The Environmental Fluid Dynamics Code
Theory and Computation
Volume 3: Water Quality Module

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Preface and Acknowledgements

The Environmental Fluid Dynamics Code (EFDC) is a public domain, open source, surface water modeling system, which includes hydrodynamic, sediment and contaminant, and water quality modules fully integrated in a single source code implementation. EFDC has been applied to over 100 water bodies including rivers, lakes, reservoirs, wetlands, estuaries, and coastal ocean regions in support of environmental assessment and management and regulatory requirements.

EFDC was originally developed at the Virginia Institute of Marine Science (VIMS) and School of Marine Science of The College of William and Mary, by Dr. John M. Hamrick beginning in 1988. This activity was supported by the Commonwealth of Virginia through a special legislative research initiative. Dr. Robert Byrne, the late Dr. Bruce Neilson, and Dr. Albert Kuo, of VIMS are acknowledged for their efforts in supporting the original development activity. Subsequent support for EFDC development at VIMS was provided by the U. S. Environmental Protection Agency and the National Oceanic and Atmospheric Administration's Sea Grant Program. The contributions of VIMS staff and former students including Mr. Gamble Sisson, Dr. Zaohqing Yang, Dr. Keyong Park, Dr. Jian Shen, and Dr. Sarah Rennie are gratefully acknowledged.

Tetra Tech, Inc. (Tt) became the first commercial user of EFDC in the early 1990's and upon Dr. Hamrick's joining Tetra Tech in 1996, the primary location for the continued development of EFDC. Tetra Tech has provided considerable internal research and development support for EFDC over the past 10 years and Mr. James Pagenkopf, Dr. Mohamed Lahlou, and Dr. Leslie Shoemaker are gratefully acknowledged for this. Mr. Michael Morton of Tetra Tech is particularly recognized for his many contributions to EFDC development and applications. The efforts Tetra Tech colleagues including Dr. Jeff Ji, Dr. Hugo Rodriguez, Mr. Steven Davie, Mr. Brain Watson, Dr. Ruiz Zou, Dr. Sen Bai, Dr. Yuri Pils, Mr. Peter von Lowe, Mr. Will Anderson, and Dr. Silong Lu are also recognized. Their wide-ranging applications of EFDC have contributed to the robustness of the model and lead to many enhancements.

Primary external support of both EFDC development and maintenance and applications at Tetra Tech over the past 10 years has been generously provided by the U.S. Environmental Protection Agency including the Office of Science and Technology, the Office of Research and Development and Regions 1 and 4. In particular, Dr. Earl Hayter (ORD), Mr. James Greenfield (R4), Mr. Tim Wool (R4) and Ms. Susan Svirsky (R1) are recognized for their contributions in managing both EFDC developmental and application work assignments.

The ongoing evolution of the EFDC model has to a great extent been application driven and it is appropriate to thank Tetra Tech's many clients who have funded EFDC applications over the past 10 years. Of these many clients, the South Florida Water Management District (SFWMD) and Dr. Mohamed Moustafa of SFWMD, are recognized for SFWMD's support of numerous EFDC applications. The benefits of ongoing interaction with a diverse group of EFDC users in the academic, governmental, and private sectors are also acknowledged.

The history of EFDC water quality applications dates to the early 1990's with the development of an EFDC hydrodynamic linkage to the WASP 5.1 water quality model by Mr. Michael Morton of Tt and Dr. John Hamrick. The EFDC linkage capability with subsequent versions of WASP has been maintained and enhanced by Dr. Hugo Rodriguez of Tt in cooperation with Mr. Tim Wool of US EPA R4, and numerous EFDC-WASP coupled applications have been successfully conducted. Following the success of the Chesapeake Bay water quality modeling effort using the CH3D-WES hydrodynamic model, externally linked to the CE-QUAL-ICM water quality model it became evident that many water quality modeling applications could benefit form the extended water quality kinetic formulation and sediment diagenesis or flux sub-model of CE-QUAL-ICM. Although coupled hydrodynamic and water quality modeling efforts had traditionally used separate externally linked models, such as DYNHYD or EFDC and WASP and CH3D-WES and CE-QUAL-ICM, the alternative of a transparent, internally linked hydrodynamic and water quality modeling was adopted along with the CE-QUAL-ICM formulation for implementation in EFDC.

The original development of the internally linked EFDC water quality module was lead by Dr. Keyong Park at VIMS in 1995. Dr. Park, working in collaboration with Dr. Carl Cerco of the U.S. Army Corps of Engineers Research and Development Center (ERDC) adopted the CE-QUAL-ICM eutrophication kinetic formulation and sediment flux model into the EFDC code. Subsequent extensions and enhancements to Dr. Park's work have been made at Tetra Tech over the past 10 years, primarily by Mr. Michael Morton and Dr. John Hamrick. The material in this volume is based on Mr. Michael Morton's revisions to the Dr. Park's original report (Park *et al.*, 1995) with additions by Dr. Hamrick. The original notation used in CE-QUAL-ICM (Cerco and Cole, 1995) including the sediment diagenesis model (DiToro and Fitzpatrick, 1992) has been retained and the reader familiar with CE-QUAL-ICM will note striking similarities with these documents. The similarities are quite intentional and served to acknowledge the seminal contributions to the field of water quality modeling that these documents represent.

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1. Introduction

This report documents the theoretical and computational aspects of the EFDC water quality module, and is the third volume *The Environmental Fluid Dynamics Code: Theory and Computation* series of reports. Volume 1 (Hamrick, 1992; Tetra Tech, 2007a) documents the hydrodynamic and transport module and Volume 2 (Tetra Tech, 2002, 2007b) documents the sediment and sorptive contaminant transport module.

This report is organized as follows. Chapter 2 describes water column eutrophication or nutrient cycling. Chapter 2 is based on the report by Park *et al.* (1995) which in turn is based on the CE-QUAL-ICM report by Cerco and Cole (1995). An attempt has been made to follow the CE-QUAL-ICM notation and the reader is strongly encouraged to consult Cerco and Cole (1995) as well as subsequent CE-QUAL-ICM documentation listed in Table 2.2. Chapter 3 describes the generic rooted aquatic plant model. The plant model is based on the Chesapeake Bay submerged aquatic vegetation (SAV) model described in Cerco *et al*. (2002) and the Florida Bay seagrass model described by Madden and McDonald (2006) with extensions to simulate emergent plants typically found in wetlands and other shallow water environments. Notation for the rooted plant model is somewhat different from the two source documents. Chapter 4 describes the sediment diagenesis or flux model. Chapter 4 is based on the report by Park *et al.* (1995) which in turn based on the work of DiToro and Fitzpatrick (1993). The reader is strongly encouraged to consult DiToro and Fitzpatrick (1993) and DiToro (2003) for a more comprehensive description of the sediment flux model. References are listed in Chapter 5. This report also contains a number of appendices. Appendix A provides supplemental material regarding use of the stationary algae variable to simulate macroalgae and substrate attached and floating periphyton. Appendix B summarizes a least squares curve fitting procedure for the interpretation of long-term Biochemical Oxygen Demand and Nitrogen series test to estimate in situate kinetic coefficients and labile and refractory load splitting factors for source loads. Appendix C summarizes some useful statistical measures for evaluation water quality model performance and list values of the performance measures reported in a number of water quality modeling studies.

2. Water Column Eutrophication Formulation

2.1 Introduction

This section summarizes the basic theory of the water quality-eutrophication component of the EFDC model. The kinetic processes included in the EFDC water quality model are derived form the CE-QUAL-ICM water quality model (Cerco and Cole, 1995) as described in Park *et al.* (1995). This document describes the current model formulation including comparisons with subsequent published documentation of CE-QUAL-ICM model applications. Table 2.1 lists the model's complete set of state variables and their interactions are illustrated in Figure 2.1. As opposed to earlier water quality models such as WASP (Ambrose *et al.*, 1992), which use biochemical oxygen demand to represent oxygen demanding organic material, the EFDC water quality model is carbon based. The four algae species are represented in carbon units. The three organic carbon variables play an equivalent role to BOD. Organic carbon, nitrogen and phosphorous can be represented by up to three reactive sub-classes, refractory particulate, labile particulate and labile dissolve. The use of the sub-classes allows a more realistic distribution of organic material by reactive classes when data are to estimate distribution factors. The following sub-sections discuss the role of each variable and summarize their kinetic interaction processes. The kinetic processes include the exchange of fluxes at the sediment-water interface, including sediment oxygen demand. The description of the EFDC water column water quality model in this section closely follows Park *et al.* (1995).

Table 2.1 EFDC model water quality state variables

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

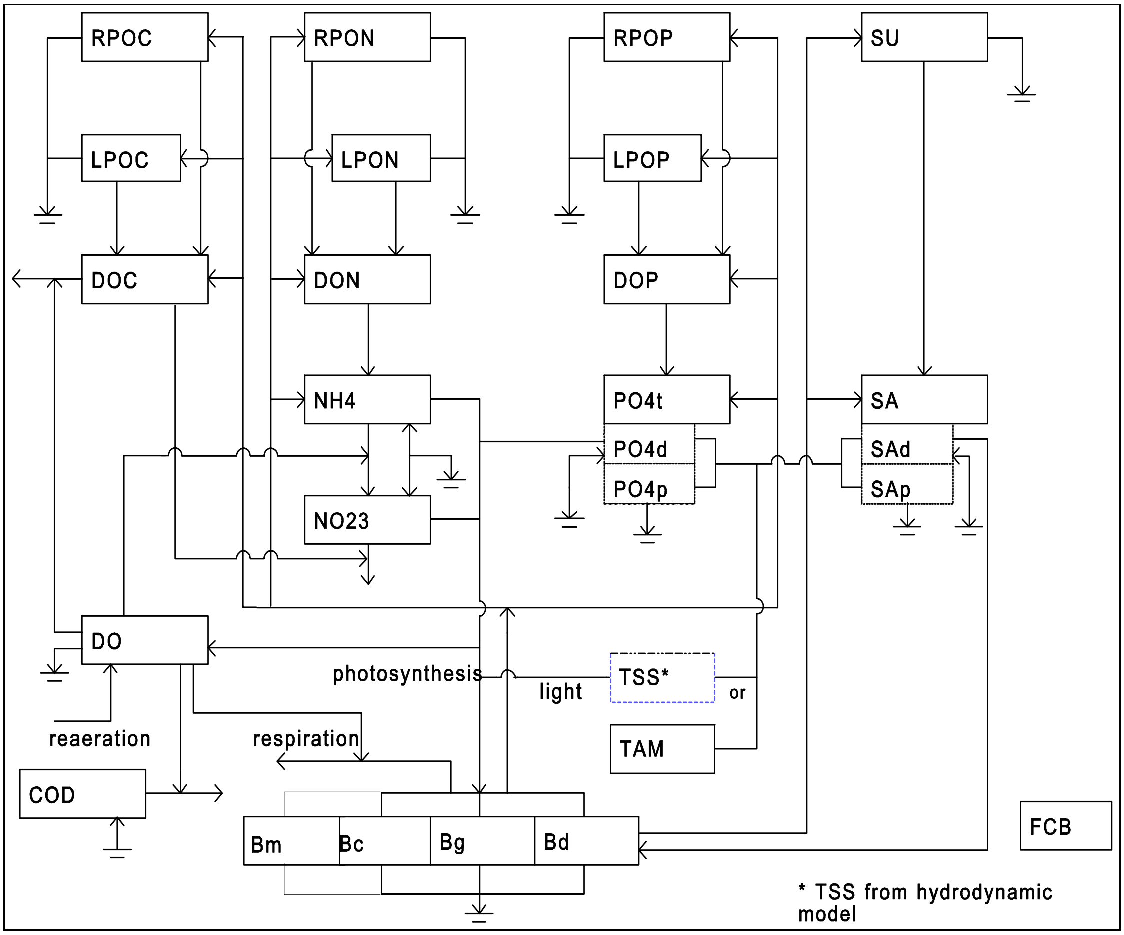

Figure 2.1 Schematic diagram of EFDC Water Quality Model Structure.

2.2 Model State Variables

2.2.1 Algae

Algae are grouped into four model classes: cyanobacteria, diatoms, greens, and stationary. The grouping is based upon the distinctive characteristics of each class and upon the significant role the characteristics play in the ecosystem. Cyanobacteria, commonly called blue-green algae, are characterized by their abundance (as picoplankton) in saline water and by their bloom-forming characteristics in fresh water. Cyanobacteria are unique in that some species fix atmospheric nitrogen, although nitrogen fixers are not believed to be predominant in many river systems. Diatoms are distinguished by their requirement of silica as a nutrient to form cell walls. Diatoms are large algae characterized by high settling velocities. Settling of spring diatom blooms to the sediments may be a significant source of carbon for sediment oxygen demand. Algae that do not fall into the preceding two groups are lumped into the heading of green algae. Green algae settle at a rate intermediate between cyanobacteria and diatoms and are subject to greater grazing pressure than cyanobacteria.

A stationary or non-transported algae variable is included in the model and has been used to simulate macroalgae. The stationary algae variable has the same kinetic formulation as the original algae groups, with the exception that it is not transported. The stationary algae group can also be used various types of bottom substrate attached or floating periphyton. It is also noted that in applications requiring simulation of multiple classes of stationary algae, one or more of the three transported algae groups can be switched to stationary model, under the restriction that the total number of transport and stationary algae classes remains less than or equal to four. Appendix A provides additional specifics with respect to model configuration simulation of macroalgae and periphyton.

2.2.2 Organic Carbon

Three organic carbon state variables are considered: dissolved, labile particulate, and refractory particulate. Labile and refractory distinctions are based upon the time scale of decomposition. Labile organic carbon decomposes on a time scale of days to weeks whereas refractory organic carbon requires more time. Labile organic carbon decomposes rapidly in the water column or the sediments. Refractory organic carbon decomposes slowly, primarily in the sediments, and may contribute to sediment oxygen demand years after deposition.

2.2.3 Nitrogen

Nitrogen is first divided into organic and mineral fractions. Organic nitrogen state variables are dissolved organic nitrogen, labile particulate organic nitrogen, and refractory particulate organic nitrogen. Two mineral nitrogen forms are considered: ammonium and nitrate. Both are utilized to satisfy algal nutrient requirements, although ammonium is preferred from thermodynamic considerations. The primary reason for distinguishing the two is that ammonium is oxidized by nitrifying bacteria into nitrate. This oxidation can be a significant sink of oxygen in the water column and sediments. An intermediate in the complete oxidation of ammonium, nitrite, also exists. Nitrite concentrations are usually much less than nitrate, and for modeling purposes, nitrite is combined with nitrate. Hence, the nitrate state variable actually represents the sum of nitrate plus nitrite.

2.2.4 Phosphorus

As with carbon and nitrogen, organic phosphorus is considered in three states: dissolved, labile particulate, and refractory particulate. Only a single mineral form, total phosphate, is considered. Total phosphate exists as several states within the model ecosystem: dissolved phosphate, phosphate sorbed to inorganic solids, and phosphate incorporated in algal cells. Equilibrium partition coefficients are used to distribute the total among the three states.

2.2.5 Silica

Silica is divided into two state variables: available silica and particulate biogenic silica. Available silica is primarily dissolved and can be utilized by diatoms. Particulate biogenic silica cannot be utilized. In the model, particulate biogenic silica is produced through diatom mortality. Particulate biogenic silica undergoes dissolution to available silica or else settles to the bottom sediments.

2.2.6 Chemical Oxygen Demand

In the context of this study, chemical oxygen demand is the concentration of reduced substances that are oxidizable by inorganic means. The primary component of chemical oxygen demand is sulfide released from sediments. Oxidation of sulfide to sulfate may remove substantial quantities of dissolved oxygen from the water column.

2.2.7 Dissolved Oxygen

Dissolved oxygen is required for the existence of higher life forms. Oxygen availability determines the distribution of organisms and the flows of energy and nutrients in an ecosystem. Dissolved oxygen is a central component of the water quality model.

2.2.8 Total Active Metal

Both phosphate and dissolved silica adsorb to inorganic solids, primarily iron and manganese. Sorption and subsequent settling is one pathway for removal of phosphate and silica from the water column. Consequently, the concentration and transport of iron and manganese are represented in the model. However, limited data do not allow a complete treatment of iron and manganese chemistry. Rather, a single-state variable, total active metal, is defined as the total concentration of metals that are active in phosphate and silica transport. Total active metal is partitioned between particulate and dissolved phases by an oxygen-dependent partition coefficient. Inorganic suspended solids can be used, in lieu of total active metal, as a sorption sited for phosphate and silica. Inorganic suspended solids concentration is provided by the sediment transport component of the EFDC modeling system.

2.2.9 Salinity

Salinity is a conservative tracer that provides verification of the transport component of the model and facilitates examination of conservation of mass. Salinity also influences the dissolved oxygen saturation concentration and is used in the determination of kinetics constants that differ in saline and fresh water. Salinity is simulated in the hydrodynamic component of the model.

2.2.10 Temperature

Temperature is a primary determinant of the rate of biochemical reactions. Reaction rates increase as a function of temperature, although extreme temperatures result in the mortality of organisms. Temperature is simulated in the hydrodynamic component of the model.

2.3 Conservation of Mass Equation

The governing mass-balance equation for each of the water quality state variables may be expressed as:

$$\begin{aligned}&\frac{\partial\left(m_x m_y HC\right)}{\partial t}+\frac{\partial}{\partial x}\left(m_y HuC\right)+\frac{\partial}{\partial y}\left(m_x HvC\right)+\frac{\partial}{\partial z}\left(m_x m_y wC\right)\\&=\frac{\partial}{\partial x}\left(\frac{m_y HA_x}{m_x}\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(\frac{m_x HA_y}{m_y}\frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(m_x m_y\frac{A_z}{H}\frac{\partial C}{\partial z}\right)+m_x m_y HS_c\end{aligned}\tag{2.1}$$

where

C = concentration of a water quality state variable

u, v, w = velocity components in the curvilinear, sigma, x-, y-, and z-directions, respectively

A_x, A_y, A_z = turbulent diffusivities in the x-, y-, and z-directions, respectively

S_c = internal and external sources and sinks per unit volume.

H = water column depth

m_x, m_y = horizontal curvilinear coordinate scale factors

The last three terms on the left-hand side (LHS) of (2.1) account for the advective transport, and the first three terms on the right-hand side (RHS) 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 (2.1) represents the kinetic processes and external loads for each of the state variables. The present model solves equation (2.1) using a fractional step procedure which decouples the kinetic terms from the physical transport terms.

$$\frac{\partial}{\partial t_P}\left(m_x m_y HC\right)+\frac{\partial}{\partial x}\left(m_y HuC\right)+\frac{\partial}{\partial y}\left(m_x HvC\right)+\frac{\partial}{\partial z}\left(m_x m_y wC\right)$$
$$=\frac{\partial}{\partial x}\left(\frac{m_y HA_x}{m_x}\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(\frac{m_x HA_y}{m_y}\frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(m_x m_y\frac{A_z}{H}\frac{\partial C}{\partial z}\right)+m_x m_y HS_{CP} \tag{2.2a}$$

$$\frac{\partial C}{\partial t_K}=S_{CK} \tag{2.2b}$$

with

$$\frac{\partial}{\partial t}\left(m_x m_y HC\right)=\frac{\partial}{\partial t_P}\left(m_x m_y HC\right)+\left(m_x m_y H\right)\frac{\partial C}{\partial t_K} \tag{2.3}$$

In equation (2.2) the source sink term has been split into physical sources and sinks which are associated in volumetric inflows and outflows, and kinetic sources and sinks. Since variations in the water column depth are coupled with the divergence of the volume transport field, the kinetic step is made at a constant water column depth corresponding to the depth field at the end for the physical transport step. This allows the depth and scale factors to be eliminated from the kinetic step (2.2b) which can be further split into reactive and internal sources and sinks.

$$\frac{\partial C_K}{\partial t}=K\cdot C+R \tag{2.4}$$

where K is kinetic rate (time^{-1}) and R represents internal source/sink term (mass volume^{-1} time^{-1}). Equation B.4 is obtained by linearizing some terms in the kinetic equations, mostly Monod type expressions. Hence, K and R are known values in equation (2.4). Equation (2.2a) is identical to, and thus its numerical method of solution is the same as, the mass-balance equation for salinity (Hamrick, 1992). The solution scheme for both the physical transport (Hamrick, 1992) and the kinetic equations is second-order accurate.

2.4 Kinetic Equations for State Variables

The remainder of this chapter details the kinetics portion of the mass-conservation equation for each state variable. Parameters are defined where they first appear. All parameters are listed, in alphabetical order, in an appendix. For consistency with reported rate coefficients, kinetics are detailed using a temporal dimension of days. Within the CE-QUAL-ICM computer code, kinetics sources and sinks are converted to a dimension of seconds before employment in the mass-conservation equation.

2.4.1 Algae

Algae, which occupy a central role in the model (Figure 2.1), are grouped into three model state variables: cyanobacteria (blue-green algae), diatoms, and green algae. The subscript, $\boldsymbol{x}$, is used to denote four algal groups: **c** for cyanobacteria, **d** for diatoms, **g** for green algae, and **m** for macroalgae. 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 the four algal groups with differences in the values of parameters in the equations. The kinetic equation describing these processes is:

$$\frac{\partial B_x}{\partial t} = \left(P_x - BM_x - PR_x\right) B_x + \frac{\partial}{\partial Z}\left(WS_x \cdot B_x\right) + \frac{WB_x}{V} \tag{2.5}$$

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

t = time (days)

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 = positive 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).

2.4.1.1 Production (Algal Growth)

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

$$P_x = PM_x \cdot f_1(N) \cdot f_2(I) \cdot f_3(T) \cdot f_4(S) \tag{2.6}$$

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

$f_1(N)$ = effect of suboptimal nutrient concentration ($0 \le f_1 \le 1$)

$f_2(I)$ = effect of suboptimal light intensity ($0 \le f_2 \le 1$)

$f_3(T)$ = effect of suboptimal temperature ($0 \le f_3 \le 1$).

$f_4(S)$ = effect of salinity on cyanobacteria growth ($0 \le f_4 \le 1$).

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 is included in the model by the salinity toxicity term in the growth equation for cyanobacteria. Activation of the salinity toxicity term, f_4 (S), is an option in the source code.

2.4.1.2 Effect of Nutrients on Algal 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:

$$f_1(N) = \left(\frac{NH4 + NO3}{KHN_x + NH4 + NO3}, \frac{PO4d}{KHP_x + PO4d}, \frac{SAd}{KHS + SAd} \right) \qquad (2.7)$$

$NH4$ = ammonium nitrogen concentration (g N m^{-3})

$NO3$ = nitrate nitrogen concentration (g N m^{-3})

KHN_x = half-saturation constant for nitrogen uptake for algal group x (g N m^{-3})

$PO4d$ = dissolved phosphate phosphorus concentration (g P m^{-3})

KHP_x = half-saturation constant for phosphorus uptake for algal group x (g P m^{-3}).

SAd = concentration of dissolved available silica (g Si m^{-3})

KHS = half-saturation constant for silica uptake for diatoms (g Si m^{-3}).

Some cyanobacteria (e.g., *Anabaena*) can fix nitrogen from atmosphere and thus are not limited by nitrogen. Hence, equation (2.7) 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 includes silica limitation.

2.4.1.3 Effect of Light on Algal Growth

The Light Field

The light field in the water column is governed by

$$\frac{\partial I}{\partial Z_*} = -Kess \cdot I \qquad (2.8)$$

where

I = light intensity (watts/meter^2)

$Kess$ = light extinction coefficient (meters^{-1})

Z_* = depth below the water surface (meters) with the light extinction coefficient being a function of the depth below the water surface.

Integration of (2.8) gives

$$I = I_{ws} \exp\left(-\int_{0}^{Z_*} Kess \cdot dZ_* \right) \tag{2.9}$$

The light intensity at the water surface, I_{ws}, is given by

$$I_{ws} = I_o \min\left(\exp\left(-Keme \cdot \left(H_{RPS} - H \right) \right), 1 \right) \tag{2.10}$$

where

I_o = light intensity at the top of the emergent aquatic plant canopy for emergent shoots or the light intensity at the water surface for submerged shoots (Watts/meter2)

$Keme$ = light extinction coefficient for emergent shoots (meters^{-1})

H_{RPS} = rooted plant shoot height (meters)

H = water column depth (meters)

When submerged aquatic plants are simulated, it is assumed that the light extinction coefficient in the water column above the canopy is given by

$$Kessac = Ke_b + Ke_{ISS} \cdot ISS + Ke_{VSS} \cdot VSS + Ke_{Chl} \sum_{m=1}^{M} \left(\frac{B_m}{CChl_m} \right) \tag{2.11}$$

and that the light extinction coefficient in the water column within the canopy is given by

$$Kessic = Ke_b + Ke_{ISS} \cdot SED + Ke_{VSS} \cdot VSS + Ke_{Chl} \sum_{m=1}^{M} \left(\frac{B_m}{CChl_m} \right) + Ke_{RPS} \cdot RPS \tag{2.12}$$

where

Ke_b = background light extinction (m^{-1})

Ke_{ISS} = light extinction coefficient for inorganic suspended solid (m^{-1} per g m^{-3})

SED = inorganic suspended solid concentration (g m^{-3}) provided from the hydrodynamic model

Ke_{VSS} = light extinction coefficient for volatile suspended solid (m^{-1} per g m^{-3})

VSS = volatile suspended solid concentration (g m^{-3}) provided from the water quality model

$CChl_{RPE}$ = carbon-to-chlorophyll ratio for epiphytes (g C per mg Chl).

Ke_{Chl} = light extinction coefficient for algae chlorophyll (m^{-1} per mg Chl m^{-3})

B_m = concentration of algae group m (g C per ml)

$CChl_m$ = carbon-to-chlorophyll ratio in algal group m (g C per mg Chl).

Ke_{RPS} = light extinction coefficient for rooted plant shoots (m^{-1} per gm C m^{-2})

RPS = concentration of plant shoots (g C per meter^2)

The forms (2.11) and (2.12) are quite general and readily allow inclusion of algae biomass into the volatile suspended solids or visa-versa. The form of (2.12) assumes that the rooted plant shoots are primarily self-shading and that epiphyte effect are manifest only on the shoot surface.

The solutions of (2.9) above and in the rooted plant shoot canopy are

$$I = I_{ws} \exp\left(-Kessac \cdot Z_*\right) \quad ; \quad 0 \le Z_* \le H - H_{RPS} \tag{2.13}$$

$$\begin{aligned} & I = I_{ct} \cdot \exp\left(-Kessic \cdot \left(Z_* - H + H_{RPS}\right)\right) \\ & I_{ct} = I_{ws} \cdot \exp\left(-Kessac \cdot \left(H - H_{RPS}\right)\right) \\ & H - H_{RPS} \le Z_* \le H \end{aligned} \tag{2.14}$$

Steele's Equation for Light Limitation

The original version of CE-QUAL-ICM (Cerco and Cole, 1995) used Steele's equation

$$f_2\left(I\right) = \frac{I}{I_{sx}} \exp\left(1 - \frac{I}{I_{sx}}\right) \tag{2.15}$$

to express light limitation. A daily and vertically integrated form of Steele's equation, in the absences of a plant canopy is:

$$f_2 = \frac{\exp\left(1\right) \cdot FD}{Kess \cdot \left(ZB - ZT\right)} \left(\exp\left(-\alpha_b\right) - \exp\left(-\alpha_T\right)\right) \tag{2.16}$$

$$\alpha_B = \left(\frac{I_{wsavg}}{FD \cdot I_{sx}}\right) \exp\left(-Kess \cdot ZB\right) \tag{2.17}$$

$$\alpha_T = \left(\frac{I_{wsavg}}{FD \cdot I_{sx}}\right) \exp\left(-Kess \cdot ZT\right) \tag{2.18}$$

FD = fractional day length ($0 \le FD \le 1$)

$Kess$ = total light extinction coefficient (m^{-1})

ZT = distance from water surface to layer top (m)

ZB = distance from water surface to layer bottom (m)

I_{wavgs} = daily total light intensity at water surface (langleys day^{-1})

I_{sx} = optimal light intensity for algal group x (langleys day^{-1})

Optimal light intensity I_{sx} for photosynthesis depends on algal taxonomy, duration of exposure, temperature, nutritional status, and previous acclimation. Variations in I_s 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 percent) of daily intensity. Kremer and 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:

$$I_{sx} = \min\left(I_{wsavg} \cdot \exp\left(-Kess \cdot D_{optx}\right), I_{sxmin}\right) \tag{2.19}$$

D_{optx} = depth of maximum algal growth for algal group x (m)

I_{wsavg} = adjusted surface light intensity (watts/meter^2)

I_{sxmin} = minimum optimum light intensity (watts/meter^2)

A minimum, I_{sxmin}, in equation (2.19) 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_{sxmin} based on a time-weighted average of daily light intensity:

$$I_{0avg} = CI_a \cdot I_0 + CI_b \cdot I_1 + CI_c \cdot I_2 \tag{2.20}$$

I_1 = daily light intensity 1 day preceding model day (langleys day^{-1})

I_2 = daily light intensity 2 days preceding model day (langleys day^{-1})

CI_a, CI_b, CI_c = weighting factors for I_0, I_1 and I_2, respectively: $CI_a + CI_b + CI_c = 1$.

Equations (2.16-18) can be applied instantaneously by setting the fraction of daylight to unity. It can also be applied within a canopy by replacing I_{ws} with I_{ct} defined by (2.14).

Alternate Formulations for Light Limitation

Subsequent applications of CE-QUAL-ICM (Bunch *et al.*, 2000) used a Monod type limitation

$$f_2(I) = \frac{I}{KHI + I} \tag{2.21}$$

or a modified Monod limitation (Cerco *et al.*, 2000, 2002, 2004; Tillman *et al.*, 2004)

$$f_2\left(I\right)=\frac{I}{\sqrt{KHI^2+I^2}} \tag{2.22}$$

where

KHI = half saturation for light limitation (Watts/m^2).

Equation (2.22) was used in the CE-QUAL-ICM Florida Bay water quality modeling study (Cerco *et al.*, 2000). Equation (2.21) can be directly averaged over a water column layer to give

$$f_{2avg}=\frac{1}{Kess\left(ZB-ZT\right)}\ln\left(\frac{KHI+I_{ws}\exp\left(-Kess\cdot ZT\right)}{KHI+I_{ws}\exp\left(-Kess\cdot ZB\right)}\right) \tag{2.23}$$

while the average of (2.22) is

$$f_{2avg}=\frac{1}{Kess}\frac{1}{\left(ZB-ZT\right)}\left(\begin{array}{l}\sqrt{1+\left(\dfrac{I_{ws}}{KHI}\exp\left(-Kess\cdot ZT\right)\right)^2}\\ -\sqrt{1+\left(\dfrac{I_{ws}}{KHI}\exp\left(-Kess\cdot ZB\right)\right)^2}\end{array}\right) \tag{2.24}$$

with ZT and ZB defined following equation (2.14). Equations (2.23) and (2.24) can be applied within a canopy by replacing I_{ws} with I_{ct} and use of the appropriate light extinction coefficient.

2.4.1.4 Effect of Temperature on Algal Growth

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

$$f_3(T)=\begin{cases}\exp\left(-KTG1_x\left(T-TM1_X\right)^2\right) & : \quad T\le TM1_X\\ 1 & : \quad TM1_X<T<TM2_X\\ \exp\left(-KTG2_x\left(T-TM2_X\right)^2\right) & : \quad T\ge TM2_X\end{cases} \tag{2.25}$$

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

TM_x = optimal temperature for algal growth for algal group *x* (°C)

$KTG1_x$ = effect of temperature below $TM1_x$ on growth for algal group *x* (°C^{-2})

$KTG2_x$ = effect of temperature above $TM2_x$ on growth for algal group *x* (°C^{-2}).

The formulation (2.25) represents a modification to the CE-QUAL-ICM formulation to allow for temperature range specification of optimum growth.

2.4.1.5 Effect of Salinity on Growth of Freshwater Cyanobacteria

The growth of freshwater cyanobacteria in salt water is limited by:

$$f_4(S) = \frac{STOXS^2}{STOXS^2 + S^2} \tag{2.26}$$

$STOX$ = salinity at which Microcystis growth is halved (psu)

S = salinity in water column (psu) provided from the hydrodynamic model.

2.4.1.6 Effect of Temperature on Algal 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:

$$BM_x = BMR_x \cdot \exp\left(KTB_x\left[T - TR_x\right]\right) \tag{2.27}$$

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).

2.4.1.7 Effect of Algal Biomass and Temperature on Algal Predation

The present model does not include zooplankton. Instead, a constant rate can be specified for algal predation, which implicitly assumes zooplankton biomass is a constant fraction of algal biomass. Alternately, the predation rate can be taken as proportional to the algae biomass. Using a temperature effect similar to that for metabolism, the predation rate is given

$$PR_x = PRR_x \cdot \left(\frac{B_x}{B_{xP}}\right)^{\alpha_P} \cdot \exp\left(KTP_x\left[T - TR_x\right]\right) \tag{2.28}$$

PRR_x = reference predation rate at B_{xP} and TR_x for algal group x (day^{-1})

B_{xP} = reference algae concentration for predation (g C/m^3)

α_P = exponential dependence factor

KTP_x = effect of temperature on predation for algal group x (°C^{-1}).

The difference between predation and basal metabolism lies in the distribution of the end products of the 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. It is also noted that predation in the EFDC water quality model follows the original formulation in CE-QUAL-ICM (Cerco and Cole, 1995) which uses a predation rate constant with total predation loss being proportional to algae concentration. Subsequent CE-QUAL-ICM documentation, Cerco *et al.*, (2000), appear to define predation independent of algae concentration.

2.4.1.8 Algal Settling

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

2.4.2 Organic Carbon

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

2.4.2.1 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 a 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 (Figure 2.1):

- Algal predation
- Dissolution to dissolved organic carbon
- Settling
- External loads.

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

$$\frac{\partial RPOC}{\partial t} = \sum_{x=c,d,g,m} FCRP_X \cdot PR_X \cdot B_X - K_{RPOC} \cdot RPOC + \frac{\partial}{\partial Z}\left(WS_{RP} \cdot RPOC\right) + \frac{WRPOC}{V} \qquad (2.29)$$

$$\frac{\partial LPOC}{\partial t} = \sum_{x=c,d,g,m} FCLP_X \cdot PR_X \cdot B_X - K_{LPOC} \cdot LPOC + \frac{\partial}{\partial Z}\left(WS_{LP} \cdot LPOC\right) + \frac{WLPOC}{V} \qquad (2.30)$$

$RPOC$ = 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}).

2.4.2.2 Dissolved Organic Carbon

Sources and sinks for dissolved organic carbon included in the model are (Figure 2.1):

- 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:

$$\frac{\partial DOC}{\partial t} = \sum_{x=c,d,g,m} \left(\begin{array}{l} \left[FCD_X + (1 - FCD_X) \left(\dfrac{KHR_X}{KHR_X + DO} \right) \right] \cdot BM_X \\ + FCDP_X \cdot PR_X \end{array} \right) \cdot B_X \qquad (2.31)$$

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

where

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})

BFDOC = benthic flux of dissolved organic carbon in bottom layer only (g C m^{-2} day^{-1})

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

The remainder of this section explains each term in equations (2.29-31).

2.4.2.3 Effect of Algae on Organic Carbon

The terms within summation (∑) in equations (2.29-31) account for the effects of algae on organic carbon through basal metabolism and predation.

2.4.2.4 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

$$\frac{\partial B_x}{\partial t} = -BM_x \cdot B_x \tag{2.32}$$

that 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:

$$\left(1 - FCD_x\right) \cdot BM_x \cdot B_x \quad : \quad \mathit{respiration} \tag{2.33}$$

$$FCD_x \cdot BM_x \cdot B_x \quad : \quad \mathit{excretion} \tag{2.34}$$

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, equation (2.32), 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, equation (2.33) represents the loss by respiration only at high oxygen levels. In general, equation (2.33) can be decomposed into two fractions as a function of dissolved oxygen availability:

$$\left(1 - FCD_x\right)\left(\frac{DO}{KHR_x + DO}\right) \cdot BM_x \cdot B_x \quad : \quad \mathit{respiration} \tag{2.35}$$

$$\left(1-FCD_x\right)\left(\frac{KHR_x}{KHR_x+DO}\right)\cdot BM_x\cdot B_x \quad : \quad excretion \tag{2.36}$$

where

$KHRx$ = metabolic DO coefficient (g/m^3 O$_2$)

Equation (2.35) represents the loss of algal biomass by respiration, and equation (2.36) 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 equation (2.31), can also be defined as the half-saturation constant of dissolved oxygen for algal respiration in equation (2.36).

Combining equations (2.34) and (2.36), the total loss due to excretion is:

$$\left[FCD_X+\left(1-FCD_X\right)\left(\frac{KHR_X}{KHR_X+DO}\right)\right]\cdot BM_X\cdot B_X \tag{2.37}$$

Equations (2.35) and (2.37) combine to give the total loss of algal biomass due to basal metabolism, $BM_x \cdot B_x$, equation (2.32). The definition of FCD_x in equation (2.31) becomes apparent in equation (2.37), (i.e., fraction of basal metabolism exuded as dissolved organic carbon at infinite dissolved oxygen concentration). At zero oxygen level, 100 percent 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, equation (2.37), that appears in equation (2.31), 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 (2.29) and (2.30).

Although this general formulation is incorporate for consistency with the original CE-QUAL-IMC formulation (Cerco and Cole, 1995), most of the subsequent applications of CE-QUAL-ICM have simplified the basal metabolism in the published DOC and DO equations or specified input parameters which effective set KHRx and FCDx to zero, see Table 2.2, which result in simplifying the DOC equation to

$$\begin{aligned}\frac{\partial DOC}{\partial t} &= \sum_{x=c,d,g,m} FCDP_X\cdot PR_X\cdot B_X \\ &+K_{RPOC}\cdot RPOC+K_{LPOC}\cdot LPOC-K_{HR}\cdot DOC-Denit\cdot DOC+\frac{WDOC}{V}\end{aligned} \tag{2.38}$$

2.4.2.5 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 (2.29) to (2.31); *FCRP*, *FCLP*, and *FCDP*. The sum of these three predation fractions should be unity.

Table 2.2 Basal Metabolism Formulations and Parameter in CE-QUAL-ICM

Study	FCDx and KHRx in DOC Equation	FCDx and KHRx in from DO Equation
Cerco and Cole, 1995 (Chesapeake Bay)	General	General
Bunch, 2000 (San Juan Bay, PR)	General (used FCD=0, KHRx=0.5)	General (used FCD=0, KHRx=0.5)
Cerco *et al.*, 2000 (Florida Bay)	No BMx source in equation, implies FCDx=0, KHRx=0	Consistent with FCDx=0, KHRx=0
Cerco *et al.*, 2002 (Ches Bay, Trib. Refinements)	No BMx source in equation, implies FCDx=0, KHRx=0	Consistent with FCDx=0, KHRx=0
Cerco *et al.*, 2004 (Lake Washington)	Equation implies KHRx =0 (used FCDx=0)	Consistent with KHRx =0 (used FCDx=0)
Tillman *et al.*, 2004 (St. Johns River)	No BMx source in equation, implies FCDx=0, KHRx=0	Consistent with FCDx=0, KHRx=0

2.4.2.6 Heterotrophic Respiration and Dissolution

The refractory and labile particulate organic carbon equations, (2.29) and (2.31) contain decay terms that represent dissolution of particulate material into dissolved material. These terms appear in equation (2.31) as sources. The third sink term in the DOC equation (2.31) 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:

$$K_{HR} = \left(\frac{DO}{KHOR_{DO} + DO} \right) K_{DOC} \tag{2.39}$$

$KHOR_{DO}$ = oxic respiration half-saturation constant for dissolved oxygen (g O_2 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:

$$K_{RPOC} = \left(K_{RC} + K_{RCalg} \sum_{x=c,d,g} B_x \right) \exp\left(KT_{HDR} \left(T - TR_{HDR} \right) \right) \tag{2.40}$$

$$K_{LPOC} = \left(K_{LC} + K_{LCalg} \sum_{x=c,d,g} B_x \right) \exp\left(KT_{HDR} \left(T - TR_{HDR} \right) \right) \tag{2.41}$$

$$K_{DOC} = \left(K_{DC} + K_{DCalg} \sum_{x=c,d,g} B_x \right) \exp\left(KT_{MIN} \left(T - TR_{MIN} \right) \right) \tag{2.42}$$

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 (2.40) to (2.42) 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 B.28 and B.29) and nitrogen (equations B.53 and B.54). 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_{MNL} and TR_{MNL}, are also used for the temperature effects on mineralization of dissolved phosphorus (equation B.45) and nitrogen (equation B.55).

2.4.2.7 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 and Morgan, 1981):

$$4NO_3^- + 4H^+ + 5CH_2O \rightarrow 2N_2 + 7H_2O + 5CO_2 \qquad (2.43)$$

The last term in equation B.22 accounts for the effect of denitrification on dissolved organic carbon. The kinetics of denitrification in the model are first-order:

$$Denit = \left(\frac{KROR_{DO}}{KROR_{DO} + DO}\right)\left(\frac{NO3}{KHDN_N + NO3}\right) AANOX \cdot K_{DOC} \qquad (2.44)$$

$KROR_{DO}$ = denitrification half-saturation constant for dissolved oxygen (g O m^{-3})

$KHDN_N$ = denitrification half-saturation constant for nitrate (g N m^{-3})

$AANOX$ = ratio of denitrification rate to oxic dissolved organic carbon respiration rate.

In equation B.34, 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 equation B.32, includes the temperature effect on denitrification.

2.4.2.8 Labile and Refractory Splitting of Dissolved Organic Carbon

A number of water quality models, including the CE-QUAL-ICM application to the St. Johns River, Florida (Tillman *et al.*, 2004) split dissolved organic carbon into labile and refractory components. The refractory component equation is

$$\frac{\partial RDOC}{\partial t} = \sum_{x=c,d,g,m} FCRDP_X \cdot PR_X \cdot B_X - K_{RDOC} \cdot RDOC + \frac{WRDOC}{V} \qquad (2.45)$$

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

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

K_{RDOC} = respiration rate of refractory dissolved organic carbon (day^{-1})

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

The decay term in (2.45) can include a photoreaction component. The labile component equation retains the general form of the DOC equation

$$\begin{aligned}\frac{\partial\, LDOC}{\partial t} &= \sum_{x=c,d,g,m} FCLDP \cdot PR_X \cdot B_X + K_{RPOC} \cdot RPOC \\ &+ K_{LPOC} \cdot LPOC - K_{LDOC} \cdot LDOC - Denit \cdot LDOC + \frac{WLDOC}{V}\end{aligned} \tag{2.46}$$

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

FCLDP = fraction of predated carbon produced as dissolved organic carbon

K_{LDOC} = respiration rate of labile dissolved organic carbon (day^{-1})

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

Equations (2.45) and (2.46) follow from Tillman *et al.*, (2004), but are not currently implemented in the EFDC water quality model.

2.4.3 Phosphorus

The present model has four state variables for phosphorus: three organic forms (refractory particulate, labile particulate, and dissolved) and one inorganic form representing the sum of dissolved and particulate phosphate in the water phase, but exclude phosphate in algae cells.

2.4.3.1 Particulate Organic Phosphorus

For refractory and labile particulate organic phosphorus, sources and sinks included in the model are (Figure B.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:

$$\begin{aligned}\frac{\partial\, RPOP}{\partial t} &= \sum_{x=c,d,g,m} \left(FPR_X \cdot BM_X + FPRP_X \cdot PR_X \right) \cdot APC_X \cdot B_X \\ &- K_{RPOP} \cdot RPOP + \frac{\partial}{\partial Z}\left(WS_{RP} \cdot RPOP \right) + \frac{WRPOP}{V}\end{aligned} \tag{2.47}$$

$$\begin{aligned}\frac{\partial\, LPOP}{\partial t} &= \sum_{x=c,d,g,m} \left(FPL_X \cdot BM_X + FPLP_X \cdot PR_X \right) \cdot APC_X \cdot B_X \\ &- K_{LPOP} \cdot LPOP + \frac{\partial}{\partial Z}\left(WS_{RP} \cdot LPOP \right) + \frac{WLPOP}{V}\end{aligned} \tag{2.48}$$

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 algal phosphorus-to-carbon ratio for all algal groups (g P per g C)

K_{RPOP} = hydrolysis rate of refractory particulate organic phosphorus (day^{-1})

K_{LPOP} = hydrolysis rate of labile particulate organic phosphorus (day^{-1})

$WRPOP$ = external loads of refractory particulate organic phosphorus (g P day^{-1})

$WLPOP$ = external loads of labile particulate organic phosphorus (g P day^{-1}).

2.4.3.2 Dissolved Organic Phosphorus

Sources and sinks for dissolved organic phosphorus included in the model are (Figure B.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:

$$\begin{aligned}\frac{\partial DOP}{\partial t} &= \sum_{x=c,d,g,m} \left(FPD_X \cdot BM_X + FPDP_X \cdot PR_X \right) \cdot APC_X \cdot B_X \\ &+ K_{RPOP} \cdot RPOP + K_{LPOP} \cdot LPOP - K_{DOP} \cdot DOP + \frac{WDOP}{V}\end{aligned} \tag{2.49}$$

DOP = concentration of dissolved organic phosphorus (g P m^{-3})

FPD_x = fraction of metabolized phosphorus by algal group *x* produced as dissolved organic phosphorus

$FPDP_x$ = fraction of predated phosphorus produced as dissolved organic phosphorus

K_{DOP} = mineralization rate of dissolved organic phosphorus (day^{-1})

$WDOP$ = external loads of dissolved organic phosphorus (g P day^{-1}).

2.4.3.3 Total Water Phase Phosphate

For total phosphate that includes both dissolved and sorbed phosphate in the water phase, sources and sinks included in the model are (Figure 2.1):

- 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:

$$\begin{aligned}\frac{\partial}{\partial t}\left(PO4p+PO4d\right) &= \sum_{x=c,d,g,m}\left(FPI_X \cdot BM_X + FPIP_X \cdot PR_X - P_X\right) \cdot APC_X \cdot B_X \\ &+ K_{DOP} \cdot DOP + \frac{\partial}{\partial Z}\left(WS_{TSS} \cdot PO4p\right) + \frac{BFPO4d}{\Delta Z} + \frac{WPO4p}{V} + \frac{WPO4d}{V}\end{aligned} \qquad (2.50)$$

Where

$PO4t$ = total phosphate (g P m^{-3}) = $PO4d + PO4p$

$PO4d$ = dissolved phosphate (g P m^{-3})

$PO4p$ = particulate (sorbed) phosphate (g P m^{-3})

FPI_x = fraction of metabolized phosphorus by algal group x produced as inorganic phosphorus

$FPIP$ = fraction of predated phosphorus produced as inorganic phosphorus

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

$BFPO4d$ = sediment-water exchange flux of phosphate (g P m^{-2} day^{-1}), applied to the bottom layer only

$WPO4t$ = external loads of total phosphate (g P day^{-1}).

In equation (2.50), 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. The remainder of this section explains each term in equations (2.47-50). The benthic flux term is discussed in Chapter 4. Alternate forms of the total phosphate equation are discussed in section 2.4.3.8.

2.4.3.4 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 buffers phosphate concentration in the water column and enhances the transport of phosphate away from its external sources (Carritt and Goodgal, 1954; Froelich, 1988). 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, equation (2.50), 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 a 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 and 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. 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:

$$
\begin{aligned}
PO4p &= \left(\frac{K_{PO4p} \cdot SORPS}{1 + K_{PO4p} \cdot SORPS} \right) \left(PO4p + PO4d \right) \\
PO4d &= \left(\frac{1}{1 + K_{PO4p} \cdot SORPS} \right) \left(PO4p + PO4d \right) \qquad (2.51) \\
SORPS &= SED \text{ or } TAM_P
\end{aligned}
$$

where

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

SED = inorganic sediment concentration (mg/L)

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

The definition of the partition coefficient alternately follows form (2.51)

$$K_{PO4p} = \frac{PO4p}{PO4d}\frac{1}{TSS}$$
$$or \tag{2.52}$$
$$K_{PO4p} = \frac{PO4p}{PO4d}\frac{1}{TAMp}$$

where the meaning of $K_{PO}4p$ 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).

2.4.3.5 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 and Cole (1993) showed that the variation of nitrogen-to-carbon stoichiometry was small and thus used a constant algal nitrogen-to-carbon ratio, ANC_x. Large variations, however, were observed for algal phosphorus-to-carbon ratio indicating the adaptation of algae to ambient phosphorus concentration (Cerco and Cole, 1993): 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 groups, *APC*, is described by an empirical approximation to the trend observed in field data (Cerco and Cole, 1994):

$$APC = \left(CP1_{prm} + CP2_{prm} \cdot \exp\left(-CP3_{prm} \cdot PO4d\right)\right)^{-1} \tag{2.53}$$

$CP1_{prm}$ = minimum carbon-to-phosphorus ratio (g C per g P)

$CP2_{prm}$ = difference between minimum and maximum carbon-to-phosphorus ratio (g C per g P)

$CP3_{prm}$ = effect of dissolved phosphate concentration on carbon-to-phosphorus ratio (per g P m^{-3}).

2.4.3.6 Effect of Algae on Phosphorus

The terms within summation in equations (2.47-50) 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 ($BM_x \cdot B_x$) is distributed using distribution coefficients (FPR_x, FPL_x, FPD_x, and FPI_x). The total loss by predation ($PR_x \cdot B_x$), is also distributed using distribution coefficients

(*FPRP, FPLP, FPDP*, and *FPIP*). The sum of four distribution coefficients for basal metabolism should be unity, and as is the sum 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 equation (2.50).

2.4.3.7 Mineralization and Hydrolysis

The third term on the RHS of equations (2.47) and (2.48) represents hydrolysis of particulate organic phosphorus and the last term in equation (2.49) represents mineralization of dissolved organic phosphorus. Mineralization of organic phosphorus is mediated by the release of nucleotidase and phosphatase enzymes by bacteria (Chróst and 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 the model formulation is that algae stimulate production of an enzyme that mineralizes organic phosphorus to phosphate when phosphate is scarce (Chróst and Overbek, 1987, Boni *et al.*, 1989). The formulations for hydrolysis and mineralization rates including these processes are:

$$K_{RPOP} = \left(K_{RP} + \left(\frac{KHP}{KHP + PO4d} \right) K_{RPalg} \sum_{x=c,d,g,m} B_x \right) \exp\left(KT_{HDR} \left(T - TR_{HDR} \right) \right) \qquad (2.54)$$

$$K_{LPOP} = \left(K_{LP} + \left(\frac{KHP}{KHP + PO4d} \right) K_{LPalg} \sum_{x=c,d,g,m} B_x \right) \exp\left(KT_{HDR} \left(T - TR_{HDR} \right) \right) \qquad (2.55)$$

$$K_{DOP} = \left(K_{DP} + \left(\frac{KHP}{KHP + PO4d} \right) K_{DPalg} \sum_{x=c,d,g,m} B_x \right) \exp\left(KT_{HDR} \left(T - TR_{HDR} \right) \right) \qquad (2.56)$$

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_{RPalg}, K_{LPalg} = constants that relate hydrolysis of refractory and labile particulate organic phosphorus, respectively, to algal biomass (day^{-1} per g C m^{-3})

K_{DPalg} = constant that relates mineralization to algal biomass (day^{-1} per g C m^{-3})

KHP = mean half-saturation constant for algal phosphorus uptake (g P m^{-3})

$$KHP = \frac{\sum_{x=c,d,g,m} KHP_X}{\sum_{x=c,d,g,m} x} \qquad (2.57)$$

When phosphate is abundant relative to *KHP*, the rates are 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 (2.54-56) have exponential functions that relate rates to temperature.

2.4.3.8 Alternate Forms of the Total Phosphate Equation

In the CE-QUAL-ICM model (Cerco and Cole, 1995), total phosphate is defined to include dissolved phosphate in algae cells. The phosphate in algae cells is given by

$$
\begin{aligned}
\frac{\partial PO4a}{\partial t} &= \sum_{x=c,d,g,m} \left(APC \cdot B_X \right) \\
&= \sum_{x=c,d,g,m} \left(P_X - FPI_X \cdot BM_X - FPIP \cdot PR_X \right) \cdot APC_X \cdot B_X \\
&\quad - \sum_{x=c,d,g,m} \left(FPR_X \cdot BM_X + FPRP \cdot PR_X \right) \cdot APC_X \cdot B_X \\
&\quad - \sum_{x=c,d,g,m} \left(FPL_X \cdot BM_X + FPLP \cdot PR_X \right) \cdot APC_X \cdot B_X \\
&\quad - \sum_{x=c,d,g,m} \left(FPD_X \cdot BM_X + FPDP \cdot PR_X \right) \cdot APC_X \cdot B_X \\
&\quad + \frac{\partial}{\partial Z} \left(\sum_{x=c,d,g,m} WS_{AlgX} \cdot APC_X \cdot B_X \right)
\end{aligned}
\tag{2.58}
$$

Where the first term on the right side represents net uptake of phosphate from the water column, and the subsequent three terms represent loss of organic phosphorous. Noting that the distribution factors for basal metabolism and predation must sum to unity, (2.58) reduces to

$$
\begin{aligned}
\frac{\partial PO4a}{\partial t} &= \sum_{x=c,d,g,m} \left(P_X - BM_X - PR_X \right) \cdot APC_X \cdot B_X \\
&\quad + \frac{\partial}{\partial Z} \left(\sum_{x=c,d,g,m} WS_{AlgX} \cdot APC_X \cdot B_X \right)
\end{aligned}
\tag{2.59}
$$

which is simply equation (2.5) multiplied by the algae phosphorous to carbon ratio and summed over all algae species. Combining (2.59) with (2.50) gives

$$\begin{aligned}
&\frac{\partial}{\partial t}\left(PO4p + PO4d + PO4a\right) = K_{DOP}\cdot DOP \\
&- \sum_{x=c,d,g,m}\left(\left(1 - FPI_X\right)\cdot BM_X + \left(1 - FPIP\right)\cdot PR_X\right)\cdot APC_X\cdot B_X \\
&+ \frac{\partial}{\partial Z}\left(WS_{TSS}\cdot PO4p + \sum_{x=c,d,g,m} WS_{AlgX}\cdot APC_X\cdot B_X\right) \\
&+ \frac{BFPO4d}{\Delta Z} + \frac{WPO4p}{V} + \frac{WPO4d}{V}
\end{aligned} \qquad (2.60)$$

It is noted that this equation differs from equation (3-51) in Cerco and Cole (1995), which is in error, but is identical to the subsequently corrected equation (35) in Cerco *et al.*, (2000) which documents the Florida Bay CE-QUAL-ICM model application. Thus, either equations (2.50) or (2.60) can be used for total phosphate as long as partitioning between particulate and dissolved phosphate in the water phase is appropriately represented by equations (2.51) and (2.52).

2.4.3.9 Labile and Refractory Splitting of Dissolve Organic Phosphorous

A number of water quality models, including the CE-QUAL-ICM application to the St. Johns River, Florida (Tillman *et al.*, 2004) split dissolved organic phosphorous into labile and refractory components. The refractory component equation is

$$\begin{aligned}
\frac{\partial RDOP}{\partial t} &= \sum_{x=c,d,g,m}\left(FPRD_X\cdot BM_X + FPRDP_X\cdot PR_X\right)\cdot APC_X\cdot B_X \\
&\qquad - K_{RDOP}\cdot RDOP + \frac{WRDOP}{V}
\end{aligned} \qquad (2.61)$$

RDOP = concentration of refractory dissolved organic phosphorus (g P m^{-3})

FPRD$_x$ = fraction of metabolized phosphorus by algal group *x* produced as refractory dissolved organic phosphorus

FPRDP = fraction of predated phosphorus produced as refractory dissolved organic phosphorus

K_{RDOP} = mineralization rate of refractory dissolved organic phosphorus (day^{-1})

WRDOP = external loads of refractory dissolved organic phosphorus (g P day^{-1}).

The labile component equation is:

$$\begin{aligned}
\frac{\partial\, LDOP}{\partial t} &= \sum_{x=c,d,g,m}\left(FPLD_X\cdot BM_X + FPLDP_X\cdot PR_X\right)\cdot APC_X\cdot B_X \\
&+ K_{RPOP}\cdot RPOP + K_{LPOP}\cdot LPOP - K_{LDOP}\cdot LDOP + \frac{WLDOP}{V}
\end{aligned} \qquad (2.62)$$

$LDOP$ = concentration of dissolved organic phosphorus (g P m^{-3})

$FPLD_x$ = fraction of metabolized phosphorus by algal group x produced as dissolved organic phosphorus

$FPLDP$ = fraction of predated phosphorus produced as dissolved organic phosphorus

K_{LDOP} = mineralization rate of dissolved organic phosphorus (day^{-1})

$WLDOP$ = external loads of dissolved organic phosphorus (g P day^{-1}).

Equations (2.61) and (2.62) follow from Tillman *et al.*, (2004), but are not currently implemented in the EFDC water quality model.

2.4.4 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.

2.4.4.1 Particulate Organic Nitrogen

For refractory and labile particulate organic nitrogen, sources and sinks included in the model are (Figure 2.1):

- Algal basal metabolism and predation
- Dissolution to dissolved organic nitrogen
- Settling
- External loads

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

$$\begin{aligned}\frac{\partial\, RPON}{\partial t} = & \sum_{x=c,d,g,m}\left(FNR_X \cdot BM_X + FNRP_X \cdot PR_X\right) \cdot ANC_X \cdot B_X \\ & - K_{RPON} \cdot RPON + \frac{\partial}{\partial Z}\left(WS_{RP} \cdot RPON\right) + \frac{WRPON}{V}\end{aligned} \tag{2.63}$$

$$\begin{aligned}\frac{\partial\, LPON}{\partial t} = & \sum_{x=c,d,g,m}\left(FNL_X \cdot BM_X + FNLP_X \cdot PR_X\right) \cdot ANC_X \cdot B_X \\ & - K_{LPON} \cdot LPON + \frac{\partial}{\partial Z}\left(WS_{LP} \cdot LPON\right) + \frac{WRLON}{V}\end{aligned} \tag{2.64}$$

where

$RPON$ = concentration of refractory particulate organic nitrogen (g N m^{-3})

$LPON$ = concentration of labile particulate organic nitrogen (g N m^{-3})

FNR_x = fraction metabolized nitrogen by algal group x as refractory particulate organic nitrogen

FNL_x = fraction of metabolized nitrogen by algal group x produced as labile particulate organic nitrogen

$FNRP$ = fraction of predated nitrogen produced as refractory particulate organic nitrogen

$FNLP$ = fraction of predated nitrogen produced as labile particulate organic nitrogen

ANC_x = nitrogen-to-carbon ratio in algal group x (g N per g C)

K_{RPON} = hydrolysis rate of refractory particulate organic nitrogen (day^{-1})

K_{LPON} = hydrolysis rate of labile particulate organic nitrogen (day^{-1})

$WRPON$ = external loads of refractory particulate organic nitrogen (g N day^{-1})

$WLPON$ = external loads of labile particulate organic nitrogen (g N day^{-1})

2.4.4.2 Dissolved Organic Nitrogen

Sources and sinks for dissolved organic nitrogen included in the model are (Figure 2.1)

- Algal basal metabolism and predation
- Dissolution from refractory and labile particulate organic nitrogen
- Mineralization to ammonium
- External loads.

The kinetic equation describing these processes is:

$$\begin{aligned}\frac{\partial DON}{\partial t} &= \sum_{x=c,d,g,m} \left(FND_X \cdot BM_X + FNDP_X \cdot PR_X \right) \cdot ANC_X \cdot B_X \\ &+ K_{RPON} \cdot RPON + K_{LPON} \cdot LPON - K_{DON} \cdot DON + \frac{BFDON}{\Delta Z} + \frac{WDON}{V}\end{aligned} \qquad (2.65)$$

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_{DON} = mineralization rate of dissolved organic nitrogen (day^{-1})

$BFDON$ = benthic flux of dissolved organic nitrogen in bottom layer only (g C m^{-2} day^{-1}).

$WDON$ = external loads of dissolved organic nitrogen (g N day^{-1}).

2.4.4.3 Ammonium Nitrogen

Sources and sinks for ammonia nitrogen included in the model are (Figure 2.1):

- 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:

$$\begin{aligned}\frac{\partial NH4}{\partial t} &= \sum_{x=c,d,g,m}\left(FNI_X \cdot BM_X + FNIP_X \cdot PR_X - PN_X \cdot P_X\right)\cdot ANC_X \cdot B_X \\ &\quad + K_{DON}\cdot DON - KNit \cdot NH4 + \frac{BFNH4}{\Delta Z} + \frac{WNH4}{V}\end{aligned} \tag{2.66}$$

FNI_x = fraction of metabolized nitrogen by algal group x produced as inorganic nitrogen

$FNIP$ = fraction of predated nitrogen produced as inorganic nitrogen

PN_x = preference for ammonium uptake by algal group x ($0 \le PN_x \le 1$)

$KNit$ = nitrification rate (day^{-1}) given in equation (2.74)

$BFNH4$ = sediment-water exchange flux of ammonium (g N m^{-2} day^{-1}), applied to the bottom layer only

$WNH4$ = external loads of ammonium (g N day^{-1})

The form of the nitrification sink in (2.66) and the subsequent source in the nitrate equation (2.67) differ from that in CE-QUAL-ICM as will be explained in section 2.4.4.7.

2.4.4.4 Nitrate Nitrogen

Sources and sinks for nitrate nitrogen included in the model are (Figure 2.1):

- 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:

$$\begin{aligned}\frac{\partial NO3}{\partial t} = & \sum_{x=c,d,g,m} \left(PN_X - 1\right) \cdot P_X \cdot ANC_X \cdot B_X + KNit \cdot NH4 \\ & - ANDC \cdot Denit \cdot DOC + \frac{BFNO3}{\Delta Z} + \frac{WNO3}{V}\end{aligned} \tag{2.67}$$

ANDC = mass of nitrate nitrogen reduced per mass of dissolved organic carbon oxidized (0.933 g N per g C)

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 (2.63-67) with the benthic fluxes, *BFNH4* and *BFNO3* described in Chapter 3.

2.4.4.5 Effect of Algae on Nitrogen

The terms within summation in equations (2.63-67) 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 the four distribution coefficients for basal metabolism should be unity; the sum of the predation distribution coefficients should also be unity.

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

$$\begin{aligned}PN_X = & NH4\left(\frac{NO3}{\left(KHN_X + NH4\right)\left(KHN_X + NO3\right)}\right) \\ & + NH4\left(\frac{KHN_X}{\left(NH4 + NO3\right)\left(KHN_X + NO3\right)}\right)\end{aligned} \tag{2.68}$$

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

2.4.4.6 Mineralization and Hydrolysis

The third term on the RHS of equations (2.63) and (2.64) represents hydrolysis of particulate organic nitrogen and the last term in equation (2.65) represents mineralization of dissolved organic nitrogen. Including a mechanism for accelerated hydrolysis and mineralization during nutrient-limited conditions, the formulations for these processes are:

$$K_{RPON} = \left(K_{RN} + \left(\frac{KHN}{KHN + NH4 + NO3} \right) K_{RNalg} \sum_{x=c,d,g,m} B_x \right) \exp\left(KT_{HDR} \left(T - TR_{HDR} \right) \right) \tag{2.69}$$

$$K_{LPON} = \left(K_{LN} + \left(\frac{KHN}{KHN + NH4 + NO3} \right) K_{LNalg} \sum_{x=c,d,g,m} B_x \right) \exp\left(KT_{HDR} \left(T - TR_{HDR} \right) \right) \tag{2.70}$$

$$K_{DON} = \left(K_{DN} + \left(\frac{KHN}{KHN + NH4 + NO3} \right) K_{DNalg} \sum_{x=c,d,g,m} B_x \right) \exp\left(KT_{HDR} \left(T - TR_{HDR} \right) \right) \tag{2.71}$$

where

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

$$KHN = \frac{\sum_{x=c,d,g,m} KHN_X}{\sum_{x=c,d,g,m} x} \tag{2.72}$$

Equations (2.69-71) have exponential functions that relate rates to temperature.

2.4.4.7 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):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \tag{2.73}$$

The first term in the second line of equation (2.64) and its corresponding term in equation (2.67) represent the effect of nitrification on ammonium and nitrate, respectively. The kinetics of the complete nitrification process are formulated as a function of available ammonium, dissolved oxygen and temperature:

$$KNit \cdot NH4 = fNit\left(T\right) \cdot \left(\frac{DO}{KHNit_{DO} + DO}\right)\left(\frac{NH4}{KHNit_{N} + NH4}\right) Nit_{m} \qquad (2.74)$$

where

$KHNit_{DO}$ = 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})

This follows that in the CE-QUAL-ICM model formulation for nitrification. The Monod function of dissolved oxygen in equation (2.72) 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 the availability of nitrifying bacteria.

In the EFDC water quality model a reference value of KNit is input into the model instead of Nit_m by writing (2.74) as

$$KNit = fNit\left(T\right) \cdot \left(\frac{DO}{KHNit_{DO} + DO}\right)\left(\frac{KHNit_{N}}{KHNit_{N} + NH4}\right) \cdot KNit_{m} \qquad (2.75)$$

where

$$KNit_{m} = \frac{Nit_{m}}{KHNit_{N}} \qquad (2.76)$$

is interpreted as the linear kinetic rate corresponding to $KHNit_N$ equal to unity, since NH4 is always must less than unit, and DO effects eliminated by setting $KHNit_{DO}$ to zero. In certain applications, particularly those having long-term BOD and Nitrogen series test results, *KNitm* is observable.

The temperature function for nitrification in equation (2.74) is given by

$$f_{Nit}(T) = \begin{cases} \exp\left(-KNit1\left(T - TNit1\right)^{2}\right) & : \quad T \le TNit1 \\ 1 & : \quad TNit1 < T < TNit2 \\ \exp\left(-KNit2\left(T - TNit2\right)^{2}\right) & : \quad T \ge TNit2 \end{cases} \qquad (2.77)$$

Tnit1 = lower optimum temperature for nitrification (°C)

Tnit2 = upper 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 effect of suboptimal temperature is represented using Gaussian form.

2.4.4.8 Denitrification

The effect of denitrification on dissolved organic carbon was described in Section 2.4.2.7. Denitrification removes nitrate from the system in stoichiometric proportion to carbon removal as determined by equation (2.43). The sink term in (2.67) represents this removal of nitrate.

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2.4.4.8 Labile and Refractory Splitting of Dissolved Organic Nitrogen

A number of water quality models, including the CE-QUAL-ICM application to the St. Johns River, Florida (Tillman *et al.*, 2004) split dissolved organic phosphorous into labile and refractory components. The refractory component equation is

$$\frac{\partial RDON}{\partial t} = \sum_{x=c,d,g,m} \left(FNRD_X \cdot BM_X + FNRDP_X \cdot PR_X \right) \cdot ANC_X \cdot B_X - K_{RDON} \cdot RDON + \frac{WRDON}{V} \qquad (2.78)$$

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

$FNRD_x$ = fraction of metabolized nitrogen by algal group *x* produced as dissolved organic nitrogen

FNRDP = fraction of predated nitrogen produced as dissolved organic nitrogen

K_{RDON} = mineralization rate of dissolved organic nitrogen (day^{-1})

WRDON = external loads of dissolved organic nitrogen (g N day^{-1}).

The equation for the labile component is

$$\frac{\partial LDON}{\partial t} = \sum_{x=c,d,g,m} \left(FNLD_X \cdot BM_X + FNLDP_X \cdot PR_X \right) \cdot ANC_X \cdot B_X + K_{RPON} \cdot RPON + K_{LPON} \cdot LPON - K_{LDON} \cdot LDON + \frac{WDON}{V} \qquad (2.79)$$

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_{DON} = mineralization rate of dissolved organic nitrogen (day^{-1})

WDON = external loads of dissolved organic nitrogen (g N day^{-1}).

Equations (2.78) and (2.79) follow from Tillman *et al.*, (2004), but are not currently implemented in the EFDC water quality model.

2.4.5 Silica

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

2.4.5.1 Particulate Biogenic Silica

Sources and sinks for particulate biogenic silica included in the model are (Figure 2.1):

- Diatom basal metabolism and predation
- Dissolution to available silica
- Settling
- External loads

The kinetic equation describing these processes is:

$$\begin{aligned}\frac{\partial SU}{\partial t} &= \left(FSP_d \cdot BM_d + FSPP \cdot PR_d\right) ASC_d \cdot B_d - K_{SUA} \cdot SU \\ &\quad + \frac{\partial}{\partial Z}\left(WS_d \cdot SU\right) + \frac{WSU}{V}\end{aligned} \tag{2.80}$$

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_{SUA} = dissolution rate of particulate biogenic silica (day^{-1})

WSU = external loads of particulate biogenic silica (g Si day^{-1})

2.4.5.2 Available Silica

Sources and sinks for available silica included in the model are (Figure 2.1):

- 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:

$$\begin{aligned}\frac{\partial SA}{\partial t} &= \left(FSI_d \cdot BM_d + FSIP \cdot PR_d - P_d\right) ASC_d \cdot B_d + K_{SUA} \cdot SU \\ &\quad + \frac{\partial}{\partial Z}\left(WS_{TSS} \cdot SAp\right) + \frac{BFSAd}{\Delta Z} + \frac{WSA}{V}\end{aligned} \tag{2.81}$$

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 bottom layer only

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

In equation (2.81), 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.

2.4.5.3 Available Silica System

Analysis of Chesapeake Bay monitoring data indicates that silica shows similar behavior as phosphate in the adsorption-desorption process (Cerco and Cole, 1993). As in phosphate, therefore, available silica is defined to include both dissolved and sorbed fractions. 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:

$$\begin{aligned}SAp &= \left(\frac{K_{SAp} \cdot SORPS}{1 + K_{SAp} \cdot SORPS}\right) SA \\ SAd &= \left(\frac{1}{1 + K_{SAp} \cdot SORPS}\right) SA \\ SORPS &= TSS \ or \ TAM_P\end{aligned} \tag{2.82}$$

$$SA = SAp + SAd \tag{2.83}$$

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

2.4.5.4 Effect of Diatoms on Silica

In equations (2.80) and (2.82), 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 (FSP_d, FSI_d, $FSPP$, and $FSIP$). 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 equation (2.81).

2.4.5.5 Dissolution

The term ($- K_{SUA} \cdot SU$) in equation (2.80) and its corresponding term in equation (2.81) represent dissolution of particulate biogenic silica to available silica. The dissolution rate is expressed as an exponential function of temperature:

$$K_{SUA} = K_{SU} \cdot \exp\left(KT_{SUA}\left(T - TR_{SUS}\right)\right) \qquad (2.84)$$

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

KT_{SUA} = effect of temperature on dissolution of particulate biogenic silica (°C^{-1})

TR_{SUA} = reference temperature for dissolution of particulate biogenic silica (°C)

2.4.6 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 fresh water, 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:

$$\frac{\partial COD}{\partial t} = -\left(\frac{DO}{KH_{COD} + DO}\right) \cdot K_{COD} \cdot COD + \frac{BFCOD}{\Delta Z} + \frac{WCOD}{V} \qquad (2.85)$$

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 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:

$$K_{COD} = K_{CD} \cdot \exp\left(KT_{COD}\left(T - TR_{COD}\right)\right) \tag{2.86}$$

K_{CD} = oxidation rate of chemical oxygen demand at TR_{COD} (day^{-1})

KT_{COD} = effect of temperature on oxidation of chemical oxygen demand (°C^{-1})

TR_{COD} = reference temperature for oxidation of chemical oxygen demand (°C)

2.4.7 Dissolved Oxygen

Sources and sinks of dissolved oxygen in the water column included in the model are (Figure B.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:

$$\begin{aligned} \frac{\partial DO}{\partial t} = & \sum_{x=c,d,g,m} \left(\begin{array}{c} \left(1+0.3\left(1-PN_x\right)\right)P_x \\ -\left(1-FCD_x\right)\left(\dfrac{DO}{KHR_x+DO}\right)BM_x \end{array} \right) \cdot AOCR \cdot B_x \\ & - AONT \cdot Nit \cdot NH4 - AOCR \cdot K_{HR} \cdot DOC - \left(\frac{DO}{KH_{COD}+DO}\right) \cdot K_{COD} \cdot COD \\ & + K_R\left(DO_S - DO\right) + \frac{SOD}{\Delta Z} + \frac{WDO}{V} \end{aligned} \tag{2.87}$$

$AONT$ = mass of dissolved oxygen consumed per unit mass of ammonium nitrogen nitrified (4.33 g O_2 per g N; see Section 5.9.2)

$AOCR$ = dissolved oxygen-to-carbon ratio in respiration (2.67 g O_2 per g C; see Section 5.9.1)

K_r = reaeration coefficient (day^{-1}): the reaeration term is applied to the surface layer only

DO_s = saturated concentration of dissolved oxygen (g O_2 m^{-3})

SOD = sediment oxygen demand (g O_2 m^{-2} day^{-1}), applied to the bottom layer only; positive is to the water column

WDO = external loads of dissolved oxygen (g O_2 day^{-1})

PN_x = preference for ammonia uptake by algae group x ($0<PN_x<1$)

The two sink terms in equation (2.87), heterotrophic respiration and chemical oxygen demand, are explained in Section 2.4.2.6 and Section 2.4.6 respectively. The remainder of this section explains the effects of algae, nitrification, and surface reaeration.

2.4.7.1 Effect of Algae on Dissolved Oxygen

The first line on the RHS of equation (2.87) 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):

$$106CO_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O \rightarrow protoplasm + 106O_2 + 15H^+ \qquad (2.88)$$

$$106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O \rightarrow protoplasm + 138O_2 \qquad (2.89)$$

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 equation (2.87) 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 equation (2.87) accounts for the oxygen consumption due to algal respiration. A simple representation of respiration process is:

$$CH_2O + O_2 = CO_2 + H_2O \qquad (2.90)$$

from which, $AOCR$ = 2.67 g O_2 per g C.

2.4.7.2 Effect of Nitrification on Dissolved Oxygen

The stoichiometry of nitrification reaction, equation (2.73) 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 (Wezernak and Gannon, 1968), i.e., $AONT = 4.33$ g O_2 per g N.

2.4.7.3 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, (DO_s - 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):

$$\begin{aligned} DO_s &= 14.5532 - 0.38217 \cdot T + 5.4258 \times 10^{-3} \cdot T^2 \\ &- CL \cdot (1.665 \times 10^{-4} - 5.866 \times 10^{-6} \cdot T + 9.796 \times 10^{-8} \cdot T^2) \end{aligned} \tag{2.91}$$

CL = chloride concentration (mg/L) = S/1.80655.

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

$$K_r = \frac{1}{\Delta z}\left(K_{ro}\sqrt{\frac{ueq}{heq}} + W_{rea}\right) \cdot \left(KT_r\right)^{(T-20)} \tag{2.92}$$

K_{ro} = proportionality constant = 3.933 in SI unit

u_{eq} = weighted velocity over cross-section (m sec^{-1}) = $\sum(u_k V_k)/\sum(V_k)$

h_{eq} = weighted depth over cross-section (m) = $\sum(V_k)/B_\eta$

B_η = width at the free surface (m)

W_{rea} = wind-induced reaeration (m day^{-1})

$$W_{rea} = 0.728\sqrt{U_w} - 0.317U_w + 0.0372U_w^2 \tag{2.93}$$

U_w = wind speed (m sec^{-1}) at the height of 10 m above surface

KT_r = constant for temperature adjustment of dissolved oxygen reaeration rate.

2.4.7.4 Simplified Equation for Dissolved Oxygen

The simplified DO equation for KHRx and FCDx equal to zero is

$$\begin{aligned}\frac{\partial DO}{\partial t} = &\sum_{x=c,d,g,m}\left((1.3-0.3PN_x)P_x - BM_x\right)\cdot AOCR\cdot B_x \\ &-AONT\cdot Nit\cdot NH4 - AOCR\cdot K_{HR}\cdot DOC - \left(\frac{DO}{KH_{COD}+DO}\right)\cdot K_{COD}\cdot COD \\ &+K_R\left(DO_S - DO\right) + \frac{SOD}{\Delta Z} + \frac{WDO}{V}\end{aligned} \qquad (2.94)$$

which is consistent with equation (2.38).

2.4.8 Total Active Metal

The present model requires simulation of total active metal for adsorption of phosphate and silica if that option is chosen (Figure 2.1). 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 (see Chapter 5), 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:

$$\begin{aligned}\frac{\partial TAM}{\partial t} = &\left(\frac{KHbmf}{KHbmf + DO}\right)\left(\exp\left(Ktam\left(T - Ttam\right)\right)\right)\frac{BFTAM}{\Delta z} \\ &+\frac{\partial}{\partial Z}\left(WS_s\cdot TAMp\right) + \frac{WTAM}{V}\end{aligned} \qquad (2.95)$$

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})

$KHbmf$ = 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

$Ktam$ = effect of temperature on sediment release of total active metal ($°C^{-1}$)

$Ttam$ = reference temperature for sediment release of total active metal (°C)

WS_s = 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 particulate and dissolved forms depending on dissolved oxygen concentration. In oxygenated water, most of the 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:

$$TAMd = \min\left(TAMdmx \exp\left(-Kdotam \cdot DO\right), TAM\right) \tag{2.96}$$

$$TAMp = TAM - TAMd \tag{2.97}$$

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

$Kdotam$ = constant that relates total active metal solubility to dissolved oxygen (per g O_2 m^{-3})

2.4.9 Fecal Coliform Bacteria

The fecal coliform variable is completely decoupled from the rest of the water quality model and is included in the model for convenience in TMDL applications which consider both nutrient and pathogen impairments. 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 and 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:

$$\frac{\partial FCB}{\partial t} = KFCB \cdot \left(TFCB^{(T-20)}\right) \cdot FCB + \frac{WFCB}{V} \tag{2.98}$$

FCB = bacteria concentration (MPN per 100 ml)
$KFCB$ = first order die-off rate at 20°C (day^{-1})
$TFCB$ = effect of temperature on decay of bacteria (°C^{-1})
$WFCB$ = external loads of fecal coliform bacteria (MPN per 100 ml m^3 day^{-1})

2.5 Settling, Deposition and Resuspension of Particulate Matter

The kinetic equations for particulate matter, including particulate organic matter, total phosphate, the two silica state variables and total active metal, contain settling term. A representative generic equation is

$$\frac{\partial PM}{\partial t} = \frac{\partial}{\partial z}\left(WS_{PM} \cdot PM\right) + PM_{SS} \tag{2.99}$$

where PM_{SS} represents the additional terms in the equation. Integration of equation (2.99) over the bottom layer gives

$$\frac{\partial PM_1}{\partial t} = \frac{WS_{PM}}{\Delta Z_1} \cdot PM_2 - \frac{WS_{PM}}{\Delta Z_1} \cdot PM_1 + PM_{SS1} \tag{2.100}$$

The original CE-QUAL-ICM and EFDC water quality models were formulated with settling velocities representing long-term average net settling. In the subsequent application of CE-QUAL-ICM to Florida Bay (Cerco *et al.*, 2000), the resuspension or erosion of particulate material form the sediment bed was added and has also been added to the EFDC water quality model.

The EFDC model allows the use of the net settling formulation (2.100) and a formulation allowing resuspension with equation (2.100) modified

$$\frac{\partial PM_1}{\partial t} = \frac{WS_{POM}}{\Delta Z_1} \cdot PM_2 - \frac{P_{depPM} \cdot WS_{PM}}{\Delta Z_1} \cdot PM_1 + \frac{E_{PM}}{\Delta Z_1} + PM_{SS1} \tag{2.101}$$

to include a probability of deposition factor and an erosion term, E_{PM} having units of mass per unit time-unit area. For EFDC model applications with erosion of particulate material in the water quality module, sediment transport must be active in the hydrodynamic model. The erosion term is then defined by

$$E_{PM} = \left(\frac{PM_{bed}}{SED_{bed}} \right) \max \left(J_{ERO}, 0 \right) \tag{2.102}$$

where

PM_{bed} = particulate material concentration in bed (g PM m^{-2} or g PM m^{-3})

SED_{bed} = concentration finest sediment class in bed (g PM m^{-2} or g PM m^{-3})

P_{depPM} = probability of deposition of the specific particulate matter variable ($0 \leq P_{depPM} \leq 1$)

J_{ERO} = mass rate of erosion or resuspension of the finest sediment class (g SED day^{-1} m^{-2})

Use the ratio of the water quality model particulate state variable concentration to the finest sediment size class concentration rather than the total solids concentration is based on the reality that finest sediment class (general less than 63 μm) includes both inorganic and organic material and field observations of settling, deposition and resuspension, when available for model calibration account for this. If simultaneous deposition and erosion are not permitted, the probability of deposition is defined as zero when the sediment erosion flux is greater than zero.

In conclusion, it is noted that in the CE-QUAL-ICM documentation which includes particulate matter resuspension (Cerco *et al.*, 2000), resuspension is explicitly included in various state variable equations, while in this document it is included implicitly as described in this section.

2.6 Method of Solution for Kinetics Equations

The kinetic equations for the 20 state variables, excluding fecal coliform, in the EFDC water column water quality model can be expressed in a 20 × 20 system of partial differential equations in each model cell, after linearizing some terms, mostly Monod type expressions:

$$\frac{\partial}{\partial t}\{C\}=[K]\{C\}+\frac{\partial}{\partial z}\left([W]\{C\}\right)+\{R\} \tag{2.103}$$

where $\{C\}$ is in mass volume^{-1}, $[K]$ is in time^{-1}, $[W]$ is in length time^{-1}, and $\{R\}$ is in mass volume^{-1} time^{-1}. The ordering of variables follows that in Table 2.1 which results in $[K]$ being lower triangular. Integrating (2.103) over layer k, gives

$$\begin{gathered}\frac{\partial}{\partial t}\{C\}_k=[K1]_k\{C\}_k+\delta_k[K2]_k\{C\}_{k+1}+\{R\}_k\\ [K1]_k=[K]_k-\frac{1}{\Delta z}[W]\\ [K2]_k=\frac{1}{\Delta z}[W]\end{gathered} \tag{2.104}$$

which indicates that the settling of particulate matter from the overlying cell acts as an input for a given cell. For the layer of cells adjacent to the bed, the erosion term in (2.101) is included in the $\{R\}$ vector. The matrices and vectors in (2.103 and 2.104) are defined in Appendix A of Park *et al.*, (1995). The layer index k increases upward with KC vertical layers; $k = 1$ is the bottom layer and $k = KC$ is the surface layer. Then $\delta_k = 0$ for k = KC; otherwise, $\delta_k = 1$. The matrix $[K2]$ is a diagonal matrix, and the non-zero elements account for the settling of particulate matter from the overlying cell.

Equation (2.104) is solved using a generalized trapezoidal scheme over a time step of θ, which may be expressed as:

$$\begin{gathered}\{C\}_k^N-\{C\}_k^O=\lambda\theta\left([K1]_k^O\{C\}_k^N+\delta_k[K2]_k^O\{C\}_{k+1}^N+\{R\}_k^N\right)\\ +(1-\lambda)\theta\left([K1]_k^O\{C\}_k^O+\delta_k[K2]_k^O\{C\}_{k+1}^O+\{R\}_k^O\right)\end{gathered} \tag{2.105}$$

Or

$$\begin{gathered}\left([I]-\lambda\theta[K1]_k^O\right)\{C\}_k^N=\left([I]+(1-\lambda)\theta[K1]_k^O\right)\{C\}_k^O\\ +\theta\delta_k[K2]_k^O\left(\lambda\{C\}_{k+1}^N+(1-\lambda)\{C\}_{k+1}^O\right)+\theta\left(\lambda\{R\}_k^N+(1-\lambda)\{R\}_k^O\right)\end{gathered} \tag{2.106}$$

where λ is an implicitness factor ($0 \le \lambda \le 1$), $\theta = 2\cdot m\cdot\Delta t$ is the time step for the kinetic equations; [I] is a unit matrix; the superscripts O and N designate the variables before and after being adjusted for the relevant kinetic processes. Since equation (2.105) is solved from the surface layer downward, the term with $\{C\}^{N}_{k+1}$ is known for the k^{th} layer and thus placed on the RHS. In equation (2.106), inversion of a matrix can be avoided when the 20 state variables are solved in the order given in Table 2.1.

2.7 Application Specific Parameter Tables

This section includes application specific parameter tables for algae (Table 2.4), organic carbon (Table 2.5), phosphorous (Table 2.6), nitrogen (Table 2.7), silica (Table 2.8), chemical oxygen demand and dissolved oxygen (Table 2.9). The Table contents may vary between various application specific distributions of this document. The reader is referred to the references listed in Table 2.3, for a list of various CE-QUAL-ICM and EFDC water quality model application specific parameter tables.

Table 2.3 Water Quality Model Applications

Application Site	Description	Study
Chesapeake Bay	Middle Atlantic Estuary System	Cerco and Cole, 1995; Park *et al.*, 1995
San Juan Bay, Puerto Rico	Sub-Tropical Estuary	Bunch *et al.*, 2000
Florida Bay	Sub-Tropical Estuary/Ocean	Cerco *et al.*, 2000
Chesapeake Bay Refinement	Middle Atlantic Estuary System	Cerco *et al.*, 2002
Lake Washington, WA	Pacific Northwest Freshwater Lake	Cerco *et al.*, 2004
St. Johns River	Southern Atlantic Estuary	Tillman *et al.*, 2004
Peconic Bays, NY	New England Estuary/Ocean	Tetra Tech, 1999
Christina River, DE/PA	Middle Atlantic Freshwater River	Tetra Tech, 2000a
Tenkiller Lake, OK	Mid-West Freshwater Lake	Tetra Tech, 2000b
Cape Fear River, NC	Middle Atlantic Estuary	Tetra Tech, 2001
Mashpouge Pond, MA	New England Freshwater Lake	Tetra Tech, 2002c
Charles River, MA	New England Estuary/River	Tetra Tech, 2006b
Charleston Harbor, SC	Mid-Southern Atlantic Estuary	Tetra Tech, 2006c

Table 2.4 Water Quality Parameters Related to Algae in the Water Column

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
PM_c (day^{-1})	4		
PM_d (day^{-1})	N/A		
PM_g (day^{-1})	N/A		
KHN_x (g N m^{-3})	0.03		
KHP_x (g P m^{-3})	0.005		
FD	1		
Ke_b (m^{-1})	0.13		
Ke_{ISS} (m^{-1} per g m^{-3})	0.085		
Ke_{VSS} (m^{-1} per g m^{-3})	0.085		
Ke_{Chl} (m^{-1} / mg Chl m^{-3})	N/A		
$CChl_x$ (g C / mg Chl)	75		
$(D_{opt})_x$ (m)	N/A		
I_{sx} (Watts/m^2)	N/A		
I_{sxmin} (Watts/m^2)	N/A		
KHI (Watts/m^2)	60 (E/ meter^2-day)		
CI_a, CI_b & CI_c	1.0, 0.0, 0.0		
$TMlow_c$, $TMupp_c$ (°C)	25, 25		
$TMlow_d$, $TMupp_d$ (°C)	N/A		
$TMlow_g$, $TMupp_g$ (°C)	N/A		
$KTG1_c$, $KTG2_c$ (°C^{-2})	0.004, 0.012		
$KTG1_d$, $KTG2_d$ (°C^{-2})	N/A		
$KTG1_g$, $KTG2_g$ (°C^{-2})	N/A		
$STOX$ (psu)	1.0		
BMR_c (day^{-1})	0.1		
BMR_d (day^{-1})	N/A		
BMR_g (day^{-1})	N/A		
TR_x (°C)	20		
KTB_x (°C^{-1})	0.0322		
PRR_c (day^{-1})	0.02		2.28
PRR_d (day^{-1})	N/A		
PRR_g (day^{-1})	N/A		

Table 2.4 Continued

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
B_{xP} (g C/m^3)	1		2.28
α_P	1		2.28
WS_c (m day^{-1})	0.01		
WS_d (m day^{-1})	N/A		
WS_g (m day^{-1})	N/A		

Table 2.5 Parameters Related to Organic Carbon in the Water Column

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
$FCRP$	0.25		
$FCLP$	0.50		
$FCDP$	0.25		
FCD	0.0[a]		
KHR_x (g O$_2$ m^{-3})	0.0		
WS_{RP} (m day^{-1})	0.03		
WS_{LP} (m day^{-1})	0.03		
$KHOR_{DO}$ (g O$_2$ m^{-3})	0.5		
K_{RC} (day^{-1})	0.005		
K_{LC} (day^{-1})	0.02		
K_{DC} (day^{-1})	0.01		
K_{RCalg} (day^{-1}/ g C m^{-3})	0.0[a]		
K_{LCalg} (day^{-1}/ g C m^{-3})	0.0[a]		
K_{DCalg} (day^{-1}/ g C m^{-3})	0.0[a]		
TR_{HDR} (°C)	20.0		
TR_{MNL} (°C)	20.0		
KT_{HDR} (°C^{-1})	0.069		
KT_{MNL} (°C^{-1})	0.069		
$AANOX$	0.0[b]		
$KROR_{DO}$ (g O m^{-3})	0.0[b]		
$KHDN_N$ (g N m^{-3})	0.0[b]		

[a] Not reported. Assumed value of zero
[b] Not reported. Assumed no simulation of denitrification

Table 2.6 Parameters Related to Phosphorus in the Water Column

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
$FPRP$	0.03		
$FPLP$	0.07		
$FPDP$	0.4		
$FPIP$	0.5[a]		
FPR_x	0.0		
FPL_x	0.0		
FPD_x	0.5		
FPI_x	0.5[a]		
APC_x (g P per g C)	0.0167		
WS_s (m/day)	0.03		
K_{PO4p} (m^3/g) for TSS	0.2		
CP_{prm1} (g C per g P)	60		
CP_{prm2} (g C per g P)	0 [b]		
CP_{prm3} (per g P m^{-3})	0 [b]		
K_{RP} (day^{-1})	0.005		
K_{LP} (day^{-1})	0.12		
K_{DP} (day^{-1})	0.2		
K_{RPalg}(day^{-1} per g C m^{-3})	0.2		
K_{LPalg}(day^{-1} per g C m^{-3})	0.0[b]		
K_{DPalg}(day^{-1} per g C m^{-3})	0.0[b]		

[a] Not reported. Value inferred from constraint.

[b] Not reported. Value assumed to be zero.

Table 2.7 Parameters Related to Nitrogen in the Water Column

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
$FNRP$	0.15		
$FNLP$	0.25		
$FNDP$	0.5		
$FNIP$	0.1		
FNR_x	0.15		
FNL_x	0.25		
FND_x	0.5		
FNI_x	0.1		
ANC_x (g N per g C)	0.175		
$ANDC$ (g N per g C)	0.933		
K_{RN} (day^{-1})	0.005		
K_{LN} (day^{-1})	0.03		
K_{DN} (day^{-1})	0.01		
K_{RNalg} (day^{-1} /g C m^{-3})	0.0[a]		
K_{LNalg} (day^{-1} /g C m^{-3})	0.0[a]		
K_{DNalg} (day^{-1} /g C m^{-3})	0.0[a]		
Nit_m (g N m^{-3} day^{-1})	0.01		
$KNit$ (day^{-1})	0.01		
$KHNit_{DO}$ (g O_2 m^{-3})	3.0		
$KHNit_N$ (g N m^{-3})	1.0		
$TNit1$ (°C)	30		
$TNit2$ (°C)	30		
$KNit1$ (°C^{-2})	0.003		
$KNit2$ (°C^{-2})	0.003		

[a] Not reported. Assumed value of zero.

Table 2.8 Parameters Related to Silica in the Water Column

Parameter	St. Johns River (Tillman *et al.*, 2004)	Florida Bay (Current Study)	Equation Ref
FSI_d	0.5		
$FSIP$	0.5^a		
FSP_d	0.5		
$FSPP$	0.5^a		
ASC_d (g Si/g C)	0.8		
K_{SUA} (days^{-1})	0.03		
K_{Sap} (m^3/g)	0.2^a		
KHS (g Si/m^3)	0.03		

[a] Not Reported. Values assumed

Table 2.9 Parameters Related to Chemical Oxygen Demand and Dissolved Oxygen in the Water Column

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
KH_{COD} (g O$_2$ m^{-3})	0.5		
K_{CD} (day^{-1})	20		
TR_{COD} (°C)	20a		
KT_{COD} (°C^{-1})	0.069a		
$AOCR$ (g O$_2$ per g C)	2.67		
$AONT$ (g O$_2$ per g N)	4.33		
K_{ro} (in SI unit)	3.933		
KT_r	20		

3. Rooted Aquatic Plants Formulation

4. Sediment Diagenesis and Flux Formulation

5. References

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A. Supplementary Material on Macroalgae and Periphyton Formulations

A.1 Introduction

This appendix provides some supplementary material on simulation of macroalgae and substrate attached and floating periphyton using the stationary algae variable in the EFDC water quality model. Section A.2 addresses alternative conceptualizations using mass per unit area and mass per unit volume representations of biomass showing that with some care, the two formulations are equivalent. Section A.3 provides additional description the mass per unit volume formulation in EFDC focusing of kinetic processes and parameters specific to representation of stationary algae.

A.2 Conceptualization

Stationary or essentially stationary algae, including macroalgae and substrate attached or floating periphyton, can be modeled using either mass per unit area or mass per unit volume units. Both conceptualizations have their merits. Mass per unit area, supplemented with areal coverage or patchiness, is more consistent with field observational data. Mass per unit volume readily allows kinetic formulations which are equivalent to those used for suspended algae. The purpose of this section is to show that the two conceptual formulations are equivalent when care is taken to properly identify the meaning of the kinetic processes.

To facilitate discussion, consider the case of a bed substrate attached periphyton or benthic algae interacting with dissolved oxygen, dissolve and particulate organic carbon, the dissolved and particulate organic forms of a nutrient, and the dissolved inorganic form of the nutrient and corresponding benthic fluxes associated with sediment diagenesis. The kinetic equation for a mass per unit area benthic algae can be written as

$$\frac{\partial (HB)_{bam}}{\partial t} = \left(P_{ba} - BM_{ba} - PR_{ba} \right) \cdot (HB)_{bam} \qquad \text{(A.1)}$$

where

$(HB)_{bam} = H_{bam} \cdot B_{bam}$ = algal biomass per unit area (g C m^{-2})

H_{bam} = thickness of benthic algae mat (m)

B_{bam} = mass of algae per unit volume of the mat (g C m^{-3})

and the other terms have previously defined definitions. Equation (A.1) follows Cerco *et al.* (2000) with the exception of a slight difference in the definition of the predation rate. Also, the state variable $(HB)_{bam}$ is defined to emphasize the mass per unit area form as well as to arrive at an equivalence between the mass per unit volume state variable used in the EFDC model. Following Cerco *et al.* (2000) it if further assumed that the benthic algae occupy only a constant fraction, *Pat_{bam}* of the total bottom area, *A*, of a horizontal model cell. Under these assumptions the mass of benthic algae per total bottom layer area follows from (A.1) and is

$$Pat_{bam}\frac{\partial(HB)_{bam}}{\partial t}=(P_{ba}-BM_{ba}-PR_{ba})\cdot Pat_{bam}\cdot(HB)_{bam} \qquad (A.2)$$

Using the EFDC formulation of mass per unit volume, the benthic algae is defined by an equivalent concentration in the bottom layer of a model cell. It is noted that although the benthic algae is not transport, the thickness of the bottom layer varies in the EFDC sigma vertical coordinate formulation. Requiring that this layer thickness variation be accounted for, the mass of algae in the bottom layer is given by the sigma coordinate form of equation (2.5)

$$\frac{\partial(H\cdot B_{ba})}{\partial t}=(P_{ba}-BM_{ba}-PR_{ba})\cdot H\cdot B_{ba}+\frac{\partial}{\partial z}(WS_{ba}\cdot B_{ba}) \qquad (A.3)$$

where

B_{ba} = mass of benthic algae per volume of model cell (g C m^{-3})

H = depth of the water column (m)

WS_{ba} = settling velocity (m/s)

And z is the dimensionless vertical sigma coordinate. It is noted that is not necessary to write (2.5) in the sigma form for transported state variables since the fractional step solution procedure accounts for cell volume variation in a mass conservative manner and future allows the kinetic step to be made at a constant cell volume. Integrating (A.3) over the bottom layer gives

$$\Delta_b\frac{\partial(H\cdot B_{ba})}{\partial t}=(P_{ba}-BM_{ba}-PR_{ba})\cdot\Delta_b\cdot H\cdot B_{ba}-WS_{ba}\cdot B_{ba} \qquad (A.4)$$

Where Δ_b is the constant dimensionless thickness of the bottom layer. The role of the last term associated downward settling will be further defined. Benthic algae exist only in the bottom layer of the water column, however the state variable is dimensioned to exist in all vertical layer for three-dimensional applications. Thus in three-dimensional applications, the concentration is set to zero in all layers above the bottom layer and the integrating of the settling term automatically sets settling flux into bottom layer to zero.

To define the meaning of the settling term in (A.4) and arrive at an equivalence with equation (A.2), the time derivative in equation (A.4) is expanded and a constant reference water column depth is introduced to give

$$\begin{aligned}&\frac{H}{H_o}\frac{\partial}{\partial t}(H_o\cdot\Delta_b\cdot B_{ba})+(H_o\cdot\Delta_b\cdot B_{ba})\frac{1}{H_o}\frac{\partial H}{\partial t}\\&=(P_{ba}-BM_{ba}-PR_{ba})\cdot(\Delta_b\cdot H\cdot B_{ba})-WS_{ba}\cdot B_{ba}\end{aligned} \qquad (A.5)$$

The settling term may be eliminated by requiring that the second and last terms in (A.5) cancel, which defines the settling velocity as

$$WS_{ba} = -\Delta_b \frac{\partial H}{\partial t} \tag{A.6}$$

With (A.6) becoming

$$\frac{\partial}{\partial t}\left(H_o \cdot \Delta_b \cdot B_{ba}\right) = \left(P_{ba} - BM_{ba} - PR_{ba}\right) \cdot \left(\Delta_b \cdot H_o \cdot B_{ba}\right) \tag{A.7}$$

Or

$$\frac{\partial B_{ba}}{\partial t} = \left(P_{ba} - BM_{ba} - PR_{ba}\right) \cdot B_{ba} \tag{A.8}$$

There are two noteworthy points to be made here. The first is that equation (A.8) is identical to equation (2.5) with a zero settling velocity and no source term. Thus the generic form (2.5) can be used to simulate benthic algae by specifying a zero settling velocity. The definition of settling by (A.6) simply served to reduce the mass conservative sigma form to the generic form.

The second point is that (A.7) conforms to the mass per unit area form (A.2) when the relationship between the variables in (A.2) and (A.7) is defined by

$$\Delta_b \cdot H_o \cdot B_{ba} = Pat_{bam} \cdot \left(HB\right)_{bam} \tag{A.9}$$

Writing (A.9) in the form

$$\left(HB\right)_{bam} = \frac{\Delta_b \cdot H_o \cdot B_{ba}}{Pat_{bam}} \tag{A.10}$$

Readily allows the model predicted mass per cell volume state variable to be converted to the observable mass per unity area of mat surface with corresponding observations for patchiness. For estuarine and coastal applications, the constant scaling depth is appropriately defined as the local depth relative to long-term mean sea level.

We now consider simplified equations for the previously listed state variables in the form presented by Cerco *et al*. (2000) consistent with equations (A.1) and (A.2). The equations for dissolved organic carbon and nitrogen, ammonia, nitrate and dissolved oxygen are

$$\frac{\partial DOC}{\partial t} = K_{POC} \cdot POC - K_{HR} \cdot DOC + \frac{BFDOC^T}{\Delta Z} \tag{A.11}$$

$$\frac{\partial DON}{\partial t} = K_{PON} \cdot PON - K_{DON} \cdot DON + \frac{BFDON^T}{\Delta Z} \tag{A.12}$$

$$\frac{\partial NH4}{\partial t} = K_{DON} \cdot DON - KNit \cdot NH4 + \frac{BFNH4^T}{\Delta Z} \tag{A.13}$$

$$\frac{\partial NO3}{\partial t} = KNit \cdot NH4 + \frac{BFN03^T}{\Delta Z} \tag{A.14}$$

$$\frac{\partial DO}{\partial t} = -AOCR \cdot K_{HR} \cdot DOC - AONT \cdot Nit \cdot NH4 - K_{COD} \cdot COD + \frac{SOD^T}{\Delta Z} \tag{A.15}$$

In equations (A.11-15) terms associated with transported suspended algae have been omitted and particulate organic source terms have been lumped, to simplify notation. The superscript *T* associated with the benthic fluxes denotes the flux to the water column at the top of the benthic algae mat. Following Cerco *et al.* (2000), the fluxes at the top of the benthic algae mat are defined as

$$BFDOC^T = \left(FCD_{ba} \cdot BM_{ba} + FCDP_{ba} \cdot PR_{ba} \right) \cdot Pat_{bam} \cdot \left(HB \right)_{bam} \tag{A.15}$$

$$BFDON^T = \left(FNP_{ba} \cdot BM_{ba} + FNPP_{ba} \cdot PR_{ba} \right) \cdot ANC_{ba} \cdot Pat_{bam} \cdot \left(HB \right)_{bam} \tag{A.17}$$

$$BFNH4^T = BFNH4^S + \begin{pmatrix} FNI_{bam} \cdot BM_{ba} - PN_{bam} \cdot P_{ba} \\ +FNIP_{ba} \cdot PR_{ba} \end{pmatrix} \cdot ANC_{ba} \cdot Pat_{bam} \cdot \left(HB \right)_{bam} \tag{A.18}$$

$$BFN03^T = BFN03^S + \left(PN_{ba} - 1 \right) \cdot P_{ba} \cdot ANC_{ba} \cdot Pat_{bam} \cdot \left(HB \right)_{bam} \tag{A.19}$$

$$SOD^T = SOD^S + \begin{pmatrix} \left(1.3 - 0.3 PN_x \right) P_x \\ -\left(1 - FCD_x \right) BM_x \end{pmatrix} \cdot AOCR \cdot Pat_{bam} \cdot \left(HB \right)_{bam} \tag{A.20}$$

with the superscript S denoting fluxes from the sediment diagenesis model. Inserting equations (A.16-20) into equations (A.11-12) gives

$$\begin{aligned} \frac{\partial DOC}{\partial t} = & \left(\frac{H_o}{H} \right) \left(FCD_{ba} \cdot BM_{ba} + FCDP_{ba} \cdot PR_{ba} \right) \cdot B_{ba} \\ & + K_{POC} \cdot POC - K_{HR} \cdot DOC \end{aligned} \tag{A.21}$$

$$\begin{aligned} \frac{\partial DON}{\partial t} = & \left(\frac{H_o}{H} \right) \left(FNP_{ba} \cdot BM_{ba} + FNPP_{ba} \cdot PR_{ba} \right) \cdot ANC_{ba} \cdot B_{ba} \\ & + K_{PON} \cdot PON - K_{DON} \cdot DON \end{aligned} \tag{A.22}$$

$$\begin{aligned}\frac{\partial NH4}{\partial t} &= \left(\frac{H_o}{H}\right)\left(FNI_{bam}\cdot BM_{ba} - PN_{bam}\cdot P_{ba} + FNIP_{ba}\cdot PR_{ba}\right)\cdot ANC_{ba}\cdot B_{ba} \\ &\quad + K_{DON}\cdot DON - KNit\cdot NH4 + \frac{BFNH4^S}{\Delta Z}\end{aligned} \tag{A.23}$$

$$\frac{\partial NO3}{\partial t} = \left(\frac{H_o}{H}\right)\left(PN_{ba} - 1\right)\cdot P_{ba}\cdot ANC_{ba}\cdot B_{ba} + KNit\cdot NH4 + \frac{BFN03^S}{\Delta Z} \tag{A.24}$$

$$\begin{aligned}\frac{\partial DO}{\partial t} &= \left(\frac{H_o}{H}\right)\left(\left(1.3 - 0.3PN_x\right)P_x - \left(1 - FCD_x\right)BM_x\right)\cdot AOCR\cdot B_{am} \\ &\quad - AOCR\cdot K_{HR}\cdot DOC - AONT\cdot Nit\cdot NH4 - K_{COD}\cdot COD + \frac{SOD^S}{\Delta Z}\end{aligned} \tag{A.25}$$

Where use has been made of (A.9) and

$$\Delta Z = \Delta_b H \tag{A.26}$$

Comparison of equations (A.21-25) with their counter parts in Chapter 2 indicate that inclusion of the mass per unit volume representation of benthic algae in the algae source-sink terms follows the same formulation with the exception of the H_o/H multiplier required for the source-sink terms associated with benthic algae. Another benefit of this formulation for interaction of benthic algae with dissolved water column state variables is that it has the flexibility of being applicable to macroalgae and floating periphytons. For completeness, the corresponding simplified equations for dissolved organic phosphorous and total water phase phosphate are

$$\begin{aligned}\frac{\partial DOP}{\partial t} &= \left(\frac{H_o}{H}\right)\left(FPD_{ba}\cdot BM_{ba} + FPDP_{ba}\cdot PR_{ba}\right)\cdot APC_{ba}\cdot B_{ba} \\ &\quad + K_{POP}\cdot POP - K_{DOP}\cdot DOP\end{aligned} \tag{A.27}$$

$$\begin{aligned}\frac{\partial}{\partial t}\left(PO4p + PO4d\right) &= \left(\frac{H_o}{H}\right)\left(FPI_{ba}\cdot BM_{ba} + FPIP_{ba}\cdot PR_{ba} - P_{ba}\right)\cdot APC_{ba}\cdot B_{ba} \\ &\quad + K_{DOP}\cdot DOP + \frac{\partial}{\partial Z}\left(WS_{TSS}\cdot PO4p\right) + \frac{BFPO4d^S}{\Delta Z}\end{aligned} \tag{A.28}$$

In Cerco *et al.* (2000) particulate organic materials produced by algae metabolism and predation are directly incorporated into the sediment bed as sources to the diagenesis model, rather than represented as a flux or source to the water column as was done for dissolved organic material and nutrients. This is a reasonable approach, however it is also reasonable that a portion of this material enter the water column by predation of water column organisms and erosion of particulate material in the benthic algae mat. The formulation in the EFDC model adopts a partitioning approach for flexibility when the stationary algae variable is used to represent macroalgae and floating periphyton mats. By analogy with the dissolve organic variables, the simplified equations for particulate organic material are

$$\frac{\partial POC}{\partial t} = F_{bapw}\left(\frac{H_o}{H}\right) FCPP_{ba} \cdot PR_{ba} \cdot B_{ba} - K_{POC} \cdot POC + \frac{\partial}{\partial Z}\left(WS_P \cdot POC\right) \tag{A.29}$$

$$\begin{aligned}\frac{\partial POP}{\partial t} = F_{bapw}\left(\frac{H_o}{H}\right)\left(FPP_{ba} \cdot BM_{ba} + FPPP_{ba} \cdot PR_{ba}\right) \cdot APC_{ba} \cdot B_{ba} \\ -K_{POP} \cdot POP + \frac{\partial}{\partial Z}\left(WS_{RP} \cdot RPOP\right)\end{aligned} \tag{A.30}$$

$$\begin{aligned}\frac{\partial PON}{\partial t} = F_{bapw}\left(\frac{H_o}{H}\right)\left(FNP_{ba} \cdot BM_{ba} + FNPP_{ba} \cdot PR_{ba}\right) \cdot ANC_{ba} \cdot B_{ba} \\ -K_{PON} \cdot PON + \frac{\partial}{\partial Z}\left(WS_{RP} \cdot PON\right)\end{aligned} \tag{A.31}$$

Where F_{bapw} is the fraction of particular organic material produced by benthic algae entering the water column. Full equations for labile and refractory components readily follow from these forms. The remainder of the particulate organic material produced by benthic algae is incorporated into the sediment organic classes depositional flux terms (A.29-31)

$$J_{POC,i} = \left(\frac{FSCP_i}{H_{2sed}}\right)\left(1 - F_{bapw}\right)\left(\frac{H_o}{H}\right) FCPP_{ba} \cdot PR_{ba} \cdot B_{ba} \tag{A.29}$$

$$J_{POP,i} = \left(\frac{FSPP_i}{H_{2sed}}\right)\left(1 - F_{bapw}\right)\left(\frac{H_o}{H}\right)\left(FPP_{ba} \cdot BM_{ba} + FPPP_{ba} \cdot PR_{ba}\right) \cdot APC_{ba} \cdot B_{ba} \tag{A.30}$$

$$J_{PON,i} = \left(\frac{FSNP_i}{H_{2sed}}\right)\left(1 - F_{bapw}\right)\left(\frac{H_o}{H}\right)\left(FNP_{ba} \cdot BM_{ba} + FNPP_{ba} \cdot PR_{ba}\right) \cdot ANC_{ba} \cdot B_{ba} \tag{A.31}$$

where

$J_{POX,i}$ = depositional flux of particulate organic material X into sediment model reactive class i (g/m^2-s)

$FSXP_i$ = fraction of deposited particulate organic material X assigned to reactive class i

H_{2sed} = depth of sediment diagenesis model layer 2 (meters)

A.3 Kinetic Formulation

The kinetic formulation for stationary algae follows that for suspended transported algae, with a few exceptions, which are described in the following subsections.

A.3.1 Effect of Nutrients on Algal 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 is expressed as:

$$f_1(N) = \left(\frac{NH4_{bm} + NO3_{bm}}{KHN_{bm} + NH4_{bm} + NO3_{bm}}, \frac{PO4d_{bm}}{KHP_{bm} + PO4d_{bm}} \right) \tag{A.32}$$

$NH4_{bm}$ = ammonium nitrogen concentration in benthic micro-algae layer (g N m^{-3})

$NO3_{bm}$ = nitrate nitrogen concentration in benthic micro-algae layer (g N m^{-3})

KHN_{bm} = half-saturation constant for nitrogen uptake (g N m^{-3})

$PO4_{bm}$ = dissolved phosphate phosphorus concentration in benthic micro-algae layer (g P m^{-3})

KHP_{bm} = half-saturation constant for phosphorus uptake (g P m^{-3}).

Since benthic micro-algae experience both the water column nutrient concentration and a benthic boundary layer concentration associated with nutrient flux form the bed, it is appropriate to define the nutrient concentrations in a manner consistent with Cerco *et al.* (2000), by

$$\begin{aligned} NH4_{bm} &= NH4 + FN_{bm} \cdot \left(\frac{\theta}{\Delta Z} \right) \cdot BFNH4 \\ NO3_{bm} &= NO3 + FN_{bm} \cdot \left(\frac{\theta}{\Delta Z} \right) \cdot BFNO3 \\ PO4d_{bm} &= PO4d + FN_{bm} \cdot \left(\frac{\theta}{\Delta Z} \right) \cdot BFPO4d \end{aligned} \tag{A.33}$$

where

ΔZ = thickness for bottom layer (m)

θ = model time step (days)

FN_{bm} = on or off factor having a value of 1 or 0

It is noted that Cerco *et al.* (2000) actually expressed (A.32) and (A.33) in area forms

$$f_1(N) = \left(\frac{\Delta Z \cdot (NH4_{bm} + NO3_{bm})}{\Delta Z \cdot KHN_{bm} + \Delta Z \cdot (NH4_{bm} + NO3_{bm})}, \frac{\Delta Z \cdot PO4d_{bm}}{\Delta Z \cdot KHP_{bm} + \Delta Z \cdot PO4d_{bm}} \right) \tag{A.34}$$

$$\begin{aligned} \Delta Z \cdot NH4_{bm} &= \Delta Z \cdot NH4 + FN_{bm} \cdot \theta \cdot BFNH4 \\ \Delta Z \cdot NO3_{bm} &= \Delta Z \cdot NO3 + FN_{bm} \cdot \theta \cdot BFNO3 \\ \Delta Z \cdot PO4d_{bm} &= \Delta Z \cdot PO4d + FN_{bm} \cdot \theta \cdot BFPO4d \end{aligned} \tag{A.35}$$

with the half-saturation parameters defined in area form as

$\Delta Z * KHN_{bm}$ = half-saturation constant for nitrogen uptake (g N m^{-2})

$\Delta Z * KHP_{bm}$ = half-saturation constant for phosphorus uptake (g P m^{-2})

input to the model.

A.3.2 Effect of Light on Growth

Following the approach used to define the light field in Section 2.4.1.3, the average light intensity in the micro-algae layer is defined by

$$I_{bm} = \frac{I_{bmt}}{Kessbm \cdot H_{bm}} \left(1 - \exp\left(-Kessbm \cdot H_{bm}\right)\right) \qquad (A.36)$$
$$I_{bmt} = I_{ws} \cdot \exp\left(-Kessac \cdot \left(H - H_{RPS}\right) - Kessic \cdot H_{RPS}\right)$$

Since the actual thickness for the micro-algae is not readily defined, the product of the light extinction coefficient in the layer and the layer thickness are required as model input and also viewed as a calibration parameter. Light limitation on growth is then specified by the modified Monod function (Cerco *et al.*, 2000; 2002; 2004; Tillman *et al.*, 2004)

$$f_2\left(I\right) = \frac{I_{bm}}{\sqrt{KHI_{bm}^2 + I_{bm}^2}} \qquad (2.22)$$

where

KHI_{bm} = half saturation for light limitation (watts/meter^2).

A.4 Kinetic Parameters for Benthic Micro Algae

Tables A.1-A.4 summarizes kinetic parameters for benthic micro-algae reported by Cerco *et al.* (2000).

Table A.1 Kinetic Parameters Related to Benthic Micro Algae

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
PM_{bm} (day^{-1})	4	x	
KHN_{bm} (g N m^{-3})	0.025 (g N m^{-2})	x	
KHP_{bm} (g P m^{-3})	0.005 (g P m^{-2})	x	
Ke_{SSBM} (m^{-1} per g m^{-3})	0.25	x	

$CChl_{bm}$ (g C / mg Chl)	75	x	
KHI_{bm} (Watts/m^2)	60 (E/ meter^2-day)	x	
$TMlow_{bm}$, $TMupp_{bm}$ (°C)	25, 25	x	
$KTG1_{bm}$, $KTG2_{bm}$ (°C^{-2})	0.004, 0.012	x	
BMR_{bm} (day^{-1})	0.05	x	
TR_x (°C)	20	x	
KTB_x (°C^{-1})	0.032	x	
PRR_c (day^{-1})	0.005	x	2.28
B_{xP} (g C/m^3)	1		2.28
α_P	1		2.28
APC_x (g P per g C)	0.0167		
ANC_x (g N per g C)	0.175		

Table A.2 Benthic Micro Algae Carbon Interaction Parameters

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
FCRP	0.25		
FCLP	0.50		
FCDP	0.25		
FCD	0.10		

Table A.3 Benthic Micro Algae Phosphorous Interaction Parameters

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
FPRP	0.10		
FPLP	0.15		
FPDP	0.25		
FPIP	0.50		
FPR	0.10		
FPL	0.15		
FPD	0.25		
FPI	0.50		

Table A.4 Benthic Micro Algae Nitrogen Interaction Parameters

Parameter	Florida Bay (Cerco *et al.*, 2000)	Florida Bay (Current Study)	Equation Ref
FNRP	0.20		
FNLP	0.40		
FNDP	0.15		
FNIP	0.35		
FNR	0.20		
FNL	0.40		
FND	0.15		
FNI	0.35		

B. Water Quality Model Performance Measures

B.1 Introduction

This appendix summarizes various error measures useful for evaluating water quality model calibration, validation and predictive performance. Measures considered include time series error measures, dimensionless skill parameters and linear regression.

B.2 Standard Time Series Error Measures

Using O to denote observations and P to denote model predictions at the corresponding locations and times, the means of the observed and predicted variables for N observations at a single or multiple observing stations is given by

$$\bar{O} = \frac{1}{N}\sum_{n=1}^{N} O_n \qquad \text{(B.1)}$$

$$\bar{P} = \frac{1}{N}\sum_{n=1}^{N} P_n \qquad \text{(B.2)}$$

The mean bias error of the model predictions is given by

$$MBE = \bar{O} - \bar{P} \qquad \text{(B.3)}$$

which is often referred to as the mean error and often write as observed minus predicted. Tabulation of the observed and predicted means is an alternate to eliminating confusion regarding the sign convention. The mean bias error is a measure of systematic model over or under prediction. It is noted that the *MBE* can be small in situations where there is large disagreement between predictions and observations. The mean absolute error

$$MAE = \frac{1}{N}\sum_{n=1}^{N} \left| O_n - P_n \right| \qquad \text{(B.4)}$$

and the root mean square error

$$RMSE = \sqrt{\frac{1}{N}\sum_{n=1}^{N} \left(O_n - P_n \right)^2} \qquad \text{(B.5)}$$

provide measures of the average differences between predictions and observations without regard to over or under prediction.

Normalization of the *MBE*, *MAE* and *RMSE* is often useful in facilitating the comparison of model performance between different application sites. The mean bias error may be normalized to define a fractional mean bias error

$$FMBE_{P+O} = \frac{\bar{O} - \bar{P}}{\frac{1}{2}\left(\bar{P} + \bar{O}\right)} \tag{B.6a}$$

$$FMBE_{PO} = \frac{\bar{O} - \bar{P}}{\bar{O}} \tag{B.6b}$$

with the choice of the denominator not being unique in the literature. The choice for normalization of the *MAE* is even less unique.

$$FMAE_{P+O} = \frac{MAE}{\frac{1}{2}\left(\bar{P} + \bar{O}\right)} \tag{B.7a}$$

$$FMAE_{O} = \frac{MAE}{\bar{O}} \tag{B7.b}$$

$$FMAE_{|P+O|} = \frac{MAE}{\frac{1}{2N}\sum_{n=1}^{N}\left|P_n + O_n\right|} \tag{B7.c}$$

$$FMAE_{|O|} = \frac{MAE}{\frac{1}{N}\sum_{n=1}^{N}\left|O_n\right|} \tag{B7.d}$$

Choices for normalization of the *RMSE* include

$$FRMSE_{PO} = \frac{RMSE}{\frac{1}{N}\sum_{n=1}^{N} P_n O_n} \tag{B.8a}$$

$$FRMSE_{O} = \frac{RMSE}{\frac{1}{N}\sum_{n=1}^{N} O_n^2} \tag{B8.b}$$

Given the various alternatives for defining fractional errors, care should be made in assuring that fractional or normalized errors are consistently defined in making comparisons between different model application sites.

The comparison of observed and predicted standard deviations is also useful in assessing the model has the same level of variability as the observations. Deviations form the means are defined by

$$O_n' = O_n - \bar{O} \tag{B.9}$$

$$P_n' = P_n - \bar{P} \tag{B.10}$$

With the standard deviations of the observations and predictions given by

$$SDO = \sqrt{\frac{1}{N-1}\sum_{n=1}^{N}\left(O_n'\right)^2} \tag{B.11}$$

$$SDP = \sqrt{\frac{1}{N-1}\sum_{n=1}^{N}\left(P_n'\right)^2} \tag{B.12}$$

The standard deviation of the differences is defined by

$$SDD = \sqrt{\frac{1}{N-1}\sum_{n=1}^{N}\left(O_n' - P_n'\right)^2} \tag{B.13}$$

Consideration of the difference between standard deviations along with the difference between means allows evaluation of the model's predictive ability in the probabilistic sense without regard for absolute predictive ability.

B.3 Dimensionless Skill Measures

As alternatives or complements to normalized or fractional error measures, a number of skill parameters have been utilized for the evaluation of hydrodynamic and ecological models. The index of agreement

$$IA = 1 - \frac{\sum_{n=1}^{N}\left(O_n - P_n\right)^2}{\sum_{n=1}^{N}\left(\left|P_n - \bar{O}\right| + \left|O_n - \bar{O}\right|\right)^2} \tag{B.14}$$

was proposed by Wilmott (1980; 1982; 1985) and been extensively used to evaluate salinity, temperature and current prediction performance for hydrodynamic models (Blumberg and Goodrich, 1990). It is noted that *IA* is essentially unity minus an alternate normalization of the *RMSE* defined by

$$RMSE_{IA} = \frac{\sum_{n=1}^{N}\left(O_n - P_n\right)^2}{\sum_{n=1}^{N}\left(\left|P_n - \bar{O}\right| + \left|O_n - \bar{O}\right|\right)^2} \tag{B.16}$$

The index of agreement, IA, falls between 0 and 1, with a value one indicating complete agreement.

The reliability index, defined by

$$RI = \frac{1 + \sqrt{\sum_{n=1}^{N} \left(\frac{O_n - P_n}{O_n + P_n} \right)^2}}{1 - \sqrt{\sum_{n=1}^{N} \left(\frac{O_n - P_n}{O_n + P_n} \right)^2}} \tag{B.16}$$

has also been used to evaluate the performance of ecological and hydrodynamic models (Leggett and Williams, 1981; Bedford and Lee, 1994). The *RI* has a value of one for perfect agreement and increases as the reliability of the model prediction decreases.

B.4 Linear Regression and Associated Measures

Linear regression provides another means of evaluating model predictive skill and was first proposed by Thomann (1982) for use with water quality models. Two forms of the regression analysis may the used. The first form is based on a least squares fitting of the equation

$$\hat{P}_n = a + bO_n \tag{B.17}$$

where the intercept, *a*, and slope, *b*, are defined by

$$a = \overline{P} - b\overline{O} \tag{B.18}$$

$$b = \frac{\sum_{n=1}^{N} (P'_n O'_n)}{\sum_{n=1}^{N} (O'_n O'_n)} \tag{B.19}$$

The correlation coefficient is given by

$$r = \frac{\sum_{n=1}^{N} P'_n O'_n}{\sqrt{\sum_{n=1}^{N} P'_n P'_n} \sqrt{\sum_{n=1}^{N} O'_n O'_n}} \tag{B.20}$$

that has a range between -1 and 1. The coefficient of determination is defined as the square of the correlation coefficient. For perfect agreement between the predictions and observations, the intercept and slope are one. The correlation coefficient should be judged with care in that a positive correlation approaching one can be achieved when values of the intercept and slope are quite different from one.

Using the results of the regression analysis, the systematic and unsystematic root mean square errors can be defined by

$$RMSES_{ab} = \sqrt{\frac{1}{N}\sum_{n=1}^{N}\left(\hat{P}_n - O_n\right)^2} \tag{B.21}$$

$$RMSEU_{ab} = \sqrt{\frac{1}{N}\sum_{n=1}^{N}\left(\hat{P}_n - P_n\right)^2} \tag{B.22}$$

The square of the *RMSE* (B.5) can be written as

$$RMSE^2 = \frac{1}{N}\sum_{n=1}^{N}\left(\hat{P}_n - O_n\right)^2 + \frac{1}{N}\sum_{n=1}^{N}\left(\hat{P}_n - P_n\right)^2 - \frac{2}{N}\sum_{n=1}^{N}\left(\hat{P}_n - O_n\right)\left(\hat{P}_n - P_n\right) \tag{B.23}$$

Since the last term in (B.22) can be shown to be zero, the systematic and unsystematic components of the root mean square error combine in a vector manner to form the *RMSE.*

$$RMSE^2 = RMSES_{ab}^2 + RMSEU_{ab}^2 \tag{B.24}$$

The *RMSES* describes the proportion of the error attributable to systematic errors or those contained in the model while the *RMSEU* are considered to be random or noise like. The model is defined as including the model code, parameters, boundary conditions and forcing functions. As the model's predictive ability increased, the *RMSES* should approach zero (Wilmott, 1982) and also provides insight as to where and why differences between predictions and observations occur.

An alternate form of the regression analysis is based on least squares fitting of the linear relationship

$$\hat{O}_n = \alpha + \beta P_n \tag{B.25}$$

where the intercept, α, and slope, β, are defined by

$$\alpha = \bar{O} - \beta\bar{P} \tag{B.26}$$

$$\beta = \frac{\sum_{n=1}^{N}\left(P_n' O_n'\right)}{\sum_{n=1}^{N}\left(P_n' P_n'\right)} \tag{B.27}$$

with the correlation coefficient still defined by (B.19). The square of the *RMSE* can then be written as

$$RMSE^2 = \frac{1}{N}\sum_{n=1}^{N}\left(\hat{O}_n - P_n\right)^2 + \frac{1}{N}\sum_{n=1}^{N}\left(\hat{O}_n - O_n\right)^2 - \frac{2}{N}\sum_{n=1}^{N}\left(\hat{O}_n - P_n\right)\left(\hat{O}_n - O_n\right) \tag{B.28}$$

The last term is zero and (B.27) becomes

$$RMSE^2 = \frac{1}{N}\sum_{n=1}^{N}\left(\hat{O}_n - P_n\right)^2 + \frac{1}{N}\sum_{n=1}^{N}\left(\hat{O}_n - O_n\right)^2 \tag{B.29}$$

which provides alternate definitions of the systematic and unsystematic errors

$$RMSE^2 = RMSES_{\alpha\beta}^2 + RMSEU_{\alpha\beta}^2 \tag{B.30}$$

$$RMSES_{\alpha\beta} = \sqrt{\frac{1}{N}\sum_{n=1}^{N}\left(\hat{O}_n - P_n\right)^2} \tag{B.31}$$

$$RMSEU_{\alpha\beta} = \sqrt{\frac{1}{N}\sum_{n=1}^{N}\left(\hat{O}_n - O_n\right)^2} \tag{B.32}$$

The choice now arises as to which form, (B.17) or (B.25) is most appropriate for evaluating model performance. Each form yields the same correlation coefficient, coefficient of determinism and *RMSE*. Figure B.1 shows graphical results using equations (B.17) in black and (B.25) in red. Corresponding values of the intercept, slope, systematic and unsystematic root mean square errors are shown in Table B.1. The two alternate forms are shown to give large differences in the intercepts and slopes. An *ad hoc* approach to eliminate the bias is to average the intercepts and slopes with the correlation coefficient and *RMSE* remaining unaffected. For the systematic and unsystematic components of the *RMSE*, equations (B.24) and (B.30) are averaged to give

$$RMSE^2 = \frac{1}{2}\left(RMSES_{ab}^2 + RMSES_{\alpha\beta}^2\right) + \frac{1}{2}\left(RMSEU_{ab}^2 + RMSEU_{\alpha\beta}^2\right) \tag{B.33}$$

with the *ad hoc RMSES* and *RMSEU* given by

$$RMSES_{adhoc} = \sqrt{\frac{1}{2}\left(RMSES_{ab}^2 + RMSES_{\alpha\beta}^2\right)} \tag{B.34}$$

$$RMSEU_{adhoc} = \sqrt{\frac{1}{2}\left(RMSEU_{ab}^2 + RMSEU_{\alpha\beta}^2\right)} \tag{B.35}$$

are used to define the *ad hoc* column component errors. Another alternative is to commingle the data and create a 2N value data set, with the first N values being predicted and observed and the second N values being observed and predicted, which can be used with either formulation. Figure B.1 shows the fit of the co-mingled data, represented by a blue line which visually nearly bisects the black and red lines. Table B.1 shows that the intercept and slope of the commingled fit are very closed to the averaged intercept and slope and that commingling retains the individual and averaged *RMSE*. The commingling does not preserve the correlation coefficient, but in this case does give a value extremely close. Similarly, the commingled systematic and unsystematic components of the *RMSE* are numerically close to the averages defined by (B.34) and (B.35). The concluding points to be made are that when comparing different model applications, consistency is of primary importance and when given the opportunity both forms of the linear regression should be considered with their results averaged or a commingled analysis performed.

B.5 Error Measures Report in Selected Water Quality Model Applications

Most recent applications of the CE-QUAL-ICM and EFDC water quality models report *MBE, MAE, RMSE* and *FMBE* or *FMAE.* The two fractional errors are always reported using normalization by the mean of the observations, equations, (B.6b) and (B.7b) for *FMBE* and *FMAE*, respectively. Tables B2 through B12 summarize the range of fractional mean absolute errors, *FMAE*, reported in a number of CE-QUAL-ICM and EFDC water quality modeling studies, for algae carbon, algae chlorophyll a, dissolved organic carbon, total organic carbon, dissolved inorganic nitrogen, ammonium, nitrate + nitrite, total nitrogen, dissolved inorganic phosphorous, total phosphorous, and dissolved oxygen. The single exception in these tables is that that *FMBE* instead of *FMAE* are listed for Lake Washington (Cerco *et al.*, 2004) since they were published instead of the *FMAE* errors. The tables present two columns of results. The aggregate column indicates that the summation used to determine the error is over multiple times and multiple stations and when a range of errors is listed, the values correspond to the smallest and largest reported form multiple aggregation regions. The station column is for error analyses where the summation is over a temporal observation times a specific stations with the range corresponding to the smallest and largest error from the set of reported stations. Minor exceptions to these conventions are described in table footnotes.

Table B.1 Comparison of Alternate Forms of Linear Regression Analysis

Measure	Eq (17)	Eq (25)	*Ad Hoc* Average	Co-mingled
Intercept	9.559	2.872	6.216	6.621
Slope	0.707	0.913	0.810	0.797
Correl. Coef.	0.803	0.803	0.803	0.797
RMSE	3.235	3.235	3.235	3.235
RMSES	1.580	0.414	1.155	1.032
RMSEU	2.823	3.208	3.022	3.066
*RMSE***2	10.464	10.464	10.464	10.464
*RMSE***2	2.496	0.171	1.334	1.065
*RMSE***2	7.968	10.292	9.130	9.400

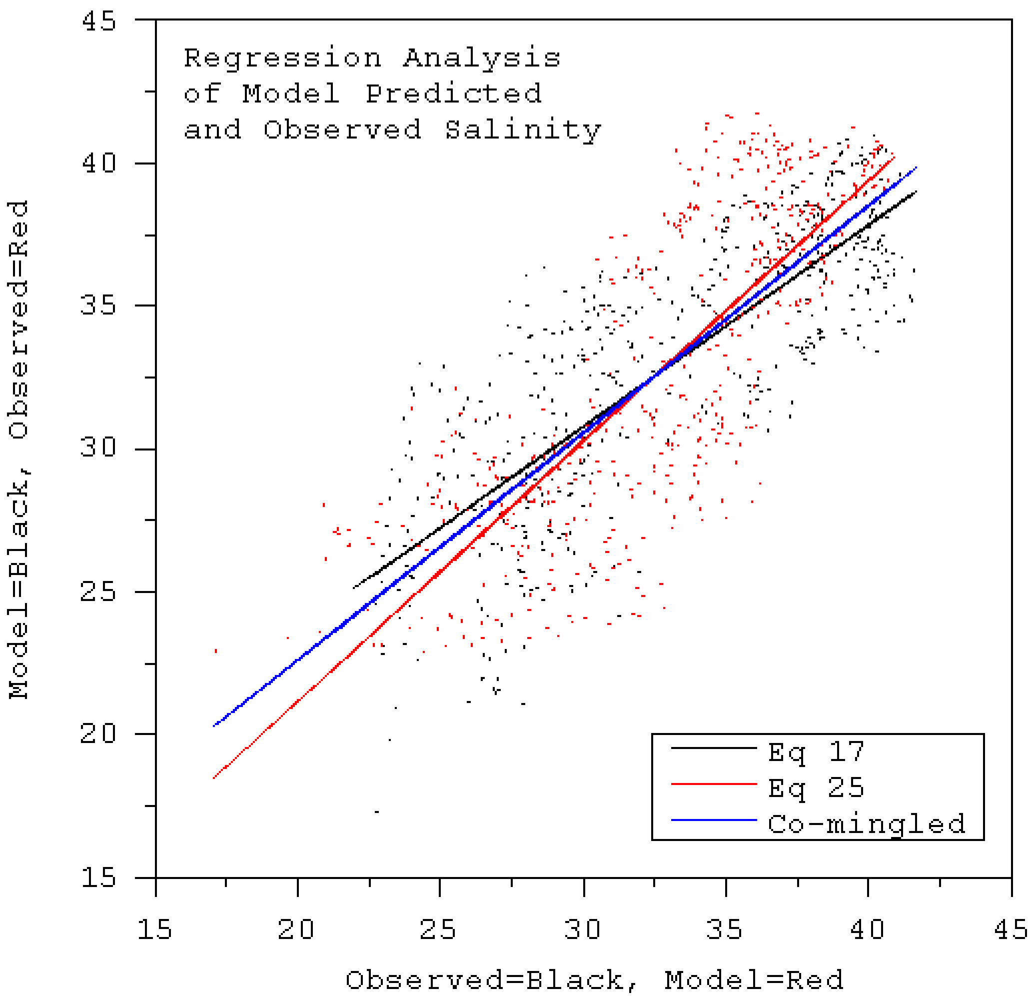

Figure B.1 Example of Linear Regression Analysis. Black points are model predicted (vertical axis) versus observed with black line being regression fix of predicted. Red points are observed (vertical axis) versus predicted with red line being regression fix of observed. Blue line is regression fix of co-mingled data.

Table B.2 Reported Fractional Mean Absolute Errors for Algae Carbon

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		
Chesapeake Bay	Cerco and Cole, 1994		
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000		
Florida Bay Tt	Tetra Tech, in prep.		
Lake Washington, WA	Cerco *et al.*, 2004		
Peconic Bays, NY	Tetra Tech, 1999		
San Juan Estuary, PR	Bunch *et al.*, 2000		
St. Johns River, FL	Tillman *et al.*, 2004	0.68-0.89	0.42-3.40

Table B.3 Reported Fractional Mean Absolute Errors for Total Algae Chla

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		0.76-1.37
Chesapeake Bay	Cerco and Cole, 1994	0.41	
Chesapeake Bay, TR	Cerco *et al.*, 2002	0.58-0.79	
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000	0.72	
Florida Bay Tt	Tetra Tech, in prep.	1.58	0.57-16.72
Lake Washington, WA	Cerco *et al.*, 2004		0.05-0.34
Peconic Bays, NY	Tetra Tech, 1999	0.37	
San Juan Estuary, PR	Bunch *et al.*, 2000	0.61	
St. Johns River, FL	Tillman *et al.*, 2004	0.46-0.52	0.37-1.10

Table B.4 Reported Fractional Mean Absolute Errors for Dissolved Organic Carbon

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		
Chesapeake Bay	Cerco and Cole, 1994		
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000		
Florida Bay Tt	Tetra Tech, in prep.		
Lake Washington, WA	Cerco *et al.*, 2004		
Peconic Bays, NY	Tetra Tech, 1999	0.20	
San Juan Estuary, PR	Bunch *et al.*, 2000		
St. Johns River, FL	Tillman *et al.*, 2004	0.18	0.09-0.45

Table B.5 Reported Fractional Mean Absolute Errors for Total Organic Carbon

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		
Chesapeake Bay	Cerco and Cole, 1994	0.49[1]	
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000	0.39	
Florida Bay Tt	Tetra Tech, in prep.	0.91	0.18-5.91
Lake Washington, WA	Cerco *et al.*, 2004		
Peconic Bays, NY	Tetra Tech, 1999	0.21	
San Juan Estuary, PR	Bunch *et al.*, 2000		
St. Johns River, FL	Tillman *et al.*, 2004	0.18-0.19	0.10-0.41

[1] Particulate organic carbon reported

Table B.6 Reported Fractional Mean Absolute Errors for Dissolved Inorganic Nitrogen

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		
Chesapeake Bay	Cerco and Cole, 1994		
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000		
Florida Bay Tt	Tetra Tech, in prep.		
Lake Washington, WA	Cerco *et al.*, 2004		
Peconic Bays, NY	Tetra Tech, 1999		
San Juan Estuary, PR	Bunch *et al.*, 2000		
St. Johns River, FL	Tillman *et al.*, 2004	0.49-0.92	0.50-0.87

Table B.7 Reported Fractional Mean Absolute Errors for Ammonium

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		0.25-3.04
Chesapeake Bay	Cerco and Cole, 1994	0.51	
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000	0.68	
Florida Bay Tt	Tetra Tech, in prep.	1.16	0.60-8.31
Lake Washington, WA	Cerco *et al.*, 2004		0.00-0.27
Peconic Bays, NY	Tetra Tech, 1999	0.75	
San Juan Estuary, PR	Bunch *et al.*, 2000		
St. Johns River, FL	Tillman *et al.*, 2004	1.00-2.36	1.22-2.00

Table B.8 Reported Fractional Mean Absolute Errors for Nitrate and Nitrite

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		0.45-0.61 (avg)[1]
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		0.36-2.63
Chesapeake Bay	Cerco and Cole, 1994	0.39	
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000	0.85	
Florida Bay Tt	Tetra Tech, in prep.	1.36	0.57-4.04
Lake Washington, WA	Cerco *et al.*, 2004		0.13-0.21
Peconic Bays, NY	Tetra Tech, 1999	0.65	
San Juan Estuary, PR	Bunch *et al.*, 2000	2.08	
St. Johns River, FL	Tillman *et al.*, 2004	0.52-1.09	0.57-0.75

[1] For the Cape Fear River, stations averages are presented and the range corresponds to separate calibration and validation analyses. This convention is used for subsequent Caper Fear River results.

Table B.9 Reported Fractional Mean Absolute Errors for Other Total Organic Nitrogen

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		0.26-0.31 (avg)
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		0.06-0.32
Chesapeake Bay	Cerco and Cole, 1994		
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000		
Florida Bay Tt	Tetra Tech, in prep.	1.08	0.40-5.81
Lake Washington, WA	Cerco *et al.*, 2004		
Peconic Bays, NY	Tetra Tech, 1999	0.33[1]	
San Juan Estuary, PR	Bunch *et al.*, 2000		
St. Johns River, FL	Tillman *et al.*, 2004		

[1] Report value is for dissolved organic nitrogen

Table B.10 Reported Fractional Mean Absolute Errors for Total Nitrogen

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		0.18-0.23 (avg)
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		0.07-0.59
Chesapeake Bay	Cerco and Cole, 1994	0.19	
Chesapeake Bay, TR	Cerco *et al.*, 2002	0.21-0.46	
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000	0.39	
Florida Bay Tt	Tetra Tech, in prep.	0.98	0.33-5.56
Lake Washington, WA	Cerco *et al.*, 2004		0.06-0.15
Peconic Bays, NY	Tetra Tech, 1999	0.24	
San Juan Estuary, PR	Bunch *et al.*, 2000	0.70	
St. Johns River, FL	Tillman *et al.*, 2004	0.28-0.30	0.18-0.38

Table B.11 Reported Fractional Mean Absolute Errors for Dissolved Inorganic Phosphorous

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		
Chesapeake Bay	Cerco and Cole, 1994	0.36	
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000	2.12	
Florida Bay Tt	Tetra Tech, in prep.		
Lake Washington, WA	Cerco *et al.*, 2004		0.20-0.47
Peconic Bays, NY	Tetra Tech, 1999	0.66	
San Juan Estuary, PR	Bunch *et al.*, 2000	0.82	
St. Johns River, FL	Tillman *et al.*, 2004	0.45-0.47	0.31-1.03

Table B.12 Reported Fractional Mean Absolute Errors for Total Inorganic Phosphorous

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		0.48-1.64
Chesapeake Bay	Cerco and Cole, 1994		
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000		
Florida Bay Tt	Tetra Tech, in prep.	1.06	0.71-2.57
Lake Washington, WA	Cerco *et al.*, 2004		
Peconic Bays, NY	Tetra Tech, 1999		
San Juan Estuary, PR	Bunch *et al.*, 2000		
St. Johns River, FL	Tillman *et al.*, 2004		

Table B.13 Reported Fractional Mean Absolute Errors for Total Organic Phosphorous

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		0.12-0.56
Chesapeake Bay	Cerco and Cole, 1994		
Chesapeake Bay, TR	Cerco *et al.*, 2002		
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000		
Florida Bay Tt	Tetra Tech, in prep.		
Lake Washington, WA	Cerco *et al.*, 2004		
Peconic Bays, NY	Tetra Tech, 1999	0.48[1]	
San Juan Estuary, PR	Bunch *et al.*, 2000		
St. Johns River, FL	Tillman *et al.*, 2004		

[1] Report value is for dissolved organic phosphorous

Table B.14 Reported Fractional Mean Absolute Errors for Total Phosphorous

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		
Charleston Harbor, SC	Tetra Tech, 2006c		
Charles River, MA	Tetra Tech, 2006b		0.12-0.54
Chesapeake Bay	Cerco and Cole, 1994	0.39	
Chesapeake Bay, TR	Cerco *et al.*, 2002	0.39-0.68	
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000	0.31	
Florida Bay Tt	Tetra Tech, in prep.	1.17	0.48-3.04
Lake Washington, WA	Cerco *et al.*, 2004		0.04-0.40
Peconic Bays, NY	Tetra Tech, 1999	0.30	
San Juan Estuary, PR	Bunch *et al.*, 2000	0.58	
St. Johns River, FL	Tillman *et al.*, 2004	0.26-0.28	0.25-0.31

Table B.15 Reported Fractional Mean Absolute Errors for Dissolved Oxygen

Application Site	Reference	Aggregated Range	Station Range
Cape Fear River, NC	Tetra Tech, 2001		0.12-0.15 (avg)
Charleston Harbor, SC	Tetra Tech, 2006c		0.08-0.21
Charles River, MA	Tetra Tech, 2006b		0.07-0.21
Chesapeake Bay	Cerco and Cole, 1994	0.15	
Chesapeake Bay, TR	Cerco *et al.*, 2002	0.26-0.32	
Christiana River, DE	Tetra Tech, 2000a		
Florida Bay ERDC	Cerco *et al.*, 2000	0.07	
Florida Bay Tt	Tetra Tech, in prep.	0.11	0.07-0.18
Lake Washington, WA	Cerco *et al.*, 2004		0.04-0.12
Peconic Bays, NY	Tetra Tech, 1999	0.06	
San Juan Estuary, PR	Bunch *et al.*, 2000	0.40	
St. Johns River, FL	Tillman *et al.*, 2004	0.09	0.06-0.13