A Three-Dimensional Hydrodynamic-Eutrophication Model (HEM-3D): Description of water quality and sediment process submodels

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A THREE-DIMENSIONAL HYDRODYNAMIC-EUTROPHICATION MODEL (HEM-3D): DESCRIPTION OF WATER QUALITY AND SEDIMENT PROCESS SUBMODELS

by

Kyeong Park, Albert Y. Kuo, Jian Shen and John M. Hamrick

Special Report in Applied Marine Science and Ocean Engineering No. 327

School of Marine Science
Virginia Institute of Marine Science
College of William and Mary
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I. Introduction

Virginia Institute of Marine Science (VIMS) has been developing a general purpose three-dimensional hydrodynamic and sediment transport model, Environmental Fluid Dynamics Computer Code (EFDC; Hamrick 1992). The real-time model simulates density and topographically-induced circulation as well as tidal and wind-driven flows, and spatial and temporal distributions of salinity, temperature and sediment concentration. The model also is capable of handling the wetting and drying of shallow area, hydraulic control structures, vegetation resistance for wetlands and Lagrangian particle tracking. The information of physical transport processes, both advective and diffusive, simulated by the hydrodynamic model can be used to account for the transport of passive substances including non-conservative water quality parameters.

A water quality model with twenty-one state variables has been developed and integrated with EFDC to form a three-dimensional Hydrodynamic-Eutrophication Model (HEM-3D) of the VIMS. The model, upon receiving the information of physical transport from EFDC, simulates the spatial and temporal distributions of water quality parameters including dissolved oxygen, suspended algae (3 groups), various components of carbon, nitrogen, phosphorus and silica cycles, and fecal coliform bacteria. A sediment process model with twenty-seven state variables has also been developed. The sediment process model, upon receiving the particulate organic matter deposited from the overlying water column, simulates their diagenesis and the resulting fluxes of inorganic substances (ammonium, nitrate, phosphate and silica) and sediment oxygen demand back to the water column. The coupling of the sediment process model with the water quality model not only enhances the model’s predictive capability of water quality parameters but also enables it to simulate the long-term changes in water quality conditions in response to changes in nutrient loadings. This report documents the water quality model, including the sediment process model, for the formulations of the kinetic processes being simulated and their numerical methods of solution.

The governing mass-balance equation for each of the water quality state variables may be expressed as:
\[
\frac{\partial C}{\partial t} + \frac{\partial (uC)}{\partial x} + \frac{\partial (vC)}{\partial y} + \frac{\partial (wC)}{\partial z} = \\
\frac{\partial}{\partial x}\left(K_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial C}{\partial z}\right) + S_c
\]  

(1-1)

\(C\) = concentration of a water quality state variable
\(u, v \& w\) = velocity components in the x-, y- and z-directions, respectively
\(K_x, K_y \& K_z\) = turbulent diffusivities in the x-, y- and z-directions, respectively
\(S_c\) = internal and external sources and sinks per unit volume.

The last three terms on the left-hand side (LHS) of Eq. 1-1 account for the advective transport and the first three terms on the right-hand side (RHS) of Eq. 1-1 account for the diffusive transport. These six terms for physical transport are analogous to, and thus the numerical method of solution is the same as, those in the mass-balance equation for salinity in the hydrodynamic model (Hamrick 1992). The last term in Eq. 1-1 represents the kinetic processes and external loads for each of the state variables. The present model solves Eq. 1-1 after decoupling the kinetic terms from the physical transport terms. The solution scheme for both the physical transport (Hamrick 1992) and the kinetic equations (Chapter II and Section III-10) is second-order accurate. Chapter II describes the decoupling and the method of solution for Eq. 1-1.

The kinetic processes included in this model use the formulations in the tidal prism water quality model, TPM-VIMS (Kuo & Park 1994), which are mostly from the Chesapeake Bay three-dimensional water quality model, CE-QUAL-ICM (Cerco & Cole 1994). The kinetic sources and sinks, and external loads for each state variable are described in Chapter III. The kinetic processes include the exchange fluxes at the sediment-water interface. A sediment process model, which was developed for the Chesapeake Bay three-dimensional modeling effort (DiToro & Fitzpatrick 1993), was slightly modified and incorporated into the tidal prism model (Kuo & Park 1994). This sediment process model is incorporated into the present model to simulate the sediment-water exchange fluxes, and is described in Chapter IV. A simplified version of the water quality model with only nine state variables, including the corresponding sediment process model, is described in Chapter V. Brief comments are given in Chapter VI.
II. Solution Method of Governing Mass-Balance Equation

The governing mass-balance equation for water quality state variables (Eq. 1-1) consists of physical transport, advective and diffusive, and kinetic processes. When solving Eq. 1-1, the kinetic terms are decoupled from the physical transport terms. The mass-balance equation for physical transport only, which takes the same form as the salt-balance equation, is:

\[
\frac{\partial C}{\partial t} + \frac{\partial(uC)}{\partial x} + \frac{\partial(vC)}{\partial y} + \frac{\partial(wC)}{\partial z} = \frac{\partial}{\partial x}\left(K_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial C}{\partial z}\right)
\]  

(2-1)

The equation for kinetic processes only, which will be referred to as kinetic equation, is:

\[
\frac{\partial C}{\partial t} = S_c
\]  

(2-2)

which may be expressed as (see Eq. 3-20):

\[
\frac{\partial C}{\partial t} = K \cdot C + R
\]  

(2-3)

where \(K\) is kinetic rate (time\(^{-1}\)) and \(R\) is source/sink term (mass volume\(^{-1}\) time\(^{-1}\)). Equation 2-3 is obtained by linearizing some terms in the kinetic equations (Section III-10 and Appendix A), mostly Monod type expressions. Hence, \(K\) and \(R\) are known values in Eq. 2-3. Equation 2-1 is identical with, and thus its numerical method of solution is the same as, the mass-balance equation for salinity (Hamrick 1992). This chapter describes the method of solution for Eq. 1-1 in terms of interfacing Equations 2-1 and 2-3.

The hydrodynamic model employs a second-order accurate three time-level advection scheme after integrating Eq. 2-1 over a cell volume (Hamrick 1992), and thus its time step is \(2 \cdot \Delta t\) where \(\Delta t = t_{n+1} - t_n\). To achieve the same second-order accuracy, the solution scheme of the kinetic equation (Eq. 2-3) is derived by dividing the solution procedure over a time period of \(2 \cdot \Delta t\) into two steps, alternating between explicit and implicit schemes. Figure 2-1a illustrates the solution procedure over the time period from \(t_{n-1}\) to \(t_{n+1}\).

The first step, \(S_1\), solves Eq. 2-3 over \(\Delta t\) from \(t_{n-1}\) to \(t_n\) by the explicit scheme:
\[ C_{P}^{n} - C^{\ast n} = \Delta t \cdot K^{n-1} \cdot C^{n-1} + \Delta t \cdot R^{\ast n-1} \]  
(2-4-1)

which subjects the conditions at \( t = t_{n+1} \), \( C^{n+1} \), to the kinetic processes alone to give \( C_{P}^{n+i} \). The superscript designates the time step. The subscript -P designates an intermediate concentration that lacks the physical transport over \( \Delta t \), whereas the subscript +P will designate one with surplus physical transport over \( \Delta t \). In Fig. 2-1, the subscript -K designates an intermediate concentration that lacks the kinetic update over \( \Delta t \), whereas the subscript +K designates one with surplus kinetic update over \( \Delta t \). In Fig. 2-1a, hence, \( C_{P}^{n} = C_{K}^{n+1} \).

Next, the intermediate concentration fields, \( C_{K}^{n+1} \), are physically transported over \( 2 \cdot \Delta t \) from \( t_{n+1} \) to \( t_{n+2} \) in step S2 (Fig. 2-1a) by the finite difference form of Eq. 2-1 after being integrated over the cell volume (Hamrick 1992):

\[ C_{K}^{n+1} - C_{K}^{n-1} = 2 \cdot \Delta t \cdot PT \]  
(2-4-2)

where PT is a physical transport operator over \( 2 \cdot \Delta t \) from \( t_{n} \) to \( t_{n+1} \), and \( C_{K}^{n+1} \) is another intermediate concentration at \( t = t_{n+1} \) lacking the kinetic update over \( \Delta t \) from \( t_{n} \) to \( t_{n+1} \).

Finally, the step S3 solves Eq. 2-3 over \( \Delta t \) from \( t_{n} \) to \( t_{n+1} \) by the implicit scheme:

\[ C^{\ast n+1} - C^{\ast n} = \Delta t \cdot K^{n-1} \cdot C^{n-1} + \Delta t \cdot R^{\ast n+1} \]  
(2-4-3)

where \( C^{\ast n} \) is the concentration at \( t = t_{n+1} \). In the linearized kinetic equation (Eq. 2-3 or Eq. 3-20), the kinetic rate is evaluated using old conditions, i.e., \( K^{n-1} \). Also note in Eq. 2-4-3, \( C_{P}^{n} = C_{K}^{n+1} \) (Fig. 2-1a).

In principle, the same three-step procedure, S1, S2 and S3, may be repeated for the next time period from \( t_{n+1} \) to \( t_{n+3} \), with the equation for the step S4 given by:

\[ C_{P}^{n+2} - C^{\ast n+1} = \Delta t \cdot K^{n-1} \cdot C^{n-1} + \Delta t \cdot R^{\ast n+1} \]  
(2-4-4)

where \( C_{P}^{n+2} \) is an intermediate concentration at \( t = t_{n+2} \) lacking the physical transport over \( \Delta t \) from \( t_{n+1} \) to \( t_{n+2} \). In practice, the computational steps S3 and S4 may be combined by adding Equations 2-4-3 and 2-4-4 to arrive at (Fig. 2-1b):

\[ C_{P}^{n+2} - C_{P}^{n} = \Delta t \cdot (K^{n-1} + K^{n+1}) \cdot C^{n-1} + 2 \cdot \Delta t \cdot R^{\ast n+1} \]  
(2-5)

which may be approximated by:

4
\[
C_{p}^{n+2} - C_{p}^{n} = \Delta t \cdot K \cdot \left( C_{p}^{n} + C_{p}^{n+2} \right) + 2 \cdot \Delta t \cdot R^n
\]
(2-6)

or

\[
C_{K}^{n+1} - C_{K}^{n} = \Delta t \cdot K \cdot \left( C_{K}^{n} + C_{K}^{n+1} \right) + 2 \cdot \Delta t \cdot R^n
\]
(2-7)

by assuming:

\[
K^{n} + K^{n+1} = 2 \cdot K^n
\]
(2-8-1)

\[
C^{n+1} = \frac{1}{2} \left( C_{p}^{n} + C_{p}^{n+2} \right) = \frac{1}{2} \left( C_{K}^{n} + C_{K}^{n+1} \right)
\]
(2-8-2)

\[
R^{n+1} = R^n
\]
(2-8-3)

Equation 2-6, or Eq. 2-7, is a second-order accurate trapezoidal solution of Eq. 2-3 over\(2 \cdot \Delta t\) from \(t_n\) to \(t_{n+2}\), with the concentration at \(t = t_{n+1}\) given by Eq. 2-8-2. The source/sink term \(R\) consists of external loads and sediment-water exchange fluxes (Section III-10 and Appendix A). In model application, external loads are usually specified as a daily input and sediment-water exchange fluxes have a time scale of days and months. Since \(\Delta t\) in a three-dimensional real-time model is on the order of minutes, the assumption in Eq. 2-8-3 does not significantly affect the accuracy of the solution.

With the combination of computational steps S3 and S4 in Fig. 2-1a, the solution scheme for Equations 2-1 and 2-3 becomes an alternate solution of the physical transport (Eq. 2-4-2) and the kinetic processes (Eq. 2-7), as illustrated in Fig. 2-1b. Both Equations 2-4-2 and 2-7 are second-order accurate. It should be noted that the intermediate concentration with the subscripts, either \(\pm K\) or \(\pm P\), are not real concentrations at their time steps. For example, \(C_{K, n+1}\) and \(C_{K, n+1}\) are imaginary concentrations at \(t = t_{n+1}\), with the former lacking the kinetic update from \(t_n\) to \(t_{n+1}\) and the latter with surplus kinetic update from \(t_{n+1}\) to \(t_{n+2}\). The real concentrations at \(t = t_{n+1}\), \(C^{n+1}\), may be evaluated by the average of these two (Eq. 2-8-2).

Finally, the solution scheme may be generalized into the one illustrated in Fig. 2-1c. Since the water quality kinetic processes have much longer time scales than the allowable \(\Delta t\) in the real-time hydrodynamic model, the kinetic equation (Eq. 2-3) may be solved not
as often as the physical transport equation (Eq. 2-1). In general, then, $\theta = m (2 \cdot \Delta t)$ where $m$ is a positive integer. In Fig. 2-1c, the kinetic equation is solved once over a time interval of $\theta$ from $t_n$ to $t_{n+2m}$ for every $m$ steps of computation of physical transport. It, however, should be cautioned that $\theta$ should not be large enough to cause instability by consuming all materials within a cell over a time period of $\theta$.

The decoupling of the kinetic processes from the physical transport results in a simple and efficient computational procedure as described above (Park & Kuo submitted). The decoupling of the governing equations not only simplifies the solution scheme but also makes the model more flexible with respect to the addition of new water quality state variables and to the modification of the kinetic formulations. The solution scheme for the physical transport equation needs to be obtained and validated only once for conservative substance such as salt. Later addition of new water quality state variables or modification of the kinetic formulations would require only simple modification in the solution scheme for kinetic equations.
Figure 2-1. A solution method for the governing mass-balance equation of water quality state variables, employing an alternate solution of physical transport and kinetic processes. (The subscripts K and P indicate kinetic processes and physical transport respectively. The subscript + indicates surplus process over $\Delta t$, while the subscript - indicates lacking of process over $\Delta t$. Solid-line arrow indicates either kinetic processes or physical transport, while dotted-line arrow displaces the same intermediate concentrations to a different notation.)
III. Kinetic Equations

The present water quality model has twenty-one model state variables, and this chapter describes the kinetic equations (Eq. 2-3) for each of the state variables.

1) cyanobacteria (blue-green algae)  
2) diatoms  
3) green algae (others)  
4) refractory particulate organic carbon  
5) labile particulate organic carbon  
6) dissolved organic carbon  
7) refractory particulate organic phosphorus  
8) labile particulate organic phosphorus  
9) dissolved organic phosphorus  
10) total phosphate  
11) refractory particulate organic nitrogen  
12) labile particulate organic nitrogen  
13) dissolved organic nitrogen  
14) ammonium nitrogen  
15) nitrate nitrogen  
16) particulate biogenic silica  
17) available silica  
18) chemical oxygen demand  
19) dissolved oxygen  
20) total active metal  
21) fecal coliform bacteria

The nitrate state variable in the model represents the sum of nitrate and nitrite nitrogen. The three variables, salinity, water temperature and total suspended solid, that are needed for the computation of the above twenty-one state variables, are provided by the hydrodynamic model.

Figure 3-1 illustrates the interactions between state variables. The kinetic processes included in this model use the formulations in the tidal prism water quality model, TPM-VIMS (Kuo & Park 1994), which are mostly from the Chesapeake Bay three-dimensional water quality model, CE-QUAL-ICM (Cerco & Cole 1994). The kinetic sources and sinks, and external loads for each state variable are described in Sections III-1 to III-9. The kinetic processes include the exchange fluxes at the sediment-water interface including sediment oxygen demand, which are explained in the sediment process model (Chapter IV). The solution method of the kinetic equations is described in Section III-10. The parameter values used in Chesapeake Bay modeling (Cerco & Cole 1994) are presented in Section III-11.
III-1. Algae

Algae, which occupies a central role in the model (Fig. 3-1), are grouped into three model state variables: cyanobacteria (blue-green algae), diatoms and green algae. The subscript, \( x \), is used to denote three algal groups: \( c \) for cyanobacteria, \( d \) for diatoms and \( g \) for green algae. Sources and sinks included in the model are:

- growth (production)
- basal metabolism
- predation
- settling
- external loads

Equations describing these processes are largely the same for three algal groups with differences in the values of parameters in the equations. The kinetic equation describing these processes is:

\[
\frac{\partial B_x}{\partial t} = (P_x - BM_x - PR_x)B_x + \frac{\partial}{\partial z}(WS_x \cdot B_x) + \frac{WB_x}{V}
\]  

(3-1)

\( B_x \) = algal biomass of algal group \( x \) (g C m\(^{-3}\))

\( t \) = time (day)

\( P_x \) = production rate of algal group \( x \) (day\(^{-1}\))

\( BM_x \) = basal metabolism rate of algal group \( x \) (day\(^{-1}\))

\( PR_x \) = predation rate of algal group \( x \) (day\(^{-1}\))

\( WS_x \) = settling velocity of algal group \( x \) (m day\(^{-1}\))

\( WB_x \) = external loads of algal group \( x \) (g C day\(^{-1}\))

\( V \) = cell volume (m\(^3\)).

III-1-1. Growth (Production)

Algal growth depends on nutrient availability, ambient light and temperature. The effects of these processes are considered to be multiplicative:

\[
P_x = PM_x \cdot f_1(N) \cdot f_2(I) \cdot f_3(T)
\]  

(3-1a)

\( PM_x \) = maximum growth rate under optimal conditions for algal group \( x \) (day\(^{-1}\))

\( f_1(N) \) = effect of suboptimal nutrient concentration (0 \( \leq \) \( f_1 \) \( \leq \) 1)
\[ f_2(I) = \text{effect of suboptimal light intensity (} 0 \leq f_2 \leq 1) \]
\[ f_3(T) = \text{effect of suboptimal temperature (} 0 \leq f_3 \leq 1) \].

The freshwater cyanobacteria may undergo rapid mortality in salt water, e.g., freshwater organisms in the Potomac River (Thomann et al. 1985). For the freshwater organisms, the increased mortality may be included in the model by retaining the salinity toxicity term in the growth equation for cyanobacteria:

\[
P_c = PM_c \cdot f_1(N) \cdot f_2(I) \cdot f_3(T) \cdot f_4(S) \tag{3-1b} \]

\[ f_4(S) = \text{effect of salinity on cyanobacteria growth (} 0 \leq f_4 \leq 1) \].

Activation of the salinity toxicity term, \( f_4(S) \), is an option in the source code.

III-1-1a. Effect of nutrients on growth

Using Liebig's "law of the minimum" (Odum 1971) that growth is determined by the nutrient in least supply, the nutrient limitation for growth of cyanobacteria and green algae is expressed as:

\[
f_1(N) = \text{minimum } \left( \frac{NH_4 + NO_3}{KHN_x + NH_4 + NO_3}, \frac{PO_4d}{KHP_x + PO_4d} \right) \tag{3-1c} \]

\( NH_4 = \text{ammonium nitrogen concentration (} \text{g N m}^{-3} \) \\
\( NO_3 = \text{nitrato nitrogen concentration (} \text{g N m}^{-3} \) \\
\( KHN_x = \text{half-saturation constant for nitrogen uptake for algal group } x \ (\text{g N m}^{-3}) \) \\
\( PO_4d = \text{dissolved phosphate phosphorus concentration (} \text{g P m}^{-3} \) \\
\( KHP_x = \text{half-saturation constant for phosphorus uptake for algal group } x \ (\text{g P m}^{-3}). \)

Some cyanobacteria, e.g., \textit{Anabaena}, can fix nitrogen from atmosphere and thus is not limited by nitrogen. Hence, Eq. 3-1c is not applicable to the growth of nitrogen fixers.

Since diatoms require silica as well as nitrogen and phosphorus for growth, the nutrient limitation for diatoms is expressed as:

\[
f_1(N) = \text{minimum } \left( \frac{NH_4 + NO_3}{KHN_d + NH_4 + NO_3}, \frac{PO_4d}{KHP_d + PO_4d}, \frac{SAd}{KHS + SAd} \right) \tag{3-1d} \]

\( SAd = \text{concentration of dissolved available silica (} \text{g Si m}^{-3} \) \\
\( KHS = \text{half-saturation constant for silica uptake for diatoms (} \text{g Si m}^{-3}). \)
The daily and vertically integrated form of Steele’s equation is:

\[ f_2(I) = \frac{2.718 \cdot FD}{Kess \cdot \Delta z} \left( e^{-\alpha_b} - e^{-\alpha_r} \right) \]  

(3-1e)

\[ \alpha_b = \frac{I_o}{FD \cdot \langle I_x \rangle} \cdot \exp\left( -Kess \cdot H_r + \Delta z \right) \]  

(3-1f)

\[ \alpha_r = \frac{I_o}{FD \cdot \langle I_x \rangle} \cdot \exp\left( -Kess \cdot H_r \right) \]  

(3-1g)

FD = fractional daylength (0 ≤ FD ≤ 1)
Kess = total light extinction coefficient (m⁻¹)
Δz = layer thickness (m)
I₀ = daily total light intensity at water surface (langleyes day⁻¹)
(⟨I⟩ₓ) = optimal light intensity for algal group x (langleyes day⁻¹)
H_r = depth from the free surface to the top of the layer (m).

Light extinction in the water column consists of three fractions in the model: a background value dependent on water color, extinction due to suspended particles and extinction due to light absorption by ambient chlorophyll:

\[ Kess = K_{eb} + K_{eTSS} \cdot TSS + K_{eChl} \cdot \sum_{x=x_{algal}} \left( \frac{B_x}{CChl_x} \right) \]  

(3-1h)

K_{eb} = background light extinction (m⁻¹)
K_{eTSS} = light extinction coefficient for total suspended solid (m⁻¹ per g m⁻³)
TSS = total suspended solid concentration (g m⁻³) provided from the hydrodynamic model
K_{eChl} = light extinction coefficient for chlorophyll 'a' (m⁻¹ per mg Chl m⁻³)
CChl_x = carbon-to-chlorophyll ratio in algal group x (g C per mg Chl).

For a model that does not simulate TSS, K_{eTSS} may be set to zero and K_{eb} may be estimated to include light extinction due to suspended solid.

Optimal light intensity (I_{o}) for photosynthesis depends on algal taxonomy, duration of exposure, temperature, nutritional status and previous acclimation. Variations in I_{o} are
largely due to adaptations by algae intended to maximize production in a variable environment. Steel (1962) noted the result of adaptations is that optimal intensity is a consistent fraction (approximately 50%) of daily intensity. Kremer & Nixon (1978) reported an analogous finding that maximum algal growth occurs at a constant depth (approximately 1 m) in the water column. Their approach is adopted so that optimal intensity is expressed as:

\[ (I_x)_{opt} = \min \left\{ (I_x)_{avg} \cdot e^{-K_{opt}(D_{opt})}, (I_x)_{min} \right\} \]  

(3-1i)

\( (D_{opt})_x \) = depth of maximum algal growth for algal group x (m)

\( (I_x)_{avg} \) = adjusted surface light intensity (langleyes day\(^{-1}\)).

A minimum, \( (I_x)_{min} \), in Eq. 3-1i is specified so that algae do not thrive at extremely low light levels. The time required for algae to adapt to changes in light intensity is recognized by estimating \( (I_x)_{avg} \) based on a time-weighted average of daily light intensity:

\[ (I_x)_{avg} = C_{I_o}I_o + C_{I_1}I_1 + C_{I_2}I_2 \]  

(3-1j)

\( I_o \) = daily light intensity one day preceding model day (langleyes day\(^{-1}\))

\( I_1 \) = daily light intensity two days preceding model day (langleyes day\(^{-1}\))

\( C_{I_o}, C_{I_1} \& C_{I_2} \) = weighting factors for \( I_o, I_1 \) and \( I_2 \), respectively: \( C_{I_o} + C_{I_1} + C_{I_2} = 1 \).

III-1-1c. Temperature

A Gaussian probability curve is used to represent temperature dependency of algal growth:

\[ f_3(T) = \exp\left(-K_{T,G1x}(T - T_{M_x})^2\right) \quad \text{if} \quad T \leq T_{M_x} \]

\[ = \exp\left(-K_{T,G2x}(T_{M_x} - T)^2\right) \quad \text{if} \quad T > T_{M_x} \]  

(3-1k)

\( T \) = temperature (°C) provided from the hydrodynamic model

\( T_{M_x} \) = optimal temperature for algal growth for algal group x (°C)

\( K_{T,G1x} \) = effect of temperature below \( T_{M_x} \) on growth for algal group x (°C\(^{-2}\))

\( K_{T,G2x} \) = effect of temperature above \( T_{M_x} \) on growth for algal group x (°C\(^{-2}\)).

III-1-1d. Effect of salinity on growth of freshwater cyanobacteria

The growth of freshwater cyanobacteria in salt water is limited by:
\[ f_s(S) = \frac{STOX^2}{STOX^2 + S^2} \]  
(3-11)

STOX = salinity at which Microcystis growth is halved (ppt)
S = salinity in water column (ppt) provided from the hydrodynamic model.

III-1-2. Basal Metabolism

Algal biomass in the present model decreases through basal metabolism (respiration and excretion) and predation. Basal metabolism in the present model is the sum of all internal processes that decrease algal biomass, and consists of two parts; respiration and excretion. In basal metabolism, algal matter (carbon, nitrogen, phosphorus and silica) is returned to organic and inorganic pools in the environment, mainly to dissolved organic and inorganic matter. Respiration, which may be viewed as a reversal of production, consumes dissolved oxygen. Basal metabolism is considered to be an exponentially increasing function of temperature:

\[ BM_x = BMR_x \cdot \exp(KTB_x[T - TR_x]) \]  
(3-1m)

BMR\(_x\) = basal metabolism rate at TR\(_x\) for algal group \(x\) (day\(^{-1}\))

KTB\(_x\) = effect of temperature on metabolism for algal group \(x\) (°C\(^{-1}\))

TR\(_x\) = reference temperature for basal metabolism for algal group \(x\) (°C).

III-1-3. Predation

The present model does not include zooplankton. Instead, a constant rate is specified for algal predation, which implicitly assumes zooplankton biomass is a constant fraction of algal biomass. An equation similar to that for basal metabolism (Eq. 3-1m) is used for predation:

\[ PR_x = PRR_x \cdot \exp(KTB_x[T - TR_x]) \]  
(3-1n)

PRR\(_x\) = predation rate at TR\(_x\) for algal group \(x\) (day\(^{-1}\)).

The difference between predation and basal metabolism lies in the distribution of the end products of two processes. In predation, algal matter (carbon, nitrogen, phosphorus and silica) is returned to organic and inorganic pools in the environment, mainly to particulate
organic matter.

III-1-4. Settling

Settling velocities for three algal groups, \( WS_c \), \( WS_d \) and \( WS_g \), are specified as an input. Seasonal variations in settling velocity of diatoms can be accounted for by specifying time-varying \( WS_d \).

III-2. Organic Carbon

The present model has three state variables for organic carbon: refractory particulate, labile particulate and dissolved.

A. Particulate organic carbon: Labile and refractory distinctions are based on the time scale of decomposition. Labile particulate organic carbon with a decomposition time scale of days to weeks decomposes rapidly in the water column or in the sediments. Refractory particulate organic carbon with longer-than-weeks decomposition time scale decomposes slowly, primarily in the sediments, and may contribute to sediment oxygen demand years after decomposition. For labile and refractory particulate organic carbon, sources and sinks included in the model are (Fig. 3-1):

: algal predation
: dissolution to dissolved organic carbon
: settling
: external loads

The governing equations for refractory and labile particulate organic carbons are:

\[
\frac{\partial RPOC}{\partial t} = \sum_{x = c, d, g} FCRP \cdot PR \cdot B_x \cdot RPOC - K_{RPOC} \cdot RPOC + \frac{\partial}{\partial z} \left( WS_{RPOC} \cdot RPOC \right) + \frac{WRPOC}{V} \quad (3-2)
\]

\[
\frac{\partial LPOC}{\partial t} = \sum_{x = c, d, g} FCLP \cdot PR \cdot B_x \cdot LPOC - K_{LPOC} \cdot LPOC + \frac{\partial}{\partial z} \left( WS_{LPOC} \cdot LPOC \right) + \frac{WLPOC}{V} \quad (3-3)
\]

\( RPOC \) = concentration of refractory particulate organic carbon (g C m\(^{-3}\))

\( LPOC \) = concentration of labile particulate organic carbon (g C m\(^{-3}\))

\( FCRP \) = fraction of predated carbon produced as refractory particulate organic carbon

\( FCLP \) = fraction of predated carbon produced as labile particulate organic carbon
$K_{RPOC} =$ dissolution rate of refractory particulate organic carbon (day$^{-1}$)

$K_{LPOC} =$ dissolution rate of labile particulate organic carbon (day$^{-1}$)

$WS_{RP} =$ settling velocity of refractory particulate organic matter (m day$^{-1}$)

$WS_{LP} =$ settling velocity of labile particulate organic matter (m day$^{-1}$)

$WRPOC =$ external loads of refractory particulate organic carbon (g C day$^{-1}$)

$WLPOC =$ external loads of labile particulate organic carbon (g C day$^{-1}$).

**B. Dissolved organic carbon:** Sources and sinks included in the model are (Fig. 3-1):

- algal excretion (exudation) and predation
- dissolution from refractory and labile particulate organic carbon
- heterotrophic respiration of dissolved organic carbon (decomposition)
- denitrification
- external loads

The kinetic equation describing these processes is:

$$\frac{dDOC}{dt} = \sum_{x \in alg} \left( FCD_x + (1 - FCD_x) \frac{KHR_x}{KHR_x + DO} \right) BM_x + FCDP \cdot PR_x \cdot B_x$$

$$+ K_{RPOC} \cdot RPOC + K_{LPOC} \cdot LPOC - K_{HR} \cdot DOC - Denit \cdot DOC + \frac{WDOC}{V}$$ (3-4)

$DOC =$ concentration of dissolved organic carbon (g C m$^{-3}$)

$FCD_x =$ fraction of basal metabolism exuded as dissolved organic carbon at infinite dissolved oxygen concentration for algal group $x$

$KHR_x =$ half-saturation constant of dissolved oxygen for algal dissolved organic carbon excretion for group $x$ (g O$_2$ m$^{-3}$)

$DO =$ dissolved oxygen concentration (g O$_2$ m$^{-3}$)

$FCDP =$ fraction of predated carbon produced as dissolved organic carbon

$K_{HR} =$ heterotrophic respiration rate of dissolved organic carbon (day$^{-1}$)

$Denit =$ denitrification rate (day$^{-1}$) given in Eq. 3-41

$WDOC =$ external loads of dissolved organic carbon (g C day$^{-1}$)

The remaining of this section explains each term in Equations 3-2 to 3-4.
III-2-1. Effect of algae on organic carbon

The terms within summation ($\sum$) in Equations 3-2 to 3-4 account for the effects of algae on organic carbon through basal metabolism and predation.

A. Basal metabolism: Basal metabolism, consisting of respiration and excretion, returns algal matter (carbon, nitrogen, phosphorus and silica) back to the environment. Loss of algal biomass through basal metabolism is (Eq. 3-1):

$$\frac{\partial B_s}{\partial t} = -BM_s \cdot B_s$$

which indicates that the total loss of algal biomass due to basal metabolism is independent of ambient dissolved oxygen concentration. In this model, it is assumed that the distribution of total loss between respiration and excretion is constant as long as there is sufficient dissolved oxygen for algae to respire. Under that condition, the losses by respiration and excretion may be written as:

$$FCD \cdot BM_s \cdot B_s$$

due to respiration

$$BM_s \cdot B_s$$

due to excretion

where $FCD_x$ is a constant of value between 0 and 1. Algae cannot respire in the absence of oxygen, however. Although the total loss of algal biomass due to basal metabolism is oxygen-independent (Eq. 3-4a), the distribution of total loss between respiration and excretion is oxygen-dependent. When oxygen level is high, respiration is a large fraction of the total. As dissolved oxygen becomes scarce, excretion becomes dominant. Thus, Eq. 3-4b represents the loss by respiration only at high oxygen levels. In general, Eq. 3-4b can be decomposed into two fractions as a function of dissolved oxygen availability:

$$\frac{DO}{KHR_x + DO} BM_s \cdot B_s$$

due to respiration

$$\frac{KHR_x}{KHR_x + DO} BM_s \cdot B_s$$

due to excretion

Equation 3-4d represents the loss of algal biomass by respiration and Eq. 3-4e represents additional excretion due to insufficient dissolved oxygen concentration. The parameter $KHR_x$, which is defined as the half-saturation constant of dissolved oxygen for algal
dissolved organic carbon excretion in Eq. 3-4, can also be defined as the half-saturation constant of dissolved oxygen for algal respiration in Eq. 3-4d.

Combining Equations 3-4c and 3-4e, the total loss due to excretion is:

\[
\text{Total loss due to excretion} = \left( FCD + (1 - FCD) \frac{KHR}{KHR + DO} \right) B_x \text{B}_x
\]

Equations 3-4d and 3-4f combine to give the total loss of algal biomass due to basal metabolism, \( BM_x \cdot B_x \) (Eq. 3-4a). The definition of \( FCD_x \) in Eq. 3-4 becomes apparent in Eq. 3-4f; i.e., fraction of basal metabolism exuded as dissolved organic carbon at infinite dissolved oxygen concentration. At zero oxygen level, 100% of total loss due to basal metabolism is by excretion regardless of \( FCD_x \).

The end carbon product of respiration is primarily carbon dioxide, an inorganic form not considered in the present model, while the end carbon product of excretion is primarily dissolved organic carbon. Therefore, Eq. 3-4f, that appears in Eq. 3-4, represents the contribution of excretion to dissolved organic carbon, and there is no source term for particulate organic carbon from algal basal metabolism in Equations 3-2 and 3-3.

**B. Predation:** Algae produce organic carbon through the effects of predation. Zooplankton take up and redistribute algal carbon through grazing, assimilation, respiration and excretion. Since zooplankton are not included in the model, routing of algal carbon through zooplankton predation is simulated by empirical distribution coefficients in Equations 3-2 to 3-4; FCRP, FCLP and FCDP. The sum of these three predation fractions should be unity.

**III-2-2. Heterotrophic respiration and dissolution**

The second term on the RHS of Equations 3-2 and 3-3 represents dissolution of particulate to dissolved organic carbon and the third term in the second line of Eq. 3-4 represents heterotrophic respiration of dissolved organic carbon. The oxic heterotrophic respiration is a function of dissolved oxygen: the lower the dissolved oxygen, the smaller the respiration term becomes. Heterotrophic respiration rate, therefore, is expressed using a Monod function of dissolved oxygen:
\[ K_{HR} = \frac{DO}{KHOR_{DO} + DO} K_{DOC} \]  
(3-4g)

\( KHOR_{DO} \) = oxic respiration half-saturation constant for dissolved oxygen (g O₂ m⁻³)
\( K_{DOC} \) = heterotrophic respiration rate of dissolved organic carbon at infinite dissolved oxygen concentration (day⁻¹).

Dissolution and heterotrophic respiration rates depend on the availability of carbonaceous substrate and on heterotrophic activity. Algae produce labile carbon that fuels heterotrophic activity: dissolution and heterotrophic respiration do not require the presence of algae though, and may be fueled entirely by external carbon inputs. In the model, algal biomass, as a surrogate for heterotrophic activity, is incorporated into formulations of dissolution and heterotrophic respiration rates. Formulations of these rates require specification of algal-dependent and algal-independent rates:

\[ K_{RPOC} = (K_{RC} + K_{RCalg} \sum_{x<alg} B_x) \cdot \exp(KT_{HDR} [T - TR_{HDR}]) \]  
(3-4h)

\[ K_{LPOC} = (K_{LC} + K_{LCalg} \sum_{x<alg} B_x) \cdot \exp(KT_{HDR} [T - TR_{HDR}]) \]  
(3-4i)

\[ K_{DOC} = (K_{DC} + K_{DCalg} \sum_{x<alg} B_x) \cdot \exp(KT_{MNL} [T - TR_{MNL}]) \]  
(3-4j)

\( K_{RC} \) = minimum dissolution rate of refractory particulate organic carbon (day⁻¹)
\( K_{LC} \) = minimum dissolution rate of labile particulate organic carbon (day⁻¹)
\( K_{DC} \) = minimum respiration rate of dissolved organic carbon (day⁻¹)
\( K_{RCalg} \) & \( K_{LCalg} \) = constants that relate dissolution of refractory and labile particulate organic carbon, respectively, to algal biomass (day⁻¹ per g C m⁻³)
\( K_{DCalg} \) = constant that relates respiration to algal biomass (day⁻¹ per g C m⁻³)
\( KT_{HDR} \) = effect of temperature on hydrolysis of particulate organic matter (°C⁻¹)
\( TR_{HDR} \) = reference temperature for hydrolysis of particulate organic matter (°C)
\( KT_{MNL} \) = effect of temperature on mineralization of dissolved organic matter (°C⁻¹)
\( TR_{MNL} \) = reference temperature for mineralization of dissolved organic matter (°C).

Equations 3-4h to 3-4j have exponential functions that relate rates to temperature.

In the present model, the term "hydrolysis" is defined as the process by which
particulate organic matter is converted to dissolved organic form, and thus includes both
dissolution of particulate carbon and hydrolysis of particulate phosphorus and nitrogen.
Therefore, the parameters, KT_{HDR} and TR_{HDR}, are also used for the temperature effects on
hydrolysis of particulate phosphorus (Equations 3-8f and 3-8g) and nitrogen (Equations 3-
13b and 3-13c). The term "mineralization" is defined as the process by which dissolved
organic matter is converted to dissolved inorganic form, and thus includes both
heterotrophic respiration of dissolved organic carbon and mineralization of dissolved
organic phosphorus and nitrogen. Therefore, the parameters, KT_{MINL} and TR_{MINL}, are also
used for the temperature effects on mineralization of dissolved phosphorus (Eq. 3-8h) and
nitrogen (Eq. 3-13d).

III-2-3. Effect of denitrification on dissolved organic carbon

As oxygen is depleted from natural systems, organic matter is oxidized by the
reduction of alternate electron acceptors. Thermodynamically, the first alternate acceptor
reduced in the absence of oxygen is nitrate. The reduction of nitrate by a large number of
heterotrophic anaerobes is referred to as denitrification, and the stoichiometry of this
reaction is (Stumm & Morgan 1981):

\[
4\text{NO}_3^- + 4\text{H}^+ + 5\text{CH}_2\text{O} \rightarrow 2\text{N}_2 + 7\text{H}_2\text{O} + 5\text{CO}_2
\]  

(3-4k)

The last term in Eq. 3-4 accounts for the effect of denitrification on dissolved organic
carbon. The kinetics of denitrification in the model are first-order:

\[
\text{Denit} = \frac{K_{HOR_D} \text{NO}_3}{K_{HOR_D} \text{DO} + \text{DO} K_{HDN_N} + \text{NO}_3} \times AANOX \times K_{DOC} \tag{3-41}
\]

K_{HDN_N} = denitrification half-saturation constant for nitrate (g N m\(^{-3}\))
AANOX = ratio of denitrification rate to oxic dissolved organic carbon respiration rate.
In Eq. 3-41, the dissolved organic carbon respiration rate, K_{DOC}, is modified so that
significant decomposition via denitrification occurs only when nitrate is freely available
and dissolved oxygen is depleted. The ratio, AANOX, makes the anoxic respiration
slower than oxic respiration. Note that K_{DOC}, defined in Eq. 3-4j, includes the temperature
effect on denitrification.
III-3. Phosphorus

The present model has four state variables for phosphorus: three organic forms (refractory particulate, labile particulate and dissolved) and one inorganic form (total phosphate).

A. Particulate organic phosphorus: For refractory and labile particulate organic phosphorus, sources and sinks included in the model are (Fig. 3-1):

- algal basal metabolism and predation
- dissolution to dissolved organic phosphorus
- settling
- external loads

The kinetic equations for refractory and labile particulate organic phosphorus are:

\[
\frac{\partial RPOP}{\partial t} = \sum_{x\in\mathcal{A}_g} (FPR_x \cdot BM_x + FPRP \cdot PR_x)APC_x \cdot B_x - K_{RPOP} \cdot RPOP \\
+ \frac{\partial}{\partial z} (WS_{RP} \cdot RPOP) + \frac{WRPOP}{V}
\]  

(3-5)

\[
\frac{\partial LPOP}{\partial t} = \sum_{x\in\mathcal{A}_g} (FPL_x \cdot BM_x + FPLP \cdot PR_x)APC_x \cdot B_x - K_{LPOP} \cdot LPOP \\
+ \frac{\partial}{\partial z} (WS_{LP} \cdot LPOP) + \frac{WLPOP}{V}
\]  

(3-6)

RPOP = concentration of refractory particulate organic phosphorus (g P m\(^{-3}\))
LPOP = concentration of labile particulate organic phosphorus (g P m\(^{-3}\))
FPR\(_x\) = fraction of metabolized phosphorus by algal group \(x\) produced as refractory particulate organic phosphorus
FPL\(_x\) = fraction of metabolized phosphorus by algal group \(x\) produced as labile particulate organic phosphorus
FPRP = fraction of predated phosphorus produced as refractory particulate organic phosphorus
FPLP = fraction of predated phosphorus produced as labile particulate organic phosphorus
APC = mean phosphorus-to-carbon ratio in all algal groups (g P per g C)
\[ K_{\text{RPOP}} = \text{hydrolysis rate of refractory particulate organic phosphorus (day}^{-1}) \]
\[ K_{\text{LPOP}} = \text{hydrolysis rate of labile particulate organic phosphorus (day}^{-1}) \]
\[ \text{WRPOP} = \text{external loads of refractory particulate organic phosphorus (g P day}^{-1}) \]
\[ \text{WLPOP} = \text{external loads of labile particulate organic phosphorus (g P day}^{-1}). \]

**B. Dissolved organic phosphorus:** Sources and sinks included in the model are (Fig. 3-1):
- algal basal metabolism and predation
- dissolution from refractory and labile particulate organic phosphorus
- mineralization to phosphate phosphorus
- external loads

The kinetic equation describing these processes is:

\[
\frac{dDOP}{dt} = \sum_{x=g,d} \left( FPD_x \cdot BM_x + FPDP \cdot PR \right) \cdot APC \cdot B_x
\]
\[ + K_{\text{RPOP}} \cdot \text{RPOP} + K_{\text{LPOP}} \cdot \text{LPOP} - K_{\text{DOP}} \cdot \text{DOP} + \frac{WDOP}{V} \tag{3-7} \]

\[ \text{DOP} = \text{concentration of dissolved organic phosphorus (g P m}^{-3} \)
\[ \text{FPD}_x = \text{fraction of metabolized phosphorus by algal group x produced as dissolved organic phosphorus} \]
\[ \text{FPDP} = \text{fraction of predated phosphorus produced as dissolved organic phosphorus} \]
\[ K_{\text{DOP}} = \text{mineralization rate of dissolved organic phosphorus (day}^{-1}) \]
\[ \text{WDOP} = \text{external loads of dissolved organic phosphorus (g P day}^{-1}). \]

**C. Total phosphate:** For total phosphate that includes both dissolved and sorbed phosphate (Section III-3-1), sources and sinks included in the model are (Fig. 3-1):
- algal basal metabolism, predation, and uptake
- mineralization from dissolved organic phosphorus
- settling of sorbed phosphate
- sediment-water exchange of dissolved phosphate for the bottom layer only
- external loads

The kinetic equation describing these processes is:
\[
\frac{\partial \text{PO}4t}{\partial t} = \sum_{x \in X} (\text{FPI}_x \cdot \text{BM}_x + \text{FPIP} \cdot \text{PR}_x - \text{P}_x \cdot \text{APC} \cdot \text{B}_x + K_{\text{DOP}} \cdot \text{DOP})
\]

\[
+ \frac{\partial}{\partial z} (\text{WS}_{\text{TSS}} \cdot \text{PO}4p) + \frac{\text{BFPO}4d}{\Delta z} + \frac{\text{WPO}4t}{V}
\]

(3-8)

\text{PO}4t = \text{total phosphate} (\text{g P m}^{-3}) = \text{PO}4d + \text{PO}4p \quad (3-8a)

\text{PO}4d = \text{dissolved phosphate} (\text{g P m}^{-3})

\text{PO}4p = \text{particulate (sorbed) phosphate} (\text{g P m}^{-3})

\text{FPI}_x = \text{fraction of metabolized phosphorus by algal group } x \text{ produced as inorganic phosphorus}

\text{FPIP} = \text{fraction of predated phosphorus produced as inorganic phosphorus}

\text{WS}_{\text{TSS}} = \text{settling velocity of suspended solid} (\text{m day}^{-1}), \text{provided by the hydrodynamic model}

\text{BFPO}4d = \text{sediment-water exchange flux of phosphate} (\text{g P m}^{-2} \text{ day}^{-1}), \text{applied to the bottom layer only}

\text{WPO}4t = \text{external loads of total phosphate} (\text{g P day}^{-1}).

In Eq. 3-8, if total active metal is chosen as a measure of sorption site, the settling velocity of total suspended solid, \text{WS}_{\text{TSS}}, is replaced by that of particulate metal, \text{WS}_{s} (\text{Sections III-3-1 and III-8}). The remainder of this section explains each term in Equations 3-5 to 3-8, except \text{BFPO}4d described in Chapter IV.

III-3-1. Total phosphate system

Suspended and bottom sediment particles (clay, silt and metal hydroxides) adsorb and desorb phosphate in river and estuarine waters. This adsorption-desorption process has been suggested to buffer phosphate concentration in water column and to enhance the transport of phosphate away from its external sources (Carritt & Goodgal 1954; Froelich 1988; Lebo 1991). To ease the computational complication due to the adsorption-desorption of phosphate, dissolved and sorbed phosphate are treated and transported as a single state variable. Therefore, the model phosphate state variable, total phosphate, is defined as the sum of dissolved and sorbed phosphate (Eq. 3-8a), and the concentrations for each fraction are determined by equilibrium partitioning of their sum.
In CE-QUAL-ICM, sorption of phosphate to particulate species of metals including iron and manganese was considered based on phenomenon observed in the monitoring data from the mainstem of the Chesapeake Bay: phosphate was rapidly depleted from anoxic bottom waters during the autumn reaeration event (Cerco & Cole 1994). Their hypothesis was that reaeration of bottom waters caused dissolved iron and manganese to precipitate, and phosphate sorbed to newly-formed metal particles and rapidly settled to the bottom. One state variable, total active metal, in CE-QUAL-ICM was defined as the sum of all metals that act as sorption sites, and the total active metal was partitioned into particulate and dissolved fractions via an equilibrium partitioning coefficient (Section III-8). Then, phosphate was assumed to sorb to only the particulate fraction of the total active metal.

In the treatment of phosphate sorption in CE-QUAL-ICM, the particulate fraction of metal hydroxides was emphasized as a sorption site in bottom waters under anoxic conditions. Phosphorus is a highly particle-reactive element, and phosphate in solution reacts quickly with a wide variety of surfaces, being taken up by and released from particles (Froelich 1988). The present model has two options, total suspended solid and total active metal, as a measure of a sorption site for phosphate, and dissolved and sorbed fractions are determined by equilibrium partitioning of their sum as a function of total suspended solid or total active metal concentration:

\[
P_{O4p} = \frac{K_{PO4p} \cdot TSS}{1 + K_{PO4p} \cdot TSS} \cdot P_{O4t} \quad \text{or} \quad P_{O4p} = \frac{K_{PO4p} \cdot TAMp}{1 + K_{PO4p} \cdot TAMp} \cdot P_{O4t} \quad (3-8b)
\]

\[
P_{O4d} = \frac{1}{1 + K_{PO4p} \cdot TSS} \cdot P_{O4t} \quad \text{or} \quad P_{O4d} = \frac{1}{1 + K_{PO4p} \cdot TAMp} \cdot P_{O4t}
\]

\[
= P_{O4t} - P_{O4p} \quad (3-8c)
\]

\[K_{PO4p} = \text{empirical coefficient relating phosphate sorption to total suspended solid (per g m}^{-3}) \text{ or particulate total active metal (per mol m}^{-3}) \text{ concentration}\]

\[TAMp = \text{particulate total active metal (mol m}^{-3}).\]

Dividing Eq. 3-8b by Eq. 3-8c gives:

\[
K_{PO4p} = \frac{P_{O4p}}{P_{O4d} \cdot TSS} \quad \text{or} \quad K_{PO4p} = \frac{P_{O4p}}{P_{O4d} \cdot TAMp} \quad (3-8d)
\]
where the meaning of $K_{\text{RO4}}$ becomes apparent, i.e., the ratio of sorbed to dissolved phosphate per unit concentration of total suspended solid or particulate total active metal (i.e., per unit sorption site available).

III-3-2. Algal phosphorus-to-carbon ratio (APC)

Algal biomass is quantified in units of carbon per volume of water. In order to express the effects of algal biomass on phosphorus and nitrogen, the ratios of phosphorus-to-carbon and nitrogen-to-carbon in algal biomass must be specified. Although global mean values of these ratios are well known (Redfield et al. 1963), algal composition varies especially as a function of nutrient availability. As phosphorus and nitrogen become scarce, algae adjust their composition so that smaller quantities of these vital nutrients are required to produce carbonaceous biomass (DiToro 1980; Parsons et al. 1984). Examining the field data from the surface of upper Chesapeake Bay, Cerco & Cole (1994) showed that the variation of nitrogen-to-carbon stoichiometry was small and thus used a constant algal nitrogen-to-carbon ratio, $\text{ANC}_x$. Large variations, however, were observed for algal phosphorus-to-carbon ratio indicating the adaptation of algae to ambient phosphorus concentration (Cerco & Cole 1994): algal phosphorus content is high when ambient phosphorus is abundant and is low when ambient phosphorus is scarce. Thus, a variable algal phosphorus-to-carbon ratio, APC, is used in model formulation. A mean ratio for all algal group, APC, is described by an empirical approximation to the trend observed in field data (Cerco & Cole 1994):

$$\text{APC} = \left( \text{CP}_{\text{prm1}} + \text{CP}_{\text{prm2}} \cdot \exp\left[-\text{CP}_{\text{prm3}} \cdot P_{\text{O4d}}\right]\right)^{-1} \quad (3-8e)$$

$\text{CP}_{\text{prm1}} = \text{minimum carbon-to-phosphorus ratio (g C per g P)}$

$\text{CP}_{\text{prm2}} = \text{difference between minimum and maximum carbon-to-phosphorus ratio (g C per g P)}$

$\text{CP}_{\text{prm3}} = \text{effect of dissolved phosphate concentration on carbon-to-phosphorus ratio (per g P m}^{-3}\text{)}$.

III-3-3. Effect of algae on phosphorus

The terms within summation ($\Sigma$) in Equations 3-5 to 3-8 account for the effects of
algae on phosphorus. Both basal metabolism (respiration and excretion) and predation are considered, and thus formulated, to contribute to organic and phosphate phosphorus. That is, the total loss by basal metabolism ($BM_x \cdot B_x$ in Eq. 3-1) is distributed using distribution coefficients; $FPR_x$, $FPL_x$, $FPD_x$ and $FPI_x$. The total loss by predation ($PR_x \cdot B_x$ in Eq. 3-1), is also distributed using distribution coefficients; $FPRP$, $FPLP$, $FPDP$ and $FPIP$. The sum of four distribution coefficients for basal metabolism should be unity, and so is that for predation. Algae take up dissolved phosphate for growth, and algae uptake of phosphate is represented by $(- \sum P_x \cdot APC \cdot B_x)$ in Eq. 3-8.

III-3-4. Mineralization and hydrolysis

The third term on the RHS of Equations 3-5 and 3-6 represents hydrolysis of particulate organic phosphorus and the last term in Eq. 3-7 represents mineralization of dissolved organic phosphorus. Mineralization of organic phosphorus is mediated by the release of nucleotidase and phosphatase enzymes by bacteria (Chröst & Overbek 1987) and algae (Boni et al. 1989). Since the algae themselves release the enzymes and bacterial abundance is related to algal biomass, the rate of organic phosphorus mineralization is related to algal biomass in model formulation. Another mechanism included in model formulation is that algae stimulate production of an enzyme that mineralizes organic phosphorus to phosphate when phosphate is scarce (Chröst & Overbek 1987; Boni et al. 1989). The formulations for hydrolysis and mineralization rates including these processes are:

\[
K_{RPOP} = (K_{RP} + \frac{KHP}{KHP + PO4d} K_{RP_{alg}} \sum_{x=0, g} B_x \cdot \exp(KT_{HDR}[T - TR_{HDR}])) \quad (3-8f)
\]

\[
K_{LPOP} = (K_{LP} + \frac{KHP}{KHP + PO4d} K_{LP_{alg}} \sum_{x=0, g} B_x \cdot \exp(KT_{HDR}[T - TR_{HDR}])) \quad (3-8g)
\]

\[
K_{DOP} = (K_{DP} + \frac{KHP}{KHP + PO4d} K_{DP_{alg}} \sum_{x=0, g} B_x \cdot \exp(KT_{MNL}[T - TR_{MNL}])) \quad (3-8h)
\]

$K_{RP}$ = minimum hydrolysis rate of refractory particulate organic phosphorus (day\(^{-1}\))

$K_{LP}$ = minimum hydrolysis rate of labile particulate organic phosphorus (day\(^{-1}\))

$K_{DP}$ = minimum mineralization rate of dissolved organic phosphorus (day\(^{-1}\))
\[ K_{rPa_b} \text{ and } K_{lPa_b} = \text{constants that relate hydrolysis of refractory and labile particulate organic phosphorus, respectively, to algal biomass (day}^{-1} \text{per g C m}^{-3}) \]

\[ K_{dPa_b} = \text{constant that relates mineralization to algal biomass (day}^{-1} \text{per g C m}^{-3}) \]

\[ K_{HP} = \text{mean half-saturation constant for algal phosphorus uptake (g P m}^{-3}) \]

\[ = \frac{1}{3} \sum_{x=c,d,g} K_{HP_x} \quad (3-8i) \]

When phosphate is abundant relative to KHP, the rates become to be close to the minimum values with little influence from algal biomass. When phosphate becomes scarce relative to KHP, the rates increase with the magnitude of increase depending on algal biomass. Equations 3-8f to 3-8h have exponential functions that relate rates to temperature.

III-4. Nitrogen

The present model has five state variables for nitrogen: three organic forms (refractory particulate, labile particulate and dissolved) and two inorganic forms (ammonium and nitrate). The nitrate state variable in the model represents the sum of nitrate and nitrite.

A. Particulate organic nitrogen: For refractory and labile particulate organic nitrogen, sources and sinks included in the model are (Fig. 3-1):

- algal basal metabolism and predation
- dissolution to dissolved organic nitrogen
- settling
- external loads

The kinetic equations for refractory and labile particulate organic nitrogen are:

\[
\frac{\partial RPO_N}{\partial t} = \sum_{x=c,d,g} (FNR_x \cdot BM_x + FNRP-PR_x)ANC_x \cdot B_x - K_{RPON} \cdot RPO_N
\]

\[
+ \frac{\partial}{\partial z} (W_{RP} \cdot RPO_N) + \frac{W_{RPON}}{V} \]

\[
\frac{\partial LPO_N}{\partial t} = \sum_{x=c,d,g} (FNL_x \cdot BM_x + FNLP-PR_x)ANC_x \cdot B_x - K_{LPON} \cdot LPO_N
\]

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\[ \frac{\partial \text{DON}}{\partial t} = \sum_{x=r,d,g} (\text{FND}_x \cdot \text{BM}_x + \text{FNDP} \cdot \text{PR}) \cdot \text{ANC}_x \cdot \text{B}_x \]

\[ + \frac{K_{\text{RPON}} \cdot \text{RPON} + K_{\text{LPON}} \cdot \text{LPON} - K_{\text{DON}} \cdot \text{DON} + \frac{\text{WDON}}{V}}{\text{ANC}_x \cdot \text{B}_x} \]  

(3-11)

DON = concentration of dissolved organic nitrogen (g N m\(^{-3}\))

FND\(_x\) = fraction of metabolized nitrogen by algal group \(x\) produced as dissolved organic nitrogen

FNDP = fraction of predated nitrogen produced as dissolved organic nitrogen

K\(_{\text{DON}}\) = mineralization rate of dissolved organic nitrogen (day\(^{-1}\))
WOON = external loads of dissolved organic nitrogen (g N day\(^{-1}\)).

C. Ammonium nitrogen: Sources and sinks included in the model are (Fig. 3-1):

- algal basal metabolism, predation, and uptake
- mineralization from dissolved organic nitrogen
- nitrification to nitrate
- sediment-water exchange for the bottom layer only
- external loads

The kinetic equation describing these processes is:

\[
\frac{\partial NH_4}{\partial t} = \sum_{x \in \text{alg}} (FN_{I_x} \cdot BM_x + FN_{IP} \cdot PR_x - PN_x \cdot P \cdot ANC_x \cdot B_x + K_{DON} \cdot DON - \text{Nit}\cdot NH_4 + \frac{BFNH_4}{\Delta z} + \frac{WNH_4}{V}) \tag{3-12}
\]

FN_{I_x} = fraction of metabolized nitrogen by algal group x produced as inorganic nitrogen

FN_{IP} = fraction of predated nitrogen produced as inorganic nitrogen

PN_x = preference for ammonium uptake by algal group x (0 ≤ PN_x ≤ 1)

Nit = nitrification rate (day\(^{-1}\)) given in Eq. 3-13g

BFNH_4 = sediment-water exchange flux of ammonium (g N m\(^{-2}\) day\(^{-1}\)), applied to the bottom layer only

WNH_4 = external loads of ammonium (g N day\(^{-1}\)).

D. Nitrate nitrogen: Sources and sinks included in the model are (Fig. 3-1):

- algal uptake
- nitrification from ammonium
- denitrification to nitrogen gas
- sediment-water exchange for the bottom layer only
- external loads

The kinetic equation describing these processes is:

\[
\frac{\partial NO_3}{\partial t} = - \sum_{x \in \text{alg}} (1 - PN_x) P \cdot ANC_x \cdot B_x + \text{Nit}\cdot NH_4 - ANDC\cdot Denit\cdot DOC + \frac{BFNO_3}{\Delta z} + \frac{WN_3}{V} \tag{3-13}
\]
ANDC = mass of nitrate nitrogen reduced per mass of dissolved organic carbon oxidized
(0.933 g N per g C from Eq. 3-4k)
BFNO3 = sediment-water exchange flux of nitrate (g N m\(^{-2}\) day\(^{-1}\)), applied to the bottom layer only
WNO3 = external loads of nitrate (g N day\(^{-1}\)).
The remainder of this section explains each term in Equations 3-9 to 3-13, except BFNH4 and BFNO3 described in Chapter IV.

III-4-1. Effect of algae on nitrogen

The terms within summation (\(\sum\)) in Equations 3-9 to 3-13 account for the effects of algae on nitrogen. As in phosphorus, both basal metabolism (respiration and excretion) and predation are considered, and thus formulated, to contribute to organic and ammonium nitrogen. That is, algal nitrogen released by both basal metabolism and predation are represented by distribution coefficients; FNR\(_x\), FNL\(_x\), FND\(_x\), FNI\(_x\), FNRP, FNLP, FNDP and FNIP. The sum of four distribution coefficients for basal metabolism should be unity, and so is that for predation.

Algae take up ammonium and nitrate for growth, and ammonium is preferred from thermodynamic considerations. The preference of algae for ammonium is expressed as:

\[
P_{N_x} = \frac{NH_4}{(KHN_x + NH_4)(KHN_x + NO_3)} + \frac{KHN_x}{(NH_4 + NO_3)(KHN_x + NO_3)}
\]  

(3-13a)

This equation forces the preference for ammonium to be unity when nitrate is absent, and to be zero when ammonium is absent.

III-4-2. Mineralization and hydrolysis

The third term on the RHS of Equations 3-9 and 3-10 represents hydrolysis of particulate organic nitrogen and the last term in Eq. 3-11 represents mineralization of dissolved organic nitrogen. Including a mechanism for accelerated hydrolysis and mineralization during nutrient-limited conditions (Section III-3-4), the formulations for these processes are:
\[ K_{\text{RPN}} = (K_{\text{RN}} + \frac{KHN}{KHN + NH_4 + NO_3} \sum_{x=1}^{d} B_x) \cdot \exp(KT_{\text{HDR}}(T - TR_{\text{HDR}})) \]  
(3-13b)

\[ K_{\text{LPON}} = (K_{\text{LN}} + \frac{KHN}{KHN + NH_4 + NO_3} \sum_{x=1}^{d} B_x) \cdot \exp(KT_{\text{HDR}}(T - TR_{\text{HDR}})) \]  
(3-13c)

\[ K_{\text{DON}} = (K_{\text{DN}} + \frac{KHN}{KHN + NH_4 + NO_3} \sum_{x=1}^{d} B_x) \cdot \exp(KT_{\text{MN}}(T - TR_{\text{MN}})) \]  
(3-13d)

- \( K_{\text{RN}} \) = minimum hydrolysis rate of refractory particulate organic nitrogen (day\(^{-1}\))
- \( K_{\text{LN}} \) = minimum hydrolysis rate of labile particulate organic nitrogen (day\(^{-1}\))
- \( K_{\text{DN}} \) = minimum mineralization rate of dissolved organic nitrogen (day\(^{-1}\))
- \( K_{\text{RN}alg} \) & \( K_{\text{LN}alg} \) = constants that relate hydrolysis of refractory and labile particulate organic nitrogen, respectively, to algal biomass (day\(^{-1}\) per g C m\(^{-3}\))
- \( K_{\text{DN}alg} \) = constant that relates mineralization to algal biomass (day\(^{-1}\) per g C m\(^{-3}\))
- \( K_{\text{HN}} \) = mean half-saturation constant for algal nitrogen uptake (g N m\(^{-3}\))

\[ K_{\text{HN}} = \frac{1}{3} \sum_{x=1}^{d} K_{\text{HN}_x} \]  
(3-13e)

Equations 3-13b to 3-13d have exponential functions that relate rates to temperature.

### III-4-3. Nitrification

Nitrification is a process mediated by autotrophic nitrifying bacteria that obtain energy through the oxidation of ammonium to nitrite and of nitrite to nitrate. The stoichiometry of complete reaction is (Bowie et al. 1985):

\[ \text{NH}_4^+ + 2 \text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ \]  
(3-13f)

The first term in the second line of Eq. 3-12 and its corresponding term in Eq. 3-13 represent the effect of nitrification on ammonium and nitrate, respectively. The kinetics of complete nitrification process are formulated as a function of available ammonium, dissolved oxygen and temperature:

\[ \text{Nit} = \frac{DO}{KHNit_{DO} + DO \cdot KHNit_{N} + NH_4} \cdot \frac{1}{f_{\text{Nit}}(T)} \]  
(3-13g)

\[ f_{\text{Nit}}(T) = \exp(-KNit1(T - TNit)^2) \quad \text{if} \quad T \leq TNit \]
\[
= \exp(-KNit2[TNit - T]^2) \quad \text{if} \quad T > TNit 
\]

\(KHNit_{bo} = \) nitrification half-saturation constant for dissolved oxygen (g O\(_2\) m\(^{-3}\))

\(KHNit_{n} = \) nitrification half-saturation constant for ammonium (g N m\(^{-3}\))

\(Nit_m = \) maximum nitrification rate at TNit (g N m\(^{-3}\) day\(^{-1}\))

\(TNit = \) optimum temperature for nitrification (°C)

\(KNit1 = \) effect of temperature below TNit on nitrification rate (°C\(^{-2}\))

\(KNit2 = \) effect of temperature above TNit on nitrification rate (°C\(^{-2}\)).

The Monod function of dissolved oxygen in Eq. 3-13g indicates the inhibition of nitrification at low oxygen level. The Monod function of ammonium indicates that when ammonium is abundant, the nitrification rate is limited by availability of nitrifying bacteria. The effect of suboptimal temperature is represented using Gaussian form.

III-4-4. Denitrification

The effect of denitrification on dissolved organic carbon is described in Section III-2-3. Denitrification removes nitrate from the system in stoichiometric proportion to carbon removal as determined by Eq. 3-4k. The last term in the first line of Eq. 3-13 represent this removal of nitrate.

III-5. Silica

The present model has two state variables for silica: particulate biogenic silica and available silica.

A. **Particulate biogenic silica**: Sources and sinks included in the model are (Fig. 3-1):

\(\text{diatom basal metabolism and predation}\)

\(\text{dissolution to available silica}\)

\(\text{settling}\)

\(\text{external loads}\)

The kinetic equation describing these processes is:

\[
\frac{\partial SU}{\partial t} = (FSP_\text{d} \cdot BM_\text{d} + FSPP \cdot PR_\text{d})ASCD_\text{d} \cdot B_d - K_{\text{SU}} \cdot SU + \frac{\partial}{\partial z} (WS_d \cdot SU) + \frac{WSU}{V} 
\]

\(SU = \) concentration of particulate biogenic silica (g Si m\(^{-3}\)).
FSP_d = fraction of metabolized silica by diatoms produced as particulate biogenic silica
FSPP = fraction of predated diatom silica produced as particulate biogenic silica
ASC_d = silica-to-carbon ratio of diatoms (g Si per g C)
K_{SIA} = dissolution rate of particulate biogenic silica (day^-1)
WSU = external loads of particulate biogenic silica (g Si day^-1).

B. Available silica: Sources and sinks included in the model are (Fig. 3-1):
- diatom basal metabolism, predation, and uptake
- settling of sorbed (particulate) available silica
- dissolution from particulate biogenic silica
- sediment-water exchange of dissolved silica for the bottom layer only
- external loads

The kinetic equation describing these processes is:

\[
\frac{\partial S_A}{\partial t} = (FSI_d \cdot BM_d + FSIP \cdot PR_d - P_d)ASC_d \cdot B_d + K_{SIA} \cdot SU + \frac{\partial}{\partial z} (WS_{TSS} \cdot SAp) + \frac{BFSAd}{\Delta z} + \frac{WSA}{V}
\]  

(3-15)

SA = concentration of available silica (g Si m^-3) = SAd + SAp  
SAd = dissolved available silica (g Si m^-3)  
SAp = particulate (sorbed) available silica (g Si m^-3)  
FSI_d = fraction of metabolized silica by diatoms produced as available silica  
FSIP = fraction of predated diatom silica produced as available silica  
BFSAd = sediment-water exchange flux of available silica (g Si m^-2 day^-1), applied to the bottom layer only.

WSA = external loads of available silica (g Si day^-1).

In Eq. 3-15, if total active metal is chosen as a measure of sorption site, the settling velocity of total suspended solid, WS_{TSS}, is replaced by that of particulate metal, WS_s (Sections III-5-1 and III-8). The remainder of this section explains each term in Equations 3-14 and 3-15, except BFSAd described in Chapter IV.

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III-5-1. Available silica system

Analysis of Chesapeake Bay monitoring data indicates that silica shows similar behavior as phosphate in the adsorption-desorption process (Cerco & Cole 1994). As in phosphate, therefore, available silica is defined to include both dissolved and sorbed fractions (Eq. 3-15a). Treatment of available silica is the same as total phosphate and the same method to partition dissolved and sorbed phosphate is used to partition dissolved and sorbed available silica:

\[
S_{Ap} = \frac{K_{Sp} \cdot TSS}{1 + K_{Sp} \cdot TSS} \cdot SA
\]

or

\[
S_{Ap} = \frac{K_{Sp} \cdot TAMp}{1 + K_{Sp} \cdot TAMp} \cdot SA
\] (3-15b)

\[
S_{Ad} = \frac{1}{1 + K_{Sp} \cdot TSS} \cdot SA
\]

or

\[
S_{Ad} = \frac{1}{1 + K_{Sp} \cdot TAMp} \cdot SA
\] (3-15c)

\[
K_{Sp} = \text{empirical coefficient relating available silica sorption to total suspended solid (per g m}^{-3} \text{) or particulate total active metal (per mol m}^{-3} \text{) concentration.}
\]

As in \(K_{PO4}\) in Section III-3-1, \(K_{Sp}\) is the ratio of sorbed to dissolved available silica per unit sorption site available.

III-5-2. Effect of diatoms on silica

In Equations 3-14 and 3-15, those terms expressed as a function of diatom biomass \(B_d\) account for the effects of diatoms on silica. As in phosphorus and nitrogen, both basal metabolism (respiration and excretion) and predation are considered, and thus formulated, to contribute to particulate biogenic and available silica. That is, diatom silica released by both basal metabolism and predation are represented by distribution coefficients; \(F_{SPd}, F_{SIp}, F_{SP}, \text{ and } F_{SI}.\) The sum of two distribution coefficients for basal metabolism should be unity, and so is that for predation. Diatoms require silica as well as phosphorus and nitrogen, and diatom uptake of available silica is represented by \((- P_d \cdot ASC_d \cdot B_d)\) in Eq. 3-15.
III-5-3. Dissolution

The term \(- K_{SU}A\) in Eq. 3-14 and its corresponding term in Eq. 3-15 represent dissolution of particulate biogenic silica to available silica. The dissolution rate is expressed as an exponential function of temperature:

\[
K_{SU}A = K_{SU} \cdot \exp(K_{T_{SU}}(T - TR_{SU}))
\]  
(3-15d)

\(K_{SU}\) = dissolution rate of particulate biogenic silica at \(TR_{SU}A\) (day\(^{-1}\))

\(K_{T_{SU}}\) = effect of temperature on dissolution of particulate biogenic silica (°C\(^{-1}\))

\(TR_{SU}A\) = reference temperature for dissolution of particulate biogenic silica (°C).

III-6. Chemical Oxygen Demand

In the present model, chemical oxygen demand is the concentration of reduced substances that are oxidizable through inorganic means. The source of chemical oxygen demand in saline water is sulfide released from sediments. A cycle occurs in which sulfate is reduced to sulfide in the sediments and reoxidized to sulfate in the water column. In freshwater, methane is released to the water column by the sediment process model. Both sulfide and methane are quantified in units of oxygen demand and are treated with the same kinetic formulation. The kinetic equation including external loads, if any, is:

\[
\frac{\partial COD}{\partial t} = -\frac{DO}{KH_{COD}} + \frac{DO}{KH_{COD}} KCOD \cdot COD + \frac{BFCOD}{\Delta z} + \frac{WCOD}{V}
\]  
(3-16)

COD = concentration of chemical oxygen demand (g O\(_2\)-equivalents m\(^{-3}\))

\(KH_{COD}\) = half-saturation constant of dissolved oxygen required for oxidation of chemical oxygen demand (g O\(_2\) m\(^{-3}\))

\(KCOD\) = oxidation rate of chemical oxygen demand (day\(^{-1}\))

\(BFCOD\) = sediment flux of chemical oxygen demand (g O\(_2\)-equivalents m\(^2\) day\(^{-1}\)), applied to the bottom layer only

\(WCOD\) = external loads of chemical oxygen demand (g O\(_2\)-equivalents day\(^{-1}\)).

An exponential function is used to describe the temperature effect on the oxidation rate of chemical oxygen demand:

\[
KCOD = K_{CD} \cdot \exp(K_{T_{COD}}(T - TR_{COD}))
\]  
(3-16a)
$K_{CD} = \text{oxidation rate of chemical oxygen demand at } TR_{CD} \text{ (day}^{-1})$

$KT_{CD} = \text{effect of temperature on oxidation of chemical oxygen demand (°C})$

$TR_{CD} = \text{reference temperature for oxidation of chemical oxygen demand (°C}).$

III-7. Dissolved Oxygen

Sources and sinks of dissolved oxygen in the water column included in the model are (Fig. 3-1):

- algal photosynthesis and respiration
- nitrification
- heterotrophic respiration of dissolved organic carbon
- oxidation of chemical oxygen demand
- surface reaeration for the surface layer only
- sediment oxygen demand for the bottom layer only
- external loads

The kinetic equation describing these processes is:

$$\frac{\partial DO}{\partial t} = \sum_{x=cd,g} \left( (1.3 - 0.3 \cdot PN) P_x - (1 - FCD) \frac{DO}{KHR_x + DO} BM_x \right) AOCR \cdot B_x$$

$$- AONT \cdot \text{Nit-NH}_4 - AOCR \cdot K_{hr} \cdot DOC - \frac{DO}{KH_{COO} + DO} \cdot KCOD \cdot COD$$

$$+ K_{r} (DO_s - DO) + \frac{SOD}{\Delta z} + \frac{WDO}{V}$$

(3-17)

$AONT = \text{mass of dissolved oxygen consumed per unit mass of ammonium nitrogen nitrified (4.33 g O}_2 \text{ per g N: Section III-7-2)}$

$AOCR = \text{dissolved oxygen-to-carbon ratio in respiration (2.67 g O}_2 \text{ per g C: Section III-7-1)}$

$K_{r} = \text{reaeration coefficient (day}^{-1}); \text{ the reaeration term is applied to the surface layer only}$

$DO_s = \text{saturated concentration of dissolved oxygen (g O}_2 \text{ m}^{-3})$

$SOD = \text{sediment oxygen demand (g O}_2 \text{ m}^{-2} \text{ day}^{-1}); \text{ applied to the bottom layer only: positive is to the water column}$
WDO = external loads of dissolved oxygen (g O₂ day⁻¹).

The two sink terms in Eq. 3-17, heterotrophic respiration and chemical oxygen demand, are explained in Sections III-2-2 (Eq. 3-4g) and III-6 (Eq. 3-16), respectively. The remainder of this section explains the effects of algae, nitrification and surface reaeration.

III-7-1. Effect of algae on dissolved oxygen

The first line on the RHS of Eq. 3-17 accounts for the effects of algae on dissolved oxygen. Algae produce oxygen through photosynthesis and consume oxygen through respiration. The quantity produced depends on the form of nitrogen utilized for growth. Equations describing production of dissolved oxygen are (Morel 1983):

\[106CO_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O \rightarrow protoplasm + 106O_2 + 15H^+\]  
\[106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O + 17H^+ \rightarrow protoplasm + 138O_2\]

When ammonium is the nitrogen source, one mole of oxygen is produced per mole of carbon dioxide fixed. When nitrate is the nitrogen source, 1.3 moles of oxygen are produced per mole of carbon dioxide fixed. The quantity, \(1.3 - 0.3 \cdot PN_x\), in the first term of Eq. 3-17 is the photosynthesis ratio and represents the molar quantity of oxygen produced per mole of carbon dioxide fixed. It approaches unity as the algal preference for ammonium approaches unity.

The last term in the first line of Eq. 3-17 accounts for the oxygen consumption due to algal respiration (Eq. 3-4d). A simple representation of respiration process is:

\[CH_2O + O_2 \rightarrow CO_2 + H_2O\]

from which, AOCR = 2.67 g O₂ per g C.

III-7-2. Effect of nitrification on dissolved oxygen

The stoichiometry of nitrification reaction (Eq. 3-13f) indicates that two moles of oxygen are required to nitrify one mole of ammonium into nitrate. However, cell synthesis by nitrifying bacteria is accomplished by the fixation of carbon dioxide so that less than two moles of oxygen are consumed per mole ammonium utilized (Wezemak & Gannon 1968): AONT = 4.33 g O₂ per g N.
III-7-3. Effect of surface reaeration on dissolved oxygen

The reaeration rate of dissolved oxygen at the air-water interface is proportional to the oxygen gradient across the interface, \((\text{DO}_s - \text{DO})\), when assuming the air is saturated with oxygen. The saturated concentration of dissolved oxygen, which decreases as temperature and salinity increase, is specified using an empirical formula (Genet et al. 1974):

\[
\text{DO}_s = 14.5532 - 0.38217 \cdot T + 5.4258 \times 10^{-3} \cdot T^2 \\
- CL \cdot (1.665 \times 10^{-4} - 5.866 \times 10^{-6} \cdot T + 9.796 \times 10^{-8} \cdot T^2)
\]

(3-17d)

\(\text{CL} = \) chloride concentration = \(S/1.80655\).

The reaeration coefficient includes the effect of turbulence generated by bottom friction (O’Connor & Dobbins 1958) and that by surface wind stress (Banks & Herrera 1977):

\[
K_r = \left( K_{no} \sqrt{\frac{u_{eq}}{h_{eq}}} + W_{rea} \right) \frac{1}{\Delta z} \cdot KT_r^{-20}
\]

(3-17e)

\(K_{no} = \) proportionality constant = 3.933 in MKS unit
\(u_{eq} = \) weighted velocity over cross-section (m sec\(^{-1}\)) = \(\Sigma (u_k \cdot V_k) / \Sigma (V_k)\)
\(h_{eq} = \) weighted depth over cross-section (m) = \(\Sigma (V_k) / B_h\)
\(B_h = \) width at the free surface (m)
\(W_{rea} = \) wind-induced reaeration (m day\(^{-1}\))

\[
= 0.728 U_w^{14} - 0.317 U_w + 0.0372 U_w^2
\]

(3-17f)

\(U_w = \) wind speed (m sec\(^{-1}\)) at the height of 10 m above surface
\(KT_r = \) constant for temperature adjustment of DO reaeration rate.

III-8. Total Active Metal

The present model requires simulation of total active metal for adsorption of phosphate and silica if that option is chosen (Fig. 3-1). The total active metal state variable is the sum of iron and manganese concentrations, both particulate and dissolved. In the model, the origin of total active metal is benthic sediments. Since sediment release of metal is not explicit in the sediment model (Chapter IV), release is specified in the
kinetic portion of the water column model. The only other term included is settling of the particulate fraction. Then, the kinetic equation for total active metal including external loads, if any, may be written as:

\[
\frac{\partial TAM}{\partial t} = \frac{KH_{bfm}}{KH_{bfm} + DO} \frac{BFTAM}{e^{KTam(T - T_{tam})}} + \frac{\partial}{\partial z} (WS \cdot TAM) + \frac{WTAM}{V} \quad (3-18)
\]

TAM = total active metal concentration (mol m\(^{-3}\)) = TAMd + TAMp

TAMd = dissolved total active metal (mol m\(^{-3}\))

TAMp = particulate total active metal (mol m\(^{-3}\))

KH_{bfm} = dissolved oxygen concentration at which total active metal release is half the anoxic release rate (g O\(_2\) m\(^{-3}\))

BFTAM = anoxic release rate of total active metal (mol m\(^{-2}\) day\(^{-1}\)), applied to the bottom layer only

K_{tam} = effect of temperature on sediment release of total active metal (°C\(^{-1}\))

T_{tam} = reference temperature for sediment release of total active metal (°C).

WS = settling velocity of particulate metal (m day\(^{-1}\))

WTAM = external loads of total active metal (mol day\(^{-1}\)).

In estuaries, iron and manganese exist in particular and dissolved forms depending on dissolved oxygen concentration. In the oxygenated water, most of iron and manganese exist as particulate while under anoxic conditions, large fractions are dissolved although solid-phase sulfides and carbonates exist and may predominate. The partitioning between particulate and dissolved phases is expressed using a concept that total active metal concentration must achieve a minimum level, which is a function of dissolved oxygen, before precipitation occurs:

\[
TAMd = \min\{TAMdmx \exp(-K_{dotam} \cdot DO), TAM\} \quad (3-18b-1)
\]

\[
TAMp = TAM - TAMd \quad (3-18b-2)
\]

TAMdmx = solubility of total active metal under anoxic conditions (mol m\(^{-3}\))

K_{dotam} = constant that relates total active metal solubility to dissolved oxygen concentration (per g O\(_2\) m\(^{-3}\)).

The behavior of Eq. 3-19b is illustrated in Fig. 4-19 of Cerco & Cole (1994).
III-9. Fecal Coliform Bacteria

Fecal coliform bacteria are indicative of organisms from the intestinal tract of humans and other animals and can be used as an indicator bacteria as a measure of public health (Thomann & Mueller 1987). In the present model, fecal coliform bacteria have no interaction with other state variables, and have only one sink term, die-off. The kinetic equation including external loads may be written as:

$$\frac{\partial FCB}{\partial t} = -K_{FCB} \cdot T_{FCB} \cdot 20 \cdot FCB + \frac{W_{FCB}}{V}$$ (3-19)

FCB = bacteria concentration (MPN per 100 ml)
K_{FCB} = first order die-off rate at 20°C (day⁻¹)
T_{FCB} = effect of temperature on decay of bacteria (°C⁻¹)
W_{FCB} = external loads of fecal coliform bacteria (MPN per 100 ml m³ day⁻¹).

III-10. Method of Solution

The kinetic equations for the 21 state variables (Sections III-1 to III-9) can be expressed in a 21×21 matrix after linearizing some terms, mostly Monod type expressions:

$$\frac{\partial [C]}{\partial t} = [K] \cdot [C] + [R]$$ (3-20)

where [C] is in mass volume⁻¹, [K] is in time⁻¹ and [R] is in mass volume⁻¹ time⁻¹. Since the settling of particulate matter from the overlying cell acts as an input for a given cell, when Eq. 3-20 is applied to a cell of finite volume, it may be expressed as:

$$\frac{\partial [C]_k}{\partial t} = [K1]_k \cdot [C]_k + \lambda \cdot [K2]_k \cdot [C]_{k+1} + [R]_k$$ (3-21)

where the four matrices [C], [K1], [K2] and [R] are defined in Appendix A. The subscript k designates a cell at the kᵗʰ vertical layer. The layer index k increases upward: with KC vertical layers, k = 1 is the bottom layer and k = KC is the surface layer. Then, λ = 0 for k = KC, otherwise λ = 1. The matrix [K2] is a diagonal matrix, and the non-zero elements account for the settling of particulate matter from the overlying cell.

As explained in Chapter II, Eq. 3-21 is solved using a second-order accurate trapezoidal scheme over a time step of 0, which may be expressed as:

39
\[ [C]^N_k = \left( [I] - \frac{\theta}{2} [K I]^O_k \right)^{-1} \left( [C]^O_k + \frac{\theta}{2} \left( [K I]^O_k [C]^O_k + \lambda [K^2]^O_k [C]^O_{k+1} \right) + \theta [R]^O_k \right) \]  

(3-22)

where \( \theta = 2 \cdot m \cdot \Delta t \) is the time step for the kinetic equations (Fig. 2-1); \([I]\) is a unit matrix; \([C]^A = [C]^N + [C]^O\); the superscripts O and N designate the variables before and after being adjusted for the relevant kinetic processes. Since Eq. 3-22 is solved from the surface layer downward, the term with \([C]^A_k+1\) is known for the \(k\)th layer and thus placed on the RHS. In Eq. 3-22, inversion of a matrix can be avoided if the 21 state variables are solved in a proper order. The kinetic equations are solved in the order of the variables in the matrix \([C]\) defined in Appendix A. The final forms of Eq. 3-22 are also listed for each of the state variables in Appendix A.

III-11. Parameter Evaluation

The present water quality model involves many parameters that need to be evaluated from field data or through model calibration. The parameter values found from the model application to the Chesapeake Bay (Cerco & Cole 1994) are listed in Tables 3-1 to 3-7. These values, which were established after analyzing extensive data sets and model calibration, may serve as an excellent starting point for model application to estuaries of the eastern United States.
### Table 3-1. Parameters related to algae in water column.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value*</th>
<th>Equation Numberb</th>
</tr>
</thead>
<tbody>
<tr>
<td>*PM(_e) (day(^{-1}))</td>
<td>2.5 (upper Potomac only)</td>
<td>3-1a</td>
</tr>
<tr>
<td>*PM(_d) (day(^{-1}))</td>
<td>2.25</td>
<td>3-1a</td>
</tr>
<tr>
<td>*PM(_s) (day(^{-1}))</td>
<td>2.5</td>
<td>3-1a</td>
</tr>
<tr>
<td>KHN(_x) (g N m(^{-3}))</td>
<td>0.01 (all groups)</td>
<td>3-1c</td>
</tr>
<tr>
<td>KHP(_x) (g P m(^{-3}))</td>
<td>0.001 (all groups)</td>
<td>3-1c</td>
</tr>
<tr>
<td>KHS (g Si m(^{-3}))</td>
<td>0.05</td>
<td>3-1d</td>
</tr>
<tr>
<td>FD</td>
<td>temporally-varying input</td>
<td></td>
</tr>
<tr>
<td>I(_o) (langley(s) day(^{-1}))</td>
<td>temporally-varying input</td>
<td>3-1f</td>
</tr>
<tr>
<td>*Ke(_e) (m(^{-1}))</td>
<td>spatially-varying input</td>
<td>3-1h</td>
</tr>
<tr>
<td>Ke(_ess) (m(^{-1}) per g m(^{-3}))</td>
<td>NA(^{c})</td>
<td>3-1h</td>
</tr>
<tr>
<td>Ke(_cml) (m(^{-1}) per mg Chl m(^{-3}))</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>CChl(_x) (g C per mg Chl)</td>
<td>0.06 (all groups)</td>
<td>3-1h</td>
</tr>
<tr>
<td>(D(_{opt}))(_x) (m)</td>
<td>1.0 (all groups)</td>
<td>3-1i</td>
</tr>
<tr>
<td>((I)<em>(</em>{\infty})) (langley(s) day(^{-1}))</td>
<td>40.0</td>
<td>3-1i</td>
</tr>
<tr>
<td>Cl(_{cml}), Cl(<em>e), &amp; Cl(</em>{c})</td>
<td>0.7, 0.2 &amp; 0.1</td>
<td>3-1j</td>
</tr>
<tr>
<td>TM(_c), TM(_d), &amp; TM(_g) ((^\circ C))</td>
<td>27.5, 20.0 &amp; 25.0</td>
<td></td>
</tr>
<tr>
<td>KTG1(_f) &amp; KTG2(_e) ((^\circ C(^{-1})))</td>
<td>0.005 &amp; 0.004</td>
<td>3-1k</td>
</tr>
<tr>
<td>KTG1(_f) &amp; KTG2(_d) ((^\circ C(^{-1})))</td>
<td>0.004 &amp; 0.006</td>
<td>3-1k</td>
</tr>
<tr>
<td>KTG1(_g) &amp; KTG2(_g) ((^\circ C(^{-1})))</td>
<td>0.008 &amp; 0.01</td>
<td>3-1k</td>
</tr>
<tr>
<td>STOX (ppt)</td>
<td>1.0</td>
<td>3-1l</td>
</tr>
<tr>
<td>*BMR(_e) (day(^{-1}))</td>
<td>0.04</td>
<td>3-1m</td>
</tr>
<tr>
<td>*BMR(_d) (day(^{-1}))</td>
<td>0.01</td>
<td>3-1m</td>
</tr>
<tr>
<td>*BMR(_f) (day(^{-1}))</td>
<td>0.003 (Jan. - May in saltwater only)</td>
<td>3-1m</td>
</tr>
<tr>
<td>TR(_x) ((^\circ C))</td>
<td>20.0 (all groups)</td>
<td>3-1m</td>
</tr>
<tr>
<td>KTB(_x) ((^\circ C(^{-1})))</td>
<td>0.069 (all groups)</td>
<td>3-1m</td>
</tr>
<tr>
<td>*PRR(_e) (day(^{-1}))</td>
<td>0.01</td>
<td>3-1n</td>
</tr>
<tr>
<td>*PRR(_d) (day(^{-1}))</td>
<td>0.215</td>
<td>3-1n</td>
</tr>
<tr>
<td>*PRR(_f) (day(^{-1}))</td>
<td>0.065 (Jan. - May in saltwater only)</td>
<td>3-1n</td>
</tr>
<tr>
<td>*WS(_d) (m day(^{-1}))</td>
<td>0.35 (January - May)</td>
<td>3-1</td>
</tr>
<tr>
<td>*WS(_d) (m day(^{-1}))</td>
<td>0.1 (June - December)</td>
<td>3-1</td>
</tr>
<tr>
<td>*WS(_s) (m day(^{-1}))</td>
<td>0.1</td>
<td>3-1</td>
</tr>
</tbody>
</table>

* The evaluation of these values are detailed in Chapter IX of Cerco & Cole (1994).

b The equation number where the corresponding parameter is first shown and defined.

c Not available in Cerco & Cole (1994) since their formulations do not include these parameters.

* The parameters declared as an array in the source code.
Table 3-2. Parameters related to organic carbon in water column.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Valuea</th>
<th>Equation Numberb</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCRP</td>
<td>0.35</td>
<td>3-2</td>
</tr>
<tr>
<td>FCLP</td>
<td>0.55</td>
<td>3-3</td>
</tr>
<tr>
<td>FCDP</td>
<td>0.10</td>
<td>3-4</td>
</tr>
<tr>
<td>FCD</td>
<td>0.0 (all groups)</td>
<td>3-4</td>
</tr>
<tr>
<td>WS_{RP} (m day⁻¹)</td>
<td>1.0</td>
<td>3-2</td>
</tr>
<tr>
<td>WS_{LP} (m day⁻¹)</td>
<td>1.0</td>
<td>3-3</td>
</tr>
<tr>
<td>KHR_{x} (g O₂ m⁻³)</td>
<td>0.5 (all groups)</td>
<td>3-4</td>
</tr>
<tr>
<td>KHOR_{DO} (g O₂ m⁻³)</td>
<td>0.5</td>
<td>3-4g</td>
</tr>
<tr>
<td>K_{RC} (day⁻¹)</td>
<td>0.005</td>
<td>3-4h</td>
</tr>
<tr>
<td>K_{LC} (day⁻¹)</td>
<td>0.075</td>
<td>3-4i</td>
</tr>
<tr>
<td>K_{DC} (day⁻¹)</td>
<td>0.01</td>
<td>3-4j</td>
</tr>
<tr>
<td>K_{RC_{CA}} (day⁻¹ per g C m⁻³)</td>
<td>0.0</td>
<td>3-4h</td>
</tr>
<tr>
<td>K_{LC_{CA}} (day⁻¹ per g C m⁻³)</td>
<td>0.0</td>
<td>3-4i</td>
</tr>
<tr>
<td>K_{DC_{CA}} (day⁻¹ per g C m⁻³)</td>
<td>0.0</td>
<td>3-4j</td>
</tr>
<tr>
<td>TR_{HDR} (°C)</td>
<td>20.0</td>
<td>3-4h</td>
</tr>
<tr>
<td>TR_{MNL} (°C)</td>
<td>20.0</td>
<td>3-4j</td>
</tr>
<tr>
<td>KT_{HDR} (°C⁻¹)</td>
<td>0.069</td>
<td>3-4h</td>
</tr>
<tr>
<td>KT_{MNL} (°C⁻¹)</td>
<td>0.069</td>
<td>3-4j</td>
</tr>
<tr>
<td>KHDN_{N} (g N m⁻³)</td>
<td>0.1</td>
<td>3-4l</td>
</tr>
<tr>
<td>AANOX</td>
<td>0.5</td>
<td>3-4l</td>
</tr>
</tbody>
</table>

* The evaluation of these values are detailed in Chapter IX of Cerco & Cole (1994).
* The equation number where the corresponding parameter is first shown and defined.
* The parameters declared as an array in the source code.
Table 3-3. Parameters related to phosphorus in water column.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value*</th>
<th>Equation Numberb</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPRP</td>
<td>0.1</td>
<td>3-5</td>
</tr>
<tr>
<td>FPLP</td>
<td>0.2</td>
<td>3-6</td>
</tr>
<tr>
<td>FPDP</td>
<td>0.5</td>
<td>3-7</td>
</tr>
<tr>
<td>FPIP</td>
<td>0.2e</td>
<td></td>
</tr>
<tr>
<td>FPR_x</td>
<td>0.0 (all groups)</td>
<td>3-5</td>
</tr>
<tr>
<td>FPI_x</td>
<td>0.0 (all groups)</td>
<td>3-6</td>
</tr>
<tr>
<td>FPD_x</td>
<td>1.0 (all groups)</td>
<td>3-7</td>
</tr>
<tr>
<td>FPI_x</td>
<td>0.0e (all groups)</td>
<td>3-8</td>
</tr>
<tr>
<td>&quot;WS_x (m day(^{-1}))&quot;</td>
<td>1.0</td>
<td>3-8</td>
</tr>
<tr>
<td>K(<em>{P</em>{O4}}) (per g m(^{-3})) for TSS</td>
<td>NAe</td>
<td>3-8b</td>
</tr>
<tr>
<td>K(<em>{P</em>{O4}}) (per mol m(^{-3})) for TAM</td>
<td>6.0</td>
<td>3-8b</td>
</tr>
<tr>
<td>CP(_{prmt}) (g C per g P)</td>
<td>42.0</td>
<td>3-8e</td>
</tr>
<tr>
<td>CP(_{prm2}) (g C per g P)</td>
<td>85.0</td>
<td>3-8e</td>
</tr>
<tr>
<td>CP(_{prm3}) (per g P m(^{-3}))</td>
<td>200.0</td>
<td>3-8e</td>
</tr>
<tr>
<td>K(_{RP}) (day(^{-1}))</td>
<td>0.005</td>
<td>3-8f</td>
</tr>
<tr>
<td>K(_{LP}) (day(^{-1}))</td>
<td>0.075</td>
<td>3-8g</td>
</tr>
<tr>
<td>K(_{DP}) (day(^{-1}))</td>
<td>0.1</td>
<td>3-8h</td>
</tr>
<tr>
<td>K(_{RPalg}) (day(^{-1}) per g C m(^{-3}))</td>
<td>0.0</td>
<td>3-8f</td>
</tr>
<tr>
<td>K(_{LPalg}) (day(^{-1}) per g C m(^{-3}))</td>
<td>0.0</td>
<td>3-8g</td>
</tr>
<tr>
<td>K(_{DPalg}) (day(^{-1}) per g C m(^{-3}))</td>
<td>0.2</td>
<td>3-8h</td>
</tr>
</tbody>
</table>

* The evaluation of these values are detailed in Chapter IX of Cervo & Cole (1994).

b The equation number where the corresponding parameter is first shown and defined.

c Not available in Cervo & Cole (1994) since their formulations do not include these parameters.

: FPI\_x is estimated from FPR\_x + FPL\_x + FPD\_x + FPI\_x = 1.

* The parameters declared as an array in the source code.
Table 3-4. Parameters related to nitrogen in water column.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value*</th>
<th>Equation Number(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FNRP</td>
<td>0.35</td>
<td>3-9</td>
</tr>
<tr>
<td>FNLP</td>
<td>0.55</td>
<td>3-10</td>
</tr>
<tr>
<td>FNDP</td>
<td>0.10</td>
<td>3-11</td>
</tr>
<tr>
<td>FNIP</td>
<td>0.0</td>
<td>3-12</td>
</tr>
<tr>
<td>FNR(_x)</td>
<td>0.0 (all groups)</td>
<td>3-9</td>
</tr>
<tr>
<td>FNL(_x)</td>
<td>0.0 (all groups)</td>
<td>3-10</td>
</tr>
<tr>
<td>FND(_x)</td>
<td>1.0 (all groups)</td>
<td>3-11</td>
</tr>
<tr>
<td>FNI(_x)</td>
<td>0.0 (all groups)</td>
<td>3-12</td>
</tr>
<tr>
<td>ANC(_x) (g N per g C)</td>
<td>0.167 (all groups)</td>
<td>3-9</td>
</tr>
<tr>
<td>ANDC (g N per g C)</td>
<td>0.933</td>
<td>3-13</td>
</tr>
<tr>
<td>(K_{RN}) (day(^{-1}))</td>
<td>0.005</td>
<td>3-13b</td>
</tr>
<tr>
<td>(K_{LN}) (day(^{-1}))</td>
<td>0.075</td>
<td>3-13c</td>
</tr>
<tr>
<td>(K_{DN}) (day(^{-1}))</td>
<td>0.015</td>
<td>3-13d</td>
</tr>
<tr>
<td>(K_{RNalb}) (day(^{-1}) per g C m(^{-3}))</td>
<td>0.0</td>
<td>3-13b</td>
</tr>
<tr>
<td>(K_{LNalb}) (day(^{-1}) per g C m(^{-3}))</td>
<td>0.0</td>
<td>3-13c</td>
</tr>
<tr>
<td>(K_{DNalb}) (day(^{-1}) per g C m(^{-3}))</td>
<td>0.0</td>
<td>3-13d</td>
</tr>
<tr>
<td>(N_{itn}) (g N m(^{-3}) day(^{-1}))</td>
<td>0.07</td>
<td>3-13g</td>
</tr>
<tr>
<td>KHNit(_{DO}) (g O(_2) m(^{-3}))</td>
<td>1.0</td>
<td>3-13g</td>
</tr>
<tr>
<td>KHNit(_N) (g N m(^{-3}))</td>
<td>1.0</td>
<td>3-13g</td>
</tr>
<tr>
<td>TNit (°C)</td>
<td>27.0</td>
<td>3-13g-1</td>
</tr>
<tr>
<td>KNit1 (°C(^{-2}))</td>
<td>0.0045</td>
<td>3-13g-1</td>
</tr>
<tr>
<td>KNit2 (°C(^{-2}))</td>
<td>0.0045</td>
<td>3-13g-1</td>
</tr>
</tbody>
</table>

\(^a\) The evaluation of these values are detailed in Chapter IX of Cerco & Cole (1994).

\(^b\) The equation number where the corresponding parameter is first shown and defined.
# Table 3-5. Parameters related to silica in water column.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value*</th>
<th>Equation Numberb</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSPP</td>
<td>1.0c</td>
<td>3-14</td>
</tr>
<tr>
<td>FSIP</td>
<td>0.0c</td>
<td>3-15</td>
</tr>
<tr>
<td>FSPd</td>
<td>1.0c</td>
<td>3-14</td>
</tr>
<tr>
<td>FSId</td>
<td>0.0c</td>
<td>3-15</td>
</tr>
<tr>
<td>ASCd (g Si per g C)</td>
<td>0.5</td>
<td>3-14</td>
</tr>
<tr>
<td>KsAP (per g m(^{-3})) for TSS</td>
<td>NA(^e)</td>
<td>3-15b</td>
</tr>
<tr>
<td>KsAP (per mol m(^{-3})) for TAM</td>
<td>6.0</td>
<td>3-15b</td>
</tr>
<tr>
<td>Ks (day(^{-1}))</td>
<td>0.03</td>
<td>3-15d</td>
</tr>
<tr>
<td>TRsia ((^\circ)C)</td>
<td>20.0</td>
<td>3-15d</td>
</tr>
<tr>
<td>KTsia ((^\circ)C(^{-1}))</td>
<td>0.092</td>
<td>3-15d</td>
</tr>
</tbody>
</table>

* The evaluation of these values are detailed in Chapter IX of Cereo & Cole (1994).

b The equation number where the corresponding parameter is first shown and defined.

c Not available in Cereo & Cole (1994) since their formulations do not include these parameters:
- FSP and FSIP are estimated from FSPP + FSIP = 1
- FSPd and FSId are estimated from FSPd + FSId = 1.

# Table 3-6. Parameters related to chemical oxygen demand and dissolved oxygen in water column.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value*</th>
<th>Equation Numberb</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHcod (g O(_2) m(^{-3}))</td>
<td>1.5</td>
<td>3-16</td>
</tr>
<tr>
<td>Kcd (day(^{-1}))</td>
<td>20.0</td>
<td>3-16a</td>
</tr>
<tr>
<td>TRcod ((^\circ)C)</td>
<td>20.0</td>
<td>3-16a</td>
</tr>
<tr>
<td>KTcod ((^\circ)C(^{-1}))</td>
<td>0.041</td>
<td>3-16a</td>
</tr>
<tr>
<td>AOCR (g O(_2) per g C)</td>
<td>2.67</td>
<td>3-17</td>
</tr>
<tr>
<td>AONT (g O(_2) per g N)</td>
<td>4.33</td>
<td>3-17</td>
</tr>
<tr>
<td>Km (in MKS unit)</td>
<td>3.933e</td>
<td>3-17e</td>
</tr>
<tr>
<td>KT(_r)</td>
<td>1.024e (1.005 - 1.030)</td>
<td>3-17e</td>
</tr>
</tbody>
</table>

* The evaluation of these values are detailed in Chapter IX of Cereo & Cole (1994).

b The equation number where the corresponding parameter is first shown and defined.

c Not available in Cereo & Cole (1994) since their formulations do not include these parameters:
- Km is from O'Connor & Dobbins (1958)
- KT\(_r\) is from Thomann & Mueller (1987).
Table 3-7. Parameters related to total active metal and fecal coliform bacteria in water column.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value(^a)</th>
<th>Equation Number(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHbfm (g O(_2) m(^3))</td>
<td>0.5</td>
<td>3-18</td>
</tr>
<tr>
<td>BFTAM (mol m(^2) day(^{-1}))</td>
<td>0.01</td>
<td>3-18</td>
</tr>
<tr>
<td>Ttam (°C)</td>
<td>20.0</td>
<td>3-18</td>
</tr>
<tr>
<td>Ktam (°C(^{-1}))</td>
<td>0.2</td>
<td>3-18</td>
</tr>
<tr>
<td>TAMdx (mol m(^3))</td>
<td>0.015</td>
<td>3-18b-1</td>
</tr>
<tr>
<td>Kdotam (per g O(_2) m(^3))</td>
<td>1.0</td>
<td>3-18b-1</td>
</tr>
<tr>
<td>KFCB (day(^{-1}))</td>
<td>0.0 - 6.1(^c) (seawater)</td>
<td>3-19</td>
</tr>
<tr>
<td>TFCB (°C(^{-1}))</td>
<td>1.07(^c)</td>
<td>3-19</td>
</tr>
</tbody>
</table>

\(^a\) The evaluation of these values are detailed in Chapter IX of Cerco & Cole (1994).
\(^b\) The equation number where the corresponding parameter is first shown and defined.
\(^c\) Not available in Cerco & Cole (1994) since their formulations do not include these parameters

: KFCB and TFCB are from Thomann & Mueller (1987)
Figure 3-1. A schematic diagram for water column water quality model.
IV. Sediment Process Model

A sediment process model developed by DiToro & Fitzpatrick (1993; hereinafter this report is referred to as D&F) and coupled with CE-QUAL-ICM for Chesapeake Bay water quality modeling (Cerco & Cole 1994) was slightly modified and incorporated into the tidal prism model, TPM-VIMS (Kuo & Park 1994). This sediment process model is included in the present model to simulate the processes in the sediment and at the sediment-water interface. The sediment process model has twenty-seven water quality related state variables and fluxes.

1-3) particulate organic carbon, $G_1$, $G_2$, and $G_3$ classes in Layer 2
4-6) particulate organic nitrogen, $G_1$, $G_2$ and $G_3$ classes in Layer 2
7-9) particulate organic phosphorus, $G_1$, $G_2$ and $G_3$ classes in Layer 2
10) particulate biogenic silica in Layer 2
11-12) sulfide/methane, Layer 1 and 2
13-14) ammonium nitrogen, Layer 1 and 2
15-16) nitrate nitrogen, Layer 1 and 2
17-18) phosphate phosphorus, Layer 1 and 2
19-20) available silica, Layer 1 and 2
21) ammonium nitrogen flux
22) nitrate nitrogen flux
23) phosphate phosphorus flux
24) silica flux
25) sediment oxygen demand
26) release of chemical oxygen demand
27) sediment temperature

The nitrate state variables, (15), (16) and (22), in the model represent the sum of nitrate and nitrite nitrogen. The three $G$ classes for particulate organic matter (POM) in Layer 2, and the two layers for inorganic substances are described below.

In the sediment model, benthic sediments are represented as two layers (Fig. 4-1). The upper layer (Layer 1) is in contact with the water column and may be oxic or anoxic depending on dissolved oxygen concentration in the overlying water. The lower layer (Layer 2) is permanently anoxic. The upper layer depth, which is determined by the penetration of oxygen into the sediments, is at its maximum only a small fraction of the total depth. Because $H_1 (~0.1 \text{ cm}) < H_2$, 

\[(4-1)\]
where $H$ is the total depth (approximately 10 cm: see Section IV-7-2D), $H_1$ is the upper layer depth and $H_2$ is the lower layer depth.

The model incorporates three basic processes (Fig. 4-2): 1) depositional flux of POM, 2) their diagenesis and 3) the resulting sediment flux. The sediment model is driven by net settling of particulate organic carbon, nitrogen, phosphorus and silica from the overlying water to the sediments (depositional flux). Because of the negligible thickness of the upper layer (Eq. 4-1), deposition is considered to be proceeded from the water column directly to the lower layer. Within the lower layer, the model simulates the diagenesis (mineralization or decay) of deposited POM, which produces oxygen demand and inorganic nutrients (diagenesis flux). The third basic process is the flux of substances produced by diagenesis (sediment flux). Oxygen demand, as sulfide (in saltwater) or methane (in freshwater), takes three paths out of the sediments: 1) oxidation at the sediment-water interface as sediment oxygen demand, 2) export to the water column as chemical oxygen demand or 3) burial to deep, inactive sediments. Inorganic nutrients produced by diagenesis takes two paths out of the sediments: 1) release to the water column or 2) burial to deep, inactive sediments (Fig. 4-2).

This chapter describes the three basic processes with reactions and sources/sinks for each state variable. The method of solution including finite difference equations, solution scheme, boundary and initial conditions, and stand alone model are explained in Section IV-6. Parameter evaluation and some limitations of the model formulations found in D&F are described in Section IV-7. Complete model documentation can be found in D&F.

IV-1. Depositional Flux

Deposition is one process that couples the water column model with the sediment model. Consequently, deposition is represented in both the water column and sediment models. In the water column model, the governing mass-balance equations for the following state variables:

- three algal groups, cyanobacteria, diatoms and green algae (Eq. 3-1)
- refractory and labile particulate organic carbon (Equations 3-2 and 3-3)
- refractory and labile particulate organic phosphorus (Equations 3-5 and 3-6) and total phosphate (Eq. 3-8)
refractory and labile particulate organic nitrogen (Equations 3-9 and 3-10)
particulate biogenic silica (Eq. 3-14) and available silica (Eq. 3-15)
contain settling terms, which represent the depositional fluxes.

The sediment model receives these depositional fluxes of particulate organic carbon (POC), particulate organic nitrogen (PON), particulate organic phosphorus (POP) and particulate biogenic silica (PSi). Because of the negligible thickness of the upper layer (Eq. 4-1), deposition is considered to proceed from the water column directly to the lower layer. Since the sediment model has three G classes of POM, $G_i$ ($i = 1, 2$ or $3$), depending on the time scales of reactivity (Section IV-2), the POM fluxes from the water column should be mapped into three G classes based on their reactivity. Then, the depositional fluxes for the $i^{th}$ G class ($i = 1, 2$ or $3$) may be expressed as:

$$J_{POC,i} = FCLP_i \cdot WS_{LP} \cdot LPOC^N + FCRP_i \cdot WS_{RP} \cdot RPOC^N + \sum_{x=cdg} FCB_{xi} \cdot WS_x \cdot B_x^N \quad (4-2)$$

$$J_{PON,i} = FNLP_i \cdot WS_{LP} \cdot LPON^N + FNRP_i \cdot WS_{RP} \cdot RPNON^N + \sum_{x=cdg} FNB_{xi} \cdot ANC_x \cdot WS_x \cdot B_x^N \quad (4-3)$$

$$J_{POP,i} = FPLP_i \cdot WS_{LP} \cdot LPOP^N + FPFP_i \cdot WS_{RP} \cdot RPOP^N + \sum_{x=cdg} FFB_{xi} \cdot APC \cdot WS_x \cdot B_x^N$$

$$+ \gamma_i \cdot WS_{TSS} \cdot PO4p^N \quad (4-4)$$

$$J_{PSi} = WS_{d} \cdot SU^N + ASC_d \cdot WS_{d} \cdot B_d^N + WS_{TSS} \cdot SAP^N \quad (4-5)$$

$J_{POM,i}$ = depositional flux of POM ($M = C, N$ or $P$) routed into the $i^{th}$ G class (g m$^{-2}$ day$^{-1}$)
$J_{PSi}$ = depositional flux of PSi (g Si m$^{-2}$ day$^{-1}$)

$FCLP_i, FNLP_1, FPLP_i = \text{fraction of water column labile POC, PON and POP,}$
respectively, routed into the $i^{th}$ G class in sediment

$FCRP_i, FNRP_i, FPFP_i = \text{fraction of water column refractory POC, PON and POP,}$
respectively, routed into the $i^{th}$ G class in sediment

$FCB_{xi}, FNB_{xi}, FFB_{xi} = \text{fraction of POC, PON and POP, respectively, in the algal}$
group $x$ routed into the $i^{th}$ G class in sediment

$\gamma_i = 1 \text{ for } i = 1$
$0 \text{ for } i = 2 \text{ or } 3.$

50
In the source code, the sediment process model is solved after the water column water quality model, and the calculated fluxes using the water column conditions at \( t = t_s \) are used for the computation of the water quality variables at \( t = t + \theta \). The superscript \( N \) indicates the variables after being updated for the kinetic processes, as defined in Eq. 3-21.

The settling of sorbed phosphate is considered to contribute to the labile \( G_1 \) pool in Eq. 4-4, and settling of sorbed silica contributes to \( J_{\text{psi}} \) in Eq. 4-5 to avoid creation of additional depositional fluxes for inorganic particulates. The sum of distribution coefficients should be unity:

\[
\sum_i FCLP_i = \sum_i FNLP_i = \sum_i FPLP_i = \sum_i FCNP_i = \sum_i FNRNP_i = \sum_i FPRNP_i = \sum_i FCNP_i = \sum_i FNBNP_i = \sum_i FPBNP_i = 1.
\]

The settling velocities, \( WS_{LP} \), \( WS_{RP} \), \( WS_x \) and \( WS_{TSS} \) as defined in the water column model (Chapter III), are net settling velocities. If total active metal is selected as a measure of sorption site, \( WS_{TSS} \) is replaced by \( WS_x \) in Equations 4-4 and 4-5 (see Sections III-3 and III-5).

IV-2. Diagenesis Flux

Another coupling point of the sediment model to the water column model is the sediment flux, which is described in Section IV-3. The computation of sediment flux requires that the magnitude of the diagenesis flux be known. The diagenesis flux is explicitly computed using mass-balance equations for deposited POC, PON and POP. (Dissolved silica is produced in the sediments as the result of the dissolution of PSi. Since the dissolution process is different from the bacterial-mediated diagenesis process, it is presented separately in Section IV-4.) In the mass-balance equations, the depositional fluxes of POM are the source terms and the decay of POM in the sediments produces the diagenesis fluxes. The integration of the mass-balance equations for POM provides the diagenesis fluxes that are the inputs for the mass-balance equations for ammonium, nitrate, phosphate and sulfide/methane in the sediments (Section IV-3).

The difference in decay rates of POM is accounted for by assigning a fraction of POM to various decay classes (Westrish & Berner 1984). POM in the sediments is divided into three \( G \) classes, or fractions, representing three scales of reactivity. The \( G_1 \) (labile) fraction has a half life of 20 days, and the \( G_2 \) (refractory) fraction has a half life of one year. The \( G_3 \) (inert) fraction is non-reactive, i.e., undergoes no significant decay
before burial into deep, inactive sediments. The varying reactivity of the G classes controls the time scale over which changes in depositional flux will be reflected in changes in diagenesis flux. If the G_1 class would dominate the POM input into the sediments, then there would be no significant time lag introduced by POM diagenesis and any changes in depositional flux would be readily reflected in diagenesis flux.

Because the upper layer thickness is negligible (Eq. 4-1) and thus depositional flux is considered to proceed directly to the lower layer (Equations 4-2 to 4-5), diagenesis is considered to occur in the lower layer only. The mass-balance equations are similar for POC, PON and POP, and for different G classes. The mass-balance equation in the anoxic lower layer for the i\textsuperscript{th} G class (i = 1, 2 or 3) may be expressed as:

\[ H_2 \frac{dG_{\text{POM}i}}{dt} = -K_{\text{POM}i} \cdot \theta_{\text{POM}i} \cdot G_{\text{POM}i} \cdot H_2 - W \cdot G_{\text{POM}i} + J_{\text{POM}i} \]  \hspace{1cm} (4-6)

\( G_{\text{POM}i} \) = concentration of POM (M = C, N or P) in the i\textsuperscript{th} G class in Layer 2 (g m\textsuperscript{-3})

\( K_{\text{POM}i} \) = decay rate of the i\textsuperscript{th} G class POM at 20°C in Layer 2 (day\textsuperscript{-1})

\( \theta_{\text{POM}i} \) = constant for temperature adjustment for \( K_{\text{POM}i} \)

\( T \) = sediment temperature (°C)

\( W \) = burial rate (m day\textsuperscript{-1}).

Since the G_3 class is inert, \( K_{\text{POM}3} = 0 \).

Once the mass-balance equations for \( G_{\text{POM}1} \) and \( G_{\text{POM}2} \) are solved, the diagenesis fluxes are computed from the rate of mineralization of the two reactive G classes:

\[ J_M = \sum_{i=1}^{2} K_{\text{POM}i} \cdot \theta_{\text{POM}i} \cdot \theta_{\text{POM}i} \cdot G_{\text{POM}i} \cdot H_2 \]  \hspace{1cm} (4-7)

\( J_M \) = diagenesis flux (g m\textsuperscript{2} day\textsuperscript{-1}) of carbon (M = C), nitrogen (M = N) or phosphorus (M = P).

IV-3. Sediment Flux

The mineralization of POM produces soluble intermediates, which are quantified as diagenesis fluxes in the previous section. The intermediates react in the oxic and anoxic layers, and portions are returned to the overlying water as sediment fluxes. Computation of sediment fluxes requires mass-balance equations for ammonium, nitrate, phosphate,
sulfide/methane and available silica. This section describes the flux portion for ammonium, nitrate, phosphate and sulfide/methane of the model. Available silica is described in Section IV-4.

In the upper layer, the processes included in the flux portion are (Fig. 4-1):
- exchange of dissolved fraction between Layer 1 and the overlying water
- exchange of dissolved fraction between Layer 1 and 2 via diffusive transport
- exchange of particulate fraction between Layer 1 and 2 via particle mixing
- loss by burial to the lower layer (Layer 2)
- removal (sink) by reaction
- internal sources.

Since the upper layer is quite thin, $H_1 \approx 0.1 \text{ cm}$ (Eq. 4-1) and the surface mass transfer coefficient ($s$) is on the order of $0.1 \text{ m day}^{-1}$, then the residence time in the upper layer is: $H_1/s \approx 10^2 \text{ days}$. Hence, a steady-state approximation is made in the upper layer. Then, the mass-balance equation for ammonium, nitrate, phosphate or sulfide/methane in the upper layer is:

$$H_1 \frac{\partial C_{t_1}}{\partial t} = 0 = s(f_{d_0} \cdot C_{t_0} - f_{d_1} \cdot C_{t_1}) + KL(f_{d_2} \cdot C_{t_2} - f_{d_1} \cdot C_{t_1})$$

$$+ \varpi(f_{p_2} \cdot C_{t_2} - f_{p_1} \cdot C_{t_1}) - W \cdot C_{t_1} - \frac{\kappa_1^2}{s} C_{t_1} + J_1$$

(4-8)

$C_{t_1}$ & $C_{t_2}$ = total concentrations in Layer 1 and 2, respectively ($\text{g m}^{-3}$)

$C_{t_0}$ = total concentration in the overlying water ($\text{g m}^{-3}$)

$s$ = surface mass transfer coefficient ($\text{m day}^{-1}$)

$KL$ = diffusion velocity for dissolved fraction between Layer 1 and 2 ($\text{m day}^{-1}$)

$\varpi$ = particle mixing velocity between Layer 1 and 2 ($\text{m day}^{-1}$)

$f_{d_0}$ = dissolved fraction of total substance in the overlying water ($0 \leq f_{d_0} \leq 1$)

$f_{d_1}$ = dissolved fraction of total substance in Layer 1 ($0 \leq f_{d_1} \leq 1$)

$f_{p_1}$ = particulate fraction of total substance in Layer 1 ($= 1 - f_{d_1}$)

$f_{d_2}$ = dissolved fraction of total substance in Layer 2 ($0 \leq f_{d_2} \leq 1$)

$f_{p_2}$ = particulate fraction of total substance in Layer 2 ($= 1 - f_{d_2}$)

$\kappa_1$ = reaction velocity in Layer 1 ($\text{m day}^{-1}$)
\[ J_1 = \text{sum of all internal sources in Layer 1 (g m}^{-2}\text{ day}^{-1}). \]

The first term on the RHS of Eq. 4-8 represents the exchange across sediment-water interface. Then, the sediment flux from Layer 1 to the overlying water, which couples the sediment model to the water column model, may be expressed as:

\[ J_{sw} = s(fd_1 \cdot C_{t1} - fd_o \cdot C_{t2}) \] (4-9)

\[ J_{aq} = \text{sediment flux of ammonium, nitrate, phosphate or sulfide/methane to the overlying water (g m}^{-2}\text{ day}^{-1}). \]

The convention used in Eq. 4-9 is that positive flux is from the sediment to the overlying water.

In the lower layer, the processes included in the flux portion are (Fig. 4-1): exchange of dissolved fraction between Layer 1 and 2 via diffusive transport, exchange of particulate fraction between Layer 1 and 2 via particle mixing, deposition from Layer 1, and burial to the deep inactive sediments, removal (sink) by reaction, internal sources including diagenetic source.

The mass-balance equation for ammonium, nitrate, phosphate or sulfide/methane in the lower layer is:

\[ H_2 \frac{\partial C_{t2}}{\partial t} = -KL(fd_2 \cdot C_{t2} - fd_1 \cdot C_{t1}) - \omega(fp_2 \cdot C_{t2} - fp_1 \cdot C_{t1}) \]

\[ + W(C_{t1} - C_{t2}) - \kappa_2 \cdot C_{t2} + J_2 \] (4-10)

\[ \kappa_2 = \text{reaction velocity in Layer 2 (m day}^{-1}) \]

\[ J_2 = \text{sum of all internal sources including diagenesis in Layer 2 (g m}^{-2}\text{ day}^{-1}). \]

The substances produced by mineralization of POM in sediments may be present in both dissolved and particulate phases. This distribution directly affects the magnitude of the substance that is returned to the overlying water. In Equations 4-8 to 4-10, the distribution of a substance between the dissolved and particulate phases in a sediment is parameterized using a linear partitioning coefficient. The dissolved and particulate fractions are computed from the partitioning equations:
\[ fd_1 = \frac{1}{1 + m_1 \cdot \pi_1} \quad fp_1 = 1 - fd_1 \]  
\[ fd_2 = \frac{1}{1 + m_2 \cdot \pi_2} \quad fp_2 = 1 - fd_2 \] (4-11-1) (4-11-2)

\[ m_1 \& m_2 = \text{solid concentrations in Layer 1 and 2, respectively (kg L}^{-1}\text{)} \]
\[ \pi_1 \& \pi_2 = \text{partition coefficients in Layer 1 and 2, respectively (per kg L}^{-1}\text{)} \]

The partition coefficient is the ratio of particulate to dissolved fraction per unit solid concentration (i.e., per unit sorption site available).

All terms, except the last two terms, in Equations 4-8 and 4-10 are common to all state variables and are described in Section IV-3-1. The last two terms represent the reaction and source/sink terms, respectively. These terms, which take different mathematical formulations for different state variables, are described in Sections IV-3-2 to IV-3-5 for ammonium, nitrate, phosphate and sulfide/methane, respectively.

IV-3-1. Common parameters for sediment flux

Parameters that are needed for the sediment fluxes are \( s, \omega, KL, W, H_2, m_1, m_2, \pi_1, \pi_2, \kappa_1, \kappa_2, J_1 \) and \( J_2 \) in Equations 4-8 to 4-11. Of these, \( \kappa_1, \kappa_2, J_1 \) and \( J_2 \) are variable-specific. Among the other common parameters, \( W \) (Section IV-7-2C), \( H_2 \) (Section IV-7-2D), and \( m_1 \) and \( m_2 \) (Section IV-7-3B), are specified as input. The modeling of the remaining three parameters, \( s, \omega, KL \), are described in this section.

A. Surface mass transfer coefficient: Owing to the observation that the surface mass transfer coefficient, \( s \), can be related to the sediment oxygen demand, SOD (DiToro et al. 1990), \( s \) can be estimated from the ratio of SOD and overlying water oxygen concentration:

\[ s = \frac{D_1}{H_1} = \frac{SOD}{DO_0} \] (4-12)

\( D_1 = \text{diffusion coefficient in Layer 1 (m}^2\text{ day}^{-1}\text{)} \).

Knowing \( s \), it is possible to estimate the other model parameters.
B. Particulate phase mixing coefficient: The particle mixing velocity between Layer 1 and 2 is parameterized as:

$$w = \frac{D_p \cdot \theta_{DP}^{20}}{H_2} \cdot \frac{G_{POC,1}}{G_{POC,R}} \cdot \frac{DO_0}{K_M_{dp} + DO_0}$$

(4-13)

$D_p$ = apparent diffusion coefficient for particle mixing (m$^2$ day$^{-1}$)

$\theta_{DP}$ = constant for temperature adjustment for $D_p$

$G_{POC,R}$ = reference concentration for $G_{POC,1}$ (g C m$^{-3}$)

$K_M_{dp}$ = particle mixing half-saturation constant for oxygen (g O$_2$ m$^{-3}$).

The enhanced mixing of sediment particles by macrobenthos (bioturbation) is quantified by estimating $D_p$. The particle mixing appears to be proportional to the benthic biomass (Matisoff 1982), which is correlated to the carbon input to the sediment (Robbins et al. 1989). This is parameterized by assuming that benthic biomass is proportional to the available labile carbon, $G_{POC,1}$, and $G_{POC,R}$ is the reference concentration at which the particle mixing velocity is at its nominal value. The Monod-type oxygen dependency accounts for the oxygen dependency of benthic biomass.

It has been observed that a hysteresis exists in the relationship between the bottom water oxygen and benthic biomass. Benthic biomass increases as the summer progresses. However, the occurrence of anoxia/hypoxia reduces the biomass drastically and also imposes stress on benthic activities. After full overturn, the bottom water oxygen increases but the population does not recover immediately. Hence, the particle mixing velocity, which is proportional to the benthic biomass, does not increase in response to the increased bottom water oxygen. Recovery of benthic biomass following hypoxic events depends on many factors including severity and longevity of hypoxia, constituent species and salinity (Diaz & Rosenberg 1995).

This phenomenon of reduced benthic activities and hysteresis is parameterized based on the idea of stress that low oxygen imposes on the benthic population. It is analogous to the modeling of the toxic effect of chemicals on organisms (Mancini 1983). A first order differential equation is employed, in which the benthic stress 1) accumulates only when overlying oxygen is below $K_M_{dp}$ and 2) is dissipated at a first order rate (Fig. 4-3a):
\[
\frac{\partial ST}{\partial t} = -K_{st}\cdot ST + \left(1 - \frac{DO_0}{KM_{dp}}\right) \quad \text{if } DO_0 < KM_{dp}
\]

\[
\frac{\partial ST}{\partial t} = -K_{st}\cdot ST \quad \text{if } DO_0 > KM_{dp}
\]

\(ST\) = accumulated benthic stress (day)

\(K_{st}\) = first order decay rate for \(ST\) (day\(^{-1}\)).

The behavior of this formulation can be understood by evaluating the steady-state stresses at two extreme conditions of overlying water oxygen, \(DO_0\):

- as \(DO_0 = 0\) \(K_{st}\cdot ST = 1\) \(f(ST) = (1 - K_{st}\cdot ST) = 0\)
- as \(DO_0 \geq KM_{dp}\) \(K_{st}\cdot ST = 0\) \(f(ST) = (1 - K_{st}\cdot ST) = 1\)

The dimensionless expression, \(f(ST) = 1 - K_{st}\cdot ST\), appears to be the proper variable to quantify the effect of benthic stress on benthic biomass and thus particle mixing (Fig. 4-3b).

The final formulation for the particle mixing velocity including the benthic stress is:

\[
\varpi = \frac{D_p \cdot \theta_{dp}^{\cdot20}}{H_2} \frac{G_{POC,1}}{G_{POC,R}} \frac{DO_0}{KM_{dp}} + \frac{DO_0}{KM_{dp}} f(ST) + \frac{D_{p,\text{min}}}{H_2}
\]

\(D_{p,\text{min}}\) = minimum diffusion coefficient for particle mixing (m\(^2\) day\(^{-1}\)).

The reduction in particle mixing due to the benthic stress, \(f(ST)\), is estimated by employing the following procedure. The stress, \(ST\), is normally calculated with Eq. 4-14. Once \(DO_0\) drops below a critical concentration, \(DO_{st,c}\) for \(NC_{hypoxia}\) consecutive days or more, the calculated stress is not allowed to decrease until \(t_{MBS}\) days of \(DO_0 > DO_{st,c}\).

That is, only when hypoxic days are longer than critical hypoxia days (\(NC_{hypoxia}\)), the maximum stress, or minimum \((1 - K_{st}\cdot ST)\), is retained for a specified period (\(t_{MBS}\) days) after \(DO_0\) recovery (Fig. 4-3). No hysteresis occurs if \(DO_0\) does not drop below \(DO_{st,c}\) or if hypoxia lasts shorter than \(NC_{hypoxia}\) days. When applying maximum stress for \(t_{MBS}\) days, the subsequent hypoxic days are not included in \(t_{MBS}\). This parameterization of hysteresis essentially assumes seasonal hypoxia, i.e., one or two major hypoxic events during summer, and might be unsuitable for systems with multiple hypoxic events throughout a year.
Three parameters relating to hysteresis, \( \text{DO}_{\text{ST,c}} \), \( \text{NC}_{\text{hypoxia}} \) and \( \text{t}_{\text{MBS}} \), are functions of many factors including severity and longevity of hypoxia, constituent species and salinity, and thus have site-specific variabilities (Diaz & Rosenberg 1995). The critical overlying oxygen concentration, \( \text{DO}_{\text{ST,c}} \), also depends on the distance from the bottom of the location of \( \text{DO}_b \) measurement, which is discussed in section for parameter evaluation (Section IV-7-3B). The critical hypoxia days, \( \text{NC}_{\text{hypoxia}} \), depends on tolerance of benthic organisms to hypoxia and thus on benthic community structure (Diaz & Rosenberg 1995). The time lag for the recovery of benthic biomass following hypoxic events, \( \text{t}_{\text{MBS}} \), tends to be longer for higher salinity. Since the present tidal prism model is intended to be applied to relatively small systems, the above three parameters are considered to be spatially constant input parameters.

C. Dissolved phase mixing coefficient: Dissolved phase mixing between Layer 1 and 2 is via passive molecular diffusion, which is enhanced by the mixing activities of the benthic organisms (bio-irrigation). This is modeled by increasing the diffusion coefficient relative to the molecular diffusion coefficient:

\[ KL = \frac{D_d \cdot \theta_B - 20}{H^2} + R_{BLBT} \cdot w \]  

(4-16)

\( D_d \) = diffusion coefficient in pore water (m² day⁻¹)
\( \theta_{BL} \) = constant for temperature adjustment for \( D_d \)
\( R_{BLBT} \) = ratio of bio-irrigation to bioturbation.

The last term in Eq. 4-16 accounts for the enhanced mixing by organism activities.

IV-3-2. Ammonium nitrogen

Diagenesis is assumed not to occur in the upper layer because of its shallow depth, and ammonium is produced by diagenesis in the lower layer:

\[ J_{1,\text{NH}_4} = 0 \]
\[ J_{2,\text{NH}_4} = J_N \quad (\text{from Eq. 4-7}) \]  

(4-17)

Ammonium is nitrified to nitrate in the presence of oxygen. A Monod-type expression is used for the ammonium and oxygen dependency of the nitrification rate. Then, the oxic
layer reaction velocity in Eq. 4-8 for ammonium may be expressed as:

\[ \frac{\kappa_{1\text{NH}_4}^2}{2} = \frac{DO_0}{2 \cdot KM_{\text{NH}_4, O_2}} \frac{KM_{\text{NH}_4}}{DO_0} \frac{\kappa_{1\text{NH}_4}^2 \cdot \theta_{\text{NH}_4}^{T - 20}}{KM_{\text{NH}_4} + NH_4_1} \]  

(4-18)

and then the nitrification flux becomes:

\[ J_{\text{Na}} = \frac{\kappa_{1\text{NH}_4}^2}{s} \cdot NH_4_1 \]  

(4-19)

\( KM_{\text{NH}_4, O_2} \) = nitrification half-saturation constant for dissolved oxygen (g O₂ m⁻³)

\( NH_4_1 \) = total ammonium nitrogen concentration in Layer 1 (g N m⁻³)

\( KM_{\text{NH}_4} \) = nitrification half-saturation constant for ammonium (g N m⁻³)

\( \kappa_{\text{NH}_4} \) = optimal reaction velocity for nitrification at 20°C (m day⁻¹)

\( \theta_{\text{NH}_4} \) = constant for temperature adjustment for \( \kappa_{\text{NH}_4} \)

\( J_{\text{Na}} \) = nitrification flux (g N m⁻² day⁻¹).

Nitrification does not occur in the anoxic lower layer:

\[ \kappa_{2\text{NH}_4} = 0 \]  

(4-20)

Once Equations 4-8 and 4-10 are solved for \( \text{NH}_4_1 \) and \( \text{NH}_4_2 \), the sediment flux of ammonium to the overlying water, \( J_{\text{aq.NH}_4} \), can be calculated using Eq. 4-9. Note that it is not \( \text{NH}_4_1 \) and \( \text{NH}_4_2 \) that determine the magnitude of \( J_{\text{aq.NH}_4} \) (Section X-B-2 in D&F). The magnitude is determined by 1) the diagenesis flux, 2) the fraction that is nitrified and 3) surface mass transfer coefficient \( (s) \) that mixes the remaining portion.

IV-3-3. Nitrate nitrogen

Nitrification flux is the only source of nitrate in the upper layer, and there is no diagenetic source for nitrate in both layers:

\[ J_{\text{LNO}_3} = J_{\text{Na}} \quad (\text{from Eq. 4-19}) \quad J_{2\text{NO}_3} = 0 \]  

(4-21)

Nitrate is present in sediments as dissolved substance, i.e., \( \pi_{\text{LNO}_3} = \pi_{2\text{NO}_3} = 0 \), making \( f_{\text{dLNO}_3} = f_{\text{d2NO}_3} = 1 \) (Eq. 4-11): it also makes \( \varpi \) meaningless, hence \( \varpi = 0 \). Nitrate is removed by denitrification in both oxic and anoxic layers with the carbon required for denitrification supplied by carbon diagenesis. The reaction velocities in Equations 4-8 and
4-10 for nitrate may be expressed as:

\[ \kappa^{2}_{1,NO3} = \kappa^{2}_{NO3,1} \cdot \theta^{T}_{NO3} \cdot 20 \]  
\[ \kappa^{2}_{2,NO3} = \kappa^{2}_{NO3,2} \cdot \theta^{T}_{NO3} \cdot 20 \]  

and the denitrification flux out of sediments as a nitrogen gas becomes:

\[ J_{NO3(s)} = \frac{\kappa^{2}_{1,NO3}}{s} NO3_1 + \kappa_{2,NO3} \cdot NO3_2 \]  

\( \kappa_{NO3,1} \) = reaction velocity for denitrification in Layer 1 at 20°C (m day\(^{-1}\))
\( \kappa_{NO3,2} \) = reaction velocity for denitrification in Layer 2 at 20°C (m day\(^{-1}\))
\( \theta_{NO3} \) = constant for temperature adjustment for \( \kappa_{NO3,1} \) and \( \kappa_{NO3,2} \)
\( J_{NO3(s)} \) = denitrification flux (g N m\(^{-2}\) day\(^{-1}\))
\( NO3_1 \) = total nitrate nitrogen concentration in Layer 1 (g N m\(^{-3}\))
\( NO3_2 \) = total nitrate nitrogen concentration in Layer 2 (g N m\(^{-3}\)).

Once Equations 4-8 and 4-10 are solved for NO3\(_1\) and NO3\(_2\), the sediment flux of nitrate to the overlying water, \( J_{aq,NO3} \), can be calculated using Eq. 4-9. The steady-state solution for nitrate showed that the nitrate flux is a linear function of NO3\(_0\) (Eq. III-15 in D&F): the intercept quantifies the amount of ammonium in the sediment that is nitrified but not denitrified (thus releases as \( J_{aq,NO3} \)), and the slope quantifies the extent to which overlying water nitrate is denitrified in the sediment. It also revealed that if the internal production of nitrate is small relative to the flux of nitrate from the overlying water, the normalized nitrate flux to the sediment, \( -J_{aq,NO3}/NO3_0 \), is linear in \( s \) for small \( s \) and constant for large \( s \) (Section III-C in D&F). For small \( s \) (~ 0.01 m day\(^{-1}\)), \( H_1 \) is large (Eq. 4-12) so that oxic layer denitrification predominates and \( J_{aq,NO3} \) is essentially zero independent of NO3\(_0\) (Fig. III-4 in D&F).

IV-3-4. Phosphate phosphorus

Phosphate is produced by the diagenetic breakdown of POP in the lower layer:

\[ J_{1,PO4} = 0 \quad J_{2,PO4} = J_P \quad (from \ Eq. \ 4-7) \]  

A portion of the liberated phosphate remains in the dissolved form and a portion becomes
particulate phosphate, either via precipitation of phosphate-containing minerals (Troup 1974), e.g., vivianite, Fe₂(PO₄)₂(s), or by partitioning to phosphate sorption sites (Lijklema 1980; Barrow 1983; Giordani & Astorri 1986). The extent of particulate formation is determined by the magnitude of the partition coefficients, π₁,PO₄ and π₂,PO₄, in Eq. 4-11. Phosphate flux is strongly affected by DO₀, the overlying water oxygen concentration. As DO₀ approaches zero, the phosphate flux from the sediments increases. This mechanism is incorporated by making π₁,PO₄ larger, under oxic conditions, than π₂,PO₄. In the model, when DO₀ exceeds a critical concentration, (DO₀)ₐₐ₉,PO₄, sorption in the upper layer is enhanced by an amount Δπ₉,PO₄:

\[
\pi₁,PO₄ = \pi₂,PO₄ \cdot (Δπ₉,PO₄,₁) \quad DO₀ > (DO₀)ₐ₉,PO₄
\]  
(4-25-1)

When oxygen falls below (DO₀)ₐ₉,PO₄, then:

\[
\pi₁,PO₄ = \pi₂,PO₄ \cdot (Δπ₉,PO₄,₁) \cdot \text{DO₀}/(DO₀)ₐ₉,PO₄ \quad DO₀ ≤ (DO₀)ₐ₉,PO₄
\]  
(4-25-2)

which smoothly reduces π₁,PO₄ to π₂,PO₄ as DO₀ goes to zero. There is no removal reaction for phosphate in both layers:

\[
κ₁,PO₄ = κ₂,PO₄ = 0
\]  
(4-26)

Once Equations 4-8 and 4-10 are solved for PO₄₁ and PO₄₂, the sediment flux of phosphate to the overlying water, Jₐ₉,PO₄, can be calculated using Eq. 4-9.

IV-3-5. Sulfide/methane and oxygen demand
A. Sulfide: No diagenetic production of sulfide occurs in the upper layer. In the lower layer, sulfide is produced by carbon diagenesis (Eq. 4-7) decremented by the organic carbon consumed by denitrification (Eq. 4-23). Then:

\[
J₁,H₂S = 0 \quad J₂,H₂S = a_{O₂C} \cdot Jₐ₉ \cdot (1 - a_{O₂N₃}) \cdot Jₐ₉(g)
\]  
(4-27)

\[
a_{O₂C} = \text{stoichiometric coefficient for carbon diagenesis consumed by sulfide oxidation (2.6667 g O₂-equivalents per g C)}
\]

\[
a_{O₂N₃} = \text{stoichiometric coefficient for carbon diagenesis consumed by denitrification (2.8571 g O₂-equivalents per g N)}
\]

A portion of the dissolved sulfide that is produced in the anoxic layer reacts with the iron.
to form particulate iron monosulfide, FeS(s) (Morse et al. 1987). The particulate fraction is mixed into the oxic layer where it can be oxidized to ferric oxyhydroxide, Fe$_2$O$_3$(s). The remaining dissolved fraction also diffuses into the oxic layer where it is oxidized to sulfate. Partitioning between dissolved and particulate sulfide in the model represents the formation of FeS(s), which is parameterized using partition coefficients, $\pi_{1,\text{H}_2\text{S}}$ and $\pi_{2,\text{H}_2\text{S}}$, in Eq. 4-11.

The present sediment model has three pathways for sulfide, the reduced end product of carbon diagenesis: 1) sulfide oxidation, 2) aqueous sulfide flux and 3) burial. The distribution of sulfide among the three pathways is controlled by the partitioning coefficients and the oxidation reaction velocities (Section V-E in D&F). Both dissolved and particulate sulfide are oxidized in the oxic layer, consuming oxygen in the process. In the oxic upper layer, the oxidation rate that is linear in oxygen concentration is used (Cline & Richards 1969; Millero 1986; Boudreau 1991). In the anoxic lower layer, no oxidation can occur. Then, the reaction velocities in Equations 4-8 and 4-10 may be expressed as:

$$\kappa^2_{1,\text{H}_2\text{S}} = \left(\kappa^2_{\text{H}_2\text{S},d_1} f_{d_{1,\text{H}_2\text{S}}} + \kappa^2_{\text{H}_2\text{S},p_1} f_{p_{1,\text{H}_2\text{S}}}\right) \theta^2_{\text{H}_2\text{S}} \frac{D\text{O}_9}{2 \cdot K_{\text{H}_2\text{S},02}}$$

(4-28-1)

$$\kappa^2_{2,\text{H}_2\text{S}} = 0$$

(4-28-2)

$\kappa_{\text{H}_2\text{S},d_1} =$ reaction velocity for dissolved sulfide oxidation in Layer 1 at 20°C (m day$^{-1}$)

$\kappa_{\text{H}_2\text{S},p_1} =$ reaction velocity for particulate sulfide oxidation in Layer 1 at 20°C (m day$^{-1}$)

$\theta_{\text{H}_2\text{S}} =$ constant for temperature adjustment for $\kappa_{\text{H}_2\text{S},d_1}$ and $\kappa_{\text{H}_2\text{S},p_1}$

$K_{\text{H}_2\text{S},02} =$ constant to normalize the sulfide oxidation rate for oxygen (g O$_2$ m$^{-3}$).

The constant, $K_{\text{H}_2\text{S},02}$, which is included for convenience only, is used to scale the oxygen concentration in the overlying water. At $D\text{O}_9 = K_{\text{H}_2\text{S},02}$, the reaction velocity for sulfide oxidation rate is at its nominal value.

The oxidation reactions in the oxic upper layer cause oxygen flux to the sediment, which exerts SOD. By convention, SOD is positive: SOD = -J$_{\text{aq,02}}$. The SOD in the model consists of two components, carbonaceous sediment oxygen demand (CSOD) due to sulfide oxidation and nitrogenous sediment oxygen demand (NSOD) due to nitrification:

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\[ SOD = CSOD + NSOD = \frac{k_{HDS}^2}{s}H2S_1 + a_{O2,NH4}J_{NH4} \] (4-29)

\( H2S_1 \) = total sulfide concentration in Layer 1 (g O₂-equivalents m⁻³)
\( a_{O2,NH4} \) = stoichiometric coefficient for oxygen consumed by nitrification (4.33 g O₂ per g N: Section III-7-2).

Equation 4-29 is nonlinear for SOD because the RHS contains \( s \) (= SOD/DOₐ) so that SOD appears on both sides of the equation: note that \( J_{NH4} \) (Eq. 4-19) is also a function of \( s \).

A simple back substitution method is used, as explained in Section IV-6-1.

If the overlying water oxygen is low, then the sulfide that is not completely oxidized in the upper layer can diffuse into the overlying water. This aqueous sulfide flux out of the sediments, which contributes to the chemical oxygen demand in the water column model, is modeled using
\[ J_{aq,HDS} = s(f\dot{d}_{HDS} \cdot H2S_1 - COD) \] (4-30)

The sulfide released from the sediment reacts very quickly in the water column when oxygen is available, but can accumulate in the water column under anoxic conditions. The COD, quantified as oxygen equivalents, is entirely supplied by benthic release in the water column model (Eq. 3-16). Since sulfide also is quantified as oxygen equivalents, COD is used as a measure of sulfide in the water column in Eq. 4-30.

**B. Methane:** When sulfate is used up, methane can be produced by carbon diagenesis and methane oxidation consumes oxygen (DiToro et al. 1990). Owing to the abundant sulfate in the saltwater, only the aforementioned sulfide production and oxidation are considered to occur in the saltwater. Since the sulfate concentration in the freshwater is generally insignificant, methane production is considered to replace sulfide production in the freshwater. In the freshwater, methane is produced by carbon diagenesis in the lower layer decremented by the organic carbon consumed by denitrification, and no diagenetic production of methane occurs in the upper layer (Eq. 4-27):

\[ (4-31) \]

The dissolved methane produced takes two pathways: 1) oxidation in the oxic upper layer
causing CSOD or 2) escape from the sediment as aqueous flux or as gas flux:

$$J_{2,CH4} = CSOD + J_{aq,CH4} + J_{CH4(g)}$$ (4-32)

$J_{aq,CH4} =$ aqueous methane flux (g O$_2$-equivalents m$^{-2}$ day$^{-1}$)

$J_{CH4(g)} =$ gaseous methane flux (g O$_2$-equivalents m$^{-2}$ day$^{-1}$).

A portion of dissolved methane that is produced in the anoxic layer diffuses into the oxic layer where it is oxidized. This methane oxidation causes CSOD in the freshwater sediment (DiToro et al. 1990):

$$CSOD = CSOD_{max} \left( 1 - sech\left[ \frac{\kappa_{CH4} \cdot \theta_{CH4} - 20}{S} \right] \right)$$ (4-33)

$$CSOD_{max} = \text{minimum}\left\{ \sqrt{2 \cdot KL \cdot CH4_{sat} \cdot J_{2,CH4}}, J_{2,CH4} \right\}$$ (4-33-1)

$$CH4_{sat} = 100 \left( 1 + \frac{h + H_2}{10} \right) 1.024^{20 - T}$$ (4-33-2)

$CSOD_{max} =$ maximum CSOD occurring when all the dissolved methane transported to the oxic layer is oxidized

$\kappa_{CH4} =$ reaction velocity for dissolved methane oxidation in Layer 1 at 20°C (m day$^{-1}$)

$\theta_{CH4} =$ constant for temperature adjustment for $\kappa_{CH4}$

$CH4_{sat} =$ saturation concentration of methane in the pore water (g O$_2$-equivalents m$^{-3}$).

The term, $(h + H_2)/10$ where $h$ and $H_2$ are in meters, in Eq. 4-33-2 is the depth from the water surface that corrects for the in situ pressure. Equation 4-33-2 is accurate to within 3% of the reported methane solubility between 5 and 20°C (Yamamoto et al. 1976).

If the overlying water oxygen is low, the methane that is not completely oxidized can escape the sediment into the overlying water either as aqueous flux or as gas flux.

The aqueous methane flux, which contributes to the chemical oxygen demand in the water column model, is modeled using (DiToro et al. 1990):

$$J_{aq,CH4} = CSOD_{max} \cdot sech\left[ \frac{\kappa_{CH4} \cdot \theta_{CH4} - 20}{S} \right] = CSOD_{max} - CSOD$$ (4-34)

Methane is only slightly soluble in water. If its solubility, $CH4_{sat}$ given by Eq. 4-33-2, is
exceeded in the pore water, it forms a gas phase that escapes as bubbles. The loss of 
methane as bubbles, i.e., the gaseous methane flux, is modeled using Eq. 4-32 with \( J_{z,CH4} \) from Eq. 4-31, CSOD from Eq. 4-33 and \( J_{m,CH4} \) from Eq. 4-34 (DiToro et al. 1990).

IV-4. Silica

The production of ammonium, nitrate and phosphate in sediments is the result of the 
mineralization of POM by bacteria. The production of dissolved silica in sediments is the result of the dissolution of particulate biogenic or opaline silica, which is thought to be independent of bacterial processes.

The depositional flux of particulate biogenic silica from the overlying water to the 
sediments is modeled using Eq. 4-5. With this source, the mass-balance equation for 
particulate biogenic silica may be written as:

\[
H_2 \frac{\partial PSi}{\partial t} = -S_{si} \cdot H_2 - W \cdot PSt + J_{PSi} + J_{DSi}
\]  

(4-35)

\( PSi \) = concentration of particulate biogenic silica in the sediment (g Si m\(^{-3}\))
\( S_{si} \) = dissolution rate of PSi in Layer 2 (g Si m\(^{-3}\) day\(^{-1}\))
\( J_{PSi} \) = depositional flux of PSi (g Si m\(^{-2}\) day\(^{-1}\)) given by Eq. 4-5
\( J_{DSi} \) = detrital flux of PSi (g Si m\(^{-2}\) day\(^{-1}\)) to account for PSi settling to the sediment that

is not associated with the algal flux of biogenic silica.

The processes included in Eq. 4-35 are dissolution (i.e., production of dissolved silica), 
burial, and depositional and detrital fluxes from the overlying water. Equation 4-35 can 
be viewed as the analog of the diagenesis equations for POM (Eq. 4-6). The dissolution 
rate is formulated using a reversible reaction that is first order in silica solubility deficit 
and follows a Monod-type relationship in particulate silica:

\[
S_{si} = K_{si} \cdot \theta_{si} \cdot \frac{PSi}{PSi + KM_{PSi}} (Si_{sat} - fU_{2,si} \cdot Si)
\]  

(4-36)

\( K_{si} \) = first order dissolution rate for PSi at 20°C in Layer 2 (day\(^{-1}\))
\( \theta_{si} \) = constant for temperature adjustment for \( K_{si} \)
\( KM_{PSi} \) = silica dissolution half-saturation constant for PSi (g Si m\(^{-3}\))
\( Si_{sat} \) = saturation concentration of silica in the pore water (g Si m\(^{-3}\)).
The mass-balance equations for mineralized silica can be formulated using the general forms, Equations 4-8 and 4-10. There is no source/sink term and no reaction in the upper layer:

\[ J_{1,\text{Si}} = k_{1,\text{Si}} = 0 \]  

(4-37)

In the lower layer, silica is produced by the dissolution of particulate biogenic silica, which is modeled using Eq. 4-36. The two terms in Eq. 4-36 correspond to the source term and reaction term in Eq. 4-10:

\[ J_{2,\text{Si}} = K_{\text{Si}} \cdot \psi_{\text{Si}} \cdot \frac{PSi}{PSi + KM_{PSi}} \cdot Si_{\text{surf}} \cdot H_2 \]  

(4-38-1)

\[ k_{2,\text{Si}} = K_{\text{Si}} \cdot \psi_{\text{Si}} \cdot \frac{PSi}{PSi + KM_{PSi}} \cdot f_{d,\text{Si}} \cdot H_2 \]  

(4-38-2)

A portion of silica dissolved from particulate silica sorbs to solids and a portion remains in the dissolved form. Partitioning using the partition coefficients, \( \pi_{1,\text{Si}} \) and \( \pi_{2,\text{Si}} \), in Eq. 4-11 controls the extent to which dissolved silica sorbs to solids. Since silica shows similar behavior as phosphate in adsorption-desorption process, the same partitioning method as applied to phosphate (Section IV-3-4) is used for silica. That is, when \( DO_0 \) exceeds a critical concentration, \( (DO_0)_{\text{crit,si}} \), sorption in the upper layer is enhanced by an amount \( \Delta \pi_{1,\text{Si}} \):

\[ \pi_{1,\text{Si}} = \pi_{2,\text{Si}} \cdot (\Delta \pi_{1,\text{Si}}) \quad DO_0 > (DO_0)_{\text{crit,si}} \]  

(4-39-1)

When oxygen falls below \( (DO_0)_{\text{crit,si}} \), then:

\[ \pi_{1,\text{Si}} = \pi_{2,\text{Si}} \cdot (\Delta \pi_{1,\text{Si}})^{DO_0/(DO_0)_{\text{crit,si}}} \quad DO_0 \leq (DO_0)_{\text{crit,si}} \]  

(4-39-2)

which smoothly reduces \( \pi_{1,\text{Si}} \) to \( \pi_{2,\text{Si}} \) as \( DO_0 \) goes to zero.

Once Equations 4-8 and 4-10 are solved for \( Si_1 \) and \( Si_2 \), the sediment flux of silica to the overlying water, \( J_{aq,\text{Si}} \), can be calculated using Eq. 4-9.

IV-5. Sediment temperature

All rate coefficients in the aforementioned mass-balance equations are expressed as a function of sediment temperature, \( T \). The sediment temperature is modeled based on the
diffusion of heat between the water column and sediment:

$$\frac{\partial T}{\partial t} = \frac{D_T}{H^2}(T_w - T)$$  \hspace{1cm} (4-40)

$D_T =$ heat diffusion coefficient between the water column and sediment ($m^2 \text{ sec}^{-1}$)

$T_w =$ temperature in the overlying water column ($^\circ C$) calculated by Eq. 3-21.

The model application in D&F and Cerco & Cole (1994) used $D_T = 1.8 \times 10^{-7} m^2 \text{ sec}^{-1}$.

**IV-6. Method of Solution**

**IV-6-1. Finite difference equations and solution scheme**

An implicit integration scheme is used to solve the governing mass-balance equations. The finite difference form of Eq. 4-8 may be expressed as:

$$0 = s(fd_0 \cdot C_{t_0} - fd_1 \cdot C_{t_1}) + KL(fd_2 \cdot C_{t_2} - fd_1 \cdot C_{t_1}) + \omega(fp_2 \cdot C_{t_2} - fp_1 \cdot C_{t_1})$$

$$- W \cdot C_{t_1} - \frac{\kappa_1^2}{s} C_{t_1} + J_1'$$  \hspace{1cm} (4-41)

where the primed variables designate the values evaluated at $t+\theta$ and the unprimed variables are those at $t$, where $\theta$ is defined in Eq. 3-21. The finite difference form of Eq. 4-10 may be expressed as:

$$0 = - KL(fd_2 \cdot C_{t_2} - fd_1 \cdot C_{t_1}) - \omega(fp_2 \cdot C_{t_2} - fp_1 \cdot C_{t_1}) + W(C_{t_1} - C_{t_2})$$

$$-(\kappa_2 + \frac{H_2}{\theta})C_{t_2}' + \left( J_2' + \frac{H_2}{\theta}C_{t_2} \right)$$  \hspace{1cm} (4-42)

The two terms, $-(H_2/\theta)C_{t_2}'$ and $(H_2/\theta)C_{t_2}$, are from the derivative term, $H_2(\partial C_{t_2}/\partial t)$ in Eq. 4-10, each of which simply adds to the Layer 2 removal rate and the forcing function, respectively. Setting these two terms equal to zero results in the steady-state model. The two unknowns, $C_{t_1}'$ and $C_{t_2}'$, can be calculated at every time step using:
The solution of Eq. 4-43 requires an iterative method since the surface mass transfer coefficient, s, is a function of the SOD (Eq. 4-12), which also is a function of s (Eq. 4-29). A simple back substitution method is used:

1. Start with an initial estimate of SOD: for example, SOD = \( a_{ozc} \cdot J_c \) or the previous time step SOD.
2. Solve Eq. 4-43 for ammonium, nitrate and sulfide/methane.
3. Compute the SOD using Eq. 4-29.
4. Refine the estimate of SOD: a root finding method (Brent’s method in Press et al. 1986) is used to make the new estimate.
5. Go to (2) if no convergence.
6. Solve Eq. 4-43 for phosphate and silica.

For the sake of symmetry, the equations for diagenesis, particulate biogenic silica and sediment temperature are also solved in implicit form. The finite difference form of the diagenesis equation (Eq. 4-6) may be expressed as:

\[
G'_{POM,i} = \left( G'_{POM,i} + \frac{\theta}{H_2} f_{POM,i} \right) \left( 1 + \theta \cdot K'_{POM,i} \cdot \theta^{-20} + \frac{\theta}{H_2} W \right)^{-1} \tag{4-44}
\]

The finite difference form of the PSi equation (Eq. 4-35) may be expressed as:

\[
PSi' = \left( PSi + \frac{\theta}{H_2} (J_{PSi} + J_{DSi}) \right) \left( 1 + \theta \cdot K_{Si} \cdot \theta^{-20} \frac{Si_{sat} - f_{d,PSi} \cdot Si_2}{PSi + K_{PSi}^{-1} M_{Si}} + \frac{\theta}{H_2} W \right)^{-1} \tag{4-45}
\]

using Eq. 4-32 for the dissolution term, in which PSi in the Monod-type term has been kept at time level \( t \) to simplify the solution. The finite difference form of the sediment temperature equation (Eq. 4-40) may be expressed as:
IV-6-2. Boundary and initial conditions

The above finite difference equations constitute an initial boundary-value problem. The boundary conditions are the depositional fluxes \( J_{\text{POM}} \) and \( J_{\text{PSi}} \) and the overlying water conditions \( C_{\text{f}}, T_{\text{w}} \) as a function of time, which are provided from the water column water quality model. The initial conditions are the concentrations at \( t = 0 \), \( G_{\text{POM}}(0), \text{PSi}(0), C_{\text{t}}(0), C_{\text{t}}(0) \) and \( T(0) \), to start the computations. Strictly speaking, these initial conditions should reflect the past history of the overlying water conditions and depositional fluxes, which often is impractical because of lack of field data for these earlier years. The procedure to evaluate the initial conditions using the stand-alone model is described in Section IV-6-3.

IV-6-3. Stand-alone model

For the purposes of estimating initial conditions and "stand alone" application (Section IV-7), a stand-alone version of sediment model is included in the present model package. The stand-alone model application also requires initial and boundary conditions. The steady-state solution for the average conditions on the first year, for which the field data are available, is obtained and used as an arbitrary set of initial conditions. The solution scheme in Section IV-6-1 becomes the steady-state one as \( \theta \to \infty \).

The boundary conditions are the overlying water conditions including temperature and the depositional fluxes. The overlying water conditions in the stand-alone model have to be based on observations collected at the time sediment-water fluxes are measured. These conditions as a function of time can be obtained using a four-term Fourier series:

\[
C_{\text{d}}(t) = a_0 + \sum_{k=1}^{4} \left( a_k \cdot \sin \left( \frac{2\pi kt}{T_p} \right) + b_k \cdot \cos \left( \frac{2\pi kt}{T_p} \right) \right)
\]  

Since the field data are often sampled at irregular intervals, the nine coefficients, \( a_0, a_1, a_2, a_3, a_4 \) and \( b_1, b_2, b_3, b_4 \), may be estimated using a multiple linear regression. For multiple year data,
the data for each year may be fitted separately so that the period, $T_p$, is one year.

The stand-alone model may use the observed depositional fluxes, if available, as boundary conditions. If the depositional flux of nitrogen, $J_{\text{PON}} (= \sum_i J_{\text{PON},i})$, is measured, the depositional fluxes of carbon, phosphorus and silica can be established using suitable stoichiometric ratios. However, the measurements of $J_{\text{PON}}$ for the entire model simulation period are impractical and hardly exist. Two possibilities are available. One is to derive $J_{\text{POM}}$ using the observed water column POM and estimate of settling velocity of POM. The other is to assume that the depositional fluxes are constant within a year and that seasonal variations in diagenesis fluxes are accounted for by the temperature dependency of the diagenesis rate constants (Section VIII-E in D&F). Yearly average depositional fluxes can be derived from the observed $J_{\text{aq,NH}_4}$, DO_0, SOD and NH_4O by estimating the ammonium diagenesis flux, $J_N$. The procedure is described below.

From the observed $J_{\text{aq,NH}_4}$, $J_N$ can be estimated using (Sections II-D and VIII-E in D&F):

$$J_{\text{aq,NH}_4} = J_{\text{aq,NH}_4} + \frac{K_{1,NH}^2}{s} NH_4$$

$$J_{\text{aq,NH}_4} = J_{\text{aq,NH}_4} + \frac{DO_0}{2 \cdot K_{M,NH}_4} + \frac{DO_0}{K_{M,NH}_4} \cdot \frac{\theta_{k_{M,NH}_4} - 20}{s} \cdot \frac{\theta_{NH}^T - 20}{s} \cdot NH_4$$

(4-48)

where $\theta_{k_{M,NH}_4}$, a constant for temperature adjustment for $K_{M,NH}_4$, accounts for the effect of temperature on $K_{M,NH}_4$: $\theta_{k_{M,NH}_4} = 1.125$ is used in D&F. Equation 4-48, which can be obtained by adding Equations 4-8 and 4-10 assuming steady-state and no burial, states that $J_N$ is the sum of $J_{\text{aq,NH}_4}$ and the quantity of ammonium that is nitrified to nitrate.

Rearrangement of Eq. 4-9 gives the oxic layer ammonium concentration:

$$NH_4 = \frac{1}{\frac{1}{J_{\text{aq,NH}_4} + NH_4} + \frac{1}{s}$$

(4-49)

Equations 4-48 and 4-49 can be applied pointwise to each measurement of $J_{\text{aq,NH}_4}$ and the resulting time series estimates of $J_N$ serve as the calibration data for estimating $J_{\text{PON}}$.

With the initial conditions estimated from the steady-state solution for the average conditions on the first year, the diagenesis portion of the model (Equations 4-6 and 4-7) is
solved to compute $J_N$ for an assumed $J_{PON}$. Through the comparison of the model calculated $J_N$ to the time series estimates, yearly average $J_{PON}$ can be evaluated. The location-specific, yearly average $J_{PON}$ estimated using the Chesapeake Bay data set (1985-1988) ranged 0.03 to 0.125 g N m$^{-2}$ day$^{-1}$ (Table 8-6 in D&F). The other depositional fluxes, $J_{POC}$, $J_{POP}$ and $J_{PSi}$, can be established using constant stoichiometric ratios:

$$J_{POC} = a_{c,N} \cdot J_{PON} \quad J_{POP} = \frac{1}{a_{c,P}} \cdot J_{POC} \quad J_{PSi} = \frac{1}{a_{c,si}} \cdot J_{POC}$$

(4-50)

$a_{c,N}$ = stoichiometric ratio of carbon to nitrogen in POM (g C per g N)

$a_{c,P}$ = stoichiometric ratio of carbon to phosphorus in POM (g C per g P)

$a_{c,si}$ = stoichiometric ratio of carbon to silica in POM (g C per g Si).

The above procedure may be viewed as being indexed by $J_{aq,NH_4}$, since it starts from an observed $J_{aq,NH_4}$.

Once the depositional fluxes are evaluated to reproduce the estimated $J_N$, they are distributed into the three $G$ classes. Then, using the initial and boundary conditions evaluated above for the first year average conditions, the stand-alone model is solved for one year. The final concentrations at the end of the first year are then used as the initial conditions and the stand-alone mode is solved again for the first year. This procedure is repeated until the final concentrations at the end of the year are equal, within a tolerance, the initial conditions at the beginning of the year. The final conditions represent the situation that would be reached if the conditions for the first year repeatedly occurred and the sediment had equilibrated to these conditions. When the kinetic coefficients need to be changed to improve the calibration, the initial conditions are recalculated with the new coefficients.

IV-7. Parameter Evaluation

The present sediment model involves many parameters that need to be evaluated from field data or through model calibration. The parameter evaluation, which is at least as important as model formulations, is described in this section. Some limitations of the model formulations and the parameter values found from the model application to the Chesapeake Bay are also presented.
As in Chesapeake Bay water quality modeling effort (Cerco & Cole 1994), it is desirable that the sediment model is operated in a "stand alone" model during initial application. Spatially-constant values are to be evaluated for model parameters in a "stand alone" application. Then, the parameters not employed or only roughly evaluated in the "stand alone" application are to be determined through the application of the coupled sediment-water column model. The sediment model application in a coupled model, which receives spatially-varying water column conditions, may require spatially-varying sediment model parameters.

IV-7-1. Parameters for depositional flux

The "stand alone" sediment model application determines the depositional fluxes of POM sufficient to reproduce the diagenesis rates that drive the stand-alone sediment model (Section IV-6-3). Constant stoichiometric ratios used in Eq. 4-50 are required to estimate \( J_{\text{POC}} \), \( J_{\text{POP}} \) and \( J_{\text{PSi}} \) from \( J_{\text{PON}} \). These ratios can be estimated using the pore water profiles of ammonium, phosphate and sulfate (Section VIII-C in D&F). The values used in D&F are:

\[
\begin{align*}
3c.\ N &= 5.68 \text{ g C per g N} \\
3c.\ Si &= 2.0 \text{ g C per g Si} \\
3c.\ P &= 41.0 \text{ g C per g P}
\end{align*}
\]

where \( a_{\text{CN}} \) and \( a_{\text{CP}} \) are Redfield ratios, and \( a_{\text{CSi}} \) is based on a limited amount of overlying water PSi data (Section VIII-E in D&F). The distribution coefficients of POM into three \( G \) classes are described in Section IV-7-2A.

In the coupled model application, parameters that need to be estimated for the depositional fluxes are the settling velocities in Equations 4-2 to 4-5: \( W_{\text{SI}} \), \( W_{\text{RP}} \), \( W_{\text{TSS}} \) and \( W_{\text{S}} \). These settling velocities, in principle, are determined from the water column model application. The values determined for the Chesapeake Bay water quality modeling (Cerco & Cole 1994) are listed in Tables 3-1 and 3-2. The depositional fluxes determined from the "stand alone" application may help determining the settling velocities in the water column model application.

IV-7-2. Parameters for diagenesis flux

Parameters that need to be estimated for the diagenesis fluxes are \( \text{FMLP}_i \), \( \text{FMRP}_i \)
and FMB\textsubscript{x1} in Equations 4-2 to 4-5, and $K_{\text{POM}i}$, $\theta_{\text{POM}i}$, W and H\textsubscript{2} in Eq. 4-6 for carbon ($M = C$), nitrogen ($M = N$) and phosphorus ($M = P$). The data from the kinetic experiments, measuring the rate at which reactants are consumed and end-products accumulate in a closed reaction vessel (Section VIII-D in D&F), can be used to confirm the determination of the reactive fractions ($FMLP_{p}$, $FMRP_{i}$ and $FMB_{x1}$) and decay rates ($K_{\text{POM}i}$).

A. Assignment to $G$ classes: The sediment model has three classes: $G_1$ (labile), $G_2$ (refractory) and $G_3$ (inert). In the "stand alone" application, the depositional fluxes are estimated using the ammonium diagenesis flux and constant stoichiometric ratios. The distribution of the depositional fluxes into the three $G$ classes used for the "stand alone" application (D&F) is listed in Table 4-1.

In the coupled model application, the deposited POM expressed in terms of the water column model state variables, upon deposition in the sediments, needs to be converted to the sediment model state variables. The water column model has two classes of POM based on the time scale of decomposition, labile and refractory (Section III-2A). Labile POM from the water column model is transferred directly into the $G_1$ class in the sediment model owing to the similar time scales of their reactivity, e.g., $FMLP_1 = 1$ and $FMLP_2 = FMLP_3 = 0$. Experiments by Westrich & Berner (1984) noted an even split of refractory POC in the water column into $G_2$ and $G_3$ classes in the sediment. The initial even distribution may be further modified from model calibration.

The results from the Chesapeake Bay water quality modeling (Cerco & Cole 1994) are listed in Table 4-1. The observed carbon enrichment of sediment particles relative to the water column was reflected by making nitrogen to be slightly more reactive than carbon or phosphorus. Splits of refractory POM were spatially-varying. To reproduce the observed water column nutrient concentrations, POM immediately below the fall lines (Bay and Tributary Zones 1) was considered largely inert. Routing of algae settled to the sediments into the sediment state variables also is listed in Table 4-1. The algal fraction assigned to the $G_1$ class was equivalent to the fraction of algal matter assigned to the labile particles following mortality in the water column (Tables 3-2 to 3-5). Split of refractory algae into $G_2$ and $G_3$ classes was equivalent to the split employed for refractory POM for most of the Bay away from the fall lines (i.e., except Bay Zones 1, 2 and 10,
B. Decay rate: Differences in reactivity of deposited POM are accounted for by assigning them to three G classes: e.g., FNRP > FCRP and FNB > FCB in Table 4-1. For any G class, the same values, that are representative of reported literature values, may be used for the decay of POC, PON and POP. The values used in D&F are:

\[
\begin{align*}
K_{POC,1} &= K_{PON,1} = K_{POP,1} = 0.035 \text{ day}^{-1} \\
K_{POC,2} &= K_{PON,2} = K_{POP,2} = 0.0018 \text{ day}^{-1} \\
K_{POC,3} &= K_{PON,3} = K_{POP,3} = 0.0 \text{ day}^{-1}
\end{align*}
\]

\[
\begin{align*}
\theta_{POC,1} &= \theta_{PON,1} = \theta_{POP,1} = 1.10 \\
\theta_{POC,2} &= \theta_{PON,2} = \theta_{POP,2} = 1.15 \\
\theta_{POC,3} &= \theta_{PON,1} = \theta_{POP,1} = \text{not available.}
\end{align*}
\]

C. Burial (sedimentation) rate: Burial rates can be measured using a number of methods (\(^{210}\text{Pb}, ^{239}\text{Pu}, ^{137}\text{Cs}, \text{Pollen}, \text{etc.})\). The measurements tend to have considerable variability since the rate at which solids are sedimented can depend on site specific features. From the "stand alone" calibration, an average value of \(W = 0.25 \text{ cm yr}^{-1}\) was determined (D&F). For the coupled model application, spatially-varying values listed in Table 4-2 were used (Cerco & Cole 1994). The values were calibrated, within the range of observations, for the concentrations of sediment organic particles. In the Bay, burial rates were highest near the Susquehanna, least in the central Bay and moderate near the Bay mouth, in general agreement with Officer et al. (1984). In tributaries, burial rates had the decreasing trend with distance away from the fall lines in general agreement with Brush (1984).

D. Active layer depth: The active layer depth, \(H\), controls the volume of the anoxic layer reservoir. From Eq. 4-1, \(H = H_2\). The mechanisms that influence the depth to which solids are mixed determine \(H\). These mixing mechanisms establish a homogeneous layer within which the diagenesis and other reactions take place. The principal agents of deep sediment mixing are the larger benthic organisms, and \(H\) is chosen to represent the depth of organism mixing. Active layer depths of 5 to 15 cm have been reported for estuaries (Aller 1982). A value of \(H_2 = 10 \text{ cm}\) was used in D&F.

E. Comparisons with field data: The most important validation of the diagenesis
portion of the model is the comparison to ammonium diagenesis. However, the composition of sediment POM is also important. The gross sediment composition is almost entirely due to $G_3$ class POM since the reactive fractions, $G_1$ and $G_2$, have decayed to produce the diagenesis flux: the median reactive fraction has been shown to be on the order of 10% of the sediment POM in Chesapeake Bay (Section VIII-D in D&F). Therefore, if measurements of the sediment composition are available, they can be compared to model predictions of $G_3$ class organic matter (Section VIII-F in D&F).

The $G_2$ class POM dominates the reactive portion: the $G_2$ class has been shown to be on the order of 90% of the reactive portion of sediment POM, i.e., $G_1 + G_2$ (Section VIII-D in D&F). Hence, the data from anoxic mineralization experiments can be used to estimate the quantity of $G_2$ fraction (Section VIII-D in D&F).

The primary source of POC in the sediments of Chesapeake Bay is algal POC. The decay kinetics of algal chlorophyll in the sediments has been found to be relatively independent of temperature with a first order decay constant of approximately 0.03 day$^{-1}$. Since this decay rate coincides with the mean mineralization rate of $G_1$ class carbon (Section IV-7-2B), the concentration of sediment chlorophyll should be a direct measure of the concentration of $G_1$ class carbon in the sediment (Section VIII-G in D&F).

The above three comparisons using measurements of sediment composition and algal POC may serve as additional measures of the reliability of the diagenesis portion of the model.

IV-7-3. Common Parameters for sediment flux

Parameters that need to be estimated for the sediment fluxes are $s$, $KL$, $\omega$, $m_1$, $m_2$, $\pi_1$, $\pi_2$, $W$, $H_2$, $\kappa_1$, $\kappa_2$, $J_1$ and $J_2$ in Equations 4-8 to 4-11 for ammonium, nitrate, phosphate and sulfide/methane. Among these, $s$, $KL$, $\omega$, $m_1$, $m_2$, $W$ and $H_2$ are the same for different variables. The parameter $s$ is estimated using Eq. 4-12. The estimation of the parameters, $W$ and $H_2$, has been described in Section IV-7-2.

A. Particulate and dissolved phase mixing coefficients: Evaluation of $\omega$ involves six new parameters (Eq. 4-15). The values used in D&F are:

$$D_p = 1.2 \times 10^{-4} \text{ m}^2 \text{ day}^{-1} \text{ (from calibration)} \quad D_{p_{\text{min}}} = 3.0 \times 10^{-6} \text{ m}^2 \text{ day}^{-1}$$
\[ \theta_{dp} = 1.117 \text{ (from data)} \]
\[ KM_{dp} = 4.0 \text{ g } O_2 \text{ m}^{-3} \text{ (from data)} \]
\[ G_{POC,R} = 100 \text{ g } C \text{ m}^{-3} \]
\[ K_{ST} = 0.03 \text{ day}^{-1} \]
Detailed vertical profiles of sediment chlorophyll can be used to quantify the rate of particle mixing by estimating the ratio of surface to depth averaged chlorophyll (Section VIII-G in D&F). Large ratio indicates little particle mixing, while the ratio approaching unity indicates intense mixing.

Three more parameters, DO\textsubscript{ST,c}, NC\textsubscript{hypoxia} and \textit{t\textsubscript{MBS}}, need to be evaluated to account for the benthic stress and hysteresis explained in Section IV-3-1B. These parameters depend on severity and longevity of hypoxia, constituent species and salinity (Diaz & Rosenberg 1995). Benthic infaunal mortality was suggested to be initiated when the oxygen concentration drops below about 2.8 g O\textsubscript{2} m\textsuperscript{-3} (Rosenberg 1980). However, Diaz & Rosenberg (1995) pointed out that the oxygen measurements in several of the field studies referred to in Rosenberg (1980) were made at some distance above the bottom. In areas with seasonal hypoxia (e.g., estuaries), the critical oxygen concentration for benthic organisms is closer to about 1 g O\textsubscript{2} m\textsuperscript{-3} (Llansó 1992). The present model simulates segment mean dissolved oxygen concentration and thus oxygen concentration immediately above bottom is not available. Hence, DO\textsubscript{ST,c} = 3 g O\textsubscript{2} m\textsuperscript{-3} may be used as an initial estimate when DO\textsubscript{0} is the vertical mean. The critical hypoxia days, NC\textsubscript{hypoxia}, depends on tolerance of benthic organisms to hypoxia (Diaz & Rosenberg 1995): NC\textsubscript{hypoxia} = 1 week will be used as an initial estimate. The time lag, \textit{t\textsubscript{MBS}}, for the recovery of benthic biomass following hypoxic events tends to be longer for higher salinity and shorter for lower salinity: about 3 to 4 weeks for low salinity water, e.g., < 20 ppt, and about 3 to 4 months for high salinity water, e.g., > 20 ppt (Diaz, personal communication).

Evaluation of KL involves three new parameters (Eq. 4-16). The values used in D&F are:
\[ D_d = 0.001 \text{ m}^2 \text{ day}^{-1} \text{ (from calibration)} \]
\[ \theta_{dl} = 1.08 \]
\[ R_{BLRT} = 0.0 \]
The value of \( D_d \) was estimated directly using observed \( J_{aq,NO}\textsubscript{3}, NH_4\textsubscript{0}, NH_4\textsubscript{2} \) and estimated \( J_N \) and \( s \) (Eq. III-42 in D&F). The resulting diffusion coefficient, which is roughly ten times the molecular diffusivity, indicates the importance of benthic enhancement. The temperature coefficient was chosen to be typical of biological reactions.
B. Solids concentration: The dissolved and particulate fractions are computed from the partitioning equations (Eq. 4-11), which require the concentration of sorbing solids. After analyzing field data, D&F used a solids concentration of $m_1 = m_2 = 0.5 \text{ kg L}^{-1}$, which are representative of the upper Bay conditions. This solids concentration is equivalent to approximately 81% porosity assuming dry sediment density of 2.65 kg L$^{-1}$ (Mackin & Aller, 1984).

IV-7-4. Parameters for ammonium flux

The parameters that need to be estimated specifically for the ammonium flux are $J_{\text{NH}_4}$, $J_{2\text{NH}_4}$, $\kappa_{\text{NH}_4}$, $\kappa_{2\text{NH}_4}$, $\pi_{\text{NH}_4}$ and $\pi_{2\text{NH}_4}$ in Equations 4-8 to 4-11. As described in Section IV-3-2:

\[
\begin{align*}
J_{\text{NH}_4} &= 0 \\
\kappa_{\text{NH}_4} & \text{from Eq. 4-18} \\
\pi_{\text{NH}_4} &= \pi_{2\text{NH}_4} = 1.0 \text{ L kg}^{-1}.
\end{align*}
\]

Partitioning is included although it has a negligible effect on the computation: from $m_1 = m_2 = 0.5 \text{ kg L}^{-1}$ (Section IV-7-3B) and Eq. 4-11, the partition coefficients, $\pi = 1$, indicate that approximately 67% of ammonium exists as dissolved form in sediments. For the parameters in Eq. 4-18 for $\kappa_{\text{NH}_4}$, the median values from a number of previous studies were used for the "stand alone" application in D&F:

\[
\begin{align*}
\kappa_{\text{NH}_4} &= 0.131 \text{ m day}^{-1} \\
\theta_{\text{NH}_4} &= 1.08 \\
KM_{\text{NH}_4} &= 1.5 \text{ g N m}^{-3} \\
KM_{\text{NH}_4\text{O}_2} &= 3.68 \text{ g O}_2 \text{ m}^{-3}.
\end{align*}
\]

The parameters $\kappa_{\text{NH}_4}$ and $J_N$ (Eq. 4-48) can be estimated from observed DO, SOD, $J_{aq\text{NH}_4}$, NH$_4$ (or NH$_4$ and Eq. 4-49) and $T$, and estimated $KM_{\text{NH}_4}$, $KM_{\text{NH}_4\text{O}_2}$ and $\theta_{\text{NH}_4}$ (Section II-D in D&F). If direct measurements of the nitrification rate in the sediments are available, these can be compared to model predictions for $J_{N\text{it}}$ computed using Eq. 4-19. This comparison may be used to confirm the estimated model parameters as well as model formulation for nitrification (Section II-F in D&F). The "stand alone" application in D&F showed that approximately 76% of the depositional nitrogen flux was returned to the water column as ammonium flux, and the remaining 24% was lost either as PON burial or became nitrate via nitrification (Section X-B-3 in D&F).

In the coupled model application, predicted ammonium flux from the sediment
during hypoxic/anoxic intervals often exceeded observations (Cerceo & Cole 1994). The excess anoxic release, which was due to blocking of the nitrification portion of the nitrification-denitrification process that removes nitrogen from the sediments, was reduced by lowering $K_{\text{M}_{\text{NH}_4,\text{O}_2}}$ to a value consistent with that for the water column model, $K_{\text{HNit}_{\text{do}}}$ in Table 3-4. In saltwater, a significant portion of the nitrogen is released as ammonium, while in freshwater, most of the mineralized nitrogen is often released from the sediments as nitrogen gas (Gardner et al 1991). Sediments adjacent to fall lines appeared to retain larger fractions of deposited phosphorus than sediments elsewhere. These variations were parameterized in the coupled model by assigning larger values for nitrification and denitrification rates, and phosphorus sorption coefficient in freshwater relative to saltwater (Cerceo & Cole 1994). The division between two regimes was set at 1 ppt salinity, the same salinity that separates sulfide or methane in the SOD kinetics (Section IV-3-5). Small adjustment was made for $\kappa_{\text{NH}_4}$ in the final calibration of the coupled model. The coupled model had (Cerceo & Cole 1994):

$$
\kappa_{\text{NH}_4} = \begin{cases} 
0.14 \text{ m day}^{-1} & \text{for saltwater (} S > S_{\text{crit,NH}_4} \text{)} \\
0.20 \text{ m day}^{-1} & \text{for freshwater (} S < S_{\text{crit,NH}_4} \text{)}
\end{cases} \\
K_{\text{M}_{\text{NH}_4,\text{O}_2}} = 1.0 \text{ g O}_2 \text{ m}^{-3} \\
S_{\text{crit,NH}_4} = 1 \text{ ppt.}
$$

IV-7-5. Parameters for nitrate flux

The parameters that need to be estimated specifically for the nitrate flux are $J_{\text{LNO}_3}$, $J_{\text{2NO}_3}$, $\kappa_{\text{1NO}_3}$, $\kappa_{\text{2NO}_3}$, $\pi_{\text{LNO}_3}$ and $\pi_{\text{2NO}_3}$ in Equations 4-8 to 4-11. As described in Section IV-3-3:

$$
J_{\text{LNO}_3} = \text{J}_{\text{Nit}} \text{ from Eq. 4-19} \\
\kappa_{\text{NO}_3,1} \text{ from Eq. 4-22-1} \\
\omega = 0 \\
J_{\text{2NO}_3} = 0 \\
\kappa_{\text{NO}_3,2} \text{ from Eq. 4-22-2} \\
\pi_{\text{LNO}_3} = \pi_{\text{2NO}_3} = 0.
$$

The parameters for $\kappa_{\text{1NO}_3}$ (Eq. 4-22-1) and $\kappa_{\text{2NO}_3}$ (Eq. 4-22-2) can be estimated from observed NO$_3$ (or NO$_3$ and Eq. 4-9), $J_{\text{aq,NO}_3}$ and $J_{\text{aq,NH}_4}$, and estimated $s$, $J_{\text{N}}$ (Eq. 4-48) and $\theta_{\text{NO}_3}$ (Section III-H in D&F). If direct measurements of the denitrification rate in the sediments are available, these may be compared to model predictions for $J_{\text{NO}_3(0)}$ (Eq. 4-23): estimation of NO$_3$ and NO$_3$ is described in Section III-I in D&F. This comparison may be used to confirm the estimated model parameters as well as model formulation for denitrification (Section III-I in D&F). The "stand alone" model (D&F) had:
\( \kappa_{\text{NO3,1}} = 0.10 \text{ m day}^{-1} \) \( \kappa_{\text{NO3,2}} = 0.25 \text{ m day}^{-1} \)
\( \theta_{\text{NO3}} = 1.08 \) (median value from previous studies).

The "stand alone" application showed that 76% of \( J_N \) is returned as \( J_{\text{aqNH}} \) and the rest is either denitrified or returned as \( J_{\text{aqNO3}} \) (Section III-K in D&F). Large fraction of the nitrate produced by nitrification escapes as \( J_{\text{N2(a)}} \) while small fraction is returned as \( J_{\text{aqNO3}} \): 22% of \( J_N \) escapes as \( J_{\text{N2(a)}} \) but this includes the denitrification of overlying water nitrate as well (Sections III-J and III-K in D&F). For large \( \text{NO3}_o \), \( J_{\text{aqNO3}} \) is negative (to the sediment) and \( J_{\text{N2(a)}} \) is large owing to the denitrification of overlying water nitrate transported to the sediment (Section III-J in D&F). One surprising result was that the primary site of denitrification is in the oxic layer: mass transfer of nitrate to the anoxic lower layer is insufficient for significant denitrification to occur in that layer (Section III-H in D&F). This finding, which contradicts some measurements (e.g., Sørensen & Revsbech 1990), may have resulted from an artifact of the two layer segmentation and deserves further investigation.

As in nitrification rate in Section IV-7-4, spatially-varying values, larger in freshwater, were used for \( \kappa_{\text{NO3,1}} \) in the final calibration of the coupled model (Cerco & Cole 1994):

\[
\begin{align*}
\kappa_{\text{NO3,1}} &= 0.125 \text{ m day}^{-1} \text{ for saltwater (} S > S_{\text{crit,NO3}} \text{)} \\
&= 0.300 \text{ m day}^{-1} \text{ for freshwater (} S < S_{\text{crit,NO3}} \text{)}.
\end{align*}
\]

IV-7-6. Parameters for phosphate flux

The parameters that need to be estimated specifically for the phosphate flux are \( J_{\text{LPO4}}, J_{\text{2PO4}}, \kappa_{\text{LPO4}}, \kappa_{\text{2PO4}}, \pi_{\text{LPO4}} \) and \( \pi_{\text{2PO4}} \) in Equations 4-8 to 4-11. As described in Section IV-3-4:

\[
\begin{align*}
J_{\text{LPO4}} &= 0 \\
J_{\text{2PO4}} &= J_P \text{ from Eq. 4-7} \\
\kappa_{\text{LPO4}} &= \kappa_{\text{2PO4}} = 0.
\end{align*}
\]

Evaluation of the partition coefficients involves three parameters (Eq. 4-25). The "stand alone" model (D&F) had:

\[
\begin{align*}
\pi_{\text{2PO4}} &= 100.0 \text{ L kg}^{-1} \\
\Delta\pi_{\text{PO4,1}} &= 300.0 \\
(\text{DO})_{\text{crit,PO4}} &= 2.0 \text{ g O}_2 \text{ m}^3.
\end{align*}
\]

Any set of laboratory or field measurements that include simultaneous measurements
of ammonium and phosphate fluxes can be compared to model predictions using the stand-alone model (Section IV-6-3, and Section VI-E in D&F). It has been shown in D&F (Section VI-E), the steady-state model cannot produce the excess anoxic $J_{aq,PO_4}$ which is due to the phosphate stored in the sediment during oxic periods. In time-varying "stand alone" application, D&F noted that the formulation for phosphate partitioning (Eq. 4-25) was not complete although the phosphate cycle still was representative (Section X-F-2 in D&F). A number of cases occurred where the model predicted a negative phosphate flux whereas the observation was positive. This discrepancy occurred just after turnover when the overlying water oxygen increased. The model recreated the oxic layer immediately with its high partition coefficient and the resulting phosphate concentration in the oxic layer caused a flux to the sediment. They suggested that a more realistic formulation would involve a model of the iron cycle, in which the formation of iron oxyhydroxide would take place more slowly and the oxic layer partition coefficient would increase more slowly.

Spatial variation in the ratio of dissolved to particulate sediment phosphate was observed in the mainstem Chesapeake Bay: at the most upriver station, pore water phosphate was lowest while particulate inorganic phosphate was highest (Fig. X-22 in D&F). It suggests that the partition coefficient was largest at the upriver station and decreased in the downriver direction (Fig. X-23 in D&F). Thus, as in the nitrification rate in Section IV-7-4, spatially-varying values, larger in freshwater, were used for $\Delta \pi_{PO_4}$ in the final calibration of the coupled model (Cerco & Cole 1994):

$$\Delta \pi_{PO_4} = 300.0 \text{ for saltwater (} S > S_{crit,PO_4} \text{)}$$

$$= 3000.0 \text{ for freshwater (} S < S_{crit,PO_4} \text{)}.$$  

IV-7-7. Parameters for sulfide/methane flux and SOD

The parameters that need to be estimated specifically for the sulfide flux and SOD are $J_{1,H_2S}$, $J_{2,H_2S}$, $\kappa_{1,H_2S}$, $\kappa_{2,H_2S}$, $\pi_{1,H_2S}$ and $\pi_{2,H_2S}$ in Equations 4-8 to 4-11. As described in Section IV-3-5:

$$J_{1,H_2S} = 0$$

$J_{2,H_2S}$ from Eq. 4-27

$$\kappa_{1,H_2S} = 0.$$  

$$\kappa_{2,H_2S} = 0.$$  

Evaluation of $\kappa_{1,H_2S}$ involves six parameters (Eq. 4-28). The values used in D&F are:
\[ \pi_{\text{H}_2\text{S}} = 100.0 \text{ L kg}^{-1} \]
\[ \kappa_{\text{H}_2\text{S}} = 0.2 \text{ m day}^{-1} \]
\[ \theta_{\text{H}_2\text{S}} = 1.08 \]
\[ \pi_{2,\text{H}_2\text{S}} = 100.0 \text{ L kg}^{-1} \]
\[ \kappa_{\text{H}_2\text{S,p}} = 0.4 \text{ m day}^{-1} \]
\[ \text{KM}_{\text{H}_2\text{S,02}} = 4.0 \text{ g O}_2 \text{ m}^3. \]

No adjustment was made for the parameters in the final calibration of the coupled model application.

The methane flux in the freshwater (Equations 4-31 to 4-34) requires the following parameters:
\[ J_{1,\text{CH}_4} = 0 \]
\[ J_{2,\text{CH}_4} \text{ from Eq. 4-31} \]
\[ \kappa_{\text{CH}_4} = 0.2 \text{ m day}^{-1} \]
\[ \theta_{\text{CH}_4} = 1.08. \]

The "stand alone" application in D&F showed that approximately 18% of the depositional carbon flux was not returned as either CSOD or as a \( J_{\text{aq,H}_2\text{S}} \). Among 18% loss, 15% was due to the burial of the G class carbon (Table 4-1) and 3% was lost by burial of particulate sulfide. The "stand alone" application also noted that neither data nor the model show any strong temperature dependency of SOD (Fig. X-19 in D&F). As in phosphate flux, simultaneous measurements of ammonium and oxygen fluxes can be used to compare to model predictions using the stand-alone model (Section IV-6-3, and Section V-G in D&F).

It has been shown in D&F (Fig. V-4A), the steady-state model cannot produce the excess SOD, which is due to the oxidation of particulate sulfide stored in the sediment during periods where carbon diagenesis exceeds SOD. In time-varying "stand alone" application, D&F noted that the sulfur cycle in the model was not complete although it still was representative (Section X-D-2 in D&F). The model calculated particulate sulfide concentrations higher than the observed FeS (acid volatile sulfide) but lower than the observed FeS+FeS\(_2\) (chromate reducible sulfide) (Fig. X-13B in D&F). The model forms FeS(s) only using a partitioning equilibria, which is considered to be reactive and oxidized. However, FeS can also react with elemental sulfur to form iron pyrite, FeS\(_2\), which is much less reactive and thus builds up in the sediment. They suggested that inclusion of the reaction for FeS\(_2\) formation would lower the computed FeS concentrations, thus improving the agreement with the observations, and would increase the computed total sulfide owing to the build-up of FeS\(_2\). Another limitation of the model found in D&F was that the model predicted almost no seasonal variation whereas the pore
water sulfide data appeared to indicate a seasonal variation (Fig. X-16 in D&F). It was both due to omission of FeS2 formation process and to use of constant linear partitioning.

IV-7-8. Parameters for silica

The parameters that need to be estimated for the particulate biogenic silica are S_Si, H2, W, J_\text{PSi} and J_DSi in Eq. 4-35. The parameters, H2 and W, are described in Section IV-7-2, and J_\text{PSi} is estimated from Eq. 4-5. D&F had:

\[ J_DSi = 0.1 \text{ g Si m}^{-2} \text{ day}^{-1}. \]

Evaluation of S_Si involves five parameters (Eq. 4-36). The values used in D&F are:

\[
\begin{align*}
K_Si &= 0.5 \text{ day}^{-1} \\
\theta_{Si} &= 1.1 \\
\text{Si}_{\text{sat}} &= 40.0 \text{ g Si m}^{-3} \\
\pi_{2, Si} &= 100.0 \text{ L kg}^{-1} \\
\text{KM}_{\text{PSi}} &= 5 \times 10^4 \text{ g Si m}^{-3}.
\end{align*}
\]

The \text{KM}_{\text{PSi}} value is equivalent to 0.1 g Si g\(^{-1}\) if solid concentration is 0.5 kg L\(^{-1}\) (Section IV-7-3B).

The parameters that need to be estimated specifically for the silica flux are J_{1, Si}, J_{2, Si}, \kappa_{1, Si}, \kappa_{2, Si}, \pi_{1, Si} and \pi_{2, Si} in Equations 4-8 to 4-11. As described in Section IV-4:

\[
\begin{align*}
J_{1, Si} &= 0 \\
J_{2, Si} &= \text{from Eq. 4-38-1} \\
\kappa_{1, Si} &= 0 \\
\kappa_{2, Si} &= \text{from Eq. 4-38-2}.
\end{align*}
\]

Evaluation of the partition coefficients involves three parameters, \pi_{2, Si}, \Delta\pi_{Si, 1} and \text{(DO}_0\text{) crit. Si} (Eq. 4-39). The values used in D&F are:

\[
\Delta\pi_{Si, 1} = 10.0
\]

\[
\text{(DO}_0\text{) crit. Si} = 1.0 \text{ g O}_2 \text{ m}^{-3}.
\]

Evaluation of J_{2, Si} (Eq. 4-38-1) and \kappa_{2, Si} (Eq. 4-38-2) requires five parameters, K_Si, \theta_{Si}, \text{KM}_{\text{PSi}}, \text{Si}_{\text{sat}} and \pi_{2, Si}. The values used in D&F are given above. All the above values were estimated from field data, previous studies or model calibration. No adjustment was made for the parameters in the final calibration of the coupled model application.

As in phosphate flux and SOD, simultaneous measurements of ammonium and silica fluxes can be used to compare to model predictions using the stand-alone model (Section IV-6-3, and Section VII-D in D&F). In the "stand alone" application, D&F showed that approximately 76% of the depositional nitrogen flux was returned as a J_{aq, \text{NH}_4} (Section IV-7-4) and approximately 82% of the depositional carbon flux was returned as either CSOD or as a J_{aq, \text{H}_2\text{S}} (Section IV-7-7). However, the fraction of recycled silica (J_{aq, Si}) to the total...
silica input ($J_{psil} + J_{dsil}$) was quite variable and did not appear to be strongly related to the total input (Section X-G-2 in D&F). This is because there is a limitation to the quantity of silica that can be recycled, which is determined by the silica solubility.

IV-7-9. Comments

The parameter values presented in this section were established after analyzing extensive data sets and model calibration (D&F; Cerco & Cole 1994). These values may serve as an excellent starting point for model application to estuaries of the eastern United States. However, since no two systems are exactly the same, it might be necessary to alter the values of some parameters when applying this sediment model for different systems. The parameters that one may want to alter include:

: split of POM settling from the overlying water to three G classes ($FMLP_i$, $FMRP_i$, and $FMB_k$ in Equations 4-2 to 4-4)
: burial rate ($W$ in Eq. 4-6)
: nitrification rate ($\kappa_{NH_4}$ in Eq. 4-19) and denitrification rate ($\kappa_{NO_3,1}$ and $\kappa_{NO_3,2}$ in Eq. 4-22), particularly as a function of salinity
: phosphate sorption in oxic upper layer ($\pi_{2,PO_4}$, $\Delta_{PO_4}$, and $(DO)_{oxl,PO_4}$ in Eq. 4-25).
Table 4-1. Assignment of water column particulate organic matter (POM) to sediment G classes used in Cereo & Cole (1994).

<table>
<thead>
<tr>
<th>WCM Variable</th>
<th>Carbon &amp; Phosphorus</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G₁</td>
<td>G₂</td>
</tr>
<tr>
<td>A. &quot;stand alone&quot; model</td>
<td>0.65</td>
<td>0.20</td>
</tr>
<tr>
<td>B. coupled model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labile Particulate</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Refractory Particulate*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>: Bay and Tributary Zones 1</td>
<td>0.0</td>
<td>0.11</td>
</tr>
<tr>
<td>: Bay Zones 2 and 10</td>
<td>0.0</td>
<td>0.43</td>
</tr>
<tr>
<td>: All Other Zones</td>
<td>0.0</td>
<td>0.73</td>
</tr>
<tr>
<td>Algae</td>
<td>0.65</td>
<td>0.255</td>
</tr>
</tbody>
</table>

* See Figure 10-6 in Cereo & Cole (1994) for the definition of Zones.

Table 4-2. Sediment burial rates (W) used in Cereo & Cole (1994).

<table>
<thead>
<tr>
<th>Bay Zones¹</th>
<th>Rate (cm yr⁻¹)</th>
<th>Tributary Zones¹</th>
<th>Rate (cm yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2, 10</td>
<td>0.50</td>
<td>1</td>
<td>0.50</td>
</tr>
<tr>
<td>3, 6, 9</td>
<td>0.25</td>
<td>2, 3</td>
<td>0.25</td>
</tr>
<tr>
<td>7, 8</td>
<td>0.37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ See Figure 10-6 in Cereo & Cole (1994) for the definition of Zones.
Figure 4-1. Sediment layers and processes included in sediment process model.
Figure 4-2. A schematic diagram for sediment process model.
Figure 4-3. Benthic stress (a) and its effect on particle mixing (b) as a function of overlying dissolved oxygen concentration.
V. Simplified Version

The water quality model has twenty-one model state variables (Chapter III), and the sediment process model has twenty-seven state variables (Chapter IV). When applying this model package, the amount of field data to evaluate the kinetic coefficients, to estimate the external loads for all state variables, to compare the model results with, etc is not trivial. Not many systems currently have such a data set. Hence, a simplified version of the water quality model, including sediment process model, is developed and described in this chapter. The model described in Chapter III and IV will be referred to as "full version" while the model described in this chapter as "simplified version".

The simplified version of the water quality model, which simulates reduced number of state variables, has nine state variables:

1) algae
2) organic carbon
3) organic phosphorus
4) total phosphate
5) organic nitrogen
6) ammonium nitrogen
7) nitrate nitrogen
8) chemical oxygen demand
9) dissolved oxygen

The nitrate state variable represents the sum of nitrate and nitrite nitrogen. The state variables and their interactions in the simplified version are shown in Fig. 5-1. All algal groups are represented by one state variable, algae. Organic matter is represented by one state variable, distinguishing neither particulate and dissolved organic nor refractory and labile particulate. Since diatoms are not explicitly simulated, neither is the silica cycle. Total active metal is not included in the simplified version, meaning that total suspended solid provided by the hydrodynamic model is the only possible sorption site for phosphate. The 9 state variables are virtually the same as those in some previous models (e.g., Thomann & Fitzpatrick 1982; Ambrose et al. 1988; Kuo et al. 1991; Park & Kuo 1993). This type of models have been widely used to help waste load allocation.

Now that the water column water quality model does not include silica cycle, the sediment process model in the simplified version has twenty-three state variables, with the 4 variables, particulate biogenic silica, available silica in Layer 1 and 2, and silica flux, excluded in the simplified version. In the simplified version, there is no distinction
between refractory particulate, labile particulate and dissolved organic matter in the water column water quality model. Hence, the organic matter deposited from the overlying water column is assigned to all three G classes in the sediment.

The remainder of this chapter describes the changes in kinetic formulations and in the meaning of kinetic coefficients caused by the reduction in state variables in both water quality and sediment process models.

V-1. Water Column Water Quality Model

V-1-1. Algae

The governing kinetic equation for algae remains the same as that in the full version (Eq. 3-1), with each term representing the process for all algal groups. Equation 3-1b is used for algal growth, with the salinity toxicity term as an option in the source code. Equation 3-1c, which does not include the silica limitation, is used for nutrient limitation for algal growth. Equations 3-1e to 3-1n in the full version remain the same in the simplified version. All kinetic coefficients in the simplified version are representative of all algal groups.

V-1-2. Organic carbon

One state variable, organic carbon, represents both particulate and dissolved organic carbon. For organic carbon, the processes included in the simplified version are:

- algal excretion (exudation) and predation
- settling of particulate organic carbon
- decomposition of organic carbon, consuming oxygen
- denitrification
- external loads

The governing kinetic equation is:

\[
\frac{\partial OC}{\partial t} = \left( FCD + (1 - FCD) \frac{KHR}{KHR + DO} \right) BM + PR \cdot B + \frac{\partial}{\partial z} \left( WS_{oc} \cdot OC \right) - K_{HRO} \cdot OC - Denit \cdot DOC + \frac{WOC}{V}
\]  

(5-1)
OC = concentration of organic carbon (g C m\(^{-3}\))
WS\(_{OC}\) = settling velocity of organic carbon (m day\(^{-1}\))
\(K_{HRO}\) = decomposition rate of organic carbon (day\(^{-1}\))
Denit = denitrification rate (day\(^{-1}\))
WOC = external loads of organic carbon (g C day\(^{-1}\)).

The variables BM, PR and B are equivalent to \(BM_x\), \(PR_x\) and \(B_x\) (Eq. 3-1) for all algal groups respectively. FCD and KHR are equivalent to \(FCD_x\) and \(KHR_x\) (Eq. 3-4) for all algal groups respectively. Denitrification rate, Denit, in the simplified version is given by Eq. 3-41 after replacing \(K_{DOC}\) with \(K_{OC}\).

In the simplified version, the term "decomposition" is defined as the process by which organic matter is converted to inorganic form. That is, decomposition includes both hydrolysis and mineralization defined in the full version (Section III-2-2). From Equations 3-4g to 3-4j, the decomposition rate of organic carbon is expressed as:

\[
K_{HRO} = \frac{DO}{KHOR_{DO} + DO} \cdot K_{OC}\]  
(5-1a)

\[
K_{OC} = (K_{OCmin} + K_{OCalg} \cdot B) \cdot \exp(KT_{DEC}\left[T - TR_{DEC}\right])\]  
(5-1b)

\(K_{OCmin}\) = minimum decomposition rate of organic carbon (day\(^{-1}\))
\(K_{OCalg}\) = constant that relates decomposition of organic carbon to algal biomass (day\(^{-1}\) per g C m\(^{-3}\))

\(KT_{DEC}\) = effect of temperature on decomposition of organic matter (°C\(^{-1}\))
\(TR_{DEC}\) = reference temperature for decomposition of organic matter (°C).

The behavior of Equations 5-1a and 5-1b is described in Section III-2-2.

V-1-3. Phosphorus

A. Organic phosphorus: One state variable, organic phosphorus, represents both particulate and dissolved organic phosphorus. For organic phosphorus, the processes included in the simplified version are:

: algal basal metabolism and predation
: settling of particulate organic phosphorus
: hydrolysis (mineralization) of organic phosphorus
The kinetic equation is:

\[
\frac{\partial OP}{\partial t} = (FPO \cdot BM + FPOP \cdot PR)APC \cdot B + \frac{\partial}{\partial z}(WS_{OP} \cdot OP) - K_{OP} \cdot OP + \frac{WOP}{V} \quad (5-2)
\]

OP = concentration of organic phosphorus (g P m\(^{-3}\))
FPO = fraction of metabolized phosphorus produced as organic phosphorus
FPOP = fraction of predated phosphorus produced as organic phosphorus
WS\(_{OP}\) = settling velocity of organic phosphorus (m day\(^{-1}\))
K\(_{OP}\) = hydrolysis rate of organic phosphorus (day\(^{-1}\))
WOP = external loads of organic phosphorus (g P day\(^{-1}\)).

Note that FPO = FPR\(_x\) + FPL\(_x\) + FPD\(_x\) and FPOP = FPRP + FPLP + FPDP for all algal groups.

From Equations 3-8f to 3-8h, the decomposition rate of organic phosphorus is expressed as:

\[
K_{OP} = \left( K_{OP_{min}} + \frac{K_{HP}}{K_{HP} + PO_{4d}} K_{OP_{alg}} \cdot B \right) \cdot \exp(K_{T_{DEC}}[T - T_{R_{DEC}}]) \quad (5-2a)
\]

K\(_{OP_{min}}\) = minimum decomposition rate of organic phosphorus (day\(^{-1}\))
K\(_{OP_{alg}}\) = constant that relates decomposition of organic phosphorus to algal biomass (day\(^{-1}\) per g C m\(^{-3}\)).

The behavior of Eq. 5-2a is described in Section III-3-4.

B. Total Phosphate: For total phosphate, the processes included in the simplified version are the same as those in the full version (Section III-3). The kinetic equation is:

\[
\frac{\partial PO_{4t}}{\partial t} = (FPI \cdot BM + FPIP \cdot PR - P)APC \cdot B + K_{OP} \cdot OP
\]

\[
+ \frac{\partial}{\partial z}(WS_{RSS} \cdot PO_{4t}) + BFPO_{4d} \cdot \frac{\Delta z}{V} + \frac{WPO_{4t}}{V} \quad (5-3)
\]

where FPI and P are equivalent to FPI\(_x\) (Eq. 3-8) and P\(_x\) (Eq.3-1) for all algal groups respectively. Note that FPO + FPI = 1 and FPOP + FPIP = 1, and that the sediment-water exchange term, BFPO\(_{4d}\), is applied to the bottom layer only.
For the total phosphate system and algal phosphorus-to-carbon ratio (APC), no change is needed from the full version to simplified version. Equations 3-8b to 3-8e in the full version are used without modification.

V-1-4. Nitrogen

A. Organic nitrogen: One state variable, organic nitrogen, represents both particulate and dissolved organic nitrogen. For organic nitrogen, the processes included in the simplified version are:

- algal basal metabolism and predation
- settling of particulate organic nitrogen
- ammonification (mineralization) of organic nitrogen
- external loads

The kinetic equation is:

\[
\frac{\partial ON}{\partial t} = (FNO \cdot BM + FNOP \cdot PR) \cdot ANC \cdot B + \frac{\partial}{\partial z} (WS_{ON} \cdot ON) - K_{ON} \cdot ON + \frac{WON}{V} \tag{5-4}
\]

ON = concentration of organic nitrogen (g N m\(^{-3}\))
FNO = fraction of metabolized nitrogen produced as organic nitrogen
FNOP = fraction of predated nitrogen produced as organic nitrogen
WS\(_{ON}\) = settling velocity of organic nitrogen (m day\(^{-1}\))
K\(_{ON}\) = ammonification rate of organic nitrogen (day\(^{-1}\))
WON = external loads of organic nitrogen (g N day\(^{-1}\)).

Note that FNO = FNR\(_x\) + FNL\(_x\) + FND\(_x\) and FNOP = FNRP + FNLP + FNDP for all algal groups.

From Equations 3-13b to 3-13d, the decomposition rate of organic nitrogen is expressed as:

\[
K_{ON} = (K_{ON_{min}} + \frac{KHN}{KHN + NH4 + NO3} \cdot K_{ON_{alg}} \cdot B) \cdot \exp(K_{T,DEC} [T - TR_{DEC}]) \tag{5-4a}
\]

\(K_{ON_{min}}\) = minimum decomposition rate of organic nitrogen (day\(^{-1}\))
\(K_{ON_{alg}}\) = constant that relates decomposition of organic nitrogen to algal biomass (day\(^{-1}\) per g C m\(^{-3}\)).
The behavior of Eq. 5-4a is described in Section III-4-2.

B. Ammonium nitrogen: For ammonium nitrogen, the processes included in the simplified version are the same as those in the full version (Section III-4). The kinetic equation is:

\[
\frac{dNH_4}{dt} = (FNI \cdot BM + FNIP \cdot PR - PN \cdot P)ANC \cdot B + K_{ON} \cdot ON
\]

\[\text{where } FNI, PN \text{ and } ANC \text{ are equivalent to } FN_x, PN_x \text{ and } ANC_x \text{ (Eq. 3-12) for all algal groups respectively. Note that } FNO + FNI = 1 \text{ and } FNOP + FNIP = 1, \text{ and that the sediment-water exchange term, } BFNH_4, \text{ is applied to the bottom layer only. Nitrification rate, } Nit, \text{ in the simplified version is the same as that in the full version (Eq. 3-13g).}
\]

C. Nitrate nitrogen: For nitrate nitrogen, the processes included in the simplified version are the same as those in the full version (Section III-4). The kinetic equation is:

\[
\frac{dNO_3}{dt} = - (1 - PN)P \cdot ANC \cdot B + Nit \cdot NH_4 - ANDC \cdot Denit \cdot OC
\]

\[\text{No other change from the full version is necessary in the simplified version. In Eq. 5-6, the sediment-water exchange term, } BFN03, \text{ is applied to the bottom layer only.}
\]

V-1-5. Chemical oxygen demand and dissolved oxygen

The kinetic equation for chemical oxygen demand remains the same as that in the full version (Eq. 3-16). The temperature dependency in oxidation rate of chemical oxygen demand is evaluated using Eq. 3-16a.

For dissolved oxygen, the processes included in the simplified version are the same as those in the full version (Section III-7). The governing kinetic equation is:
\[
\frac{\partial DO}{\partial t} = \left( 1.3 - 0.3 \cdot PN \right) P - (1 - FCD) \frac{DO}{K_{HR} + DO} BM AOCR \cdot B - AONT \cdot Nit \cdot NH4 - AOCR \cdot K_{oc} \cdot OC - \frac{DO}{K_{COD} + DO} KCOD \cdot COD \\
+ K_s(DO_s - DO) + \frac{SOD}{\Delta z} + \frac{WDO}{V}
\]  

(5-7)

No other change from the full version is necessary in the simplified version. In Eq. 5-7, the sediment oxygen demand, SOD, is applied to the bottom layer only.

V-1.6. Comments

In the source code, the variables defined for cyanobacteria in the full version are used for algal biomass in the simplified version. The variables defined for inorganic nutrients (total phosphate, and ammonium and nitrate nitrogen), chemical oxygen demand and dissolved oxygen in the full version are also used in the simplified version. New variables are defined for organic matter since the kinetic equations for organic matter in the simplified version take different forms from those for particulate and dissolved organic matter in the full version. The kinetic coefficients for the full version listed in Section III-11 (Tables 3-1 to 3-7) may guide the evaluation of those in the simplified version.

V-2. Sediment Process Model

In the full version, the labile particulate organic matter (POM) deposited from the overlying water is transferred directly into the G_1 class in the sediment model, and the refractory POM is split into G_2 and G_3 classes. The deposited algal POM is split into all three classes (Section IV-7-2A). Now that the water column water quality model has only one state variable to represent the organic matter (carbon, phosphorus or nitrogen), all organic matter deposited from the overlying water column should be assigned to three G classes in the sediment. From Equations 4-2 to 4-4, the depositional fluxes for the i\textsuperscript{th} G class in the simplified version is:

\[ J_{POM_i} = FCOP_i \cdot WS_{OC} \cdot OC^N + FCB_i \cdot WS \cdot B^N \]  

(5-8)
\[ J_{\text{PON}_i} = F\text{NOP}_i \cdot WS_{\text{ON}} \cdot ON^N + F\text{NB}_i \cdot ANC \cdot WS \cdot B^N \] (5-9)

\[ J_{\text{POP}_i} = F\text{POP}_i \cdot WS_{\text{OP}} \cdot OP^N + F\text{PB}_i \cdot APC \cdot WS \cdot B^N + \gamma_i \cdot WS_{\text{TSS}} \cdot PO4p^N \] (5-10)

FCOP\(_i\), FNOP\(_i\) & FPOP\(_i\) = fraction of water column OC, ON and OP, respectively, routed into the \(i^{th}\) G class in sediment

FCB\(_i\), FNB\(_i\) & FPB\(_i\) = fraction of OC, ON and OP, respectively, in all algal groups routed into the \(i^{th}\) G class in sediment.

The variable WS is equivalent to WS\(_x\) (Eq. 3-1) for all algal groups. The parameter values in Table 4-1 may guide the evaluation of distribution coefficients (FCOP\(_i\), FNOP\(_i\), FPOP\(_i\), FCB\(_i\), FNB\(_i\) and FPB\(_i\)) in the simplified version.

Exclusion of the 4 state variables related to silica in the sediment process model is straightforward, and it affects neither the mathematical formulations of the remaining portion of the model, nor the meaning of the kinetic coefficients. No change from the full version is necessary for the diagenesis and sediment flux formulations in the simplified version.
Figure 5-1. A schematic diagram for simplified water quality model.
VI. Comments

The Virginia Institute of Marine Science's three-dimensional Hydrodynamic-Eutrophication Model (HEM-3D) consists of the hydrodynamic model, the water column water quality model and the sediment process model. The hydrodynamic model is the EFDC described in Hamrick (1992). Application of the hydrodynamic model involves grid generation, data analysis for initial and boundary conditions, model calibration/verification, and interpretation of model results. The application of the hydrodynamic model to the Indian River Lagoon/Turkey Creek region is described in Tetra Tech (1993).

The model formulations and their method of solution for the water column water quality model and sediment process model are described in this report. Application of the water quality and sediment process models involves data analysis for initial and boundary conditions, evaluation of external loadings, model calibration/verification, and interpretation of model results. The application of the water quality and sediment process models to an idealized, hypothetical system will be described in another report. Description of input data files is given in Appendix B of this report, which is provided in a disk.
References


Llansó, R.J. 1992. Effects of hypoxia on estuarine benthos: the lower Rappahannock River (Chesapeake Bay), a case study. Estuarine, Coastal and Shelf Science, 35: 491-515.


Troup, R. 1974. The interaction of iron with phosphate, carbonate and sulfide in


The matrices in Eq. 3-21, $[C]_k$ in mass volume$^{-1}$, $[K1]_k$ and $[K2]_k$ in time$^{-1}$ and $[R]_k$ in mass volume$^{-1}$ time$^{-1}$, are defined below. For the diagonal matrix $[K2]_k$, which accounts for the settling of particulate matter from the overlying cell, only the diagonal terms are shown. In the matrix $[C]_k$, the LHS of the equal sign lists the names of the state variables used in this report, while the RHS lists the names used in the source code.
The non-zero elements in $[K1]_k$, $[K2]_k$, and $[R]_k$ are given below. As explained in Section III-10, the layer index $k$ increases upward: $k = 1$ is the bottom layer and $k = KC$ is the surface layer. Hereinafter the subscript $k$ to designate the $k^{th}$ layer is omitted.

$$
[K1]_k =
\begin{pmatrix}
    a_{1,c} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & a_{2,d} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & a_{3,g} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{4,c} & a_{4,d} & a_{4,g} & b_4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{5,c} & a_{5,d} & a_{5,g} & 0 & c_5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{6,c} & a_{6,d} & a_{6,g} & b_6 & c_6 & d_6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{7,c} & a_{7,d} & a_{7,g} & 0 & 0 & 0 & e_7 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{8,c} & a_{8,d} & a_{8,g} & 0 & 0 & 0 & f_8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{9,c} & a_{9,d} & a_{9,g} & 0 & 0 & 0 & e_9 & f_9 & g_9 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{10,c} & a_{10,d} & a_{10,g} & 0 & 0 & 0 & 0 & g_{10} & h_{10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{11,c} & a_{11,d} & a_{11,g} & 0 & 0 & 0 & 0 & 0 & 0 & i_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{12,c} & a_{12,d} & a_{12,g} & 0 & 0 & 0 & 0 & 0 & 0 & j_{12} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{13,c} & a_{13,d} & a_{13,g} & 0 & 0 & 0 & 0 & 0 & 0 & i_{13} & j_{13} & k_{13} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{14,c} & a_{14,d} & a_{14,g} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{15,c} & a_{15,d} & a_{15,g} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & a_{16,d} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & a_{17,d} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    a_{19,c} & a_{19,d} & a_{19,g} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix}
$$

The non-zero elements in $[K1]_k$, $[K2]_k$ and $[R]_k$ are given below. As explained in Section III-10, the layer index $k$ increases upward: $k = 1$ is the bottom layer and $k = KC$ is the surface layer. Hereinafter the subscript $k$ to designate the $k^{th}$ layer is omitted.

$$
\begin{align*}
    a_{1,c} &= P_c^0 - BM_c^0 - PR_c^0 - \frac{W_S^0}{\Delta z^0} \\
    t_{1,c} &= \frac{(W_S^0)_{k+1}}{\Delta z^0} \\
    r_{1,c} &= \frac{WB_c^0}{V^0}
\end{align*}
$$

A-2
\[ a_{zd} = P_{zd} - BM_{zd} - PR_{zd} - \frac{WS_{zd}}{\Delta z} \]
\[ a_{zs} = P_{zs} - BM_{zs} - PR_{zs} - \frac{WS_{zs}}{\Delta z} \]
\[ a_{x} = FCRP \cdot PR_{x} \]
\[ b_{4} = - b_{6} - \frac{WS_{RP}}{\Delta z} \]
\[ c_{5} = - c_{6} - \frac{WS_{LP}}{\Delta z} \]
\[ d_{6} = - K_{HR} - Densit \]
\[ e_{7} = - e_{9} - \frac{WS_{RP}}{\Delta z} \]
\[ f_{8} = - f_{9} - \frac{WS_{LP}}{\Delta z} \]
\[ t_{7} = t_{4} \]
\[ t_{8} = t_{5} \]
\[ a_{9x} = (FPD_x \cdot BM_x^o + FPDP \cdot PR_x^o) \cdot APC^o \]
\[ f_9 = K_{LPOP}^o \]
\[ r_9 = \frac{WDOP^o}{V^o} \]

\[ a_{10x} = (FPI_x \cdot BM_x^o + FPPIP \cdot PR_x^o - P_x^o) \cdot APC^o \]
\[ g_{10} = K_{DPOP}^o \]

\[ h_{10} = -\frac{WS_{TSS}^o}{\Delta z^o} \cdot \frac{K_{P04P} \cdot TSS^o}{1 + K_{P04P} \cdot TSS^o} \]

\[ t_{10} = \frac{(WS_{TSS})_{k+1}^o \cdot K_{P04P} \cdot TSS_{k+1}^o}{\Delta z^o} \cdot \frac{1}{1 + K_{P04P} \cdot TSS_{k+1}^o} \]

\[ i_{11} = -i_{13} - \frac{WS_{RP}^o}{\Delta z^o} \]
\[ r_{11} = \frac{WRPON^o}{V^o} \]

\[ a_{12x} = (FNL_x \cdot BM_x^o + FNLP \cdot PR_x^o) \cdot ANC_x \]
\[ j_{12} = -j_{13} - \frac{WS_{LP}^o}{\Delta z^o} \]
\[ r_{12} = \frac{WLPON^o}{V^o} \]

\[ a_{13x} = (FND_x \cdot BM_x^o + FNDP \cdot PR_x^o) \cdot ANC_x \]
\[ i_{13} = K_{RPON}^o \]
\[ k_{13} = -k_{14} \]
\[ r_{13} = \frac{WDON^o}{V^o} \]

\[ a_{14x} = (FNI_x \cdot BM_x^o + FNIP \cdot PR_x^o - PN_x^o \cdot P_x^o) \cdot ANC_x \]
\[ k_{14} = K_{DON}^o \]

A-4
\[ l_{14} = - N_{it}^o \]
\[ a_{15x} = -(1 - P_{N_k}^o)P_x^o \cdot ANC_x \]
\[ l_{15} = N_{it}^o \]
\[ a_{16d} = (FS_{d}^o \cdot BM_d^o + FS_{PP-PR_d}^o)ASC_d \]
\[ t_{16} = \frac{(WS_d^o)_{x+1}}{\Delta z^o} \]
\[ a_{17d} = (FS_{d}^o \cdot BM_d^o + FS_{IP-PR_d}^o - P_d^o)ASC_d \]
\[ n_{17} = - \frac{WS_{TSS}^o}{\Delta z^o} K_{StP} \cdot TSS^o \]
\[ t_{17} = \frac{(WS_{TSS})_{x+1}^o}{\Delta z^o} K_{StP} \cdot TSS_{x+1}^o \]
\[ \alpha_{18} = - \frac{DO^o}{KH_{COD} + DO^o} \cdot KCOD^o \]
\[ r_{18} = \frac{BFCOD^o}{\Delta z^o} + \frac{WCOD^o}{V^o} \]
\[ a_{19x} = \left(1.3 - 0.3 P_{N_k}^o\right)P_x^o - (1 - F_{CD_x}^o) \frac{DO^o}{KH_{R_x} + DO^oBM_x^o} \cdot AOCR \]
\[ d_{19} = - AOCR \cdot K_{HR}^o \]
\[ l_{19} = - AONT \cdot N_{it}^o \]
\[ \alpha_{19} = \alpha_{18} \]
\[ r_{19} = \frac{K_r^o \cdot DO_x^o}{\Delta z^o} + \frac{SOD^o}{V^o} + \frac{WDO^o}{V^o} \]
\[ d_{15} = - ANDC \cdot Denit^o \]
\[ r_{15} = \frac{BFNO3^o}{\Delta z^o} + \frac{WNO3^o}{V^o} \]
\[ m_{16} = - m_{17} - \frac{WS_d^o}{\Delta z^o} \]
\[ r_{16} = \frac{WSU^o}{V^o} \]
\[ m_{17} = K_{StU}^o \]
\[ r_{17} = \frac{BFSA^o}{\Delta z^o} + \frac{WSA^o}{V^o} \]

A-5
The diagonal matrix \([K2]_k\) is applied only when \(k \neq KC\), as indicated by \(\lambda\) in Eq. 3-21, and so is the second term on the RHS of \(r_{20}\). The sediment-water exchange terms in the matrix \([R]_k\) are applied only when \(k = 1\) (bottom layer), and the terms for dissolved oxygen reaeration in \(p_{19}\) and \(r_{19}\) are applied only when \(k = KC\) (surface layer).

Equation 3-21 is solved using a second-order accurate trapezoidal scheme over a time step of \(\theta\) (Eq. 3-22). To avoid inversion of a matrix in Eq. 3-22, the kinetic equations are solved in the order of the variables in the matrix \([C]\). The final forms of Eq. 3-22 for each of the state variables are:

\[
B_c^N = \left(B_c^O + \frac{\theta}{2} \left( a_{k,c} \cdot B_c^O + \lambda \cdot t_{1,c} \cdot (B_c)^A_{k+1} \right) + \theta \cdot r_{k,c} \right) \left(1 - \frac{\theta}{2} a_{k,c} \right)^{-1}
\]

\[
B_d^N = \left(B_d^O + \frac{\theta}{2} \left( a_{2,d} \cdot B_d^O + \lambda \cdot t_{2,d} \cdot (B_d)^A_{k+1} \right) + \theta \cdot r_{2,d} \right) \left(1 - \frac{\theta}{2} a_{2,d} \right)^{-1}
\]

\[
B_g^N = \left(B_g^O + \frac{\theta}{2} \left( a_{3,g} \cdot B_g^O + \lambda \cdot t_{3,g} \cdot (B_g)^A_{k+1} \right) + \theta \cdot r_{3,g} \right) \left(1 - \frac{\theta}{2} a_{3,g} \right)^{-1}
\]

\[
RPOC^N = \left(RPOC^O + \frac{\theta}{2} \cdot TT_{RPOC} + \theta \cdot r_4 \right) \left(1 - \frac{\theta}{2} b_4 \right)^{-1}
\]

\[
TT_{RPOC} = \sum_{x,c,d,g} a_{4,x} \cdot B_x^A + b_4 \cdot RPOC^O + \lambda \cdot t_4 \cdot RPOC_{k+1}^A
\]

\[
LPOC^N = \left(LPOC^O + \frac{\theta}{2} \cdot TT_{LPOC} + \theta \cdot r_5 \right) \left(1 - \frac{\theta}{2} c_5 \right)^{-1}
\]

\[
TT_{LPOC} = \sum_{x,c,d,g} a_{5,x} \cdot B_x^A + c_5 \cdot LPOC^O + \lambda \cdot t_5 \cdot LPOC_{k+1}^A
\]
\[ DOC^N = \left( DOC^O + \frac{\theta}{2} \cdot TT_{DOC} + \theta \cdot r_6 \right) \left( 1 - \frac{\theta}{2} d_6 \right)^{-1} \]

\[ TT_{DOC} = \sum_{x \in d_8} a_{6x} \cdot B_x^A + b_6 \cdot RPOC^A + c_6 \cdot LPOC^A + d_6 \cdot DOC^O \]

\[ RPOP^N = \left( RPOP^O + \frac{\theta}{2} \cdot TT_{RPOP} + \theta \cdot r_7 \right) \left( 1 - \frac{\theta}{2} e_7 \right)^{-1} \]

\[ TT_{RPOP} = \sum_{x \in d_8} a_{7x} \cdot B_x^A + e_7 \cdot RPOP^O + \lambda \cdot t_7 \cdot RPOP_{k+1}^A \]

\[ LPOP^N = \left( LPOP^O + \frac{\theta}{2} \cdot TT_{LPOP} + \theta \cdot r_8 \right) \left( 1 - \frac{\theta}{2} f_8 \right)^{-1} \]

\[ TT_{LPOP} = \sum_{x \in d_8} a_{8x} \cdot B_x^A + f_8 \cdot LPOP^O + \lambda \cdot t_8 \cdot LPOP_{k+1}^A \]

\[ DOP^N = \left( DOP^O + \frac{\theta}{2} \cdot TT_{DOP} + \theta \cdot r_9 \right) \left( 1 - \frac{\theta}{2} g_9 \right)^{-1} \]

\[ TT_{DOP} = \sum_{x \in d_8} a_{9x} \cdot B_x^A + e_9 \cdot RPOP^O + f_9 \cdot LPOP^O + g_9 \cdot DOP^O \]

\[ PO4t^N = \left( PO4t^O + \frac{\theta}{2} \cdot TT_{PO4t} + \theta \cdot r_{10} \right) \left( 1 - \frac{\theta}{2} h_{10} \right)^{-1} \]

\[ TT_{PO4t} = \sum_{x \in d_8} a_{10x} \cdot B_x^A + g_{10} \cdot DOP^O + h_{10} \cdot PO4t^O + \lambda \cdot t_{10} \cdot PO4t_{k+1}^A \]

\[ RPON^N = \left( RPON^O + \frac{\theta}{2} \cdot TT_{RPON} + \theta \cdot r_{11} \right) \left( 1 - \frac{\theta}{2} i_{11} \right)^{-1} \]

\[ TT_{RPON} = \sum_{x \in d_8} a_{11x} \cdot B_x^A + i_{11} \cdot RPON^O + \lambda \cdot t_{11} \cdot RPON_{k+1}^A \]

\[ LPON^N = \left( LPON^O + \frac{\theta}{2} \cdot TT_{LPON} + \theta \cdot r_{12} \right) \left( 1 - \frac{\theta}{2} j_{12} \right)^{-1} \]

\[ TT_{LPON} = \sum_{x \in d_8} a_{12x} \cdot B_x^A + j_{12} \cdot LPON^O + \lambda \cdot t_{12} \cdot LPON_{k+1}^A \]
\[
DON^N = \left( DON^O + \frac{\theta}{2} \cdot TT_{DON} + \theta \cdot r_{13} \right) \left( 1 - \frac{\theta}{2} k_{13} \right)^{-1}
\]

\[
TT_{DON} = \sum_{x \in d_3} a_{13x} \cdot B_x^A + i_{13} \cdot RPON^A + j_{13} \cdot LPON^A + k_{13} \cdot DON^O
\]

\[
NH4^N = \left( NH4^O + \frac{\theta}{2} \left( \sum_{x \in d_6} a_{14x} \cdot B_x^A + k_{14} \cdot DON^A + l_{14} \cdot NH4^O \right) + \theta \cdot r_{14} \right) \left( 1 - \frac{\theta}{2} l_{14} \right)^{-1}
\]

\[
NO3^N = NO3^O + \frac{\theta}{2} \left( \sum_{x \in d_5} a_{15x} \cdot B_x^A + d_{15} \cdot DOC^A + l_{15} \cdot NH4^A \right) + \theta \cdot r_{15}
\]

\[
SU^N = \left( SU^O + \frac{\theta}{2} \left[ a_{16d} \cdot B_d^A + m_{16} \cdot SU^O + \lambda \cdot t_{16} \cdot SU_{i+1}^A \right] + \theta \cdot r_{16} \right) \left( 1 - \frac{\theta}{2} m_{16} \right)^{-1}
\]

\[
SA^N = \left( SA^O + \frac{\theta}{2} \left[ a_{17d} \cdot B_d^A + m_{17} \cdot SU^A + n_{17} \cdot SA^O + \lambda \cdot t_{17} \cdot SA_{i+1}^A \right] + \theta \cdot r_{17} \right) \left( 1 - \frac{\theta}{2} n_{17} \right)^{-1}
\]

\[
COD^N = \left( COD^O + \frac{\theta}{2} \cdot o_{18} \cdot COD^O + \theta \cdot r_{18} \right) \left( 1 - \frac{\theta}{2} o_{18} \right)^{-1}
\]

\[
DO^N = \left( DO^O + \frac{\theta}{2} \cdot TT_{DO} + \theta \cdot r_{19} \right) \left( 1 - \frac{\theta}{2} p_{19} \right)^{-1}
\]

\[
TT_{DO} = \sum_{x \in d_8} a_{19x} \cdot B_x^A + d_{19} \cdot DOC^A + l_{19} \cdot NH4^A + o_{19} \cdot COD^A + p_{19} \cdot DO^O
\]

\[
TAM^N = \left( TAM^O + \frac{\theta}{2} \left[ q_{20} \cdot TAM^O + \lambda \cdot t_{20} \cdot TAM_{i+1}^A \right] + \theta \cdot r_{20} \right) \left( 1 - \frac{\theta}{2} q_{20} \right)^{-1}
\]

\[
FCB^N = \left( FCB^O + \frac{\theta}{2} \cdot s_{21} \cdot FCB^O + \theta \cdot r_{21} \right) \left( 1 - \frac{\theta}{2} s_{21} \right)^{-1}
\]

where $C^A = C^N + C^O$. 

A-8