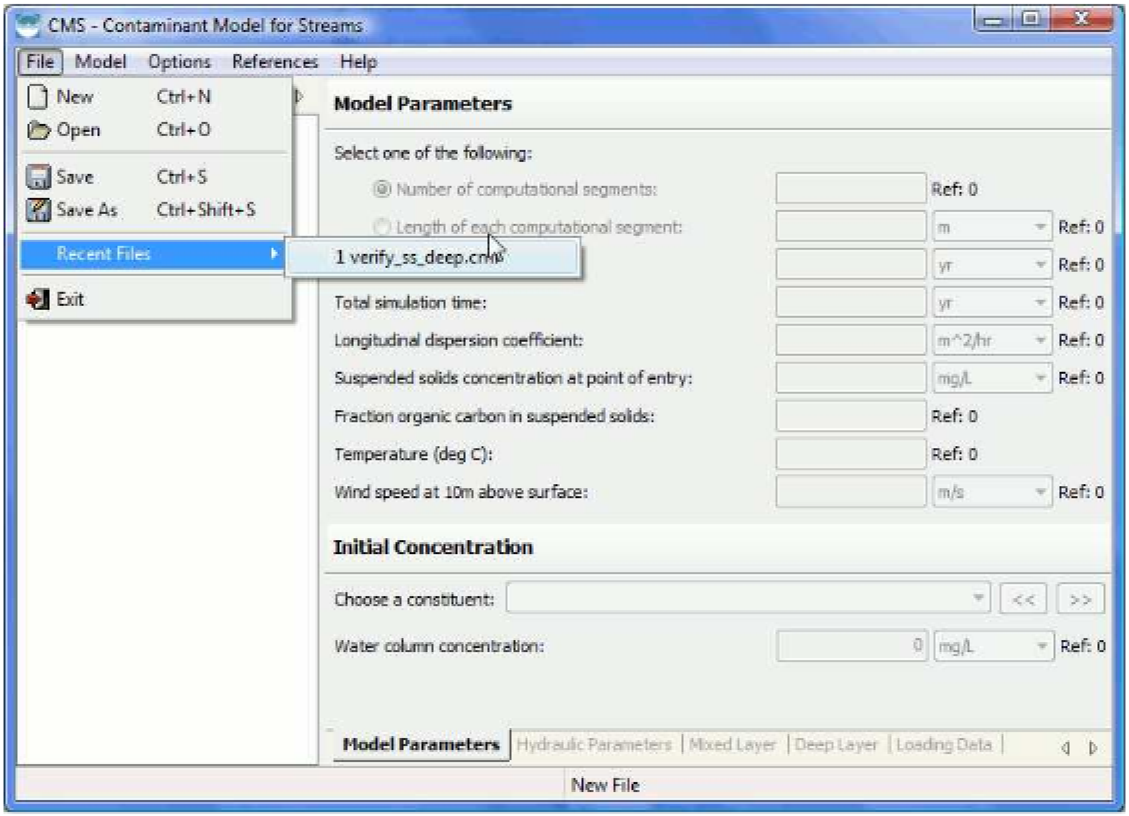


Figure C.7: Recent file menu

The current project may be saved at any time by selecting ”File → Save” from the main menu as shown in Figure C.8.

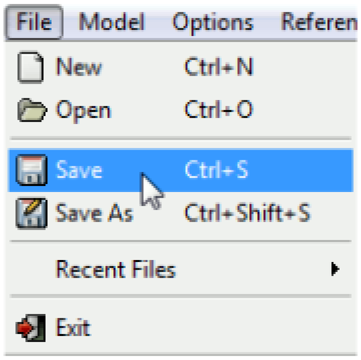
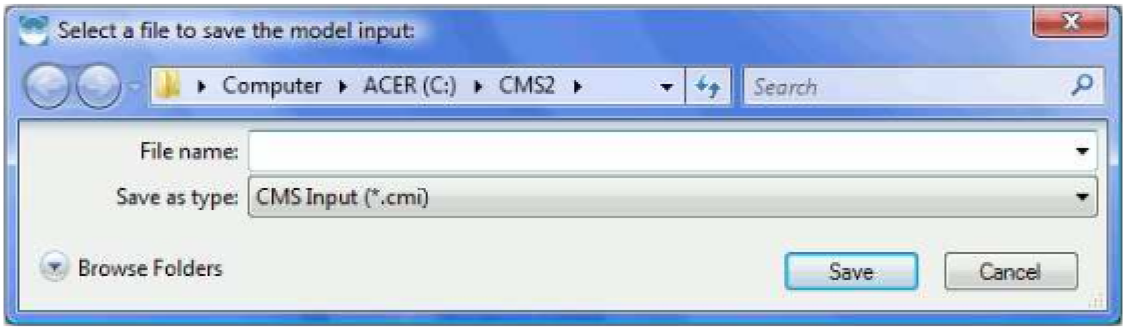


Figure C.8: Save file menu

If the project has not been saved previously, such as for a new project, the dialog shown in Figure C.9 will be displayed allowing the user to select the location and the name of the file where the project data will be stored. The user should select an appropriate directory and enter the desired file name into the File name box at the bottom of the dialog. This dialog can also be displayed by selecting ”File → Save As” from the main menu in order to save the current project under a different file name.


Select a file to save the model input:

Computer ▸ ACER (C:) ▸ CMS2 ▸

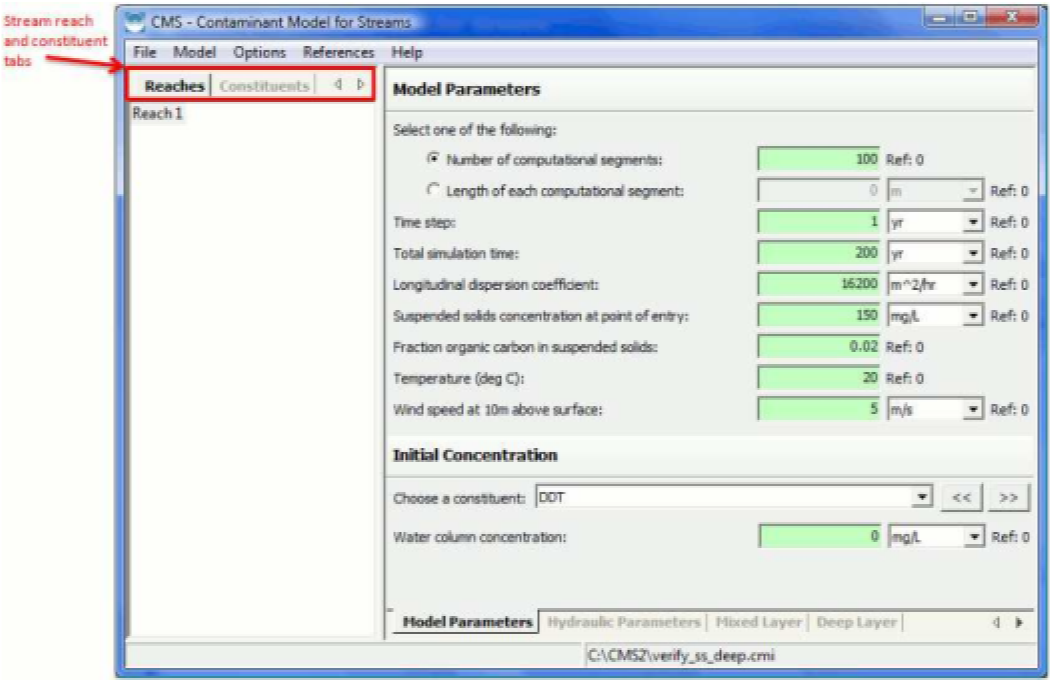
File name:

Save as type: CMS Input (*.cmi)

Figure C.9: Save file dialog

C.2 Data Entry

Data entry is performed through the six main screens of the CMS interface. One screen is dedicated to the constituents and their properties, while the remaining five screens are specific to the reaches and their properties. To switch between the stream reach and constituent screens, use the tabs on the upper left hand side of the interface as shown in Figure C.10.



Stream reach and constituent tabs

CMS - Contaminant Model for Streams

Model Parameters

Select one of the following:

● Number of computational segments: 100 Ref: 0

○ Length of each computational segment: 0 m Ref: 0

Time step: 1 yr Ref: 0

Total simulation time: 200 yr Ref: 0

Longitudinal dispersion coefficient: 16200 m^2/hr Ref: 0

Suspended solids concentration at point of entry: 150 mg/L Ref: 0

Fraction organic carbon in suspended solids: 0.02 Ref: 0

Temperature (deg C): 20 Ref: 0

Wind speed at 10m above surface: 5 m/s Ref: 0

Initial Concentration

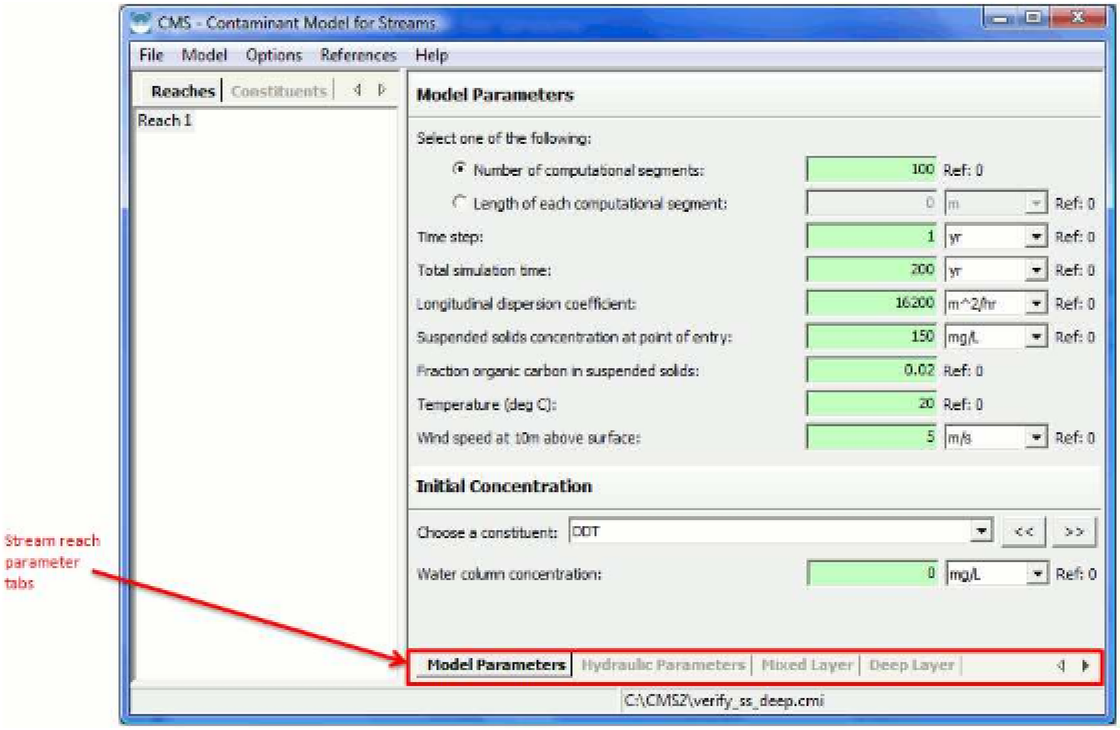
Choose a constituent: DDT

Water column concentration: 0 mg/L Ref: 0

C:\CMS2\verify_ss_deep.cmi

Figure C.10: Stream reach and constituent tabs

There are five individual screens accessible to enter properties for the stream reaches to be modeled when the ”Reaches” tab is selected. To activate these screens, use the tabs at the bottom of the main screen as shown in Figure C.11.



Stream reach parameter tabs

Model Parameters

Select one of the following:

● Number of computational segments: 100 Ref: 0

○ Length of each computational segment: 0 m Ref: 0

Time step: 1 yr Ref: 0

Total simulation time: 200 yr Ref: 0

Longitudinal dispersion coefficient: 16200 m^2/hr Ref: 0

Suspended solids concentration at point of entry: 150 mg/L Ref: 0

Fraction organic carbon in suspended solids: 0.02 Ref: 0

Temperature (deg C): 20 Ref: 0

Wind speed at 10m above surface: 5 m/s Ref: 0

Initial Concentration

Choose a constituent: DDT

Water column concentration: 0 mg/L Ref: 0

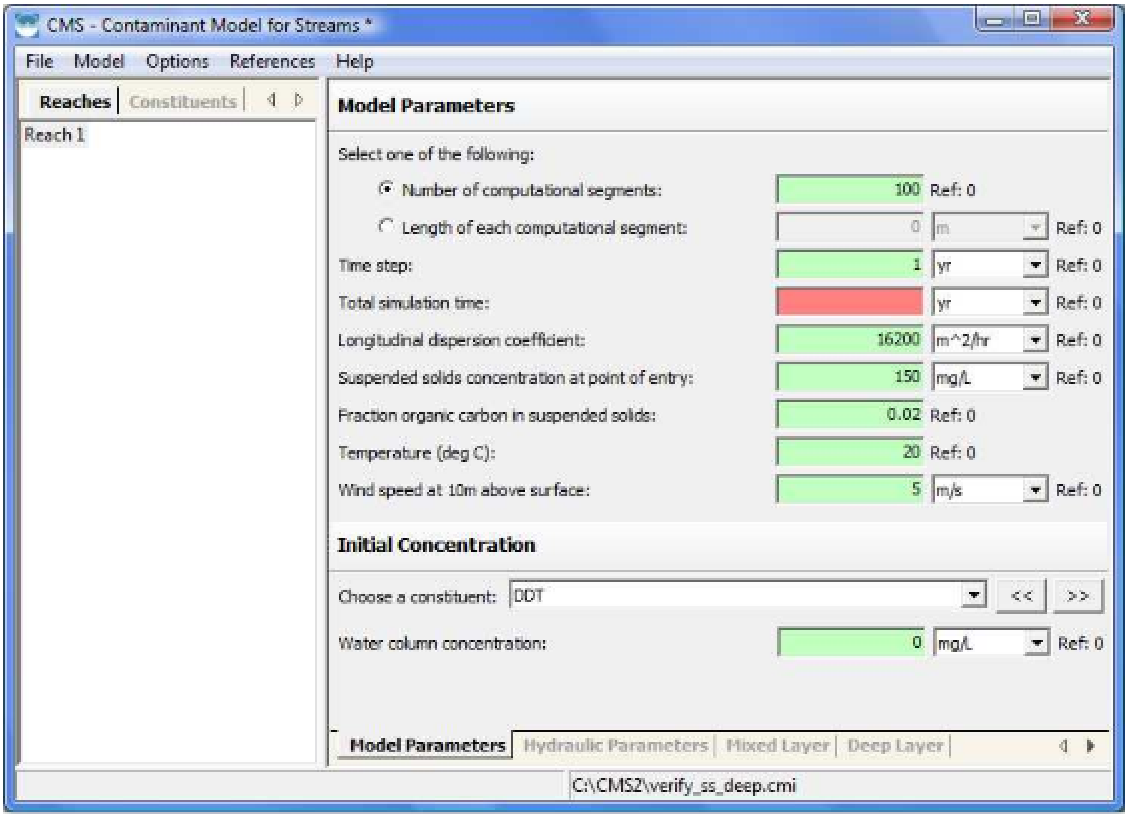
Figure C.11: Stream reach property tabs

C.2.1 *Stream Reach Parameters*

The data entry parameters for the stream reaches are divided into five different areas: model parameters, hydraulic parameters, mixed sediment layer parameters, deep sediment layer parameters, and loading parameters. Each category has its own input screen for data relevant to the specified category.

C.2.1.1 Model Parameters

The model parameters screen consists of entry forms for most of the general parameters including time step, spatial step, total simulation time, etc. The model parameters screen is shown in Figure C.12, and an explanation of the input fields is given below.



Model Parameters

Select one of the following:

● Number of computational segments: 100 Ref: 0

○ Length of each computational segment: 0 m Ref: 0

Time step: 1 yr Ref: 0

Total simulation time: yr Ref: 0

Longitudinal dispersion coefficient: 16200 m^2/hr Ref: 0

Suspended solids concentration at point of entry: 150 mg/L Ref: 0

Fraction organic carbon in suspended solids: 0.02 Ref: 0

Temperature (deg C): 20 Ref: 0

Wind speed at 10m above surface: 5 m/s Ref: 0

Initial Concentration

Choose a constituent: DDT << >>

Water column concentration: 0 mg/L Ref: 0

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Figure C.12: Model parameters screen

Model Parameter Field Description

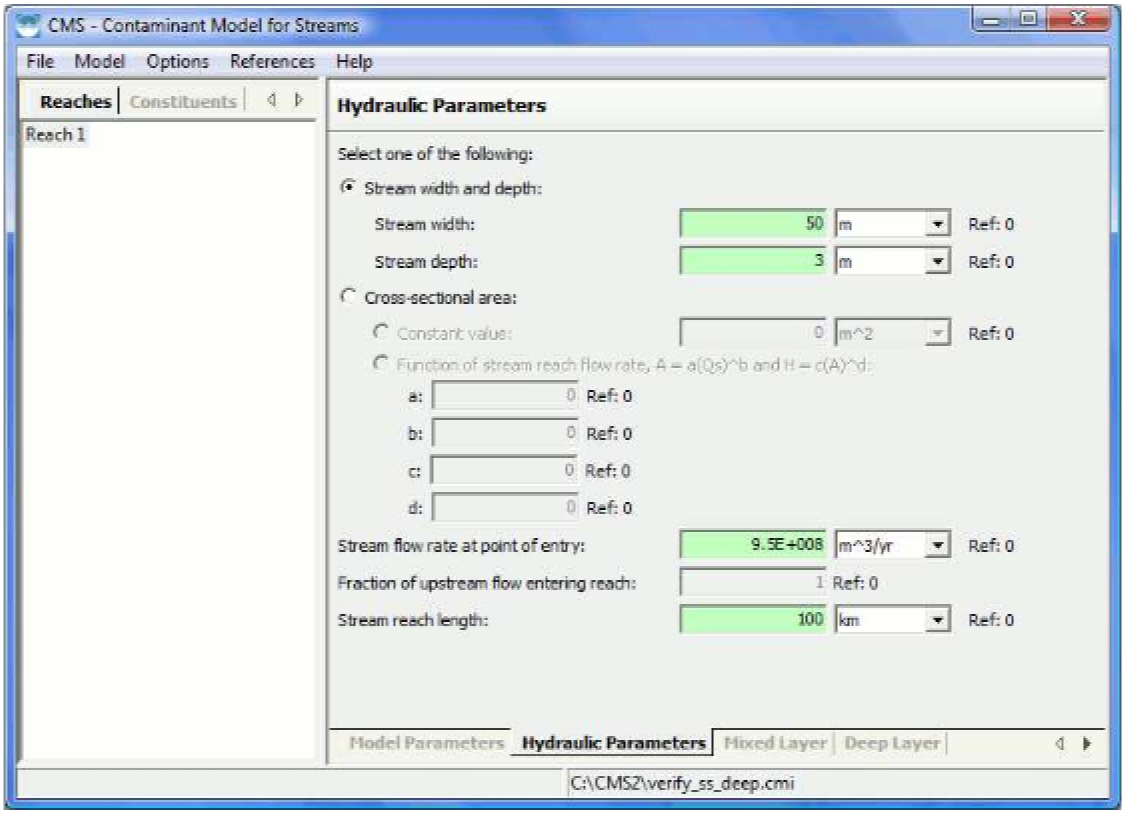
- **Segment Length Options** - One of the following options must be selected.
  - **Number of Computational Segments** - Specifies the number of segments in the stream reach; the segment length will automatically be calculated.

  - **Length of Computational Segment** - Specifies the length of the segments in the stream reach (units may be specified in combo box). The number of segments will automatically be calculated.

- **Time Step** - Specifies the length of the time step to be used (units may be specified in combo box).
- **Total Simulation Time** - Specifies the total length of the simulation (units may be specified in combo box).
- **Longitudinal Dispersion Coefficient** - Specifies the longitudinal dispersion coefficient to be used (units may be specified in combo box).
- **Suspended solids concentration at point of entry** - Specifies the concentration of suspended solids in the stream at the point of entry (units may be specified in combo box). Solids concentration loading data will be specified on the Loading Data screen.
- **Fraction Organic Carbon in Suspended Solids (Water Column)** - Specifies the fraction of organic carbon present in the suspened solids in the water column.
- **Temperature** ($^{\circ}C$) - Specifies the temperature in degrees Celsius. This is required if the ”Calculate” option is specified for the volatilization rate or the mass transfer velocity for any constituent.
- **Wind Speed at 10m above Surface** - Specifies the wind speed at 10m above the surface of the stream. This is required if the ”Calculate” option is specified for the volatilization rate for any constituent.
- **Inital Concentration** - Specifies the initial concentration of the constituents in the water column.

C.2.1.2 Hydraulic Parameters

The hydraulic parameters screen consists of entry forms for hydraulic parameters including width, depth, cross-sectional area, etc. The hydraulic parameters screen is shown in Figure C.13, and an explanation of the input fields is given below.



Hydraulic Parameters

Select one of the following:

● Stream width and depth:

Stream width: 50 m Ref: 0

Stream depth: 3 m Ref: 0

○ Cross-sectional area:

○ Constant value: 0 m^2 Ref: 0

○ Function of stream reach flow rate, A = a(Qs)^b and H = c(A)^d:

a: 0 Ref: 0

b: 0 Ref: 0

c: 0 Ref: 0

d: 0 Ref: 0

Stream flow rate at point of entry: 9.5E+008 m^3/yr Ref: 0

Fraction of upstream flow entering reach: 1 Ref: 0

Stream reach length: 100 km Ref: 0

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Figure C.13: Hydraulic parameters screen

Hydraulic Parameter Field Descriptions

- **Cross-sectional area options** - One of the following options must be selected.
  - **Surface water width and depth**
    - **Stream width** - Specifies the width of the stream for the maximum extent of the reach (units may be specified in combo box).
    - **Stream depth** - Specifies the depth of the stream for the maximum extent of the reach (units may be specified in combo box).
  - **Cross-sectional area** - One of the following options must be selected.
    - **Constant value** - Specifies a constant cross-sectional area of the stream for the maximum extent of the reach (units may be specified in combo box).
    - **Function of stream reach flow rate,** $a(Q_s)^b$ - Q_s is the stream flow rate including any flows supplied on the loading data screen.
      - **a** - Specifies the first coefficient in this function.

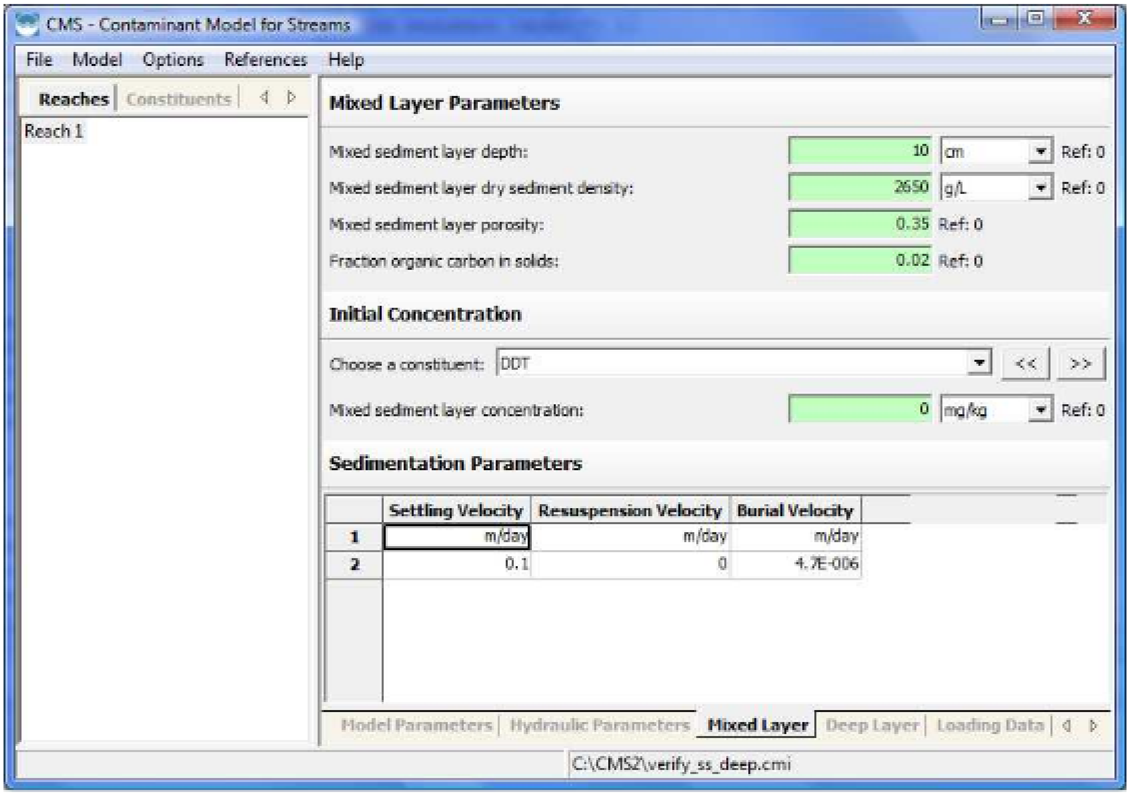
    - **b** - Specifies the second coefficient in this function.
    - **c** - Specifies the first coefficient in this function.
    - **d** - Specifies the second coefficient in this function.

  When using this method, the stream depth can be related to the cross-sectional area by $H = cA^d$ where H is the stream depth, A is the cross-sectional area, and c and d are coefficients supplied by the user.

- **Stream flow rate at point of entry** - Specifies the flow rate of the stream (units may be specified in combo box).
- **Fraction of upstream flow entering reach** - Since there is no hydraulic routing included in the model, the fraction of the upstream flow entering the reach must be specified. For the first reach in the model, this value will be ”1”.
- **Stream reach length** - Specifies the total longitudinal distance for the current reach.

C.2.1.3 Mixed Layer Parameters

The mixed layer parameters screen consists of entry fields for mixed sediment layer parameters including the layer depth, dry sediment density, porosity, etc. The mixed layer parameters screen is shown in Figure C.14, and an explanation of the input fields is given below.



Reach 1

Mixed Layer Parameters

Mixed sediment layer depth: 10 cm Ref: 0

Mixed sediment layer dry sediment density: 2650 g/L Ref: 0

Mixed sediment layer porosity: 0.35 Ref: 0

Fraction organic carbon in solids: 0.02 Ref: 0

Initial Concentration

Choose a constituent: DDT

Mixed sediment layer concentration: 0 mg/kg Ref: 0

Sedimentation Parameters

	Settling Velocity	Resuspension Velocity	Burial Velocity
1	m/day	m/day	m/day
2	0.1	0	4.7E-006

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Figure C.14: Mixed layer parameters screen

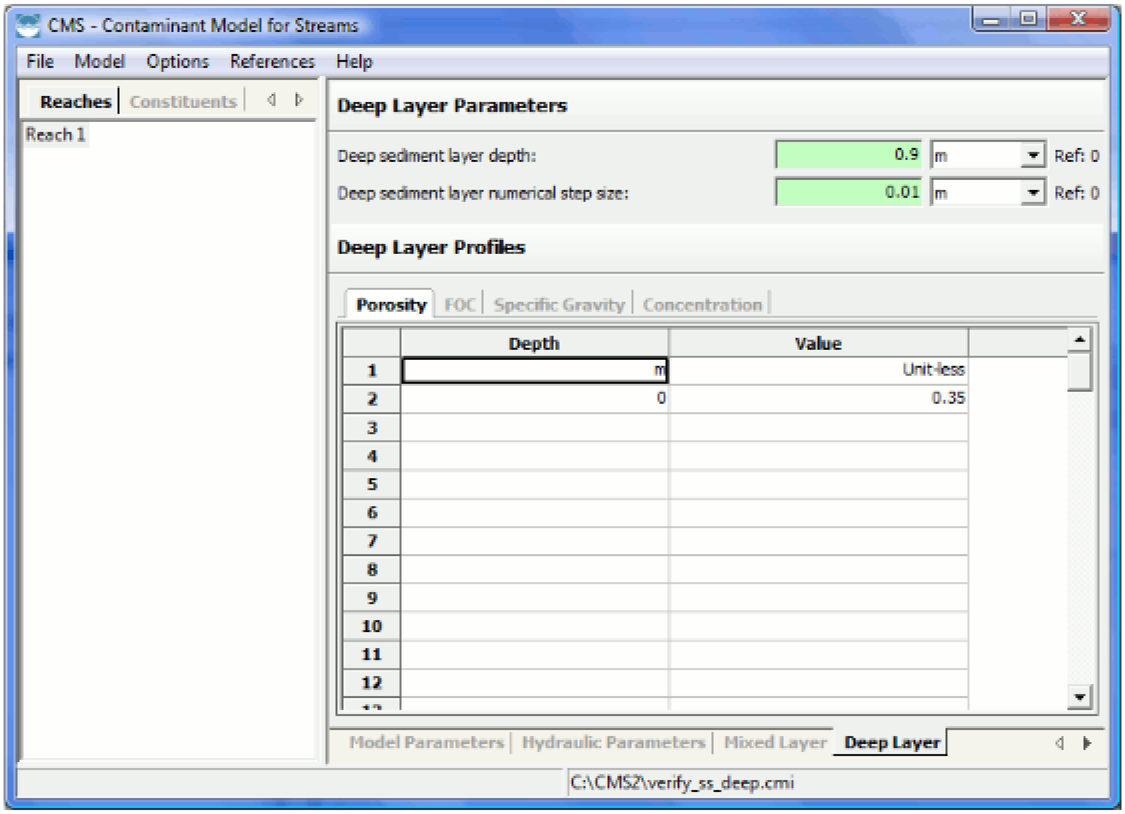
Mixed Layer Parameter Field Descriptions

- **Mixed sediment layer depth** - Defines the depth of the fully mixed sediment bed layer where most of the biological activity occurs.
- **Dry sediment density** - Specifies the density of the sediment bed in mass per volume dry weight (units may be specified in combo box).
- **Mixed sediment layer porosity** - Specifies the porosity of the mixed sediment bed layer.
- **Fraction organic carbon in solids** - Specifies the fraction of organic carbon present in the solids in the sediment bed.
- **Sedimentation parameters** - Two of these three parameters must be specified. The third parameter should be set to ”0”.
  - **Settling velocity** - Specifies the settling velocity for suspended particles (units may be specified in combo box).

- **Resuspension velocity** - Specifies the resuspension velocity for particles resuspended from the mixed layer of the sediment bed (units may be specified in combo box).
- **Burial velocity** - Specifies the burial velocity for particles in the sediment bed (units may be specified in combo box).

C.2.1.4 Deep Layer Parameters

The deep layer parameters screen consists of entry fields for parameters that are specific to the deep sediment layer including the layer depth, porosity, specific gravity, etc. The deep layer parameters screen is shown in Figure C.15, and an explanation of the input fields is given below.



Deep sediment layer depth: 0.9 m Ref: 0

Deep sediment layer numerical step size: 0.01 m Ref: 0

	Depth	Value
1	m	Unit-less
2	0	0.35
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		

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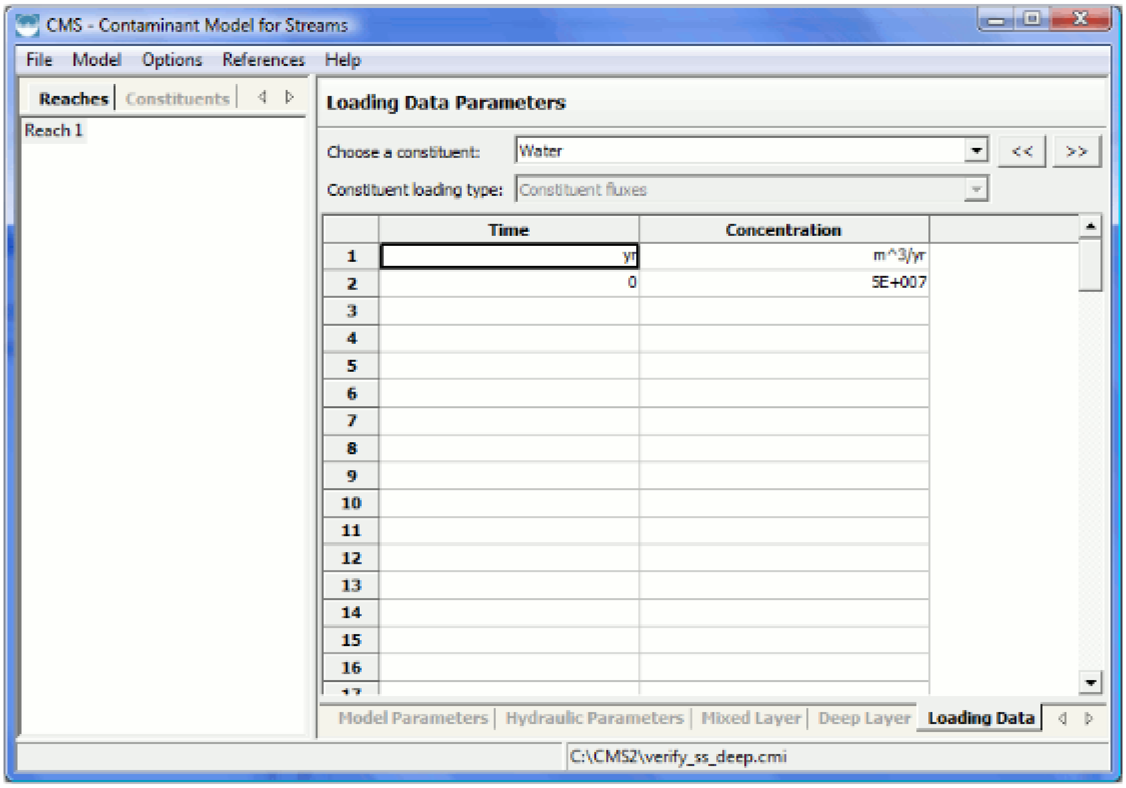
Figure C.15: Deep layer parameters screen

Deep Layer Parameter Field Descriptions

- **Deep sediment layer depth** - Defines the depth of the fully mixed sediment bed layer where most of the biological activity occurs.
- **Deep sediment layer numerical step size** - Specifies the vertical step size for the deep sediment layer model calculations.
- **Depth varying parameters** - These parameters are allowed to vary with depth in the deep sediment layer and are entered as a depth/value pair.
  - **Porosity** - Specifies the porosity of the deep sediment layer.
  - **Fraction organic carbon (FOC) in solids** - Specifies the fraction of organic carbon present in the solids in the deep layer.
  - **Specific Gravity** - Specifies the specific gravity of the deep sediment layer.
  - **Concentration** - Specifies the concentrations of the constituents.

C.2.1.5 Loading Data Parameters

The loading data parameters screen contains entry fields for entering flux or concentration loadings for water, suspended solids, and the model constituents. The loading data parameters screen is shown in Figure C.16, and an explanation of the input fields is given below.



Loading Data Parameters

Choose a constituent: Water

Constituent loading type: Constituent fluxes

	Time	Concentration
1	yr	m^3/yr
2	0	5E+007
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		
13		
14		
15		
16		

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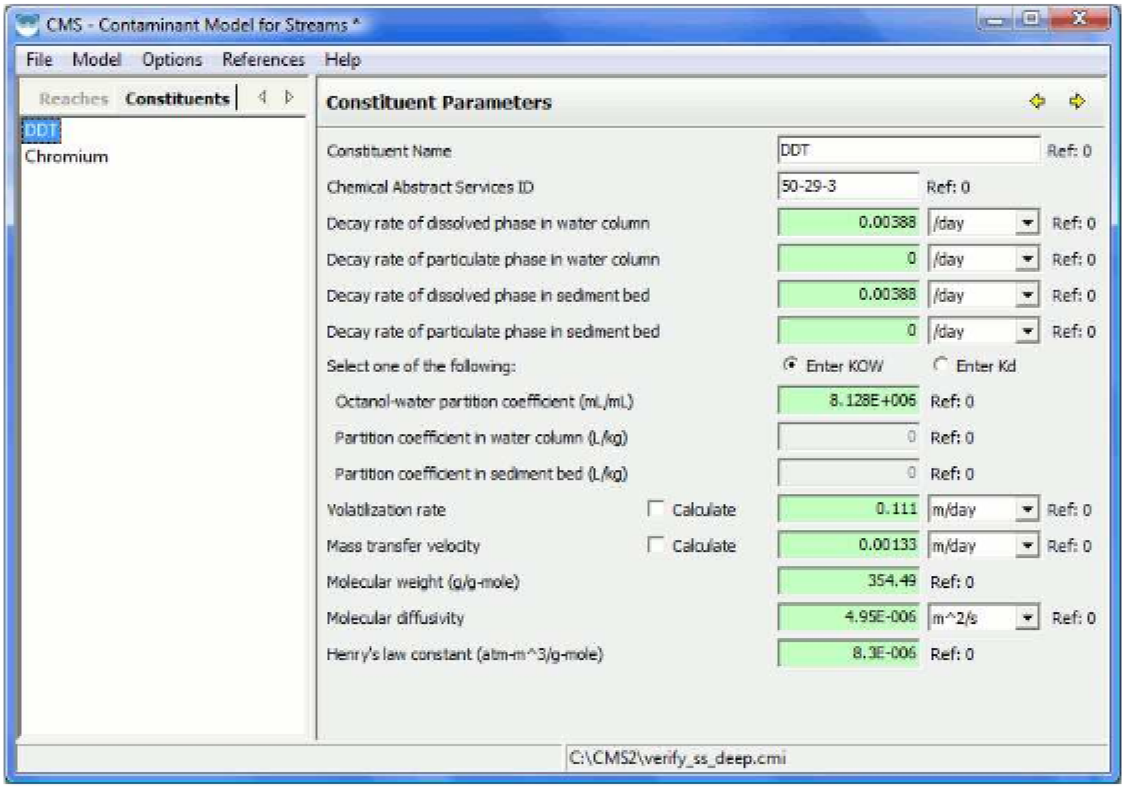
Figure C.16: Loading data parameters screen

Loading Data Parameter Field Descriptions

- **Constituent selection** - Selects the constituent for which the loading data will be entered.
- **Constituent loading type** - Specifies if the loading data will be entered as a flux or a concentration.
- **Data grid** - Allows the user to enter time/value pairs for constituent loading data.

C.2.2 Constituent Parameters

The constituent parameters screen consists of entry forms for all of the constituent-specific parameters such as decay rates, partition coefficients, etc. Constituents can be added, modified, or removed by clicking the right mouse button in the list box at the left of the screen. The constituent parameters screen is shown in Figure C.17, and an explanation of the input fields is given below.



Constituent Name	DDT		Ref: 0
Chemical Abstract Services ID	50-29-3		Ref: 0
Decay rate of dissolved phase in water column	0.00388	/day	Ref: 0
Decay rate of particulate phase in water column	0	/day	Ref: 0
Decay rate of dissolved phase in sediment bed	0.00388	/day	Ref: 0
Decay rate of particulate phase in sediment bed	0	/day	Ref: 0
Select one of the following:	● Enter KOW	○ Enter Kd	
Octanol-water partition coefficient (mL/mL)	8.128E+006		Ref: 0
Partition coefficient in water column (L/kg)	0		Ref: 0
Partition coefficient in sediment bed (L/kg)	0		Ref: 0
Volatilization rate ☐ Calculate	0.111	m/day	Ref: 0
Mass transfer velocity ☐ Calculate	0.00133	m/day	Ref: 0
Molecular weight (g/g-mole)	354.49		Ref: 0
Molecular diffusivity	4.95E-006	m^2/s	Ref: 0
Henry's law constant (atm-m^3/g-mole)	8.3E-006		Ref: 0

C:\CMS2\verify_ss_deep.cmi

Figure C.17: Constituent parameters screen

Constituent Parameter Field Descriptions

- **Constituent Name** - Specifies the name of the selected constituent.
- **Constituent CAS ID** - Specifies the Chemical Abstract Services identification number for the currently selected constituent.

  Note - The following decay rates do not include physical losses such as volatilization, settling, burial, etc. They are a summation of degradation mechanisms such as biodegradation, hydrolysis, photolysis, etc.

- **Decay rate of dissolved phase in water column** - Specifies the decay rate of the dissolved phase/fraction of the currently selected constituent in the water column (units may be specified in combo box).
- **Decay rate of particulate phase in water column** - Specifies the decay rate of the particulate phase/fraction of the currently selected constituent in the water column (units may be specified in combo box).
- **Decay rate of dissolved phase in sediment bed** - Specifies the decay rate of the dissolved phase/fraction of the currently selected constituent in the sediment bed (units may be specified in combo box).
- **Decay rate of particulate phase in sediment bed** - Specifies the decay rate of the particulate phase/fraction of the currently selected constituent in the sediment bed (units may be specified in combo box).
- The user may enter either the Octanol-water partition coefficient or partition coefficients in the water column and sediment bed:
  - **Octanol-water partition coefficient** - Specifies the octanol-water partition coefficient for the currently selected constituent in units of mL Octanol/mL Water. The octanol-water partition coefficient, or KOW, is a measure of the preference of the constituent to bind to organic materials or to remain in the water column. If the KOW is specified, it will be used to calculate the partition coefficients in the water column and sediment bed.
  - **Partition coefficient in water column** - Specifies the partition coefficient of the currently selected constituent in the water column in units of L/kg. This value will be ignored if the KOW is specified above.
  - **Partition coefficient in sediment bed** - Specifies the partition coefficient of the currently selected constituent in the sediment bed in units of L/kg. This value will be ignored if the KOW is specified above.
- **Volatilization rate** - Specifies the rate of volatilization of the currently selected constituent from the water column (units may be specified in combo box). Note*: only the dissolved fraction of the constituent will be considered in the volatilization calculations. Select the ”Calculate” option to have this value automatically calculated by the model.
- **Mass transfer velocity** - Specifies the mass transfer velocity of the currently selected constituent across the sediment-water interface (units may be specified in combo box). Note*: only the dissolved fraction of the constituent will be considered in mass transfer calculations. Select the ”Calculate” option to have this value automatically calculated by the model.
- **Molecular Weight** ($g/gmole$) - Specifies the molecular weight of the selected constituent. This value is required if the ”Calculate” option is specified for the volatilization rate.

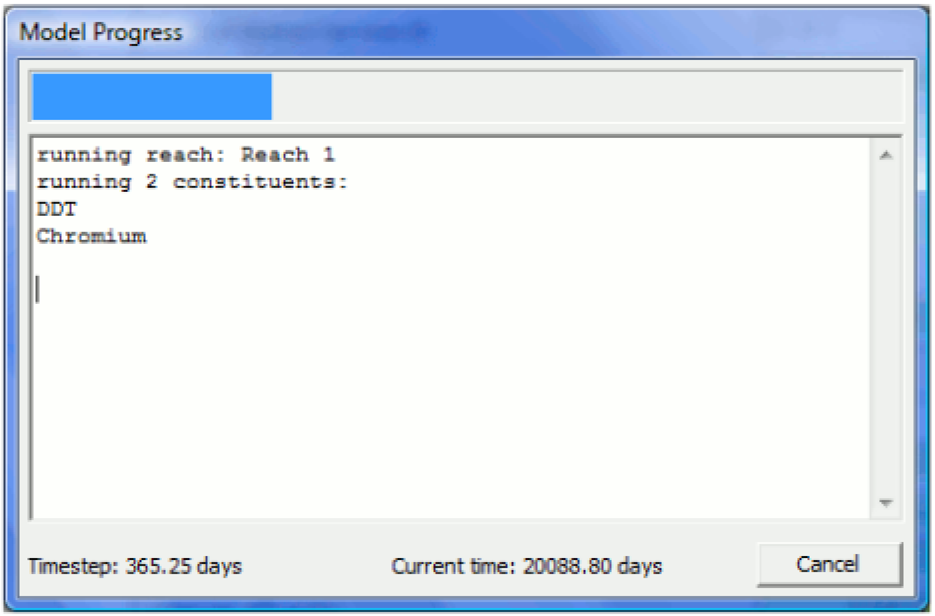
- **Molecular Diffusivity** - Specifies the molecular diffusivity of the selected constituent. This is required if the ”Calculate” option is specified for the mass transfer velocity.
- **Henry’s Law Constant** ($atm\ m^3/g\text{-}mole$) - Specifies the Henry’s law constant for the selected constituent. This is required if the ”Calculate” option is specified for the volatilization rate.

C.3 Model Execution

The model execution process is described in this section. This includes running the model and explaining how errors will be handled that occur during the execution process.

C.3.1 Running the Model

The model is run by selecting ”Model → Run” from the main menu or pressing the F5 key. When the model is executing, a new dialog will be displayed indicating the progress of the model, the current model time step, and the current simulation time during the execution (Figure C.18). The model run can be terminated by clicking the ”Cancel” button at any point during the execution process.



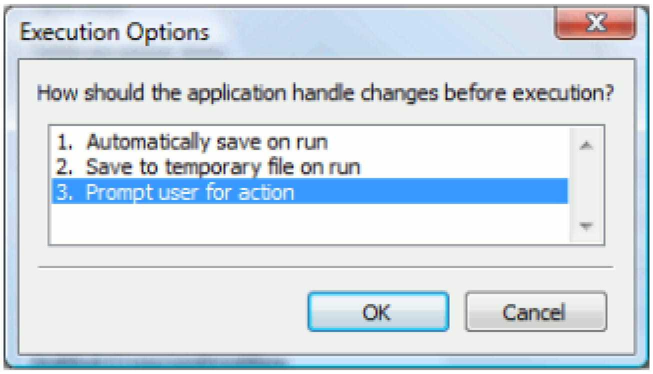
```
running reach: Reach 1
running 2 constituents:
DDT
Chromium
```

Figure C.18: Model progress dialog

The execution options dialog allows the user to specify the action that is to be taken when running the model with data that has been modified. If the current project has been modified and the changes have not been saved, the application can perform one of three tasks:

- **Automatically save on run** - Specifies that the model will automatically save any changes to the original file before running the model.
- **Save to temporary file on run** - Specifies that the model will use a temporary file with all of the current project settings and leave the original file unmodified. This is useful to see what effect a certain change will have on the model results without modifying the original file.
- **Prompt user for action** - Specifies that the model is to prompt the user for an action to take whenever the model is run and there are changes that have not been saved.

The default setting is to use a temporary file if this situation arises, but the user can modify this by using the ”Execution Options” dialog. The execution options dialog and all available options are shown in Figure C.19.


Execution Options

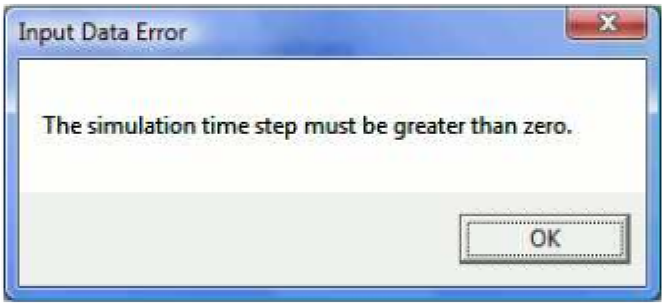
How should the application handle changes before execution?

1. Automatically save on run
2. Save to temporary file on run
3. Prompt user for action

Figure C.19: Execution options dialog

C.3.2 Model Errors

Before the model is run, the program checks to insure that all required data has been entered. This prevents errors from occurring during model execution and informs the user about the data that needs to be entered. When a problem is found in the current data set, a dialog such as the one shown in Figure C.20 will be displayed. The user should then proceed to correct the problem and try running the model again.

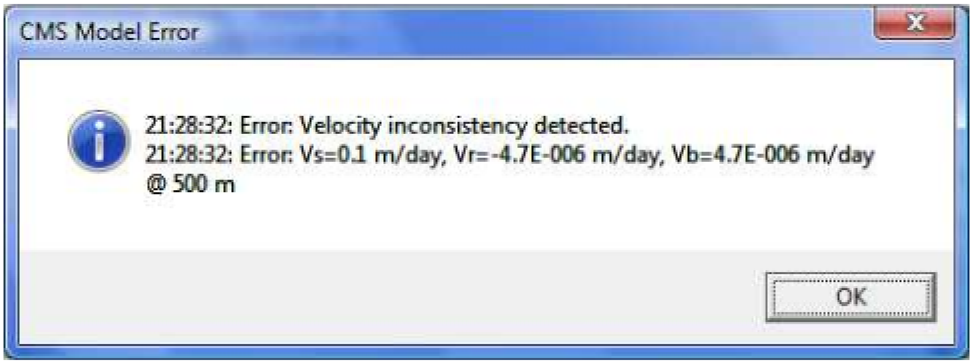

Input Data Error

The simulation time step must be greater than zero.

Figure C.20: CMS input error

In addition to the message given for input data errors, the input fields on each screen change colors to indicate if the data that has been entered is valid for the current parameter. This can be seen in Figure C.12 above where the model time step input field is light red instead of the green color shown for other fields.

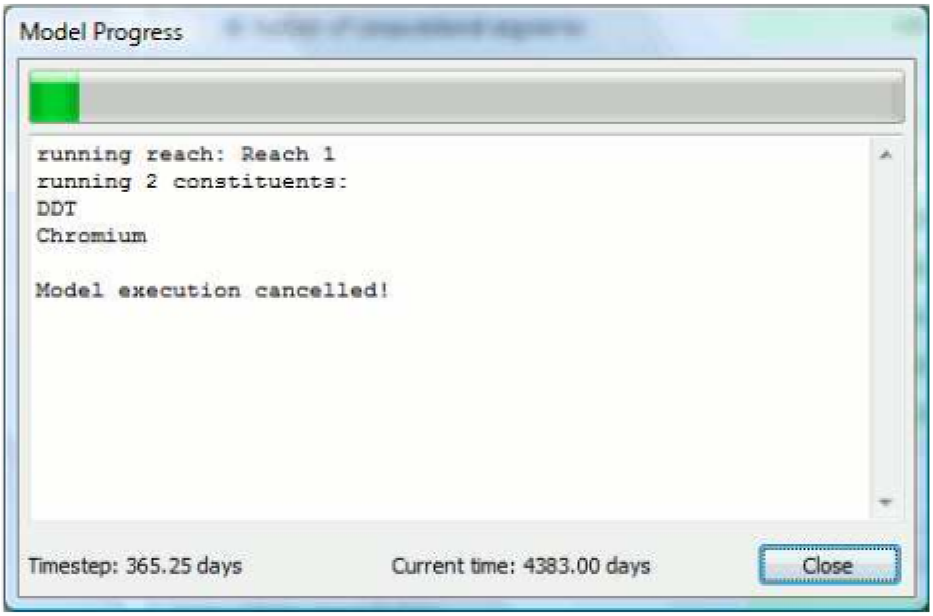
Once model execution has begun, errors may occur due to many factors such as an imbalance in the suspended solids, an error reading or writing to a data file, or even due to the user pressing the ”Cancel” button. When an error occurs during model execution, a message dialog will be displayed that indicates what error occurred (Figure C.21). The user can then take steps to correct the error and re-run the model.



21:28:32: Error: Velocity inconsistency detected.
21:28:32: Error: Vs=0.1 m/day, Vr=-4.7E-006 m/day, Vb=4.7E-006 m/day @ 500 m

Figure C.21: Model execution error

If the error was caused by user intervention, pressing the ”Cancel” button, the error message will appear as shown in Figure C.22. No action is required by the user since the only error that occurred was an interruption in the model execution process.



```
running reach: Reach 1
running 2 constituents:
DDT
Chromium

Model execution cancelled!
```

Timestep: 365.25 days

Current time: 4383.00 days

Figure C.22: User intervention error

C.4 Model Results

After the model has been run successfully, the ”Results” menu item under the ”Model” menu will be enabled (Figure C.23). This menu item is also enabled when loading an input file that has been run successfully and when loading a results data file. If the model was not run successfully, and no results file was created, the menu item will not be enabled.

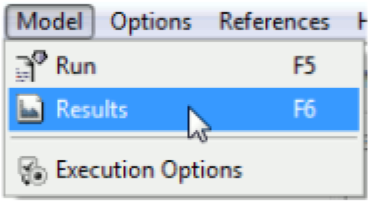
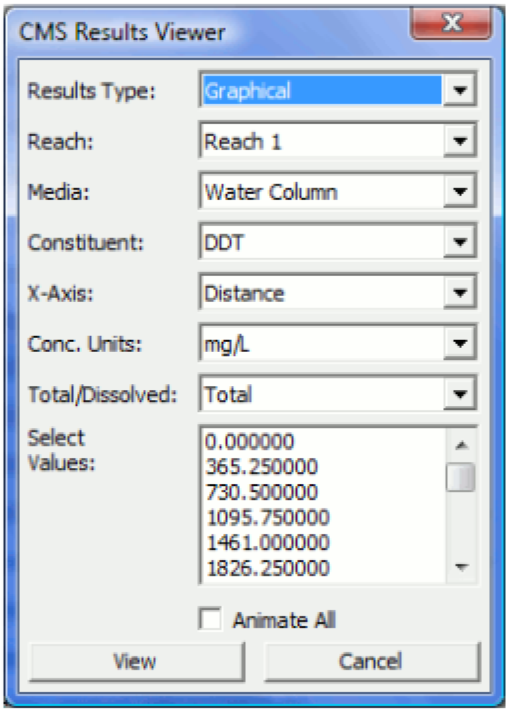


Figure C.23: View results menu item

C.4.1 Results Form

To view the model results, select ”Model → Results” from the main menu. The results form shown in Figure C.24 will then be loaded. This form will allow the user to view the model results in a variety of ways, both text and graphical. Descriptions of the form fields and the functions they perform are listed below. Once all of the required information has been specified, click the ”View” button to load the plot dialog.



Results Type: Graphical

Reach: Reach 1

Media: Water Column

Constituent: DDT

X-Axis: Distance

Conc. Units: mg/L

Total/Dissolved: Total

Select Values:
0.000000
365.250000
730.500000
1095.750000
1461.000000
1826.250000

☐ Animate All

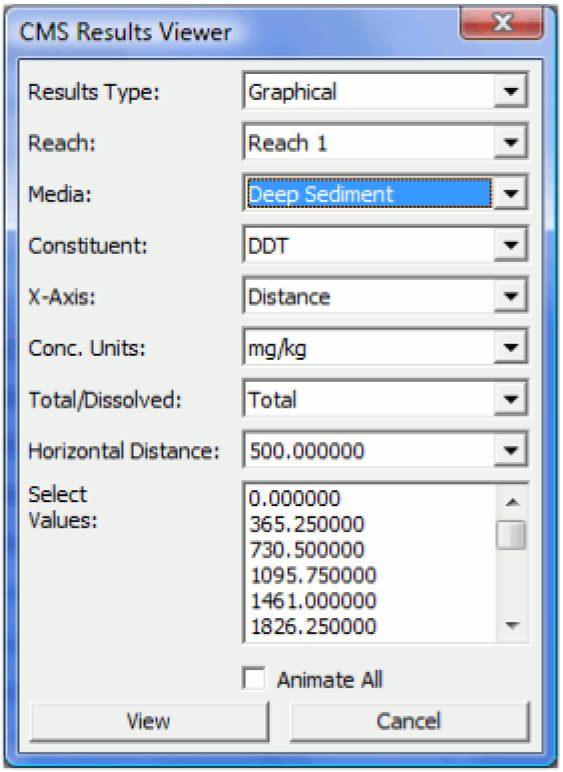
Figure C.24: Results form

Results Form Field Descriptions

- **Results Type** - Specifies how the results will be displayed to the user. The two available options are: Graphical and Text. The graphical option will display a plot with the user-specified information, and the text option will display the same user-specified information in a tabular view.

- **Reach** - Selects the stream reach for viewing results.
- **Media** - Specifies the values that are to be displayed. The two available options are: Water and Sediment. The water option will display the values for the specified constituent in the water column. The sediment option will display the values for the specified constituent in the sediment bed.
- **Constituent** - Specifies the constituent for which the model results will be displayed. This list contains all of the constituents specified in the model input and also contains a ”Suspended Solids” entry when the media type is specified as ”water.” This allows the user to view the suspended solids concentration in the water column.
- **X-Axis** - Specifies the values for the x-axis on the plot. The two available options are: Distance and Time. The distance option will plot concentration values on the y-axis versus downstream distance along the x-axis. The time option will plot concentration values on the y-axis versus time on the x-axis.
- **Conc. Units** - Specifies the unit of measure for the selected constituent.
- **Total/Dissolved** - Specifies if the concentration will be the total concentration for the selected media or only the concentration that is in the dissolved phase. The dissolved phase concentration in the sediment bed refers to the concentration in the pore water. Therefore, the dissolved concentration can only be viewed in units of mg/L and refers to the mass dissolved in the pore water per volume of pore water.
- **Select Values** - The label for this input option will vary depending upon the value that is chosen for the x-axis. If the x-axis option is specified as ”Distance”, this list will allow the selection of times for which the concentration vs. distance plots are to be displayed. If the x-axis option is specified as ”Time”, this list will allow the selection of distances for which the concentration vs. time plots are to be displayed. The user may select a series of values from this list by selecting the first value and holding down the shift key while selecting the last value. Multiple values may also be selected individually by holding down the control key while selecting the values.
- **Animate All** - This option is used to animate the series of plots for concentration vs. time or concentration vs. distance. If this option is selected, the list box containing all of the values will be disabled since all values will be used in the animation.

When the selected media is the deep sediment layer, an extra input option is available as shown in Figure C.25.



Results Type: Graphical
Reach: Reach 1
Media: Deep Sediment
Constituent: DDT
X-Axis: Distance
Conc. Units: mg/kg
Total/Dissolved: Total
Horizontal Distance: 500.000000
Select Values:
0.000000
365.250000
730.500000
1095.750000
1461.000000
1826.250000
☐ Animate All

Figure C.25: Results form for viewing deep sediment concentrations

- **Horizontal Distance** - Specifies the numerical model segment for which the deep sediment results should be displayed.

C.4.2 Plot Dialog

The plot dialog will appear as shown in Figure C.26 for a single time or distance value. A plot for multiple distance values is shown in Figure C.27.

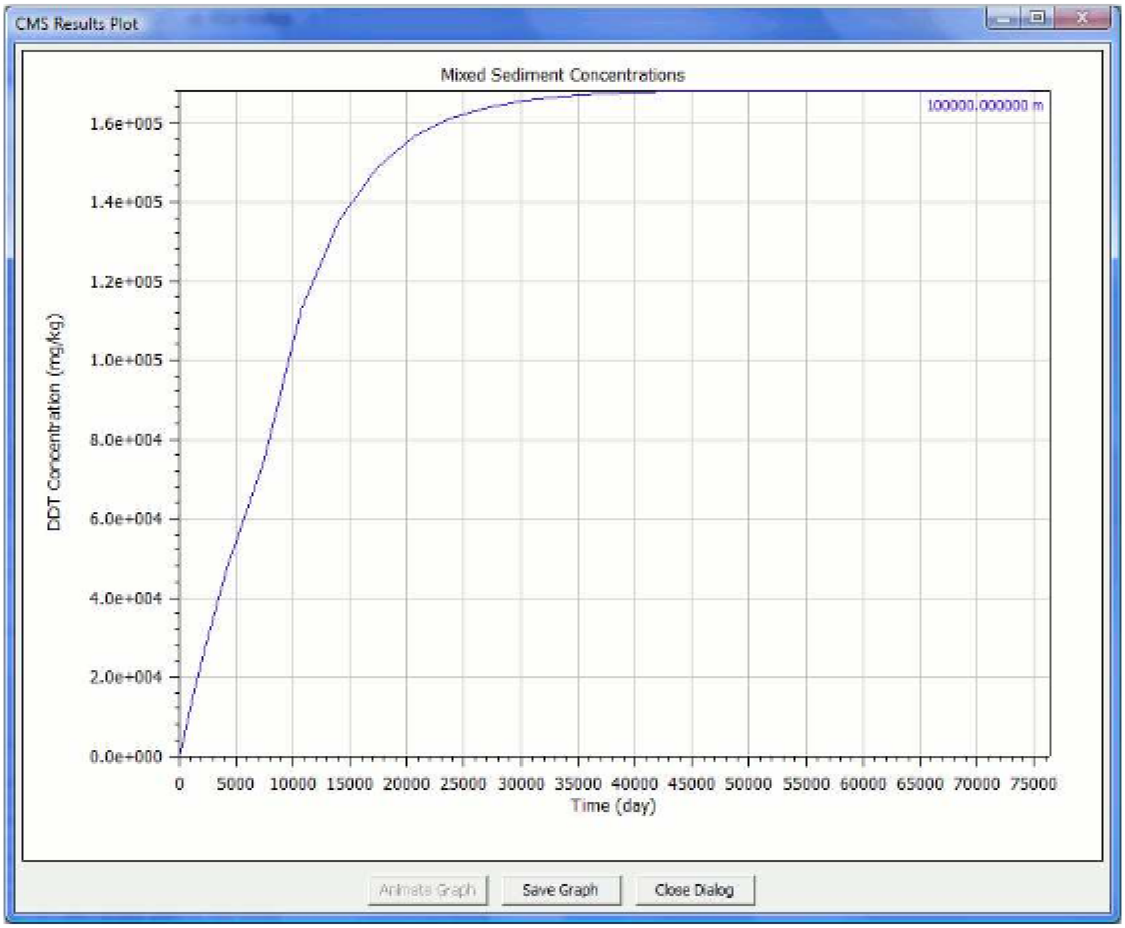


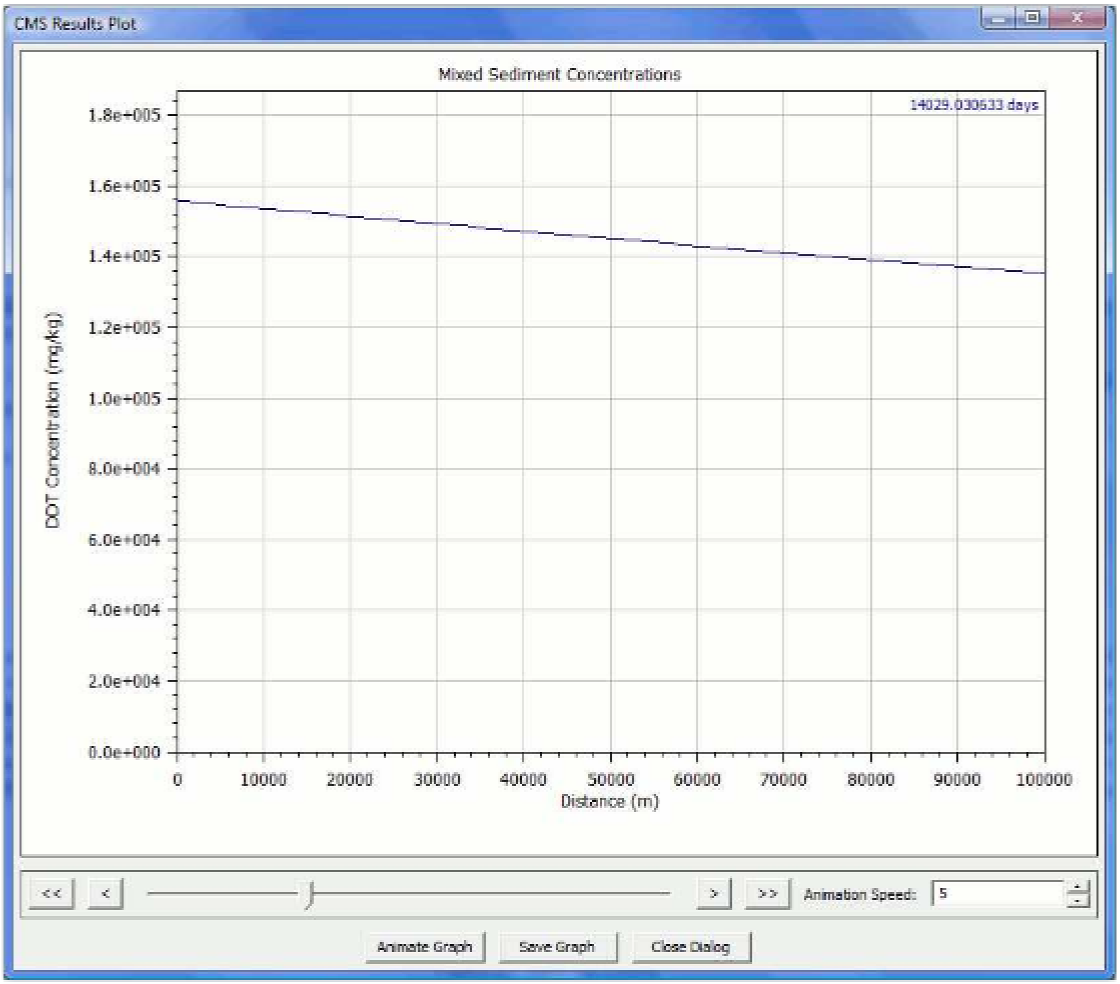
Figure C.26: Plot dialog for a single distance

Figure C.27: Plot dialog for multiple distance values

Time values on the x-axis are always in days and distance values on the x-axis are always in meters. The label for the y-axis indicates the constituent for which the concentration is being plotted as well as the units that were selected. The concentration values always indicate total concentration (dissolved and particulate).

There are buttons at the bottom of the dialog. The ”Animate Graph” button is not enabled unless the ”Animate All” selection was made on the results form. The ”Save Graph” button is used to save the current plot to an image file. The ”Print Graph” button is used to print out a hard copy of the current plot. The ”Close Dialog” button will close the plot dialog and return the user to the results form.

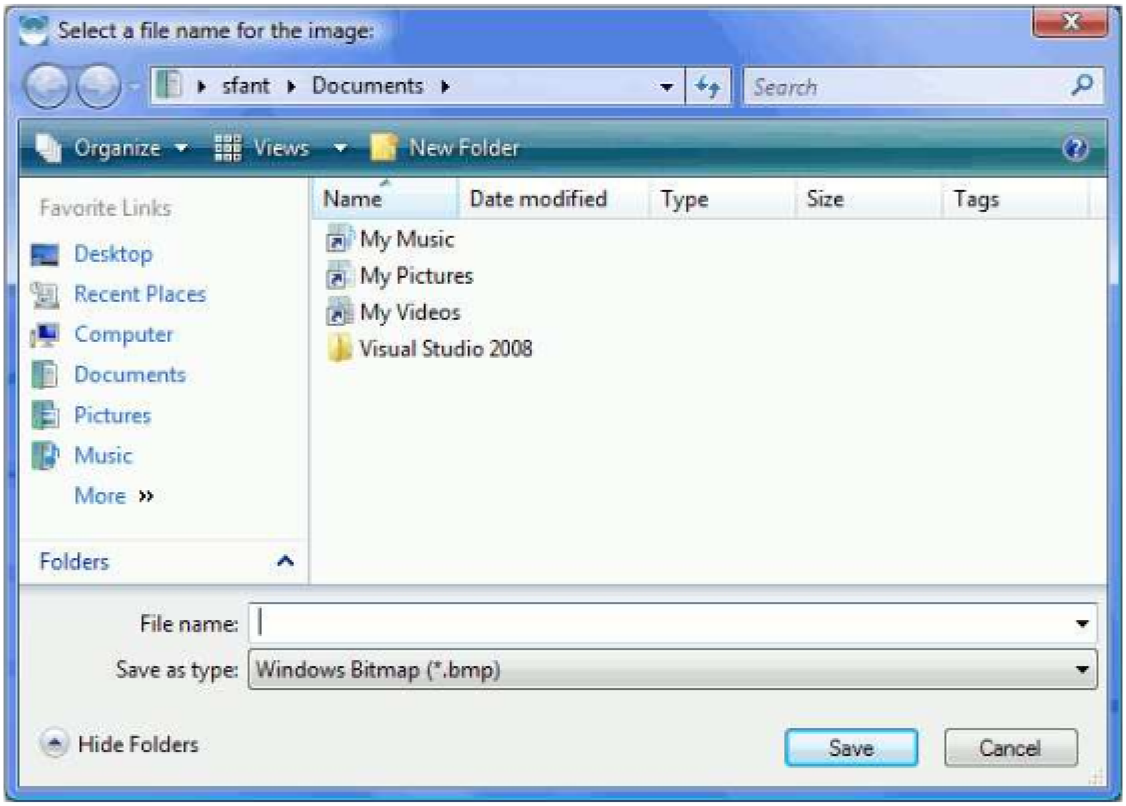
If the ”Animate All” selection is made on the results form, the plot dialog will appear as shown below in Figure C.28.



Animation Speed: 5

Figure C.28: Plot dialog in animation mode

The ”Animate Graph” button is now enabled, and several additional controls appear on the dialog. When the animate button is clicked, the plots will be displayed in order for each time or distance value (depending upon which value was chosen for the x- axis) beginning with the first value. While the animation is playing, the caption of the ”Animate Graph” button will change to display ”Cancel.” This button can be clicked during the animation to cancel playback. The box labeled ”Animation Speed” is used to control the speed of the animation. The default value is ”5” and ranges from a low value (slowest) of 1 to a high value (fastest) of 10. The slider control is used to move through the plots without actually playing the animation. The two buttons on the left side of the slider control, from left to right, are used to move to the first image in the animation or to the previous image in the animation. The two buttons on the right side of the slider control, from left to right, are used to move to the next image in the animation or to the last image in the animation. If the ”Save Graph” button is clicked for an animation, the user has the option to save the current from of the animation or to save the entire animation as an MPEG file. The action that is taken is determined by the type of file chosen in the save file dialog (Figure C.29). If the *.mpg extension is chosen, the entire animation is saved. Otherwise, the current plot is saved.

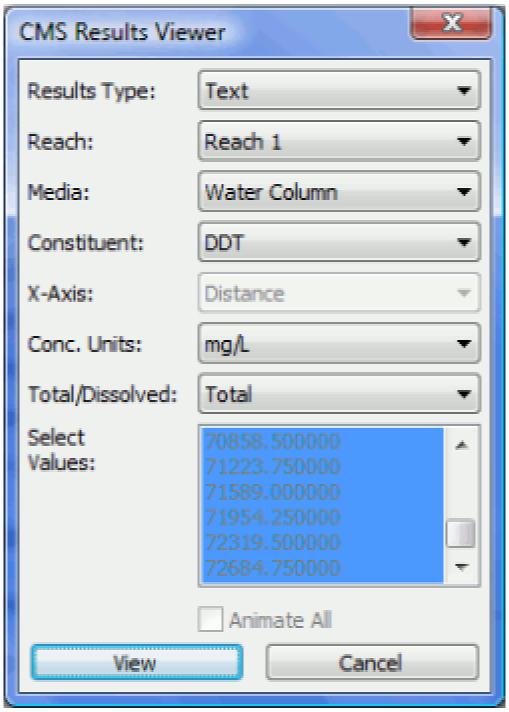


Save as type: Windows Bitmap (*.bmp)

Figure C.29: Save file dialog

C.4.3 Text Viewer

The text viewer displays the concentration data in a tabular format allowing the user to view any point in the data series. When the ”Text” option is chosen for the results type on the results form, some of the options available for graphical results are no longer available. The results form will appear as shown in Figure C.30.


CMS Results Viewer

Results Type: Text

Reach: Reach 1

Media: Water Column

Constituent: DDT

X-Axis: Distance

Conc. Units: mg/L

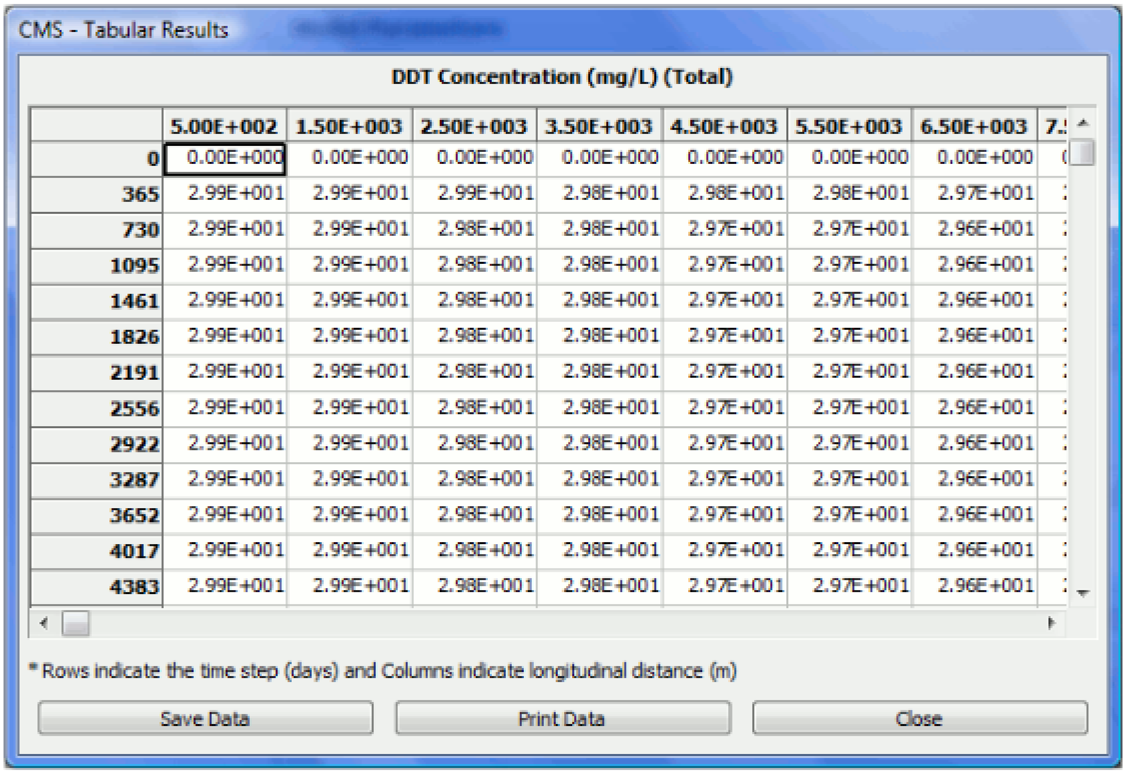
Total/Dissolved: Total

Select Values:
70858.500000
71223.750000
71589.000000
71954.250000
72319.500000
72684.750000

☐ Animate All

Figure C.30: Results form for text results

The user may select the media type, constituent and concentration type and units as was done for the graphical results. The ”View” button is then used to open the text viewer form (Figure C.31). This form displays the downstream distance (or vertical distance for the deep sediment layer) in meters in the column header (top row) and the time in days in the first column. The user can scroll to any point to view data values. The data can be printed using the ”Print Data” button or exported to a comma separated file using the ”Save Data” button.



DDT Concentration (mg/L) (Total)

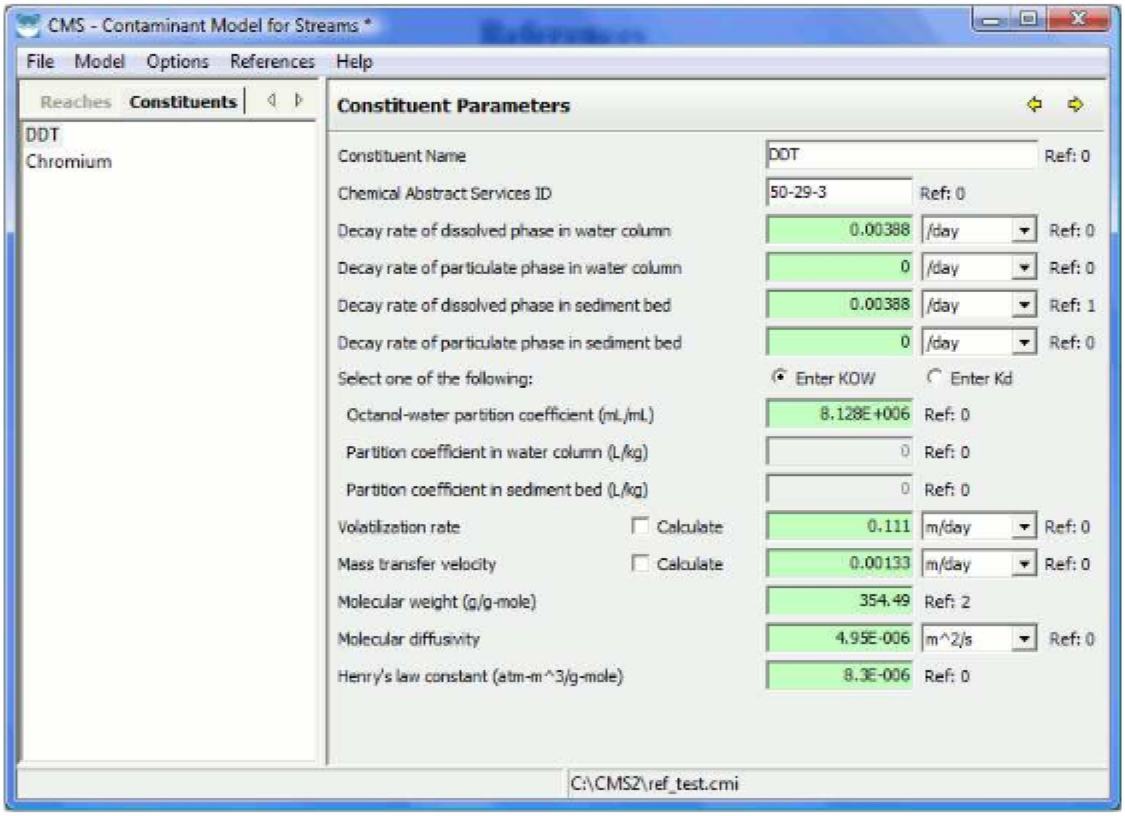
	5.00E+002	1.50E+003	2.50E+003	3.50E+003	4.50E+003	5.50E+003	6.50E+003
0	0.00E+000	0.00E+000	0.00E+000	0.00E+000	0.00E+000	0.00E+000	0.00E+000
365	2.99E+001	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.98E+001	2.97E+001
730	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
1095	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
1461	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
1826	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
2191	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
2556	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
2922	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
3287	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
3652	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
4017	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001
4383	2.99E+001	2.99E+001	2.98E+001	2.98E+001	2.97E+001	2.97E+001	2.96E+001

* Rows indicate the time step (days) and Columns indicate longitudinal distance (m)

Figure C.31: Text viewer

C.5 References

References can be useful to indicate where or how a certain value in the model input was obtained. References can be added for most fields in the model, and the reference number will be shown to the right of the field as in Figure C.32 below for the molecular weight.



Constituent Name	DDT		Ref: 0
Chemical Abstract Services ID	50-29-3		Ref: 0
Decay rate of dissolved phase in water column	0.00388	/day	Ref: 0
Decay rate of particulate phase in water column	0	/day	Ref: 0
Decay rate of dissolved phase in sediment bed	0.00388	/day	Ref: 1
Decay rate of particulate phase in sediment bed	0	/day	Ref: 0
Select one of the following:	● Enter KOW	○ Enter Kd	
Octanol-water partition coefficient (mL/mL)	8.128E+006		Ref: 0
Partition coefficient in water column (L/kg)	0		Ref: 0
Partition coefficient in sediment bed (L/kg)	0		Ref: 0
Volatilization rate ☐ Calculate	0.111	m/day	Ref: 0
Mass transfer velocity ☐ Calculate	0.00133	m/day	Ref: 0
Molecular weight (g/g-mole)	354.49		Ref: 2
Molecular diffusivity	4.95E-006	m^2/s	Ref: 0
Henry's law constant (atm-m^3/g-mole)	8.3E-006		Ref: 0

Figure C.32: Reference number indicator

C.5.1 Viewing References

To view all references used in the current project, select ”References → View” from the main menu (Figure C.33).

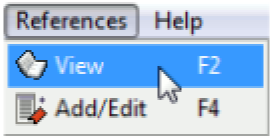
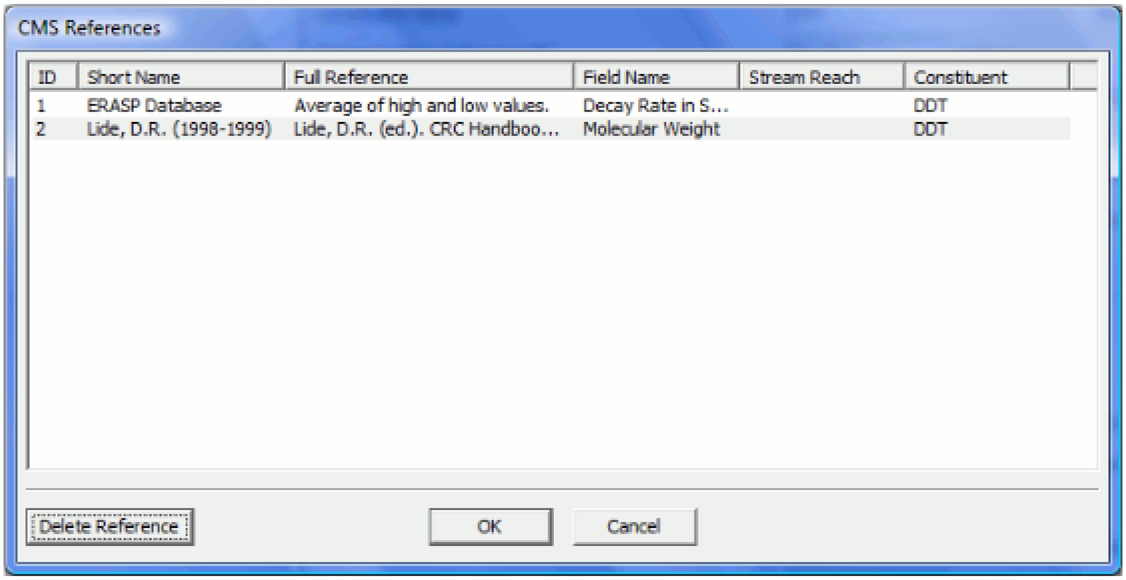


Figure C.33: References menu

The references dialog will then be displayed as shown in Figure C.34. The user can click on the column labels to sort the references in either ascending or descending order according to any of the columns. This dialog is also used to delete references. To delete a reference, select the appropriate reference in the list and click the ”Delete Reference” button at the bottom left corner of the dialog. If a reference is being used by multiple fields, it will be displayed once for each field with the field name and constituent name (where applicable) listed in the appropriate columns. A reference cannot be deleted if it is currently being used by one or more fields. Therefore, a reference can only be deleted if the ”Field Name” column is empty.

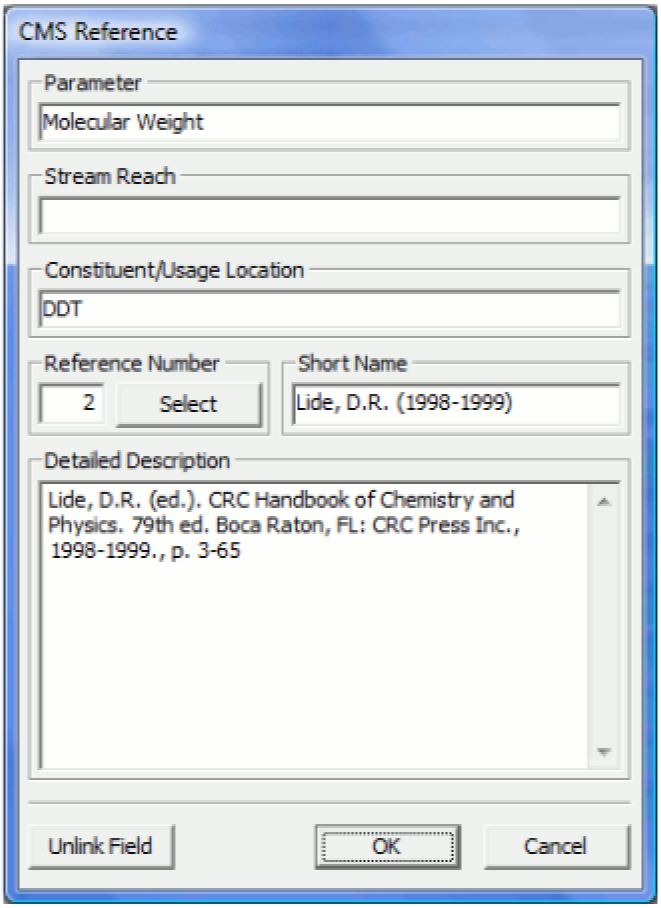


ID	Short Name	Full Reference	Field Name	Stream Reach	Constituent
1	ERASP Database	Average of high and low values.	Decay Rate in S...		DDT
2	Lide, D.R. (1998-1999)	Lide, D.R. (ed.). CRC Handboo...	Molecular Weight		DDT

Figure C.34: CMS References

C.5.2 Entering and Editing References

To enter a new reference or edit an existing reference for a field in the current project, make sure that the desired field is selected and choose ”References → Add/Edit” from the main menu. The reference dialog (Figure C.35) will then appear as shown below.



Parameter: Molecular Weight

Stream Reach:

Constituent/Usage Location: DDT

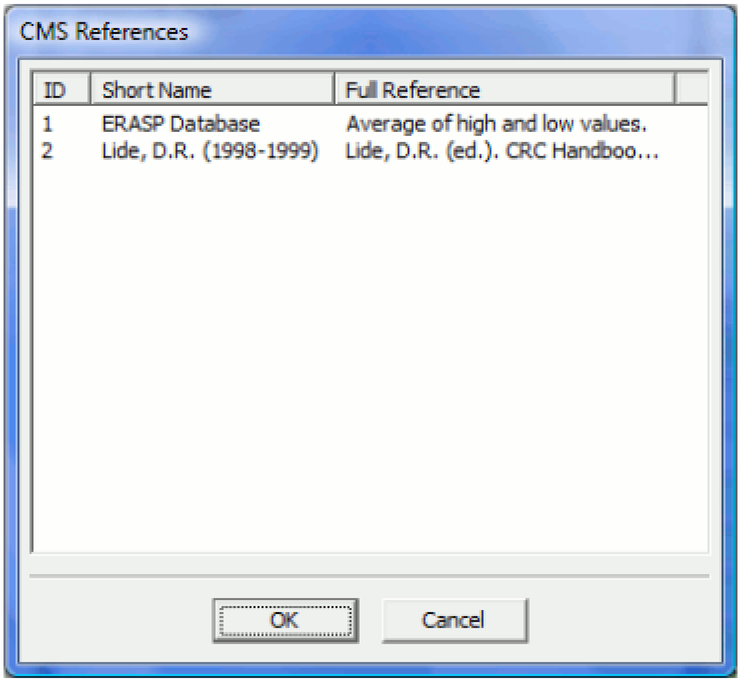
Reference Number: 2

Short Name: Lide, D.R. (1998-1999)

Detailed Description: Lide, D.R. (ed.). CRC Handbook of Chemistry and Physics. 79th ed. Boca Raton, FL: CRC Press Inc., 1998-1999., p. 3-65

Figure C.35: Reference dialog

The reference number is automatically generated and cannot be modified. An existing reference can be used for the current field by clicking the ”Select” button. The dialog shown in Figure C.36 will be displayed allowing the user to select from the list of existing references.



ID	Short Name	Full Reference
1	ERASP Database	Average of high and low values.
2	Lide, D.R. (1998-1999)	Lide, D.R. (ed.). CRC Handboo...

Figure C.36: References selection dialog

To remove the reference from the current field, click the ”Unlink Field” button at the bottom left corner of the reference dialog shown in Figure C.35. This will remove the reference number from the field but will not delete the reference information so that it may be used with other fields.

C.6 Configuration

CMS numerical solution options and settings can be modified through the ”Options” menu (Figure C.37). Through these menu options, users can modify numerical solution scheme settings, solids balance type, and print interval/frequency settings.

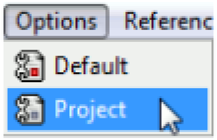
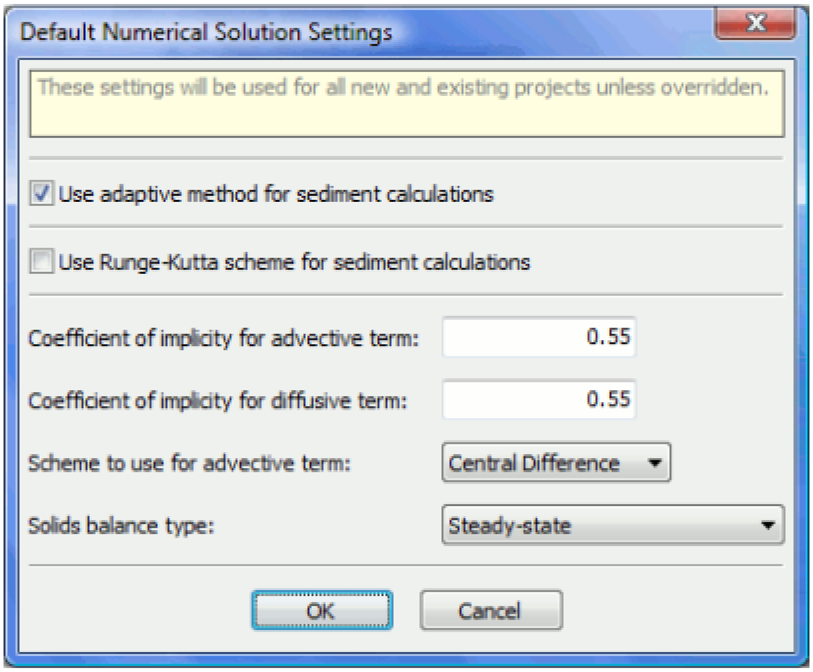


Figure C.37: Tools menu

C.6.1 Default Numerical Solution Settings

The default numerical solution settings dialog allows the user to modify the numerical solution scheme and solids balance settings. These settings will be used for all new projects and all existing projects that have not overridden the default settings. The default numerical solution settings dialog is shown in Figure C.38, and the field descriptions are given below.



Default Numerical Solution Settings

These settings will be used for all new and existing projects unless overridden.

☑ Use adaptive method for sediment calculations

☐ Use Runge-Kutta scheme for sediment calculations

Coefficient of implicity for advective term: 0.55

Coefficient of implicity for diffusive term: 0.55

Scheme to use for advective term: Central Difference

Solids balance type: Steady-state

Figure C.38: Default numerical solution settings dialog

Default Numerical Solution Settings Field Descriptions

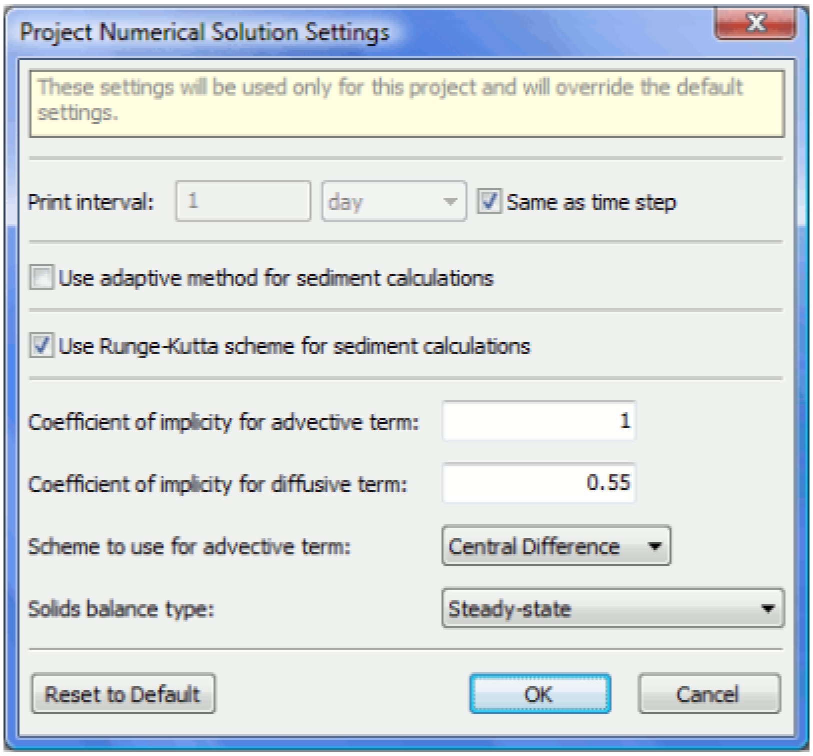
- **Use adaptive method for sediment calculations** - Specifies that the model should use an adaptive method for performing the sediment bed calculations. This will allow the model to modify the time step in order to maintain the stability of the calculations. This will apply to both the first order Euler and fourth order Runge-Cutta schemes.
- **Use Runge-Cutta scheme sediment calculations** - Specifies that the model should use the fourth order Runge-Cutta scheme for the sediment calculations instead of the default first order Euler scheme.
- **Coefficient of implicity for advective term** - Specifies the division of the advection numerical solution scheme into explicit and implicit parameters. A value of "0" specifies a fully explicit scheme and uses only values from the current time step. A value of "1" specifies a fully implicit scheme and uses only values from the future time step.
- **Coefficient of implicity for diffusive term** - Specifies the division of the diffusion numerical solution scheme into explicit and implicit parameters. A value of "0" specifies a fully explicit scheme and uses only values from the current time step. A

value of ”1” specifies a fully implicit scheme and uses only values from the future time step.

- **Scheme to use for advective term** - Specifies the numerical solution scheme to use for the solution of the advective terms. The diffusive terms are always solved using the second-order accurate Crank-Nicolson centered-time, centered-space method. The advective terms can be solved using either the Crank-Nicolson method or the first-order accurate upwind method. The upwind method is not as sensitive to large changes in the concentration gradient, but it induces numerical diffusion.
- **Solids balance type** - Specifies if the suspended solids in the water column are assumed to be at steady-state or if the solids should be modeled in the same manner as the constituents. The steady-state option will use the value entered for the total solids concentration at the point of entry as the steady-state concentration. The unsteady-state option combines this value with the values entered on the loading data screen to model the solids concentration along the stream reach. *Note - The only option currently available while the model is running under ARAMS/FRAMES is the steady-state solids balance. The solid transport code is under development and will be available in a later release.

C.6.2 Project Numerical Solution Settings

The project numerical solution settings dialog allows the user to modify the numerical solution scheme settings, the solids balance type, and the print interval for the current project. These settings will only be used for the current project and can be reset to use the default system settings at any point by clicking the button labeled ”Reset to Default.” The project numerical solution settings dialog is shown in Figure C.39, and the field descriptions are listed below.



These settings will be used only for this project and will override the default settings.

Print interval: 1 day ☑ Same as time step

☐ Use adaptive method for sediment calculations

☑ Use Runge-Kutta scheme for sediment calculations

Coefficient of implicity for advective term: 1

Coefficient of implicity for diffusive term: 0.55

Scheme to use for advective term: Central Difference

Solids balance type: Steady-state

Figure C.39: Project numerical solution settings dialog

Project Numerical Solution Settings Field Descriptions

- **Print interval** - Specifies how frequently data will be written to the output file when running the model. This value is specified in a similar fashion as the time step. By default, the ”Same as time step” option is selected. This will print a data point for every time step. If this option is not selected, the data will only be output on the print interval specified here. *Note - this does not apply when the adaptive method is selected. The adaptive method will modify the time step as necessary and may not be able to output data at the exact times specified. In this case, the model will attempt to output data at the time step interval originally specified by the user on the Model Parameters screen.
- **Use adaptive method for sediment calculations** - Specifies that the model should use an adaptive method for performing the sediment bed calculations. This will allow the model to modify the time step in order to maintain the stability of the calculations. This will apply to both the first order Euler and fourth order Runge-Cutta schemes.

- **Use Runge-Cutta scheme sediment calculations** - Specifies that the model should use the fourth order Runge-Cutta scheme for the sediment calculations instead of the default first order Euler scheme.

- **Coefficient of implicity for advective term** - Specifies the division of the advection numerical solution scheme into explicit and implicit parameters. A value of ”0” specifies a fully explicit scheme and uses only values from the current time step. A value of ”1” specifies a fully implicit scheme and uses only values from the future time step.

- **Coefficient of implicity for diffusive term** - Specifies the division of the diffusion numerical solution scheme into explicit and implicit parameters. A value of ”0” specifies a fully explicit scheme and uses only values from the current time step. A value of ”1” specifies a fully implicit scheme and uses only values from the future time step.

- **Scheme to use for advective term** - Specifies the numerical solution scheme to use for the solution of the advective terms. The diffusive terms are always solved using the second-order accurate Crank-Nicolson centered-time, centered-space method. The advective terms can be solved using either the Crank-Nicolson method or the first-order accurate upwind method. The upwind method is not as sensitive to large changes in the concentration gradient, but it induces numerical diffusion.

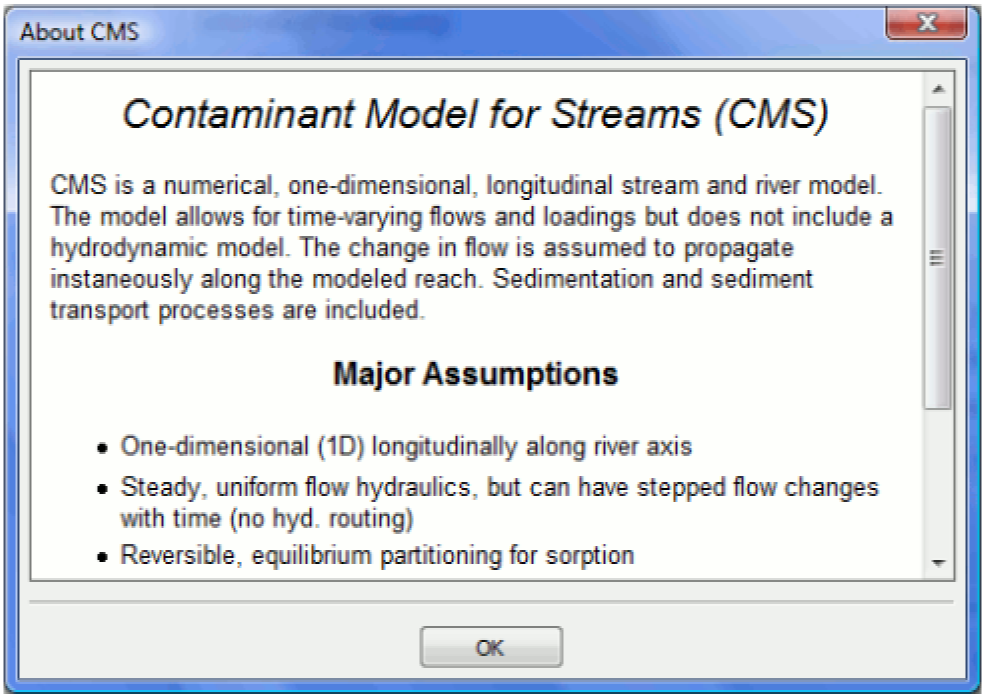
- **Solids balance type** - Specifies if the suspended solids in the water column are assumed to be at steady-state or if the solids should be modeled in the same manner as the constituents. The steady-state option will use the value entered for the total solids concentration at the point of entry as the steady-state concentration. The unsteady-state option combines this value with the values entered on the loading data screen to model the solids concentration along the stream reach. *Note - The only option currently available while the model is running under ARAMS/FRAMES is the steady-state solids balance. The solids transport code is under development and will be available in a later release.

C.7 Help

The Help menu provides access to information concerning the CMS model. Selecting ”Contents” from the help menu or pressing the ”F1” key will display the CMS help file. The initial location displayed in the help file will depend upon the current data screen and field that are selected. This allows for help to be displayed for a specific data field simply by clicking into the field and pressing the ”F1” key. The Help menu is shown in Figure C.40.

Figure C.40: Help menu

The ”About” item in the help menu will display an informational dialog containing a brief description of the model, the current version number, and a link to a web site with more information pertaining to the model. The About dialog is shown in Figure C.41.



Contaminant Model for Streams (CMS)

CMS is a numerical, one-dimensional, longitudinal stream and river model. The model allows for time-varying flows and loadings but does not include a hydrodynamic model. The change in flow is assumed to propagate instaneously along the modeled reach. Sedimentation and sediment transport processes are included.

Major Assumptions

- One-dimensional (1D) longitudinally along river axis
- Steady, uniform flow hydraulics, but can have stepped flow changes with time (no hyd. routing)
- Reversible, equilibrium partitioning for sorption

Figure C.41: About Dialog

APPENDIX D

FINITE DIFFERENCE APPROXIMATIONS

The derivatives in the water column governing equations and the deep sediment layer governing equations are approximated for each computation cell using finite difference techniques. This appendix will cover the development of the approximations for both advection and diffusion for internal cells, the upstream boundary cell, and the downstream boundary cell. Due to the fact that the equations for the water column and the deep sediment layer are solved in essentially the same manner, the development of the approximations will only be shown for the water column. The approximations are developed using the interfacial concentrations at the cell boundaries. However, the upstream and downstream boundary cells are unique since they are not bounded on both sides by other computational cells. Therefore, the boundary conditions given in section 2.2.3 are applied at the boundaries to complete the approximations.

D.1 Cell Definition for Internal Segments

The following figure for internal segment i shows its bounding cells, the interfacial concentrations, and the segment lengths.

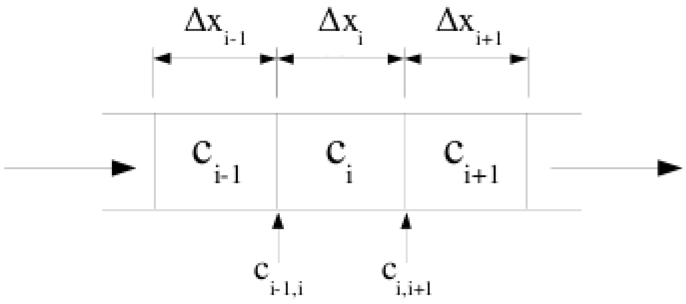


Figure D.1: Representation of internal segment i

A central difference for cell i is given by

$$\left.\frac{\partial c}{\partial x}\right|_i \cong \frac{c_{i,i+1} - c_{i-1,i}}{\Delta x} \tag{D.1}$$

where $c_{i+1,i}$ and $c_{i,i-1}$ are the interfacial concentrations at the downstream and upstream boundaries of cell i, respectively. These values are defined in terms of the cell concentrations as given below in Equations D.2 and D.3.

$$c_{i,i+1} = \frac{\Delta x_i}{\Delta x_i + \Delta x_{i+1}} c_i + \frac{\Delta x_{i+1}}{\Delta x_i + \Delta x_{i+1}} c_{i+1} = \frac{1}{2} c_i + \frac{1}{2} c_{i+1} \tag{D.2}$$

$$c_{i-1,i} = \frac{\Delta x_{i-1}}{\Delta x_{i-1} + \Delta x_i} c_{i-1} + \frac{\Delta x_i}{\Delta x_{i-1} + \Delta x_i} c_i = \frac{1}{2} c_{i-1} + \frac{1}{2} c_i \tag{D.3}$$

The final step in Equations D.2 and D.3 is a simplification due to the constant spatial step size (Δx) used in the model.

D.2 Advection (Central Difference)

The central difference approximation of the advection term for segment i is given as

$$\frac{\partial c}{\partial t} = \left(-\frac{Q}{A}\frac{\partial c}{\partial x}\right)_i \cong -\frac{Q}{A}\left(\frac{c_{i,i+1} - c_{i-1,i}}{\Delta x}\right) \tag{D.4}$$

Substituting the definitions for the interfacial concentrations given above in Equations D.2 and D.3 yields

$$\begin{aligned} \frac{\partial c}{\partial t} &\cong -\frac{Q}{A}\left(\frac{c_{i,i+1} - c_{i-1,i}}{\Delta x}\right) = -\frac{Q}{A\Delta x}\left(\frac{c_{i+1} + c_i}{2} - \frac{c_i + c_{i-1}}{2}\right) \\ &= -\frac{Q}{A2\Delta x}\left(c_{i+1} - c_{i-1}\right) = -\frac{U}{2\Delta x}\left(c_{i+1} - c_{i-1}\right) \end{aligned} \tag{D.5}$$

Since the model uses no hydraulic or hydrologic routing, the interfacial areas (A) of all cells are assumed to be the same and constant with a given flow rate (Q). Therefore, the velocity (U) can be used for all approximations in place of the flow rate and interfacial area term. Implementing time weighting using the coefficient of implicity (θ) gives the final approximation in Equation D.6.

$$\frac{c_i^{n+1} - c_i^n}{\Delta t} = -\frac{U}{2\Delta x}\left[(1-\theta)\left(c_{i+1}^n - c_{i-1}^n\right) + \theta\left(c_{i+1}^{n+1} - c_{i-1}^{n+1}\right)\right] \tag{D.6}$$

Grouping terms and rearranging again to get the unknown, or future, values on the left hand side and the known, or current, values on the right side gives the version of the equation used in the matrix solution.

$$-\gamma\theta c_{i-1}^{n+1} + 1 + \gamma\theta c_{i+1}^{n+1} = \gamma(1-\theta)c_{i-1}^n + 1 - \gamma(1-\theta)c_{i+1}^n \tag{D.7}$$

where,

$$\gamma = \frac{U\Delta t}{2\Delta x} \tag{D.8}$$

D.3 Advection (Upwind)

The upwind method uses only the values at the current cell (i) and the previous cell ($i-1$), so the interfacial concentrations are not required. Using upwind differencing, the advection term can be approximated as follows:

$$\frac{\partial c}{\partial t} = \left(-\frac{Q}{A}\frac{\partial c}{\partial x}\right)_i \cong -\frac{Q}{A}\left(\frac{c_i - c_{i-1}}{\Delta x}\right) \tag{D.9}$$

Rearranging the equation and implementing time weighting using the coefficient of implicity (θ) gives

$$\frac{c_i^{n+1} - c_i^n}{\Delta t} = -\frac{U}{\Delta x}\left[(1-\theta)\left(c_i^n - c_{i-1}^n\right) + \theta\left(c_i^{n+1} - c_{i-1}^{n+1}\right)\right] \tag{D.10}$$

Grouping terms and rearranging again to get the future values on the left hand side and the current values on the right hand side yields

$$-\gamma_u \theta c_{i-1}^{n+1} + \left(1 + \gamma_u \theta\right) c_i^{n+1} = \gamma_u \left(1 - \theta\right) c_{i-1}^{n} + \left(1 - \gamma_u \left(1 - \theta\right)\right) c_i^{n} \tag{D.11}$$

where,

$$\gamma_u = \frac{U \Delta t}{\Delta x} = \text{Courant number} \tag{D.12}$$

D.4 Diffusion (Central Difference)

Using Equation D.1, the spatial derivative for the diffusion term is given as

$$\frac{\partial c}{\partial t} = \left[\frac{\partial}{A \partial x}\left(AD\frac{\partial c}{\partial c}\right)\right]_i \cong \frac{1}{A}\left[\frac{\left(AD\frac{\partial c}{\partial x}\right)_{i,i+1} - \left(AD\frac{\partial c}{\partial x}\right)_{i-1,i}}{\Delta x}\right] \tag{D.13}$$

Since the cross-sectional area and diffusion coefficient are assumed to be constant along the length of the stream reach, these variables can be taken outside of the differentials giving the following:

$$\frac{\partial c}{\partial t} \cong \frac{1}{\Delta x}\left[D\frac{c_{i+1} - c_i}{\Delta x} - D\frac{c_i - c_{i-1}}{\Delta x}\right] = D\left[\frac{c_{i+1} - 2c_i - c_{i-1}}{\left(\Delta x\right)^2}\right] \tag{D.14}$$

Implementing time weighting using the coefficient of implicity (θ) gives

$$\frac{c_i^{n+1} - c_i^{n}}{\Delta t} = \frac{D_x}{\left(\Delta x\right)^2}\left[\left(1 - \theta\right)\left(c_{i+1}^{n} - 2c_i^{n} + c_{i-1}^{n}\right) + \theta\left(c_{i+1}^{n+1} - 2c_i^{n+1} + c_{i-1}^{n+1}\right)\right] \tag{D.15}$$

Grouping terms and rearranging again to get the future values on the left hand side and the current values on the right hand side yields

$$\begin{aligned} -\lambda\theta c_{i-1}^{n+1} + \left(1 + 2\lambda\theta\right) c_i^{n+1} - \lambda\theta c_{i+1}^{n+1} \\ = \lambda\left(1 - \theta\right) c_{i-1}^{n} + \left(1 - 2\lambda\left(1 - \theta\right)\right) c_i^{n} + \lambda\left(1 - \theta\right) c_{i+1}^{n} \end{aligned} \tag{D.16}$$

where,

$$\lambda = \frac{D_x \Delta t}{(\Delta x)^2} \tag{D.17}$$

D.5 Combined Central Advection and Central Diffusion

Combining Equations D.6 and D.15 gives the following for a combined central advection and central diffusion finite difference approximation:

$$\begin{aligned} \frac{c_i^{n+1} - c_i^n}{\Delta t} &= -\frac{U}{2\Delta x}\left[(1-\theta)\left(c_{i+1}^n - c_{i-1}^n\right) + \theta\left(c_{i+1}^{n+1} - c_{i-1}^{n+1}\right)\right] \\ &\quad + \frac{D_x}{(\Delta x)^2}\left[(1-\theta)\left(c_{i+1}^n - 2c_i^n + c_{i-1}^n\right) + \theta\left(c_{i+1}^{n+1} - 2c_i^{n+1} + c_{i-1}^{n+1}\right)\right] \end{aligned} \tag{D.18}$$

Rearranging yields the following equation, which is a combination of Equations D.7 and D.16.

$$\begin{aligned} &-(\gamma+\lambda)\,\theta c_{i-1}^{n+1} + (1+2\lambda\theta)\,c_i^{n+1} - (\lambda-\gamma)\,\theta c_{i+1}^{n+1} \\ &= (\lambda+\gamma)(1-\theta)\,c_{i-1}^n + (1-2\lambda(1-\theta))\,c_i^n + (\lambda-\gamma)(1-\theta)\,c_{i+1}^n \end{aligned} \tag{D.19}$$

D.6 Combined Upwind Advection and Central Diffusion

Combining equations D.10 and D.15 gives the following for a combined upwind advection and central diffusion finite difference approximation:

$$\begin{aligned} \frac{c_i^{n+1} - c_i^n}{\Delta t} &= -\frac{U}{\Delta x}\left[(1-\theta)\left(c_i^n - c_{i-1}^n\right) + \theta\left(c_i^{n+1} - c_{i-1}^{n+1}\right)\right] \\ &\quad + \frac{D_x}{(\Delta x)^2}\left[(1-\theta)\left(c_{i+1}^n - 2c_i^n + c_{i-1}^n\right) + \theta\left(c_{i+1}^{n+1} - 2c_i^{n+1} + c_{i-1}^{n+1}\right)\right] \end{aligned} \tag{D.20}$$

Rearranging yields the following equation, which is a combination of equations D.11 and D.16.

$$
\begin{aligned}
-\left(\lambda+\gamma_u\right)\theta c_{i-1}^{n+1}+\left(1+2\lambda\theta+\gamma_u\theta\right)c_i^{n+1}-\lambda\theta c_{i+1}^{n+1}\\
=\left(\lambda+\gamma_u\right)\left(1-\theta\right)c_{i-1}^{n}+\left(1-2\lambda\left(1-\theta\right)-\gamma_u\left(1-\theta\right)\right)c_i^{n}+\lambda\left(1-\theta\right)c_{i+1}^{n}
\end{aligned}
\tag{D.21}
$$

D.7 Cell Definition for Upstream Boundary Segment

Figure D.2 gives a graphical representation of the upstream boundary cell including cell widths and boundary and interfacial concentrations.

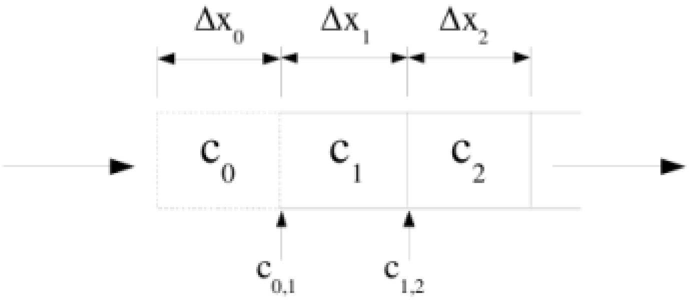


Figure D.2: Representation of upstream boundary cell

The central difference for the upstream boundary cell is defined in a similar manner to the interior cells given in Equation D.1. The central difference for cell 1 at the upstream boundary is given by

$$
\left.\frac{\partial c}{\partial x}\right|_i \cong \frac{c_{1,2}-c_{0,1}}{\Delta x} \tag{D.22}
$$

where $c_{1,2}$ and $c_{0,1}$ are the interfacial concentrations at the downstream and upstream boundaries of cell 1, respectively. The value of $c_{0,1}$ is determined in the same manner as the upstream cell boundary concentration for internal cells given in equation D.1. However, the value of c_0 will be specified by the user as the upstream boundary concentration, c_b, or calculated using a mass balance if an upstream loading is specified as explained in Section 2.2.3. Cell 0 is not an actual model cell. However, when a loading is specified at the upstream boundary rather than a concentration, the associated concentration is determined using a mass balance for the theoretical cell, Cell 0. This is consistent with the fact that numerical solutions generally define concentrations at the center of the model cells while analytical models define them at the cell boundaries.

D.8 Advection at Upstream Boundary (Central Difference)

The central difference for the advection term at the upstream boundary can then be approximated by the following:

$$\frac{\partial c}{\partial t} = \left(-\frac{Q}{A}\frac{\partial c}{\partial x}\right)_1 \cong -\frac{Q}{A}\left(\frac{c_{1,2}-c_{0,1}}{\Delta x}\right) \tag{D.23}$$

Substituting the definitions for the boundary and interfacial concentrations as given above yields

$$\frac{\partial c}{\partial t} \cong -\frac{Q}{A}\left(\frac{c_{1,2}-c_{0,1}}{\Delta x}\right) = -\frac{Q}{A}\left(\frac{c_2+c_1}{2\Delta x}-\frac{c_1+c_b}{2\Delta x}\right) = -\frac{U}{2\Delta x}\left(c_2-c_b\right) \tag{D.24}$$

Rearranging the equation and implementing time weighting using the coefficient of implicity (θ) gives

$$\frac{c_1^{n+1}-c_1^{n}}{\Delta t} = -\frac{U}{2\Delta x}\left[(1-\theta)\left(c_2^n+c_b^n\right)+\theta\left(c_2^{n+1}+c_b^{n+1}\right)\right] \tag{D.25}$$

Although the boundary concentration at time $n+1$ is a future value, it is also a known value. Therefore it is placed with the other known, or current, values. Grouping terms and rearranging again to get the unknown values on the left hand side and the known values on the right hand side yields

$$c_i^{n+1} + \gamma\theta c_2^{n+1} = c_1^n - \gamma\left(1-\theta\right)c_2^n + \gamma\left(1-\theta\right)c_b^n + \gamma\theta c_b^{n+1} \tag{D.26}$$

where,

c_b^n = upstream boundary concentration at current time step

c_b^{n+1} = upstream boundary concentration at future time step

D.9 Advection at Upstream Boundary (Upwind)

Using upwind differencing, the advection term at the upstream boundary can be approximated as follows:

$$\frac{\partial c}{\partial t} = \left(-\frac{Q}{A}\frac{\partial c}{\partial x}\right)_1 \cong -\frac{Q}{A}\left(\frac{c_1 - c_b}{\Delta x}\right) \tag{D.27}$$

Rearranging the equation and implementing time weighting using the coefficient of implicity (θ) gives

$$\frac{c_1^{n+1} - c_1^n}{\Delta t} = -\frac{U}{\Delta x}\left[\left(1-\theta\right)\left(c_1^n - c_b^n\right) + \theta\left(c_1^{n+1} - c_b^{n+1}\right)\right] \tag{D.28}$$

Grouping terms and rearranging again to get the future values on the left hand side and the current values on the right hand side yields

$$\left(1+\gamma_u\theta\right)c_1^{n+1} = \left(1-\gamma_u\left(1-\theta\right)\right)c_1^n + \gamma_u\left(1-\theta\right)c_b^n + \gamma_u\theta c_b^{n+1} \tag{D.29}$$

D.10 Diffusion at Upstream Boundary

The spatial derivative for the diffusion term at the upstream boundary is given as

$$\frac{\partial c}{\partial t} = \left[\frac{\partial}{A\partial x}\left(AD\frac{\partial c}{\partial x}\right)\right]_1 \cong \frac{1}{A}\left[\frac{\left(AD\frac{\partial c}{\partial x}\right)_{1,2} - \left(AD\frac{\partial c}{\partial x}\right)_{0,1}}{\Delta x}\right] \tag{D.30}$$

As with the term for the internal cells, the cross-sectional area and diffusion coefficient can be taken outside of the differentials. However, since it was stated in Section 2.2.3 that no diffusion would be allowed across the upstream boundary, the boundary term can be eliminated from Equation D.30. Substituting Equation D.2 for the spatial derivative of the $c_{1,2}$ interfacial concentration then gives the following:

$$\frac{\partial c}{\partial t} \cong \frac{1}{\Delta x}\left[D\frac{c_2 - c_1}{\Delta x}\right] \tag{D.31}$$

Implementing time weighting using the coefficient of implicity (θ) gives

$$\frac{c_1^{n+1} - c_1^n}{\Delta t} = \frac{D_x}{(\Delta x)^2}\left[(1-\theta)\left(c_2^n - c_1^n\right) + \theta\left(c_2^{n+1} - c_1^{n+1}\right)\right] \tag{D.32}$$

Grouping terms and rearranging again to get the future values on the left hand side and the current values on the right hand side yields

$$(1+\lambda\theta)\, c_1^{n+1} - \lambda\theta c_2^{n+1} = (1-\lambda(1-\theta))\, c_1^n + \lambda(1-\theta)\, c_2^n \tag{D.33}$$

D.11 Combined Central Advection and Central Diffusion at Upstream Boundary

Combining Equations D.25 and D.32 gives the following for a combined central advection and central diffusion finite difference approximation:

$$\begin{aligned}\frac{c_1^{n+1} - c_1^n}{\Delta t} &= -\frac{U}{2\Delta x}\left[(1-\theta)\left(c_2^n + c_0^n\right) + \theta\left(c_2^{n+1} + c_0^{n+1}\right)\right] \\ &\quad + \frac{D_x}{(\Delta x)^2}\left[(1-\theta)\left(c_2^n - c_1^n\right) + \theta\left(c_2^{n+1} - c_1^{n+1}\right)\right]\end{aligned} \tag{D.34}$$

Rearranging yields the following equation, which is a combination of Equations D.26 and D.33.

$$\begin{aligned}&(1+\lambda\theta)\, c_1^{n+1} + (\gamma - \lambda)\,\theta c_2^{n+1} \\ &= (1-\lambda(1-\theta))\, c_1^n + (\gamma+\lambda)(1-\theta)\, c_2^n + \lambda\theta c_b^{n+1} + \gamma(1-\theta)\, c_b^n\end{aligned} \tag{D.35}$$

D.12 Combined Upwind Advection and Central Diffusion at Upstream Boundary

Combining equations D.28 and D.32 gives the following for a combined upwind advection and central diffusion finite difference approximation:

$$\begin{aligned}\frac{c_1^{n+1}-c_1^n}{\Delta t} &= -\frac{U}{\Delta x}\left[(1-\theta)\left(c_1^n-c_b^n\right)+\theta\left(c_1^{n+1}-c_b^{n+1}\right)\right] \\ &\quad +\frac{D_x}{\left(\Delta x\right)^2}\left[(1-\theta)\left(c_2^n-c_1^n\right)+\theta\left(c_2^{n+1}-c_1^{n+1}\right)\right] \qquad \text{(D.36)}\end{aligned}$$

Rearranging yields the following equation, which is a combination of equations D.29 and D.33.

$$\begin{aligned}&\left(1+\gamma_u\theta+\lambda\theta\right)c_1^{n+1}-\lambda\theta c_2^{n+1} \\ &=\left(1-\gamma_u\left(1-\theta\right)-\lambda\left(1-\theta\right)\right)c_1^n+\lambda\left(1-\theta\right)c_2^n+\gamma_u\left(1-\theta\right)c_b^n+\gamma_u\theta c_b^{n+1} \qquad \text{(D.37)}\end{aligned}$$

D.13 Cell Definition for Downstream Boundary Segment

Figure D.3 gives a graphical representation of the downstream boundary cell including cell widths and boundary and interfacial concentrations.

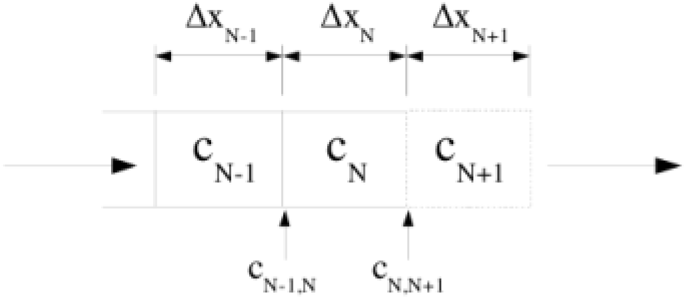


Figure D.3: Representation of downstream boundary cell

The central difference for any cell i was given in Equation D.1. In order to eliminate the boundary concentration, $c_{N,N+1}$, for the downstream cell we define the dispersive flux across the boundary as

$$\left(D\frac{\partial c}{\partial x} \right) \Big|_{N,N+1} = D_b \tag{D.38}$$

We also define the spatial derivative at the downstream boundary as

$$\frac{\partial c}{\partial x}\Big|_{N,N+1} = \frac{2\left(c_{N+1} - c_N\right)}{\Delta x + \Delta x_{N+1}} = \frac{c_{N+1} - c_N}{\Delta x} \tag{D.39}$$

Combining Equations D.38 and D.39 and solving for the concentration of the downstream cell, c_{N+1}, yields

$$c_{N+1} = \frac{D_b \Delta x}{D} + C_N \tag{D.40}$$

As given in Section 2.2.3, the downstream boundary condition is defined as a zero-concentration gradient. In this instance, the dispersive flux at the boundary, D_b, is actually zero. Setting D_b to zero in Equation D.40 shows that, for a zero-concentration gradient, the concentration of the theoretical downstream cell, $N + 1$, is the same as that of the last computation cell, N

$$c_{N+1} = c_N \tag{D.41}$$

D.14 Advection at Downstream Boundary (Central Difference)

Derivation of the central difference for the advection term begins at the downstream boundary proceeds in the same manner as that for the internal cells. Therefore, we begin with Equation D.5 and use Equation D.41 to eliminate the concentration of the downstream cell, $N + 1$, from the equation giving the following:

$$\frac{\partial c}{\partial t} = -\frac{U}{2\Delta x} \left(c_N - c_{N-1} \right) \tag{D.42}$$

Rearranging the equation and implementing time weighting using the coefficient of implicity (θ) gives

$$\frac{c_N^{n+1} - c_N^n}{\Delta t} = -\frac{U}{2\Delta x} \left[(1-\theta) \left(c_N^n - c_{N-1}^n \right) + \theta \left(c_N^{n+1} - c_{N-1}^{n+1} \right) \right] \tag{D.43}$$

Grouping terms and rearranging again to get the future values on the left hand side and the current values on the right hand side yields

$$-\gamma\theta c_{N-1}^{n+1} + (1+\gamma\theta) c_N^{n+1} = \gamma (1-\theta) c_{N-1}^n + (1 - \gamma (1-\theta)) c_N^n \tag{D.44}$$

D.15 Advection at Downstream Boundary (Upwind)

Since the upwind method does not involve the concentration of the downstream boundary or downstream cells, the finite difference approximation for the downstream cell is essentially the same as that for the internal cells given in Section D.3.

$$\frac{\partial c}{\partial t} = \left(-\frac{Q}{A} \frac{\partial c}{\partial x} \right)_N \cong -\frac{Q}{A} \left(\frac{c_N - c_{N-1}}{\Delta x} \right) \tag{D.45}$$

Rearranging the equation and implementing time weighting using the coefficient of implicity (θ) gives

$$\frac{c_N^{n+1} - c_N^n}{\Delta t} = -\frac{U}{\Delta x} \left[(1-\theta) \left(c_N^n - c_{N-1}^n \right) + \theta \left(c_N^{n+1} - c_{N-1}^{n+1} \right) \right] \tag{D.46}$$

Grouping terms and rearranging again to get the future values on the left hand side and the current values on the right hand side yields

$$-\gamma_u \theta c_{N-1}^{n+1} + (1 + \gamma_u \theta)\, c_N^{n+1} = \gamma_u (1 - \theta)\, c_{N-1}^{n} + (1 - \gamma_u (1 - \theta))\, c_N^{n} \tag{D.47}$$

D.16 Diffusion at Downstream Boundary

The spatial derivative for the diffusion term at the downstream boundary is given as

$$\frac{\partial c}{\partial t} = \left[\frac{\partial}{A \partial x}\left(AD\frac{\partial c}{\partial x}\right)\right]_N \cong \frac{1}{A}\left[\frac{\left(AD\frac{\partial c}{\partial x}\right)_{N,N+1} - \left(AD\frac{\partial c}{\partial x}\right)_{N-1,N}}{\Delta x}\right] \tag{D.48}$$

The cross-sectional area and diffusion coefficient can be taken outside of the differentials. Substituting Equation D.2 for the spatial derivatives of the concentration at the interfaces gives the following:

$$\frac{\partial c}{\partial t} \cong \frac{D}{(\Delta x)^2}\left[c_{N+1} - 2c_N + c_{N-1}\right] \tag{D.49}$$

However, due to the zero-concentration gradient, Equation D.31 reduces to

$$\frac{\partial c}{\partial t} \cong \frac{D}{(\Delta x)^2}\left[c_{N-1} - c_N\right] \tag{D.50}$$

Rearranging the equation and implementing time weighting using the coefficient of implicity (θ) gives

$$\frac{c_N^{n+1} - c_N^{n}}{\Delta t} = \frac{D_x}{(\Delta x)^2}\left[(1 - \theta)\left(c_{N-1}^{n} - c_N^{n}\right) + \theta\left(c_{N-1}^{n+1} - c_N^{n+1}\right)\right] \tag{D.51}$$

Grouping terms and rearranging again to get the future values on the left hand side and the current values on the right hand side yields

$$-\lambda \theta c_{N-1}^{n+1} + (1 + \lambda \theta)\, c_N^{n+1} = \lambda (1 - \theta)\, c_{N-1}^{n} + (1 - \lambda (1 - \theta))\, c_N^{n} \tag{D.52}$$

D.17 Combined Central Advection and Central Diffusion at Downstream Boundary

Combining Equations D.43 and D.51 gives the following for a combined central advection and central diffusion finite difference approximation:

$$\begin{aligned}\frac{c_N^{n+1}-c_N^n}{\Delta t} &= -\frac{U}{2\Delta x}\left[(1-\theta)\left(c_N^n-c_{N-1}^n\right)+\theta\left(c_N^{n+1}-c_{N-1}^{n+1}\right)\right]\\ &\quad +\frac{D_x}{(\Delta x)^2}\left[(1-\theta)\left(c_{N-1}^n-c_N^n\right)+\theta\left(c_{N-1}^{n+1}-c_N^{n+1}\right)\right] \qquad \text{(D.53)}\end{aligned}$$

Rearranging yields the following equation, which is a combination of Equations D.44 and D.52.

$$\begin{aligned}&-(\gamma+\lambda)\,\theta c_{N-1}^{n+1}+(1+\gamma\theta+\lambda\theta)\,c_N^{n+1}\\ &=(\gamma+\lambda)(1-\theta)\,c_{N-1}^n+(1-\gamma(1-\theta)-\lambda(1-\theta))\,c_N^n \qquad \text{(D.54)}\end{aligned}$$

D.18 Combined Upwind Advection and Central Diffusion at Downstream Boundary

Combining equations D.46 and D.51 gives the following for a combined upwind advection and central diffusion finite difference approximation:

$$\begin{aligned}\frac{c_N^{n+1}-c_N^n}{\Delta t} &= -\frac{U}{\Delta x}\left[(1-\theta)\left(c_N^n-c_{N-1}^n\right)+\theta\left(c_N^{n+1}-c_{N-1}^{n+1}\right)\right]\\ &\quad +\frac{D_x}{(\Delta x)^2}\left[(1-\theta)\left(c_{N-1}^n-c_N^n\right)+\theta\left(c_{N-1}^{n+1}-c_N^{n+1}\right)\right] \qquad \text{(D.55)}\end{aligned}$$

Rearranging yields the following, which is a combination of equations D.47 and D.52.

$$\begin{aligned}&-(\gamma_u+\lambda)\,\theta c_{N-1}^{n+1}+(1+\gamma_u\theta+\lambda\theta)\,c_N^{n+1}\\ &=(\gamma_u+\lambda)(1-\theta)\,c_{N-1}^n+(1-\gamma_u(1-\theta)-\lambda(1-\theta))\,c_N^n \qquad \text{(D.56)}\end{aligned}$$