Three-Dimensional Eutrophication Model of the Lower St. Johns River, Florida

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ABSTRACT: The CE-QUAL-ICM three-dimensional eutrophication model was applied to the lower, estuarine, portion of the St. Johns River, Florida. Transport processes were obtained from the Environmental Fluid Dynamics Code. Model application period was December 1996 through November 1998. The model activated 28 state variables in the water column including physical variables, three algal groups, multiple forms of carbon, nitrogen, phosphorus and silica, and dissolved oxygen. Several features were added to the model for this application. These included representation of the internal algal phosphorus pool, distinction of labile and refractory organic matter, and representation of nitrogen fixation. The water column was coupled to a predictive sediment diagenesis model that computed sediment-water fluxes of dissolved oxygen, chemical oxygen demand, ammonium, nitrate, phosphate, and silica, based on computed inputs of particulate organic matter. Model results were compared to an extensive suite of observations in the water column and benthic sediments.

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

<table>
<thead>
<tr>
<th>Multiply</th>
<th>By</th>
<th>To Obtain</th>
</tr>
</thead>
<tbody>
<tr>
<td>miles (U.S. statute)</td>
<td>1.609347</td>
<td>kilometers</td>
</tr>
<tr>
<td>square miles</td>
<td>2,589,998</td>
<td>square meters</td>
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Preface

This study was conducted as part of a feasibility cost share agreement between the U.S. Army Engineer District, Jacksonville, and the St. Johns River Water Management District related to protecting and restoring the Lower St. Johns River. The project was assigned to the U.S. Army Engineer Research and Development Center (ERDC) under the purview of the Environmental Laboratory (EL).

This report was prepared by the Water Quality and Contaminant Modeling Branch, Environmental Processes and Effects Division, EL. The study was supervised by Barry Bunch, Chief, Water Quality and Contaminant Modeling Branch, Environmental Processes and Effects Division, EL. General supervision was provided by Dr. Edwin A. Theriot, Director, EL. Technical reviewers were Toni Toney, Carlos Ruiz, and Billy Johnson.

COL James R. Rowan, EN, was Commander and Executive Director of ERDC. Dr. James R. Houston was Director.
1 Introduction

Background

The U.S. Army Engineer District, Jacksonville (CESAJ)\(^1\) and the St. Johns River Water Management District (SJRWMD) have a feasibility cost share agreement related to protecting and restoring the Lower St. Johns River (LSJR). The agreement includes a need to identify maximum acceptable levels of point and nonpoint source pollutant loadings. As designated in the 1987 Surface Water Improvement and Management (SWIM) Act, the Lower St. Johns River basin is in need of restoration and special protection. The Florida Department of Environmental Protection (FDEP) and the U.S. Environmental Protection Agency (EPA) have listed it as an impaired waterbody, which requires the establishment of a Total Maximum Daily Load (TMDL) (303d listed for nutrients, total suspended solids, turbidity, coliform bacteria, and other causes).

As part of Phase 3, Amendment 4 in the cost share agreement, written specifications for an LSJR water quality model have been determined and described. The U.S. Army Engineering Research and Development Center, Environmental Laboratory (EL) was requested by CESAJ to support development of a three-dimensional (3D) hydrodynamic and water quality model for the LSJR system.

In addition to determining acceptable levels of pollutant loadings and assessing the effects of these loadings on the LSJR, the model will be used as a means to separate natural variations from human impacts. Other potential model uses are:

- \(a.\) Gaining a basic understanding of the physical and some of the chemical and biological dynamics of the river.
- \(b.\) Evaluating the sensitivity of the river to changes in tributary inflows and pollutant loadings.
- \(c.\) Ranking areas for load reductions in accordance with management priorities.
- \(d.\) Developing recommendations for practical and feasible river restoration actions and plans for management.

\(^1\) For convenience unusual abbreviations used in this report are listed and defined in Appendix A, Acronyms.
e. Developing recommendations to the Florida Department of Environmental Protection in support of Total Maximum Daily Loads and other pollutant loading limitations.

To meet the requirements of the CESAJ/SJRWMD scope-of-work (SOW), the modeling system had to contain coupled, 3D hydrodynamic and water quality models that were capable of running multi-year simulations on workstations. The hydrodynamic model (HM) had to include salinity transport and baroclinic coupling to momentum. The SOW also requested that the 3D finite difference models use a boundary-fitted grid, and the grid for the water quality model (WQM) must be the same as for the HM. The modules in the WQM had to include kinetics for: (1) water column eutrophication processes including multiple phytoplankton groups; (2) littoral processes involving growth of submerged aquatic vegetation (SAV) and organic matter flux; and (3) sediment dynamics including deposition and resuspension, flocculation of organic matter, sediment diagenesis, and dissolved oxygen (DO) and nutrient fluxes between bottom sediments and the water column.

St. Johns River

The SJRWMD manages the LSJR basin, which represents approximately 22 percent of the SJRWMD managed area. The LSJR flows from the confluence of Florida’s Ocklawaha River to the north and east toward Jacksonville, eventually flowing into the Atlantic Ocean (Figure 1-1). Due to the large tidal range near its mouth, the St. Johns has never been precisely flow-gauged, though mean annual discharge is believed to be between 170 to 225 m³/s (Morris 1995). In periods of low water, tides may cause a reverse flow as far south as Lake Monroe, 161 miles upstream from the river’s mouth.

The St. Johns River is the longest northern flowing river in the United States and the longest river in Florida at 300 miles in length. The LSJR represents approximately one-third of the total length of the St. Johns River (100 miles) and less than one-third of the total watershed area of 9,562 sq miles. The water surface area of the LSJR is 34,817 ha (85,967 acres) including tributary mouths below tide head (Hendrickson and Konwinski 1998). Hendrickson and Konwinski (1998) segment the LSJR into three riverine salinity and limnologic zones: a fresh tidal lacustrine zone extending from Palatka to Orange Park; a predominantly oligohaline, lacustrine zone extending from Orange Park north toward Fuller Warren Bridge (Interstate 95) in Jacksonville; and a mesohaline, riverine zone extending from Jacksonville to the Atlantic Ocean.

The LSJR basin is between the subtropical climate of southern Florida and the humid continental climate of the southeastern United States. Its climate is classified as humid subtropical, having an average summer maximum daily temperature of 32.2 °C (90 °F). During the winter season, below freezing temperatures occur 10-15 times per year. The average annual rainfall in the LSJR basin is approximately 132 cm (52 in.) with most of the precipitation occurring June through September from convective activity.
Land use patterns within the basin vary from the southern portion to the northern portion. The southern portion is predominantly rural with land uses ranging from forestry to row crop agriculture. In the northern portion of the basin, the heavily urbanized cities of Jacksonville, Orange Park, and Middleburg dominate land uses. Approximately three quarters (64 to 82 percent) of the heavily urbanized areas of the LSJR drain to the oligohaline and mesohaline zones of the river, compared with the 62 to 98 percent of agricultural land draining to the fresh tidal lacustrine zone (Hendrickson and Konwinski 1998).

Water quality of the LSJR varies depending on location (e.g., poor in the urbanized areas to good in the sparsely populated areas). Water quality problems identified on the LSJR include low DO, excessive nutrients that induce algal blooms (confined to the area from Palatka to 15 miles north at Tocoi Creek and from Doctor’s Inlet north to the Fuller Warren Bridge), and elevated bacterial populations. The primary culprits causing degradation are point and nonpoint sources such as industrial dischargers, municipal water treatment plants, stormwater runoff from agriculture and dairy farms, and septic tanks (SAD and SJRWMD 1994).

Study Objective

The objective of this 2-year study was the development of a 3D calibrated water quality model, with the capabilities discussed above coupled to the SJRWMD hydrodynamic model of the LSJR. For the 2-year simulation period, the SJRWMD selected December 1996 through November 1998 because more observed data had been collected during this period for the water quality constituents of interest.

Reference


Figure 1-1. Lower St. Johns River Basin
2 Data Bases

Observed Data

Observed water quality data are required by Corps of Engineers Integrated Compartment Water Quality Model (CE-QUAL-ICM) to set initial and boundary conditions for each constituent modeled in a simulation. Observed data (preferably water column profile data) are also required to evaluate model performance. The SJRWMD provided all observed data for this study. Much of the data were extracted from STOrage and RETrieval (STORET) into a Microsoft® Excel spreadsheet. This file contained data for 50 water quality parameters at 303 stations on the St. Johns River and its tributaries. Although data span many years (1959-1999), not every water quality constituent was measured each year. Of the 50 water quality parameters, only data for constituents being modeled (Table 2-1) were extracted from the spreadsheet and plotted to examine data trends and consistency. A Statistical Analysis System (SAS) program was run on the data to calculate mean, maximum, and minimum values for each year. Most observed data were measured in the surface layer, although a few stations had observations at middle and bottom depths.

<table>
<thead>
<tr>
<th>Table 2-1</th>
<th>CE-QUAL-ICM Water Quality Model State Variables</th>
</tr>
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<tbody>
<tr>
<td>Temperature</td>
<td>Salinity</td>
</tr>
<tr>
<td>Fixed Solids</td>
<td>Cyanobacteria</td>
</tr>
<tr>
<td>Diatoms</td>
<td>Other Phytoplankton</td>
</tr>
<tr>
<td>Zooplankton Group 1</td>
<td>Zooplankton Group 2</td>
</tr>
<tr>
<td>Labile Dissolved Organic Carbon</td>
<td>Refractory Dissolved Organic Carbon</td>
</tr>
<tr>
<td>Labile Particulate Organic Carbon</td>
<td>Refractory Particulate Organic Carbon</td>
</tr>
<tr>
<td>Ammonium</td>
<td>Nitrate + Nitrite Nitrogen</td>
</tr>
<tr>
<td>Refractory Dissolved Organic Nitrogen</td>
<td>Labile Dissolved Organic Nitrogen</td>
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<tr>
<td>Refractory Particulate Organic Nitrogen</td>
<td>Labile Particulate Organic Nitrogen</td>
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<tr>
<td>Labile Dissolved Organic Phosphorus</td>
<td>Total Phosphate</td>
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<td>Labile Particulate Organic Phosphorus</td>
<td>Refractory Dissolved Organic Phosphorus</td>
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<td>Internal Phosphorus, Algal Group 2</td>
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<td>Chemical Oxygen Demand</td>
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<td>Dissolved Silica</td>
<td>Internal Phosphorus, Algal Group 3</td>
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<tr>
<td>Particulate Biogenic Silica</td>
<td>Dissolved Oxygen</td>
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The SJRWMD identified two consecutive simulation periods to be modeled during this study, 1 December 1996 to 30 November 1997 and 1 December 1997 to 30 November 1998. Table 2-2 was generated from data extracted from the Excel spreadsheet provided by SJRWMD and contains a number of observations for each modeled water quality constituent for each water level of the main stem stations (Figure 1-1) used for comparison during calibration.

Table 2-2
St. Johns River Water Quality Main Stem Stations (Hendrickson 1999)

<table>
<thead>
<tr>
<th>Station ID</th>
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<th>NH4T</th>
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Note:

- NH4D: Ammonium-Dissolved, MG/L as N
- NH4T: Ammonium-Total, MG/L as N
- NOXT: Nitrate&Nitrite-Total, MG/L as N
- NOXD: Nitrate&Nitrite-Diss, MG/L as N
- TPT: Total Phosphorus-T, MG/L as P
- TPD: Total Phosphorus-D, MG/L as P
- PO4D: Ortho-Phosphate-D, MG/L as P
- TOC: Total Organic Carbon, MG/L as C
- DOC: Dissolved Organic Carbon, MG/L as C
- CL: Chloride, MG/L
- CHLA: Chlorophyll-A, MG/M3
- CHLAC: Chlorophyll-Corrected, MG/M3
In addition to the Excel spreadsheet, the SJRWMD provided files containing continuous monitored data by the U.S. Geological Survey (USGS) for the following constituents:

- Temperature,
- DO,
- Salinity,
- Barometric pressure,
- Air temperature,
- Relative humidity,
- Net radiation,
- Photo-active radiation,
- Rainfall,
- Wind speed/wind direction.

Table 2-3 lists the station names and locations, water levels and time periods of salinity, DO, and temperature samples.

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Note: S = surface; M = middle; B = bottom.

Light Attenuation Data

SJRWMID provided light attenuation observations for a number of stations on the LSJR (Table 2-4). A designation of N/A for a segment number in Table 2-4 indicates the station was outside the study grid. Comparisons of light attenuation values predicted by CE-QUAL-ICM were made to data collected at stations designated on Figure 1-1. Data collection at most of the stations used in comparisons began mid-1997 or later and continued into late 2000. Some stations did not have any data collected during the simulation period.
### Table 2-4
Light Attenuation Stations on the St. Johns River

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<td>N/A</td>
</tr>
<tr>
<td>SJRM70C</td>
<td>06/14/2000 – 08/23/2000</td>
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<td>SAVDRLKO</td>
<td>11/18/1999 – 10/24/2000</td>
<td>5</td>
</tr>
</tbody>
</table>
Meteorological Data

Table 2-5 contains station name and locations where meteorological data were supplied by the SJRWMD. Specific meteorological data (e.g., dew point temperature and cloud cover) not provided by the SJRWMD were requested from the Air Force Combat Climatology Center in order to calculate heat exchange coefficients and equilibrium temperatures required by CE-QUAL-ICM. Data were requested for Jacksonville and Gainesville, FL. A comparison of the parameters at these two stations showed minimal difference; thus information at the Jacksonville Airport was used in the calculations.

<table>
<thead>
<tr>
<th>Station Name</th>
<th>Dates</th>
<th>River Miles</th>
<th>RF</th>
<th>AT</th>
<th>RH</th>
<th>BP</th>
<th>WD</th>
<th>WS</th>
<th>NR</th>
<th>PAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dames Point</td>
<td>10/4/95-9/30/98</td>
<td>10</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Acosta Bridge</td>
<td>10/4/95-9/30/98</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shands Bridge</td>
<td>10/4/95-9/30/98</td>
<td>50</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Buckman Bridge</td>
<td>10/4/95-9/30/98</td>
<td>56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dancy Point</td>
<td>10/4/95-9/30/98</td>
<td>70</td>
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<td></td>
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<td>Buffalo Bluff</td>
<td>10/4/95-9/30/98</td>
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<td></td>
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</tbody>
</table>

Note: X indicates availability at station; RF = rainfall; AT = air temperature; RH = relative humidity; BP = barometric pressure; WD = wind direction; WS = wind speed; PAR = photo active radiation.
3 Hydrodynamic Model

Introduction

The foundation of the CE-QUAL-ICM model is the solution to the 3D mass-conservation equation for a control volume. The CE-QUAL-ICM control volumes correspond to cells on the model grid. CE-QUAL-ICM solves, for each volume and for each state variable, the equation:

$$\frac{\partial V_j C_j}{\partial t} = \sum_{k=1}^{n} Q_k C_k + \sum_{k=1}^{n} A_k D_k \frac{\partial C}{\partial x_k} + \sum S_j$$  \hspace{1cm} (3-1)

in which:

- $V_j$ = volume of $j^{th}$ control volume (m$^3$)
- $C_j$ = concentration in $j^{th}$ control volume (g m$^{-3}$)
- $t$, $x$ = temporal and spatial coordinates
- $n$ = number of flow faces attached to $j^{th}$ control volume
- $Q_k$ = volumetric flow across flow face $k$ of $j^{th}$ control volume (m$^3$ s$^{-1}$)
- $C_k$ = concentration in flow across face $k$ (g m$^{-3}$)
- $A_k$ = area of flow face $k$ (m$^2$)
- $D_k$ = diffusion coefficient at flow face $k$ (m$^2$ s$^{-1}$)
- $S_j$ = external loads and kinetic sources and sinks in $j^{th}$ control volume (g s$^{-1}$)

CE-QUAL-ICM is an integrated compartment model that uses an unstructured grid. The user can specify the grid and transport information for the solution of the discretized form of Equation 3-1. More typically, the grid structure and transport information is derived from the application of a hydrodynamic model and the information passed to CE-QUAL-ICM through linkage files. The linkage information required includes:

- Mapping information to identify relative cell locations,
- Geometry information such as interface areas and lengths,
- Rates of flows and dispersion across cell boundaries, and
- Cell volumes for comparison with computed volumes.
The linkage information is provided to CE-QUAL-ICM in three input files. A map file contains the flow and cell mapping between the hydrodynamic model's volumetric elements and unstructured CE-QUAL-ICM model. A geometry file contains cell-mapping information (e.g., cells numbers above particular cells). A binary linkage file contains time-variable geometry (interfacial areas and volumes) as well as rates of flow and diffusion.

CE-QUAL-ICM has previously been linked with a variety of hydrodynamic models. One of the most frequently used hydrodynamic models is CH3D. Initial project plans called for SJRWMD to apply CH3D to the Lower St. Johns River. However, prior to the initiation of the current phase of the CE-QUAL-ICM project, the SJRWMD successfully applied the Environmental Fluid Dynamics Code (EFDC), developed by Dr. John Hamrick (Tetra Tech), to the Lower St. Johns River. Rather than switch to CH3D, it was decided following the initial project in October 1999 that the SJRWMD would continue the use of EFDC and that linkage routines would be developed between EFDC and CE-QUAL-ICM. The linkage was supported in part by U.S. EPA Region 4 with funding for Dr. Hamrick to assist in the linkage development. The initial linkage was developed by Dr. Hamrick and then tested and modified by EL. This chapter describes the development and testing of the linkage. A summary of the linkage procedure developed by Dr. Hamrick is provided below, followed by a summary of the linkage's implementation and testing.

Summary of CE-QUAL-ICM Linkage Interface Procedure

The volume continuity equation in EFDC can be written as:

\[ \frac{dV_{1,k}}{dt} = Q_{lw,k} - Q_{le,k} + Q_{ls,k} + Q_{ln,k} + Q_{i,k-1} - Q_{i,k} + S_{i,k} \]  

(3-2)

where \( V \) is the cell column, the first four \( Q \)s on the right side are the horizontal flows in compass notation, the fifth and sixth \( Q \)s are the vertical flows, and \( S \) is a volume source term that includes volumetric inflows and outflows including direct rainfall and water surface evaporation. The cell volume is given by:

\[ V_{1,k} = A_i \Delta_i H \]  

(3-3)

where \( A_i \) is the horizontal cell area, \( \Delta_i \) is the dimensionless sigma layer thickness, and \( H \) is the water column depth. The sigma layer formulation requires that the vertical flows at the bottom of the lowest layer \( (k = 1, \text{ in EFDC}) \) and at the top surface layer \( (k = K, \text{ in EFDC}) \) be identically zero:

\[ Q_{l,0} = 0 \]

\[ Q_{l,K} = 0 \]  

(3-4)
The discrete form of Equation 3-2 over a hydrodynamic model time step is:

$$\frac{(V_{l,k}^n - V_{l,k}^{n-1})}{\theta} = (Q_{lv,k} - Q_{ir,k} + Q_{ls,k} - Q_{in,k} + Q_{i,k-1} - Q_{i,k} + S_{l,k})^{n,n-1}$$

(3-5)

where \( n, n-1 \) denotes an average of the right side variables over the time interval \( \theta \) between time levels \( n-1 \) and \( n \). The interface procedure is based on averaging Equation 3-5 over \( N \) time steps. For example, over the first \( N \) time steps of the simulation the result is:

$$\frac{(V_{l,k}^N - V_{l,k}^0)}{N\theta} = \frac{1}{N} \sum_{n=1}^{N} (Q_{lv,k} - Q_{ir,k} + Q_{ls,k} - Q_{in,k} + Q_{i,k-1} - Q_{i,k} + S_{l,k})^{n,n-1}$$

(3-6)

or

$$\frac{(V_{l,k}^N - V_{l,k}^0)}{N\theta} = \tilde{Q}_{lv,k} - \tilde{Q}_{ir,k} + \tilde{Q}_{ls,k} - \tilde{Q}_{in,k} + \tilde{Q}_{i,k-1} - \tilde{Q}_{i,k} + \tilde{S}_{l,k}$$

(3-7)

where the tilde denotes the corresponding average.

To provide continuity consistent interface information, EFDC accumulates only the horizontal flows and the volume source term. Equation 3-7 can be rewritten as:

$$\tilde{Q}_{l,k} - \tilde{Q}_{l,k-1} + \frac{V_{l,k}^N}{N\theta} = \frac{V_{l,k}^0}{N\theta} + \tilde{Q}_{lv,k} - \tilde{Q}_{ir,k} + \tilde{Q}_{ls,k} - \tilde{Q}_{in,k} + \tilde{S}_{l,k}$$

(3-8)

where the terms on the right include the known initial volume and the accumulated averages. Note that had the averaged vertical flows been accumulated and combined with the final volume on the left side of Equation 3-8, the equation would not likely have been satisfied due to round off in the averaging process. An alternate implemented in the EFDC interfaces is determination of the vertical flows and the final volume such that Equation 3-8 is satisfied to machine precision. Equation 3-8 for the bottom layer of a cell stack is:

$$\tilde{Q}_{l,1} = \tilde{Q}_{l,1} + \frac{A_l A_f H^N}{N\theta} + \frac{V_{l,1}^0}{N\theta} + \tilde{Q}_{lv,1} - \tilde{Q}_{ir,1} + \tilde{Q}_{ls,1} - \tilde{Q}_{in,1} + \tilde{S}_{l,1}$$

(3-9)
where * denotes a readily calculated temporary variable. Combining Equation 3-8 written for the second layer with Equation 3-9 gives:

\[ \tilde{Q}_{i,2} = \tilde{Q}_{i,2} + \frac{A_i(\Delta_i + \Delta_2)H_i^N}{N\theta} = \frac{V_{i,k}^0}{N\theta} + \frac{V_{i,2}^0}{N\theta} + \tilde{Q}_{iw,1} - \tilde{Q}_{iw,1} + \tilde{Q}_{i,1} - \tilde{Q}_{i,1} + \tilde{S}_{i,1} + \tilde{S}_{i,2} + \tilde{Q}_{iw,2} - \tilde{Q}_{iw,2} + \tilde{Q}_{i,2} - \tilde{Q}_{i,2} + \tilde{S}_{i,2} \]

(3-10)

and identifies the general recursion

\[ \tilde{Q}_{i,k} = \tilde{Q}_{i,k} + \frac{A_iH_i^N}{N\theta} \sum_{j=1}^{k} \Delta_j = \frac{\sum_{j=1}^{k} \left( \frac{V_{i,j}^0}{N\theta} + \tilde{Q}_{iw,j} - \tilde{Q}_{iw,j} + \tilde{Q}_{i,j} - \tilde{Q}_{i,j} + \tilde{S}_{i,j} \right)}{3-11} \]

For the top layer, \( k = K \), Equation 3-11 gives

\[ \tilde{Q}_{i,K} = \frac{A_iH_i^N}{N\theta} = \sum_{j=1}^{K} \left( \frac{V_{i,j}^0}{N\theta} + \tilde{Q}_{iw,j} - \tilde{Q}_{iw,j} + \tilde{Q}_{i,j} - \tilde{Q}_{i,j} + \tilde{S}_{i,j} \right) \]

(3-12)

due to Equation 3-4 and the summation of \( D \) over \( K \) being unity. Thus Equation 3-12 is readily solved for the interface corrected depth at the end of the averaging interval. The interior vertical flows for \( k = 1, K - 1 \) are then determined from:

\[ \tilde{Q}_{i,k} = \tilde{Q}_{i,k} - \frac{A_iH_i^N}{N\theta} \sum_{j=1}^{k} \Delta_j \]

(3-13)

The issue of determining the water column depth at the end of the averaging period, simultaneously with the vertical flows, rather than using the value provided directly by the hydrodynamic simulation deserves some clarification. First, reconsider Equation 3-8:

\[ \tilde{Q}_{i,k} - \tilde{Q}_{i,k-1} + \frac{V_{i,k}^N}{N\theta} = \frac{V_{i,k}^0}{N\theta} + \tilde{Q}_{iw,k} - \tilde{Q}_{iw,k} + \tilde{Q}_{i,k} - \tilde{Q}_{i,k} + \tilde{S}_{i,k} \]

(3-8, bis)

which corresponds to a system of \( K \) equations. If the volume at the end of the averaging interval determined by hydrodynamic model is used in Equation 3-8, the equation is appropriately written as:

\[ \tilde{Q}_{i,k} - \tilde{Q}_{i,k-1} = \frac{V_{i,k}^0}{N\theta} - \frac{V_{i,k}^{N\text{Hyd}}}{N\theta} + \tilde{Q}_{iw,k} - \tilde{Q}_{iw,k} + \tilde{Q}_{i,k} - \tilde{Q}_{i,k} + \tilde{S}_{i,k} \]

(3-14)
which is a system of $K$ equations with $K - 1$ unknowns if the $k = 0$ and $k = K$
vertical flows are presumed identically zero consistent with the sigma
formulation. The problem posed by Equation 3-14 is over-determined, having
fewer unknowns than equations. Note also that summing Equation 3-14 over the
vertical layer stack to give an external model continuity equation

$$0 = \frac{A_i}{N\theta} (H_i^{i\text{Hyd}} - H_i^0) - \sum_{k=1}^{K} \left( \bar{Q}_{lw,k} - \bar{Q}_{lr,k} + \bar{Q}_{ls,k} - \bar{Q}_{ln,k} + \bar{S}_{l,k} \right)$$  (3-15)  

does not necessarily resolve the problem in that, even though the external
continuity equation is solved identically over each hydrodynamic time step,
rounding errors can accumulate in the averaging of the depth integrate horizontal
transports with Equation 3-15 not being identically satisfied. Alternately,
Equation 3-15 can be solved for the interface corrected depth at the end of the
averaging interval

$$\frac{A_i}{N\theta} H_i^N = \frac{A_i}{N\theta} H_i^0 + \sum_{k=1}^{K} \left( \bar{Q}_{lw,k} - \bar{Q}_{lr,k} + \bar{Q}_{ls,k} - \bar{Q}_{ln,k} + \bar{S}_{l,k} \right)$$  (3-16)  

and subtracted from the first $K - 1$ equations of the set (Equation 3-8) giving

$$\bar{Q}_{l,k} - \bar{Q}_{l,k-1} = \bar{Q}_{lw,k} - \bar{Q}_{lr,k} + \bar{Q}_{ls,k} - \bar{Q}_{ln,k} + \bar{S}_{l,k}$$  
$$- \sum_{k=1}^{K} \left( \bar{Q}_{lw,k} - \bar{Q}_{lr,k} + \bar{Q}_{ls,k} - \bar{Q}_{ln,k} + \bar{S}_{l,k} \right) : k = 1, K - 1$$  (3-17)  

which is in principle identical to the procedure defined by Equations 3-11 to 3-13
but involves more arithmetic operations.

The interfacing is expanded to subsequent averaging periods by saving the
interface-corrected water column depth at the end of the previous averaging
period to define the initial volume at the start of the next averaging period. As a
final overall check, the interface procedure essentially implements a secondary
continuity tracking to that of the hydrodynamic model. If the procedure is
robust, one would expect that water column depths predicted by the
hydrodynamic model after $m$ averaging periods would be consistent with the
final interface-adjusted depths locally

$$|H_i^{m\text{Hyd}} - H_i^{mN}| \leq \varepsilon$$  (3-18)  

and globally

$$\left| \sum_{l=1}^{L} A_i H_i^{m\text{Hyd}} - \sum_{l=1}^{L} A_i H_i^{mN} \right| \leq \varepsilon_g$$  (3-19)
Summary of Implementation

The implementation of the linkage was accomplished in an interface program and a subroutine of EFDC. The interface program is run first and used to create input files for both EFDC and CE-QUAL-ICM. The EFDC program reads these files and, during its execution, creates the binary linkage files read by CE-QUAL-ICM.

Interface program

The interface program reads two input files, a general input file (EFDC_ICM.INP), and a map file. The map file (CELL.INP) contains the I and J coordinates for the EFDC grid, where the number at a particular I, J location designates the type of cell (0=dry land cell not bordering a water cell, 9=dry land cell bordering a water cell), and where 1 ≤ number ≤ 5 indicates a water cell. The general input file contains:

a. Grid and flow transfer parameters, such as the I (pseudo X), J (pseudo Y) and K (pseudo Z) dimensions of the grid.

b. The number and I,J coordinates of the flow boundary conditions.

c. The number and I,J coordinates of the open boundary conditions.

d. The number and I,J coordinates of the EFDC cells that are not included in the CE-QUAL-ICM grid. This input was included to allow elimination of EFDC cells not needed for the CE-QUAL-ICM grid, such as the upstream "sponge" for Buffalo Bluff. The elimination of the sponge cells results in there not being a one-one correspondence in the numbering of the EFDC and CE-QUAL-ICM grid cells.

The output from the interface program includes two files read by EFDC and two by CE-QUAL-ICM. The output files used for EFDC input include an EFDC to CE-QUAL-ICM cell mapping file (EFDC_C_ICM) and a flow mapping file (EFDC_F_ICM). Files are also created to aid in generating the map (MAP_W_ICM) and geometry files (GEO_W_ICM) read by CE-QUAL-ICM. Once the interface program is run and the output files are created, they are copied to directories for input to EFDC or CE-QUAL-ICM, as appropriate. An additional output file (TESTGRID.PRN) contains the cell numbers at each I,J location for comparison of the EFDC and CE-QUAL-ICM grids.

EFDC

A subroutine developed for EFDC by Dr. Hamrick and modified by EL reads the input files created by the interface program and creates the binary linkage files read by CE-QUAL_ICM. An additional input file (EFDC.ICM) controls the linkage. This file contains:

a. Control information (controlling creation of diagnostic files).

b. Number of ICM cells, horizontal and vertical flow faces.

c. I,J locations of tributaries in EFDC input and flag indicating if they are to be written to CE-QUAL-ICM.
d. Flag for mapping internal EFDC boundaries to CE-QUAL-ICM open
boundaries for areas where the EFDC cells are not used in CE-QUAL-
ICM simulations.

Within the main EFDC input file (EFDC.INP), flags indicate whether a
linkage file is to be created (variable ISWASP), and a variable indicates the
number of reference time steps over which the variables written to the linkage
file are averaged. During the execution of EFDC, two binary linkage files are
created and updated. The first file (EFDCRME.INP) contains the net rates of
precipitation and evaporation over the averaging period. The second file
(EFDCHYD.INP) contains both time-invariant and time-variant information.
The time-invariant data for the sigma grid include:

- Surface areas,
- Vertical water column interfacial areas,
- Cell dimensions, and
- Sigma layer thickness (fraction).

The time-variant data include:

- Rates of flow and diffusion,
- Total water column volumes (converted to cell volumes), for comparison
  with ICM predictions (computed from continuity).

Additional files may be output containing diagnostic information and the results
of EFDC salinity and dye tracer simulations for comparison with CE-QUAL-
ICM predictions.

Testing of the EFDC/CE-QUAL-ICM Model Linkage

The linkage between EFDC and CE-QUAL-ICM was tested using four grids
developed for the Lower St. Johns River. They included:

a. A grid consisting of 5,230 water cells in the horizontal and 5 vertical
layers, with 15 open boundary and 79 tributary inflows for each layer,
developed by the SJRWMD and modified by Dr. Hamrick. The
CE-QUAL-ICM grid was a one-one overlay.

b. A grid consisting of 5,230 EFDC cells in the horizontal with 8 vertical
layers, with 17 open boundary and 76 tributary inflows for each layer,
developed by the SJRWMD. The CE-QUAL-ICM grid was a one-one
overlay.

c. A grid consisting of 2,210 EFDC cells in the horizontal with 8 vertical
layers, with 17 open boundary and 76 tributary inflows for each layer,
developed by the SJRWMD. The CE-QUAL-ICM grid was a one-one
overlay.

d. A grid consisting of 2,210 EFDC cells in the plan, with 6 layers and with
17 open boundary cells and 76 tributary inflows for each layer. For
CE-QUAL-ICM, by eliminating the cells used to represent volume
upstream of Palatka, the number of horizontal cells was reduced to 2,120, and tributary inflows reduced to 64. This was the final grid (Figure 3-1) and will be used in all further CE-QUAL-ICM simulations.

For each of the above grids, the EFDC model was executed and linkage files created. CE-QUAL-ICM input files were developed for the simulation of salinity and a conservative tracer.
Testing first consisted of comparisons of volumes predicted by EFDC with those predicted by CE-QUAL-ICM after a 60-day simulation period. CE-QUAL-ICM takes the initial volumes from the linkage file and then computes new volumes from continuity using the flows contained in the linkage file. The volumes were compared at the end of simulations for the entire grid and over time for individual model cells. For selected cells, all flows and volume changes were output and examined.

Initial simulations with EFDC indicated a volume imbalance. This was reported and the EFDC linkage routines modified by Dr. Hamrick to correct the volume imbalance.

For the corrected EFDC, the total volume at the end of the 396-day simulation for the period of 1 October 1997 to 31 October 1998 for the 2210 X 6 layer grid (the final grid) was 3.82E+09 m³, with a difference in total grid volume between EFDC and CE-QUAL-ICM of -7.8E-04 percent. The maximum difference between the computed EFDC and CE-QUAL-ICM volumes for any cell was 0.08 percent. Similar differences were noted in other simulations, indicating that the volume balance was acceptable (near machine accuracy).

Comparisons were also made between salinities and dye tracer concentrations predicted by EFDC and CE-QUAL-ICM. In general, the predicted concentrations were very similar but not identical. Generally, CE-QUAL-ICM predicted stronger gradients than those predicted by EFDC. This was attributed to the numerical solution technique used in CE-QUAL-ICM being less dispersive than that used in EFDC. Representative comparisons of salinities predicted by CE-QUAL-ICM and EFDC, and observed data, are provided in Figures 3-2 to 3-11. Note in these figures that the CE-QUAL-ICM predictions are at the midpoint of each day, while the EFDC predictions are hourly.

Predicted concentrations and volumes were sufficiently close to conclude that the linkage was successfully completed.
Figure 3-2. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Shands Bridge (surface)

Figure 3-3. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Shands Bridge (bottom)
Figure 3-4. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Buckman Bridge (surface)

Figure 3-5. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Buckman Bridge (bottom)
Figure 3-6. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Acosta Bridge (surface)

Figure 3-7. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Acosta Bridge (bottom)
Figure 3-8. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Dames Bridge (surface)

Figure 3-9. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Dames Bridge (bottom)
Figure 3-10. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Bar Pilot (surface)

Figure 3-11. Comparison of CE-QUAL-ICM predictions at midpoint of each day to EFDC predictions and observations for the simulation period at Bar Pilot (bottom)
4 Loads and Boundary Conditions

Introduction

Boundaries and loads provided the forcing functions for water quality in the application of CE-QUAL-ICM to the Lower St. Johns River Estuary. Loads are the product of Q and C, where Q (V/T) is the rate of water flow and C (M/A) the constituent concentration. The loads (M/T) can be provided directly to ICM. This would be required, for example, where the rates of inflow are not specified to the ICM model through the hydrodynamic linkage file. Alternatively, where the rates of inflow are included in the hydrodynamic linkage file, the concentrations can be specified as a boundary condition and the load (QC) computed internally.

In the application of CE-QUAL-ICM to the Lower St. Johns River Estuary, boundary conditions or loads were provided for the 17 horizontal segments comprising the ocean boundary, 36 point sources (PS), and 65 tributaries or non-point sources (NPS). For each of these locations, boundary conditions or loads were also specified for each of the six vertical layers in the model grid.

For PS, the rates of inflow were not considered in the EFDC hydrodynamic simulations. For these sources, all forcings were included as loads in this application. For the ocean boundary, all forcings were specified as boundary conditions. For tributaries and NPS, the forcings were specified as either loads or boundary conditions, based upon either convenience or the form of the data supplied by the SJRWMD. A series of boundary and loading files were developed for each source and constituent simulated, and the correspondence of the constituents and input files tabulated in Table 4-1. For time-varying data, individual files were created for each of the 2 years of simulation: 1 December 1996 to 30 November 1997 and 1 December 1997 to 30 November 1998 (indicated by 9* in Table 4-1). The methods and assumptions to create these files are discussed in the following sections.

Boundary Conditions

Boundary conditions were specified at the 17 horizontal segments comprising the ocean boundary and for selected constituents for the 65 NPS. Boundary conditions were also specified for each of the six vertical layers
<table>
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<tr>
<th>Variable Number</th>
<th>Variable Name</th>
<th>Buffalo Bluff and Dunn's Creek</th>
<th>Other NPS</th>
<th>PS</th>
<th>Ocean Boundary</th>
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<td>OCN_BC.NPT</td>
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<td>NPS_96B.NPT</td>
<td>PS1_9*.NPT, PS29*.NPT</td>
<td>OCN_BC.NPT</td>
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<td>BUFF9<em>B.NPT, DUNN9</em>_B.NPT</td>
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<td>BUFF9<em>B.NPT, DUNN9</em>_B.NPT</td>
<td>NPS_96B.NPT</td>
<td>PS1_9*.NPT</td>
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<td>BUFF9<em>B.NPT, DUNN9</em>_B.NPT</td>
<td>NPS_96B.NPT</td>
<td>PS1_9*.NPT</td>
<td>OCN_BC.NPT</td>
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<td>NPS_96B.NPT</td>
<td>PS1_9*.NPT</td>
<td>OCN_BC.NPT</td>
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<td>NPS_96B.NPT</td>
<td>PS1_9*.NPT</td>
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<td>PS1_9*.NPT</td>
<td>OCN_BC.NPT</td>
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<td>OCN_BC.NPT</td>
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<td>OCN_BC.NPT</td>
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<tr>
<td>15</td>
<td>Urea</td>
<td>Not simulated</td>
<td>Not simulated</td>
<td>Not simulated</td>
<td>Not simulated</td>
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<td>NPS_96B.NPT</td>
<td>PS1_9*.NPT</td>
<td>OCN_BC.NPT</td>
</tr>
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<td>NPS_96B.NPT</td>
<td>PS1_9*.NPT</td>
<td>OCN_BC.NPT</td>
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<td>BUFF9<em>B.NPT, DUNN9</em>_B.NPT</td>
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<tr>
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<td>PS1_9*.NPT</td>
<td>OCN_BC.NPT</td>
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</tbody>
</table>

(Continued)
in the model grid. Typically, all boundary conditions are specified to CE-QUAL-ICM in a single time-varying file. The structure of the standard file allows specification of the boundary locations for each water quality constituent followed by a time series of concentrations for those constituents and locations. The standard approach requires that all updates be at the same frequency. For the application of CE-QUAL-ICM to the Lower St. Johns Estuary, where the frequency of updates varied between sources from hourly to monthly values, reducing all data for the large number of sources to the same update frequency for incorporation into a single loading file would have resulted in an excessively large file. Instead, the CE-QUAL-ICM model was modified to allow specification of multiple boundary condition files. The files used and the assumptions used in their development are described below.

Salinity

All salinities were specified in boundary condition files. Separate files were developed for the salinities at the ocean boundary, Dunns Creek, and Buffalo Bluff. As with the EFDC hydrodynamic model, the salinities for all other sources were assumed to be zero.

Time-varying salinities, extracted from the input file (SSER.INP) to the EFDC hydrodynamic model, for Dunns Creek and Buffalo Bluff were specified in the boundary condition files DUNN96_N.NPT or DUNN97_N.NPT and BUFF96_N.NPT or BUFF97_N.NPT for the 2 years of simulation.
The frequency of the updates varied but averaged 6 to 12 hours. The salinities were assumed to be constant with depth.

The ocean salinities used in the water quality simulations were also extracted from input (SSER.INP) to the hydrodynamic model. The salinities for each of the six layers, from the surface downward, were 35.00, 35.10, 35.25, 35.50, 35.75, and 36.00 ppt. The salinities were assumed to remain constant and were specified in the boundary file OCN_BC.NPT.

**Water temperature**

All water temperatures were specified as boundary conditions in a single file for each year simulated (TEMP96_BC.NPT and TEMP97_BC.NPT) based upon observed data provided by SJWMD. For each of these files, the update frequency for water temperatures was hourly. The water temperatures were assumed constant with depth.

Since PS flows were not included in hydrodynamic simulations, no boundary conditions were specified for these sources. Hourly varying temperature values were specified at the ocean boundary, Buffalo Bluff, and Dunns Creek. The ocean temperatures were based upon National Oceanic and Atmospheric Administration (NOAA) data collected at Jacksonville Beach. For the remaining 63 tributaries and NPS, the SJRWMD estimated hourly temperatures based upon the best fit for stations located on the east or west bank of the estuary. The west bank stations used to create time-series included:

- NBC - North Fork of Black Creek
- BSF - South Fork of Black Creek
- BLC - Black Creek @ Hwy 209
- SPCR - Swimming Pen Creek
- PTC - Peters Creek @ Hwy 209
- RCB - Rice Creek @ US 17

The east bank stations used to create time-series included:

- SMC - Six Mile Creek @ SR 13
- MOB - Moccasin Branch @ SR 13
- DPB - Deep Creek @ RR
- OHD - Hastings Drainage District Outlet
- DCH - Deep Creek Headwaters
- DBR - Dog Branch

The estimated temperatures were then assigned to east or west bank stations as indicated in Table 4-2.
Table 4-2
Specification of West and East Bank Tributary Stations for Water Temperatures

| Trib. No. | Cell No. | IC  | JC  | Name          | T
<table>
<thead>
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<td>45</td>
<td>112</td>
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</table>

| Trib. No. | Cell No. | IC  | JC  | Name          | T
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<td>67</td>
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</tbody>
</table>

(Continued)
Other ocean boundary conditions

Concentrations of other water quality constituents simulated were specified as boundary input at the ocean boundary. These conditions were based on analysis by the SJRWMD, where averaged conditions were computed from a limited number of samples collected over six dates near the ocean model boundary. The averaged values were assumed to remain constant over the 2-year period of simulation and were assumed to be constant with depth. They were specified in the input file OCN_BC.NPT. Boundary conditions were specified for total suspended solids, each of the three algal groups, Labile dissolved organic carbon (DOC), Refractory DOC, Labile dissolved organic phosphorus (POC), Refractory POC, Ammonium, Nitrate, Labile dissolved organic nitrogen (DON), Refractory DON, Labile PON, Refractory PON, Total Phosphorus (TP), Labile DOP, Refractory DOP, Labile POP, Refractory POP, DO, Particulate Si (silica), and Dissolved Si. Since only dissolved silica data were available, the total and particulate fractions were estimated based upon the assumption that 70 percent of the silica was in the dissolved form.

Other boundary conditions for Buffalo Bluff and Dunns Creek

Concentrations of other water quality constituents simulated were specified as boundary input for Buffalo Bluff and Dunns Creek based upon data provided by the SJRWMD. These time-varying conditions were based on data collected at varying frequencies, but averaging approximately two to three weeks. The time-varying values were assumed to remain constant with depth, and were specified in the input files BUFF96_B.NPT, BUFF97_B.NPT, DUNN96_B.NPT and DUNN97_B.NPT. Boundary conditions were specified for total suspended solids, each of the three algal groups, Labile DOC, Refractory DOC, Labile POC, Refractory POC, Ammonium, Nitrate, Labile DON, Refractory DON, Labile PON, Refractory PON, Total P, Labile DOP, Refractory DOP, Labile POP, Refractory POP, DO, Particulate Si, and Dissolved Si. As discussed above, only dissolved silica data were available, so the total and particulate fractions were estimated based upon the assumption that 70 percent of the silica was in the dissolved form.
Other boundary conditions for non-point sources

Concentrations of silica and DO were also specified separately as boundary conditions for 63 of the tributaries and NPS (see Table 4-2). Silica and DO concentrations for Buffalo Bluff, Dunns Creek, and ocean boundary were specified separately, as described above. No boundary conditions were provided for PS, as PS flows were not included in hydrodynamic simulations.

DO concentrations for the 63 tributaries and NPS were based on single monthly averages of DNC and RCB observed values. These averages were assumed to be applicable to all of the 63 NPS and assumed constant with depth. The monthly values were specified in the files TRBC9697.NPT and TRBC9798.NPT for the two simulation years.

Total estimated silica concentrations were provided by the SJRWMD for 63 of the tributaries and NPS. These values were assumed constant with time and over the six modeled layers. The total silica was subdivided into dissolved and particulate fractions based upon the assumption that 70 percent of the silica was in the dissolved form. The estimated values were provided to the model in the input file SI_BC.NPT.

Point and Non-point Source Loads

Point source loads

Data were provided by the SJRWMD for the 36 point sources listed in Table 4-3. Also listed in Table 4-3 are the facility locations, I and J grid coordinates, and the surface cell number in the ICM model grid corresponding

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<th>Facility ID</th>
<th>Facility Name</th>
<th>Data Freq.</th>
<th>Facility Latitude</th>
<th>Facility Longitude</th>
<th>IC</th>
<th>JC</th>
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<td>ARLINGTON EAST WWTF</td>
<td>Daily</td>
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<td>-81.54316</td>
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<td>48</td>
<td>1464</td>
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<td>JAX DISTRICT 11 WWTF</td>
<td>Daily</td>
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<td>STONE CONTAINER CORPORATION</td>
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to the loading location. The St. Johns River study area was divided into six segments as denoted on Figure 4-1. Monthly PS loads for Total P and Total N were summed for each segment and are presented in Figures 4-2 through 4-13. As noted in Figures 4-2 through 4-7, segment 4 received the majority of the Total P loads (approximately 1,200 kg/day) while the Total P loads to the other segments ranged from 30 to 210 kg/day. Similar to Total P loads, maximum Total N loads (approximately 4,200 kg/day) to the system were received in segment 4 as shown in Figure 4-11, while loads to the other segments range from 60 to 950 kg/day (Figures 4-8 through 4-13 except Figure 4-11).

Figure 4-1. Six colored reaches represent segmentation of the St. Johns River, showing location of observed water quality stations.
Figure 4-2. Mean monthly TP PS loads into Segment 1, 1996-1998

Figure 4-3. Mean monthly TP PS loads into Segment 2, 1996-1998
Figure 4-4. Mean monthly TP PS loads into Segment 3, 1996-1998

Figure 4-5. Mean monthly TP PS loads into Segment 4, 1996-1998
Figure 4-6. Mean monthly TP PS loads into Segment 5, 1996-1998

Figure 4-7. Mean monthly TP PS loads into Segment 6, 1996-1998
Figure 4-8. Mean monthly TN PS loads into Segment 1, 1996-1998

Figure 4-9. Mean monthly TN PS loads into Segment 2, 1996-1998
Figure 4-10. Mean monthly TN PS loads into Segment 3, 1996-1998

Figure 4-11. Mean monthly TN PS loads into Segment 4, 1996-1998
Figure 4-12. Mean monthly TN PS loads into Segment 5, 1996-1998

Figure 4-13. Mean monthly TN PS loads into Segment 6, 1996-1998
The data provided by the SJWMD varied from monthly to daily between the point-source dischargers. Two input files were developed for each year of simulation, one for the monthly and one for the daily updated discharges (PS1_96B.NPT, PS1_97B.NPT, PS2_96B.NPT and PS2_97.NPT). The computed total loadings were subdivided into loadings to each of the vertical layers at the specified locations based upon the fraction of layer thickness for each of the six layers in the sigma grid.

Flows and constituent concentrations were provided by the SJRWMD for each of the dischargers listed in Table 4-3. Loads were computed as the product of the flow and specified concentrations for each state variable simulated (Table 4-4). Where only total data were provided and ICM required partitioning among dissolved and particulate fractions, the totals were partitioned using the fractions listed in Table 4-4.

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Non-point source loads

Data were provided by the SJRWMD for the 63 non-point sources listed in Table 4-5. Also listed in Table 4-4 are the I and J grid coordinates and the surface cell number in the ICM model grid corresponding to the loading location. As previously discussed for point source monthly loads of Total P and N, Total P and N NPS monthly loads were summed for each of the six river segments (Figure 4-1) and are presented in Figures 4-14 through 4-25. As noted in Figures 4-14 through 4-19, segments 3 through 6 received the majority of the Total P loads (average between 500 to 600 kg/day) while the Total P loads to the other segments were small in comparison (<120 kg/day). Similar to Total P loads, most of the Total N loads came into segments 3 through 6 on average approximately 2,500 kg/day as shown in Figures 4-22 through 4-25, while loads to the most downstream segments were on average around 200 kg/day (Figures 4-20 and 4-21).

All loading data varied daily. Two input files were developed for the non-point source loads; for the 2 years of simulation (NPS_96B.NPT and NPS_97B.NPT). The specified loadings were subdivided into loadings to each of the vertical layers at the specified locations based upon the fraction of layer thickness for each of the six layers in the sigma grid.

Constituent loads were provided by the SJRWMD for each of the discharge locations listed in Table 4-5. The loads were provided in units varying from milligrams per day to kilograms per day and were converted to ICM input units of kilograms per day. Where only total data were provided and ICM required partitioning among dissolved and particulate fractions, the totals were partitioned using the fractions listed in Table 4-4. The constituents provided by the

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Table 4-5
Non-point Loading Sources Included In Model Simulations

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SJRWMD and fractions for partitioning to ICM state variables were identical to those used for the PS with the exception of ammonia and nitrate. For the NPS, only total inorganic nitrogen loadings were provided, which were partitioned assuming that 0.75 of the loading was nitrate-nitrogen.
Figure 4-14. Mean monthly TP NPS loads into Segment 1, 1996-1998

Figure 4-15. Mean monthly TP loads into Segment 2, 1996-1998
Figure 4-16. Mean monthly TP NPS loads into Segment 3, 1996-1998

Figure 4-17. Mean monthly TP NPS loads into Segment 4, 1996-1998
Figure 4-18. Mean monthly TP NPS loads into Segment 5, 1996-1998

Figure 4-19. Mean monthly TP NPS loads into Segment 6, 1996-1998
Figure 4-20. Mean monthly TN NPS loads into Segment 1, 1996-1998

Figure 4-21. Mean monthly TN NPS loads into Segment 2, 1996-1998

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Figure 4-22. Mean monthly TN NPS loads into Segment 3, 1996-1998

Figure 4-23. Mean monthly TN NPS loads into Segment 4, 1996-1998
Figure 4-24. Mean monthly TN NPS loads into Segment 5, 1996-1998

Figure 4-25. Mean monthly TN NPS loads into Segment 6, 1996-1998
Determination of labile and refractory organic carbon and organic nutrient loads

The approach to partitioning labile and refractory organic carbon and nutrients described below was extracted from a report by Hendrickson et al. (2002). Refer to the report for details on the procedure.

**Organic carbon.** To partition labile and refractory organic carbon, tributary runoff and point source effluent water quality monitoring data collected between 1993 to 1999 within the lower St. Johns River basin were compiled to create a data base of biological oxygen demand (BOD), nutrients, and organic carbon. Station description and number of events sampled are included in Hendrickson et. al (2002). Stations were included in the analysis if the sample constituent suite included carbonaceous biological oxygen demand (CBOD), total organic carbon, total phosphorus, orthophosphate, total ammonia and total nitrate+nitrite nitrogen. In all, 789 samples were available for 28 surface water stations and 22 point sources.

Total organic carbon (TOC) within a sample was considered to be a combination of labile total organic carbon (LTOC) and refractory total organic carbon (RTOC), the proportions of which are determinable through the simultaneous expression of their rates of decomposition, as indicated by oxygen consumption in the CBOD₅ test. Using the rates of decomposition of the first-order decay model of 0.075 day⁻¹ for labile substrates, and 0.001 day⁻¹ for refractory, a pair of equations for the simultaneous solution of labile and refractory portions can be set up in the form (Chapra 1997):

\[ C_t = C_{0,7} (1 - e^{-0.001 t}) + C_{0,1} (1 - e^{-0.075 t}) \]  

Solving the equation for organic carbon, at time = 5 days, the sum of the carbon consumed was considered = CBOD₅/2.67, while at t = ∞, Cₜ = TOC = RTOC + LTOC. The resulting paired equation was simplified for computation to the following:

\[ \text{LTOC} = \frac{(\text{CBOD}_5 \times 74.906 - \text{TOC})}{61.54} \]  
\[ \text{RTOC} = \text{TOC} - \text{LTOC} \]

In calculations, two of the 88 point source samples and six of the 702 tributary samples had CBOD₅ values that indicated decay rates less than 0.001 day⁻¹; conversely, 3 point source samples in the data set exhibited CBOD₅ values that, when converted to TOC, exceeded the TOC at the maximum decomposition rate of 0.075 day⁻¹. These values were omitted from subsequent calculations.

**Organic nutrients.** To determine labile and refractory organic nitrogen and phosphorus in tributary runoff and point source effluents, the relationships between labile organic C content and organic C:N and C:P ratios were examined.
to partition organic nitrogen (TON = TKN − NH₄) and non-orthophosphate P (TNOP = TP − PO₄) into these respective pools. Organic C:N and C:P ratios for the tributary and point source data set were plotted against percent LTOC [(LTOC/TOC)*100] to determine if a relationship existed between proportional nutrient content and lability. One data point omitted from this analysis was from stream runoff draining a large dairy and intensive pasture lands in which the organic C:P was 4225:1. Figures in Hendrickson et. al (2002) suggest a significant partitioning of carbon-to-nutrient ratios based upon their content of LTOC, with high LTOC samples exhibiting low organic C:N and C:P ratios.

To determine the organic C:N and C:P for hypothetical, purely labile or refractory substrates, the data set was subdivided into samples with %LTOC less than or equal to 15, and those with %LTOC equal to or greater than 25. Linear regressions using the mean carbon-to-nutrient ratio within 5 percentage-point classes were computed, and the regression equation used to extrapolate the organic C:N and C:P when the %LTOC = 0% and when %LTOC = 100%. This yielded an organic mass (OM) C:N ratio of 33.6 for a completely refractory substrate, and a ratio of 3.6 for a completely labile substrate. In the case of non-orthophosphate phosphorous, the OM C:P ratios obtained were 662.9 for refractory OM and 22.4 for labile.

To constrain predictions of labile and refractory organic nutrients by the computed analytical laboratory fractions (e.g., TON = TKN−NH₄; TNOP = TP−PO₄), and to utilize original measured values and already computed watershed model loads, organic C:N and C:P ratios were used to partition existing TON and TNOP concentrations into labile and refractory fractions, rather than developing separate specific land use loading rates. TON was partitioned by establishing a proportional relationship of the form:

\[
\text{LTON} = \left[ \frac{\text{LTOC}}{\text{TOC} \times 3.6} \right] \times \text{TON} + \left[ \frac{\text{LTOC}}{\text{TOC} \times 33.6} \right] \times \text{TON} \times \frac{\text{LTOC}}{\text{TOC} \times 3.6} (4-4)
\]

Following this calculation, RTON could be calculated by difference with the relationship

\[
\text{RTON} = \text{TON} - \text{LTON} (4-5)
\]

or with the complementary partitioning equation of the form

\[
\text{RTON} = \left[ \frac{\text{RTOC}}{\text{TOC} \times 33.6} \right] \times \text{TON} \times \frac{\text{RTOC}}{\text{TOC} \times 336} + \left[ \frac{\text{LTOC}}{\text{TOC} \times 3.6} \right] \times \text{TON} (4-6)
\]
Similarly, TNOP was partitioned with the relationship

\[
RTON = \left[ \frac{LTNOP}{(TOC \times 22.4)} \right] \left( \frac{RTNOP}{(TOC \times 662.9)} + \frac{LTNOP}{(TOC \times 22.4)} \right)^{-1} \times TNOP
\]  

(4-7)

The concentrations of labile and refractory organic nitrogen, phosphorus, and carbon calculated using this methodology, for the 22 tributary surface water stations, and domestic waste and industrial waste point sources are listed in Hendrikson et al. (2002).

**Atmospheric loads**

Atmospheric loads to the water surface were treated as a distinctive nutrient source. Atmospheric loads to the watershed were merged with other distributed loads and were not distinguished. Information on atmospheric loads was provided by the sponsor. Monthly wet loads of ammonium and nitrate, dry loads of ammonium and nitrate, and loads of phosphorus were provided for 23 sites. These were averaged into spatially uniform monthly values. No loads were provided for organic nitrogen although these can be substantial (Peierls and Paerl 1997). The nitrogen loads were increased by 20 percent to account for organic nitrogen, and then split the total into 25 percent ammonium, 60 percent nitrate, and 15 percent dissolved organic nitrogen. The amount of organic nitrogen and the fractions were based on atmospheric loads used in the Chesapeake Bay model (Cerco et al. 2002). Loads were input to the model as areal quantities (Table 4-6). These were multiplied internally by cell surface area to produce mass loading to each surface cell in the computational grid. Summaries of the mass loads are presented in Chapter 10.

**References**


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5 Water Quality Model Formulation

Introduction

CE-QUAL-ICM was designed to be a flexible, widely-applicable eutrophication model. The initial application of the model was to Chesapeake Bay (Cerco and Cole 1994). Subsequent applications included the Delaware Inland Bays (Cerco et al. 1994), Newark Bay (Cerco and Bunch 1997), the San Juan Estuary (Bunch et al. 2000), and Florida Bay (Cerco et al. 2000). Each model application employed a different combination of model features and required addition of system-specific capabilities. This chapter describes general features and site-specific developments of the model as applied to the water column of the St. Johns River.

Conservation of Mass Equation

The foundation of CE-QUAL-ICM is the solution to the 3D mass-conservation equation for a control volume. Control volumes correspond to cells on the model grid. CE-QUAL-ICM solves, for each volume and each state variable, the equation:

\[
\frac{\delta V_j \cdot C_j}{\delta t} = \sum_{k=1}^{n} Q_k \cdot C_k + \sum_{k=1}^{n} A_k \cdot D_k \cdot \frac{\delta C}{\delta x_k} + \sum S_j
\]  

(5-1)

in which:

- \( V_j \) = volume of \( j \)th control volume (m\(^3\))
- \( C_j \) = concentration in \( j \)th control volume (g m\(^{-3}\))
- \( t, x \) = temporal and spatial coordinates
- \( n \) = number of flow faces attached to \( j \)th control volume
- \( Q_k \) = volumetric flow across flow face \( k \) of \( j \)th control volume (m\(^3\) s\(^{-1}\))
- \( C_k \) = concentration in flow across face \( k \) (g m\(^{-3}\))
- \( A_k \) = area of flow face \( k \) (m\(^2\))
Solution of Equation 5-1 on a digital computer requires specification of parameter values and discretization of the continuous derivatives. The equation is solved using the QUICKEST algorithm (Leonard 1979) in the horizontal plane and a fully implicit central-difference scheme in the vertical direction. The time step, determined by stability requirements, is usually 5 to 15 minutes. The remainder of this chapter is devoted to detailing the kinetics sources and sinks. For notational simplicity, the transport terms are dropped in the reporting of kinetics formulations.

State Variables

CE-QUAL-ICM, as applied to St. Johns River, incorporates 28 state variables in the water column including physical variables, multiple algal groups, and multiple forms of carbon, nitrogen, phosphorus, and silica (Table 5-1). Two zooplankton groups, microzooplankton and mesozooplankton, are available and can be activated when desired.

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Algae

Algae are grouped into three model classes: cyanobacteria, diatoms, and others. 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 often distinguished as having negligible settling velocity and are subject to low predation pressure.
Cyanobacteria are unique in that some species fix atmospheric nitrogen. Diatoms are distinguished by their requirement for 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 other algae. Other algae settle at a rate intermediate between cyanobacteria and diatoms and are subject to greater grazing pressure than cyanobacteria.

Each algal group is quantified as carbonaceous biomass. Carbon-to-chlorophyll ratio may be specified or computed for comparison of computed algal carbon to observed chlorophyll.

**Organic carbon**

Four organic carbon state variables are considered: labile dissolved, refractory 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 while refractory organic carbon requires more time. Labile particulate organic carbon decomposes rapidly in the water column or the sediments. Refractory particulate organic carbon decomposes slowly, primarily in the sediments, and may contribute to sediment oxygen demand years after deposition.

**Phosphorus**

As with carbon, organic phosphorus in the water column is considered in four states: labile dissolved, refractory dissolved, labile particulate, and refractory particulate. A single mineral form, total phosphate, is considered. Total phosphate exists as two states within the model ecosystem: dissolved phosphate and phosphate sorbed to inorganic solids. Phosphorus incorporated in the cells of each algal group is also computed as a state variable. Computation of internal phosphorus provides for variable algal composition and allows luxury phosphorus uptake.

**Nitrogen**

Nitrogen is first divided into organic and mineral fractions. Organic nitrogen state variables are: labile dissolved, refractory dissolved, labile particulate, and refractory particulate. Two mineral nitrogen forms are considered: ammonium and nitrate. Both are utilized to fulfill 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 often much less than nitrate and, for modeling purposes, nitrite is combined with nitrate; therefore, the nitrate state variable actually represents the sum of nitrate plus nitrite.
Silica

Silica is divided into two state variables: dissolved silica and particulate biogenic silica. Dissolved silica is available for utilization 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.

Chemical oxygen demand

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.

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.

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 DO saturation concentration and may be used in the determination of kinetics constants that differ in saline and fresh water.

Temperature

Temperature is a primary determinant of the rate of biochemical reactions. Reaction rates increase as a function of temperature, although extreme temperatures may result in the mortality of organisms and a decrease in kinetics rates.

Fixed solids

Fixed solids are the mineral fraction of total suspended solids. The solids contribute to light attenuation and may play a role in sediment-water phosphorus transfer and in buffering water column phosphorus concentration.

Algae

Algae play a central role in the carbon and nutrient cycles comprised by the model ecosystem. Equations governing the three groups are largely the same. Differences among the groups are expressed through the magnitudes of
parameters in the equations. Algal sources and sinks in the conservation equation include production, respiration, predation, and settling. These are expressed as:

\[
\frac{\delta}{\delta t} B = \left( G - R - W_a \frac{\delta}{\delta z} \right) B - PR
\]

(5-2)

in which:

- \( B \) = algal biomass, expressed as carbon (g C m\(^{-3}\))
- \( G \) = growth (d\(^{-1}\))
- \( R \) = respiration (d\(^{-1}\))
- \( W_a \) = algal settling velocity (m d\(^{-1}\))
- \( PR \) = predation (g C m\(^{-3}\) d\(^{-1}\))

**Production**

Production by phytoplankton is determined by the intensity of light, by the availability of nutrients, and by the ambient temperature.

**Light**

The influence of light on phytoplankton production is represented by a chlorophyll-specific production equation (Jassby and Platt 1976):

\[
P^B = Pm^B \frac{I}{\sqrt{I^2 + Ik^2}}
\]

(5-3)

in which:

- \( P^B \) = production (g C g\(^{-1}\) Chl d\(^{-1}\))
- \( Pm^B \) = production at optimal illumination (g C g\(^{-1}\) Chl d\(^{-1}\))
- \( I \) = irradiance (E m\(^{-2}\) d\(^{-1}\))

Parameter \( Ik \) is defined as the irradiance at which the initial slope of the production versus irradiance relationship (Figure 5-1) intersects the value of \( Pm^B \):

\[
Ik = \frac{Pm^B}{\alpha}
\]

(5-4)

in which \( \alpha \) is the initial slope of production versus irradiance relationship (g C g\(^{-1}\) Chl (E m\(^{2}\))\(^{-1}\)).
Chlorophyll-specific production rate is readily converted to carbon-specific growth rate, for use in Equation 5-2 through division by the carbon-to-chlorophyll ratio:

\[ G = \frac{P_n}{C_{Chl}} \]  

(5-5)

in which \( C_{Chl} \) is the carbon-to-chlorophyll ratio (g C g\(^{-1}\) chlorophyll \(a\)).

**Carbon-to-chlorophyll ratio**

The carbon-to-chlorophyll ratio is determined by an empirical relationship presented by Cloern et al. (1995). They related the chlorophyll-to-carbon ratio to temperature, light, and nutrient limitation:

\[ \frac{Chl}{C} = \frac{Chl}{C_{min}} + A \cdot e^{B \cdot T} \cdot e^{C \cdot \text{Itot}} \cdot \mu' \]  

(5-6)

in which:

- \( Chl / C_{min} \) = minimum chlorophyll to carbon ratio (g Chl g\(^{-1}\) C)
- \( \text{Itot} \) = total daily irradiance (E m\(^{-2}\))
- \( \mu' \) = nutrient limitation to growth (0 ≤ \( \mu' \) ≤ 1)
- \( A, B, C \) = empirical parameters
The model takes the inverse of Equation 5-6 since carbon-to-chlorophyll ratio is required. Parameters are treated as input variables to be specified for each algal group. (Cloern et al. provided parameter values for coastal diatoms and noted that dinoflagellates have smaller chlorophyll to carbon ratios than diatoms.) A constant carbon-to-chlorophyll ratio can be employed by specifying parameter \( A \) as zero.

Examination of the computed ratio, using parameters for coastal diatoms, indicates the carbon-to-chlorophyll ratio takes values from less than 50 to more than 300 (Figures 5-2, 5-3, and 5-4). Light has the greatest influence on the ratio while the effect of temperature is least. The ratio increases as irradiance increases and decreases as a function of temperature. The ratio decreases as nutrients move from severely-limiting to non-limiting conditions. The effect of nutrient limitation on carbon-to-chlorophyll exhibits a strong interaction with irradiance. At low irradiance, the ratio is more sensitive to nutrient limitation than at high irradiance.

**Nutrients**

Carbon, nitrogen, and phosphorus are the primary nutrients required for algal growth. Diatoms require silica as well. Inorganic carbon is usually available in excess and is not considered in the model.

![Figure 5-2. Effect of temperature and nutrient limitation on carbon-to-chlorophyll ratio](image)
Figure 5-3. Effect of irradiance and temperature on carbon-to-chlorophyll ratio

Figure 5-4. Effect of nutrient limitation and irradiance on carbon-to-chlorophyll ratio
Nitrogen and silica. The effects of nitrogen and silica on growth are described by the formulation commonly referred to as "Monod kinetics" (Monod 1949):

\[
f(N) = \frac{D}{KHd + D}
\]  

(5-7)

in which:

- \( f(N) \) = nutrient limitation on algal production \( (0 \leq f(N) \leq 1) \)
- \( D \) = concentration of dissolved inorganic nutrient \( (\text{g m}^{-3}) \)
- \( KHd \) = half-saturation constant for nutrient uptake \( (\text{g m}^{-3}) \)

In the Monod formulation (Figure 5-5) growth is dependent upon nutrient availability at low nutrient concentrations but is independent of nutrients at high concentrations. A key parameter in the formulation is the "half-saturation concentration." Growth rate is half the maximum when available nutrient concentration equals the half-saturation concentration.

Phosphorus. The effect of phosphorus on growth is modeled with a formulation commonly known as "Droop kinetics" (Droop 1973). Droop kinetics relate algal growth to the concentration of internal rather than external nutrients. For phosphorus, using terminology employed in the model, the limit is:

\[
Plim = \frac{Q - Qo}{Q}
\]  

(5-8)

Figure 5-5. Monod formulation for nutrient-limited growth
in which:

\[ Plim = \text{phosphorus limitation on algal production} \quad (0 \leq Plim \leq 1) \]
\[ Q = \text{cell quota (g P g}^{-1} \text{ algal C)} \]
\[ Qo = \text{minimum cell quota (g P g}^{-1} \text{ algal C)} \]

As noted by Droop, his formula (Figure 5-6) is equivalent to a Monod formulation in which the nutrient concentration is expressed as excess cell quota and the half-saturation concentration is the minimum cell quota:

\[ Plim = \frac{Q - Qo}{Qo + (Q - Qo)} \quad (5-9) \]

Figure 5-6. Droop formulation for nutrient-limited growth

The original formulation of the Droop model expresses internal nutrients as mass of nutrient per algal cell. The present model quantifies algae as carbon per unit volume, not as discrete cells. The internal phosphorus state variable is also expressed as mass per unit volume. Cell quota is mass of internal phosphorus per unit volume divided by mass of algal carbon per unit volume or mass phosphorus per mass carbon.

Phosphorus is transported from the external pool to the internal pool in accordance with an uptake relationship that is identical to the Monod formula:

\[ Pup = V_{max} \cdot \frac{PO_4}{KHp + PO_4^d} \quad (5-10) \]
in which:

\[ P_{up} = \text{phosphorus uptake by algae (g P g}^{-1}\text{ algal C d}^{-1}) \]
\[ V_{max} = \text{maximum uptake rate (g P g}^{-1}\text{ algal C d}^{-1}) \]
\[ PO_{4d} = \text{dissolved portion of total phosphate external to cell (g P m}^{-3}) \]
\[ K_{Hp} = \text{half saturation concentration for phosphorus uptake (g P m}^{-3}) \]

**Effect of internal phosphorus calculation.** The model was applied to a closed, well-mixed system (Table 5-2) supplied with inorganic nitrogen and light in excess quantities. Phosphorus recycling was eliminated so that only the initial phosphate was available to the algae. The system was simulated for 30 days. Midway through the simulation, a phosphate load equivalent to the initial mass was injected. Three simulations were conducted. The first used the internal phosphorus algorithm. In the second, algal composition was fixed equivalent to the initial cell quota in the internal phosphorus computation (0.025 g P g\(^{-1}\) C). In the third, algal composition was fixed equivalent to the minimum cell quota in the internal phosphorus computation (0.007 g P g\(^{-1}\) C).

| Table 5-2
| Properties of Well-Mixed System |
| --- | --- | --- |
| Property | Value | Units |
| Volume | 1.0 | m\(^3\) |
| Initial phosphate | 0.09 | g P m\(^{-3}\) |
| Initial internal phosphorus | 0.0125 | g P m\(^{-3}\) |
| Initial algal biomass | 0.5 | g C m\(^{-3}\) |
| Growth rate | 1.0 | d\(^{-1}\) |
| Basal metabolism | 0.1 | d\(^{-1}\) |
| Photo-respiration | 0.1 | |
| K_{Hp} | 0.01 | g P m\(^{-3}\) |
| Phosphorus-to-carbon ratio (fixed composition) | 0.007, 0.025 | g P g\(^{-1}\) C |
| Q_a (variable composition) | 0.007 | g P g\(^{-1}\) C |
| V_{max} | 0.01 | g P g\(^{-1}\) C d\(^{-1}\) |

Biomass for the fixed-composition calculations took off more rapidly than the internal phosphorus calculation (Figure 5-7). Algae with the high, fixed composition quickly exhausted the available phosphorus (Figure 5-8) and attained peak biomass roughly a third of the other simulations. The effect of the internal phosphorus calculation was to reduce amplitude of biomass fluctuations and delay their occurrence, relative to the computation with minimum, fixed composition (Figure 5-7). Fluctuations in external phosphate were also damped and delayed (Figure 5-8).

Growth of algae with fixed composition stopped abruptly when external phosphorus was exhausted (Figures 5-7 and 5-8). Growth of algae with internal phosphorus continued after external phosphorus was depleted, fueled by the internal pool, and did not cease until internal cell quota reached the minimum (Figures 5-9 and 5-10).
Figure 5-7. Algal biomass with fixed and variable internal phosphorus

Figure 5-8. Dissolved phosphate with fixed and variable internal phosphorus
Figure 5-9. Biomass and cell quota for algae with variable internal phosphorus

Figure 5-10. Internal and external phosphorus for simulation with variable internal phosphorus
This simulation suggests that application of the internal phosphorus model to a real system will result in damped oscillations in algal biomass and phosphate relative to a model with fixed composition. Peak biomass will not differ substantially, however, from that attained using a model with fixed, minimal phosphorus-to-carbon ratio. The actual impact in a system with multiple, time varying inputs and with recycling is impossible to predict, however, and should be tested in one or more sensitivity runs.

Temperature

Algal production increases as a function of temperature until an optimum temperature or temperature range is reached. Above the optimum, production declines until a temperature lethal to the organisms is attained. Numerous functional representations of temperature effects are available. Inspection of growth versus temperature curves indicates a function similar to a Gaussian probability curve (Figure 5-11) provides a good fit to observations:

\[
 f(T) = e^{-KTg1 \cdot (T - Topt)} \text{ when } T \leq Topt \\
 = e^{-KTg2 \cdot (Topt - T)^2} \text{ when } T > Topt
\]

in which:

- \( T \) = temperature (°C)
- \( Topt \) = optimal temperature for algal growth (°C)
- \( KTg1 \) = effect of temperature below Topt on growth (°C^-1)
- \( KTg2 \) = effect of temperature above Topt on growth (°C^-2)

![Figure 5-11. Relation of algal production to temperature](image)
Combining effects of light, nutrients, and temperature

A production versus irradiance relationship (Figure 5-12) is constructed for each model cell at each time step. First, \( Pm^g \) is determined as a function of ambient temperature and nutrient concentrations:

\[
Pm^g = P_{\text{max}} \cdot f(T) \cdot \min\left(\frac{NH_4 + NO_3}{KHn + NH_4 + NO_3}, \frac{Q - Q_o}{Q}, \frac{Si}{KHS + Si}\right)
\]

in which:

\( Pm^g \) = production subject to light and nutrient limitations (g C g\(^{-1}\) Chl d\(^{-1}\))

\( P_{\text{max}} \) = production at optimal temperature in the absence of light and nutrient limitations (g C g\(^{-1}\) Chl d\(^{-1}\))

\( NH_4 \) = ammonium concentration (g N m\(^{-3}\))

\( NO_3 \) = nitrate concentration (g N m\(^{-3}\))

\( KHn \) = half-saturation concentration for nitrogen uptake (g N m\(^{-3}\))

\( Si \) = dissolved silica concentration (g Si m\(^{-3}\))

\( KHS \) = half-saturation concentration for silica uptake (g P m\(^{-3}\))

\[\text{Figure 5-12. Combined effects of light and nutrient limitations. In region A, nutrient limitation has no effect. In region B, light and nutrient limitations exhibit strong interactions. In region C, light exhibits little or no influence on production}\]
Next, parameter \( I_k \) is derived from Equation 5-4. Finally, production, as a function of temperature, nutrients, and light, is derived from Equation 5-3. The resulting production versus irradiance curve exhibits three regions (Figure 5-12).

For \( I \gg I_k \), the value of the term \( I/\sqrt{I^2 + I_k^2} \) approaches unity and temperature and nutrients are the primary factors that influence production. For \( I \ll I_k \), production is determined solely by \( \alpha \) and irradiance \( I \). In the region where the initial slope of the production versus irradiance curve intercepts the line indicating production at optimal illumination, \( I \cdot I_k \), production is determined by the combined effects of temperature, nutrients, and light.

The model requires, for each phytoplankton group, specification of parameters \( P_{\text{max}}, \alpha, T_{\text{opt}}, K_{T_g}, K_{H_n}, K_{H_p}, \) and (for diatoms) \( K_{H_s} \). Parameters \( P^0, P_{\text{m}0}, \) and \( I_k \) are derived. It is assumed that \( \alpha \) is constant. Although this assumption is not entirely true, specification of the functional variation of \( \alpha \) is beyond the data availability of most model applications.

**Irradiance**

Irradiance at the water surface is evaluated at each model time step. Instantaneous irradiance is computed by fitting a sin function to daily total irradiance:

\[
I_0 = \frac{\Pi}{2 \cdot FD} \cdot IT \cdot \sin \left( \frac{\Pi \cdot DSSR}{FD} \right)
\]

in which:

\( I_0 \) = irradiance at water surface (E m\(^{-2}\) d\(^{-1}\))

\( FD \) = fractional daylength (0 \( \leq FD \leq 1 \))

\( DSSR \) = time since sunrise (day)

\( Io \) is evaluated only during the interval:

\[
\frac{1 - FD}{2} \leq DSM \leq \frac{1 + FD}{2}
\]

in which \( DSM \) is the time since midnight (day). Outside the specified interval, \( Io \) is set to zero.

**Respiration**

Two forms of respiration are considered in the model: photo-respiration and basal metabolism. Photo-respiration represents the energy expended by carbon fixation and is a fixed fraction of production. In the event of no production (e.g., at night), photo-respiration is zero. Basal metabolism is a continuous energy expenditure to maintain basic life processes. In the model, metabolism is
considered to be an exponentially increasing function (Figure 5-13) of temperature. Total respiration is represented:

\[ R = P_{resp} \cdot G + B_{Mr} \cdot e^{K_{Tb} \cdot (T - T_r)} \]  

(5-15)

in which:

- \( P_{resp} \) = photo-respiration (0 ≤ \( P_{resp} \) ≤ 1)
- \( B_{Mr} \) = metabolic rate at reference temperature \( T_r \) (d⁻¹)
- \( K_{Tb} \) = effect of temperature on metabolism (°C⁻¹)
- \( T_r \) = reference temperature for metabolism (°C).

Figure 5-13. Relation of algal metabolism to temperature

**Predation**

Predation is modeled by assuming zooplankton and other predators clear a specific volume of water per unit biomass:

\[ PR = F \cdot B \cdot Z \]  

(5-16)

in which:

- \( F \) = filtration rate (m³ g⁻¹ zooplankton C day⁻¹)
- \( Z \) = zooplankton biomass (g C m⁻³).

Absent an explicit zooplankton model, specification of the spatial and temporal distribution of the predator population is impossible. One approach is to assume zooplankton biomass is proportional to algal biomass, \( Z = \gamma B \), in which case Equation 5-16 can be rewritten:
\[ PR = \gamma \cdot F \cdot B^2 \] (5-17)

Since neither \( \gamma \) nor \( F \) are known precisely, the logical approach is to combine their product into a single unknown, \( Ph_{tl} \), determined during the model calibration procedure. Effect of temperature on predation is represented with the same formulation as the effect of temperature on respiration.

**Effect of algae on phosphorus**

Model phosphorus state variables include total phosphate (dissolved and sorbed), internal phosphorus, labile dissolved organic phosphorus, refractory dissolved organic phosphorus, labile particulate organic phosphorus, and refractory particulate organic phosphorus. Thus, total phosphorus in the model is expressed as:

\[ TotP = P_{O4t} + PI_B + LDOP + RDOP + LPOP + RPOP \] (5-18)

in which:

- \( TotP \) = total phosphorus (g P m\(^{-3}\))
- \( P_{O4t} \) = total phosphate (g P m\(^{-3}\))
- \( PI_B \) = internal phosphorus (g P m\(^{-3}\))
- \( LDOP \) = labile dissolved organic phosphorus (g P m\(^{-3}\))
- \( RDOP \) = refractory dissolved organic phosphorus (g P m\(^{-3}\))
- \( LPOP \) = labile particulate organic phosphorus (g P m\(^{-3}\))
- \( RPOP \) = refractory particulate organic phosphorus (g P m\(^{-3}\)).

Algal uptake transfers dissolved phosphate to the internal pool while respiration releases internal phosphorus as dissolved phosphate and organic phosphorus. The division of respired phosphorus into mineral and organic fractions is determined by empirical distribution coefficients. A second set of distribution coefficients determines the fate of algal phosphorus lost through predation.

**Effect of algae on nitrogen**

Model nitrogen state variables include ammonium, nitrate, labile dissolved organic nitrogen, refractory dissolved organic nitrogen, labile particulate organic nitrogen, and refractory particulate organic nitrogen. The amount of nitrogen incorporated in algal biomass is quantified through a stoichiometric ratio. Thus, total nitrogen in the model is expressed as:

\[ TotN = NH_4 + NO_3 + Anc \cdot B + DON + LPON + RPON \] (5-19)

in which:

- \( TotN \) = total nitrogen (g N m\(^{-3}\))
\[ \text{NH}_4 = \text{ammonium (g N m}^{-3}\text{)} \]
\[ \text{NO}_3 = \text{nitrate (g N m}^{-3}\text{)} \]
\[ \text{Anc} = \text{Igal nitrogen-to-carbon ratio (g N g}^{-1}\text{ C)} \]
\[ \text{DON} = \text{dissolved organic nitrogen (g N m}^{-3}\text{)} \]
\[ \text{LPON} = \text{lable particulate organic nitrogen (g N m}^{-3}\text{)} \]
\[ \text{RPON} = \text{refractory particulate organic nitrogen (g N m}^{-3}\text{)} \].

Algae take up ammonium and nitrate during production and release ammonium and organic nitrogen through respiration. Nitrate is internally reduced to ammonium before synthesis into biomass occurs (Parsons et al. 1984). Trace concentrations of ammonium inhibit nitrate reduction so that, in the presence of ammonium and nitrate, ammonium is utilized first. The “preference” of algae for ammonium is expressed by an empirical function (Thomann and Fitzpatrick 1982) with two limiting values (Figure 5-14). When nitrate is absent, the preference for ammonium is unity. When ammonium is absent, the preference is zero. In the presence of ammonium and nitrate, the preference depends on the abundance of both forms relative to the half-saturation constant for nitrogen uptake. When both ammonium and nitrate are abundant, the preference for ammonium approaches unity. When ammonium is scarce but nitrate is abundant, the preference decreases in magnitude and a significant fraction of algal nitrogen requirement comes from nitrate.

As with phosphorus, the fate of algal nitrogen released by respiration and predation is represented by distribution coefficients.

![Figure 5-14. Algal ammonium preference](image_url)
Organic Carbon

Organic carbon undergoes innumerable transformations in the water column. The model carbon cycle (Figure 5-15) consists of the following elements:

- Phytoplankton production
- Phytoplankton exudation
- Predation on phytoplankton
- Dissolution of particulate carbon
- Heterotrophic respiration
- Photo-oxidation
- Coagulation
- Settling and resuspension.

Algal production is the primary carbon source although carbon also enters the system through external loading. Predation on algae releases particulate and dissolved organic carbon to the water column. A fraction of the particulate organic carbon undergoes first-order dissolution to dissolved organic carbon. Dissolved organic carbon produced by phytoplankton exudation, by predation, and by dissolution is respired at a first-order rate to inorganic carbon. Light-mediated reactions convert dissolved organic carbon to inorganic form (photo-oxidation) and induce coagulation to particulate organic carbon. Particulate organic carbon that does not undergo dissolution settles to the bottom sediments.

Figure 5-15. Model carbon cycle
Labile dissolved organic carbon

The complete representation of labile dissolved organic carbon sources and sinks in the model ecosystem is:

\[
\frac{\delta}{\delta t} LDOC = FCLDP \cdot PR + Klpoc \cdot LPOC + Krpoc \cdot RPOC
\]

\[
- Kldoc \cdot LDOC + \frac{BENLDOC}{\Delta z} + \frac{SAVLDOC}{\Delta z}
\]

in which:

\(LDOC\) = labile dissolved organic carbon (g m\(^{-3}\))

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

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

\(FCLDP\) = fraction of predation on algae released as \(LDOC\) (0 < \(FCLDP\) < 1)

\(Klpoc\) = dissolution rate of \(LPOC\) (d\(^{-1}\))

\(Krpoc\) = dissolution rate of \(RPOC\) (d\(^{-1}\))

\(Kldoc\) = respiration rate of \(LDOC\) (d\(^{-2}\))

\(BENLDOC\) = release of DOC from sediments and benthic algae (g C m\(^{-2}\) d\(^{-1}\))

\(SAVLDOC\) = release of DOC from seagrass (g C m\(^{-2}\) d\(^{-1}\))

\(\Delta z\) = model layer thickness (m).

The fate of refractory particulate organic carbon that is converted to dissolved form is uncertain. Potentially, both labile and refractory dissolved carbon may be produced. The model formulation assumes that all dissolved carbon produced by bacterial hydrolysis is labile whatever the source. The nature of refractory particulate organic carbon is reflected in very low hydrolysis rates rather than in the end product of the dissolution process.

Refractory dissolved organic carbon

Processes that influence refractory dissolved organic carbon are analogous to those for the labile dissolved fraction. In addition, refractory dissolved organic carbon is subject to photoreactions (oxidation and coagulation). The complete representation of refractory dissolved organic carbon sources and sinks in the model ecosystem is:

\[
\frac{\delta}{\delta t} RDOC = FCRDP \cdot PR - Krdoc \cdot RDOC
\]

\[
- lavg \cdot Krclit \cdot RDOC + \frac{BENRDOC}{\Delta z} + \frac{SAVRDOC}{\Delta z}
\]

(5-21)
in which:

\[ RDOC = \text{refractory dissolved organic carbon (g m}^{-3}) \]
\[ FCRDP = \text{fraction of predation on algae released as } RDOC \]
\[ (0 < FCRDP < 1) \]
\[ Krdoc = \text{respiration rate of } RDOC \text{ (d}^{-1}) \]
\[ lavg = \text{irradiance averaged over thickness of model cell (E m}^{-2} \text{ d}^{-1}) \]
\[ Krelit = \text{photoreaction rate (E m}^{-2})^{-1} \]
\[ BENRDOC = \text{release of } RDOC \text{ from sediments and benthic algae (g C m}^{-2} \text{ d}^{-1}) \]
\[ SAVRDOC = \text{release of } RDOC \text{ from seagrass (g C m}^{-2} \text{ d}^{-1}). \]

The photoreactions that affect dissolved organic matter are complex. As a first approach, it is assumed here that the reaction rate is linearly proportional to ambient light and to dissolved organic carbon. Investigation in one southeast river (Gao and Zepp 1998) indicates that photo-oxidation of dissolved organic carbon consumes oxygen and produces dissolved inorganic carbon in rough stoichiometric proportions. The same investigation illustrates the existence of an iron-mediated reaction that results in coagulation of dissolved organic carbon into particulate form. Iron is not considered in the model. An input parameter, \( Fcoag \), determines the fraction of the photoreacted dissolved organic carbon that coagulates. The remainder is oxidized to mineral form with concurrent consumption of dissolved oxygen.

**Labile particulate organic carbon**

The complete representation of labile particulate organic carbon sources and sinks in the model ecosystem is:

\[
\frac{\delta}{\delta t} LPOC = FCLPP \cdot PR - Krpoc \cdot LPOC
\]

\[
-WI \cdot \frac{\delta}{\delta z} LPOC + \frac{BENLPOC}{\Delta z} + \frac{SAVLPOC}{\Delta z}
\]

in which:

\[ FCLPP = \text{fraction of predation on algae released as } LPOC \]
\[ (0 < FCLPP < 1) \]
\[ WI = \text{settling velocity of labile particles (m d}^{-1}) \]
\[ BENLPOC = \text{resuspension of } LPOC \text{ from sediments (g C m}^{-2} \text{ d}^{-1}) \]
\[ SAVLPOC = \text{release of } LPOC \text{ from seagrass (g C m}^{-2} \text{ d}^{-1}). \]
Refractory particulate organic carbon

The complete representation of refractory particulate organic carbon sources and sinks in the model ecosystem is:

\[
\frac{\delta}{\delta t} \text{RPOC} = 
\]

\[
\text{FCRPP} \cdot \text{PR} \cdot \text{Krroc} \cdot \text{RPOC} + \text{Fcoag} \cdot \text{Iavg} \cdot \text{Krclit} \cdot \text{RDOC} 
\]

\[
- \text{Wr} \cdot \frac{\delta}{\delta z} \frac{\text{RPOC} + \text{BENRPOC}}{\Delta z} + \frac{\text{SAVRPOC}}{\Delta z} 
\]

in which:

- \text{FCRPP} = \text{fraction of predation on algae released as RPOC (0 < FCRP < 1)}
- \text{Fcoag} = \text{fraction of photo-oxidized RDOC that coagulates (0 < Fcoag < 1)}
- \text{Wr} = \text{settling velocity of refractory particles (m d\textsuperscript{-1})}
- \text{BENRPOC} = \text{resuspension of RPOC from sediments (g C m\textsuperscript{-2} d\textsuperscript{-1})}
- \text{SAVRPOC} = \text{release of RPOC from seagrass (g C m\textsuperscript{-2} d\textsuperscript{-1}).}

Phosphorus

The model phosphorus cycle (Figure 5-16) includes the following processes:

- Algal uptake and respiration
- Predation
- Hydrolysis of particulate organic phosphorus
- Mineralization of dissolved organic phosphorus
- Settling
- Exchange with inorganic solids.
External loads provide the ultimate source of phosphorus to the system. Dissolved phosphate is taken up by algae to sustain growth and released as phosphate and organic phosphorus through respiration and predation. A portion of the particulate organic phosphorus hydrolyzes to dissolved organic phosphorus. The balance settles to the sediments. Dissolved organic phosphorus is mineralized to phosphate. A portion of the phosphate sorbs to inorganic solids and settles to the sediments. Within the sediments, particulate phosphorus is mineralized and recycled to the water column as dissolved phosphate.

Hydrolysis and mineralization

Within the model, hydrolysis is defined as the process by which particulate organic substances are converted to dissolved organic form. Mineralization is defined as the process by which dissolved organic substances are converted to dissolved inorganic form. Conversion of particulate organic phosphorus to phosphate proceeds through the sequence of hydrolysis and mineralization. Direct mineralization of particulate organic phosphorus does not occur. Analogous to the reasoning applied to dissolved organic carbon, it is assumed hydrolysis of both labile and refractory particulate organic phosphorus produces labile dissolved organic phosphorus. Mineralization of both labile and refractory dissolved organic phosphorus produces phosphate.

Mineralization of organic phosphorus is mediated by the release of nucleotidase and phosphatase enzymes by bacteria (Ammerman and Azam 1985; Chrost and Overbeck 1987) and algae (Matavulj and Flint 1987; Chrost and Overbeck 1987; Boni et al. 1989). Since the algae themselves release the enzyme...
and since bacterial abundance is related to algal biomass, the rate of labile
organic phosphorus mineralization is related, in the model, to algal biomass. A
most remarkable property of the enzyme process is that alkaline phosphatase
activity is inversely proportional to ambient phosphate concentration (Chrost and
Overbeck 1987; Boni et al. 1989). Put in different terms, when phosphate is
scarce, algae stimulate production of an enzyme that mineralizes organic
phosphorus to phosphate. This phenomenon is simulated by relating
mineralization to the algal phosphorus nutrient limitation. Mineralization is
highest when algae are strongly phosphorus limited and is least when no
limitation occurs.

The expression for mineralization rate is:

\[ K_{ldop} = K_{ldp} + \frac{K_{Hp}}{K_{Hp} + P_{04d}} \cdot K_{dpalg} \cdot B \tag{5-24} \]

in which:

- \( K_{ldop} = \) mineralization rate of labile dissolved organic phosphorus (d\(^{-1}\))
- \( K_{ldp} = \) minimum mineralization rate (d\(^{-1}\))
- \( K_{Hp} = \) half-saturation concentration for algal phosphorus uptake (g P m\(^{-3}\))
- \( P_{04d} = \) dissolved phosphate (g P m\(^{-3}\))
- \( K_{dpalg} = \) constant that relates mineralization to algal biomass (m\(^{3}\) g\(^{-1}\) C d\(^{-1}\)).

Potential effects of algal biomass and nutrient limitation on the
mineralization rate are shown in Figure 5-17. When nutrient concentration
greatly exceeds the half-saturation concentration for algal uptake, the rate
roughly equals the minimum. Algal biomass has little influence. As nutrient
becomes scarce relative to the half-saturation concentration, the rate increases.
The magnitude of increase depends on algal biomass. Factor of two to three
increases are feasible.

An exponential function (Figure 5-13) relates mineralization and hydrolysis
rates to temperature.

The total phosphate system

The model phosphate state variable is defined as the sum of dissolved and
sorbed phosphate:

\[ P_{04t} = P_{04d} + P_{04p} \tag{5-25} \]

in which:

- \( P_{04t} = \) total phosphate (g P m\(^{-3}\))
- \( P_{04d} = \) dissolved phosphate (g P m\(^{-3}\))
- \( P_{04p} = \) particulate (sorbed) phosphate (g P m\(^{-3}\))
Figure 5-17. Effect of algal biomass and nutrient concentration on phosphorus mineralization

Particulate and dissolved fractions of total phosphate are determined by equilibrium partitioning:

\[ PO_4^d = \frac{1}{1 + K_{adpo4} \cdot ISS} \cdot PO_4^t \]  

(5-26)

and

\[ PO_4^p = \frac{K_{adpo4} \cdot ISS}{1 + K_{adpo4} \cdot ISS} \cdot PO_4^t \]  

(5-27)

in which:

\( K_{adpo4} \) = partition coefficient (m³ g⁻¹)

\( ISS \) = inorganic (fixed) solids concentration (g m⁻³)

Total phosphate

The mass-balance equation for the total phosphate state variable is:
\[ \frac{\delta}{\delta t} \text{PO}_4 t = Kldop \cdot LDOP + Krdop \cdot RDOP \]

\[ -V_{max} \cdot \frac{PO_4 d}{Khp + PO_4 d} \cdot B + R \cdot B \cdot FPI \cdot Q_0 + PR \cdot FPPIP \cdot Q \]  

(5-28)

\[ -W_{ss} \frac{\delta}{\delta z} \text{PO}_4 P + \frac{\text{BENPO}_4}{\Delta z} + \frac{\text{SAVPPO}_4}{\Delta z} \]

in which:

- \( LDOP = \) labile dissolved organic phosphorus (g P m\(^{-3}\))
- \( RDOP = \) refractory dissolved organic phosphorus (g P m\(^{-3}\))
- \( Krdop = \) hydrolysis rate of refractory dissolved organic phosphorus (d\(^{-1}\))
- \( FPI = \) fraction of algal respiration released as total phosphate
  \( (0 \leq FPI \leq 1) \)
- \( FPPIP = \) fraction of predation released as total phosphate
  \( (0 < FPPIP < 1) \)
- \( W_{ss} = \) solids settling rate (m d\(^{-1}\))
- \( BENPO_4 = \) sum (diagenesis + benthic algae) of sediment water phosphorus transfer (g P m\(^{-2}\) d\(^{-1}\))
- \( SAVPO_4 = \) phosphate release from seagrass (g P m\(^{-2}\) d\(^{-1}\))

It is assumed that respiration releases phosphorus from the pool represented by the minimum cell quota. Since predators consume entire phytoplankton, predation releases phosphorus from the entire cell quota. The settling term represents the settling of particulate phosphate sorbed to particles.

**Internal phosphorus**

Internal phosphorus is quantified as mass per unit volume and is subject to the same transport processes as the other state variables. Internal phosphorus is created through algal uptake and depleted by respiration and predation. Algal settling removes associated internal phosphorus. The kinetics portion of the mass-balance equation is:

\[ \frac{\delta}{\delta t} \text{PIB} = V_{max} \cdot \frac{PO_4 d}{Khp + PO_4 d} \cdot B - R \cdot B \cdot Q_0 \]

\[ -PR \cdot Q \cdot Wa \cdot \frac{\delta}{\delta z} \text{PIB} \]

(5-29)

in which \( \text{PIB} \) is the internal phosphorus concentration (g P m\(^{-3}\)).
Labile dissolved organic phosphorus

\[
\frac{\delta}{\delta t} LDOP = R \cdot B \cdot FPLD \cdot Qo + PR \cdot FPLDP \cdot Q + Klpop \\
LPOP + Krpop \cdot RPOP - Klpop \cdot LDOP + \frac{BENLDOP}{\Delta z} + \frac{SAVLPOP}{\Delta z}
\] (5-30)

in which:

- \( FPLD \) = fraction of algal respiration released as \( LDOP \) \((0 < FPLD < 1)\)
- \( FPLDP \) = fraction of predation on algae released as \( LDOP \) \((0 < FPLDP < 1)\)
- \( LPOP \) = labile particulate organic phosphorus \((g \text{ P m}^{-3})\)
- \( RPOP \) = refractory particulate organic phosphorus \((g \text{ P m}^{-3})\)
- \( Klpop \) = hydrolysis rate of \( LPOP \) \((d^{-1})\)
- \( Krpop \) = hydrolysis rate of \( RPOP \) \((d^{-1})\)
- \( BENLDOP \) = release of \( LDOP \) from sediments and benthic algae \((g \text{ P m}^{-2} d^{-1})\)
- \( SAVLPOP \) = release of \( LDOP \) from seagrass \((g \text{ P m}^{-2} d^{-1})\)

Refractory dissolved organic phosphorus

\[
\frac{\delta}{\delta t} RDOP = R \cdot B \cdot FPRD \cdot Qo + PR \cdot FPRDP \cdot Q - Krpop \cdot RDOP + \frac{BENLDOP}{\Delta z} + \frac{SAVLPOP}{\Delta z}
\] (5-31)

in which:

- \( FPRD \) = fraction of algal respiration released as \( RDOP \) \((0 < FPRD < 1)\)
- \( FPRDP \) = fraction of predation on algae released as \( RDOP \) \((0 < FPRDP < 1)\)
- \( BENLDOP \) = release of \( RDOP \) from sediments and benthic algae \((g \text{ P m}^{-2} d^{-1})\)
- \( SAVLPOP \) = release of \( RDOP \) from seagrass \((g \text{ P m}^{-2} d^{-1})\)

Labile particulate organic phosphorus

\[
\frac{\delta}{\delta t} LPOP = R \cdot B \cdot FPLP \cdot Qo + PR \cdot FPLPP \cdot Q - Klpop \\
LPOP - Wt \cdot \frac{\delta}{\delta z} LPOP + \frac{BENLPOP}{\Delta z} + \frac{SAVLPOP}{\Delta z}
\] (5-32)
in which:

\[ FPLP = \text{fraction of algal respiration released as } LPOP \ (0 < FPLP < 1) \]
\[ FPLPP = \text{fraction of predation on algae released as } LPOP \ (0 < FPLPP < 1) \]
\[ BENLPOP = \text{resuspension of } LPOP \text{ from sediments (g P m}^{-2}\text{ d}^{-1}) \]
\[ SAVLPOP = \text{release of } LPOP \text{ from seagrass (g P m}^{-2}\text{ d}^{-1}) \]

**Refractory particulate organic phosphorus**

\[
\frac{\delta}{\delta t} RPOP = R \cdot B \cdot FPRP \cdot Qo + PR \cdot FPRPP \cdot Q \cdot K\text{rpop} \\
- RPOP \cdot W \cdot \frac{\delta}{\delta z} RPOP + \frac{BENRPOP}{\Delta z} + \frac{SAVRPOP}{\Delta z} \tag{5-33}
\]

in which:

\[ FPRP = \text{fraction of algal respiration released as } RPOP \ (0 < FPRP < 1) \]
\[ FPRPP = \text{fraction of predation on algae released as } RPOP \ (0 < FPRPP < 1) \]
\[ BENRPOP = \text{resuspension of } RPOP \text{ from sediments (g P m}^{-2}\text{ d}^{-1}) \]
\[ SAVRPOP = \text{release of } RPOP \text{ from seagrass (g P m}^{-2}\text{ d}^{-1}) \]

**Nitrogen**

The model nitrogen cycle (Figure 5-18) includes the following processes:

- Algal production and respiration
- Predation
- Hydrolysis of particulate organic nitrogen
- Minimization of dissolved organic nitrogen
- Settling
- Nitrification.
External loads provide the ultimate source of nitrogen to the system. Inorganic nitrogen is incorporated by algae during growth and released as ammonium and organic nitrogen through respiration and predation. A portion of the particulate organic nitrogen hydrolyzes to dissolved organic nitrogen. The balance settles to the sediments. Dissolved organic nitrogen is mineralized to ammonium. In an oxygenated water column, a fraction of the ammonium is subsequently oxidized to nitrate through the nitrification process. Particulate nitrogen that settles to the sediments is mineralized and recycled to the water column, primarily as ammonium. Nitrate moves in both directions across the sediment-water interface, depending on relative concentrations in the water column and sediment interstices.

Analogous to the reasoning applied to carbon and phosphorus, it is assumed that hydrolysis of both labile and refractory particulate organic nitrogen produces labile dissolved organic nitrogen. Mineralization of both labile and refractory dissolved organic nitrogen produces ammonium.

**Nitrification**

Nitrification is a process mediated by specialized groups of autotrophic bacteria that obtain energy through the oxidation of ammonium to nitrite and oxidation of nitrite to nitrate. A simplified expression for complete nitrification (Tchobanoglous and Schroeder 1987) is:

\[
\text{NH}_4^+ + \text{O}_2 - - > \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ 
\]

\[ (5-34) \]
The simplified stoichiometry indicates that two moles of oxygen are required to nitrify one mole of ammonium into nitrate. The simplified equation is not strictly true, however. Cell synthesis by nitrifying bacteria is accomplished by the fixation of carbon dioxide so that less than two moles of oxygen are consumed per mole ammonium utilized (Wezemak and Gannon 1968).

The kinetics of complete nitrification are modeled as a function of available ammonium, dissolved oxygen, and temperature:

\[
NT = \frac{DO}{KHont + DO} \cdot \frac{NH4}{KHnnt + NH4} \cdot f(T) \cdot NTm
\]  

(5-35)

in which:

\(NT\) = nitrification rate (g N m\(^{-3}\) d\(^{-1}\))

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

\(KHnnt\) = half-saturation constant of NH\(_4\) required for nitrification (g N m\(^{-3}\))

\(NTm\) = maximum nitrification rate at optimal temperature (g N m\(^{-3}\) day\(^{-1}\))

The kinetics formulation (Figure 5-19) incorporates the products of two "Monod" functions. The first function diminishes nitrification at low DO concentration. The second function expresses the influence of ammonium concentration on nitrification. When ammonium concentration is low relative to KHnnt, nitrification is proportional to ammonium concentration. For NH\(_4\) \(<<\) KHnnt, the reaction is approximately first-order. (The first-order decay constant \(\approx NTm/KHnnt\).) When ammonium concentration is large relative to KHnnt, nitrification approaches a maximum rate. This formulation is based on a concept proposed by Tuffey et al. (1974). Nitrifying bacteria adhere to benthic or suspended sediments. When ammonium is scarce, vacant surfaces suitable for nitrifying bacteria exist. As ammonium concentration increases, bacterial biomass increases, vacant surfaces are occupied, and the rate of nitrification increases. The bacterial population attains maximum density when all surfaces suitable for bacteria are occupied. At this point, nitrification proceeds at a maximum rate independent of additional increase in ammonium concentration.

The optimal temperature for nitrification may be less than peak temperatures that occur in coastal waters. To allow for a decrease in nitrification at superoptimal temperature, the effect of temperature on nitrification is modeled in the Gaussian form of Equation 5-11.
Nitrogen mass balance equations

The mass-balance equation for nitrogen state variables are written by summing all previously described sources and sinks:

Ammonium

\[
\frac{\delta}{\delta t} NH_4 = Anc \cdot \left[ (BM \cdot FNI - PN \cdot P) \cdot B + PR \cdot FNIP \right] + Kldon \cdot LDON + Krdon \cdot RDON - NT + \frac{BENNHH4}{\Delta z} + \frac{SAVNHH4}{\Delta z}
\]  

(5-36)

in which:

- \( LDON = \) labile dissolved organic nitrogen (g N m\(^{-3}\))
- \( RDON = \) refractory dissolved organic nitrogen (g N m\(^{-3}\))
- \( FNI = \) fraction of algal respiration released as NH\(_4\) (0 \(\leq FNI \leq 1\))
- \( PN = \) algal ammonium preference (0 \(\leq PN \leq 1\))
- \( FNIP = \) fraction of predation released as NH\(_4\) (0 \(\leq FNIP \leq 1\))
- \( BENNH4 = \) release of ammonium from sediments and benthic algae (g N m\(^{-2}\) d\(^{-1}\))
- \( SAVNH4 = \) release of ammonium from seagrass (g N m\(^{-2}\) d\(^{-1}\)).
Nitrate

\[
\frac{\delta}{\delta t} \text{NO}_3 = -\text{Anc} \cdot (1 - \text{PN}) \cdot \text{P} \cdot \text{B} + \text{NT} + \frac{\text{BENNO}_3 - \text{SAVNO}_3}{\Delta z} \Delta z
\]  \hspace{1cm} (5-37)

in which:

\text{BENNO}_3 = \text{release of nitrate from sediments and benthic algae (g N m}^{-2} \text{ d}^{-1})

\text{SAVNO}_3 = \text{nitrate uptake by seagrass (g N m}^{-2} \text{ d}^{-1}).

Labile dissolved organic nitrogen

\[
\frac{\delta}{\delta t} \text{LDON} = \text{Anc} \cdot (\text{BM} \cdot \text{B} \cdot \text{FNLD} + \text{PR} \cdot \text{FNLDP}) + \text{Klpon} \cdot \text{LPON} + \text{Krpon} \cdot \text{RPON} - \text{Kldon} \cdot \frac{\text{LDON}}{\Delta z} + \frac{\text{SAVLDON}}{\Delta z}
\]  \hspace{1cm} (5-38)

in which:

\text{LPON} = \text{labile particulate organic nitrogen (g P m}^{-3})

\text{RPON} = \text{refractory particulate organic nitrogen (g P m}^{-3})

\text{FNLD} = \text{fraction of algal respiration released as LDON (0 < FNLD < 1)}

\text{FNLDP} = \text{fraction of predation on algae released as LDON (0 < FNLDP < 1)}

\text{Klpon} = \text{hydrolysis rate of LPON (d}^{-1})

\text{Krpon} = \text{hydrolysis rate of RPON (d}^{-1})

\text{Kldon} = \text{mineralization rate of LDON (d}^{-1})

\text{BENLDON} = \text{release of LDON from sediments and benthic algae (g P m}^{-2} \text{ d}^{-1})

\text{SAVLDON} = \text{release of LDON from seagrass (g P m}^{-2} \text{ d}^{-1}).

Refractory dissolved organic nitrogen

\[
\frac{\delta}{\delta t} \text{RDON} = \text{Anc} \cdot (\text{BM} \cdot \text{B} \cdot \text{FNRD} + \text{PR} \cdot \text{FNRD}) - \text{Krten} \cdot \text{RDON} + \frac{\text{BENRDON}}{\Delta z} + \frac{\text{SAVRDON}}{\Delta z}
\]  \hspace{1cm} (5-39)

in which:

\text{FNRD} = \text{fraction of algal respiration released as RDON (0 < FNRD < 1)}
\[ FNRDP = \text{fraction of predation on algae released as } RDON \]
\[ (0 < FNRDP < 1) \]

\[ Kldon = \text{mineralization rate of } RDON \ (\text{d}^{-1}) \]

\[ BENRDON = \text{release of } RDON \text{ from sediments and benthic algae (g P m}^{-2} \text{ d}^{-1}) \]

\[ SAVRDON = \text{release of } RDON \text{ from seagrass (g P m}^{-2} \text{ d}^{-1}) \]

**Labile particulate organic nitrogen**

\[
\frac{\delta}{\delta t} LPON = Anc \cdot (BM \cdot B \cdot FNLP + PR \cdot FNLPP) - Klpon \\
\cdot LPON - WI \cdot \frac{\delta}{\delta z} LPON + \frac{BENLPON}{\Delta z} + \frac{SAVLPON}{\Delta z} \tag{5-40}
\]

in which:

\[ FNLP = \text{fraction of algal respiration released as } LPON \ (0 < FNLP < 1) \]
\[ FNLPP = \text{fraction of predation on algae released as } LPON \]
\[ (0 < FNLPP < 1) \]

\[ BENLPON = \text{resuspension of } LPON \text{ from sediments (g N m}^{-2} \text{ d}^{-1}) \]

\[ SAVLPON = \text{release of } LPON \text{ from seagrass (g N m}^{-2} \text{ d}^{-1}) \]

**Refractory particulate organic nitrogen**

\[
\frac{\delta}{\delta t} RPON = Anc \cdot (BM \cdot B \cdot FNRP + PR \cdot FNRPP) - \\
Kron \cdot RPON - Wr \cdot \frac{\delta}{\delta z} RPON + \frac{BENRPON}{\Delta z} \tag{5-41}
\]

in which:

\[ FNRP = \text{fraction of algal respiration released as } RPON \ (0 < FNRP < 1) \]
\[ FNRPP = \text{fraction of predation on algae released as } RPON \ (0 < FNRPP < 1) \]

\[ BENRPON = \text{resuspension of } RPON \text{ from sediments (g N m}^{-2} \text{ d}^{-1}) \]

\[ SAVRPON = \text{release of } RPON \text{ from seagrass (g N m}^{-2} \text{ d}^{-1}) \]

**Silica**

The model incorporates two siliceous state variables, dissolved silica and particulate biogenic silica. The silica cycle (Figure 5-20) is a simple one in which diatoms take up available silica and recycle available and particulate biogenic silica through the actions of respiration and predation. Particulate silica dissolves in the water column or settles to the bottom. A portion of the settled
particulate biogenic silica dissolves within the sediments and returns to the water column. Sources and sinks represented are:

- Diatom production and respiration
- Predation
- Dissolution of particulate to dissolved silica
- Settling

![Diagram of silica cycle](image)

**Dissolved silica.** The kinetics equation for dissolved silicia is:

\[
\frac{\partial}{\partial t} SA = \text{Asc} \cdot (-P \cdot B + FSAP \cdot PR) + Kpbs \cdot PBS + \frac{\text{BENSA}}{\Delta z} \quad (5-42)
\]

in which:

- \(SA\) = dissolved silica (g Si m\(^{-3}\))
- \(\text{Asc}\) = algal silica-to-carbon ratio (g Si g\(^{-1}\) C)
- \(FSAP\) = fraction of predation released as dissolved silica (0 < FSAP < 1)
- \(PBS\) = particulate biogenic silica (g Si m\(^{-3}\))
- \(Kpbs\) = particulate biogenic silica dissolution rate (d\(^{-1}\))
- \(\text{BENSA}\) = release of \(SA\) from sediments (g Si m\(^{-2}\) d\(^{-1}\)).

The model allows a silica-to-carbon ratio to be defined for each algal group. This flexibility provides for the definition of groups consisting of mixtures of diatoms and other phytoplankton.
Particulate biogenic silica. The kinetics equation for particulate biogenic silica is:

\[
\frac{\delta}{\delta t} PBS = Asc \cdot [R \cdot B -(1 - \text{Fsap}) \cdot PR] \\
- Kpbs \cdot PBS \cdot Wpbs \frac{\delta}{\delta z} PBS
\]  

(5-43)

in which \( Wpbs \) is the settling velocity of particulate biogenic silica (m day\(^{-1} \)).

**Chemical Oxygen Demand**

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

\[
\frac{\delta}{\delta t} COD = - \frac{DO}{KHocod + DO} \cdot Kcod \cdot COD
\]  

(5-44)

in which:

- \( COD \) = chemical oxygen demand concentration (g oxygen-equivalents m\(^{-3} \))
- \( KHocod \) = half-saturation concentration of DO required for exertion of chemical oxygen demand (g O\(_2\) m\(^{-3} \))
- \( Kcod \) = oxidation rate of chemical oxygen demand (d\(^{-1} \)).

An exponential function (Figure 5-13) describes the effect of temperature on exertion of chemical oxygen demand.

**Dissolved Oxygen**

Sources and sinks of DO in the water column (Figure 5-21) include:

- Algal photosynthesis
- Atmospheric reaeration
- Algal respiration
- Heterotrophic respiration
- Nitrification
- Chemical oxygen demand
- Photo-oxidation
Reaeration

The reaeration rate is proportional to the DO deficit in model segments that from the air-water interface:

$$\frac{\delta}{\delta t} \frac{DO}{\Delta z} = \frac{Kr}{DOs - DO}$$  \hspace{1cm} (5-45)

in which:

- $DO = \text{dissolved oxygen concentration (g O}_2 \text{ m}^{-3}$)
- $Kr = \text{reaeration coefficient (m d}^{-1}$
- $DOs = \text{dissolved oxygen saturation concentration (g O}_2 \text{ m}^{-3}$).

In freeflowing streams, the reaeration coefficient depends largely on turbulence generated by bottom shear stress (O'Connor and Dobbins 1958). In lakes and coastal waters, however, wind effects may dominate the reaeration process (O'Connor 1983). The model employs a relationship for wind-driven gas exchange (Hartman and Hammond 1985):

$$Kr = 0.157 \cdot Rv \cdot Wms^{1.5}$$  \hspace{1cm} (5-46)
in which:

\[ R_v = \frac{\text{ratio of kinematic viscosity of pure water at } 20 \, ^\circ C \text{ to kinematic viscosity of water at specified temperature and salinity}}{\text{wind speed measured at } 10 \, \text{m above water surface (m s}^{-1})).} \]

An empirical function that fits (Figure 5-22) tabulated values of \( R_v \) is:

\[ R_v = 0.54 + 0.0233 \cdot T - 0.0020 \cdot S \quad (5-47) \]

in which \( S \) is salinity (ppt).

![Figure 5-22. Computed and tabulated values of \( R_v \)](image)

Saturation DO concentration diminishes as temperature and salinity increase. An empirical formula that describes these effects (Genet et al. 1974) is:

\[ DO_s = 14.5532 - 0.38217 \cdot T + 0.0054258 \cdot T^2 \\
- CL \cdot \left( 1.665 \cdot 10^4 - 5.866 \cdot 10^6 \cdot T + 9.796 \cdot 10^3 \cdot T^2 \right) \quad (5-48) \]
in which:

\[ CL = \text{chloride concentration} \quad (= \text{salinity/}1.80655) \]
\[ T = \text{temperature (}^\circ\text{C}). \]

**Mass balance equation for DO**

\[
\frac{\delta}{\delta t} DO = Aocr \cdot (P - R) \cdot B - Aont \cdot NT
\]
\[
- Aocr \cdot (Kldoc \cdot LDOC + Krdoc \cdot RDOC)
\]
\[
- Aocr \cdot (1 - Fcoag) \cdot Iavg \cdot Krelit \cdot RDOC
\]
\[
- Kcod \cdot COD + \frac{Kr}{\Delta z} \cdot (DOs - DO) + \frac{BENDO}{\Delta z} + \frac{SAVDO}{\Delta z}
\]

in which:

\[ Aocr = \text{oxygen-to-carbon mass ratio in production, respiration, and photo-oxidation} \quad (= 2.67 \text{ g O}_2 \text{ g}^{-1} \text{ C}) \]
\[ Aont = \text{oxygen consumed per mass ammonium nitrified} \quad (= 4.33 \text{ g O}_2 \text{ g}^{-1} \text{ N}) \]
\[ BENDO = \text{sediment oxygen flux (g DO m}^{-2} \text{ d}^{-1}) \]
\[ SAVDO = \text{seagrass dissolved oxygen production (g DO m}^{-2} \text{ d}^{-1}). \]

**Temperature**

Computation of temperature uses a conservation of internal energy equation that is analogous to the conservation of mass equation. For practical purposes, the internal energy equation can be written as a conservation of temperature equation. The only source or sink of temperature considered is exchange with the atmosphere. Atmospheric exchange is considered proportional to the temperature difference between the water surface and a theoretical equilibrium temperature (Edinger et al. 1974):

\[
\frac{\delta}{\delta t} T = \frac{KT}{\rho \cdot Cp \cdot H} \cdot (Te - T)
\]

in which:

\[ T = \text{water temperature (}^\circ\text{C}) \]
\[ Te = \text{equilibrium temperature (}^\circ\text{C}) \]
\[ KT = \text{Heat exchange coefficient (watt m}^{-2} \text{ }^\circ\text{C}^{-1}) \]
\[ C_p = \text{specific heat of water (4,200 watt s kg}^{-1} \text{C}^{-1}) \]
\[ \rho = \text{density of water (1,000 kg m}^{-3}) \]

**Inorganic (Fixed) Solids**

The only internal sources and sinks of fixed solids are resuspension and settling. To account for resuspension dynamically requires a sediment transport model linked to the hydrodynamic model. In the absence of such a model, resuspension is considered in a long-term, average sense. Net settling to the bottom sediments is specified less than settling through the water column. The difference between settling through the water and settling into the sediments is the quantity resuspended:

\[
\frac{\delta}{\delta t} \text{ISS} = -Wiss \cdot \frac{\delta}{\delta z} \text{ISS} + (Wiss - Wissnet) \frac{\text{ISS}}{\Delta z}
\]

in which:

- \( \text{ISS} \) = fixed solids concentration (g m\(^{-3}\))
- \( Wiss \) = solids settling velocity (m d\(^{-1}\))
- \( Wissnet \) = net settling to sediments (m d\(^{-1}\))

Resuspension is represented by the term involving \( Wissnet \) and is evaluated in the bottom cell of the water column only.

**Light attenuation**

Fixed solids are one component of light attenuation, which is computed:

\[
Kess = Keb + Kevss \cdot VSS + Keiss \cdot \text{ISS} + Kedoc \cdot RDOC
\]

in which:

- \( Kess \) = diffuse light attenuation (m\(^{-1}\))
- \( Keb \) = background light attenuation (m\(^{-1}\))
- \( Kevss \) = attenuation coefficient for volatile solids (m\(^2\) g\(^{-1}\))
- \( VSS \) = volatile solids concentration (g m\(^{-3}\))
- \( Keiss \) = attenuation coefficient for fixed solids (m\(^2\) g\(^{-1}\))
- \( Kedoc \) = attenuation coefficient for refractory dissolved organic carbon (m\(^2\) g\(^{-1}\))

Volatile solids are computed from the sum of algal biomass and particulate organic carbon. These state variables, as carbon, are converted to solids using a ratio 2.5 g solids g\(^{-1}\) C (assuming organic matter is composed of carbon, hydrogen, and oxygen in the atomic ratio 1:2:1). Attenuation by phytoplankton chlorophyll is taken into account in the parameter that relates attenuation to volatile solids.
Salinity

Salinity is modeled by the conservation of mass equation with no internal sources or sinks.

Parameter Values

Model parameter evaluation is a recursive process. Parameters are selected from a range of feasible values, tested in the model, and adjusted until satisfactory agreement between predicted and observed variables is obtained. Ideally, the range of feasible values is determined by observation or experiment. For some parameters, however, no observations are available. Then, the feasible range is determined by parameter values employed in similar models or by the judgment of the modeler. For the St. Johns River, an initial parameter set was adapted from the Chesapeake Bay study (Cerco and Cole 1994), the most extensive model application to date. Parameter values were adjusted, where appropriate, for the subtropical environment. Subsequent adjustment was performed to improve agreement between model and observations. A complete set of parameter values is provided in Table 5-3.

Table 5-3
Parameters in Kinetics Equations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>AANOX</td>
<td>ratio of anoxic to oxic respiration</td>
<td>0.5</td>
<td>0 &lt; AANOX ≤ 1</td>
</tr>
<tr>
<td>ANC</td>
<td>nitrogen-to-carbon ratio of algae</td>
<td>0.135 (diatoms), 0.175 (other)</td>
<td>g N g^-1 C</td>
</tr>
<tr>
<td>AOCR</td>
<td>dissolved oxygen-to-carbon ratio in respiration</td>
<td>2.67</td>
<td>g O2 g^-1 C</td>
</tr>
<tr>
<td>AONT</td>
<td>mass DO consumed per mass ammonium nitrified</td>
<td>4.33</td>
<td>g O2 g^-1 N</td>
</tr>
<tr>
<td>Qo</td>
<td>minimum cell quota</td>
<td>0.004 (blue greens), 0.005 (other)</td>
<td>g P g^-1 C</td>
</tr>
<tr>
<td>Vmax</td>
<td>maximum uptake rate</td>
<td>0.006 (diatoms), 0.0033 (cyan), 0.0044 (greens)</td>
<td>g P g^-1 C</td>
</tr>
<tr>
<td>Areaer</td>
<td>empirical constant in reaeration equation</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>ASC</td>
<td>algal silica-to-carbon ratio</td>
<td>0.0 (cyan), 0.8 (diatom), 0.0 (green)</td>
<td>g Si g^-1 C</td>
</tr>
<tr>
<td>BMr</td>
<td>basal metabolic rate of algae at reference temperature</td>
<td>0.05 (cyan), 0.05 (diatom), 0.05 (green)</td>
<td>d^-1</td>
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<tr>
<td>FCLDP</td>
<td>fraction of labile dissolved carbon produced by predation</td>
<td>0.1</td>
<td>0 ≤ FCLDP ≤ 1</td>
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<tr>
<td>FCRDP</td>
<td>fraction of refractory dissolved carbon produced by predation</td>
<td>0.2</td>
<td>0 ≤ FCRDP ≤ 1</td>
</tr>
<tr>
<td>FCLPP</td>
<td>fraction of labile particulate carbon produced by predation</td>
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<td>0 ≤ FCLPP ≤ 1</td>
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(Sheet 1 of 4)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCRPP</td>
<td>fraction of refractory particulate carbon produced by predation</td>
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<td>$0 \leq \text{FCRPP} \leq 1$</td>
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<tr>
<td>FNI</td>
<td>fraction of inorganic nitrogen produced by algal metabolism</td>
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<td>$0 \leq \text{FNI} \leq 1$</td>
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<td>FNIP</td>
<td>fraction of inorganic nitrogen produced by predation</td>
<td>0.4</td>
<td>$0 \leq \text{FNIP} \leq 1$</td>
</tr>
<tr>
<td>FNLD</td>
<td>fraction of labile dissolved organic nitrogen produced by algal metabolism</td>
<td>0.18</td>
<td>$0 \leq \text{FNLD} \leq 1$</td>
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<tr>
<td>FNLDP</td>
<td>fraction of labile dissolved organic nitrogen produced by predation</td>
<td>0.18</td>
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<td>fraction of refractory dissolved organic nitrogen produced by algal metabolism</td>
<td>0.02</td>
<td>$0 \leq \text{FNRD} \leq 1$</td>
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<tr>
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<td>0.2</td>
<td>$0 \leq \text{FNRDP} \leq 1$</td>
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<tr>
<td>FNLP</td>
<td>fraction of labile particulate organic nitrogen produced by algal metabolism</td>
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<td>$0 \leq \text{FNLP} \leq 1$</td>
</tr>
<tr>
<td>FNLP</td>
<td>fraction of labile particulate organic nitrogen produced by predation</td>
<td>0.2</td>
<td>$0 \leq \text{FNLP} \leq 1$</td>
</tr>
<tr>
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<td>0.05</td>
<td>$0 \leq \text{FNRP} \leq 1$</td>
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<tr>
<td>FNRPP</td>
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<td>0.1</td>
<td>$0 \leq \text{FNRPP} \leq 1$</td>
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<tr>
<td>FPLD</td>
<td>fraction of labile dissolved organic phosphorus produced by algal metabolism</td>
<td>0.2</td>
<td>$0 \leq \text{FPLD} \leq 1$</td>
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<td>0.36</td>
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<tr>
<td>FPRD</td>
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<td>$0 \leq \text{FPRD} \leq 1$</td>
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<td>0.04</td>
<td>$0 \leq \text{FPRDP} \leq 1$</td>
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<tr>
<td>FPI</td>
<td>fraction of dissolved inorganic phosphorus produced by algal metabolism</td>
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<td>FPIP</td>
<td>fraction of dissolved inorganic phosphorus produced by predation</td>
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<td>$0 \leq \text{FPIP} \leq 1$</td>
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<td>FPLP</td>
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<td>$0 \leq \text{FPLP} \leq 1$</td>
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<td>fraction of refractory particulate phosphorus produced by predation</td>
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<td>oxidation rate of chemical oxygen demand</td>
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<td>constant that relates mineralization rate to algal biomass</td>
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<td>half-saturation concentration for nitrogen uptake by algae</td>
<td>0.02 (cyan), 0.03 (diatoms), 0.025 (greens)</td>
<td>g N m$^{-3}$</td>
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Table 5-3 (Continued)

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<td>0.1</td>
<td>g N m(^{-3})</td>
</tr>
<tr>
<td>KHnnt</td>
<td>half-saturation concentration of NH(_4) required for nitrification</td>
<td>1.0</td>
<td>g N m(^{-3})</td>
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<tr>
<td>KHocod</td>
<td>half-saturation concentration of dissolved oxygen required for exertion of COD</td>
<td>0.5</td>
<td>g O(_2) m(^{-3})</td>
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<td>0.5</td>
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<td>half-saturation concentration of dissolved oxygen required for nitrification</td>
<td>1.0</td>
<td>g O(_2) m(^{-3})</td>
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<td>g P m(^{-3})</td>
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<tr>
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<td>half-saturation concentration for silica uptake by algae</td>
<td>0.0 (cyan), 0.03 (diatom), 0.01 (green)</td>
<td>g Si m(^{-3})</td>
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<td>KIst</td>
<td>salinity at which algal mortality is half maximum value</td>
<td>2.0 (cyan), 2.0 (diatom), 35.0 (green)</td>
<td>ppt</td>
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<td>Klpoc</td>
<td>labile particulate organic carbon dissolution rate</td>
<td>0.075</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>KIdoc</td>
<td>labile dissolved organic carbon dissolution rate</td>
<td>0.05</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Klp</td>
<td>labile particulate organic nitrogen hydrolysis rate</td>
<td>0.0375</td>
<td>d(^{-1})</td>
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<tr>
<td>KIdon</td>
<td>labile dissolved organic nitrogen hydrolysis rate</td>
<td>0.025</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Klpop</td>
<td>labile particulate organic phosphorus hydrolysis rate</td>
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<td>d(^{-1})</td>
</tr>
<tr>
<td>KIdop</td>
<td>labile dissolved organic phosphorus hydrolysis rate</td>
<td>0.1</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Kbpoc</td>
<td>refractory particulate organic carbon dissolution rate</td>
<td>0.0025</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Kbdoc</td>
<td>refractory dissolved organic carbon dissolution rate</td>
<td>0.0025</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Kbp</td>
<td>refractory particulate organic nitrogen hydrolysis rate</td>
<td>0.0025</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Kbdon</td>
<td>refractory dissolved organic nitrogen hydrolysis rate</td>
<td>0.0025</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Kbpop</td>
<td>refractory particulate organic phosphorus hydrolysis rate</td>
<td>0.005</td>
<td>d(^{-1})</td>
</tr>
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<td>Kbdop</td>
<td>refractory dissolved organic phosphorus hydrolysis rate</td>
<td>0.01</td>
<td>d(^{-1})</td>
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<td>Kpbs</td>
<td>biogenic silica dissolution rate</td>
<td>0.03</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Ktb</td>
<td>effect of temperature on basal metabolism of algae</td>
<td>0.032</td>
<td>°C(^{-1})</td>
</tr>
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<td>KTood</td>
<td>effect of temperature on exertion of chemical oxygen demand</td>
<td>0.041</td>
<td>d(^{-1})</td>
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<td>KTg1</td>
<td>effect of temperature below Tm on growth of algae</td>
<td>0.007 (cyan), 0.006 (diatoms), 0.004 (green)</td>
<td>°C(^{-2})</td>
</tr>
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<td>KTg2</td>
<td>effect of temperature above Tm on growth of algae</td>
<td>0.004 (cyan), 0.003 (diatoms), 0.010 (green)</td>
<td>°C(^{-2})</td>
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<tr>
<td>KThdr</td>
<td>effect of temperature on hydrolysis rates</td>
<td>0.092</td>
<td>°C(^{-1})</td>
</tr>
<tr>
<td>KTMn1</td>
<td>effect of temperature on mineralization rates</td>
<td>0.092</td>
<td>°C(^{-1})</td>
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<tr>
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<td>°C(^{-1})</td>
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<tr>
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<td>°C(^{-1})</td>
</tr>
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<td>KTSua</td>
<td>effect of temperature on biogenic silica dissolution</td>
<td>0.092</td>
<td>°C(^{-1})</td>
</tr>
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<td>Krclt</td>
<td>photoreaction rate</td>
<td>0.0</td>
<td>(Em(^{-1}))(^{-1})</td>
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<td>Fcoag</td>
<td>fraction of dissolved organic carbon coagulated</td>
<td>0.0</td>
<td>0 ≤ Fcoag • 1</td>
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(Sheet 3 of 4)
<table>
<thead>
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<th>Symbol</th>
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<th>Value</th>
<th>Units</th>
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<tr>
<td>NTm</td>
<td>maximum nitrification rate at optimal temperature</td>
<td>0.1 to 0.5</td>
<td>g N m(^{-3}) d(^{-1})</td>
</tr>
<tr>
<td>Phtl</td>
<td>predation rate on algae</td>
<td>0.05 (cyan), 1.0 (diatom), 1.0 (green)</td>
<td>m(^3) g(^{-1}) C d(^{-1})</td>
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<tr>
<td>Pm(^b)</td>
<td>maximum photosynthetic rate</td>
<td>200 (cyan), 350 (diatom), 200 (green)</td>
<td>g C g(^{-1}) Chi d(^{-1})</td>
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<td>Presp</td>
<td>photo-respiration fraction</td>
<td>0.25</td>
<td>0 &lt; Presp &lt; 1</td>
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<td>STF</td>
<td>salinity toxicity factor</td>
<td>0.2 (cyan), 0.1 (others)</td>
<td>d(^{-1})</td>
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<td>optimal temperature for growth of algae</td>
<td>35 (cyan), 25 (diatom), 35 (green)</td>
<td>°C</td>
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<tr>
<td>Tmnt</td>
<td>optimal temperature for nitrification</td>
<td>30</td>
<td>°C</td>
</tr>
<tr>
<td>Tr</td>
<td>reference temperature for metabolism</td>
<td>20</td>
<td>°C</td>
</tr>
<tr>
<td>Trhdr</td>
<td>reference temperature for hydrolysis</td>
<td>20</td>
<td>°C</td>
</tr>
<tr>
<td>Trml</td>
<td>reference temperature for mineralization</td>
<td>20</td>
<td>°C</td>
</tr>
<tr>
<td>Trsua</td>
<td>reference temperature for biogenic silica dissolution</td>
<td>20</td>
<td>°C</td>
</tr>
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<td>Wa</td>
<td>algal settling rate</td>
<td>0.0 (cyan), 0.1 (other)</td>
<td>m d(^{-1})</td>
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<td>Wl</td>
<td>settling velocity of labile particles</td>
<td>0.25</td>
<td>m d(^{-1})</td>
</tr>
<tr>
<td>Wr</td>
<td>settling velocity of refractory particles</td>
<td>0.25</td>
<td>m d(^{-1})</td>
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<tr>
<td>Wiss</td>
<td>settling velocity of fixed solids</td>
<td>0.75</td>
<td>m d(^{-1})</td>
</tr>
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<td>Wbps</td>
<td>settling velocity of biogenic silica</td>
<td>0.25</td>
<td>m d(^{-1})</td>
</tr>
<tr>
<td>Keb</td>
<td>background light attenuation</td>
<td>0.03</td>
<td>m(^{-1})</td>
</tr>
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<td>Kevss</td>
<td>attenuation coefficient for volatile solids</td>
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<td>m(^2) g(^{-1})</td>
</tr>
<tr>
<td>Keiss</td>
<td>attenuation coefficient for fixed solids</td>
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<td>m(^2) g(^{-1})</td>
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<td>Kedoc</td>
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<td>0.15</td>
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<td>α</td>
<td>initial slope of production vs. irradiance relationship</td>
<td>3.15 (cyan), 8.0 (other)</td>
<td>g C g(^{-1}) Chi (E m(^{-2}))</td>
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</table>

**References**


6 Water Column Calibration Results

The Calibration Period

The SJRWMD chose 1 December 1996 to 30 November 1998 as the calibration period. Calibration is an iterative process; consequently, more than 50 model runs were made in the effort to calibrate the model. In each run, model parameters or other factors were adjusted until an adequate fit between observations and model results was obtained. Calibration was considered complete when no substantial improvement in calibration status resulted from additional adjustments. Final model parameters were presented in Chapter 5 (Table 5-3).

Hydrodynamics for the 2-year calibration period were obtained from an EFDC application by the SJRWMD. The sources and update periods of the forcing functions used to drive the hydrodynamics for the simulation period are discussed in Suscy and Morris (2002).

Wind speed during the 2-year simulation period exhibited a minor seasonal variability displayed as a rough sinusoidal pattern with higher wind speeds occurring in the winter months and lower wind speeds occurring in the late summer months (Figure 6-1). The windiest 3-month period usually occurred from February-April and the calmest from July-September, with a 24 percent difference between the two periods (Suscy and Morris 2002). Wind patterns showed deviations during the simulation period. For instance, wind speeds during summer 1997 (especially in July) were higher on the average than what had occurred in summer 1996. Moreover, winter speeds during the winter months in 1997 were of a greater magnitude than what had occurred during the winter of the previous year.

Suscy and Morris (2002) examined wind directions by creating cumulative wind-run plots for east and north components of the observed wind vector. During the simulation period for the St. Johns River, the east-west wind component showed relatively low seasonal variability, the wind-run plot indicating a long period of nearly zero net east-west wind movement (July 1996-November 1997). Predominate west winds occurred from November 1997 to August 1998. In contrast, according to Suscy and Morris (2002), the north-south wind component showed a definite seasonal variability with north winds.
Day 1 From Beginning of Simulation Year

Figure 6-1. Wind speed for both simulation years

Predominating in early fall (September-October) to early winter (December-January) and south winds predominating in early spring (February-March) to late summer (September-October).

TP and TN loads during the simulation period were separated into two source types - point (PS) and non-point source (NPS) (refer to Chapter 4). Magnitudes of TP from PS loads showed small variations from month to month for each segment (Figure 4-1), but magnitudes of loads for the six river segments ranged from a low of 85 to 1,200 kg/day. Average TP PS load values were approximately 100 kg/day for all segments except segment 4, which received the highest average loads of 1,000 kg/day. TP loads from NPSs showed the greatest deviations in loading magnitudes from month to month for each river segment. Segments 1, 2, and 4 showed similar peak TP loads during August and December 1997, and February and August 1998 (Figures 4-14, 4-15, and 4-17) while segments 3, 5, and 6 showed peak TP loads during these months as well as April and November 1997 (Figures 4-16, 4-18, and 4-19). NPS peak loads did not follow the convention of the wet season (June-October) entirely. The winter of 1997-1998 was an exceptionally wet period (Sucsy and Morris 2002) resulting in the notably higher loads.

Similar to TP loadings, TN PS and NPS loads showed similar loading patterns. Magnitudes of TN PS loads showed small variations from month to month for each segment, but values of loads per segment ranged from a low of 65 to 4,100 kg/day. While most segments received similar TP PS loads, average TN PS loads varied from 100 kg/day for segment 5, to 250 kg/day for segment 1, to 700 kg/day for segments 2 and 6, and to 2,750 kg/day for segment 4. Comparable to TP NPS loads, TN NPS loads showed the most variations in magnitude from month to month for each river segment. Segments 1, 2, and 4 showed similar peak TN loads especially during December 1997 through March.
1998 and August 1998 (Figures 4-20, 4-21, and 4-23) while segments 3, 5, and 6 showed peak TN loads during these months as well as late spring/early summer 1997 (Figures 4-22, 4-24, and 4-25). As just discussed for TP NPS peak loads, TN NPS peak loads did not follow the convention of the wet season entirely either. With the 1997-1998 winter being abnormally wet, TN NPS loads peaked during this period.

**Presentation Formats**

CE-QUAL-ICM calibration performance was evaluated by comparing model output with observed data. Numerous methods were used to present and analyze model results. Three forms of graphical comparison were used: time-series plots (Figures 6-2 through 6-4), monthly longitudinal plots (Figure 6-5), and percent cumulative frequency plots (Figure 6-6). In addition, four statistics, mean error (ME), absolute mean error (AME), root mean square error (RMSE), and relative error (RE) were calculated to further evaluate model performance.

**Statistics**

The RMSE is an indicator of the deviation between predicted water quality values and observed values. A value of zero would indicate no variation between the observed and predicted. The ME indicates on average how the model is doing. For example, a positive ME indicates predictions are less than observed and a negative ME indicates predictions exceed observed. A value of zero for ME would also indicate complete agreement between predicted and observed. The AME indicates the how model reproduces data on average. An AME of 0.5 °C means that the computed temperatures are, on average, within ± 0.5 °C of the observed temperatures. Lastly, the RE is the ratio of the AME to the mean of observations expressed as a percent. The RE is the best statistic to use to make comparisons of model performance between other study results since it has been normalized. Each statistic was calculated for all data where observed data were available; data were not distinguished by layer, thus in essence getting the overall model performance. The equations for each statistic are presented below:

\[
ME = \frac{\sum (O - P)}{n}
\]  

in which:

\[
O = \text{observation}
\]

\[
P = \text{model prediction}
\]

\[
n = \text{number of observations},
\]

\[
AME = \frac{\sum |O - P|}{n},
\]  

\[
RMSE = \sqrt{\frac{\sum (O - P)^2}{n}}
\]  

\[
RE = \frac{AME}{\bar{O}}
\]
\[ RMSE = \sqrt{\frac{\sum (O - P)^2}{n}} \]  

(6-3)

and

\[ RE = \frac{\sum |O - P|}{\sum O} \cdot 100 \]  

(6-4)

Tables 6-1 through 6-4 present the value for each statistic for a particular water quality constituent of the LSJR results.

**Graphical plots**

Three graphical plot types will be used to evaluate model performance. Beginning with Time-series plots, comparison of time-specific model output (12:00 P.M.) and observed data demonstrate model performance over time and provide indications of interactions between modeled parameters. From the model output, constituent concentrations were selected that corresponded to the day and location at which the observed data were collected. Time-series plots were generated for stations shown in Figure 1-1. Only results at three stations (Fulton Point, Piney Point, and Picolota) are presented here (Figures 6-2 through 6-4). Results for all other stations are available from the first author on CD-ROM.

Monthly longitudinal plots synopsise overall model performance along the longitudinal profile of the river. Monthly averaged concentrations were output for all cells. Comparisons were made between observed data and a monthly averaged computed value that corresponds to the location and month the data were collected. Results for longitudinal profiles were presented during a month critical to water quality (i.e., August). The remaining monthly longitudinal plots are provided on a CD-ROM. A point to consider when viewing the longitudinal comparisons is that comparison of monthly averaged constituent concentrations to time-specific observed values will make the computed values appear not as robust as the observed (missed peak and low values). This gives the appearance that the model is over- or under-predicting observed data. For example, if the observed value were collected during an extreme event but the average does not show it, this may be interpreted as poor model performance.

The third and final graphical form used to evaluate model performance is the cumulative distribution plot. The percent cumulative distribution plots (Figure 6-6) show how concentration distribution of the predicted values compare with observed data (i.e., does CE-QUAL-ICM capture the range of low to high concentrations for a particular variable).
Table 6-1
Combined Water Quality Statistics for All Stations

<table>
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<tr>
<th></th>
<th>ME (%)</th>
<th>AME (%)</th>
<th>RMSE (%)</th>
<th>RE (%)</th>
<th>Number of Observations</th>
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<tbody>
<tr>
<td>Alg1</td>
<td>-0.0995</td>
<td>0.2263</td>
<td>0.3999</td>
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<td>0.2238</td>
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<td>0.0626</td>
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<td>6.3779</td>
<td>10.5498</td>
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<td>DIN</td>
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<td>0.1058</td>
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<td>DIP</td>
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<td>0.0385</td>
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### Table 6-4 (Concluded)

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**Temperature**

Time-series plots for three stations are presented in Figures 6-2 through 6-4. Figures indicate good comparison between observed and predicted results. CEQUAL-ICM captured the cooler early summer temperatures in 1997 as compared to temperatures during the same time period in 1998. This is also noted by the RE statistic for temperature in Table 6-1 (e.g., RE approximately 3.5 percent). Having an RE similar or slightly better than REs reported for other studies (Table 6-5) signifies good model performance for this constituent.

**Salinity**

Ocean boundary conditions for salinity varied from 35-36 parts per thousand (ppt) from top to bottom year round. Ocean boundary conditions had greater influence on stations in the most downstream reaches as seen in Figures 6-2 through 6-4. Boundary conditions for 63 tributary or point sources were also included with concentrations ranging from approximately 0.03 to 0.4 ppt. Buffalo Bluff was treated as a separate boundary file with salinity concentrations of roughly 0.55 ppt developed from two stations presented in Sucsxy and Morris (2002). Salinity time-series plots show good comparison to observed data with predictions at Bar Pilot bottom layer showing the greatest difference between observed and predicted data. The model captured the wide variability of salinity in the upstream direction, especially between Dames Point and Buckman Bridge stations, and between Buckman Bridge and Shands Bridge stations.
Figure 6-2. Time-series plots at Fulton Point for top, middle, and bottom layers for all water quality constituents (Sheet 1 of 20)
Figure 6-2. (Sheet 2 of 20)
St. Johns River (01/17 - 01/19)
Fulton Pt., Mid Layer
Nitrate

![Graph showing nitrate levels](image)

St. Johns River (01/17 - 01/19)
Fulton Pt., Bottom
Nitrate

![Graph showing nitrate levels](image)

Figure 6-2. (Sheet 3 of 20)
Figure 6-2. (Sheet 4 of 20)
Figure 6-2. (Sheet 5 of 20)
Figure 6-2. (Sheet 6 of 20)
St. Johns River (01/17 - 01/19)
Fulton Pt, Surface
Dissolved Oxygen

mg/L

Days from Dec. 1, 1996

St. Johns River (01/17 - 01/19)
Fulton Pt, Mid Layer
Dissolved Oxygen

mg/L

Days from Dec. 1, 1996

Figure 6-2. (Sheet 7 of 20)
Figure 6-2. (Sheet 8 of 20)
Figure 6-2. (Sheet 9 of 20)
Chapter 6  Water Column Calibration Results

Figure 6-2. (Sheet 10 of 20)
Figure 6-2. (Sheet 11 of 20)
Figure 6-2. (Sheet 12 of 20)
Figure 6-2. (Sheet 13 of 20)
St. Johns River (01/17 - 01/19)
Fulton Pt, Bottom
Salinity

St. Johns River (01/17 - 01/19)
Fulton Pt, Surface
Total Nitrogen

Figure 6-2. (Sheet 14 of 20)
Figure 6-2. (Sheet 15 of 20)
Figure 6-2. (Sheet 16 of 20)
Figure 6-2. (Sheet 17 of 20)
Figure 6-2. (Sheet 18 of 20)
Figure 6-2. (Sheet 19 of 20)
Figure 6-2. (Sheet 20 of 20)

Figure 6-3. Time-series plots at Piney Point for top and middle layers for all water quality constituents (Sheet 1 of 14)
Figure 6-3. (Sheet 2 of 14)
St. Johns River (01/17 - 01/19)
Piney Pt., Mid Layer
Nitrate

mg/L

0 91.25 182.5 273.75 365 456.25 547.5 638.75 730
Days from Dec. 1, 1996

St. Johns River (01/17 - 01/19)
Piney Pt., Surface
Chlorophyll

ugm/L

0 91.25 182.5 273.75 365 456.25 547.5 638.75 730
Days from Dec. 1, 1996

Figure 6-3. (Sheet 3 of 14)
Figure 6-3. (Sheet 4 of 14)
Figure 6-3. (Sheet 5 of 14)
Figure 6-3. (Sheet 6 of 14)
St. Johns River (01/17 - 01/19)
Piney Pt, Mid Layer
Dissolved Organic Carbon

St. Johns River (01/17 - 01/19)
Piney Pt, Surface
Dissolved Silica

Figure 6-3. (Sheet 7 of 14)
Figure 6-3. (Sheet 8 of 14)
Figure 6-3. (Sheet 9 of 14)
Figure 6-3. (Sheet 10 of 14)
Figure 6-3. (Sheet 11 of 14)
Figure 6-3. (Sheet 12 of 14)
Figure 6-3. (Sheet 13 of 14)
Figure 6-3. (Sheet 14 of 14)

Figure 6-4. Time-series plots at Picolata for top layer for all water quality constituents (Sheet 1 of 7)
St. Johns River (01/17 - 01/19)
Picolata, Surface
Nitrate

0.3
0.25
0.2
0.15
0.1
0.05

mg/L

0   91.25  182.5  273.75  365  456.25  547.5  638.75   730

Days from Dec. 1, 1996

St. Johns River (01/17 - 01/19)
Picolata, Surface
Chlorophyll

110
100
90
80
70
60
50
40
30
20
10
0

ug/mL

0   91.25  182.5  273.75  365  456.25  547.5  638.75   730

Days from Dec. 1, 1996

Figure 6-4. (Sheet 2 of 7)
Figure 6-4. (Sheet 3 of 7)
Figure 6-4. (Sheet 4 of 7)
Figure 6-4. (Sheet 5 of 7)

Chapter 6  Water Column Calibration Results
Figure 6-4. (Sheet 6 of 7)
Figure 6-4. (Sheet 7 of 7)
Figure 6-5. Longitudinal water quality results for August 1997 and 1998
(Sheet 1 of 15)
St Johns River (01/17 - 01/19)
Surface Chlorophyll August 1997

St Johns River (01/17 - 01/19)
Surface Chlorophyll August 1998

Figure 6-5. (Sheet 2 of 15)
Figure 6-5. (Sheet 3 of 15)
Figure 6-5. (Sheet 4 of 15)
Figure 6-5. (Sheet 5 of 15)
Figure 6-5. (Sheet 6 of 15)
Figure 6-5. (Sheet 7 of 15)
Figure 6-5. (Sheet 8 of 15)
Figure 6-5. (Sheet 9 of 15)
Figure 6-5. (Sheet 10 of 15)
Figure 6-5. (Sheet 11 of 15)
St Johns River (01/17 - 01/19)
Surface Total Nitrogen August 1997

St Johns River (01/17 - 01/19)
Surface Total Nitrogen August 1998

Figure 6-5. (Sheet 12 of 15)
Figure 6-5. (Sheet 13 of 15)
Figure 6-5. (Sheet 14 of 15)
Figure 6-5. (Sheet 15 of 15)
Figure 6-6. Cumulative distribution results for all water quality constituents (Sheet 1 of 8)
St. Johns River (01/17 - 01/19)

Algal Group 1
Model
Observed

St. Johns River (01/17 - 01/19)

Algal Group 2
Model
Observed

Figure 6-6. (Sheet 2 of 8)
Figure 6-6. (Sheet 3 of 8)
Figure 6-6. (Sheet 4 of 8)
Figure 6-6. (Sheet 5 of 8)
Figure 6-6. (Sheet 6 of 8)
Figure 6-6. (Sheet 7 of 8)
Table 6-5
Comparison of Water Quality Relative Error (%) Statistics at Five CE-QUAL-ICM Study Sites

<table>
<thead>
<tr>
<th></th>
<th>LSJR RE (%)</th>
<th>Lake Washington RE (%)</th>
<th>Mainstem Bay – Chesapeake Bay RE (%)</th>
<th>Florida Bay RE (%)</th>
<th>San Juan Bay RE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl a</td>
<td>49.3</td>
<td>16.3</td>
<td>58.34</td>
<td>72.0</td>
<td>60.8</td>
</tr>
<tr>
<td>DO</td>
<td>9.3</td>
<td>6.3</td>
<td>35.7</td>
<td>7.7</td>
<td>39.8</td>
</tr>
<tr>
<td>SALT</td>
<td>27.6</td>
<td>N/A</td>
<td>11.85</td>
<td>4.7</td>
<td>12.9</td>
</tr>
<tr>
<td>TEMP</td>
<td>3.5</td>
<td>7.6</td>
<td>N/A</td>
<td>5.3</td>
<td>3.3</td>
</tr>
<tr>
<td>TN</td>
<td>29.0</td>
<td>5.1</td>
<td>24.33</td>
<td>38.9</td>
<td>70.1</td>
</tr>
<tr>
<td>TP</td>
<td>26.9</td>
<td>8.6</td>
<td>37.64</td>
<td>31.3</td>
<td>58.3</td>
</tr>
<tr>
<td>DIP</td>
<td>45.8</td>
<td>N/A</td>
<td>N/A</td>
<td>212.7</td>
<td>82.3</td>
</tr>
<tr>
<td>TOC</td>
<td>18.1</td>
<td>N/A</td>
<td>N/A</td>
<td>39.0</td>
<td>40.7</td>
</tr>
<tr>
<td>TSS</td>
<td>60.4</td>
<td>N/A</td>
<td>N/A</td>
<td>139.6</td>
<td>78.0</td>
</tr>
</tbody>
</table>

Statistically CE-QUAL-ICM is performing adequately with an ME of -0.2367 and an RMSE of 3.9605, indicating a slight overprediction of salinity. If model performance for each individual station is examined (Table 6-4), stations farthest upstream from the ocean boundary show better comparisons to observed data. Influences at these stations are mostly from tributary boundary conditions. The RE for the combined statistic for all stations is around 27 percent, which is 7 percent higher than what was reported in Sucsy and Morris (2002). It is thought that the difference in RE between reports is due to how RE...
was calculated. Sucsy and Morris looked at the median RE of tidally averaged salinity, and RE in this report was calculated from daily salinity output at 12:00 PM and daily averaged observed salinity data. Comparison of the RE for LSJR to other studies shows a higher value for LSJR. As already mentioned, the greatest differences occur at the Bar Pilot station (closest to the ocean boundary) where CE-QUAL-ICM failed to predict the variation in salinity concentrations in the bottom layer.

**Chlorophyll**

Higher observed chlorophyll values occurred in the study area’s most upstream reaches, corresponding to an absence of salinity. CE-QUAL-ICM has captured this trend as shown in time series and longitudinal plots (Figures 6-2 through 6-5). As demonstrated in the time-series figures, CE-QUAL-ICM has also reproduced the seasonality of increased chlorophyll values during the summers of each year modeled. Statistically CE-QUAL-ICM’s model performance is more than adequate for chlorophyll with an RE of 49.38 percent. This value is comparable or better to other studies reported in Table 6-5. Comparison of the RE for each year modeled shows that the 1997-1998 year is slightly better than the 1996-1997 year (i.e., 47 percent as compared to 52 percent, respectively). This may suggest that nutrients or conditions required for algal growth are being computed more realistically for the 1997-1998 year. Statistics presented for individual stations (Table 6-4) indicated that computed values compared better to observed data at stations closest to the boundaries (i.e., Palatka RE approximately 40 percent and Fulton Point RE approximately 48 percent) than at the mid-reach stations.

The cumulative distribution plot (Figure 6-6) demonstrates that CE-QUAL-ICM has a propensity to overpredict chlorophyll. This is also affirmed by an ME value of -1.2406. From the cumulative distribution plot, discrepancies between observed and predicted chlorophyll values occurred most often for chlorophyll values greater than 20 µg/L. Above this value, CE-QUAL-ICM has a tendency to overpredict concentrations.

Spatially, chlorophyll values showed similar trends during August for both simulation years (Figures 6-5). As would be expected, these plots (and additional longitudinal plots provided on a CD-ROM) illustrate how chlorophyll values increased in the upstream direction whether during cool or warm months. Higher chlorophyll values occurred during summer months and could get as high as 90 µg/L (Figure 6-5).

**Ammonia and Nitrate**

Initially, ammonia and nitrate were examined separately. Observed ammonia concentrations were usually an order of magnitude less than nitrate concentrations. There are three distinct peaks of high ammonia and nitrate values, with the highest occurring between days 273 and 547 from the start of the simulation. Ammonia and nitrate time series (Figures 6-2 through 6-4) show CE-QUAL-ICM is able to reproduce this trend, although ammonia is usually over-predicted and
nitrate underpredicted. As noted from the cumulative distribution plot (Figure 6-6), ammonia values for all concentration ranges were on the whole being overpredicted. On the other hand, nitrate values below 0.1 mg/L were accurately predicted while values above this level were underpredicted (Figure 6-6).

After consideration of the arbitrary division of dissolved inorganic nitrogen (DIN) loads (ammonia split 25 percent and nitrate split 75 percent) and the difficulty of computing reasonable results for ammonia and nitrate individually, ammonia and nitrate values were combined for the computed and observed values to arrive at computed and observed DIN values. For the remainder of this report, reference to ammonia and nitrate will be as DIN. Times series of DIN implied that combining the two variables produced more accurate comparisons (Figures 6-2 through 6-4). This accuracy is also demonstrated in the improved statistic of DIN as compared to statistics for ammonia or nitrate. The RE for DIN-combined statistics for all stations was approximately 48 percent. When the RE statistics are compared by year modeled (Tables 6-2 and 6-3), the 1996-1997 year has a much higher RE than the 1997-1998 year and is 92 percent compared to 48 percent, respectively. This difference could suggest problems in loads or boundary conditions for the first year modeled. Also, problems computing DIN in the first year may be influenced by chlorophyll values (see chlorophyll discussion above). Comparison of the RE for individual stations shows the RE varies from station to station about 20 percent, with no discernable pattern.

The cumulative distribution plots (Figure 6-6) indicate that CE-QUAL-ICM has a tendency to overpredict DIN for concentrations below 0.17 mg/L, which occur about 75 percent of the time. For values greater than this, CE-QUAL-ICM usually underpredicts.

Spatially, CE-QUAL-ICM does reasonably well in predicting DIN longitudinally. Most of the major disparities occur at stations in the middle of the study reach (i.e., Piney Point, Mandarin Point, and Racey Point). These stations are where much of the PS and NPS loads are entering the study area. During August 1997 and August 1998, summer months critical to water quality, CE-QUAL-ICM is able for the most part to reproduce the trend of higher DIN values at the downstream stations and lower values at the upstream stations (Figure 6-5). Longitudinal plots of DIN for other months of the simulation period are provided on the CD-ROM.

**Total Nitrogen (TN)**

TN appears to be dominated by the organic phase when compared to DIN. This observation is based on most of the TN values being around 1.0 mg/L or greater while DIN values are usually less than 0.3 mg/L. Hendrickson and Konwinski (1998) reported similar trends in magnitudes of observed data for TN and DIN. Hendrickson et al. (2002) stated that much of the organic nutrients were associated with anthropogenic nutrient enrichment as well as terrestrially derived, colored humic, and nonhumic substances that come primarily from vascular plants. Recently, although it is not clear what form TN is in, loads to the LSJR have been attributed to PS discharge, with most nutrient portions being bioavailable (Hendrickson et al. 2002).
All stations presented in the time-series plots (Figures 6-2 through 6-4) show a similar range of TN predictions with an overall RE of 29 percent (Table 6-1). CE-QUAL-ICM does a commendable job in representing the dominance of the organic form over the mineral form. With the RE value reported, it is comparable to published values from other studies (Table 6-5). From comparison of the RE statistics for each year modeled, there is very little difference in RE value between years (Tables 6-2 and 6-3). Comparison of the RE for individual stations indicates that the greatest RE values occur from the stations closest to the ocean boundary upstream to Mandarin Point. This may indicate problems with how loads or boundary conditions were set in these reaches. From the cumulative distribution plot (Figure 6-6), the CE-QUAL-ICM consistently underpredicts TN slightly at all concentrations.

Spatially, CE-QUAL-ICM does reasonably well in predicting TN longitudinally. As with DIN values, most of the major disparities occur at the stations in the middle of the study reach (i.e., Piney Point, Mandarin Point, and Racey Point), again implying errors in load or boundary estimates. During August 1997 and August 1998, months critical for water quality, CE-QUAL-ICM does a very good job of reproducing the trend of TN values increasing in the upstream direction (Figure 6-4). Longitudinal plots of TN for other months of the simulation period are provided on the CD-ROM.

**Dissolved Inorganic Phosphate**

Figures 6-2 through 6-4 show that the range of DIP values is similar at all stations presented. The magnitudes of DIP values are about one-third the value of DIN. The figures show that CE-QUAL-ICM does reasonably well at computing higher concentrations of DIP but consistently overpredicts the lower values. This is also indicated in the cumulative distribution plot (Figure 6-5); CE-QUAL-ICM consistently overpredicts concentrations less than 0.02 mg/L and underpredicts values greater than this. Statistics demonstrate good model performance with the RE at approximately 45 percent for the combined statistics for all stations (Table 6-1). That is comparable to or better than other study results presented in Table 6-5, implying better model performance for LSJR. Comparison of the RE statistics by year modeled illustrates that there is very little difference in model performance between years (Tables 6-2 and 6-3). When the REs for individual stations are compared, the greatest RE values occur at the stations closest to the boundary locations in the grid (i.e., Palatka and the ocean). At Palatka, the high RE reflects the low observed DIP concentration in the denominator of the error formula. Near the ocean, the RE reflects the difficulty in assigning open-mouth boundary conditions.

The CE-QUAL-ICM was reasonably able to spatially reproduce the DIP increase then decrease longitudinally through the study reach during the warm months of August 1997 and August 1998. At the most upstream stations for both years, the CE-QUAL-ICM was slightly overpredicting DIP. Longitudinal plots of DIP for other months of the simulation period are provided on the CD-ROM.
**Total Phosphorus (TP)**

TP values for the simulation period have similar magnitudes to DIN values, and approximately half of TP appears to be in the organic form. Time-series plots presented in Figures 6-2 through 6-4 show that the magnitude of observed TP values is in the same range at all stations, as was also noted for DIP above. The figures indicate two periods of increasing/decreasing TP concentrations, which CE-QUAL-ICM appears to be capturing. The RE for the combined statistics for all stations (Table 6-1) is approximately 27 percent. This RE value is better than or comparable to what has been reported for other studies (Table 6-5). When RE statistics are compared by year, the RE value is only slightly better for the first year indicating that CE-QUAL-ICM performs about the same for both years. The RE is distributed roughly uniformly among stations with no distinct trends.

As indicated in Figure 6-6, CE-QUAL-ICM consistently underpredicts TP concentrations at all levels. This trend is also demonstrated with an ME value of 0.014 mg/L.

Spatially, CE-QUAL-ICM is able to predict trends in TP values, which were similar to trends seen in DIP values during the critical months of August 1997 and August 1998. CE-QUAL-ICM reproduced reasonably well the increase then decrease of TP values longitudinally throughout the study reach. Like DIP values at the most upstream stations, CE-QUAL-ICM was slightly overpredicting TP. Longitudinal plots of TP for other months of the simulation period are provided on the CD-ROM.

**TOC and DOC**

As pointed out by Cole (1995), DOC is extremely important when addressing eutrophication-related issues in the LSJR. DOC affects light penetration in the freshwater reaches of the LSJR, limiting productivity and making it imperative that DOC loading be accurately estimated. The TOC of the LSJR system is composed of approximately 10 percent LTOC (Hendrickson et al. 2002). To address this concern, the model was modified to handle labile and refractory classes of TOC and DOC. Comparing observed values of TOC and DOC shows that most of the TOC is in the dissolved form. For this reason, the rest of this section discusses only DOC.

Figures 6-2 through 6-4 contain time series of computed versus observed data for DOC. From the figures, it can be seen that CE-QUAL-ICM is reproducing the variability in DOC values, especially the increase from early to late winter in 1997-1998. The model appears to be performing very well with the RE of DOC and TOC for the combined station statistics at approximately 18 percent (Table 6-1). Comparison of this value to reported values of RE in other studies demonstrates that CE-QUAL-ICM performs better at LSJR for this constituent. With the capability of being able to model different classes of TOC and DOC, model performance has been improved. When RE statistics are compared by year, RE values are very similar, indicating CE-QUAL-ICM performs about the same for both years. Individual station statistics shows that the station closest to
the ocean boundary, Fulton Point, has the highest RE of all stations (approximately 45 percent). Problems at boundary stations have been seen for other constituents discussed previously.

The cumulative distribution plot (Figure 6-6) shows that, for concentrations less than 8 mg/L, CE-QUAL-ICM slightly overpredicts DOC values (Figure 6-6). For greater values, CE-QUAL-ICM does an adequate job accurately predicting DOC values. This tendency is also verified with the ME of -0.17 mg/L.

Spatially, CE-QUAL-ICM was able to reproduce DOC values longitudinally during the critical months of August 1997 and August 1998. CE-QUAL-ICM was able to reproduce the trend of increased DOC concentrations from the ocean boundary to the middle of the study reach, then a leveling off of concentration magnitudes in the upstream direction (Figure 6-5). Longitudinal plots of DOC and TOC for other months of the simulation period are provided on the CD-ROM.

**Dissolved Oxygen**

Times-series plots shown in Figures 6-2 through 6-4 demonstrate that CE-QUAL-ICM has the ability to reproduce trends in seasonal DO variation (i.e., higher DO values during winter months and lower values during summer months). Influence in saturation concentrations (a function of salinity and temperature) can also be seen when comparisons are made between the lower DO values found close to the ocean boundary and the higher values found in the freshwater regions. The greatest differences are most noticeable for time-series plots showing bottom level DO results (e.g., Fulton Point or Piney Point). The RE value for LSJR was 9.3 percent. When compared to the RE value of other studies (Table 6-6), model performance is comparable to most other sites except for Chesapeake Bay’s Mainstem and San Juan Bay. CE-QUAL-ICM appears to be doing better, but this is not actually the case, since only bottom DO values were used in computing the RE statistics at Mainstem and San Juan Bays. At LSJR, all levels of DO values were used in computing the RE statistics. If only bottom DO values were used in calculating the RE at LSJR, a comparable RE would probably be obtained. When RE statistics are compared by year, RE values are very similar, indicating CE-QUAL-ICM performs about the same for both years. Like other constituents previously discussed, the individual station statistics show the greatest RE (as well as increases in other statistics) occurs at the upstream stations closest to the boundary.

The DO cumulative distribution plot (Figure 6-6) demonstrates that CE-QUAL-ICM is capturing DO values at all concentration ranges with a slight underprediction in the higher values (>7mg/L). This trend is also implied by an ME of 0.04 mg/L.

Spatially observed data for August 1997 and August 1998 show similar behavior trends in DO (Figure 6-4), a dip in DO concentrations in the downstream stations then increase to mid-stations followed by a decrease toward the most upstream station. A noted difference in the 2 years is that, during August 1998, DO values beginning at stations mid-LSJR to most of the upstream
stations are higher than those observed in August 1997. This difference is probably the result of higher observed chlorophyll values, thus more DO being produced. The model does not capture this. Longitudinal plots of DO for other months of the simulation period are provided on the CD-ROM.

**Total Suspended Solids (TSS)**

Observed TSS concentrations are highest at the most downstream station (Figure 6-2), and decrease in the upstream direction (Figure 6-4). Time-series plots all show computed TSS is underpredicted at all stations (Figure 6-2 through 6-4). It is not clear why underprediction occurs since settling is set to a low rate. Problems in computing TSS may be caused by not having PS and NPS loads correctly estimated. The RE of TSS for the combined station statistics is 60 percent (Table 6-1). When the RE statistics are compared by year, the RE value during the 1996-1997 year is slightly better than for the 1997-1998 year (i.e., 57 percent as compared to 61 percent, respectively). This indicates that CE-QUAL-ICM performs better during the first year of simulation for this variable, possibly because loads are set more accurately. Comparing individual station statistics shows the highest RE values occur from about mid-study reach in the downstream direction where much of the loads enter.

From the cumulative distribution plot, TSS is being underpredicted by CE-QUAL-ICM at all concentration levels (Figure 6-6). The ME for the combined statistics also indicates that TSS is on average approximately 10 mg/L lower than observed. If you look at ME for TSS for each year modeled, the model does better at predicting TSS in 1996-1997 (ME = 3.64 mg/L) than in 1997-1998 (ME = 16.6 mg/L).

Spatially observed data for August 1997 and August 1998 show similar behavior trends longitudinally in TSS (Figure 6-5), higher concentrations of TSS at the downstream stations, then a decrease to middle stations followed by an increase toward the most upstream station. CE-QUAL-ICM reproduces this trend better longitudinally in August 1997 than in August 1998 (Figure 6-5). This affirms the previous discussion about comparison of the RE statistic for each year modeled.

**References**


Volume 1: Calculation of the external load.” (Draft). St. Johns River Water Management District, Palatka, FL.

Introduction

The predictive benthic sediment model applied to the St. Johns River was first developed for use in Chesapeake Bay (DiToro and Fitzpatrick 1993). Management of the bay required a model with two fundamental capabilities:

- Predict effects of management actions on sediment-water exchange processes, and
- Predict time scale for alterations in sediment-water exchange processes.

The model (Figure 7-1, Table 7-1) is driven by net settling of organic matter from the water column to the sediments. In the sediments, the model simulates the diagenesis (decay) of the organic matter. Diagenesis produces oxygen.
Table 7-1  
Sediment Model State Variables and Fluxes

<table>
<thead>
<tr>
<th>State Variable</th>
<th>Sediment-Water Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>Particulate Organic Carbon</td>
<td>Sediment Oxygen Demand</td>
</tr>
<tr>
<td>Sulfide/Methane</td>
<td>Release of Chemical Oxygen Demand</td>
</tr>
<tr>
<td>Particulate Organic Nitrogen</td>
<td></td>
</tr>
<tr>
<td>Ammonium</td>
<td>Ammonium Flux</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Nitrate Flux</td>
</tr>
<tr>
<td>Particulate Organic Phosphorus</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>Phosphate Flux</td>
</tr>
<tr>
<td>Particulate Biogenic Silica</td>
<td></td>
</tr>
<tr>
<td>Available Silica</td>
<td>Silica Flux</td>
</tr>
</tbody>
</table>

Oxygen demand, as sulfide (in saltwater) or methane (in freshwater), takes three paths out of the sediments: export to the water column as chemical oxygen demand, oxidation at the sediment-water interface as sediment oxygen demand, or burial to deep, inactive sediments. Inorganic nutrients produced by diagenesis take two paths out of the sediments: release to the water column, or burial to deep, inactive sediments.

The formulation of the diagenesis model is too extensive to repeat here. Complete model documentation was provided by DiToro and Fitzpatrick (1993). More accessible documentation may be found in DiToro (2001). Details of the sediment model, required to understand the coupling of the sediment submodel to the model of the water column, are provided in this chapter.

**Coupling With the Sediment Diagenesis Model**

Benthic sediments are represented as two layers with a total depth of 10 cm (Figure 7-2). The upper layer, in contact with the water column, may be oxic or anoxic depending on DO concentration in the water. The lower layer is permanently anoxic. The thickness of the upper layer is determined by the penetration of oxygen into the sediments. At its maximum thickness, the oxic layer depth is only a small fraction of the total.

The sediment model consists of three basic processes. The first is deposition of particulate organic matter from the water column to the sediments. Due to the negligible thickness of the upper layer, deposition proceeds from the water column directly to the lower, anoxic layer. Within the lower layer, organic matter is subject to the second basic process, diagenesis. The third basic process is flux of substances produced by diagenesis to the upper sediment layer, to the water column, and to deep, inactive sediments. The flux portion of the model is the most complex. Computation of flux requires consideration of reactions in both sediment layers, of partitioning between particulate and dissolved fractions.
in both layers, of sedimentation from the upper to lower layer and from the lower layer to deep inactive sediments, of particle mixing between layers, of diffusion between layers, and of mass transfer between the upper layer and the water column.

The water quality and sediment models interact on a time scale equal to the integration time step of the water quality model. After each integration, predicted particle deposition, temperature, nutrient and DO concentrations are passed from the water quality model to the sediment model. The sediment model computes sediment-water fluxes of dissolved nutrients and oxygen based on predicted diagenesis and concentrations in the sediments and water. The computed sediment-water fluxes are incorporated by the water quality model into appropriate mass balances and kinetic reactions.
Deposition

Deposition is one process that couples the model of the water column with the model of the sediments. Consequently, deposition is represented in both the sediment and water-column models. In the water column, deposition is represented with a modification of the mass-balance equation applied only to cells that interface the sediments:

\[
\frac{\Delta C}{\Delta t} = \text{[transport]} + \frac{WS}{\Delta z} \cdot C_{up} - \frac{W_{net}}{\Delta z} \cdot C
\]  

(7-1)

in which:

- \( C \) = concentration of particulate constituent in cell above sediments (g m\(^{-3}\))
- \( WS \) = settling velocity in water column (m d\(^{-1}\))
- \( C_{up} \) = constituent concentration two cells above sediments (g m\(^{-3}\))
- \( W_{net} \) = net settling to sediments (m d\(^{-1}\))
- \( \Delta z \) = cell thickness (m)

Net settling to the sediments may be less than or equal to settling in the water column. Sediment resuspension is implied when settling to the sediments is less than settling through the water column.

Diagenesis

Organic matter in the sediments is divided into three G classes or fractions, in accordance with principles established by Westrich and Berner (1984). Division into G classes accounts for differential decay rates of organic matter fractions. The G1 (labile) fraction has a half-life of 20 days. The G2 (refractory) fraction has a half-life of 1 year. The G3 (inert) fraction undergoes no significant decay before burial into deep, inactive sediments. Each G class has its own mass-conservation equation:

\[
H \cdot \frac{\Delta G_i}{\Delta t} = W_{net} \cdot f_i \cdot C - W \cdot G_i - H \cdot K_i \cdot G_i \cdot \theta_i^{(T-20)}
\]

(7-2)

in which:

- \( H \) = total thickness of sediment layer (m)
- \( G_i \) = concentration of organic matter in G class \( i \) (g m\(^{-3}\))
- \( f_i \) = fraction of deposited organic matter assigned to G class \( i \)
- \( W \) = burial rate (m d\(^{-1}\))
- \( K_i \) = decay rate of G class \( i \) (d\(^{-1}\))
- \( \theta_i \) = constant that expresses effect of temperature on decay of G class \( i \)

Since the G3 class is inert, \( K_3 = 0 \).
Sediment-water flux

The exchange of dissolved substances between the sediments and water column is driven by the concentration difference between the surface sediment layer and the overlying water. Flux may be in either direction across the sediment-water interface, depending on concentration gradient. Sediment-water flux is computed within the diagenesis model as the product of concentration difference and an internally-computed mass-transfer coefficient. In the water column, sediment-water exchange of dissolved substances is represented with a modification of the mass-balance equation applied only to cells that interface with bottom sediments:

\[
\frac{\Delta C}{\Delta t} = \text{[transport]} + \text{[kinetics]} + \frac{\text{BENFLX}}{\Delta z}
\]

in which \(\text{BENFLX}\) is the sediment-water flux of dissolved substance (g m\(^{-2}\) d\(^{-1}\)).

By convention, positive fluxes are from sediment to water. Negative fluxes, including sediment oxygen demand, are from water to sediments.

Field and Laboratory Program

A program of field and laboratory analyses, aimed at quantifying sediment-water interactions in the St. Johns River, was conducted by personnel from the University of Florida. Numerous observations were conducted, not all of which were germane to the present model effort and domain. Relevant portions of the program included measures of sediment-water fluxes, measures of bulk sediment properties, and measures of interstitial water concentrations.

Sediment-water fluxes

Measures of sediment-water fluxes of oxygen, ammonium, and phosphate were conducted via laboratory incubation of intact cores. Cores were collected in June and October 2001 from four locations (Figure 7-3). Triplicate cores were incubated under aerobic (all substances) and anaerobic conditions (nutrients only). Blank nutrient columns, containing water only, were run for two locations during the October sampling. Cores for sediment oxygen demand analyses were incubated from 12 to 24 hours at approximately 20 °C. Sampling interval varied with more intensive measures of DO concentration early in the incubation. Cores for nutrient analyses were incubated for 5 days. Sampling interval varied with samples collected more frequently early in the incubation.
Figure 7-3. Location of sediment-water flux and interstitial water measurements.
Bulk sediment properties

Analyses of bulk sediment properties were conducted at 31 locations within the model domain. Analyses were conducted on the upper 10 cm of sediment, consistent with the layer thickness of the diagenesis model. Properties analyzed included dry density, wet density, total carbon, total nitrogen, total phosphorus, and HCL-extractable phosphorus.

Interstitial water

Sediment peepers were used for in-situ sampling of interstitial water at the four locations selected for measurement of sediment-water fluxes. Water collected in the peepers was analyzed for ammonium, nitrate, and phosphate. Interstitial water was removed from intact cores collected at eight locations within the model domain. These samples were analyzed for sulfide and silica as well as ammonium, nitrate, and phosphate.

Data Analyses

Sediment-water fluxes

Sediment-water oxygen and nutrient fluxes are measured by sampling the water overlying sediment cores. Fluxes are inferred from concentration changes in the water. Simultaneous sampling of a control or blank column, containing water only, is advisable to identify concentration changes due to processes in the water or between the water and column walls. Apparent fluxes in the blank column are then subtracted from the fluxes measured in the columns containing both sediment and water.

The time series of DO in water overlying the sediment cores showed a two-phase behavior. A very rapid decline was followed by a slower, more linear decrease. This behavior is frequently seen in flux measurements and is usually attributed to disturbance of the sediment-water interface and, perhaps, sediment resuspension. The first 2 hours of data were eliminated to allow time for initial disturbances to settle. Linear regression was used to fit a line to the remaining DO observations in each core. The slope of this line, g O₂ m⁻³ d⁻¹, multiplied by the depth of water, 0.15 m, resulted in sediment oxygen demand, g O₂ m⁻² d⁻¹. From 5 to 12 samples were in each regression. Strength of individual relationships, quantified as R², varied from essentially zero to unity. Median R², over all regressions, was 0.88. No blank column was run, so the measured demand (Table 7-2) is a combination of demand from the sediments and overlying water.

A similar process was followed to quantify the sediment-water nutrient fluxes. Observations from the first 2 hours were dropped to eliminate initial disturbances. The sample collected after 5 days was often aberrant, so this
Table 7-2
Summary of Sediment-Water Fluxes

<table>
<thead>
<tr>
<th></th>
<th>Aerobic NH4 Flux, mg m(^{-2}) d(^{-1})</th>
<th>Anoxic NH4 Flux, mg m(^{-2}) d(^{-1})</th>
<th>Aerobic PO4 Flux, mg m(^{-2}) d(^{-1})</th>
<th>SOD, g m(^{-2}) d(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Standard Dev.</td>
<td>Mean</td>
<td>Standard Dev.</td>
</tr>
<tr>
<td>June</td>
<td>-1.08</td>
<td>0.10</td>
<td>23.37</td>
<td>0.95</td>
</tr>
<tr>
<td>June</td>
<td>-14.46</td>
<td>1.51</td>
<td>13.83</td>
<td>0.85</td>
</tr>
<tr>
<td>June</td>
<td>-0.35</td>
<td>0.09</td>
<td>28.03</td>
<td>0.55</td>
</tr>
<tr>
<td>June</td>
<td>-0.71</td>
<td>0.52</td>
<td>27.37</td>
<td>0.66</td>
</tr>
<tr>
<td>October</td>
<td>-8.33</td>
<td>1.28</td>
<td>53.37</td>
<td>2.71</td>
</tr>
<tr>
<td>October</td>
<td>-11.59</td>
<td>0.61</td>
<td>102.93</td>
<td>7.29</td>
</tr>
<tr>
<td>October</td>
<td>-36.46</td>
<td>0.33</td>
<td>37.37</td>
<td>1.65</td>
</tr>
<tr>
<td>October</td>
<td>0.46</td>
<td>1.50</td>
<td>15.80</td>
<td>1.47</td>
</tr>
<tr>
<td>October</td>
<td>-0.41</td>
<td>0.08</td>
<td>11.07</td>
<td>0.54</td>
</tr>
<tr>
<td>October</td>
<td>0.00</td>
<td>0.04</td>
<td>11.53</td>
<td>0.60</td>
</tr>
</tbody>
</table>

* Corrected for activity in water.

The St. Johns River does not exhibit bottom-water anoxia. Therefore, the aerobic nutrient fluxes are the best reflection of in-situ sediment-water nutrient exchanges. The anoxic nitrogen fluxes are valuable, however, as indicators of "diagenesis flux" (DiToro 2001). Diagenesis flux is the amount of ammonium produced by decay of organic matter in the sediments. The diagenetic ammonium flux is attenuated by nitrification in the aerobic sediment layer. Nitrate produced by nitrification is subsequently reduced to gaseous nitrogen by denitrification in anoxic microzones (Jenkins and Kemp 1984). Consequently, ammonium released to overlying water, under aerobic conditions, is much less than the amount produced through diagenesis. Sediment nitrification in the St. Johns River apparently proceeds at such a rate that ammonium is often stripped from the water column (Table 7-2).

Sediment oxygen demand observed in this study, ≈0.1 to 0.4 g m\(^{-2}\) d\(^{-1}\) is low relative to other systems in which we have worked. In Chesapeake Bay, for example, the vast preponderance of sediment oxygen demand observations exceed 0.5 g m\(^{-2}\) d\(^{-1}\) (DiToro 2001) while in the St. Johns, none of the observations achieve this level.
Sediment phosphorus release is also small, consistent with the aerobic conditions of the overlying waters. Significant sediment phosphorus release usually occurs under anoxic conditions when iron oxides in surficial sediments, which adsorb phosphate and prevent its release under oxic conditions, are reduced to soluble form allowing free diffusion of phosphate to overlying water. The sediment-water phosphate fluxes in the St. Johns are, in fact, indeterminate. Phosphorus uptake in the blank columns was large relative to phosphate flux in the columns containing sediment. Subtraction of the blank flux from the sediment-water fluxes resulted in small net release from sediments to water. Due to the limited number of blank observations and the classic problem of obtaining a small difference via subtraction of two large numbers, we believe the best statement about sediment-water phosphate flux in the St. Johns is that it is so small it cannot be reliably measured.

**Interstitial water**

Concentrations in interstitial water were reported based on volume of interstitial water. Concentrations in the sediment model are computed based on bulk sediment volume. For comparison with the model, observed concentrations were converted to a bulk basis through multiplication by porosity (\(\approx 0.9\)).

**Bulk sediment properties**

Bulk sediment properties were reported based on weight (e.g., g kg\(^{-1}\)). Concentrations in the sediment model are computed based on bulk sediment volume. For comparison with the model, observed concentrations were converted to a bulk basis via the relationship:

\[
Cb = Cw \cdot (1 - \phi) \cdot \rho
\]  

(7-4)

in which:

- \(Cb\) = bulk concentration (g m\(^{-3}\))
- \(Cw\) = weight-based concentration (g g\(^{-1}\))
- \(\phi\) = porosity
- \(\rho\) = solids density (1.64 g m\(^{-3}\))

Solids density was derived from bulk density and moisture content analyses provided by the original investigators.

**Parameter Specification**

Coupling with the sediment model requires specification of net settling rates, of the G splits of organic matter, and of burial rates.
Net settling rates

Net settling for inorganic solids was specified as 0.075 m d\(^{-1}\), 10 percent of the value in the water column. This specification indicates 90 percent of the solids that initially settle to the bottom are resuspended. Net settling of organic matter was specified identical to settling in the water column: 0.25 m d\(^{-1}\) for labile and refractory detritus and 0.1 m d\(^{-1}\) for diatoms and green algae. Zero net settling was specified for the buoyant cyanobacteria. Specifications in this study indicate no resuspension occurs for organic matter.

Assignment to G classes

Upon deposition in the sediments, state variables representing particulate organic matter in the water quality model required conversion into sediment model state variables (Table 7-3). The water quality model considered two classes of particulate organic matter: labile and refractory. The sediment model was based on three classes of organic particles: labile (G1), refractory (G2), and inert (G3). Labile particles from the water quality model were transferred directly into the G1 class in the sediment model. Refractory particles from the water quality model had to be split into G2 and G3 fractions upon entering the sediments. Algae settling directly to the sediments also required routing into sediment model state variables. Initial guidance for the splits was obtained from the most recent Chesapeake Bay model calibration (Cerco and Noel 2003). Subsequently, the fraction of refractory carbon routed to the G3 class was increased to reflect the large sediment carbon concentrations observed in the St. Johns River.

<table>
<thead>
<tr>
<th>WQM Variable</th>
<th>Carbon</th>
<th>Nitrogen</th>
<th>Phosphorus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labile Particles</td>
<td>% G1</td>
<td>% G2</td>
<td>% G3</td>
</tr>
<tr>
<td>Refractory Particles</td>
<td></td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Algae</td>
<td>60</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

Burial rates

Lead-210 sedimentation rates were provided from 20 cores collected in 8 locations. Burial rates ranged from 0.19 to 3.88 cm yr\(^{-1}\) with two-thirds of the data in the range 0.4 to 1.2 cm yr\(^{-1}\). A range of options existed for employment of this data. At one extreme, the observed rates could be employed at measurement locations and the rates elsewhere obtained by interpolation/ extrapolation. At the other extreme, a single value could be used everywhere. A compromise would be to explore the data for trends that could be represented in the model. The data were too sparse for meaningful extrapolation of
individual observations and spatial patterns were difficult to distinguish. This study uses the median value, 0.9 cm yr$^{-1}$, throughout.

**Sediment model parameters**

With one exception, all parameters within the diagenesis model are exactly as derived for the original model application (DiToro and Fitzpatrick 1993). The model bulk solids density was reduced from 0.5 kg L$^{-1}$ (Chesapeake Bay) to 0.3 kg L$^{-1}$, based on data supplied by the original investigators.

**Model Results**

The field program was conducted during 2001, while the model application period was December 1996 through November 1998. For comparison with the observations, model results in the cells corresponding to sample locations were averaged over June and October of the computed years.

**Sediment-water fluxes**

Computed and observed diagenesis flux show remarkable agreement, with values centered in the range of 20 to 40 mg N m$^{-2}$ d$^{-1}$ (Figure 7-4). The close agreement indicates the model is correctly computing the rate of organic matter decomposition in the sediments. Both observations and model indicate that little or none of the diagenesis flux escapes to the water column (Figure 7-5). Observations suggest sediments strip ammonium from the water column, while the model computes $\approx$15 percent of the diagenetically produced ammonium escapes the sediments. In view of the uncertainties in the observations, uncertainties associated with comparisons of different years, and the small magnitude of the fluxes, it is concluded that the model adequately represents sediment-water ammonium flux.

Both observations and model indicate low rates of sediment oxygen demand (Figure 7-6), although the modeled rate exceeds the observed. The most likely reason for the computed excess is the difference between incubation temperature and in-situ temperature. Laboratory measures were conducted at $\approx$20 °C, while computations were based on in-situ temperatures of 22.5 °C (June) and 30 °C (October). Commonly used temperature corrections indicate laboratory oxygen demand should be increased by 12 percent to correct for June temperatures and by 62 percent to correct for October temperatures. Some small downward adjustments in computed sediment oxygen demand might still be made and could be readily accomplished by various parameter adjustments. Potential downward adjustments will cause associated declines in computed diagenesis flux, however, which is presently well-represented. The present model calibration is a compromise that provides good representation of diagenesis flux and sediment oxygen demand but not perfect representation of either.
Figure 7-4. Computed and observed sediment diagenesis flux

Figure 7-5. Computed and observed sediment-water ammonium flux
Figures 7-6. Computed and observed sediment oxygen demand

Observations indicate small sediment phosphate releases, but they are, as previously noted, too small to effectively determine. Modeled releases are also small, ≈1 mg P m⁻² d⁻¹ (Figure 7-7). It is concluded that the model well represents observed sediment-water phosphate flux, especially in view of uncertainties in the observations, uncertainties associated with comparisons of different years, and the small magnitude of the fluxes.

**Interstitial water**

The primary goal of the sediment model is to provide accurate computations of sediment-water fluxes. Comparison of other computed and observed properties provides an indication that processes within the sediment model, which lead to fluxes, are operating correctly. Matching computed and observed properties is not a goal in itself.

Computed interstitial ammonium concentration is perhaps half the observed concentration (Figure 7-8). The computed concentration can be raised by changing the ammonium partition coefficient in the model. This change would produce increased sediment ammonium release, which is already on the high side (Figure 7-5). In view of the numerous uncertainties associated with the measures and with conversion of measures into equivalent model quantities, a factor-of-two agreement between modeled and observed concentration is believed to be reasonable.
Figure 7-7. Computed and observed sediment phosphate flux

Figure 7-8. Observed versus computed interstitial ammonium concentration
Although a few elevated concentrations are present in the observations, the preponderance of observed and computed nitrate concentrations are low (Figure 7-9). These low concentrations indicate sediment nitrate is rapidly reduced to gaseous nitrogen by the denitrification process.

![Interstitial Nitrate](image)

**Figure 7-9.** Observed versus computed interstitial nitrate concentration

Computed interstitial phosphate agrees well with observed (Figure 7-10). Both observed and computed concentrations are ≈2 g P m\(^{-3}\). Computed interstitial sulfide, a component in the computation of sediment oxygen demand, is a bit larger, on average, than observed although there is a good deal of scatter in both computations and observations (Figure 7-11). As with other substances, the agreement is believed to be good in view of uncertainties in data analysis and conversion. Computed and observed interstitial silica show excellent agreement centered around 15 g Si m\(^{-3}\) (Figure 7-12). Since no silica flux measures were collected, this agreement is the best indication that the computed sediment-water silica fluxes are correct.

**Bulk concentrations**

Computed sediment nitrogen (Figure 7-13) and carbon (Figure 7-14) are an order of magnitude less than observed. Although computed sediment inorganic phosphorus agrees well with observed (Figure 7-15), computed TP is about half the observed TP (Figure 7-16). These discrepancies are too large to attribute to uncertainties in data and model. An interesting question is how the bulk concentrations can be off by a large amount but the computed fluxes can be well represented. The answer is that the preponderance of sediment organic matter is inert G3 material. This material has been described as the “ashes” of the
Figure 7-10. Observed versus computed interstitial phosphate concentration

Figure 7-11. Observed versus computed interstitial sulfide concentration
Figure 7-12. Observed versus computed interstitial silica concentration

Figure 7-13. Observed versus computed sediment bulk nitrogen concentration
Figure 7-14. Observed versus computed sediment bulk organic carbon concentration

Figure 7-15. Observed versus computed sediment bulk inorganic phosphorus concentration
Figure 7-16. Observed versus computed sediment bulk phosphorus concentration

diagenesis process. Since the material is inert, its concentration has no impact on computed fluxes. The concentration of G3 organic matter can be increased by increasing deposition, by decreasing burial, or by increasing the fraction assigned to the G3 class upon deposition. The observed bulk concentrations indicate some adjustments in processes and rates are appropriate, but these will have little or no effect on sediment-water fluxes.

One process that might account for the large concentration of inert sediment organic matter is flocculation and settling of dissolved organic matter in the water column. Some initial analyses of sensitivity to flocculation were performed, but incorporation of the process proved beyond the scope of the present model effort.

References


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8 Analysis of Water Column Kinetics

Introduction

This study added several new features to the conventional CE-QUAL-ICM kinetics. These included Droop kinetics, nitrogen fixation, and the split of dissolved organic matter into labile and refractory fractions. This chapter presents initial analysis of the influence of these improvements and also provides the opportunity for comparison of computed and observed phytoplankton primary production and water column respiration.

Droop Kinetics

Representations of the effect of nutrients on phytoplankton growth can be divided into two classes. The first class represents growth as a function of nutrient concentration external to the cell. The second represents growth as a function of nutrients internal to the cell. The formulation and implications of growth based on internal nutrients were reported 30 years ago by Droop (1973). Droop’s work was based on three postulates:

- Nutrient uptake depends on external nutrient concentration
- Growth depends on internal nutrient concentration
- At steady state, nutrient uptake must equal the product of growth rate and internal nutrient concentration

DiToro (1980) compared the effects of phytoplankton growth kinetics based on external and internal nutrient concentrations. For realistic cases, he found the growth rates computed by the two formulations were indistinguishable. Formulations based on internal nutrients did, however, provide substantial variation in algal composition relative to the constant composition used in formulations based on external nutrients.

DiToro cited one study (Bierman 1976) that considered internal nutrients in the calculation of algal growth. No additional studies that consider internal nutrients were identified. The formulation commonly known as “Droop kinetics” seems to have fallen by the wayside. Concern over the role of luxury phosphorus uptake in the propagation of the spring algal bloom caused the sponsor to request the consideration of internal nutrients in the present study. While Droop...
considered multiple internal nutrients and their interactions, this study is limited
to phosphorus. Nutrient limitations due to nitrogen and silica were modeled with
conventional relationships based on external nutrient concentrations. Our
consideration of phosphorus alone was motivated by the sponsor's concern and
by our own experience. Multiple Chesapeake Bay models have used different
phosphorus stoichiometry between spring and summer algal groups. In contrast,
nitrogen composition requires little or no difference. Experience such as that
reflected in DiToro's analyses shows that theoretical variations in algal
phosphorus content exceed by an order of magnitude theoretical variations in
nitrogen and silica content.

Initial parameter evaluation

As formulated here, the Droop kinetics require evaluation of three parameters
for each of the three algal groups. The parameters are:

- $V_{\text{max}}$, the maximum rate of algal nutrient uptake ($g \ P \ g^{-1} \ \text{algal C d}^{-1}$)
- $Q_o$, the minimum cell quota ($g \ P \ g^{-1} \ \text{algal C}$)
- $K_{Hp}$, the half-saturation concentration for phosphorus uptake ($g \ P \ m^{-3}$).

Guidance for evaluation of these parameters is minimal, no doubt due to the lack
of this model's employment. DiToro reported cell-based values (attributed to
Rhee 1973) for Scenedesmus. The reported values can be converted to our model
units using cell carbon of $1.5 \times 10^7 \ \mu\text{mol C/cell}$ (Rhee and Gotham 1981):

- $V_{\text{max}} = 0.2 \ g \ P \ g^{-1} \ \text{algal C d}^{-1}$
- $Q_o = 0.003 \ g \ P \ g^{-1} \ \text{algal C}$
- $K_{Hp} = 0.02 \ g \ P \ m^{-3}$.

The value for $Q_o$ corresponds to an algal carbon-to-phosphorus ratio of
333:1, which is enormous relative to the commonly accepted Redfield ratio of
40:1 (Redfield et al. 1966). The original Chesapeake Bay application (Cerco and
Cole 1994) used a carbon-to-phosphorus ratio of 127:1 for phosphorus-limited
phytoplankton. This ratio corresponds to a cell quota of $0.008 \ g \ P \ g^{-1} \ \text{algal C}$,
which is presumed to be close to the minimum since it represents stringently
phosphorus-limited conditions. It appears the order-of-magnitude range for $Q_o$ is
$10^{-3}$ to $10^{-2} \ g \ P \ g^{-1} \ \text{algal C}$.

$V_{\text{max}}$ can be estimated by noting that, at steady state, phosphorus uptake
must equal the algal growth rate. Maximum specific algal growth rate, averaged
over a day, is $\approx 2 \ \text{d}^{-1}$. Using the Redfield ratio for cell quota results in:

$$V_{\text{max}} = \frac{2 \ gP}{\text{day} \ 40 \ gC} = \frac{0.05 gP}{gC \text{day}}$$  \hspace{1cm} (8-1)

It appears $V_{\text{max}}$ is in the order of magnitude $10^{-1} \ g \ P \ g^{-1} \ \text{algal C d}^{-1}$.

Great care must be taken to distinguish the half-saturation concentration for
phosphorus uptake from the half-saturation concentration for algal growth
(DiToro 1980). Taft et al. (1975) reported half-saturation concentration for short-term phosphorus uptake by estuarine algae in the range of 0.003 to 0.053 g P m\(^{-3}\). It appears the order-of-magnitude range for \(K_{Hp}\) is \(10^{-3}\) to \(10^{-2}\) g P m\(^{-3}\).

**Analysis of cell quota**

Although the parameters in the Droop kinetics could be approximately evaluated, there was no insight into the response of the model to variations in these parameters. In particular, insight was lacking into how to tune the model to bring results into calibration. An analytical investigation of computation of cell quota was conducted to guide the calibration process.

At steady state, algal growth must equal respiration:

\[
G = G_{\text{max}} \left[ 1 - \frac{Q_o}{Q} \right] = r
\]  

(8-2)

in which:

\(G\) = specific growth rate (d\(^{-1}\))

\(G_{\text{max}}\) = maximum specific growth rate (d\(^{-1}\))

\(Q\) = cell quota (g P g\(^{-1}\) C)

\(Q_o\) = minimum cell quota (g P g\(^{-1}\) C)

\(r\) = specific respiration rate (d\(^{-1}\)).

At steady state also, nutrient uptake must equal nutrient release:

\[
V_{\text{max}} \cdot \frac{S}{K_{Hp} + S} = r \cdot Q_o
\]  

(8-3)

in which:

\(V_{\text{max}}\) = maximum nutrient uptake rate (g P g\(^{-1}\) C d\(^{-1}\))

\(S\) = external nutrient concentration (g P m\(^{-3}\))

\(K_{Hp}\) = half saturation concentration for nutrient uptake (g P m\(^{-3}\)).

Equations 8-2 and 8-3 can be rearranged to solve for \(Q_o\) and then equated to each other. The result is:

\[
Q \cdot \left[ 1 - \frac{r}{G_{\text{max}}} \right] = \frac{V_{\text{max}}}{r} \cdot \frac{S}{K_{Hp} + S}
\]  

(8-4)
which can be rearranged to yield:

$$Q = \frac{V_{\text{max}} \cdot S}{r \cdot \frac{KHp + S}{1 - \frac{r}{G_{\text{max}}}}} \quad (8-5)$$

Equation 8-5 yields two insights. First, cell quota is directly proportional to the maximum nutrient uptake rate. Second, minimum cell quota does not appear. This insight is remarkable. Apparently, specification of minimum cell quota does not impact cell quota at all.

The effect of substrate concentration on cell quota can be examined at two extremes. First, note that respiration is much less than the maximum growth rate so that $r/G_{\text{max}} \ll 1$, and the denominator of Equation 8-5 approaches unity. Then examine conditions of nutrients in great excess, $S \gg KHp$. In that case:

$$Q \approx \frac{V_{\text{max}}}{r} \quad (8-6)$$

Cell quota is linearly proportional to the maximum nutrient uptake rate and inversely proportional to the respiration rate.

The opposite extreme is extreme scarcity of nutrients, $S \ll KHp$. In that case:

$$Q \approx \frac{V_{\text{max}}}{r} \cdot \frac{S}{KHp} \quad (8-7)$$

When nutrients are scarce, cell quota is linearly proportional to external nutrient concentration and inversely proportional to half-saturation concentration for nutrient uptake.

The minimum cell quota can be approached but never attained. The degree to which the minimum can be approached is determined by the ratio of respiration to maximum growth rate. This result is obtained by rearranging Equation 8-2 to yield:

$$Q = Q_0\left[1 - \frac{r}{G_{\text{max}}}\right] \quad (8-8)$$

Although the ratio $r/G_{\text{max}}$ is small, it is non-zero. Increasing the respiration rate relative to growth moves the realizable cell quota away from the minimum. Increasing the growth rate relative to respiration moves the realizable cell quota towards the minimum.
Model parameter values

Following initial evaluation, model parameter values were evaluated through a recursive calibration process. Calibration was determined by visual comparison of computed and observed substrate concentrations and algal biomass, and by evaluation of computed cell quotas. Final values of minimum cell quotas and half-saturation concentrations were in the expected range. The maximum uptake rate was considerably lower than the values expected based on published quantities and on order-of-magnitude scaling.

Sensitivity analyses

Sensitivity analyses, conducted during model development (Chapter 5), indicated the following characteristics of Droop kinetics:

- Oscillations in algal biomass and in dissolved phosphate are damped, relative to a model with fixed algal stoichiometry
- Peak biomass does not differ substantially from a model with fixed, minimal phosphorus-to-carbon ratio.

The sensitivity analyses were conducted on a reduced simplified system. It was noted that analyses should be repeated on a system with multiple, time-varying inputs and with complete nutrient kinetics. The enormous effort involved in model set-up, calibration, and execution precluded comparison of Droop kinetics with a second model using fixed algal composition. It was reasoned that a model based on fixed composition could be approximated by reducing the range of computed composition. An attempt was made to reduce the range by increasing minimum cell quota and by reducing maximum nutrient uptake velocity. Minimum cell quota was doubled over the calibration value (Table 8-1). Calibration values were restored and uptake velocity was halved in a subsequent run.

<table>
<thead>
<tr>
<th>Table 8-1</th>
<th>Parameters in Droop Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algal Group</td>
<td>$V_{max}$, g P g$^{-1}$ alg C d$^{-1}$</td>
</tr>
<tr>
<td>cyanobacteria</td>
<td>0.006</td>
</tr>
<tr>
<td>diatoms</td>
<td>0.0033</td>
</tr>
<tr>
<td>other</td>
<td>0.0044</td>
</tr>
</tbody>
</table>

Results are presented at two locations: Racey Point (near the upstream end of the system) and Talleyrand (near the lower end). Nitrogen is calculated to be the predominant limiting nutrient at Racey Point except during late winter and early spring when phosphorus is predominant (Figure 8-1). Phosphorus is calculated to be the predominant limiting nutrient at Talleyrand (Figure 8-2). Cell quota and nutrient limitations, calculated individually for each algal group, are presented here as mean values, weighted by the biomass of each algal group.

Increasing the minimum cell quota had little effect on the computed cell quota (Figures 8-3, 8-4). This behavior is consistent with the analytical study.
Chapter 8  Analysis of Water Column Kinetics

01/17 – 01/19 = Base
SENS1 = Double Minimum Cell Quota
SENS2 = Halve Maximum Nutrient Uptake Rate

Figure 8-1. Computed limits to algal production at Racey Point
Figure 8.2. Computed limits to algal production at Talleyrand

01/17 – 01/19 = Base
SENS1 = Double Minimum Cell Quota
SENS2 = Halve Maximum Nutrient Uptake Rate
Figure 8.3. Computed cell quota at Racey Point

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Chapter 8: Analysis of Water Column Kinetics

Figure 8-4. Computed cell quota at Talleyrand

01/17 – 01/19 = Base
SENS1 = Double Minimum Cell Quota
SENS2 = Halve Maximum Nutrient Uptake Rate
(Equation 8-5), which indicated that specification of the minimum cell quota does not influence the computed quota. Reducing the maximum nutrient uptake rate reduced the cell quota by one-third to one-half (Figures 8-3, 8-4). This behavior is consistent with the analytical study (Equation 8-5), which indicated that cell quota is linearly proportional to maximum nutrient uptake rate.

Increasing the minimum cell quota increased phosphorus limitation on growth at both locations (Figures 8-1, 8-2). This behavior can be readily interpreted by noting the role of minimum cell quota in computed nutrient limitation:

\[ G = G_{\text{max}} \left(1 - \frac{Q_0}{Q}\right) \]  

(Equation 8-9)

Likewise, decreasing the maximum nutrient uptake rate also increased phosphorus limitation on growth (Figures 8-1, 8-2). This behavior can also be interpreted in light of Equation 8-9. Instead of diminished growth brought about by increased \( Q_0 \), however, diminished growth is induced by a reduction in cell quota, \( Q \) (Figures 8-3 and 8-4, Equation 8-5).

At Racey Point, computed chlorophyll was largely unaffected by changes in either minimum cell quota or maximum nutrient uptake rate (Figure 8-5). Close inspection indicates some small, transient differences between model runs but, for practical purposes, chlorophyll was unchanged. Certainly the agreement between computed and observed chlorophyll was unaffected by the parameter variations. To a large extent, this behavior can be attributed to the predominant nitrogen limitation at this location, but chlorophyll is not substantially altered during the periods of phosphorus limitation either. At Talleyrand, computed chlorophyll was reduced through much of the application period (Figure 8-6). This behavior can be readily interpreted as the reaction to increased phosphorus limitation in a predominantly phosphorus-limited region. The peak algal blooms were not truncated, however. These blooms were composed of cyanobacteria that predominated upstream in a largely nitrogen-limited region. Cyanobacteria were apparently transported into the lower estuary where they rapidly perished due to salinity-induced mortality. Since their presence was due to transport rather than production, they were unaffected by parameter changes that induced phosphorus limitation.

At Racey Point, increasing the minimum cell quota had minimum influence on dissolved phosphate concentration (Figure 8-7). To the extent a change was noticeable, dissolved phosphate increased. A large increase in dissolved phosphate accompanied the reduction in nutrient uptake rate, behavior that is readily understood. Close inspection indicates the increases were primarily during the periods when nitrogen was the limiting nutrient. At Talleyrand, dissolved phosphate increased in response to the parameter changes but not to the extent apparent at Racey Point (Figure 8-8). The behaviors at the two locations indicate that external phosphate is sensitive to specification of nutrient uptake velocity when phosphorus is not the limiting nutrient but is less sensitive when phosphorus is limiting.
01/17 – 01/19 = Base
SENS1 = Double Minimum Cell Quota
SENS2 = Halve Maximum Nutrient Uptake Rate

Figure 8-5. Computed and observed chlorophyll at Racey Point
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01/17 – 01/19 = Base
SENS1 = Double Minimum Cell Quota
SENS2 = Halve Maximum Nutrient Uptake Rate

Figure 8-6. Computed and observed chlorophyll at Talleyrand
Figure 8-7. Computed and observed DIP at Racey Point

01/17 - 01/19 = Base

SENS1 = Double Minimum Cell Quota

SENS2 = Halve Maximum Nutrient Uptake Rate
Chapter 8  Analysis of Water Column Kinetics

01/17 - 01/19 = Base
SENS1 = Double Minimum Cell Quota
SENS2 = Halve Maximum Nutrient Uptake Rate

Figure 8-8. Computed and observed DIP at Talleyrand
While comparison of the Droop model with a realistic model based on fixed algal composition was not possible, these sensitivity runs allow inferences to be made regarding the Droop model. Changes in parameter values had little influence on computed chlorophyll. In particular, peak chlorophyll concentrations were unaffected. This finding is consistent with earlier sensitivity runs on the reduced system and with DiToro's 1980 findings. It is concluded that employment of a Droop model to improve computed chlorophyll concentration is unnecessary. Droop model parameters exerted a major influence on dissolved phosphate concentration. Luxury uptake, in excess of algal requirements, was computed when nitrogen was limiting. Several other CE-QUAL-ICM applications are plagued with excessive phosphate concentration (Cerco 2000). Specification of a minimum phosphorus composition, necessary to compute chlorophyll correctly during phosphorus limitation, results in excessive phosphorus concentration at times and locations where phosphorus is not limiting. Use of Droop kinetics appears to offer a remedy to this problem. Ironically then, Droop kinetics present a mechanism for regulating computed nutrient concentrations rather than computed chlorophyll concentrations.

Nitrogen Fixation

Nitrogen fixation is the microbial-mediated conversion of gaseous nitrogen to ammonium. Nitrogen fixation may be conducted by heterotrophic bacteria or by autotrophic cyanobacteria (blue-green algae). Not all cyanobacteria are nitrogen fixers. In the St. Johns River, the genera *Cylindrospermopsis* and *Anabaena* fix nitrogen while *Microcystis* does not. Intuition suggests the nitrogen fixers should be dominant under strongly nitrogen-limited conditions when their ability to utilize gaseous nitrogen gives them a competitive advantage over organisms limited to the use of ammonium and nitrate. In reality, a host of factors influences the presence of nitrogen fixers, and prediction of their occurrence is problematic.

Concern for the role of nitrogen fixation in supporting algal blooms led the sponsor to adopt a two-pronged approach. Field programs were initiated to investigate cyanobacteria physiology and to measure nitrogen fixation rates (Paerl et al. 2002, Philips 2002). Incorporation of nitrogen fixation was planned as a later addition to the model. Difficulty in calibrating the model absent nitrogen fixation led to accelerating the incorporation of the process into the present model.

Observations

Measures of nitrogen fixation were obtained from the original investigator (Philips 2002). Measures were conducted in light and dark at 15 stations at monthly intervals from January through October 2000. The investigator also provided observations of conventional water quality parameters collected concurrently with the nitrogen fixation measures. The two data bases were merged and purged of observations outside of the model domain, partial records, and a few questionable measures. Nitrogen fixation was measured by an acetylene reduction method and reported as ng ethylene L^{-1} h^{-1}. From tables in the Philips report, the conversion ng ethylene L^{-1} h^{-1} * 0.33 = ng N_{2} L^{-1} h^{-1} was
derived. Subsequent units conversions resulted in a data base of light and dark nitrogen fixation, as mg N m⁻³ d⁻¹, and concurrent water temperature, salinity, chlorophyll, dissolved inorganic nitrogen, and additional parameters. Roughly 10 records were available from each of 11 stations.

**Model formulation**

Incorporation of nitrogen fixation in the model required two considerations. The first was relaxation of the nitrogen limitation to blue-green algal growth. The second was incorporation of nitrogen fixed into the total nitrogen budget. Inspection of the observations indicated significant relationships between nitrogen fixation and temperature (Figure 8-9), salinity (Figure 8-10), and dissolved inorganic nitrogen (Figure 8-11). One approach would have been to develop a function that related nitrogen fixation to these parameters. Relationships were already in place, however, that related cyanobacteria production and mortality to salinity and temperature. Creation of a new relationship for nitrogen fixation would have been redundant and, possibly, in conflict with the existing relationships. The approach taken in this study concentrated on the relationship of nitrogen fixation to dissolved inorganic nitrogen. The salinity and temperature relationships were left to the existing formulations.

Our revised nutrient limitation required specification of the fraction of nitrogen fixers in the blue-green algal population and specification of a new half-saturation coefficient:

\[
N\lim = \frac{DIN}{KHn + DIN} \cdot \left[1 - F_{\text{fix}}\right] + \frac{DIN + KHn_{\text{fix}}}{DIN + KHn + KHn_{\text{fix}}} \cdot F_{\text{fix}}
\]

in which:

- \(N\lim\) = nitrogen limitation \((0 \leq N\lim \leq 1)\)
- \(DIN\) = dissolved inorganic nitrogen \((\text{g} \ N \text{m}^{-3})\)
- \(KHn\) = half-saturation concentration for nitrogen uptake \((\text{g} \ N \text{m}^{-3})\)
- \(KHn_{\text{fix}}\) = half-saturation concentration for nitrogen fixation \((\text{g} \ N \text{m}^{-3})\)
- \(F_{\text{fix}}\) = fraction of nitrogen fixers in blue-green algal population \((0 \leq F_{\text{fix}} \leq 1)\).

Parameter \(KHn_{\text{fix}}\) is a parameter that relaxes the nitrogen limit for a portion of the population (Figure 8-12). As \(KHn_{\text{fix}}\) increases, the limitation is reduced. The influence of \(KHn_{\text{fix}}\) is greater at low nitrogen concentrations and diminishes at higher concentrations.

Computed nitrogen fixation takes place only when nitrogen is the most limiting of the potential limits (nitrogen, phosphorus, light) to algal production. Total nitrogen is incremented by first removing from the dissolved inorganic nitrogen pool the amount of nitrogen calculated by conventional limitation:
Figure 8-9. Computed and observed relationship between temperature and nitrogen fixation
Figure 8-10. Computed and observed relationship between salinity and nitrogen fixation.
Figure 8-11. Computed and observed relationship between DIN and nitrogen fixation

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Figure 8-12. Effect of parameter $KHnfix$ on nitrogen limitation computed for $KHn = 0.02 \text{ g N m}^{-3}$

\[ \text{DIN}_{up} = \frac{\text{DIN}}{KHn + \text{DIN}} \cdot G \cdot B1 \cdot \text{Anc} \] (8-11)

in which:

- $\text{DIN}_{up}$ = uptake of dissolved inorganic nitrogen by cyanobacteria (g N m$^{-3}$ d$^{-1}$)
- $G$ = maximum specific growth rate without nutrient limitation (d$^{-1}$)
- $B1$ = cyanobacteria biomass (g C m$^{-3}$)
- $\text{Anc}$ = cyanobacteria nitrogen-to-carbon ratio (g N g$^{-1}$ C)

Algal biomass is next incremented by the amount calculated using the nutrient limitation with nitrogen fixation:

\[ \frac{\delta B1}{\delta t} = N \lim G \cdot B1 \] (8-12)

The amount of nitrogen fixed is the difference between nitrogen uptake and increase in nitrogenous algal biomass:

\[ \text{Nfix} = \left[ \frac{\text{DIN} + KHnfix}{\text{DIN} + KHn + KHnfix} - \frac{\text{DIN}}{\text{DIN} + KHn} \right] \cdot \text{Fnfix} \cdot G \cdot B1 \cdot \text{Anc} \] (8-13)

in which $\text{Nfix}$ is the amount of nitrogen fixed (g N m$^{-3}$ d$^{-1}$).
Model results

Computed nitrogen fixation was extracted from the model on a daily-average basis at six locations corresponding to sampling sites. For comparison with the model, observations conducted in light and dark were averaged into a single daily value. Parameters $K_{Hnf}$ and $F_{nf}$ were evaluated visually primarily through comparison of computed and observed nitrogen fixation rates and their relation to temperature, salinity, and dissolved inorganic nitrogen. Final parameter values were $K_{Hnf} = 0.01$ g N m$^{-3}$ and $F_{nf} = 0.175$.

**Temperature.** Observations (Figure 8-9) indicate significant nitrogen fixing activity does not occur below 20 °C. Thereafter, activity increases in a rough exponential relationship to temperature. The model replicates well the temperature relationship apparent in the observations. Maximum computed nitrogen fixation rates are about double the maximum observed rates. This discrepancy can be attributed to the comparison of the model population from 1997-1998 to the observed samples from 2000. Aside from potential differences in rates between the computed and observed years, the complete computational set of over 2,000 daily rates should show greater range than the sampled set of roughly 100 observations.

**Salinity.** Virtually no nitrogen fixation was observed when salinity exceeded 1 ppt; the preponderance of nitrogen fixation occurred when salinity was less than 0.5 ppt (Figure 8-10). The model provided excellent representation of the observed dependence of nitrogen fixation on salinity.

**Dissolved inorganic nitrogen.** Nitrogen fixation was not observed when dissolved inorganic nitrogen exceeded 0.1 g N m$^{-3}$ (Figure 8-11). The rate was greatly enhanced when dissolved inorganic nitrogen was less than 0.05 g N m$^{-3}$. Computed nitrogen fixation was largely cut off when dissolved inorganic nitrogen exceeded $\leq 0.05$ g N m$^{-3}$. Below this concentration, computed nitrogen fixation increased in inverse proportion to dissolved inorganic nitrogen concentration. The model behavior well replicated the observed relationship between dissolved inorganic nitrogen and nitrogen fixation.

**Chlorophyll.** Observations indicated a loose relationship between chlorophyll and nitrogen fixation (Figure 8-13). Clearly, nitrogen fixation increased as chlorophyll increased. Highest fixation rates were observed when chlorophyll exceeded 40 mg m$^{-3}$, although significant nitrogen fixation occurred at lower chlorophyll concentrations. In one instance, a chlorophyll concentration in excess of 60 mg m$^{-3}$ was accompanied by no nitrogen fixation. The loose relationship between nitrogen fixation and chlorophyll was no doubt due to the fact that chlorophyll concentration represented the entire algal population rather than the population of nitrogen fixers alone. Model computations provided a good representation of observed characteristics. The general increase of nitrogen fixation as a function of chlorophyll was computed, although occasional outliers produced significant nitrogen fixation at low chlorophyll concentrations or else no nitrogen fixation at high chlorophyll concentrations.

Nitrogen fixation was modeled in order to represent chlorophyll (Figure 8-14) and nitrogen (Figure 8-15) concentrations during algal blooms.
Figure 8-13. Computed and observed relationship between chlorophyll and nitrogen fixation.
A model sensitivity run indicated chlorophyll (Figure 8-16) and total nitrogen (Figure 8-17) observed during the August 1998 bloom could not be replicated without nitrogen fixation. One interesting observation is that salinity (Figure 8-18).
Figure 8-16. Computed and observed chlorophyll concentration, without nitrogen fixation, along river axis, August 1998.

Figure 8-17. Computed and observed total nitrogen concentration, without nitrogen fixation, along river axis, August 1998.
restricted nitrogen fixation to the region of the river above km 40, but chlorophyll and total nitrogen increased downstream. Apparently nitrogen fixed upstream was carried into the lower portion of the river. Chlorophyll was also carried downstream and, perhaps, algal production in the lower river was stimulated by nitrogen fixed upstream.

The modeled nitrogen fixation rates do not completely replicate the August 1998 bloom; higher rates are required. The modeled rates can readily be increased but must be tempered by the requirement to match chlorophyll and total nitrogen at other times. The goal is to optimize model behavior over the 2-year calibration period rather than during one bloom event. The overall effect of nitrogen fixation on the model results is best examined in a quantitative format by using the ME statistic:

\[
ME = \frac{\sum (O - P)}{n}
\]  

in which:

- ME = mean error
- O = observation
- P = prediction
- n = number of observations
An ME of zero is ideal. Positive ME indicates observations exceed computations, on average. Negative ME indicates computations exceed observations, on average.

Nitrogen fixation increases computed chlorophyll by 0 to 5 mg m\(^{-3}\) (Figure 8-19). The greatest effect is in the reach from Mandarin Point to Picolata. The net effect on ME is close to zero. For every station in which nitrogen fixation moves ME towards zero (e.g., Picolata), there is another station in which ME moves away from zero (e.g., Mandarin Point). Nitrogen fixation increases computed total nitrogen by 0.01 to more than 0.1 g N m\(^{-3}\) (Figure 8-20). In this case, nitrogen fixation almost always moves ME close to the ideal value of zero.

The nitrogen fixation algorithm is based on a constant fraction, 17.5 percent, of nitrogen fixers in the total cyanobacteria population. No doubt, results could be improved if this fraction were variable. The fraction can readily be varied to match observed nitrogen and chlorophyll but there are no means to specify the fraction in a predictive mode. One approach to predicting the fraction of nitrogen fixers would be to increase the fraction in the presence of nitrogen limitation. But, as has been noted, prediction of the occurrence of nitrogen fixers is not so easy. An algal state variable can also be incorporated that specifically represents nitrogen fixers if sufficient information becomes available to isolate and model this population.

![Figure 8-19. Chlorophyll ME with and without nitrogen fixation](image-url)
Conclusions

It is concluded that:

- The CE-QUAL-ICM model captures apparent relationships between observed nitrogen fixation and temperature, salinity, dissolved inorganic nitrogen, and chlorophyll.
- Nitrogen fixation is required to match observed chlorophyll and total nitrogen during algal blooms.
- The major effect of computed nitrogen fixation is improvement of overall computed total nitrogen. Little or no effect on overall computed chlorophyll is apparent.
- Improved representation of nitrogen fixation and its effects requires improved information about the temporal and spatial distribution of the nitrogen fixing population.

Labile and Refractory Dissolved Organic Matter

A novel approach in the St. Johns River study was the partitioning of dissolved organic matter into labile and refractory components. These fractions were represented as distinct model state variables: labile dissolved organic carbon (DOC), refractory DOC, labile DO nitrogen, refractory DO nitrogen, labile DO phosphorus, and refractory DO phosphorus. Previous applications of the CE-QUAL-ICM model (e.g., Cerco and Cole 1994) split particulate organic matter into labile and refractory fractions but represented dissolved organic carbon and nutrients as homogenous components.
The split of particulate organic matter was driven by the need to partition organic matter for the sediment diagenesis model (DiToro and Fitzpatrick 1993). Although the existence of components of various lability within the dissolved pools was recognized, no explicit need to partition dissolved organic matter was apparent. Within the St. Johns River, the obvious difference between dissolved organic matter entering the system as “blackwater” from upstream wetlands and dissolved organic matter entering the system from algal decomposition indicated these components should be individually represented in the model. The humic material in blackwater was considered to be highly refractory, while fresh organic matter recycled from phytoplankton was expected to be more labile. The split of dissolved organic matter also presented the opportunity to apportion point-source loads and, perhaps, to provide more detailed information on the effects of point-source controls on eutrophication.

**Splitting the loads**

Guidance on defining and partitioning particulate organic matter was provided by the G model (Westrich and Berner 1984). Experiments on oxic decomposition of phytoplankton found that 50 percent of the organic matter decomposed in 70 days (first-order decay rate 0.066 d⁻¹), 16 percent decomposed over 600 days (first order decay rate 0.004 d⁻¹) and the remainder was nonreactive. For modeling purposes, the fraction that decomposed on a time scale of 2 months was defined as labile, while the remaining material, which decomposed on a time scale of 2 years or more, was defined as refractory.

The Westrich and Berner experiments were conducted over a period of 2 years. Incubations of this duration conducted on organic matter collected from multiple sources are impractical. A simpler, less time-consuming method of partitioning must be found. A method based on BOD analyses was derived by the sponsor and used to partition loads to the St. Johns River (Hendrickson 2002). Decay rates for labile and refractory material, taken from an earlier application of the CE-QUAL-ICM model, were used to apportion 5-day biochemical oxygen demand into labile and refractory contributions. Stoichiometry was used to convert oxygen consumed into equivalent labile and refractory fractions of total organic carbon (TOC). Nutrients were partitioned using distinct mass ratios for labile and refractory components. These were C:N = 3.6 for labile organic nitrogen, C:N = 33.6 for refractory organic nitrogen, C:P = 22.4 for labile organic phosphorus, and C:P = 663 for refractory organic phosphorus.

Using this approach, organic carbon runoff into the St. Johns River was determined to be largely refractory. Organic nitrogen in runoff was split roughly evenly into labile and refractory components. Organic phosphorus runoff was predominantly labile. Exact proportions varied, however, as a function of land use and other factors. Proportions of labile and refractory DOC and DON computed in the water column followed the partitioning of the loads (Figures 8-21, 8-22). Concentrations of refractory DOC were an order of magnitude greater than labile, while labile and refractory DON were about evenly split. Computed concentrations of labile and refractory DOP were also evenly split (Figure 8-23) although the labile fraction predominated in the loads. A simple explanation is that the labile load was rapidly converted to dissolved inorganic phosphorus leaving a larger fraction of the refractory material behind.
Figure 8-21. Computed labile and refractory DOC at Picolata

Figure 8-22. Computed labile and refractory DON at Picolata
Sensitivity analyses

Since the division of dissolved organic matter into labile and refractory portions was a new addition to the model, it was decided to examine the effects of the addition. The calibrated model was contrasted with three sensitivity runs (Table 8-2). In the first run, SENS4, all dissolved organic matter was considered labile. In the second, SENS5, all dissolved organic matter was considered refractory. In the third, SENS6, an average decay rate was used for all DO matter. DOC observations were available for the St. Johns River. Sensitivity analyses focused on this state variable as well as DO, since oxygen consumption is largely the result of carbon oxidation. Observations were not available for dissolved organic nutrients. Sensitivity analyses focused on inorganic nutrient forms, since these are produced in the model through mineralization of dissolved organic nutrients, and on chlorophyll, since phytoplankton production is supported by inorganic nutrients. Results were examined as time-series comparisons with observations and as cumulative plots of computed and observed properties.
Table 8-2
Dissolved Organic Matter Mineralization Rates

<table>
<thead>
<tr>
<th></th>
<th>Labile, d⁻¹</th>
<th>Refractory, d⁻¹</th>
<th>Average, d⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>St. Johns River</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>0.05</td>
<td>0.0025</td>
<td>0.011</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.025</td>
<td>0.0025</td>
<td>0.008</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.10</td>
<td>0.01</td>
<td>0.032</td>
</tr>
<tr>
<td><strong>Chesapeake Bay (Cerco and Noel 2003)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
<td>0.011</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
<td>0.025</td>
</tr>
<tr>
<td>Phosphorus</td>
<td></td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td><strong>Florida Bay (Cerco et al. 2000)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Phosphorus</td>
<td></td>
<td></td>
<td>0.20</td>
</tr>
</tbody>
</table>

**Carbon and dissolved oxygen.** Time series of comparisons of computed and observed dissolved organic carbon are different but essentially equivalent for the calibration and for the all-refractory run (Figure 8-24). Thereafter, computed DOC declines below the observed rate as the mineralization rate increases through the average and all-labile runs. Careful examination of the cumulative distributions (Figure 8-25) indicates the calibration provides superior calculation of DOC system-wide. The all-refractory run calculates DOC too high while the other sensitivity runs calculate DOC too low.

Time-series comparisons of computed and observed DO are roughly equivalent for the calibration and for the all-refractory run (Figure 8-26). Computations deteriorate as the mineralization rate increases and are obviously incorrect for the all-labile run. The cumulative plots indicate computed DO moves up or down as the mineralization rate decreases or increases (Figure 8-27). At the median, the calibration provides superior results. The all-refractory run matches the upper end of the DO distribution well but is inferior to the calibration for the lower portion of the distribution. The average run underestimates DO throughout the distribution while the all-labile run provides completely unsatisfactory results.

**Nitrogen and chlorophyll.** Highest dissolved inorganic nitrogen concentrations are computed for the all-labile run and decline thereafter as mineralization rate declines. At Picolata, visual examination indicates the calibration provides superior results (Figure 8-28). The cumulative distribution plots are not as clear (Figure 8-29). In the lower half of the observed distribution, the average run is best, although this run underestimates the upper portion of the distribution. The calibration is high on the lower end and low on the higher end of the observed distribution. In a sense, the calibration may be viewed as superior overall, although the run with average mineralization rate provides better results when nitrogen is potentially a limiting nutrient. Both the average run and the calibration are superior to the all-labile and all-refractory runs.
Figure 8-24. Computed and observed DOC at Picolata for calibration (01/10 – 01/19), all labile (SENS4), all refractory (SENS5), and average (SENS6) splits
Figure 8-25. System-wide cumulative distributions of computed and observed DOC for calibration (01/10–01/19). all labile (SENS4), all refractory (SENS5), and average (SENS6) splits.
Figure 8-26. Computed and observed DO at Picolata for calibration (01/10 – 01/19), all labile (SENS4), all refractory (SENS5), and average (SENS6) splits.
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Figure 8-27. System-wide cumulative distributions of computed and observed DO for calibration (01/10 – 01/19), all labile (SENS4), all refractory (SENS5), and average (SENS6) splits.
Figure 8-28. Computed and observed DIN at Picolata for calibration (01/10 – 01/19), all labile (SENS4), all refractory (SENS5), and average (SENS6) splits.
Figure 8-29. System-wide cumulative distributions of computed and observed DIN for calibration (01/10 - 01/19) all labile (SENS4), all refractory (SENS5), and average (SENS6) splits
The chlorophyll time series at Picolata are indistinguishable for the calibration and average runs (Figure 8-30). Computed chlorophyll is on the low side of observed for the all-refractory run and on the high side for the all-labile run. Neither can the calibration and average runs be distinguished in the cumulative plots (Figure 8-31). The all-refractory run is equivalent to the calibration and average runs up to the median observed chlorophyll but underestimates the higher end of the observations. The all-labile run is clearly inferior to all three alternatives.

**Phosphorus.** The wide range of computed dissolved inorganic phosphorus makes it impossible to select a superior run from the time series at Picolata (Figure 8-32). No dramatic differences are apparent in the cumulative distributions (Figure 8-33), although they can be ranked in order of agreement with the observed distributions, from the all-labile run through the calibration, the average run, and the all-refractory run.

**Conclusions**

The splitting of dissolved organic matter into labile and dissolved components was most successful for DOC. The split was beneficial from two aspects. First, the calibration was superior to alternatives that considered only one component. Second, the split reflected obvious differences in carbon derived from internal versus external sources.

The benefits of splitting DON and DOP were less apparent. The model results using two components could not be clearly distinguished from alternate runs using only one component. The use of a single, average mineralization rate for nitrogen and a single labile rate for phosphorus provided results as good as or superior to the calibration. These conclusions must be moderated by the fact that no observations of DON or DOP were available for comparison with the model. Also, the impact of the splits on management alternatives involving load controls was not examined.

The justification for splitting DON into two components is based more on reasoning than on results. Organic carbon and nitrogen do not exist as independent entities, although they are modeled as such. Rather, they exist together in a host of organic compounds. The processes mimicked by our first-order mineralization of DOC and DON involve activity of heterotrophic bacteria. Bacteria take up organic compounds containing carbon and nitrogen. Portions of the carbon and nitrogen are incorporated into bacterial biomass. The remainder of the carbon is respired away. Excess nitrogen, if any, is excreted as ammonium. Consequently, it is reasonable to represent organic nitrogen mineralization with a rate close to the rate used for organic carbon mineralization. If DOC is split into two components with different mineralization rates, then it is reasonable to split DON into equivalent components.

The justification for splitting DOP into two components is less clear. The process mimicked by our first-order mineralization of DOP is an enzyme-mediated reaction. Phosphatase enzymes produced by bacteria (Ammerman and Azam 1985; Chrost and Overbeck 1987) and algae (Matavulj and Flint 1987;
Figure 8.30. Computed and observed chlorophyll at Picolata for calibration (01/10 – 01/19), all labile (SENS4), all refractory (SENS5), and average (SENS6) splits
Figure 8-31. System-wide cumulative distributions of computed and observed chlorophyll for calibration (01/10 – 01/19), all labile (SENS4), all refractory (SENS5), and average (SENS6) splits.
Figure 8-32. Computed and observed DIP at Picolata for calibration (01/10-01/19), all labile (SENS4), all refractory (SENS5), and average (SENS6) splits.
Figure 8-33. System-wide cumulative distributions of computed and observed DIP for calibration (01/10 – 01/19), all labile (SENS4), all refractory (SENS5), and average (SENS6) splits.
Chrost and Overbeck 1987; Boni et al. 1989) convert DOP into phosphate. This process is distinct from heterotrophic carbon utilization and need not proceed at a similar rate. In our models, the first-order mineralization rate for DOP is usually an order-of-magnitude larger than rates for carbon and nitrogen (Table 8-2). The uncertainty in assigning fractions and the absence of distinct model improvements indicate splitting DOP into components is not worthwhile except for consistency with other dissolved organic substances.

Primary Production and Respiration

The data base

Observations were provided from three stations: Federal Point, Picolata, and Mandarin Point. The data base consisted of 25 observations at each station collected August 1994 to August 1996. Observations of interest included Gross Areal Production (GAP), Volumetric Community Respiration (VCR), and Areal Community Respiration (ACR).

Gross areal production was measured via oxygen evolution over a 3-hour period at midday. Oxygen consumed in accompanying dark bottles was added to oxygen evolved to obtain gross production. A photosynthesis quotient of 1.2 was used to convert oxygen production to carbon units. Respiration measured as oxygen consumption was converted to equivalent carbon units using a respiration quotient of unity. Respiration measured on a volumetric basis was integrated over the depth of the water column to obtain respiration on an areal basis.

The observations were collected prior to the modeled period. For comparison with the model, monthly means were computed at each station. The mean was usually taken from two observations, up to four observations were available for some months. Observations were entirely missing for several other months. Available monthly means were subsequently averaged into annual means.

Comparison with model

Model results at locations corresponding to the observations were averaged into monthly means. Since the production observations were collected at midday, model computations at noon were used. Roughly 60 individual computations (2 months × 30 days) went into each monthly mean. Monthly means were subsequently averaged into annual means.

Observed gross areal production exhibited peak values of roughly 350 mg C m\(^{-2}\) hr\(^{-1}\) at all stations (Figures 8-34 through 8-36). A strong seasonal trend was exhibited so that production during the winter months was less than 10 percent of the summer peak. The summer production maximum encompassed more months at Federal Point than further downstream so that annual production was greatest at the Federal Point station (Table 8-3). The model production cycle was “flatter” than observed. Peak model production was ≈70 percent of observed while minimum modeled production was two times larger than observed. The temporal behavior of computed production lagged the observations. Observed
Figure 8-34. Observed and computed monthly mean GAP at Federal Point

Figure 8-35. Observed and computed monthly mean GAP at Picolata
production in spring was undercomputed, while computed production exceeded observed in autumn. On an annual-average basis, modeled production exceeded observed at Mandarin Point by ≈25 percent, was nearly perfect at Picolata, and fell ≈25 percent below observed at Federal Point (Table 8-3). In view of the limited number of samples and the absence of temporal correspondence between observations and computations, the differences between computed and observed annual-average production are not considered significant.

Observed volumetric carbon respiration exhibited no seasonal trend (Figures 8-37 through 8-39). Peak values were roughly 50 mg C m\(^{-3}\) hr\(^{-1}\). Observations were erratic with multiple questionable values, notably the occurrence of zeroes (as opposed to missing observations), i.e., August 24, 1994, at Picolata. Modeled respiration exhibited seasonality that corresponded with temperature so that peak respiration occurred during the summer months.
Figure 8-37. Observed and computed monthly mean VCR at Federal Point

Figure 8-38. Observed and computed monthly mean VCR at Picolata
Magnitude of peak model respiration was roughly half observed. In view of the erratic behavior of the observations, long-term means should be the most reliable representation of respiration. On an annual-average basis, model respiration ranged from half to nearly 100 percent of the observed values (Table 8-3).

**Discussion**

On an annual-average basis, the model provides good representation of gross areal production. The production-temperature relationships presently applied in the algal component of the model can, perhaps, be revised to enhance seasonality but existing discrepancies between observations and computations must be viewed as minor compared to previous applications of this and other models. Difficulty in simultaneously computing chlorophyll concentration and primary production has been observed in previous CE-QUAL-ICM applications (Cerco 2000) and is a common characteristic of eutrophication models (Brush et al. 2002). The primary production computations in the St. Johns River present a welcome contrast to previous results. Successful computations of both chlorophyll concentration and production in the St. Johns reflect formulations and parameter values adapted from an application specifically intended to reproduce primary production (Cerco and Noel 2004).

Respiration in the model is tightly coupled to temperature and to primary production. Production is temperature-dependent and provides the substrate for heterotrophic respiration (represented as organic carbon mineralization in the model). Both algal and heterotrophic respiration are temperature dependent and enhance the influence of greater substrate availability. The coupling of respiration to production is an entirely reasonable behavior and indicates that internally produced carbon is the primary source of oxidizable substrate.
Observed respiration shows no coupling to temperature or production. In particular, peak respiration often occurs from December to April when production is low. The validity of these measures requires examination. If the respiration measures are valid, they indicate an external source of oxidizable material. To reproduce observed respiration in the model, carbon loads must be re-examined and, perhaps, re-evaluated. Alternately, the present split of loads into labile and refractory fractions may require revision.

References


9 Light Attenuation

The Data Base

A data base of more than 700 measures of light attenuation was provided by the sponsor. The majority of the observations were collected outside the spatial and temporal domains of the present model application. The data set was reduced to observations collected at eight stations located along the river axis within the model grid:

- Bar Pilot
- Fulton Point
- Talleyrand
- Piney Point
- Mandarin Point
- Picolata
- Racey Point
- Palatka.

The preponderance of observations remained outside the model application period. These observations were retained since they were often the sole characterization of conditions at the sample stations.

The Model

An additive model was applied that considered attenuation from four sources: clear water, inorganic solids, organic solids, and dissolved organic matter. Organic solids were computed as 2.5 times the sum of the model particulate organic carbon state variables. This ratio was based on the assumption that organic matter is composed of carbon, hydrogen, and oxygen in the atomic ratio 1:2:1. DOC was used as a surrogate for dissolved organic matter. The resulting model was:

\[
Ke = a_1 + a_2 \cdot ISS + a_3 \cdot VSS + a_4 \cdot DOC
\]  

(9-1)
in which:

\[ Ke = \text{coefficient of diffuse light attenuation (m}^{-1}\text{)} \]
\[ a_1 = \text{attenuation of clear water} \]
\[ a_2 = \text{contribution of inorganic solids to light attenuation (m}^2\text{ g}^{-1}\text{)} \]
\[ a_3 = \text{contribution of organic solids to light attenuation (m}^2\text{ g}^{-1}\text{)} \]
\[ a_4 = \text{contribution of dissolved organic carbon to light attenuation (m}^2\text{ g}^{-1}\text{)} \]

\[ \text{ISS} = \text{inorganic (fixed) solids concentration (g m}^{-3}\text{)} \]
\[ \text{VSS} = \text{organic (volatile) solids concentration (g m}^{-3}\text{)} \]
\[ \text{DOC} = \text{dissolved organic carbon concentration (g m}^{-3}\text{)} \]

Parameters in the model were initially adapted from published values (Pennock 1985; Kirk 1994; Cerco and Noel 2004). Good, consistent guidance was available for the contributions from clear water and solids. Little guidance was available for the contribution from DOC. Initial values were refined through visual fitting of computed and observed attenuation. Final values used in the model were: \( a_1 = 0.03 \text{ m}^{-1} \); \( a_2 = 0.08 \text{ m}^2\text{ g}^{-1} \); \( a_3 = 0.06 \text{ m}^2\text{ g}^{-1} \); and \( a_4 = 0.15 \text{ m}^2\text{ g}^{-1} \).

Light attenuation was computed in every model cell at every time step using computed values of solids and DOC concentrations.

**Model Results**

Computed and observed results were in very good agreement throughout the greater portion of the river (Figures 9-1 through 9-5). Computations departed from observations near the river mouth (Figures 9-6 through 9-8). Observations indicated a sharp and continuous decline in attenuation downstream of Piney Point while the model computed a flat spatial distribution in which the mouth of the river differed little from the headwaters (Figure 9-9).

Two factors contribute to the discrepancies between computations and observations near the mouth of the river. The first is an apparent overestimation of the parameters that relate attenuation to solids concentration. At the two most downstream stations, Bar Pilot and Fulton Point, the major component of computed attenuation is suspended solids (Figure 9-10). Reduction of computed attenuation into the observed range requires reduction of the solids contribution. Exact matching of the observed mean attenuation at these two stations requires virtual elimination of attenuation by solids. Elimination of solids attenuation is unrealistic.

The second contributor to the discrepancies between computations and observations is the assignment of attenuation to DOC. DOC is used as a surrogate for dissolved, colored organic matter. It is felt that the use of DOC overestimates the contribution of colored material in the lower river. One alternative is that color is bleached out as DOC moves downstream from the headwaters to the mouth. Another alternative, favored by us, recognizes that DOC in the river is a mixture of carbon from multiple sources. Carbon produced
Figure 9-1. Computed and observed light attenuation at Palatka

Figure 9-2. Computed and observed light attenuation at Racey Point
Figure 9-3. Computed and observed light attenuation at Picolata

Figure 9-4. Computed and observed light attenuation at Mandarin Point
Figure 9-5. Computed and observed light attenuation at Piney Point

Figure 9-6. Computed and observed light attenuation at Talleyrand
Figure 9-7. Computed and observed light attenuation at Fulton Point

Figure 9-8. Computed and observed light attenuation at Bar Pilot
Figure 9-9. Mean computed and observed light attenuation at eight stations

Figure 9-10. Components of modeled light attenuation
in-situ, expressed in the model primarily as labile DOC, is a small fraction of the total. The remaining carbon, expressed in the model primarily as refractory DOC, enters the river oceanic and upland sources.

In the tidal freshwater, the refractory DOC originates largely from upland sources. The oceanic contribution must be zero since salt is absent. As salinity increases downstream, the contribution of oceanic DOC increases. For a moment, assume that refractory DOC is conservative. Near the mouth, where salinity is ≈25 ppt, the contribution from the ocean end member is ≈70 percent of the total refractory DOC pool (obtained by ratio based on oceanic salinity of 35 ppt). Use of a single, constant, parameter value to represent DOC attenuation throughout the system assumes that attenuation by the various pools that total DOC comprises is identical. Yet fresh water is recognized as more highly colored than sea water (Kirk 1994). If attenuation is to be related to DOC, we should lower the value of parameter $a_*$ near the river mouth should be lowered to recognize that a large portion of the DOC in that vicinity is oceanic and less colored than DOC that originates in the watershed. An empirical relationship could readily be developed based on an observed relationship between attenuation and salinity (Figure 9-11).

![Figure 9-11. Observed mean light attenuation versus salinity at nine stations in the modeled domain](image)

**Discussion**

Original plans for this phase of the modeling activity called for incorporation of a state-of-the-art optical model (Gallegos 2002) into our own model. As the project progressed, implementation of nitrogen fixation gained priority. Implementation of the advanced optical model is now planned for the next phase.
of our modeling activity. We heartily support employment of the advanced technology. Our enthusiasm is based as much on the careful measures of optical properties that accompany the advanced model as on the model formulation. Additive models such as we employed here provide useful approximations for systems in which absorption is the dominant contributor to light attenuation (Kirk 1994). A major problem with additive models is in parameter evaluation through regression, visual fitting, or other methods. Employment of carefully-measured parameters will eliminate a source of uncertainty and contribute to overall improvement in model calibration and predictive power.

References


10 Analysis

Limiting Nutrients

The LSJR system has been described as a nitrogen-limited estuary with nitrogen being the primary limiting nutrient to algal growth (Hendrickson and Konwinski 1998). This description is based on observed nutrient ratios and concentrations. Nutrient limits computed by the model are based on the Monod formulation for nutrient uptake (nitrogen, silica) or the Droop formulation (phosphorus). The model limitations range from zero (growth completely inhibited by a specific nutrient) to unity (no growth inhibition by the specified nutrient). Computed limitations largely agree with observations. That is, the model computes strong nitrogen limitation during the growing season (Figure 10-1) at most locations. At times, growth is limited to less than 20 percent of its potential value by nitrogen limitation. Computed nutrient limits
Figure 10-1. (Sheet 2 of 4)
Figure 10-1. (Sheet 3 of 4)
Figure 10-1. (Sheet 4 of 4)
to growth are relaxed near the mouth of the river and indicate primarily phosphorus rather than nitrogen limitation. Examination of computed DIN at Fulton Point indicates computations tend to exceed observations. Consequently the model may underestimate nitrogen limitation at this location relative to phosphorus limitation. In view of the limited spatial extent of the computed phosphorus limitation, and the relative abundance of both nutrients near the river mouth, it is believed that the model is suited for use in examining nutrient control alternatives throughout the river.

**Variables With No Observed Data**

Several variables were analyzed that did not have observed data associated with them. Table 10-1 lists these variables. In keeping with previous discussions of computed results (see Chapter 6), only results at the Fulton Point, Piney Point, and Picolata stations presented in Figures 10-2 through 10-4 will be shown here. Results at other stations are provided on the CD-ROM.

<table>
<thead>
<tr>
<th>Table 10-1 Variables With No Observed Data</th>
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<tbody>
<tr>
<td>Algal POC</td>
</tr>
<tr>
<td>Refractory POC</td>
</tr>
<tr>
<td>Refractory POP</td>
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<tr>
<td>Refractory DON</td>
</tr>
</tbody>
</table>

Algal particulate organic matter is proportioned into three forms – algal particulate organic carbon (POC), algal particulate organic nitrogen (PON), and algal particulate organic phosphorus (POP). At each station presented (Figures 10-2 through 10-4), algal POC makes up about 90 percent of the total algal biomass, while the other elements form roughly 6 percent (algal PON) and 4 percent (algal POP) of the total biomass.

If labile and refractory portions of particulate organic matter are considered, concentrations at Fulton Point show different trends for the PON portions but similar trends for POC than what is seen at Piney Point and Picolata. At Fulton Point (Figure 10-2) for the surface and bottom layers, the refractory portion of POC was twice that of the labile portion. This trend is also seen at Piney Point and Picolata (Figures 10-3 and 10-4). The refractory portion of PON at Fulton Point is more than twice the labile portion for the surface layer and more than one order of magnitude higher in the bottom layer. Piney Point and Picolata differ from this trend with 70 percent of the PON in the labile form while 30 percent is in the refractory form.

Internal algal phosphorus can be considered a form of POP. Nearly all of the POP values at Fulton Point are equally split between refractory POP and algal POP. Labile POP at this station makes up a very minor portion (<5 percent) of this variable. At Piney Point and Picolata, POP values are almost all from algal POP. Labile and refractory forms of POP are approximately 1 percent of the total POP value at these stations.
Figure 10-2. Fulton Point computed water quality constituents that have no observed data available (Sheet 1 of 7)
St. Johns River (01/17 - 01/19)
Fulton Pt., Surface
Labile DOC
Refractory DOC

mg/L

Days from Dec. 1, 1996

St. Johns River (01/17 - 01/19)
Fulton Pt., Bottom
Labile DOC
Refractory DOC

mg/L

Days from Dec. 1, 1996

Figure 10-2. (Sheet 2 of 7)
Figure 10-2. (Sheet 3 of 7)
Figure 10-2. (Sheet 4 of 7)
Figure 10-2. (Sheet 5 of 7)
Figure 10-2. (Sheet 6 of 7)
Figure 10-2. (Sheet 7 of 7)
Figure 10-3. Piney Point computed water quality constituents that have no observed data available (Sheet 1 of 7)
Figure 10-3. (Sheet 2 of 7)
Figure 10-3. (Sheet 3 of 7)
Figure 10-3. (Sheet 4 of 7)
Figure 10-3. (Sheet 5 of 7)
Figure 10-3. (Sheet 6 of 7)
Figure 10-3. (Sheet 7 of 7)
Figure 10-4. Picolata computed water quality constituents that have no observed data available (Sheet 1 of 4)
Figure 10-4. (Sheet 2 of 4)
Figure 10-4. (Sheet 3 of 4)
The dissolved forms of organic matter show similar trends at all stations for surface and bottom layers. From comparing DOC at all stations, Figures 10-2 through 10-4 showed higher refractory DOC values than labile (90 percent as compared to 10 percent). Values for DON were about equally split between refractory and labile for all stations except that Fulton Point showed slightly higher bottom refractory DON. Finally, DOP for surface and bottom levels at Piney Point and Picolata were split approximately 55 percent refractory and 45 percent labile, while refractory DOP at Fulton Point was an order of magnitude higher than labile DOP.

Overall, the dominant form of organic matter at the stations discussed previously was refractory DOC. At all stations, the maximum value of refractory DOC computed by CE-QUAL-ICM was approximately 18 mg/L. This computed value was comparable to observed values of DOC reported.

**Transport Across Boundaries and Nutrient Budgets**

Nutrient budgets were analyzed by computing the mass balance (i.e., transfer of mass to the system and transformation within the system) for the six reach segments of the LSJR (Figure 4-1) for each simulation year. A yearly nutrient budget is composed of many components. Budgets or mass balance for TN and TP were expressed as:
Accumulation = Loadings ± Transport ± Reactions + \( \varepsilon \) 

(10-1)

in which:

**Accumulation** = Net change in mass over a year  

**Loadings** = PS, NPS, and Atmospheric loads to the segments  

**Transport** = Mass moved into or out of segments  

**Reactions** = Settling of nutrients, chemical transformation, and sediment releases of nutrients within the segments.  

\( \varepsilon \) = Error term

The error term arises due to round-off error in internal calculations, small discrepancies in loadings summarized external to the model, and other factors.

A major component of the nutrient budget was the transport across segment boundary faces. Monthly averaged output flux information for cells making up the segment boundary faces was used in from CE-QUAL-ICM computing the yearly transport values for TN and TP in and out of segments.

Figures 10-5 and 10-6 present results by year for each segment of the LSJR. Note that transport is plotted separately on a smaller plot within the plotting area showing mass components of the mass balance. Positive terms represent sources to the water column of the region. Expressions in the legend representing components of the mass balance are:

a. **TN and TP Epsilon** represent error terms for the mass balance equation.  

b. **NPS** represents mass from NPS loads.  

c. **PS** represents mass from PS loads.  

d. **Particle PNFWS and PPFWS** represent the mass of nitrogen and phosphorus, respectively, settling to the sediments.  

e. **Dissolved BENNH4, BENNO3, and BENP04** represent the mass of ammonium, nitrate, and phosphate, respectively, released from the sediments.  

f. **ATM_N and ATM_P** represent the mass of atmospheric nitrogen and phosphorus depositing to the segment.  

g. **NFIX** represents the mass of nitrogen from nitrogen fixation added to the segment.  

h. **Delta** represents net accumulation in the region, over the year.

Observations from comparison of TN and TP budgets for both years modeled are:

a. **PS, NPS, and atmospheric loads** did not show large variability from year to year.
Figure 10-5. TN budget by segments for both simulation years (Sheet 1 of 6)
Figure 10-5. (Sheet 2 of 6)
Figure 10-5. (Sheet 3 of 6)
Figure 10-5. (Sheet 4 of 6)
Figure 10-5. (Sheet 5 of 6)
Figure 10-5. (Sheet 6 of 6)
Figure 10-6. TP budget by segments for both simulation years (Sheet 1 of 6)
Figure 10-6. (Sheet 2 of 6)
Figure 10-6. (Sheet 3 of 6)
Figure 10-6. (Sheet 4 of 6)
Figure 10-6. (Sheet 5 of 6)
Figure 10-6. (Sheet 6 of 6)
b. Of the variables included in the TN and TP budgets, the budgets appear to be most affected by transport. Transport of TN and TP mass into and out of each segment is usually an order of magnitude larger than mass loads or other sources of mass. Overall transport through the system was in a downstream direction toward the ocean.

c. Besides transport for segments 1, 2, and 4, PS loads provide the largest source of TN mass for both years, and for segments 3, 5, and 6, NPS loads provide the largest source of TN mass for both years.

d. Like TN loadings, PS loads for segments 1, 2, and 4 provide the largest source of TP mass for both years after transport, and NPS loads for segments 3, 5, and 6 provide the largest source of TP mass for both years after transport.

e. Nitrogen fixation becomes a major source of TN in segments 5 and 6 during the 1997-1998-simulation year.

f. Besides transport out of the system as a mechanism of loss for nitrogen and phosphorus, particulate nitrogen and phosphorus settling is the next largest loss mechanism from the system. Losses of particulate phosphorus mass is about the same magnitude for all segments, but loss of particulate nitrogen mass from segments 4 and 5 is an order of magnitude greater than for all the other segments.

Ideally, the law of mass conservation requires that the mass balance within a segment should be zero. The $\epsilon$ is an indicator of the error amount of Equation 10-1. For this application, $\epsilon$ was found to be approximately 10 percent or less when computing TN and TP mass balance for each segment. Even though TN and TP mass balance were not zero, an error of 10 percent or less was deemed acceptable when one considers that loads are affected by numerous assumptions regarding sources, destination, attenuation, and round-off errors made during computations of the average yearly transport and mass load values.

Change in mass over a simulation year was included in the analysis as well. Estimates of delta TN and TP by year for each segment were computed by summing all components of TN (i.e., algal N, ammonium, nitrate, labile/refractory DON, and labile/refractory PON) and TP (i.e., algal internal P, labile/refractory DOP, and labile/refractory POP) for the first and last day of simulation and solving as:

$$\text{Delta TP or TN} = \text{last day TP or TN (kg)} - \text{1st TP or TN (kg)}$$  \hspace{1cm} (10-2)

The plots indicate that TP and TN mass has slightly changed over the year for all segments.

Reference

## Appendix A
### Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<td>3D</td>
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<td>ACR</td>
<td>areal community respiration</td>
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<td>AME</td>
<td>average mean error</td>
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<td>BOD</td>
<td>biochemical oxygen demand</td>
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<tr>
<td>CBOD</td>
<td>carbonaceous biochemical oxygen demand</td>
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<tr>
<td>CE-QUAL-ICM</td>
<td>Corps of Engineers Integrated Compartment Water Quality Model</td>
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<td>CESAJ</td>
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<tr>
<td>CH3D</td>
<td>computational hydrodynamics in three dimensions</td>
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<td>DIC</td>
<td>dissolved inorganic carbon</td>
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<td>EFDC</td>
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<td>ME</td>
<td>mean error</td>
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<tr>
<td>PON</td>
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<td>volumetric community respiration</td>
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<td>WQM</td>
<td>water quality model</td>
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Three-Dimensional Eutrophication Model of the Lower St. Johns River, Florida

Transport processes were obtained from the Environmental Fluid Dynamics Code. Model application period was December 1996 through November 1998. The model activated 28 state variables in the water column including physical variables, three algal groups, multiple forms of carbon, nitrogen, phosphorus and silica, and dissolved oxygen. Several features were added to the model for this application. These included representation of the internal algal phosphorus pool, distinction of labile and refractory dissolved organic matter, and representation of nitrogen fixation. The water column was coupled to a predictive sediment diagenesis model that computed sediment-water fluxes of dissolved oxygen, chemical oxygen demand, ammonium, nitrate, phosphate, and silica, based on computed inputs of particulate organic matter. Model results were compared to an extensive suite of observations in the water column and benthic sediments.