A Three-dimensional Bay/estuary Model To Simulate Water Quality Transport

2006

Jing Yu

University of Central Florida

Find similar works at: http://stars.library.ucf.edu/etd

University of Central Florida Libraries http://library.ucf.edu

Part of the Civil Engineering Commons

STARS Citation

http://stars.library.ucf.edu/etd/1031

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
A THREE-DIMENSIONAL BAY/ESTUARY MODEL TO SIMULATE WATER QUALITY TRANSPORT

by

JING YU
B.S. Tsinghua University, 1996
M.S. Loyola University of Chicago, 2002

A thesis submitted in partial fulfillment of requirements for the Degree of Master of Science in the Department of Civil and Environmental Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Fall Term
2006
ABSTRACT

This thesis presents the development of a numerical water quality model using a general paradigm of reaction-based approaches. In a reaction-based approach, all conceptualized biogeochemical processes are transformed into a reaction network. Through the decomposition of species governing equations via Gauss-Jordan column reduction of the reaction network, (1) redundant fast reactions and irrelevant kinetic reactions are removed from the system, which alleviates the problem of unnecessary and erroneous formulation and parameterization of these reactions, and (2) fast reactions and slow reactions are decoupled, which enables robust numerical integrations. The system of species transport equations is transformed to reaction-extent transport equations, which is then approximated with two subsets: algebraic equations and kinetic-variables transport equations. As a result, the model alleviates the needs of using simple partitions for fast reactions. With the diagonalization strategy, it makes the inclusion of arbitrary number of fast and kinetic reactions relatively easy, and, more importantly, it enables the formulation and parameterization of kinetic reactions one by one. To demonstrate the general paradigm, QAUL2E was recasted in the mode of a reaction network. The model then was applied to the Loxahatchee estuary to study its response to a hypothetical biogeochemical loading from its surrounding drainage. Preliminary results indicated that the model can simulate four interacting biogeochemical processes: algae kinetics, nitrogen cycle, phosphorus cycle, and dissolved oxygen balance.
To my parents
Yu Xuejun and Wang Fengqin
Who encourage me to go after my dreams forever

To my husband, Zhan
And my daughter, Yuhui (April)
Who awake up my spirit and responsibilities
ACKNOWLEDGMENTS

I would first like to express my gratitude to my advisor Dr. Gour-Tsyh (George) Yeh for his guidance and support through my graduate study. His ideas and input has enlightened me in this work. What I learned from him is not only the knowledge about civil engineering, but also spirits of seriousness, honesty, and confidence as a distinguished researcher. His way of research has impressed me and will greatly help me in my future career.

I would like to extend my appreciations to the Thesis Committee members, Dr. Scott C. Hagen and Dr. Fidelia Nnadi. Their time, inspiration, and patience were invaluable.

I would also like to thank Florida Department of Environmental Protection (FDEP) and South Florida Water Management District (SFWMD) to make this research possible.

Finally, thanks to my husband Zhan for his love and encouragement to my whole graduate study.
# TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................................................ viii

LIST OF FIGURES ...................................................................................................................................... ix

CHAPTER 1  INTRODUCTION ....................................................................................................................... 1

1.1 Background ......................................................................................................................................... 1

1.2 Objective and Scope of Work ........................................................................................................ 4

1.3 Format and Content ....................................................................................................................... 8

CHAPTER 2  MATHEMATICAL MODEL ...................................................................................................... 9

2.1 Water Flow ......................................................................................................................................... 9

2.2 Bed Sediments ........................................................................................................................... 10

2.3 Suspended Sediments ................................................................................................................ 10

2.4 Immobile Bed Species .................................................................................................................. 14

2.5 Mobile Column Species .............................................................................................................. 18

CHAPTER 3  DECOMPOSITION OF REACTIVE SYSTEMS ...................................................................... 25

3.1 Column Reactive Systems ........................................................................................................... 25

3.2 Bed Reactive Systems .................................................................................................................. 35

CHAPTER 4  NUMERICAL APPROXIMATIONS .................................................................................. 39

4.1 Bed Sediment Transport .............................................................................................................. 40

4.2 Suspended Sediment Transport .................................................................................................. 42

4.2.1 Finite Element Method in Advection Form Approach .......................................................... 42
LIST OF TABLES

Table 5.1 QUAL2E Original Working Equations ................................................................. 78
Table 5.2 QUAL2E Reaction Network ............................................................................... 79
Table 5.3 Governing Equations for the Reaction-based Diagonalization Approach .............. 80
Table 5.4 New Paradigm Working Equations for QUAL2E ................................................... 81
Table 5.5 QUAL2E Reaction Rate Parameters for the Loxahatchee Estuary ....................... 82
Table 5.6 QUAL2E Reaction Coefficients for the Loxahatchee Estuary ............................... 83
Table 5.7 River Miles for Different Reach of the Loxahatchee Estuary ................................. 85
Table 5.8 Initial and Boundary Conditions ......................................................................... 88
LIST OF FIGURES

Figure 1.1 Sediments and Biogeochemicals in a 3-D Estuary System ........................................ 5
Figure 5.1 the Loxahatchee River and Estuary with Overlapped Mesh ..................................... 86
Figure 5.2 Computation Domain and Finite Element Discretization .................................... 87
Figure 5.3 Initial Flow Velocity Distributions........................................................................ 89
Figure 5.4 Distribution of Suspended Sediment at t =1 h.................................................... 91
Figure 5.5 Distribution of Suspended Sediment at t =96 h.................................................... 91
Figure 5.6 Distribution of Bed Sediment at t =1 h............................................................... 92
Figure 5.7 Distribution of Bed Sediment at t =96 h............................................................... 92
Figure 5.8 Distribution of Chla at t =1 h............................................................................... 93
Figure 5.9 Distribution of Chla at t =96 h.............................................................................. 93
Figure 5.10 Distribution of Organic Nitrogen at t =1 h.......................................................... 94
Figure 5.11 Distribution of Organic Nitrogen at t =96 h........................................................ 94
Figure 5.12 Distribution of BOD at t =1 h............................................................................. 95
Figure 5.13 Distribution of BOD at t =96 h........................................................................... 95
Figure 5.14 Distribution of Dissolved Oxygen at t =1 h......................................................... 96
Figure 5.15 Distribution of Dissolved Oxygen at t =96 h....................................................... 96
Bay/Estuaries are undoubtedly among the most biologically productive ecosystems that exist on our planet. They also provide ecological, economic and recreational functions. Since the birth of the “chemical age”, bay/estuaries water quality has been heavily impacted worldwide by human encroachment and industrial and agricultural chemicals. Although each estuary is unique, they all face similar environmental problems and challenges, such as: oxygen depletion, nitrogen super-saturation, pathogen contamination, toxic chemicals, thermal stratification, excessive loadings of nutrients and sediments, and uncontrolled algae and aquatic plant growth. These problems tend to cause declines in water quality, living resources, and overall ecosystem health.

In order to combat the water quality problems, one of the most critical steps is to correctly identify, simulate and predict the bay/estuary water quality. Due to the rapid development of computer technology, computational models have increasingly become a primary tool for the prediction and management of water quality problems. In the last thirty years, considerable models were developed to simulate the kinetically controlled, multi-component reactive chemical and sediment transport in surface water. These models include both of sediment transport (e.g., Zheng et al, 2003; Engel et al., 1995; Paulsen and Owen, 1996; Harris and Wiberg, 2001; Zeng and Beck, 2003; and Rathburn and Wohl, 2003) and chemical transport
They are widely employed in modeling water quality in rivers/stream networks, large inland water bodies such as lakes/reservoirs, and tidal water bodies such as bays, estuaries, and coastal waters.

However, many of current coupled models for reactive transport have various capabilities (Keum and Hahn, 2003) due to computational limitations. Some models couple transport with equilibrium chemistry (e.g., Cederberg et al., 1985; Liu and Narasimhan, 1989; Yeh and Tripathi, 1991; Parkhurst, 1995; Parkhurst and Appelo, 1999; and Yeh et al., 2005), while some couple transport with kinetic chemistry (e.g., MacQuarrie et al., 1990; Tompson, 1993; Lensing et al., 1994; Wood et al., 1994; Yeh et al., 1998; and Saiers et al., 2000). Models coupling transport with both equilibrium and kinetic reactions appeared in the mid-1990s (e.g., Steefel and Lasaga, 1994; Chilakapati, 1995; Tebes-Stevens et al., 1998; Yeh et al., 2001b; Brun and Engesgaard, 2002).

Many of these models, e.g., QUAL2E (Brown and Barnwell, 1987), WASP (Di Toro et al., 1983; Connolly and Windfied, 1984; Ambrose et al., 1993; http://www.epa.gov/athens/wwqtscl/html/wasp.html), and CE-QUAL-ICM (Cerco and Cole, 1995), are mechanistically similar. All these models address several interacting biogeochemical processes: (1) biota kinetics, (2) oxygen balance, (3) carbon cycling, (4) nitrogen cycling, (5) phosphorus cycling, and (6) sediment-biogeochemical interactions. The major differences among them are the number of water quality parameters included and the number of biogeochemical processes considered. Some of these models use the lumped species rate formulation, which
implicitly assume that equilibrium reactions occur only among aqueous species or consider only limited reaction network. This assumption has the limitation that the reaction system contains specific chemicals or reactions (e.g., Ambrose et al., 1993; Brown and Barnwell, 1987; Park et al, 2003; and Bonnet and Wessen, 2001). The other models use the ad hoc rate formulation that is not able to capture key features of a natural system via several measurable parameters (Yeh et al., 2001). Such limitations will inevitably affect the generality of these models. They may provide efficient monitoring and management tools because they are calibrated for specific environments, but the extension of a calibrated model to other environmental conditions needs to be carefully evaluated.

Reaction-based models formulate the production-consumption rate of every chemical species due to every chemical reaction (both equilibrium and kinetic) for a specified reaction network (Burgos et al., 2003). And with better understanding and mathematical formulation of complex biogeochemical interactions (e.g., Chilakapati et al., 1998; Thomann, 1998; Somlyody et al., 1998; Mann, 2000; and Yeh et al., 2001a), models considering interactions among chemicals based on reaction mechanism have a better potential for application to other systems (Steefel and Cappellen, 1998). Therefore, a state-of-art general-purpose water quality models should be based on the reaction-based approach, which can simulate a generic reaction network including mixed equilibrium/kinetic biochemical and geochemical reactions quite generically and simply.

Obviously, there is a need to develop a reaction-based, fully mechanistic approached model that can simulate a generic reaction network including mixed equilibrium/kinetic biochemical and geochemical reactions (Yeh et al., 1998 and Yeh et al., 2005).
1.2 Objective and Scope of Work

This thesis presents the framework for a three-dimensional bay/estuary model to simulate sediment and reactive chemical transport. It’s a comprehensive model addressing the full range of biogeochemical reactions and transport with reaction-based formulation.

In our model, sediments are categorized based on their physical and chemical properties (Zhang, 2005). For each kind of sediment, the model includes mobile suspended sediment particles scattered in the water column and immobile bed sediment particles accumulated in the bottom. The distribution of suspended sediment and bed sediment in an estuary is controlled by complex nonlinear processes associated with the interaction between wind-induced waves, asymmetrical tidal horizontal advection and vertical mixing, short-term and long-term variations in estuarine circulation, stratification, bottom stress (resuspension), particle settling velocity (deposition), and flocculation-deflocculation processes (Postma, 1967; Dyer, 1986; Sanford et al., 1991; Geyer, 1993; Uncles and Stephens, 1993; Jay and Musiak, 1994). To simplify our model, no flocculation and deflocculation processes were considered, which allows us to neglect the interaction between different sizes of sediments. Based on this assumption, the sediments can be classified into two groups in accordance with different grain size: non-cohesive sediments (e.g., sand) with grain diameters larger than 63µm and cohesive sediments (e.g., silt and clay) with grain size smaller than 63µm, the latter having the property of forming aggregates resulting in higher settling velocities.
In a three-dimensional bay/estuary, as shown in Figure 1.1 (Zhang, 2005), the chemical species are classified according to the six phases in which they exist and the three forms they appear. The six phases are suspended sediment, bed sediment, aqueous water, pore water, suspended precipitate, and bed precipitate phases. The three forms are dissolved chemicals, precipitates, and particulate chemicals sorbed onto sediments. Chemical species in the water column (including the suspended sediment phase, the aqueous water phase and the suspension precipitate phase) are considered to be mobile. Chemical species in the bottom (including the bed sediment phase, the pore water phase and the bed precipitate phase) are considered to be immobile.

![Figure 1.1 Sediments and Biogeochemicals in a 3-D Estuary System](image)

The reactive system is completely defined by specifying biogeochemical reactions and counting the total number of species (Yeh et al., 2001). Biogeochemical reactions taken into account in the model include aqueous complexation, adsorption/desorption, ion-exchange, precipitation/dissolution, reduction/oxidation, and volatilization et al. The biogeochemical reactions are divided into two classes based on the reversibility and the comparison between reaction rate and transport time scale: fast/equilibrium reaction and slow/kinetic reactions. Any
individual reaction representing any of these chemical and physical processes may be simulated as kinetic or as equilibrium, which makes the code extremely flexible for application to a wide range of biogeochemical transport problems.

One of the most critical issues in reaction-based water quality modeling is the use of appropriate numerical methods to approximate the governing equations. For research applications, the model needs to use accurate and robust methods. For practical applications, it needs to employ efficient and robust methods. To enable the wide ranges of transport simulations (including sediment and water quality) of the model for real-world problems, two numerical options are provided to discretize the governing sediment and biogeochemical transport equations: hybrid Lagrangian-Eulerian finite element methods or conventional finite element methods. Three schemes are employed to handle the coupling between the hydrologic transport and biogeochemical reactions. These three coupling strategies are (1) fully-implicit scheme, which is an improved sequential iterative approach (SIA) (Yeh and Tripathi, 1989), (2) mixed predictor-correction/operator-splitting approach, and (3) operator-splitting approach. Some of these numerical options and coupling strategies are accurate for research applications while some are efficient for application to large practical field problems. The Newton-Raphson method was used to solve the set of algebraic equations and ordinary equations describing the evolution of all biogeochemical species.

The main objective is to (1) To develop a three-dimensional general-purpose bay/estuary model and (2) To verify the applicability of the model to simulate sediment and reactive biogeochemical transport subject to biogeochemical reactions in the Loxahatchee estuary.
Through decomposition of the system of species transport equations via Gauss-Jordan column reduction of the reaction network, fast reactions and slow reactions are decoupled, which enables robust numerical integrations and reduces problem stiffness by eliminating fast reactions from the partial differential equations governing reactive transport. Species reactive transport equations are transformed into two sets: a set of nonlinear algebraic equations representing equilibrium reactions and a set of transport equations of kinetic-variables in terms of kinetically controlled reaction rates. As a result, the model uses kinetic variables instead of biogeochemical species as primary dependent variables, which reduces the number of transport equations and simplifies reaction terms in these equations. For each time step, we first solve the advective-dispersive transport of kinetic-variables. We then solve the reactive chemical system node by node to yield concentrations of all species. Therefore the model can solve the governing equations efficiently no matter how complex the chemical part of the model is. Theoretically, the model has the capability to simulate reactive chemical transport with arbitrary number of both equilibrium reactions and kinetic reactions.

In our model, the reaction rates of elementary kinetic reactions are given by collision theory (Stumm and Morgan, 1981). For non-elementary kinetic reactions, the reaction rates can be formulated by user specified rate laws based on either empirical or mechanistic approaches. Similarly, the reaction rates of equilibrium reactions can be given by either a mass action equation or a users’ specified nonlinear algebraic equation. Therefore, the model is designed to include as many types of reactions as possible.
In our model, neither effects nor feedback of sediment and chemical transport on flow fields and heat distributions are considered. This assumption makes our model fully flexible to be linked with any flow and thermal transport model. To simplify our model, we neglect the affection of chemicals on sediment transport. Based on this assumption, the sediment fields are computed first when both sediment and reactive chemical transport are simulated. Then the reactive chemical transport is calculated using the computed sediment fields at respective times. As a general model, the sediment and chemical transport simulation can be invoked conveniently, either individually or in tandem in the model.

1.3 Format and Content

This thesis is organized as follows. Chapter 2 gives a review of the governing equations and boundary conditions used in this model. Chapter 3 introduces the decomposition procedure. Chapter 4 describes numerical approximations and numerical options used in the model. To demonstrate the flexibility and generality of the model, the widely used water quality model QUAL2E is recast in the mode of reaction networks to show that the model include it as a specific example in Chapter 5. Chapter 5 also presents a hypothetical application of QUAL2E to the Loxahatchee estuary. Chapter 6 summarizes the work presented in this thesis and outlines the opportunities for future work beyond the scope of this thesis.
CHAPTER 2 MATHEMATICAL MODEL

In this chapter, we present the governing equations derived based on the mass conservation law to simulate the sediment and reactive chemical transport in a three-dimensional coastal system.

The total derivative “$d/dt$” is

$$\frac{d\Phi}{dt} = \frac{\partial \Phi}{\partial t} + V_g \cdot \nabla \Phi$$  \hspace{1cm} (2.1)

where $V_g$ is the grid moving velocity [L/T].

2.1 Water Flow

The continuity equation of water flow can be derived based on the conservation principle of water mass as (Yeh et al., 2005)

$$\nabla \cdot V = S_s$$  \hspace{1cm} (2.2)

where $V$ is the flow velocity [L/T]; $S_s$ is the artificial source of flow [L$^3$/L$^3$/T].
2.2 Bed Sediments

The balance equation for bed sediments is simply the statement that the rate of mass change is due to erosion/deposition as (Yeh et al., 2005)

\[
\frac{\partial}{\partial t} (B \bar{M}_n) = F_{\text{src} \rightarrow B} , n \in [1, N_s] \quad \text{and} \quad \frac{\partial B}{\partial t} = \sum_{n=1}^{N_s} \frac{F_{\text{src} \rightarrow B}}{\rho_n}
\]  \( (2.3) \)

where \( B \) is the bed thickness \([L]\); \( \bar{M}_n \) is the \( n \)-th bed sediment concentration averaged over the bed thickness \([M/L^3]\); \( t \) is the time \([T]\); \( F_{\text{src} \rightarrow B} \) is the exchange rate of the \( n \)-th sediment from water column to the bed layer due to deposition/erosion and diffusion \([M/L^2/T]\); \( N_s \) is the number of sediment size-fractions; and \( \rho_n \) is the density of the \( n \)-th size-fraction \([M/L^3]\). The concentration of all bed sediments must be given initially for transient simulations. Initial concentration is obtained by field measurement or by solving a steady-state version of the governing equations. No boundary condition is needed for bed sediments.

2.3 Suspended Sediments

The continuity equation of suspended sediment can be derived based on the conservation law of material mass as (Yeh et al., 2005)

\[
\frac{\partial S_n}{\partial t} + \nabla \cdot (V S_n) - \frac{\partial}{\partial z} (W_{\text{sn}} S_n) - \nabla \cdot (K \nabla S_n) = M_n \delta , n \in [1, N_s]
\]  \( (2.4) \)
where $S_n$ is the concentration of the $n$-th suspended sediment $[\text{M/L}^3]$; $t$ is the time $[\text{T}]$; $V$ is the flow velocity $[\text{L/T}]$; $W_{sn}$ is the settling velocity of the $n$-th suspended sediment fraction $[\text{L/T}]$; $K$ is the dispersion coefficient tensor $[\text{L}^2/\text{T}]$; $M_n^{as}$ is the artificial source/sink of the $n$-th suspended sediment $[\text{M/L}^3/\text{T}]$; and $N_s$ is the number of sediment size-fractions. The concentration of all suspended sediments must be given initially for transient simulations. Initial concentration is obtained by field measurement or by solving a steady-state version of the governing equations.

Five types of boundary conditions for suspended sediments are taken into account as stated as follows.

**Dirichlet boundary condition**

This condition is applied when concentration is given at the boundary and prescribed as function of time.

$$S_n = S_{nd} (x_b,y_b,z_b,t) \text{ at } B_d$$

(2.5)

where $S_n$ is the prescribed concentration of the $n$-th suspended sediment $[\text{M/L}^3]$; $(x_b,y_b,z_b)$ is the spatial coordinate at the boundary; $S_{nd} (x_b,y_b,z_b,t)$ is the given time-dependent concentration of the $n$-th suspended sediment at the boundary $B_d [\text{M/L}^3]$; $B_d$ is the Dirichlet boundary.
**Variable boundary condition**

This boundary condition is employed when the flow direction would change with time during simulations. Two cases are considered, regarding to the flow direction.

< Case 1 > When the flow is directed into the region of the interest from outside ($\mathbf{n} \cdot V < 0$), the flushing capacity of the water bodies adjacent to the region of interest is considered in calculating the incoming concentration.

$$\mathbf{n} \cdot (V S_n - K \cdot \nabla S_n) - \mathbf{n} \cdot (V_{sn} S_n) = q_{s_{sn}}(x_h, y_h, z_h, t) \text{ at } B_v$$  \hspace{1cm} (2.6)

< Case 2 > When the flow is directed out of the region from inside ($\mathbf{n} \cdot V > 0$), the sediment mass is assumed to be transported out of the region via advection.

$$-\mathbf{n} \cdot (K \cdot \nabla S_n) = 0 \text{ at } B_v$$  \hspace{1cm} (2.7)

where $\mathbf{n}$ is an outward-pointing unit vector normal to the boundary $B_v$; $V$ is the prescribed flow velocity [L/T]; $S_n$ is the prescribed concentration of the $n$-th suspended sediment [M/L$^3$]; $V_{sn} = (0, 0, W_{sn})^T$ is the settling velocity vector of the $n$-th sediment in water column [L/T]; $K$ is the prescribed dispersion coefficient tensor [L$^2$/T]; $W_{sn}$ is the settling velocity of the $n$-th sediment [L/T]; $q_{s_{sn}}(x_h, y_h, z_h, t)$ is the given time-dependent flux of the $n$-th suspended sediment at the boundary $B_v$ [M/L$^2$/T]; $B_v$ is the Variable boundary.

**Cauchy boundary condition**

This boundary condition is employed when the total material flux is given as functions of time at the boundary. Usually, this boundary is an upstream flux boundary.
\[ \mathbf{n} \cdot \left( V S_n - K \cdot \nabla S_n \right) - \mathbf{n} \cdot \left( V_{sn} S_n \right) = q_{S_{nc}} \left( x_h, y_h, z_{h}, t \right) \text{ at } B_c \]  

(2.8)

where \( \mathbf{n} \) is an outward-pointing unit vector normal to the boundary \( B_c \); \( V \) is the prescribed flow velocity \([L/T]\); \( S_n \) is the prescribed concentration of the \( n \)-th suspended sediment \([M/L^3]\); \( K \) is the prescribed dispersion coefficient tensor \([L^2/T]\); \( V_{sn} = \{0, 0, W_{sn}\}^T \) is the settling velocity vector of the \( n \)-th sediment in water column \([L/T]\); \( W_{sn} \) is the settling velocity of the \( n \)-th sediment \([L/T]\); \( q_{S_{nc}} \left( x_h, y_h, z_{h}, t \right) \) is the given time-dependent Cauchy flux of the \( n \)-th suspended sediment at the boundary \( B_c \) \([M/L^2/T]\); \( B_c \) is the Cauchy boundary.

**Neumann boundary condition**

This boundary condition is used when the diffusive material flux is known as functions of time at the boundary node. Usually, this boundary is a downstream boundary.

\[ -\mathbf{n} \cdot \left( K \cdot \nabla S_n \right) = q_{S_{nn}} \left( x_h, y_h, z_{h}, t \right) \text{ at } B_n \]  

(2.9)

where \( \mathbf{n} \) is an outward-pointing unit vector normal to the boundary \( B_n \); \( S_n \) is the prescribed concentration of the \( n \)-th suspended sediment \([M/L^3]\); \( K \) is the prescribed dispersion coefficient tensor \([L^2/T]\); \( q_{S_{nn}} \left( x_h, y_h, z_{h}, t \right) \) is the known time-dependent Neumann diffusive flux of the \( n \)-th suspended sediment at the boundary \( B_n \) \([M/L^2/T]\); \( B_n \) is the Neumann boundary.

**Coastal surface water-coastal bed interface boundary condition**

When Equation (2.4) is solved, the following boundary condition should be applied at the interface of the water column and sediment bed layer

\[ \]
\[ \mathbf{n} \cdot (\mathbf{V} S_n - K \cdot \nabla S_n) - \mathbf{n} \cdot (\mathbf{V} s_n S_n) = F_{sc\rightarrow B} \text{ at } B_{sb} \]  

(2.10)

where \( \mathbf{n} \) is an outward-pointing unit vector pointing from column to bed; \( \mathbf{V} \) is the prescribed flow velocity \([L/T]\); \( S_n \) is the concentration of the \( n \)-th suspended sediment \([M/L^3]\); \( V_{sn} = \{0,0,W_{sn}\}^T \) is the settling velocity vector of the \( n \)-th sediment in water column; \( W_{sn} \) is the settling velocity of the \( n \)-th sediment\([L/T]\); \( B_{sb} \) is the coastal surface water-coastal bed interface boundary; \( F_{sc\rightarrow B} \) is the exchange rate of the \( n \)-th sediment from water column to the bed layer due to deposition/erosion and diffusion \([M/L^2/T]\).

If diffusion effect is negligible, \( F_{sc\rightarrow B} \) can be formulated as

\[ F_{sc\rightarrow B} = 0.5 (\mathbf{n} \cdot \mathbf{V}) \left[ (1 + \text{sign}(\mathbf{n} \cdot \mathbf{V})) S_n + (1 - \text{sign}(\mathbf{n} \cdot \mathbf{V})) \overline{M}_n \right] + D_n - R_n \]  

(2.11)

where \( \overline{M}_n \) is the \( n \)-th bed sediment concentration averaged over the bed thickness \([M/L^3]\); \( D_n \) is the deposition rate of the \( n \)-th sediment \([M/L^2/T]\); \( R_n \) is the erosion rate of the \( n \)-th sediment \([M/L^2/T]\).

### 2.4 Immobile Bed Species

The balance equation for immobile species is simply the statement that the rate of mass change is due to biogeochemical reaction and the interfacial exchange from water column to the bed layer due to diffusion (for dissolved species), settling (for precipitate species), or deposition and erosion (for particulate species) as
For Dissolved Species

\[\frac{\partial}{\partial t}\left(\rho_{pw} \theta_b C_{bdc}\right) = r_{bdc}\bigg|_{N_b} + \frac{F_{DC \rightarrow B}}{B} - \frac{P_{pw} \theta_b C_{bdc}}{B} \frac{\partial B}{\partial t}\]  \tag{2.12}

where \(\rho_{pw}\) is the density of pore water (bed water) \([M/L^3]\); \(\theta_b\) is the porosity of the bed sediment \([L^3/L^3]\); \(C_{bdc}\) is the concentration of dissolved chemical in the pore water \([M/M]\); \(t\) is the time \([T]\); \(r_{bdc}\bigg|_{N_b}\) is the production-consumption rate of the dissolved chemical due to all the \(N_b\) biogeochemical reactions in the bed \([M/L^3/t]\); \(F_{DC \rightarrow B}\) is the exchange rate of the dissolved chemical from the column water to the pore water \([M/L^2/t]\); \(B\) is the bed thickness \([L]\); and \(N_b\) is the total number of all biogeochemical reactions.

For Precipitates

\[\frac{\partial}{\partial t}\left(\rho_{pw} \theta_b C_{bp}\right) = r_{bp}\bigg|_{N_b} + \frac{F_{PC \rightarrow B}}{B} - \frac{P_{pw} \theta_b C_{bp}}{B} \frac{\partial B}{\partial t}\]  \tag{2.13}

where \(\rho_{pw}\) is the density of pore water (bed water) \([M/L^3]\); \(\theta_b\) is the porosity of the bed sediment \([L^3/L^3]\); \(C_{bp}\) is the concentration of precipitate in the pore water (bed water)\([M/M]\); \(t\) is the time \([T]\); \(r_{bp}\bigg|_{N_b}\) is the production-consumption rate of the precipitate due to all the \(N_b\) biogeochemical reactions \([M/L^3/t]\); \(F_{PC \rightarrow B}\) is the exchange rate of the precipitate from the column water to the pore(bed) water \([M/L^2/t]\); \(B\) is the bed thickness \([L]\); and \(N_b\) is the total number of all biogeochemical reactions.
For Particulate Chemicals

\[
\frac{\partial (\bar{M}_n C_{b_{pn}})}{\partial t} = r_{b_{pn}} \bigg|_{N_b} + \frac{F_{PN:C\rightarrow B}}{B} - \frac{\bar{M}_n C_{b_{pn}}}{B} \frac{\partial B}{\partial t}
\]  

(2.14)

where \( \bar{M}_n \) is the \( n \)-th bed sediment concentration averaged over the bed thickness \([M/L^3]\); \( C_{b_{pn}} \) is the concentration of particulate chemical sorbed on to the \( n \)-th bed sediment \([M/M]\); \( r_{b_{pn}} \bigg|_{N_b} \) is the production-consumption rate of the particulate chemical due to all the \( N_b \) biogeochemical reactions \([M/L^3/t]\); \( F_{PN:C\rightarrow B} \) is the exchange rate of the particulate chemicals from the suspended sediment phase to the bed sediment phase \([M/L^2/t]\).

Define

\[
\rho_b = \begin{cases} 
\rho_{pw} \theta, & \text{for } C_{bdc} \text{ and } C_{bp} \\
\bar{M}_n, & \text{for } C_{b_{pn}} 
\end{cases}
\]  

(2.15)

\[
F_{bi:C\rightarrow B} = \begin{cases} 
F_{DC:C\rightarrow B}, & \text{for } C_{bdc} \\
F_{PC:B}, & \text{for } C_{bp} \\
F_{PN:C\rightarrow B}, & \text{for } C_{b_{pn}} 
\end{cases}
\]  

(2.16)

Equation (2.12) through (2.14) can be modified as

\[
\frac{\partial (\rho_{bi} C_{bi})}{\partial t} = r_{bi} \bigg|_{N_b} + \frac{F_{bi:C\rightarrow B}}{B} \frac{\rho_{bi} C_{bi}}{B} \frac{\partial B}{\partial t}, \ i \in M_b
\]

or

\[
\frac{\partial (B \rho_{bi} C_{bi})}{\partial t} = F_{bi:C\rightarrow B} = B r_{bi} \bigg|_{N_b}
\]  

(2.17)

where \( B \) is the bed depth \([L]\); \( \rho_b = \rho_{bw} \theta \) for pore-water dissolved species and precipitated species in pore water; \( \rho_{bw} \) is the density of bed pore water \([M/L^3]\); \( \theta \) is the porosity of the bed
sediment \([L^3/L^3]\); \(\rho_b = \bar{M}_n\) for particulate species sorbed onto the \(n\)-th bed sediment; \(C_{bi}\) is the concentration of the \(i\)-th immobile chemical species \([M/M]\); \(t\) is the time \([T]\); \(F_{biC \to B}\) is exchange rate of the \(i\)-th chemical species from water column to the bed layer due to diffusion, settling, or deposition/erosion \([M/t/L^2]\); \(r_{bi}\) is the production-consumption rate of the \(i\)-th immobile chemical species due to all \(N_b\) reactions \([M/L^3/t]\); and \(M_b\) is the total number of bed chemical species.

The exchange rate \(F_{DC:C \to B}\), \(F_{PC:C \to B}\), \(F_{PN:C \to B}\) can be formulated as

\[
F_{DC:C \to B} = 0.5(n \cdot V)
\left[
\left(1 + \text{sign}(n \cdot V)\right) \rho_w C_{cdc} + \left(1 - \text{sign}(n \cdot V)\right) \rho_{pw} \theta_b C_{bdc}
\right]
+ \varepsilon_{dc:C \to B} \left(\rho_w C_{cdc} - \rho_{pw} \theta_b C_{bdc}\right), \quad [C_{cdc}] = [C_{bdc}]
\tag{2.18}
\]

where \(\rho_w\) is the density of column water \([M/L^3]\); \(\rho_{pw}\) is the density of bed water \([M/L^3]\); \(V\) is the flow velocity \([L/T]\); \([C_{cdc}]\) is the column mobile dissolved chemical; \([C_{bdc}]\) is the bed immobile dissolved chemical corresponding to \([C_{cdc}]\) \([M/M]\); \(\varepsilon_{dc:C \to B}\) is the diffusion/dispersion coefficient for dissolved species at the column-bed interface \([L/T]\).

\[
F_{PC:C \to B} = 0.5(n \cdot V)
\left[
\left(1 + \text{sign}(n \cdot V)\right) \rho_w C_{cp} + \left(1 - \text{sign}(n \cdot V)\right) \rho_{pw} \theta_b C_{bp}
\right]
+(n \cdot V_{sp}) \rho_w C_{cp} + \varepsilon_{p:C \to B} \left(\rho_w C_{cp} - \rho_{pw} \theta_b C_{bp}\right), \quad [C_{cp}] = [C_{bp}]
\tag{2.19}
\]

where \(V_{sp} = \{0,0,W_{sp}\}^T\) is the settling velocity vector of the mobile chemical species at precipitated form in water column \([L/T]\); \([C_{cp}]\) is the column mobile precipitated species; \([C_{bp}]\)
is the bed immobile precipitated species corresponding to \([C_{cpn}]\) [M/M]; \(\varepsilon_{pC\rightarrow B}\) is the diffusion/dispersion coefficient for precipitated species at the column-bed interface[L/T].

\[
F_{PN,C\rightarrow B} = 0.5(n \cdot V) \left[ (1 + \text{sign}(n \cdot V)) S_n C_{cpn} + (1 - \text{sign}(n \cdot V)) \bar{M}_n C_{bpm} \right] \\
+ \left( D_n C_{cpn} - R_n C_{bpm} \right) [C_{cpn}] = [C_{bpm}]
\]

(2.20)

where \(S_n\) is the concentration of the \(n\)-th suspended sediment [M/L^3]; \(\bar{M}_n\) is the \(n\)-th bed sediment concentration averaged over the bed thickness [M/L^3]; \([C_{cpn}]\) is the column mobile particulate chemical sorbed on to \(n\)-th suspended sediment; \([C_{bpm}]\) is the bed immobile particulate chemical sorbed on to \(n\)-th suspended sediment corresponding to \([C_{cpn}]\) [M/M]. No boundary conditions are needed for immobile species.

### 2.5 Mobile Column Species

The transport equation of mobile species can be derived based on the conservation law of material mass stating that the rate of mass change is due to both advective-dispersive transport and biogeochemical reactions as
For Dissolved Species

\[
\frac{\partial (\rho_w C_{\text{diss}})}{\partial t} + \nabla \cdot \left( V \rho_w C_{\text{diss}} \right) - \nabla \cdot \left[ K \cdot \nabla \left( \rho_w C_{\text{diss}} \right) \right] = M_{\text{diss}}^{\text{as}} + r_{\text{diss}} \bigg|_{N_c}
\] (2.21)

where \( \rho_w \) is the density of column water [M/L^3]; \( C_{\text{diss}} \) is the concentration of dissolved chemical in the column water phase [M/M]; \( t \) is the time [T]; \( V \) is the flow velocity [L/T]; \( K \) is the dispersion coefficient tensor [L^2/T]; \( M_{\text{diss}}^{\text{as}} \) is the source/sink of the dissolved chemical species in the column water [M/L^3/T]; \( r_{\text{diss}} \bigg|_{N_c} \) is the production-consumption rate of the dissolved chemical due to all the \( N_c \) biogeochemical reactions in column water [M/L^3/t]; and \( N_c \) is the total number of all biogeochemical reactions.

For Precipitates

\[
\frac{\partial (\rho_w C_{\text{precip}})}{\partial t} + \nabla \cdot \left( V \rho_w C_{\text{precip}} \right) - \frac{\partial}{\partial z} \left( W_{\text{sp}} \rho_w C_{\text{precip}} \right) - \nabla \cdot \left[ K \cdot \nabla \left( \rho_w C_{\text{precip}} \right) \right] = M_{\text{precip}}^{\text{as}} + r_{\text{precip}} \bigg|_{N_c}
\] (2.22)

where \( \rho_w \) is the density of column water [M/L^3]; \( C_{\text{precip}} \) is the concentration of precipitate in column water [M/M]; \( t \) is the time [T]; \( V \) is the flow velocity [L/T]; \( K \) is the dispersion coefficient tensor [L^2/T]; \( W_{\text{sp}} \) is the settling velocity of suspended precipitate in the column water [L/T]; \( M_{\text{precip}}^{\text{as}} \) is the source/sink of suspended precipitate in column water [M/L^3/T]; \( r_{\text{precip}} \bigg|_{N_c} \) is the production-consumption rate of the precipitate due to all the \( N_c \) biogeochemical reactions in the column water [M/L^3/t]; and \( N_c \) is the total number of all biogeochemical reactions in column water.
For Particulate Chemicals

\[ \frac{\partial}{\partial t} \left( S_n C_{\text{cpn}} \right) + \nabla \cdot \left( V S_n C_{\text{cpn}} \right) - \frac{\partial}{\partial z} \left( W_{sn} S_n C_{\text{cpn}} \right) - \nabla \cdot \left[ K \nabla \left( S_n C_{\text{cpn}} \right) \right] = M_{\text{ax}}^{\text{cpn}} + r_{\text{cpn}} \bigg|_{N_c} \]  

(2.23)

where \( S_n \) is the \( n \)-th suspended sediment concentration \([\text{M/L}^3]\); \( C_{\text{cpn}} \) is the concentration of particulate chemical sorbed on to the \( n \)-th suspended sediment \([\text{M/M}]\); \( t \) is the time \([\text{T}]\); \( V \) is the flow velocity \([\text{L/T}]\); \( K \) is the dispersion coefficient tensor \([\text{L}^2/\text{T}]\); \( W_{sn} \) is the settling velocity of \( n \)-th suspended sediment in the column water \([\text{L/T}]\); \( M_{\text{ax}}^{\text{cpn}} \) is the source/sink of particulate chemical sorbed on to the \( n \)-th suspended sediment in column water \([\text{M/L}^3/\text{T}]\); \( r_{\text{cpn}} \bigg|_{N_c} \) is the production-consumption rate of particulate chemical sorbed on to the \( n \)-th suspended sediment due to all the \( N_c \) biogeochemical reactions \([\text{M/L}^3/\text{t}]\); and \( N_c \) is the total number of all biogeochemical reactions in column water.

Define

\[ \rho = \begin{cases} \rho_n, & \text{for } C_{\text{cdc}} \ \text{and} \ C_{\text{cp}} \\ S_n, & \text{for } C_{\text{cpn}} \end{cases} \quad \text{and} \quad W_{si} = \begin{cases} 0, & \text{for } C_{\text{cdc}} \\ W_{sp}, & \text{for } C_{\text{cp}} \\ W_{sn}, & \text{for } C_{\text{cpn}} \end{cases} \]  

(2.24)

Equation (2.21) through (2.23) can be modified as

\[ \frac{\partial}{\partial t} \left( \rho_i C_i \right) + \nabla \cdot \left( V \rho_i C_i \right) - \frac{\partial}{\partial z} \left( W_{si} \rho_i C_i \right) - \nabla \cdot \left[ K \nabla \left( \rho_i C_i \right) \right] = M_{ci}^{\text{ax}} + r_{ci} \bigg|_{N_c}, \ i \in M_c \]  

(2.25)

where \( \rho_i \) is the density of the column phase (column water, suspended precipitate or suspended sediment) associated with \( i \)-th chemical species (Equation (2.24)) \([\text{M/L}^3]\); \( C_i \) is the concentration
of i-th chemical species in column water [M/M]; \( V \) is the flow velocity [L/T]; \( K \) is the dispersion coefficient tensor \([L^2/T]\); \( W_{si} \) is the settling velocity of the i-th mobile chemical species in the column phases [L/T]; \( M_{ci}^{sr} \) is the source/sink of i-th species in water column [M/L^3/T]; \( r_{ci} \) is the production-consumption rate of i-th chemical species in water column due to all \( N_c \) reactions [M/L^3/t]; and \( M_c \) is the total number of mobile chemical species in water column. Concentrations of all species must be given initially for transient simulations. Initial concentration is obtained by field measurement or by solving a steady-state version of the governing equations. Similar to suspended sediment transport, five types of boundary conditions are taken into account for mobile species.

**Dirichlet boundary condition**

This condition is applied when concentration is given at the boundary and prescribed as function of time.

\[
C_i = C_{id}(x_b, y_b, z_b, t) \quad \text{at} \quad B_d
\]  

(2.26)

where \( C_i \) is the concentration of the i-th mobile chemical species [M/L^3]; \((x_b, y_b, z_b)\) is the spatial coordinate at the boundary; \( C_{id}(x_b, y_b, z_b, t) \) is the given time-dependent concentration of the i-th mobile chemical species at the boundary \( B_d \) [M/L^3]; \( B_d \) is the Dirichlet boundary.

**Variable boundary condition**

This boundary condition is employed when the flow direction would change with time during simulations. Two cases are considered, regarding to the flow direction.
<Case 1> When the flow is directed into the region of the interest from outside \((\mathbf{n} \cdot V < 0)\), the flushing capacity of the water bodies adjacent to the region of interest is considered in calculating the incoming concentration.

\[
\mathbf{n} \cdot (V C_i - K \cdot \nabla C_i) - \mathbf{n} \cdot (V_{sp} C_i) - \mathbf{n} \cdot (V_{sn} C_i) = q_{Civ}(x_b, y_h, z_b, t) \text{ at } B_v \tag{2.27}
\]

<Case 2> When the flow is directed out of the region from inside \((\mathbf{n} \cdot V > 0)\), the sediment mass is assumed to be transported out of the region via advection.

\[
-\mathbf{n} \cdot (K \cdot \nabla C_i) = 0 \text{ at } B_v \tag{2.28}
\]

where \(\mathbf{n}\) is an outward-pointing unit vector normal to the boundary \(B_v\); \(V\) is the prescribed flow velocity \([\text{L/T}]\); \(C_i\) is the concentration of the \(i\)-th mobile chemical species \([\text{M/L}^3]\); \(K\) is the prescribed dispersion coefficient tensor \([\text{L}^2/\text{T}]\); \(V_{sp} = \{0, 0, W_{sp}\}^T\) is the settling velocity vector of the \(i\)-th mobile chemical species at precipitated form in water column \([\text{L/T}]\); \(V_{sn} = \{0, 0, W_{sn}\}^T\) is the settling velocity vector of \(n\)-th suspended sediment where the \(i\)-th mobile chemical species at particulate form particulate chemical sorbs on to \([\text{L/T}]\); \(q_{Civ}(x_b, y_h, z_b, t)\) is the given time-dependent flux of the \(i\)-th mobile chemical species at the boundary \(B_v\) \([\text{M/L}^2/\text{T}]\); \(B_v\) is the Variable boundary.

**Cauchy boundary condition**

This boundary condition is employed when the total material flux is given as functions of time at the river/stream boundary. Usually, this boundary is an upstream flux boundary.

\[
\mathbf{n} \cdot (V C_i - K \cdot \nabla C_i) - \mathbf{n} \cdot (V_{sp} C_i) - \mathbf{n} \cdot (V_{sn} C_i) = q_{Civ}(x_b, y_h, z_b, t) \text{ at } B_c \tag{2.29}
\]
where \( \mathbf{n} \) is an outward-pointing unit vector normal to the boundary \( B_c \); \( V \) is the prescribed flow velocity [L/T]; \( C_i \) is the prescribed concentration of the \( i \)-th mobile chemical species [M/L^3]; \( K \) is the prescribed dispersion coefficient tensor [L^2/T]; \( V_{sp} = \{0, 0, W_{sp}\}^T \) is the settling velocity vector of the \( i \)-th mobile chemical species at precipitated form in water column [L/T]; \( V_{sn} = \{0, 0, W_{sn}\}^T \) is the settling velocity vector of \( n \)-th suspended sediment where the \( i \)-th mobile chemical species at particulate form particulate chemical sorbs on to [L/T]; \( q_{Cic}(x_b, y_b, z_b, t) \) is the given time-dependent Cauchy flux of the \( i \)-th mobile chemical species at the boundary \( B_c \) [M/L^2/T]; \( B_c \) is the Cauchy boundary.

**Neumann boundary condition**

This boundary condition is used when the diffusive material flux is known as functions of time at the boundary node. Usually, this boundary is a downstream boundary.

\[
-n \cdot (K \cdot \nabla C_i) = q_{cin}(x_b, y_b, z_b, t) \quad \text{at } B_n
\]

where \( \mathbf{n} \) is an outward-pointing unit vector normal to the boundary \( B_n \); \( C_i \) is the prescribed concentration of the \( i \)-th mobile chemical species [M/L^3]; \( K \) is the prescribed dispersion coefficient tensor [L^2/T]; \( q_{cin}(x_b, y_b, z_b, t) \) is the time-dependent Neumann diffusive flux of the \( i \)-th mobile chemical species at the boundary \( B_n \) [M/L^2/T]; \( B_n \) is the Neumann boundary.

**Coastal surface water-coastal bed interface boundary condition**

\[
\mathbf{n} \cdot (V C_i - K \cdot \nabla C_i) - n \cdot (V_{sp} C_i) - n \cdot (V_{sn} C_i) = F_{bi:C \rightarrow B} \quad \text{at } B_{sb}
\]

(2.31)
where \( \mathbf{n} \) is an outward-pointing unit vector pointing from column to bed; \( V \) is the prescribed flow velocity [L/T]; \( C_i \) is the prescribed concentration of the \( i \)-th mobile chemical species [M/L^3]; \( K \) is the prescribed dispersion coefficient tensor [L^2/T]; \( V_{sp} = \{0,0,W_{sp}\}^T \) is the settling velocity vector of the \( i \)-th mobile chemical species at precipitated form in water column [L/T]; \( V_{sn} = \{0,0,W_{sn}\}^T \) is the settling velocity vector of \( n \)-th suspended sediment where the \( i \)-th mobile chemical species at particulate form particulate chemical sorbs on to [L/T]; \( F_{hc \rightarrow b} \) is the exchange rate of the \( i \)-th species from water column to the bed layer due to diffusion, settling, or deposition/erosion in the unit of chemical mass per unit bed area per unit time [M/T/L^2]; \( B_{sb} \) is the coastal surface water-coastal bed interface boundary.
CHAPTER 3  DECOMPOSITION OF REACTIVE SYSTEMS

From a mathematical point of view, the temporal-spatial distribution of chemical species can be described with a system of $M_b$ mass balance equations (Equation (2.17)) in bed and $M_c$ reactive transport equations (Equation (2.25)) in column. These two equations can be recast in two different forms.

3.1 Column Reactive Systems

According to the mathematical model section, a set of $M_c$ partial differential equations can be written for $M_c$ chemical species in the column reaction system as

$$\frac{\partial}{\partial t}(\rho_i C_i) + L(\rho_i C_i) = r_{ci} \bigg|_{N_c} , i \in [1, M_c]$$

(3.1)

where the operator $L$ is defined as follows

$$L(\rho_i C_i) = \left\{ \nabla \cdot (V \rho_i C_i) - \frac{\partial}{\partial z} (W_{si} \rho_i C_i) - \right\} , \quad i \in [1, M_c]$$

(3.2)

The determination of $r_{ci} \bigg|_{N_c}$ and associated parameters is a primary challenge in biogeochemical modeling. Instead of using ad hoc method to formulate $r_{ci} \bigg|_{N_c}$, we use reaction-based
formulations (Steefel and Cappellen, 1998). In a reaction-based formulation, \( r_{ci} \big|_{N_i} \) is given by the summation of rates of all reactions in which the \( i \)-th species participates.

\[
\left. \frac{dC_i}{dt} \right|_{\text{reaction}} = \sum_{k=1}^{N_c} (v_{ik} - \mu_{ik}) r_k, \ i \in M_c
\]  

(3.3)

where \( v_{ik} \) is the reaction stoichiometry of the \( i \)-th species in the \( k \)-th reaction associated with the products, \( \mu_{ik} \) is the reaction stoichiometry of the \( i \)-th species in the \( k \)-th reaction associated with the reactants, and \( r_k \) is the rate of the \( k \)-th reaction \([M/L^3]\).

Substitution of Equation (3.3) into Equation (3.1) yields

\[
\frac{\partial (\rho_i C_i)}{\partial t} + L (\rho_i C_i) = \sum_{k=1}^{N_c} (v_{ik} - \mu_{ik}) r_k, i \in M_c; \text{ or } U \left[ \frac{\partial (\rho C)}{\partial t} + L (\rho C) \right] = \nu r
\]  

(3.4)

where \( v_{ik} \) is the reaction stoichiometry of the \( i \)-th species in the \( k \)-th reaction associated with the products; \( \mu_{ik} \) is the reaction stoichiometry of the \( i \)-th species in the \( k \)-th reaction associated with the reactants; \( r_k \) is the reaction rate of the \( k \)-th reaction; \( U \) is a unit matrix; \( C \) is a vector with its components representing \( M_c \) species concentrations multiplied by the density of the column water or suspended sediment depending on the form of the chemical species (Equation (2.24)); \( \nu \) is the reaction stoichiometry matrix; and \( r \) is the reaction rate vector with \( N_c \) reaction rates as its components.

Equation (3.4) is a representation of mass balance for any species \( i \) in a reactive transport system, which states that the changing rate of any species mass is due to advection-dispersion coupled with contributing reactions that describe biogeochemical processes. In a primitive approach,
Equation (3.4) is integrated to yield the distributions and evolutions of chemical species in a region of interest. However, when some fast equilibrium reactions taking place in the system, this approach is not adequate (Fang et al., 2003). Therefore, we will take a diagonalization approach through decomposition. Equation (3.4) written in matrix form can be decomposed based on the type of biogeochemical reactions via Gauss-Jordan column reduction of reaction matrix $\mathbf{v}$ (Chilakapati, 1995).

A redundant reaction is a fast reaction that can be derived from other fast reactions. An irrelevant reaction is a slow reaction that is linearly dependent on only equilibrium reactions. Kinetic reactions that are linearly dependent on both equilibrium and kinetic reactions are relevant to the system.

In a system involving $N_e$ fast/equilibrium reactions and $N_k$ slow/kinetic reactions among $M$ chemical species, redundant fast reactions and irrelevant slow reactions should be removed from the system before the decomposition, if users inadvertently include them. The removal of redundant fast reactions avoids the singularity of the reaction matrix. The removal of irrelevant slow reactions alleviates problems associated with rate formulation uncertainty and parameterization for the reactions. As a result, only $N_E$ linearly independent equilibrium reactions and a subset of $N_K$ kinetic reactions are considered.

Perform decomposition by pivoting on equilibrium reactions represented by mass action equations and decouple them from the kinetic reactions. In other words, each fast reaction can be used to eliminate one chemical species from simultaneous consideration. An incomplete Gauss-
Jordan row decomposition of the reaction matrix pivoting on $N_E$ equilibrium reactions will result in $N_E$ equilibrium species and $M_c-N_E$ kinetic species as follows

$$\begin{bmatrix} \mathbf{A}_1 & \mathbf{O}_1 \\ \mathbf{A}_2 & \mathbf{U}_1 \end{bmatrix} \begin{bmatrix} \frac{\partial (\mathbf{C}_1)}{\partial t} + \mathbf{L}(\mathbf{C}_1) \\ \frac{\partial (\mathbf{C}_2)}{\partial t} + \mathbf{L}(\mathbf{C}_2) \end{bmatrix} = \begin{bmatrix} \mathbf{D}_1 & \mathbf{K}_1 \\ \mathbf{O}_2 & \mathbf{K}_2 \end{bmatrix} \begin{bmatrix} \mathbf{R}_1 \\ \mathbf{R}_2 \end{bmatrix}$$  \quad (3.5)

where $\mathbf{A}_1$ and $\mathbf{A}_2$ are submatrixes of the reduced $\mathbf{U}$ matrix with size of $N_E \times N_E$ and $(M_c - N_E) \times N_E$ respectively; $\mathbf{O}_1$ is a zero matrix representing a submatrix of the reduced $\mathbf{U}$ matrix with size of $N_E \times (M_c - N_E)$; $\mathbf{U}_1$ is a unit matrix representing a submatrix of the reduced $\mathbf{U}$ matrix with size of $(M_c - N_E) \times (M_c - N_E)$; $\mathbf{C}_1$ and $\mathbf{C}_2$ are subvectors of the vector $\mathbf{C}$ with size of $N_E$ and $M_c - N_E$ respectively; $\mathbf{D}_1$ is the diagonal matrix representing a submatrix of the reduced $\mathbf{v}$ with size of $N_E \times N_E$ reflecting $N_E$ linearly independent fast reactions; $\mathbf{K}_1$ is a submatrix of the reduced $\mathbf{v}$ with size of $N_E \times N_K$ reflecting the effects of $N_K$ kinetic reactions; $\mathbf{O}_2$ is a zero matrix representing a submatrix of the reduced $\mathbf{v}$ with size of $(M_c - N_E) \times N_E$; $\mathbf{K}_2$ is a submatrix of the reduced $\mathbf{v}$ with size of $(M_c - N_E) \times N_K$, $\mathbf{R}_1$ is a subvector of the vector $\mathbf{r}$ with dimension of $N_E$, and $\mathbf{R}_2$ is a subvector of the vector $\mathbf{r}$ with dimension of $N_K$.

For reactions that are fast, equilibrium may be regarded as being reached instantaneously among all the relevant species and the reaction rate can be conceptually considered as infinity. An infinite rate is mathematically represented by a mass action equation or a user specified algebraic equation. As a result, the decomposition of Equation (3.4) to Equation (3.5) effectively reduces a set of $M_c$ simultaneous reactive transport equations into two subsets of equations. The first set contains $N_E$ nonlinear algebraic equations representing mass action laws for the equilibrium
reactions, and the second set contains \((M-N_E)\) kinetic-variable transport equations. These equation subsets are defined as

**Mass action equations for equilibrium reactions**

\[
\frac{\partial E_i}{\partial t} + L(E_i) = D_{ii} r_i + \sum_{j=1}^{N_k} K_{ij} r_{2j}, \quad i \in N_E \Rightarrow r_i = \infty \quad \Rightarrow
\]

\[
\frac{\partial E_i}{\partial t} + L(E_i) \approx D_{ii} r_i = \infty \quad \exists \text{thermodynamically consistent equation}
\]

where \(E_i = \sum_{j=1}^{N_k} A_{ij} C_{1j}\) or \(E = A_i C_1\)

**Transport equations for kinetic-variables**

\[
\frac{\partial E_i}{\partial t} + L(E_i) = \sum_{j=1}^{N_k} K_{2j} r_{2j}, \quad i \in [1, M_c - N_E], \text{where}
\]

\[
E_i = \sum_{j=1}^{N_k} A_{2j} C_{1j} + C_2, \quad \text{or} \quad E = [A_2 \quad U_1] \begin{bmatrix} C_1 \\ C_2 \end{bmatrix}.
\]

Assign

\[
RA_i = \sum_{j=1}^{N_k} K_{2j} r_{2j}, \quad n \in [1, M_c - N_E]
\]

\[
[A_2 \quad U_1] = A_{ek}
\]

From Equations (3.2), (3.6) and (3.7), the \(M_c-N_E\) transport equations for kinetic-variables are specified as follows
where $E_i$ is the $i$-th kinetic variables which is the linear combination of $\rho_j C_j$ resulted from the matrix decomposition of a unit matrix $[M/L^3]$; $t$ is the time $[T]$; $V$ is the flow velocity $[L/T]$; $W_{sp}$ is the settling velocity of suspended precipitate of the $i$-th kinetic-variable $[L/T]$; $E_i^{preci}$ is the portion of $E_i$, which contains the linear combination of only precipitated species $[M/L^3]$; $W_{sn}$ is the settling velocity of particulate chemical sorbed on to $n$-th suspended sediment in the $i$-th kinetic-variable $[L/T]$; $E_i^{sn}$ is the portion of $E_i$, which contains the linear combination of only particulate species sorbed to the $n$-th sediment $[M/L^3]$; $E_i^{dc}$ is the portion of $E_i$, which contains the linear combination of only dissolved chemicals $[M/L^3]$; $K$ is the dispersion coefficient tensor $[L^2/T]$; $ME_i^{as}$ is the artificial source/sink of the $i$-th kinetic-variable, which is the linear combination of $M'_n$ $[M/L^3/T]$; $RA_i$ is the concentration changing rate of $i$-th kinetic-variable due to reaction resulting from the decomposition $[M/L^3/T]$; $M_c$ is the total number of column chemical species; and $N_E$ is the number of equilibrium chemical reactions in column.

$E_i$, $E_i^{dc}$, $E_i^{preci}$ and $E_i^{sn}$ can be formulated as

$$E_i = \sum_{j=0}^{M_c} A_{kj} (\rho_j C_j) = E_i^{dc} + E_i^{preci} + \sum_{n=1}^{N_E} E_i^{sn}, \quad i \in [1, M_c - N_E]$$  \hspace{1cm} (3.11)$$

$$E_i^{dc} = \sum_{j=1}^{M_c} A_{kj} (\rho_j C_j)$$  \hspace{1cm} (3.12)$$
\[ E_{i}^{\text{prec}} = \sum_{j=M_d+1}^{M_c+M_p} A_{ekj} (\rho_j C_j) \] (3.13)

\[ E_{i}^{sn} = \sum_{j=M_d+M_p+1}^{M_c} A_{ekj} (\rho_j C_j) \] (3.14)

\[ M_c = M_{dc} + M_p + M_{sn} \] (3.15)

where \( A_{ekj} \) is the element of a \((M_c-N_E) \times M_c\) matrix \( A_{ek} = [A_2 \ U_1] \) and it represents the coefficient of the linear combination of \( \rho_j C_j \) in \( E_i \); \( M_p \) is the total number of column precipitated species; \( M_{dc} \) is the total number of column dissolved chemicals; and \( M_{sn} \) is the total number of column species adsorbed to \( n \)-th sediment fraction. The initial and boundary conditions for chemical species need to be transformed into the corresponding initial and boundary conditions for kinetic variables, in order to solve the continuity equation for kinetic variables. They are stated in the following.

**Dirichlet boundary condition**

\[ E_i = E_{id} = \sum_{j=M_c} \ A_{ekj} \left[ \rho_j C_{jd} (x_h, y_h, z_h, t) \right] \text{ at } B_d \] (3.16)

where \( E_{id} \) is the \( i \)-th kinetic variable [M/L^3] at the dirichlet boundary; \( C_{jd} \) is the given time-dependent concentration of the \( j \)-th mobile chemical species at the boundary \( B_d \) [M/L^3]; \( B_d \) is the Dirichlet boundary.

**Variable boundary condition**

< Case 1 > When the flow is directed into the region from outside \((\mathbf{n} \cdot \mathbf{V} < 0)\),
\[ \mathbf{n} \cdot (\mathbf{V} E_i - K \cdot \nabla E_i) - \mathbf{n} \cdot (V_{sp} E_i^{\text{prec}}) - \sum_{n=1}^{N} \mathbf{n} \cdot (V_{sn} E_i^{sn}) \]

\[ = q_{E_{iv}} = \sum_{j \in M_v} A_{cikj} q_{C_{jv}}(x_h, y_h, z_h, t) \text{ at } B_v \tag{3.17} \]

< Case 2 > When the flow is directed out of the region from inside (\( \mathbf{n} \cdot \mathbf{V} > 0 \))

\[- \mathbf{n} \cdot (K \cdot \nabla E_i) = 0 \text{ at } B_v \tag{3.18} \]

where \( q_{E_{iv}} \) is the flux of the \( i \)-th kinetic variable at the boundary \( B_v \) [M/L²/T]; \( q_{C_{jv}}(x_h, y_h, z_h, t) \) is the given time-dependent flux of the \( j \)-th mobile chemical species at the boundary \( B_v \) [M/L²/T]; \( B_v \) is the Variable boundary.

**Cauchy boundary condition**

\[ \mathbf{n} \cdot (\mathbf{V} E_i - K \cdot \nabla E_i) - \mathbf{n} \cdot (V_{sp} E_i^{\text{prec}}) - \sum_{a \in N_v} \mathbf{n} \cdot (V_{sn} E_i^{sn}) \]

\[ = q_{E_{ic}} = \sum_{j \in M_v} A_{cikj} q_{C_{jc}}(x_h, y_h, z_h, t) \text{ at } B_c \tag{3.19} \]

where \( q_{E_{ic}} \) is the flux of the \( i \)-th kinetic variable at the boundary \( B_c \) [M/L²/T]; \( q_{C_{jc}}(x_h, y_h, z_h, t) \) is the given time-dependent Cauchy flux of the \( j \)-th mobile chemical species at the boundary \( B_c \) [M/L²/T]; \( B_c \) is the Cauchy boundary.

**Neumann boundary condition**

\[- \mathbf{n} \cdot (K \cdot \nabla E_i) = q_{E_{in}} = \sum_{j \in M_v} A_{cikj} q_{C_{jn}}(x_h, y_h, z_h, t) \text{ at } B_n \tag{3.20} \]
where $q_{Ein}$ is the Neumann flux of the $i$-th kinetic variable at the boundary $B_n$ [M/L^2/T]; $q_{Cjn}(x_b,y_b,z_b,t)$ is the given Neumann flux of the $j$-th mobile chemical species at the boundary $B_n$ [M/L^2/T]; $B_n$ is the Neumann boundary.

Coastal surface water-coastal bed interface boundary condition

$$
n \cdot (VE_i - K \cdot \nabla E_i) - n \cdot \left( V_{sp} E_{i}^{preci} \right) - \sum_{n \in N} n \cdot \left( V_{sn} E_{i}^{sn} \right) = F_{E_i:C \rightarrow B} \text{ at } B_{sb} \quad (3.21)
$$

where $F_{E_i:C \rightarrow B}$ is the exchange rate of the $i$-th kinetic variable in water column from water column to the bed layer due to diffusion (for dissolved species), settling (for precipitated species) and deposition/erosion (for particulate species) [M/L^2/T]. Equation (3.21) can be expressed and further decomposed into the following equations

$$
F_{E_i:C \rightarrow B} = F_{E_i^{dc}:C \rightarrow B} + F_{E_i^{preci}:C \rightarrow B} + \sum_{n=1}^{N} F_{E_i^{sn}:C \rightarrow B}, \quad i \in [1, M_c - N_E] \quad (3.22)
$$

$$
n \cdot (VE_{i}^{dc} - K \cdot \nabla E_{i}^{dc}) = F_{E_i^{dc}:C \rightarrow B} \quad (3.23)
$$

$$
n \cdot (VE_{i}^{preci} - K \cdot \nabla E_{i}^{preci}) = F_{E_i^{preci}:C \rightarrow B} \quad (3.24)
$$

$$
\sum_{n=1}^{N} \left[ n \cdot (VE_{i}^{sn} - K \cdot \nabla E_{i}^{sn}) - n \cdot (V_{sn} E_{i}^{sn}) \right] = \sum_{n=1}^{N} F_{E_i^{sn}:C \rightarrow B} \quad (3.25)
$$

where $F_{E_i^{dc}:C \rightarrow B}$, $F_{E_i^{preci}:C \rightarrow B}$, $F_{E_i^{sn}:C \rightarrow B}$ are the portion of the exchange rates $F_{E_i:C \rightarrow B}$ from water column to the bed layer corresponding to $E_i^{dc}$, $E_i^{preci}$, and $E_i^{sn}$, respectively [M/L^2/T]. They can be formulated as
\[ F_{E_\text{dc:C}\rightarrow B} = \sum_{j_\text{c}[1,M_{\text{dc}}]} A_{\text{ekij}} \varepsilon_{\text{dc:C}\rightarrow B} (\rho_w C_j - \rho_{pw} \theta_b C_{bj'}) + \sum_{j_\text{c}[1,M_{\text{dc}}]} A_{\text{ekij}} \left\{ 0.5(n \cdot V) \left[ \left(1 + \text{sign}(n \cdot V)\right) \rho_w C_j + \left(1 - \text{sign}(n \cdot V)\right) \rho_{pw} \theta_b C_{bj'} \right] \right\} \] \quad (3.26)

\[ F_{E_\text{pc:C}\rightarrow B} = \sum_{j_\text{c}[M_{\text{dc}}+1,M_{\text{dc}}+M_p]} A_{\text{ekij}} \left[ (n \cdot V) \rho_w C_j + \varepsilon_{\text{pc:C}\rightarrow B} (\rho_w C_j - \rho_{pw} \theta_b C_{bj'}) \right] + \sum_{j_\text{c}[M_{\text{dc}}+1,M_{\text{dc}}+M_p]} A_{\text{ekij}} \left\{ 0.5(n \cdot V) \left[ \left(1 + \text{sign}(n \cdot V)\right) \rho_w C_j + \left(1 - \text{sign}(n \cdot V)\right) \rho_{pw} \theta_b C_{bj'} \right] \right\} \] \quad (3.27)

\[ F_{E_\text{en:C}\rightarrow B} = \sum_{j_\text{c}[M_{\text{dc}}+1,M_{\text{dc}}+M_p]} A_{\text{ekij}} \left( D_n C_j - R_n C_{bj'} \right) + \sum_{j_\text{c}[M_{\text{dc}}+1,M_{\text{dc}}+M_p]} A_{\text{ekij}} \left\{ 0.5(n \cdot V) \left[ \left(1 + \text{sign}(n \cdot V)\right) S_n C_j + \left(1 - \text{sign}(n \cdot V)\right) \bar{M}_n C_{bj'} \right] \right\} \] \quad (3.28)

where \( \varepsilon_{\text{dc:C}\rightarrow B} \) is the diffusion/dispersion coefficient for dissolved species at the column bed interface [L/T]; \( \varepsilon_{\text{pc:C}\rightarrow B} \) is the diffusion/dispersion coefficient for precipitated species at the column-bed interface[L/T]; \([C_j]\) represents the \( j \)-th mobile column species; and \([C_{bj'}]\) represents the \( j' \)-th immobile bed species that corresponds to \([C_j]\).
3.2 Bed Reactive Systems

According to the mathematical model section, a set of Mb partial differential equations can be written for Mb chemical species in the bed reaction system as

\[
\frac{\partial (\rho_{bi} C_{bi})}{\partial t} + K(\rho_{bi} C_{bi}) = \sum_{k=1}^{N} (v_{bik} - \mu_{bik}) r_{bk}, \quad i \in M_b
\]  

(3.29)

\[
K(\rho_{bi} C_{bi}) = \frac{\rho_{bi} C_{bi}}{B} \frac{\partial B}{\partial t} - \frac{F_{bi\rightarrow B}}{B}, \quad i \in M_b
\]  

(3.30)

Using the similar procedure as in section 3.1 we can get the following equations

**Mass action equations for equilibrium reactions**

\[
\frac{\partial E_{bi}}{\partial t} + K(E_{bi}) = D_{bli} r_{bli} + \sum_{j=1}^{N_k} K_{b1j} r_{b2j}, \quad i \in N_{bE} \Rightarrow r_{bli} = \infty \Rightarrow
\]

\[
\frac{dE_{bi}}{dt} + K(E_{bi}) \approx D_{bli} r_{bli} = \infty \exists \text{thermodynamically consistent equation}
\]  

(3.31)

**where** \( E_{bi} = \sum_{j=1}^{N_j} A_{b1j} C_{b1j} \text{ or } E_b = A_{bi} C_{bi} \)

**Balance equations for kinetic variables**

\[
\frac{\partial E_{bi}}{\partial t} = R A_{bi} - \frac{E_{bi}}{B} \frac{\partial B}{\partial t} - \frac{F_{E_{bi}\rightarrow B}}{B}, \quad i \in [1, M_b - N_{bE}]
\]  

(3.32)

where \( E_{bi} \) is the i-th kinetic variables in the bed which is the linear combination of \( \rho_{bi} C_{bi} \)

resulted from the matrix decomposition of a unit matrix \([M/L^3] \); t is the time \([T] \); \( RA_{bi} \) is the
concentration changing rate of $i$-th kinetic-variable in the bed due to reaction resulting from the decomposition [M/L$^3$/T]; $F_{E_i, c \rightarrow B}$ is the exchange rate of kinetic variable $E_{bi}$ in the bed from water column to the bed layer [M/L$^2$/T]; $M_b$ is the total number of bed chemical species; $NbE$ is the number of equilibrium chemical reactions in bed.

$E_{bi}$ can be further written as

$$E_{bi} = \sum_{j=M_b} A_{bki}(\rho_{bj} C_{bj}) = E_{bi}^{dc} + E_{bi}^{preci} + \sum_{n=1}^{NbE} E_{bi}^{sn}, \quad i \in [1, M_b - NbE] \quad (3.33)$$

$$E_{bi}^{dc} = \sum_{j=1}^{M_{dc}} A_{bki}(\rho_{bj} C_{bj}) \quad (3.34)$$

$$E_{bi}^{preci} = \sum_{j=M_{dc}+1}^{M_{dc}+M_{bp}} A_{bki}(\rho_{bj} C_{bj}) \quad (3.35)$$

$$E_{bi}^{sn} = \sum_{j=M_{dc}+M_{bp}+1} A_{bki}(\rho_{bj} C_{bj}) \quad (3.36)$$

$$M_b = M_{dc} + M_{bp} + M_{bn} \quad (3.37)$$

where $E_{bi}^{preci}$ is the portion of $E_{bi}$, which contains the linear combination of only precipitated species [M/L$^3$]; $E_{bi}^{sn}$ is the portion of $E_{bi}$, which contains the linear combination of only particulate species sorbed to the $n$-th sediment[M/L$^3$]; $E_{bi}^{dc}$ is the portion of $E_{i}$, which contains the linear combination of only dissolved chemicals[M/L$^3$]; $A_{bki}$ is the element of a $(M_b-NbE) \times M_b$ matrix and it represents the coefficient of the linear combination of in $E_{bi}$; $M_{bp}$ is the total number of bed precipitated species; $M_{dc}$ is the total number of bed dissolved chemicals; $M_{bn}$ is the total number of bed species adsorbed to sediment fraction $n$. 
\[ F_{E_{iE},C\rightarrow B} \text{ can be expressed and further decomposed into the following equations} \]

\[ F_{E_{iE},C\rightarrow B} = F_{E_{iE}^{dc},C\rightarrow B} + F_{E_{iE}^{prei},C\rightarrow B} + \sum_{n=1}^{N_{hE}} F_{E_{iE}^{sn},C\rightarrow B}, \quad i \in [1, M_b - N_{hE}] \quad (3.38) \]

\[ F_{E_{iE}^{dc},C\rightarrow B} = \sum_{j \in [1,M_d]} A_{bkij} \left( \frac{1}{2} \right) \left( \rho_n C_j - \rho_{pw E} \theta_b C_j \right) \]

\[ + \sum_{j \in [1,M_d]} A_{bkij} \left\{ 0.5(n \cdot V) \left[ \begin{array}{c}
(1 + sign(n \cdot V)) \rho_n C_j + \\
(1 - sign(n \cdot V)) \rho_{pw E} \theta_b C_j 
\end{array} \right] \right\} \quad (3.39) \]

\[ F_{E_{iE}^{prei},C\rightarrow B} = \sum_{j \in [1,M_d + M_{sp}]} A_{bkij} \left( \frac{1}{2} \right) \left( \rho_n C_j - \rho_{pw E} \theta_b C_j \right) \]

\[ + \sum_{j \in [1,M_d + M_{sp}]} A_{bkij} \left\{ 0.5(n \cdot V) \left[ \begin{array}{c}
(1 + sign(n \cdot V)) \rho_n C_j + \\
(1 - sign(n \cdot V)) \rho_{pw E} \theta_b C_j 
\end{array} \right] \right\} \quad (3.40) \]

\[ F_{E_{iE}^{sn},C\rightarrow B} = \sum_{j \in [1,M_d + M_{sp} + 1,M_b]} A_{bkij} \left( D_n C_j - R_n C_j \right) \]

\[ + \sum_{j \in [1,M_d + M_{sp} + 1,M_b]} A_{bkij} \left\{ 0.5(n \cdot V) \left[ \begin{array}{c}
(1 + sign(n \cdot V)) S_n C_j + \\
(1 - sign(n \cdot V)) M_n C_j 
\end{array} \right] \right\} \quad (3.41) \]

where \( F_{E_{iE}^{dc},C\rightarrow B} \), \( F_{E_{iE}^{prei},C\rightarrow B} \), and \( F_{E_{iE}^{sn},C\rightarrow B} \) are the exchange rates in the bed from water column to the bed layer corresponding to \( E_{iE}^{dc} \), \( E_{iE}^{prei} \), and \( E_{iE}^{sn} \), respectively [M/L2/T]; \( \varepsilon_{dc,C\rightarrow B} \) is the diffusion/dispersion coefficient for dissolved species at the column-bed interface [L/T]; \( \varepsilon_{prei,C\rightarrow B} \) is
the diffusion/dispersion coefficient for precipitated species at the column-bed interface [L/T]; $[C_j]$ represents the $j$-th immobile bed species; and $[C_{j'}]$ represents the $j'$-th mobile column species that corresponds to $[C_j]$. 
In this section, we present the numerical approaches employed to solve the governing equations of reactive chemical transport. Ideally, one would like to use a numerical approach that is accurate, efficient, and robust. Thus, depending on what one intends to use the specific problem at hand for, different numerical approaches may be most suitable. For research applications, accuracy is a primary requirement, because one does not want to distort physics due to numerical errors. On the other hand, for large field practical problems, efficiency and robustness are primary concerns with accuracy remaining well within the bounds of uncertainty associated with model parameters.

For hyperbolic-dominant transport equations such as the advection-dominant scalar transport, it is well known that the semi-Lagrangian (SL) method is most efficient in discretizing the advection transport while the conventional second-order finite element or finite difference methods are sufficient to approximate the diffusive/dispersive transport. Considering that there can be wide ranges of transport conditions for real-world problems, we provide many numerical options in the model.

For transport simulations (including sediment and water quality), two options are provided to discretize the governing sediment and biogeochemical transport equations: hybrid Lagrangian-Eulerian finite element methods or conventional finite element methods. Three schemes are employed to handle the coupling between the hydrologic transport and biogeochemical reactions:
fully implicit sequential iteration approach, operator splitting, and mixed predictor-corrector and operator-splitting. The Newton-Raphson method was used to solve the set of algebraic equations and ordinary equations describing the evolution of all biogeochemical species.

4.1 Bed Sediment Transport

Modify Equation (2.3) with grid velocity \( V_g \) term and get the following equation

\[
\frac{\partial (BM_n)}{\partial t} + V G = F_{inC\rightarrow B}, n \in [1, N_s] \quad \text{and} \quad \frac{\partial B}{\partial t} = \sum_{n=1}^{N_s} \frac{F_{inC\rightarrow B}}{\rho_n}
\]  

(4.1)

where

\[
VG = V_g \cdot \nabla (BM_n) = BV_g \cdot \nabla M_n
\]

(4.2)

\[
VG \approx \hat{V} G = \sum_{j=1}^{N} VG_j(t)N_j(R)
\]

(4.3)

\[
\hat{M}_n \approx \hat{M}_n = \sum_{j=1}^{N} \hat{M}_j(t)N_j(R)
\]

(4.4)

The integration of Equation (4.2) can be written as

\[
\int_{R} N_i \sum_{j=1}^{N} VG_j(t)N_j(R)dR = \int_{R} N_i BV_g \cdot \sum_{j=1}^{N} \hat{M}_j(t)\nabla N_j(R)dR
\]

(4.5)
Assign matrices \([QA]\) and \([QV]\) as following

\[
QA_{ij} = \sum_{e=1}^{M_e} N^e_i N^e_j \mathrm{d}R \quad (4.6)
\]

\[
QV_{ij} = B \sum_{e=1}^{M_e} N^e_i \nabla N^e_j(R) \mathrm{d}R \quad (4.7)
\]

Equation (4.5) is expressed as

\[
[QA]\{VG\} = [QV]\{\vec{M}_n\} \quad (4.8)
\]

Lump matrix \([QA]\) into diagonal matrix and update

\[
QV_{ij} = QV_{ij} / QA_{ii} \quad (4.9)
\]

So that

\[
\{VG\} = [QV]\{\vec{M}_n\} \quad (4.10)
\]

At \(n+1\)-th time step, Equation (4.1) written in matrix form is then expressed as

\[
\begin{bmatrix}
\frac{B^{n+1}[U]}{\Delta t} + \sum_{n=1}^{N} \frac{W_1}{\rho_n} \left\{ F_{\text{sec}\rightarrow B} \right\}^{n+1} - WV_1 \left[ QV^{n+1} \right] \{\vec{M}_n^{n+1}\} \\
\frac{B^n[U]}{\Delta t} - \sum_{n=1}^{N} \frac{W_2}{\rho_n} \left\{ F_{\text{sec}\rightarrow B} \right\}^n + WV_2 \left[ QV^n \right] \{\vec{M}_n^n\}
\end{bmatrix} + W_1 \left\{ F_{\text{sec}\rightarrow B}^{n+1} \right\} + W_2 \left\{ F_{\text{sec}\rightarrow B}^n \right\}, n \in [1, N_s]
\]

where \([U]\) is the unit matrix; \(WV_1, WV_2, W_1\) and \(W_2\) are time weighting factors; superscripts \(^{n+1}\) and \(^n\) represent the time step number. \(B^{n+1}\) can be obtained from the following equation
\[
\frac{B^{n+1}}{\Delta t} = \frac{B^n}{\Delta t} + \sum_{n=1}^{N_s} \frac{W_1 \{ F_{snC\rightarrow B} \}^{n+1}}{\rho_n} + \sum_{n=1}^{N_s} \frac{W_2 \{ F_{snC\rightarrow B} \}^n}{\rho_n}
\] (4.12)

4.2 Suspended Sediment Transport

4.2.1 Finite Element Method in Advective Form Approach

Conversion of Equation (2.4) to advection form is expressed as

\[
\frac{\partial S_n}{\partial t} + V \cdot \nabla S_n - \frac{\partial}{\partial z} \left( W_{sn} S_n \right) - \nabla \cdot \left( K \cdot \nabla S_n \right) + \left( \nabla \cdot V \right) S_n = M_{n}^{as}, \quad n \in [1, N_s]
\] (4.13)

According to Equation (2.2), the right-hand side term RHS and left hand side term LHS can be assigned as follows.

\begin{align*}
If \quad & S_n \leq 0, \quad M_{n}^{as} = S_n \ast S_n, \quad LHS = 0, \quad RHS = 0 \\
Else \quad & S_n > 0, \quad M_{n}^{as} = M_{n}^{as}, \quad LHS = S_n, \quad RHS = M_{n}^{as}
\end{align*}
(4.14)

Then Equation (4.13) is modified as

\[
\frac{\partial S_n}{\partial t} + V \cdot \nabla S_n - \frac{\partial}{\partial z} \left( W_{sn} S_n \right) - \nabla \cdot \left( K \cdot \nabla S_n \right) + LHS \ast S_n = RHS, \quad n \in [1, N_s]
\] (4.15)
Modify the equation with grid velocity $V_g$ term and get

$$\frac{dS_n}{dt} + (V - V_g) \cdot \nabla S_n - \frac{\partial}{\partial z}(W_{sn} S_n) - \nabla \cdot (K \cdot \nabla S_n) + LHS \cdot S_n = RHS, n \in [1, N_s]$$

(4.16)

Integrate equation (4.16) in the spatial dimensions over the entire region as follows.

$$\int_{R} N_i \frac{dS_n}{dt} dR + \int_{R} W_i \left[ (V - V_g) \cdot \nabla S_n - \frac{\partial}{\partial z}(W_{sn} S_n) \right] dR + \int_{R} \nabla N_i \cdot (K \cdot \nabla S_n) dR + \int_{R} LHS \cdot S_n dR$$

(4.17)

$$= \int_{R} N_i RHS dR + \int_{B} \mathbf{n} \cdot \left[ N_i (K \cdot \nabla S_n) \right] dB$$

Substituting equation $S_n \approx \tilde{S}_n = \sum_{j=1}^{N} S_{m_i} (t) N_{j} (R)$ into Equation (4.17), we obtain

$$\sum_{j=1}^{N} \left[ \int_{R} (N_i N_j) dR \right] \frac{dS_{m_i}}{dt} dR$$

$$+ \sum_{j=1}^{N} \left[ \int_{R} W_i \left[ (V - V_g) \cdot \nabla N_j \right] dR \right] S_{m_j} (t)$$

$$+ \sum_{j=1}^{N} \left[ \int_{R} \nabla N_i \cdot (K \cdot \nabla N_j) dR + \int_{R} RHS N_j dR \right] S_{m_j} (t)$$

(4.18)

$$= \int_{R} N_i RHS dR + \int_{B} \mathbf{n} \cdot \left[ N_i (K \cdot \nabla S_n) \right] dB$$

Equation (4.18) can be written in matrix form as

$$[Q1] \left\{ \frac{dS_n}{dt} \right\} + [Q2] \{S_n\} + [Q3] \{S_n\} = \{SS\} + \{B\}$$

(4.19)

where the matrices $[Q1]$, $[Q2]$, and $[Q3]$, and load vectors $\{SS\}$ and $\{B\}$ are given by
\[
Q_{1g} = \sum_{e=1}^{M_e} \int_{R_e} N_i^e N_j^e dR
\]  
(4.20)

\[
Q_{2g} = \sum_{e=1}^{M_e} \int_{R_e} W_i^e \left( (V - V_g^e - V_{sn}) \cdot \nabla N_j^e \right) dR
\]  
(4.21)

\[
Q_{3g} = \sum_{e=1}^{M_e} \int_{R_e} \nabla N_i^e \cdot \left( K \cdot \nabla N_j^e \right) dR + \sum_{e=1}^{M_e} \int_{R_e} LHS N_i^e N_j^e dR
\]  
(4.22)

\[
SS_i = \int_{R_e} N_i^e RHS dR
\]  
(4.23)

\[
B_i = \int_{B} \mathbf{n} \cdot (N_i K \cdot \nabla S_n) dB
\]  
(4.24)

At \(n+1\)-th time step, Equation (4.19) is approximated as

\[
\begin{align*}
\left[ Q_1^{n+1} \right] \left\{ S_{n+1} \right\} - \left[ Q_1^n \right] \left\{ S_n \right\} & = \frac{\Delta t}{W_1} \left[ Q_2^{n+1} \right] \left\{ S_{n+1} \right\} + \frac{\Delta t}{W_2} \left[ Q_3^n \right] \left\{ S_n \right\} \\
& + \frac{\Delta t}{W_1} \left[ Q_2^n \right] \left\{ S_n \right\} + \frac{\Delta t}{W_2} \left[ Q_3^{n+1} \right] \left\{ S_{n+1} \right\} + W_1 \left[ S_{n+1} \right] + W_2 \left[ S_n \right] + W_1 \left[ B^{n+1} \right] + W_2 \left[ B^n \right]
\end{align*}
\]  
(4.25)

where \(WV_1, WV_2, W_1\) and \(W_2\) are time weighting factors, matrices and vectors with superscripts \(n+1\) and \(n\) are evaluated over the region at the new time step \(n+1\) and the region at the old time step \(n\), respectively.

Let \( [CMATRIX] \left\{ S_{n+1} \right\} = \{ RLD \} \)  
(4.26)
\[ [RLD] = \left( \frac{[Q_i^a]}{\Delta t} - W V_2 [Q_2^a] - W_2 [Q_3^a] \right) \{S_{n^a}\} + W_1 \{SS'^{a+1}\} + W_2 \{SS\} + W_1 \{B'^{a+1}\} + W_2 \{B^a\} \]  

(4.28)

For interior nodes i, B_i is zero, for boundary nodes i = b, B_i is calculated according to the specified boundary conditions shown as follows.

**Dirichlet boundary condition**

\[ S_n = S_{nd} (x_b, y_b, z_b, t) \]  

(4.29)

**Variable boundary condition**

< Case 1 > when flow is going in from outside (\( \mathbf{n} \cdot \mathbf{V} < 0 \))

\[ B_i = \int_B \mathbf{n} \cdot (N_i V S_n) dB - \int_B \mathbf{n} \cdot (N_i V_{sn} S_n) dB - \int_B N_i q_{svn} dB \]  

(4.30)

< Case 2 > Flow is going out from inside (\( \mathbf{n} \cdot \mathbf{V} > 0 \))

\[ B_i = 0 \]  

(4.31)

**Cauchy boundary condition**

\[ B_i = \int_B \mathbf{n} \cdot (N_i V S_n) dB - \int_B \mathbf{n} \cdot (N_i V_{sn} S_n) dB - \int_B N_i q_{snc} dB \]  

(4.32)

**Neumann boundary condition**

\[ B_i = -\int_B N_i q_{snn} dB \]  

(4.33)
Coastal surface water-coastal bed interface boundary condition

\[ B_i = \int_B n \cdot (N_i V S_n) dB - \int_B (N_i F_{sm} \rightarrow C) dB - \int_B n \cdot (N_i V_{sm} S_n) dB \]  \hspace{1cm} (4.34)

4.2.2 Lagrangian-Eulerian Approach

Equation (4.15) in hybrid Lagrangian-Eulerian form is written as follows.

In Lagrangian step,

\[ \frac{DS}{Dt} = \frac{\partial S}{\partial t} + V \cdot \nabla S_n - \frac{\partial}{\partial z} (W_{sm} S_n) = 0 \]  \hspace{1cm} (4.35)

where particle tracking velocity is the flow velocity \( V \).

In Eulerian step,

\[ \frac{DS}{Dt} - \nabla \cdot (K \cdot \nabla S_n) + LHS \cdot S_n = RHS \]  \hspace{1cm} (4.36)

Let \( D = \nabla \cdot (K \cdot \nabla S_n) \), Equation (4.36) written in a slightly different form is shown as

\[ \frac{DS}{Dt} - D + LHS \cdot S_n = RHS \]  \hspace{1cm} (4.37)

The diffusion term \( D \) expressed in term of \( S_n \) is solved by the following procedure.
Approximate Sn and D by \( S_n \approx \hat{S}_n = \sum_{j=1}^{N} S_{nj}(t)N_j(R) \) and \( D \approx \hat{D} = \sum_{j=1}^{N} D_j(t)N_j(R) \)

The integration of equation \( D = \nabla \cdot (K \cdot \nabla S_n) \) can be written as

\[
\sum_{j=1}^{N} \left[ \int_{R_j} N_i N_j dR \right] D_j(t) = -\sum_{j=1}^{N} \left[ \int_{R_j} \nabla N_i \cdot (K \cdot \nabla N_j) dR \right] S_{nj}(t) + \int_{B} n \cdot \left[ N_i (K \cdot \nabla S_n) \right] dB
\]

Assign

\[
QA_{ij} = \sum_{e=1}^{M_e} \left( \int_{R_{je}} N_{i}^{e} N_{j}^{e} dR \right)
\]

\[
QD_{ij} = \sum_{e=1}^{M_e} \left( \int_{R_{je}} \nabla N_{i}^{e} \cdot (K \cdot \nabla N_{j}^{e}) dR \right)
\]

\[
B_i = \int_{B} n \cdot \left[ N_i (K \cdot \nabla S_n) \right] dB
\]

Equation (4.38) is expressed as

\[
[QA] \{D\} = -[QD] \{S_n\} + \{B\}
\]

Lump matrix \([QA]\) into diagonal matrix and update

\[
QD_{ij} = QD_{ij} / QA_{ij}
\]

\[
B_i = B_i / QA_{ii}
\]

Then

\[
\{D\} = -[QD] \{S_n\} + \{B\}
\]
Equation (4.37) written in matrix form is then expressed as

\[
\left( \frac{[U]}{\Delta \tau} + W_1 [QD^{n+1}] + W_1 [LHS^{n+1}] \right) \{ S_n^{n+1} \} = \frac{[U]}{\Delta \tau} \{ S_n^* \} + W_2 \{ D^* \} \\
-W_2 [LHS^*] \{ S_n^* \} + W_1 \{ RHS^{n+1} \} + W_2 \{ RHS^* \} + W_1 \{ B^{n+1} \}
\] (4.46)

where [U] is the unit matrix, \( \Delta \tau \) is the tracking time, \( W_1 \) and \( W_2 \) are time weighting factors, matrices and vectors with superscript \( n+1 \) are evaluated over the region at the new time step \( n+1 \) (e.g. \( LHS^{n+1} \) is a diagonal matrix with \( LHS \) calculated over the new grid at \( n+1 \)-th time step as its diagonal components), Matrices and vectors with superscript \( * \) corresponds to the \( n \)-th time step values interpolated at the location where a node is tracked through particle tracking in Lagrangian step.

**Dirichlet boundary condition**

\[
B_i = \left( [QB] \{ S_n \} \right) \frac{1}{QA_{ij}}
\] (4.47)

where

\[
QB_{ij} = \sum_{e=1}^{M} \left\{ n \cdot \left[ N_i^e \left( K \cdot \nabla N_j^e \right) \right] dB \right\}
\] (4.48)

**Variable boundary condition**

< Case 1 > when flow is going in from outside \( (n \cdot V < 0) \)

\[
B_i = \left[ \int_{B_i} n \cdot \left( N_i V S_n \right) dB - \int_{B_i} n \cdot \left( N_i V_{sn} S_n \right) dB - \int_{B_i} N_i q_{Snv} dB \right] \frac{1}{QA_{ij}}
\] (4.49)
< Case 2 > Flow is going out from inside \((\mathbf{n} \cdot V > 0)\)

\[
B_i = 0 \quad (4.50)
\]

**Cauchy boundary condition**

\[
B_i = \left[ \int_B \mathbf{n} \cdot (N_i V S_{n}) dB - \int_B \mathbf{n} \cdot (N_i V n S_n) dB - \int_B N_i q_{Snc} dB \right] / QA_{ii} \quad (4.51)
\]

**Neumann boundary condition**

\[
B_i = -\left[ \int_B N_i q_{Snn} (x_h, y_h, z_h, t) dB \right] / QA_{ii} \quad (4.52)
\]

**Coastal surface water-coastal bed interface boundary condition**

\[
B_i = \left[ \int_B \mathbf{n} \cdot (N_i V S_{n}) dB - \int_B \mathbf{n} \cdot (V S_{n} S_n) dB - \int_B N_i F_{snc \rightarrow B} dB \right] / QA_{ii} \quad (4.53)
\]
4.3 Kinetic Variable Transport

4.3.1 Finite Element Method in Advective Form Approach

4.3.1.1 Fully-Implicit Scheme

Conversion of Equation (3.10) to advection form is expressed as

\[
\frac{\partial E_i}{\partial t} + V \cdot \nabla E_i = \frac{\partial \left( W_{sp} E_{i}^{preci} \right)}{\partial z} - \sum_{n=1}^{N} \frac{\partial \left( W_{sn} E_{i}^{sm} \right)}{\partial z} - \nabla \cdot (K \cdot \nabla E_i) + (\nabla \cdot V) E_i = M E_i^{as} + RA_i, \quad i \in [1, M_e - N_e]
\] (4.54)

According to governing Equation (2.2), the right-hand side term \( RHS \) and left hand side term \( LHS \) can be initialized and updated as follows

\[
\text{If } S_y \leq 0, M E_i^{as} = S_y \cdot E_i, \quad LHS = 0, \quad RHS = 0
\]

\[
\text{Else } S_y > 0, M E_i^{as} = M E_i^{as}, \quad LHS = S_y, \quad RHS = M E_i^{as}
\] (4.55)

Then Equation (4.54) is modified as

\[
\frac{\partial E_i}{\partial t} + V \cdot \nabla E_i = \frac{\partial \left( W_{sp} E_{i}^{preci} \right)}{\partial z} - \sum_{n=1}^{N} \frac{\partial \left( W_{sn} E_{i}^{sm} \right)}{\partial z} - \nabla \cdot (K \cdot \nabla E_i) + LHS \cdot E_i = RHS + RA_i
\] (4.56)
According to Fully-Implicit Scheme, Equation (4.56) can be separated into two equations as follows

\[
\frac{E_i^{n+1/2} - E_i^n}{\Delta t} + V \cdot \nabla E_i - \frac{\partial (W_{sp} E_{i,\text{preci}})}{\partial z} - \sum_{n=1}^{N_s} \frac{\partial (W_{sn} E_{i,n})}{\partial z} = 0
\]  

(4.57)

\[-\nabla \cdot (K \cdot \nabla E_i) + \text{LHS} \cdot E_i = \text{RHS} + R_A_i
\]

(4.58)

First, \(E_i^{n+1/2}\) can be solved through Equation (4.57). Second, we solve Equation (4.58) together with algebraic equations for equilibrium reactions using BIOGEOCHEM (Fang et al., 2003) to obtain all individual species concentrations. Iteration between these two steps is needed because the new reaction terms and the equation coefficients in Equation (4.57) need to be updated by the calculation results of Equation (4.58).

Modify Equation (4.56) with grid velocity \(V_g\) term.

\[
\frac{dE_i}{dt} + V \cdot \nabla E_i - V_g \cdot \nabla E_i - \frac{\partial (W_{sp} E_{i,\text{preci}})}{\partial z} - \sum_{n=1}^{N_s} \frac{\partial (W_{sn} E_{i,n})}{\partial z} = 0
\]  

(4.59)

\[-\nabla \cdot (K \cdot \nabla E_i) + \text{LHS} \cdot E_i = \text{RHS} + R_A_i
\]

Integrate equation (4.59) in the spatial dimensions over the entire region as follows.

\[
\int_{R} N_i \frac{dE_i}{dt} dR - \int_{R} W_{sp}(V_g \cdot \nabla E_i) dR + \int_{R} W_{sp}(V \cdot \nabla E_i) dR - \int_{R} W_{sp} \left[ \frac{\partial (W_{sp} E_{i,\text{preci}})}{\partial z} \right] dR - \sum_{n=1}^{N_s} \int_{R} W_{sn} \left[ \frac{\partial (W_{sn} E_{i,n})}{\partial z} \right] dR
\]

\[-\int_{R} \nabla E_i \cdot (K \cdot \nabla E_i) dR + \int_{R} N_i \cdot (LHS \cdot E_i) dR + \int_{R} (\text{RHS} \cdot E_i) dR
\]

(4.60)

\[= \int_{R} N_i (\text{RHS} + R_A_i) dR + \int_{R} n \cdot [N_i (K \cdot \nabla E_i)] dB
\]

51
Define

\[
W_{sE} = \begin{cases} 
0, & \text{for dissolved kinetic variable } E_i^{de} \\
W_{sp}, & \text{for suspended precipitate kinetic variable } E_i^{prec} \\
W_{sn}, & \text{for particulate kinetic variable sorbed on to } n-th \text{ suspended sediment } E_i^{sn}
\end{cases}
\]  

(4.61)

\[
V_s = \{0,0,W_{sE}\}^T 
\]  

(4.62)

Equation (4.60) can be written as

\[
\int_R \frac{dE_i}{dt} dR - \int_R W_i (V \cdot \nabla E_i) dR + \int_R W_i (V \cdot \nabla E_i) dR - \int_R W_i (V \cdot \nabla E_i) dR + \int_R N_i (LHS \cdot E_i) dR \\
+ \int_R \nabla N_i \cdot (K \cdot \nabla E_i) dR + \int_R (N_i \cdot LHS \cdot E_i) dR \\
= \int_R N_i (RHS + RA_i) dR + \int_B \nabla \cdot [N_i (K \cdot \nabla E_i)] dB 
\]  

(4.63)

Approximate solution \( E_i \) by a \( E_i \approx \hat{E}_i = \sum_{j=1}^{N} E_{ij}(t) N_j (R) \), we obtain

\[
\sum_{j=1}^{N} \left[ \int_R N_i N_j dR \frac{dE_{ij}(t)}{dt} \right] \left[ \begin{array}{c} 0 \\ W_{sp} \\ W_{sn} \end{array} \right] - \sum_{j=1}^{N} \left[ \int_R W_i (V - V_s) \cdot \nabla N_j dR \right] E_{ij} (t) \\
+ \sum_{j=1}^{N} \left[ \int_R \nabla N_i \cdot (K \cdot \nabla N_j) dR + \int_R N_iLHS \cdot N_j dR \right] E_{ij} (t) \\
= \int_R N_i (RHS + RA_i) dR + \int_B \nabla \cdot [N_i (K \cdot \nabla E_i)] dB 
\]  

(4.64)

Equation (4.64) can be written in matrix form as

\[
[Q1] \left[ \frac{dE_i}{dt} \right] + [Q2] \{E_i\} + [Q3] \{E_i\} = \{SS\} + \{B\} 
\]  

(4.65)
where the matrices \([Q1]\), \([Q2]\), \([Q3]\) and load vectors \({SS}\), and \({B}\) are given by

\[
Q_{1y} = \sum_{c=1}^{M} \int_{R_c} N_i^e N_j^e dR
\]  
(4.66)

\[
Q_{2y} = \sum_{c=1}^{M} \int_{R_c} W_i^e \left( V - V_g - V_i \right) \nabla N_j^e dR
\]  
(4.67)

\[
Q_{3y} = \sum_{c=1}^{M} \int_{R_c} \nabla N_i^e \cdot \left( K \nabla N_j^e \right) dR + \sum_{c=1}^{M} \int_{R_c} N_i^e \left( LHS \ast N_j^e \right) dR
\]  
(4.68)

\[
SS_i = \int_{R_i} N_i^e \left( RHS + RA_i \right) dR
\]  
(4.69)

\[
B_i = \int_{B} n \cdot \left[ N_i \left( K \cdot \nabla E_i \right) \right] dB
\]  
(4.70)

At \(n+1\)-th time step, Equation (4.65) is approximated as

\[
\frac{[Q_{1}^{n+1}]}{\Delta t} \{E_{1}^{n+1/2}\} - \frac{[Q_{1}^{n}]}{\Delta t} \{E_{1}^{n}\} + W_1 \left[ \frac{Q_{2}^{n+1}}{\Delta t} \right] \{E_{1}^{n+1/2}\} + W_2 \left[ \frac{Q_{2}^{n}}{\Delta t} \right] \{E_{1}^{n}\} + W_3 \left[ \frac{Q_{3}^{n+1}}{\Delta t} \right] \{E_{1}^{n+1}\} + W_4 \left[ \frac{Q_{3}^{n}}{\Delta t} \right] \{E_{1}^{n}\} = W_1 \left\{ SS^{n+1} \right\} + W_2 \left\{ SS^{n} \right\} + W_1 \left\{ B^{n+1} \right\} + W_2 \left\{ B^{n} \right\}
\]  
(4.71)

Let

\[
\{CMATRX\} \{E_{1}^{n+1/2}\} = \{RLD\}
\]  
(4.72)

where

\[
\{CMATRX\} = \frac{[Q_{1}^{n+1}]}{\Delta t} + W_1 \left[ \frac{Q_{2}^{n+1}}{\Delta t} \right] + W_1 \left[ \frac{Q_{3}^{n+1}}{\Delta t} \right]
\]  
(4.73)
\[
\{RLD\} = \left( \frac{[Q^n]}{\Delta t} - W V_2 \left[ Q_2^n \right] - W_2 \left[ Q_3^n \right] \right) \{E_i^n\} \\
+ W_1 \{S S^{n+1}_n\} + W_2 \{S S^n\} + W_1 \{B^{n+1}_i\} + W_2 \{B^n_i\}
\] 

(4.74)

For interior nodes \( i \), \( B_i \) is zero, for boundary nodes \( i = b \), \( B_i \) is calculated according to the specified boundary condition and shown as follows.

\[
B_i = \int_B \mathbf{n} \cdot \left( N_i \mathbf{K} \cdot \nabla E_i \right) dB
\]

(4.75)

**Dirichlet boundary condition**

\[
E_i = E_{id} \left( x_b, y_b, z_b, t \right) \text{ at } B_d
\]

(4.76)

**Variable boundary condition**

< Case 1 > when flow is going in from outside (\( n \cdot V < 0 \))

\[
B_i = \int_B \left[ n \cdot \left( V E_i - V_{sp} E_i^{preci} - \sum_{n \in \Omega} \left( V_{sn} E_i^{sn} \right) \right) \right] dB - \int_B \sum_{n \in \Omega} q_{E_{in}} dB
\]

(4.77)

< Case 2 > Flow is going out from inside (\( n \cdot V > 0 \))

\[
B_i = 0
\]

(4.78)

**Cauchy boundary condition**

\[
B_i = \int_B \left[ n \cdot \left( V E_i - V_{sp} E_i^{preci} - \sum_{n \in \Omega} \left( V_{sn} E_i^{sn} \right) \right) \right] dB - \int_B \sum_{n \in \Omega} q_{E_{in}} dB
\]

(4.79)
**Neumann boundary condition**

\[ B_i = -\int_B N_i q_{Ein} \, dB \quad (4.80) \]

**Coastal surface water-coastal bed interface boundary condition**

\[ B_i = \int_B n \bullet \left[ N_i \left( V E_i - V_{sp} E_{i}^{preci} - \sum_{n \in N_i} (V_{sn} E_{i}^{sn}) \right) \right] dB - \int_B N_i F_{E_i,C->B} \, dB \quad (4.81) \]

### 4.3.1.2 Mixed Predictor-Corrector and Operator-Splitting Method

According to Mixed Predictor-corrector and Operator-splitting method, Equation (4.56) can be separated into two equations as follows.

\[
\frac{E_i^{n+1/2} - E_i^n}{\Delta t} + V \bullet \nabla E_i - \frac{\partial (W_{sp} E_i^{preci})}{\partial z} - \sum_{n=1}^{N_i} \frac{\partial (W_{sn} E_i^{sn})}{\partial z} - \nabla \cdot (K \cdot \nabla E_i) + LHS_n E_i = RHS + RA_i^n 
\]

\[
\frac{E_i^{n+1} - E_i^{n+1/2}}{\Delta t} = RA_i - RA_i^n 
\]

First, solve Equation (4.82) and get \( E_i^{n+1/2} \). Second, solve Equation (4.83) using BIOGEOCHM scheme to obtain the individual species concentration.
Modify Equation (4.82) with grid velocity $V_g$ term, so that at $n+1$-th time step

$$\frac{dE_i}{dt} + (V - V_g) \cdot \nabla E_i - \frac{\partial (W_{\text{preci}} E_i)}{\partial z} - \sum_{n=1}^{N} \frac{\partial (W_{\text{inci}} E_i)}{\partial z}$$

$$- \nabla \cdot (K \cdot \nabla E_i) + LHS \cdot E_i = RHS + RA^n$$

Use Galerkin or Petrov-Galerkin Finite-Element Method for the spatial discretization of transport equation. Integrate Equation (4.84) in the spatial dimensions over the entire region as follows.

$$\int_{R} N_i \frac{dE_i}{dt} dR + \int_{R} W_i \left[ (V - V_g) \cdot \nabla E_i \right] dR$$

$$+ \int_{R} \nabla N_i \cdot \left[ K \cdot \nabla E_i \right] dR + \int_{R} N_i \cdot LHS \cdot E_i dR$$

$$= \int_{R} N_i \left( RHS + RA^n \right) dR + \int_{B} \left[ N_i \left[ K \cdot \left( \nabla E_i \right) \right] \right] dB$$

Approximate solution $E_n^m$ by a linear $E_i \approx \hat{E}_i = \sum_{j=1}^{N} E_{ij} (t) N_j (R)$, we obtain

$$\sum_{j=1}^{N} \left[ \int_{R} N_j dR \left( \frac{dE_j}{dt} (t) \right) \right] + \sum_{j=1}^{N} \left[ \int_{R} W_i \left( V - V_g \right) \cdot \nabla N_j dR \right] E_{ij} (t)$$

$$\sum_{j=1}^{N} \left[ \int_{R} \nabla N_i \cdot \left( K \cdot \nabla N_j \right) dR + \int_{R} N_i \cdot LHS N_j dR \right] E_{ij} (t)$$

$$= \int_{R} N_i \left( RHS + RA^n \right) dR + \int_{B} \left[ N_i \left[ K \cdot \left( \nabla E_i \right) \right] \right] dB$$

Equation (4.86) can be written in matrix form as

$$[Q1] \left[ \frac{dE_i}{dt} \right] + [Q2] \{ E_i \} + [Q3] \{ E_i \} = \{ SS \} + \{ B \}$$

where the matrices $[Q1]$, $[Q2]$, and $[Q3]$, and load vectors $\{ SS \}$ and $\{ B \}$ are given by
\[ Q_1 y = \sum_{e=1}^{M_e} \int_{R_e} N_i^e N_j^e dR \] (4.88)

\[ Q_2 y = \sum_{e=1}^{M_e} \int_{R_e} W_i^e (V - V_g - V_x) \cdot \nabla N_j^e dR \] (4.89)

\[ Q_3 y = \sum_{e=1}^{M_e} \left[ \int_{R_e} \nabla N_i^e \bullet (K \cdot \nabla N_j^e) \right] dR + \sum_{e=1}^{M_e} \left( N_i^e LHSN_j^e \right) dR \] (4.90)

\[ SS_i = \int_{R_e} N_i^e \left( RHS + RA_i^n \right) dR \] (4.91)

\[ B_i = \int_{B} n \bullet \{ N_i \left[ K \bullet (\nabla E_i) \right] \} dB \] (4.92)

where all the integrations are evaluated with the corresponding time weighting values.

At \( n+1 \)-th time step, Equation (4.87) is approximated as

\[
\frac{\left[ Q_1^{n+1} \right] \{(E_i)^{n+1/2}\} - \left[ Q_1^n \right] \{(E_i)^n\}}{\Delta t} + WV_1 \left[ Q_2^{n+1} \right] \{(E_i)^{n+1/2}\} + WV_2 \left[ Q_2^n \right] \{(E_i)^n\} + W_1 \left[ Q_3^{n+1} \right] \{(E_i)^{n+1/2}\} + W_2 \left[ Q_3^n \right] \{(E_i)^n\} = W_1 \{ SS^{n+1} \} + W_2 \{ SS^n \} + W_1 \{ B^{n+1} \} + W_2 \{ B^n \} \] (4.93)

So that

\[ \left[ CMATRX \right] \{(E_i)^{n+1/2}\} = \{ RLD \} \] (4.94)

where

\[ \left[ CMATRX \right] = \frac{\left[ Q_1^{n+1} \right]}{\Delta t} + WV_1 \left[ Q_2^{n+1} \right] + W_1 \left[ Q_3^{n+1} \right] \] (4.95)
\[
\{RLD\} = \left[ \frac{Q_1}{\Delta t} + W_2 \left[ O_2^2 \right] - W_2 \left[ O_3^3 \right] \right] (E_i)^n \] 
\[
+ W_1 \left\{ S_{n+1} \right\} + W_2 \left\{ S_n \right\} + W_1 \left\{ B_{n+1} \right\} + W_2 \left\{ B_n \right\} 
\] (4.96)

The boundary term \{B\} is calculated according to the specified boundary conditions the same as that in section 4.3.1.1.

**Dirichlet boundary condition**

\[
E_i = E_{id} \left( x_i, y_i, z_i, t \right) \text{ at } B_d 
\] (4.97)

**Variable boundary condition**

< Case 1 > when flow is going in from outside (\( n \cdot V < 0 \))

\[
B_i = \int_B n \cdot \left[ N_i \left( V E_i - V_{sp} E_i^{preci} - \sum_{n \in N_i} \left( V_{sn} E_i^{sn} \right) \right) \right] dB - \int_B N_i q_{E_E} dB 
\] (4.98)

< Case 2 > Flow is going out from inside (\( n \cdot V > 0 \))

\[
B_i = 0 
\] (4.99)

**Cauchy boundary condition**

\[
B_i = \int_B n \cdot \left[ N_i \left( V E_i - V_{sp} E_i^{preci} - \sum_{n \in N_i} \left( V_{sn} E_i^{sn} \right) \right) \right] dB - \int_B N_i q_{E_E} dB 
\] (4.100)
Neumann boundary condition

\[ B_i = -\int_B N_i q_{Ein} \, dB \quad (4.101) \]

Coastal surface water-coastal bed interface boundary condition

\[ B_i = \int_B n \cdot \left[ N_i \left( V E_i - V_{sp} E_{i}^{preci} - \sum_{n \in N_i} \left( V_{sn} E_{i}^{sn} \right) \right) \right] \, dB - \int_B N_i F_{E_i,C \rightarrow B} \, dB \quad (4.102) \]

4.3.1.3 Operator-Splitting Approach

According to Operator-Splitting Approach, Equation (4.56) can be separated into two equations as follows.

\[ \frac{E_i^{n+1/2} - E_i^n}{\Delta t} + V \cdot \nabla E_i - \frac{\partial \left( W_{sp} E_{i}^{preci} \right)}{\partial z} - \sum_{n=1}^{N_i} \frac{\partial \left( W_{sn} E_{i}^{sn} \right)}{\partial z} \]

\[ -\nabla \cdot (K \cdot \nabla E_i) + LHS \cdot E_i = RHS \]

\[ \frac{E_i^{n+1} - E_i^{n+1/2}}{\Delta t} = RA_i \quad (4.104) \]

Modify Equation (4.103) with grid velocity \( V_g \) term, so that at \( n+1 \)-th time step

\[ \frac{dE_i}{dt} + (V - V_g) \cdot \nabla E_i - \frac{\partial \left( W_{sp} E_{i}^{preci} \right)}{\partial z} - \sum_{n=1}^{N_i} \frac{\partial \left( W_{sn} E_{i}^{sn} \right)}{\partial z} \]

\[ -\nabla \cdot (K \cdot \nabla E_i) + LHS \cdot E_i = RHS \]

\[ \frac{E_i^{n+1} - E_i^{n+1/2}}{\Delta t} = RA_i \quad (4.105) \]
Equation (4.105) can be solved through the same procedure as that in section 4.3.1.2, except for the load vectors \{SS\}, which is calculated by the following equation.

\[
SS_i = \int_{R_i} N_i^c RHSdR \tag{4.106}
\]

4.3.2 Lagrangian–Eulerian Approach

4.3.2.1 Fully-Implicit Scheme

Equation (4.59) in Lagrangian-Eulerian form is written as follows.

In Lagrangian step,

\[
\frac{DE_i}{D\tau} = \frac{dE_i}{dt} - V_g \cdot \nabla E_i - \frac{\partial (W_{sp}E_i^{pre})}{\partial z} - \sum_{n=1}^{N} \frac{\partial (W_{sn}E_i^{n})}{\partial z} + V \cdot \nabla E_i = 0 \tag{4.107}
\]

where particle tracking velocity is the flow velocity \(V\).

In Eulerian step,

\[
\frac{DE_i}{D\tau} - \nabla \cdot (K \cdot \nabla E_i) + LHS \cdot E_i = RHS + RA_i \tag{4.108}
\]
Equation (4.108) written in a slightly different form is shown as

$$\frac{DE_i}{D\tau} - D + LHS \cdot E_i = RL \quad (4.109)$$

where

$$D = \nabla \cdot (K \cdot \nabla E_i) \quad (4.110)$$

$$RL = RHS + RA_i \quad (4.111)$$

According to Equation (4.37),

$$[QA]\{D\} = -[QD]\{E_i\} + \{B\} \quad (4.112)$$

where

$$QA_{ij} = \sum_{c=1}^{M_e} \int_{R_c} N_i^e N_j^e dR \quad (4.113)$$

$$QD_{ij} = \sum_{c=1}^{M_e} \int_{R_c} \nabla N_i^e \cdot (K \cdot \nabla N_j^e) dR \quad (4.114)$$

$$B_i = \int_B n \cdot \left[ N_i \left( K \cdot \nabla E_i \right) \right] dB \quad (4.115)$$

Lump matrix [QA] into diagonal matrix and update

$$QD_{ij} = QD_{ij} / QA_{ii} \quad (4.116)$$

$$B_i = B_i / QA_{ii} \quad (4.117)$$

Then

$$\{D\} = -[QD]\{E_i\} + \{B\} \quad (4.118)$$
Equation (4.109) written in matrix form is then expressed as

\[
\begin{align*}
\left[ U \right] + W_1 \left[ QD^{n+1} \right] &+ W_1 \left[ LHS^{n+1} \right] \{ E_i^{n+1/2} \} = \left[ U \right] \{ E_i^* \} + W_2 \{ D^* \} \\
- W_2 \left[ LHS^* \right] \{ E_i^* \} &+ W_1 \{ RL^{n+1} \} + W_2 \{ RL^* \} + W_1 \{ B^{n+1} \}
\end{align*}
\]

where \([U]\) is the unit matrix, \(\Delta \tau\) is the tracking time, \(W_1\) and \(W_2\) are time weighting factors, matrices and vectors with \(^{n+1}\) and \(^{n+1/2}\) are evaluated over the region at the new time step \(n+1\). Matrices and vectors with superscript * corresponds to the \(n\)-th time step values interpolated at the location where a node is tracked through particle tracking in Lagrangian step.

For interior nodes \(i\), \(B_i\) is zero, for boundary nodes \(i = b\), \(B_i\) is calculated according to the specified boundary condition and shown as follows.

**Dirichlet boundary condition**

\[
B_i = \left( \left[ QB \right] \{ E_i \} \right) / QA_i \tag{4.120}
\]

where

\[
QB_{ij} = \sum_{e=1}^{M_e} \left\{ n \bullet \left[ N_i^e \left( K \bullet \nabla N_j^e \right) \right] dB \right\}
\]

**Variable boundary condition**

< Case 1 > when flow is going in from outside \((n \bullet V < 0)\)

\[
B_i = \int_{\beta} n \bullet \left[ N_i \left( VE_i - V_{sp} E_i^{\text{previ}} - \sum_{n=1}^{N_i} (V_{sn} E_i^{sn}) \right) \right] dB / QA_i - \int_{\beta} N_i q_{Ein} dB / QA_i \tag{4.121}
\]
<Case 2> Flow is going out from inside \( (\mathbf{n} \cdot \mathbf{V}) > 0 \)

\[
B_i = 0 \quad \text{(4.122)}
\]

**Cauchy boundary condition**

\[
B_i = \int_B \mathbf{n} \cdot \left[ N_i \left( V_{E_i} - V_{sp} E_i^{preci} - \sum_{n=1}^{N} \left( V_{sn E_i^{mn}} \right) \right) \right] dB / QA_{ii} - \int_B N_i q_{Ei} dB / QA_{ii} \quad \text{(4.123)}
\]

**Neumann boundary condition**

\[
B_i = -\int_B N_i q_{Ei} dB / QA_{ii} \quad \text{(4.124)}
\]

**Coastal surface water-coastal bed interface boundary condition**

\[
B_i = \left\{ \int_B \mathbf{n} \cdot \left[ N_i \left( V_{E_i} - V_{sp} E_i^{preci} - \sum_{n=1}^{N} \left( V_{sn E_i^{mn}} \right) \right) \right] dB - \int_B N_i F_{Ei,C \rightarrow B} dB \right\} / QA_{ii} \quad \text{(4.125)}
\]

### 4.3.2.2 Mixed Predictor-Corrector and Operator-Splitting Method

Equation (4.82) in Lagrangian-Eulerian form is written as follows.

In Lagrangian step,

\[
\frac{DE_i}{Dt} = \frac{dE_i}{dt} + V \cdot \nabla E_i - \frac{\partial \left( W_{sp} E_i^{preci} \right)}{\partial z} - \sum_{n=1}^{N} \frac{\partial \left( W_{sn E_i^{mn}} \right)}{\partial z} = 0 \quad \text{(4.126)}
\]
where particle tracking velocity is the flow velocity \( V \).

In Eulerian step,

\[
\frac{D E_i}{D \tau} - \nabla \cdot (K \cdot \nabla E_i) + \text{LHS}^* E_i = \text{RHS} + \text{RA}_i \tag{4.127}
\]

Equation (4.127) written in a slightly different form is shown as

\[
\frac{D E_i}{D \tau} - D + \text{LHS}^* E_i = \text{RHS} + \text{RA}_i \tag{4.128}
\]

where

\[
D = \nabla \cdot (K \cdot \nabla E_i) \tag{4.129}
\]

which can be solved through the same procedure as that in section 4.2.2 by changing \( S_s \) to \( E_i \).

Equation (4.128) written in matrix form is then expressed as

\[
\begin{bmatrix}
\frac{[U]}{\Delta \tau} + \text{W}_1 \left[ QD^{n+1} \right] + \text{W}_1 \left[ \text{LHS}^{n+1} \right] \left( E_i \right)^{n+1/2}
\end{bmatrix} = \\
\begin{bmatrix}
\frac{[U]}{\Delta \tau} \left( E_i \right)^* - \text{W}_2 \left[ \text{LHS}^* \right] \left( E_i \right)^* + \text{W}_2 \left[ D^* \right] + \text{W}_1 \left[ \text{RHS}^{n+1} \right] \\
\text{W}_2 \left[ \text{RHS}^* \right] + \text{W}_1 \left[ \text{RA}_i^{n+1} \right] + \text{W}_2 \left[ \text{RA}_i^* \right] + \text{W}_1 \left[ B^{n+1} \right]
\end{bmatrix} \tag{4.130}
\]
### 4.3.2.3 Operator-Splitting Approach

Equation (4.103) can be solved through the same procedure used in section 4.3.1.3, except that reaction term is not included in the right hand side.

### 4.3.3 Finite Element Method in Conservative Form Approach

#### 4.3.3.1 Fully-Implicit Scheme

According to governing Equation (2.2), the right-hand side term RHS and left hand side term LHS can be initialized and updated as follows.

\[
\text{If } S_s \leq 0, ME_n^{as} = S_s \times E_i, LHS = -S_s, RHS = 0
\]
\[
\text{Else } S_s > 0, ME_n^{as} = ME_n^{as}, LHS = 0, RHS = ME_n^{as}
\]

(4.131)

Then Equation (3.10) is modified as

\[
\frac{\partial E_i}{\partial t} + \nabla \cdot (VE_i) - \frac{\partial (W_{sp}E_i^{prev})}{\partial z} - \sum_{n=1}^{N} \frac{\partial (W_{sn}E_i^{sn})}{\partial z}
\]

\[
-\nabla \cdot (K \cdot \nabla E_i) + LHS \times E_i = RHS + RA_i
\]

(4.132)

According to Fully-Implicit Scheme, Equation (4.132) can be separated into two equations as follows
\[
\frac{E_{n}^{n+1/2} - E_{n}^{n}}{\Delta t} + \nabla \cdot (VE_{i}) - \frac{\partial (W_{sp}^{n} E_{i}^{prec})}{\partial z} - \sum_{n=1}^{N} \frac{\partial (W_{sn} E_{i}^{sn})}{\partial z} = \nabla \cdot (K \nabla E_{i}) + LHS \ast E_{i} = RHS + RA_{i}
\] (4.133)

\[
\frac{E_{n+1}^{n+1/2} - E_{n+1}^{n}}{\Delta t} = 0
\] (4.134)

First, \(E_{n}^{n+1/2}\) can be solved through Equation (4.133). Second, we solve Equation (4.134) together with algebraic equations for equilibrium reactions using BIOGEOCHEM (Fang et al., 2003) to obtain all individual species concentrations. Iteration between these two steps is needed because the new reaction terms and the equation coefficients in Equation (4.133) need to be updated by the calculation results of Equation (4.134).

Modify Equation (4.132) with grid velocity \(V_{g}\) term.

\[
\frac{dE_{i}}{dt} + \nabla \cdot (VE_{i}) - V_{g} \cdot \nabla E_{i} - \frac{\partial (W_{sp}^{n} E_{i}^{prec})}{\partial z} - \sum_{n=1}^{N} \frac{\partial (W_{sn} E_{i}^{sn})}{\partial z} = \nabla \cdot (K \nabla E_{i}) + LHS \ast E_{i} = RHS + RA_{i}
\] (4.135)

Integrate Equation (4.135) in the spatial dimensions over the entire region as follows.

\[
\int \int \int_{R} N_{i} \frac{dE_{i}}{dt} dR - \int \int \int_{R} W_{i} (V_{g} \cdot \nabla E_{i}) dR - \int \int \int_{R} W_{i} (V_{s} \cdot \nabla E_{i}) dR - \int \int \int_{R} \nabla W_{i} \cdot (VE_{i}) dR
\]
\[
+ \int \int \int_{R} \nabla N_{i} \cdot (K \nabla E_{i}) dR + \int \int \int_{R} N_{i} LHS \ast E_{i} dR = \int \int \int_{R} N_{i} (RHS + RA_{i}) dR
\] (4.136)

\[
- \int \int \int_{B} n \cdot (W_{i} V_{E_{i}}) dB + \int \int \int_{B} n \cdot \left\{ N_{i} \left[ K \cdot (\nabla E_{i}) \right] \right\} dB
\]
Approximate solution $E_i$ by $E_i \approx \hat{E}_i = \sum_{j=1}^{N} E_{ij}(t)N_j(R)$, we obtain

\[
\sum_{j=1}^{N} \left[ N_i N_j dR \left( \frac{dE_{ij}(t)}{dt} \right) \right] + \sum_{j=1}^{N} \left[ \nabla N_i \bullet \left[ K \bullet \nabla N_j \right] \right] dR + \int_{R} N_i LHSN_j dR \left[ E_{ij}(t) \right] \\
- \sum_{j=1}^{N} \left[ \int_{R} W_i \left( V_i \bullet \nabla N_j \right) dR + \int_{R} W_i \left( V_i \bullet \nabla N_j \right) dR + \int_{R} \nabla W_i \bullet \left( V N_j \right) dR \right] E_{ij}(t) \right] \\
= \int_{R} N_i (RHS + RA) dR - \int_{B} n \bullet (WVE_i) dB + \int_{B} n \bullet (N_i K \bullet \nabla E_i) dB 
\]

(4.137)

Equation (4.137) can be written in matrix form as

\[
[Q1] \left\{ \frac{dE_i}{dt} \right\} + [Q2] \{ E_i \} + [Q3] \{ E_i \} = \{ SS \} + \{ B \} 
\]

(4.138)

where the matrices $[Q1]$, $[Q2]$, $[Q3]$ and load vectors $\{ SS \}$, and $\{ B \}$ are given by

\[
Q_{1ij} = \sum_{c=1}^{M} \int_{R_c} N_i^c N_j^c dR 
\]

(4.139)

\[
Q_{2ij} = -\sum_{c=1}^{M} \int_{R_c} W_i^c V_i \bullet \nabla N_j^c dR - \sum_{c=1}^{M} \int_{R_c} \nabla W_i^c \bullet \left( V N_j^c \right) dR - \sum_{c=1}^{M} \int_{R_c} W_i^c \bullet \nabla N_j^c dR 
\]

(4.140)

\[
Q_{3ij} = \sum_{c=1}^{M} \int_{R_c} \nabla N_i^c \bullet \left[ K \bullet \nabla N_j^c \right] dR + \sum_{c=1}^{M} \int_{R_c} N_i^c LHSN_j^c dR 
\]

(4.141)

\[
SS_i = \int_{R_i} N_i^c (RHS + RA) dR 
\]

(4.142)

\[
B_i = -\int_{B} n \bullet (WVE_i) dB + \int_{B} n \bullet (N_i K \bullet \nabla E_i) dB 
\]

(4.143)
At \(n+1\)-th time step, Equation (4.138) is approximated as

\[
\frac{Q^{n+1}}{\Delta t}\{E_i^{n+1/2}\} - \frac{Q^n}{\Delta t}\{E_i^n\} + WV_1\left[Q^{2n+1}\right]\{E_i^{n+1/2}\} + WV_2\left[Q^{2n}\right]\{E_i^n\} + W_1\left[Q^{3n+1}\right]\{E_i^{n+1/2}\} + W_2\left[Q^{3n}\right]\{E_i^n\} = 4.144
\]

Let

\[
\begin{bmatrix} CMATRIX \end{bmatrix}\{E_i^{n+1/2}\} = \{RLD\}
\]

where

\[
\begin{bmatrix} CMATRIX \end{bmatrix} = \frac{Q^{n+1}}{\Delta t} + WV_1\left[Q^{2n+1}\right] + W_1\left[Q^{3n+1}\right]
\]

\[
\{RLD\} = \frac{Q^n}{\Delta t} - WV_2\left[Q^{2n}\right] - W_2\left[Q^{3n}\right] + W_1\left[SS^{n+1}\right] + W_2\left[SS^n\right] + W_1\left[B^{n+1}\right] + W_2\left[B^n\right]
\]

For interior nodes \(i\), \(B_i\) is zero, for boundary nodes \(i = b\), \(B_i\) is calculated according to the specified boundary condition and shown as follows.

\[
B_i = -\int_B n \cdot (W_i V E_i) dB + \int_B n \cdot (N_i K \cdot \nabla E_i) dB
\]

**Dirichlet boundary condition**

\[
E_i = E_{id}
\]
Variable boundary condition

< Case 1 > when flow is going in from outside \((n \cdot V < 0)\)

\[
B_i = -\int_B n \cdot \left[ N_i \left( V_{sp,E_i}^{preci} + \sum_{n \in N_c} \left( V_{sn,E_i}^{sn} \right) \right) \right] dB - \int_B N_i q_{Ein} dB \tag{4.149}
\]

< Case 2 > Flow is going out from inside \((n \cdot V > 0)\)

\[
B_i = -\int_B n \cdot (NVE_i) dB \tag{4.150}
\]

Cauchy boundary condition

\[
B_i = -\int_B n \cdot \left[ N_i \left( V_{sp,E_i}^{preci} + \sum_{n \in N_c} \left( V_{sn,E_i}^{sn} \right) \right) \right] dB - \int_B N_i q_{Eic} dB \tag{4.151}
\]

Neumann boundary condition

\[
B_i = -\int_R n \cdot \left( WVE_i \right) dB - \int_B N_i q_{Ein} dB \tag{4.152}
\]

Coastal surface water-coastal bed interface boundary condition

\[
B_i = -\int_B n \cdot \left[ N_i \left( V_{sp,E_i}^{preci} + \sum_{n \in N_c} \left( V_{sn,E_i}^{sn} \right) \right) \right] dB - \int_B N_i F_{E;i:C \rightarrow B} dB \tag{4.153}
\]
4.3.3.2 Mixed Predictor-Corrector and Operator-Splitting Method

According to Mixed Predictor-corrector and Operator-splitting method, Equation (4.132) can be separated into two equations as follows.

\[
\frac{E_i^{n+1/2} - E_i^n}{\Delta t} + \nabla \cdot (VE_i) - \frac{\partial (W_{sp} E_i^{preci})}{\partial z} - \sum_{n=1}^{N_z} \frac{\partial (W_{sn} E_i^m)}{\partial z} = \nabla \cdot (K \cdot \nabla E_i) + LHS \ast E_i - RHS + RA_i^n \tag{4.154}
\]

First, solve equation (4.154) and get \(E_i^{n+1/2}\). Second, solve equation (4.155) using BIOGEOCHM scheme to obtain the individual species concentration.

\[
\frac{E_i^{n+1} - E_i^{n+1/2}}{\Delta t} = RA_i - RA_i^n \tag{4.155}
\]

Modify Equation (4.154) with grid velocity \(V_g\) term, so that at \(n+1\)-th time step

\[
\frac{dE_i}{dt} + \nabla \cdot (VE_i) - V_g \cdot \nabla E_i - \frac{\partial (W_{sp} E_i^{preci})}{\partial z} - \sum_{n=1}^{N_z} \frac{\partial (W_{sn} E_i^m)}{\partial z} = \nabla \cdot (K \cdot \nabla E_i) + LHS \ast E_i - RHS + RA_i^n \tag{4.156}
\]

Use Galerkin or Petrov-Galerkin Finite-Element Method for the spatial descretization of transport equation. Integrate Equation (4.156) in the spatial dimensions over the entire region as follows.

\[
\int_{R} N_i \frac{dE_i}{dt} dR - \int_{R} \Delta W_i \cdot (VE_i) dR - \int_{R} W_i V_g \cdot \nabla E_i dR - \int_{R} W_i V_s \cdot \nabla E_i dR + \int_{R} \nabla N_i \cdot \left[ K \cdot (\nabla E_i) \right] dR + \int_{R} N_i LHS \ast E_i dR
\]

\[
= \int_{R} \left( RHS + RA_i^n \right) dR + \int_{B} n \cdot \left\{ N_i \left[ K \cdot (\nabla E_i) \right] \right\} dB - \int_{B} n \cdot \left( W_i VE_i \right) dB \tag{4.157}
\]
Approximate solution $E_i$ by a linear $E_i \approx \hat{E}_i = \sum_{j=1}^{N} E_{ij}(t) N_j(R)$, we obtain

$$
\sum_{j=1}^{N} \left[ \int_{R} N_j N_j dR \frac{dE_{ij}(t)}{dt} \right] - \sum_{j=1}^{N} \left[ \int_{R} \Delta W_i \bullet (V N_j) dR + \int_{R} W_i (V_g + V_s) \bullet \nabla N_j dR \right] E_{ij}(t) \\
\sum_{j=1}^{N} \left[ \int_{R} \nabla N_j \bullet (K \bullet \nabla N_j) dR + \int_{R} N_j LHSN_j dR \right] E_{ij}(t) \\
= \int_{R} N_j \left( RHS + RA^n \right) dR + \int_{B} \left\{ \int_{R} \left[ N_j \left( K \bullet (\nabla E_i) \right) \right] dR - \int_{B} \left( WVE_i \right) dB \right\}
$$

(4.158)

Equation (4.158) can be written in matrix form as

$$
[Q1]\left( \frac{dE_i}{dt} \right) + [Q2] \{E_i\} + [Q3] \{E_i\} = \{SS\} + \{B\}
$$

(4.159)

where the matrices $[Q1]$, $[Q2]$, and $[Q3]$, and load vectors $\{SS\}$ and $\{B\}$ are given by

$$
Q1_{ij} = \sum_{e=1}^{M} \int_{R_e} N_{ij}^{e} N_{ij}^{e} dR
$$

(4.160)

$$
Q2_{ij} = -\sum_{e=1}^{M} \int_{R_e} \Delta W_{ij}^{e} \bullet (V N_{ij}^{e}) dR - \sum_{e=1}^{M} \int_{R_e} W_{ij}^{e} (V_g + V_s) \bullet \nabla N_{ij}^{e} dR
$$

(4.161)

$$
Q3_{ij} = \sum_{e=1}^{M} \int_{R_e} \nabla N_{ij}^{e} \bullet (K \bullet \nabla N_{ij}^{e}) dR + \sum_{e=1}^{M} \int_{R_e} \left( N_{ij}^{e} LHSN_{ij}^{e} \right) dR
$$

(4.162)

$$
SS_i = \int_{R_i} \left( RHS + RA^n \right) dR
$$

(4.163)

$$
B_i = \int_{B} \left\{ \int_{R_i} \left[ N_i \left( K \bullet (\nabla E_i) \right) \right] dR - \int_{B} \left( WVE_i \right) dB \right\}
$$

(4.164)

where all the integrations are evaluated with the corresponding time weighting values.
At $n+1$-th time step, Equation (4.159) is approximated as

$$
\frac{Q_{1}^{n+1}}{\Delta t}\{ (E_i)^{n+1/2} \} - \frac{Q_{1}^{n}}{\Delta t}\{ (E_i)^{n} \} + W V_1 \left[ Q_{2}^{n+1} \right] \{ (E_i)^{n+1/2} \} + W V_2 \left[ Q_{2}^{n} \right] \{ (E_i)^{n} \} + W_1 \left[ Q_{3}^{n+1} \right] \{ (E_i)^{n+1/2} \} + W_2 \left[ Q_{3}^{n} \right] \{ (E_i)^{n} \} = W_1 \left\{ S S_{n+1} \right\} + W_2 \left\{ S S_n \right\} + W_1 \left\{ B_{n+1} \right\} + W_2 \left\{ B_n \right\} 
$$

(4.165)

So that

$$
\left[ C M A T R X \right] \{ (E_i)^{n+1/2} \} = \{ R L D \}
$$

(4.166)

where

$$
\left[ C M A T R X \right] = \frac{Q_{1}^{n+1}}{\Delta t} + W V_1 \left[ Q_{2}^{n+1} \right] + W_1 \left[ Q_{3}^{n+1} \right] 
$$

(4.167)

$$
\{ R L D \} = \left( \frac{Q_{1}^{n}}{\Delta t} - W V_2 \left[ Q_{2}^{n} \right] - W_2 \left[ Q_{3}^{n} \right] \right) \{ (E_i)^{n} \} + W_1 \{ S S_{n+1} \} + W_2 \{ S S_{n} \} + W_1 \{ B_{n+1} \} + W_2 \{ B_{n} \}
$$

(4.168)

The boundary term $\{ B \}$ is calculated according to the specified boundary conditions the same as section 4.3.3.1.

**4.3.3.3 Operator-Splitting Approach**

According to Operator-Splitting Approach, Equation (4.132) can be separated into two equations as follows
\[
\frac{E_i^{n+1/2} - E_i^n}{\Delta t} + \nabla \bullet (V E_i) - \frac{\partial (W_{sp} E_i^{preci})}{\partial z} - \sum_{n=1}^{N_s} \frac{\partial (W_{sn} E_i^m)}{\partial z} = \sum \tag{4.169}
\]
\[\text{\(-\nabla \cdot (K \cdot \nabla E_i) + LHS \cdot E_i = RHS\)}\]

\[
\frac{E_i^{n+1} - E_i^{n+1/2}}{\Delta t} = RA_i \tag{4.170}
\]

Modify Equation (4.169) with grid velocity \(V\) term, so that at \(n+1\)-th time step

\[
\frac{dE_i}{dt} + \nabla \bullet (V E_i) - V_g \bullet \nabla E_i - \frac{\partial (W_{sp} E_i^{preci})}{\partial z} - \sum_{n=1}^{N_s} \frac{\partial (W_{sn} E_i^m)}{\partial z} = \sum \tag{4.171}
\]
\[\text{\(-\nabla \cdot (K \cdot \nabla E_i) + LHS \cdot E_i = RHS\)}\]

Equation (4.171) can be solved through the same procedure as that in section 4.3.3.2, except for the load vectors \(\{SS\}\), which is calculated by the following equation.

\[
SS_i = \int_{\Omega_i} N_i^c RHSdR \tag{4.172}
\]
CHAPTER 5  APPLICATION

This chapter demonstrates flexibility and generality of the model by recasting the eutrophication model QUAL2E in the mode of reaction network. Then we apply this reaction network to the Loxahatchee estuary to study its response to a hypothetical biogeochemical loading (e.g., TMDL) from its surrounding drainage and demonstrate the general paradigm.

Although the governing formulations in Chapter 2 and 3 have been derived, the implementation of these equations needs a continuing work by others. The simulation results in this chapter are obtained using old formulations from an old approach. The new approach described in above chapters considers that a 3-D estuary system contains column and bed systems. There are only column species in the column system and there are only bed species in the bed system separately. These two systems interact via interfacial conditions. There are two reaction networks corresponding to these two systems respectively. Comparing with this approach, the old approach only considers one integral system. In this integral system, all the bed and column species exist at each node. There are one reaction network which contains all the reactions occurred in the column and bed. And all the reactions are considered at each node. These reactions include the biogeochemical reactions and some physical processes such as settling. The difference between the column nodes and bed nodes is the concentration of the species. The concentration of each bed species at column nodes is 0. The concentration of each column species at bed nodes is also 0. The following are the governing equations for this old approach.
Continuity equation for bed sediment

\[ \frac{\partial M_n}{\partial t} = D_n - R_n, \quad n \in [1, N_s] \quad (5.1) \]

Continuity equation for suspended sediment

\[ \frac{\partial S_n}{\partial t} + \nabla \cdot (V S_n) - \nabla \cdot (K \cdot \nabla S_n) = M_n^{\text{ms}}, \quad n \in [1, N_s] \quad (5.2) \]

Continuity equation for bed immobile species

\[ \frac{\partial C_{bi}}{\partial t} = r_{bi} \bigg|_N \quad (5.3) \]

Continuity equation for column mobile species

\[ \frac{\partial C_i}{\partial t} + \nabla \cdot (V C_i) - \nabla \cdot (K \cdot \nabla C_i) = M_i^{\text{ms}} + r_i \bigg|_N \quad (5.4) \]

Equation (5.1) is the governing equation for bed sediment corresponding to Equation (2.3), which ignores the impact of bed thickness change on bed sediment concentration. Equation (5.2) is the governing equation for suspended sediment corresponding to Equation (2.4), which does not consider the settling process of the suspended sediment. Equation (5.3) and (5.4) are the governing equations for bed immobile species and column mobile species corresponding to Equation (2.17) and (2.25). Both of these two equations ignore some physical processes, e.g. settling, and deposition/erosion. Instead, these physical processes are considered as part of the reaction network. Comparing with the old governing formulation for bed species (Equation
the new approach considers above physical processes in the new governing formulation for bed species (Equation (2.17)). In the mean time, above physical processes are considered as boundary conditions for the new governing formulation for column species (Equation (2.25)). Equation (5.3) also ignores the impact of bed thickness change on the concentration of bed immobile chemical species.

From Chapter 3 we can see that there are two different forms of equations through the decomposition of the two reaction systems for the new approach. On the contrary, there is only one form of equations via the decomposition for the old approach, which is shown as below.

\[
\frac{\partial E_i}{\partial t} + \nabla \cdot \left( V E_i^m \right) - \nabla \cdot \left( K \nabla E_i^m \right) = ME_i^{ar} + RA_i, i \in \left[ 1, M - N_E \right] \tag{5.5}
\]

where \( E_i^m \) is the concentration of mobile part of the n-th kinetic-variable \([M/L^3]\). In this old approach, \( E_i \) is a linear combination of column and bed species concentrations. It includes mobile part which is a linear combination of column species concentrations and immobile part which is a linear combination of bed species concentrations. In the new approach, \( E_i \) in the column water is simple a linear combination of the species concentrations of the column water; \( E_i \) in the bed is simple a linear combination of the species concentrations in the bed. From above discussion we can see that the new approach is more efficient and accurate.
5.1 Reaction Paradigm of QUAL2E

The Stream Water Quality Model QUAL2E (Brown and Barnwell, 1987) is a typical eutrophication model for stream systems. It is the most recent version of the model QUAL-II (Roesner et al., 1981), which was developed from the model QUAL-I in the 1960s. QUAL2E was first released in 1985 (Brown and Barnell, 1985) and has been successfully applied in many water quality studies since then (Lung, 1986; Wagner et al., 1996; Yang et al., 2000; Ning et al., 2001; Park and Lee, 2002; McAvoy et al., 2003; Ng and Perera, 2003; and Park et al., 2003).

In the original reports, there are 9 water qualities (reagents) simulated in QUAL2E (Table 5.1). The eutrophication model in QUAL2E can be recast in the mode of reaction network (Table 5.2). There are a total of 9 reagents involved in 16 kinetic reactions in QAUL2E (Table 5.2). These 16 reactions can be classified into four groups: Algae kinetics (Reaction 1~4), Nitrogen cycle (Reaction 5~9), Phosphorus cycle (Reaction 10~12), and Dissolved Oxygen Balance (Reaction 13~16).

In the context of reaction network, there should be 19 constituents involved in QUAL2E. Substitution of this reaction network into Equation (3.1) results in 19 ordinary differential equations for 19 species in a well-mixed system. In QUAL2E, all rate equations depend on only the first 9 constituents (DO, BOD, Chla, NH₄, ON, NO₂, NO₃, OP, and OPO₄), thus, the other 10 constituents (DOₗ(b), BODₗ(b), Chlaₗ(b), NH₄ₗ(b), ONₗ(b), OPₗ(b), OPO₄ₗ(b), CO₂, H₂O, and O₂ₗ(g)) can be decoupled from the first 9 in any simulation. Thus, only the first 9 species were considered in
QUAL2E. The exclusion of the last 10 species has an important implication when QUAL2E is applied to a new system other than the one QUAL2E was developed for.

<table>
<thead>
<tr>
<th>No</th>
<th>Species</th>
<th>Notation</th>
<th>Working Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dissolved Oxygen</td>
<td>O</td>
<td>( \frac{dO}{dt} = K_0 \theta^{T-20} (O^- - O) + (\alpha_1 \theta_1^{T-20} - \alpha_2 \theta_2^{T-20}) ) Chla_\theta^{T-20} - K_0 \theta^{T-20} L - K_0 \theta^{T-20} d - \alpha_3 \beta \text{CORDO0}^{T-20} N_i - \alpha_4 \beta \text{CORDO0}^{T-20} N_i</td>
</tr>
<tr>
<td>2</td>
<td>Biochemical oxygen demand</td>
<td>L</td>
<td>( \frac{dL}{dt} = -K_0 \theta^{T-20} L - K_0 \theta^{T-20} L )</td>
</tr>
<tr>
<td>3</td>
<td>Chlorophyll a</td>
<td>Chla</td>
<td>( \frac{dChla}{dt} = \mu \theta^{T-20} Chla_\theta^{T-20} - \rho \theta^{T-20} Chla_\theta^{T-20} - \frac{\sigma_1}{d} \theta^{T-20} Chla_\theta^{T-20} )</td>
</tr>
<tr>
<td>4</td>
<td>Organic nitrogen</td>
<td>N_4</td>
<td>( \frac{dN_4}{dt} = \rho \theta^{T-20} Chla_\theta^{T-20} - \beta_4 \theta^{T-20} N_4 - \sigma_4 \theta^{T-20} N_4 )</td>
</tr>
<tr>
<td>5</td>
<td>Ammonia nitrogen</td>
<td>N_1</td>
<td>( \frac{dN_1}{dt} = \beta_1 \theta^{T-20} N_4 - \beta_2 \text{CORDO0}^{T-20} N_i + \sigma_2 \theta^{T-20} /d - \alpha_3 \mu \theta^{T-20} Chla_\theta^{T-20} )</td>
</tr>
<tr>
<td>6</td>
<td>Nitrite nitrogen</td>
<td>N_2</td>
<td>( \frac{dN_2}{dt} = \beta_1 \text{CORDO0}^{T-20} N_1 - \beta_2 \text{CORDO0}^{T-20} N_2 )</td>
</tr>
<tr>
<td>7</td>
<td>Nitrate nitrogen</td>
<td>N_3</td>
<td>( \frac{dN_3}{dt} = \beta_1 \text{CORDO0}^{T-20} N_2 - (1 - F) \alpha_1 \mu \theta^{T-20} Chla_\theta^{T-20} )</td>
</tr>
<tr>
<td>8</td>
<td>Organic phosphorus</td>
<td>P_1</td>
<td>( \frac{dP_1}{dt} = \alpha_1 \theta_1^{T-20} Chla_\theta^{T-20} - \beta_1 \theta_1^{T-20} P_1 - \sigma_1 \theta_1^{T-20} P_1 )</td>
</tr>
<tr>
<td>9</td>
<td>Dissolved phosphorous</td>
<td>P_4</td>
<td>( \frac{dP_4}{dt} = \beta_1 \theta_1^{T-20} P_1 + \sigma_2 \theta_1^{T-20} /d - \alpha_2 \mu \theta_1^{T-20} Chla_\theta^{T-20} )</td>
</tr>
</tbody>
</table>

Had evidence indicated that the rate formulation of the 16 kinetic reactions also depends on the other 10 constituents in a system, then all 19 constituents should have been modeled simultaneously.
<table>
<thead>
<tr>
<th>No.</th>
<th>Mechanism</th>
<th>Reaction</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Algae growth</td>
<td>$\alpha_i N_i + \alpha_i P_i + H_2O + CO_2(g) \rightarrow$</td>
<td>$R = \frac{\mu_i}{\alpha_i} \theta^{T-20} Chla_i$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_i Chla_i + \alpha_i O + (\alpha_i - \alpha_i) O(g)$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Diatom growth related nitrate reduction</td>
<td>$N_i + 1.5H_2O \rightarrow N_i + (\alpha_i + \alpha_i) O(g)$</td>
<td>$R = (1 - F) \alpha_i \frac{\mu_i}{\alpha_i} \theta^{T-20} Chla_i$</td>
</tr>
<tr>
<td>3</td>
<td>Algae respiration</td>
<td>$\alpha_i Chla_i + \alpha_i O \rightarrow$</td>
<td>$R = \frac{\rho}{\alpha_i} \theta^{T-20} Chla_i$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha_i N_i + \alpha_i P_i + H_2O + CO_2(g)$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Algae settling</td>
<td>$Chla_i \rightarrow Chla_{i(b)}$</td>
<td>$R = \frac{\sigma_i}{\theta} \theta^{T-20} Chla_i$</td>
</tr>
<tr>
<td>5</td>
<td>Mineralization of organic nitrogen</td>
<td>$N_i \rightarrow N_i$</td>
<td>$R = \beta_i \theta^{T-20} N_i$</td>
</tr>
<tr>
<td>6</td>
<td>Organic nitrogen settling</td>
<td>$N_i \rightarrow N_{4(b)}$</td>
<td>$R = \sigma_i \theta^{T-20} N_i$</td>
</tr>
<tr>
<td>7</td>
<td>Biological oxidation of ammonia nitrogen</td>
<td>$N_i + \alpha_i O \rightarrow N_i + 1.5H_2O$</td>
<td>$R = \beta_i CORDO \theta^{T-20} N_i$</td>
</tr>
<tr>
<td>8</td>
<td>Benthos source to ammonia nitrogen</td>
<td>$N_{4(b)} \rightarrow N_i$</td>
<td>$R = \sigma_i \theta^{T-20} / \theta$</td>
</tr>
<tr>
<td>9</td>
<td>Oxidation of nitrate nitrogen</td>
<td>$N_i + \alpha_i O \rightarrow N_i$</td>
<td>$R = \beta_i CORDO \theta^{T-20} N_i$</td>
</tr>
<tr>
<td>10</td>
<td>Organic phosphorus decay</td>
<td>$P_i \rightarrow P_2$</td>
<td>$R = \beta_i \theta^{T-20} P_i$</td>
</tr>
<tr>
<td>11</td>
<td>Organic phosphorus settling</td>
<td>$P_i \rightarrow P_{2(b)}$</td>
<td>$R = \sigma_i \theta^{T-20} P_i$</td>
</tr>
<tr>
<td>12</td>
<td>Benthos source to dissolved phosphorus</td>
<td>$P_{2(b)} \rightarrow P_2$</td>
<td>$R = \sigma_i \theta^{T-20} / \theta$</td>
</tr>
<tr>
<td>13</td>
<td>Deoxygenating of BOD</td>
<td>$O + L \rightarrow CO_{2(g)} + H_2O$</td>
<td>$R = K_0 \theta^{T-20} L$</td>
</tr>
<tr>
<td>14</td>
<td>BOD settling</td>
<td>$L \rightarrow L_{(b)}$</td>
<td>$R = K_0 \theta^{T-20} L$</td>
</tr>
<tr>
<td>15</td>
<td>Re-aeration</td>
<td>$O_{(g)} \rightarrow O$</td>
<td>$R = K_0 \theta^{T-20}(O^+ - O)$</td>
</tr>
<tr>
<td>16</td>
<td>Sediment oxygen demand</td>
<td>$O \rightarrow O_{(b)}$</td>
<td>$R = K_0 \theta^{T-20} / \theta$</td>
</tr>
</tbody>
</table>

From a reaction based approach, governing equations for all species involved in the reaction network must be considered. The diagonalization of the reaction matrix for all 19 species would result in a set of 19 kinetic-variable equations. If we substitute Equations (14) through (19) into Equations (1) through (9) in Table 5.3, the resulting first 9 equations are then decoupled from the last 10 equations. Once the resulting 9 equations are solved for $C_1$ through $C_9$, Equations (14) through (19) are used to calculate the dynamics of $Chla_{2(b)}$, $N_{4(b)}$, $P_{2(b)}$, $L_{(b)}$, $O_{2(g)}$, and $O_{(b)}$, and Equations (10) through (13) can be used to calculate the amount of $H_2O$, $CO_2$, $N_{1(b)}$, and $P_{1(b)}$ that
must be supplied to maintain the conservation principle for water, carbon dioxide, benthic organic nitrogen, and benthic organic phosphorus.

### Table 5.3 Governing Equations for the Reaction-based Diagonalization Approach

<table>
<thead>
<tr>
<th>No.</th>
<th>Decomposition Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>( \frac{dE_1}{dt} = d\left[ 0.00027(C_1 + Chla_{(b)}) + C_4 + P_{2(b)} \right] \text{dt} = -0.015R_4 + R_{10} )</td>
</tr>
<tr>
<td>(2)</td>
<td>( \frac{dE_2}{dt} = d\left[ C_4 + P_{2(b)} \right] \text{dt} = -0.015R_4 + R_{10} )</td>
</tr>
<tr>
<td>(3)</td>
<td>( \frac{dE_3}{dt} = d\left[ -0.21(C_1 - C_2 + O_{2(b)} + O_{3(b)} - L_{1(b)}) + 0.0078(C_1 + Chla_{2(b)}) - 0.77C_4 - C_7 + 5.1(C_4 + P_{2(b)}) \right] \text{dt} = R_4 + 5.1R_{10} )</td>
</tr>
<tr>
<td>(4)</td>
<td>( \frac{dE_4}{dt} = d\left[ 0.00032(C_1 + Chla_{(b)}) + 0.22\left( C_4 + N_{4(b)} \right) + 1.2\left( C_6 + P_{2(b)} \right) \right] \text{dt} = -0.22R_4 + 1.2R_{10} )</td>
</tr>
<tr>
<td>(5)</td>
<td>( \frac{dE_5}{dt} = d\left[ -0.22(C_1 - C_2 + O_{2(b)} + O_{3(b)} - L_{1(b)}) + 0.0078(C_1 + Chla_{2(b)}) + 0.23C_4 + 5.1(C_4 + P_{2(b)}) \right] \text{dt} = R_4 + 5.1R_{10} )</td>
</tr>
<tr>
<td>(6)</td>
<td>( \frac{dE_6}{dt} = d\left[ 0.0094(C_1 - C_2 + O_{2(b)} + O_{3(b)}) - 0.00033(C_1 + Chla_{(b)}) + 0.033C_4 - 0.22(C_4 + P_{2(b)}) \right] \text{dt} = -0.043R_4 - 0.22R_{10} )</td>
</tr>
<tr>
<td>(7)</td>
<td>( \frac{dE_7}{dt} = d\left[ 0.0015(C_1 + Chla_{(b)}) + C_4 + C_5 + C_6 + C_7 + N_{4(b)} \right] \text{dt} = R_4 )</td>
</tr>
<tr>
<td>(8)</td>
<td>( \frac{dE_8}{dt} = d\left[ 0.00027(C_1 + Chla_{(b)}) + C_4 + C_5 + P_{2(b)} \right] \text{dt} = -R_{11} )</td>
</tr>
<tr>
<td>(9)</td>
<td>( \frac{dE_9}{dt} = d(C_2 + L_{1(b)}) \text{dt} = -R_{13} )</td>
</tr>
<tr>
<td>(10)</td>
<td>( \frac{dE_{10}}{dt} = d(C_2 + L_{1(b)} + H_2O) \text{dt} = 0 )</td>
</tr>
<tr>
<td>(11)</td>
<td>( \frac{dE_{11}}{dt} = d(C_2 + L_{1(b)} + CO_2) \text{dt} = 0 )</td>
</tr>
<tr>
<td>(12)</td>
<td>( \frac{dE_{12}}{dt} = d(0.0015(C_1 + Chla_{(b)}) + C_4 + C_5 + C_6 + C_7 + N_{1(b)} + N_{4(b)}) \text{dt} = 0 )</td>
</tr>
<tr>
<td>(13)</td>
<td>( \frac{dE_{13}}{dt} = d\left[ 0.00027(C_1 + Chla_{(b)}) + C_4 + C_5 + P_{2(b)} + P_{2(c)} \right] \text{dt} = 0 )</td>
</tr>
<tr>
<td>(14)</td>
<td>( \frac{dE_{14}}{dt} = dChla_{(b)} \text{dt} = R_4 )</td>
</tr>
<tr>
<td>(15)</td>
<td>( \frac{dE_{15}}{dt} = dN_{4(b)} \text{dt} = R_4 )</td>
</tr>
<tr>
<td>(16)</td>
<td>( \frac{dE_{16}}{dt} = dP_{2(b)} \text{dt} = -R_{12} )</td>
</tr>
<tr>
<td>(17)</td>
<td>( \frac{dE_{17}}{dt} = dL_{1(b)} \text{dt} = R_{14} )</td>
</tr>
<tr>
<td>(18)</td>
<td>( \frac{dE_{18}}{dt} = dO_{2(c)} \text{dt} = -R_{17} )</td>
</tr>
<tr>
<td>(19)</td>
<td>( \frac{dE_{19}}{dt} = dO_{2(c)} \text{dt} = R_{18} )</td>
</tr>
</tbody>
</table>

C1 = O, C2 = L, C3 = Chla, C4 = N4, C5 = N1, C6 = N2, C7 = N3, C8 = P1, and C9 = P2

The use of diagonalization approaches allows us to formulate some rate equations one by one. For example, the reaction rate \( R_8 \) can be calculated by plotting the concentration of \( E_7 \) versus time in which \( E_7 \) is the linear combination of \( C_3, C_4, C_5, C_6, C_7, Chla_{(b)} \) and \( P_{2(b)} \) [see Equation (3.2) in Table 5.3]. Similarly, reaction rates \( R_{11}, R_{13}, R_4, R_6, R_{12}, R_{14}, R_{15}, \) and \( R_{16} \) can be calculated from the dynamics of \( E_8 \) through \( E_{15} \), respectively [see Equations (8), (9) and (14) through (19) in Table 5.3]. Because linearly dependent reactions are present in the system, we
cannot formulate all rate equations independently. To do so, we have to design an experimental system such that only linearly independent reactions are present to individually and mechanistically formulate rate equations.

Table 5.4 is the new working equation using diagonalization paradigm for QUAL2E. From it we can see that the evolution of each species is due to the combination of reaction rates. Table 5.5 and 5.6 are the reaction co rate parameters and efficiencies used in Loxahatchee estuary simulation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>Notation</th>
<th>Working Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dissolved Oxygen</td>
<td>O</td>
<td>$\frac{d[O]}{dt} = \alpha_1 R_1 - \alpha_4 R_3 - \alpha_5 R_5 - R_{16} + R_{15}$</td>
</tr>
<tr>
<td>2</td>
<td>Biochemical oxygen</td>
<td>L</td>
<td>$\frac{d[L]}{dt} = -R_{13} - R_{14}$</td>
</tr>
<tr>
<td>3</td>
<td>Chlorophyll a</td>
<td>Chla</td>
<td>$\frac{d[\text{Chla}]}{dt} = \alpha_1 R_2 - \alpha_3 R_3 - R_4$</td>
</tr>
<tr>
<td>4</td>
<td>Organic nitrogen</td>
<td>N$_4$</td>
<td>$\frac{d[N_4]}{dt} = \alpha_4 R_4$</td>
</tr>
<tr>
<td>5</td>
<td>Ammonia nitrogen</td>
<td>N$_1$</td>
<td>$\frac{d[N_1]}{dt} = -\alpha_1 R_1 + R_2 + R_3 - R_4$</td>
</tr>
<tr>
<td>6</td>
<td>Nitrite nitrogen</td>
<td>N$_2$</td>
<td>$\frac{d[N_2]}{dt} = R_3 - R_4$</td>
</tr>
<tr>
<td>7</td>
<td>Nitrate nitrogen</td>
<td>N$_3$</td>
<td>$\frac{d[N_3]}{dt} = -R_2 + R_3$</td>
</tr>
<tr>
<td>8</td>
<td>Organic phosphorus</td>
<td>P$_1$</td>
<td>$\frac{d[P_1]}{dt} = \alpha_2 R_3 - R_{10} - R_{11}$</td>
</tr>
<tr>
<td>9</td>
<td>Dissolved phosphorous</td>
<td>P$_4$</td>
<td>$\frac{d[P_4]}{dt} = -\alpha_1 R_1 + R_{16} + R_{13}$</td>
</tr>
</tbody>
</table>
Table 5.5 QUAL2E Reaction Rate Parameters for the Loxahatchee Estuary

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ</td>
<td>Algae growth rate</td>
<td>µ&lt;sub&gt;max&lt;/sub&gt;(FL) (FN) (FP)</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>µ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Maximum algae growth rate</td>
<td>2.0</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>FL</td>
<td>Algae growth limitation factor for light</td>
<td>min{(1/λ&lt;sub&gt;d&lt;/sub&gt;)ln[(KL+I)/(KL+I-e&lt;sup&gt;-λ&lt;sub&gt;d&lt;/sub&gt;d&lt;/sup&gt;)]},1}</td>
<td>-</td>
</tr>
<tr>
<td>λ</td>
<td>Light extinction coefficient</td>
<td>2.0</td>
<td>ft&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>d</td>
<td>Depth of flow</td>
<td>Variable</td>
<td>ft</td>
</tr>
<tr>
<td>KL</td>
<td>Half saturation light intensity</td>
<td>5</td>
<td>Btu/ft&lt;sup&gt;2&lt;/sup&gt;-hr</td>
</tr>
<tr>
<td>I</td>
<td>Surface light intensity</td>
<td>5</td>
<td>Btu/ft&lt;sup&gt;2&lt;/sup&gt;-hr</td>
</tr>
<tr>
<td>FN</td>
<td>Algae growth limitation factor for N</td>
<td>(N&lt;sub&gt;I&lt;/sub&gt;+N&lt;sub&gt;3&lt;/sub&gt;)/(N&lt;sub&gt;I&lt;/sub&gt;+N&lt;sub&gt;1&lt;/sub&gt;+)K&lt;sub&gt;N&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>K&lt;sub&gt;N&lt;/sub&gt;</td>
<td>Half saturation constant for N</td>
<td>0.155</td>
<td>mg-N/L</td>
</tr>
<tr>
<td>FP</td>
<td>Algae growth limitation factor for P</td>
<td>P&lt;sub&gt;2&lt;/sub&gt;/(P&lt;sub&gt;2&lt;/sub&gt;+K&lt;sub&gt;P&lt;/sub&gt;)</td>
<td>-</td>
</tr>
<tr>
<td>K&lt;sub&gt;P&lt;/sub&gt;</td>
<td>Half saturation constant for P</td>
<td>0.0255</td>
<td>mg-P/L</td>
</tr>
<tr>
<td>θ&lt;sub&gt;µ&lt;/sub&gt;</td>
<td>Temperature correction for algae growth</td>
<td>1.047</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>Fraction of algae N taken from ammonia</td>
<td>P&lt;sub&gt;N&lt;/sub&gt;N&lt;sub&gt;I&lt;/sub&gt;/P&lt;sub&gt;N&lt;/sub&gt;N&lt;sub&gt;I&lt;/sub&gt;+ (1-P&lt;sub&gt;N&lt;/sub&gt;)N&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>P&lt;sub&gt;N&lt;/sub&gt;</td>
<td>Preference factor for ammonia nitrogen</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>ρ</td>
<td>Algae respiration rate</td>
<td>0.275</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>θ&lt;sub&gt;ρ&lt;/sub&gt;</td>
<td>Temperature correction for algae respiration</td>
<td>1.047</td>
<td>-</td>
</tr>
<tr>
<td>σ&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Algae settling rate</td>
<td>3.25</td>
<td>ft/day</td>
</tr>
<tr>
<td>θ&lt;sub&gt;σ&lt;sub&gt;1&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for algae settling</td>
<td>1.024</td>
<td>-</td>
</tr>
<tr>
<td>β&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Rate constant for organic N decay</td>
<td>0.21</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>θ&lt;sub&gt;β&lt;/sub&gt;&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Temperature correction for organic N decay</td>
<td>1.047</td>
<td>-</td>
</tr>
<tr>
<td>σ&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Organic N settling rate</td>
<td>0.0505</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>θ&lt;sub&gt;σ&lt;sub&gt;4&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for organic N settling</td>
<td>1.024</td>
<td>-</td>
</tr>
<tr>
<td>β&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Rate constant for ammonia oxidation</td>
<td>0.55</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>CORDO</td>
<td>Nitrification rate correction factor</td>
<td>1-e&lt;sup&gt;-KNITRF*O&lt;/sup&gt;</td>
<td>-</td>
</tr>
<tr>
<td>θ&lt;sub&gt;β&lt;/sub&gt;&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Temperature correction for ammonia oxidation</td>
<td>1.083</td>
<td>-</td>
</tr>
<tr>
<td>KNITRF</td>
<td>First order nitrification inhibition coefficient</td>
<td>0.65</td>
<td>L/mg</td>
</tr>
<tr>
<td>σ&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Benthic source rate for ammonia</td>
<td>0</td>
<td>mg-N/ft&lt;sup&gt;2&lt;/sup&gt;/day</td>
</tr>
<tr>
<td>θ&lt;sub&gt;σ&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for ammonia source</td>
<td>1.074</td>
<td>-</td>
</tr>
<tr>
<td>β&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Rate constant for nitrite oxidation</td>
<td>1.10</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>θ&lt;sub&gt;β&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for nitrite oxidation</td>
<td>1.047</td>
<td>-</td>
</tr>
<tr>
<td>β&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Rate constant for organic P decay</td>
<td>0.355</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>θ&lt;sub&gt;β&lt;sub&gt;4&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for organic P decay</td>
<td>1.047</td>
<td>-</td>
</tr>
<tr>
<td>σ&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Organic P settling rate</td>
<td>0.0505</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>θ&lt;sub&gt;σ&lt;sub&gt;5&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for organic P settling</td>
<td>1.024</td>
<td>-</td>
</tr>
<tr>
<td>σ&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Benthic source rate for dissolved P</td>
<td>0</td>
<td>mg-P/ft&lt;sup&gt;2&lt;/sup&gt;/day</td>
</tr>
<tr>
<td>θ&lt;sub&gt;σ&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for dissolved P source</td>
<td>1.074</td>
<td>-</td>
</tr>
<tr>
<td>K&lt;sub&gt;1&lt;/sub&gt;</td>
<td>BOD deoxygenating rate constant</td>
<td>1.71</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>θ&lt;sub&gt;K&lt;sub&gt;1&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for BOD decay</td>
<td>1.047</td>
<td>-</td>
</tr>
<tr>
<td>K&lt;sub&gt;3&lt;/sub&gt;</td>
<td>BOD settling rate constant</td>
<td>0</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>θ&lt;sub&gt;K&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for BOD settling</td>
<td>1.024</td>
<td>-</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Re-aeration rate constant</td>
<td>min(5.026u&lt;sup&gt;0.369&lt;/sup&gt;q&lt;sup&gt;-1.673&lt;/sup&gt;2.31,10)</td>
<td>day&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>u</td>
<td>Flow velocity</td>
<td>Variable</td>
<td>ft/day</td>
</tr>
<tr>
<td>O*</td>
<td>Equilibrium oxygen concentration</td>
<td>-13.344+1.57578×10&lt;sup&gt;-6&lt;/sup&gt;TK&lt;sup&gt;-6.66423×10&lt;sup&gt;-10&lt;/sup&gt;TK&lt;sup&gt;-1&lt;/sup&gt;&lt;/sup&gt;</td>
<td>mg/l</td>
</tr>
<tr>
<td>T&lt;sub&gt;T&lt;/sub&gt;</td>
<td>Temperature</td>
<td>T+273.15</td>
<td>°K=°C+273.15</td>
</tr>
<tr>
<td>θ&lt;sub&gt;T&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for re-aeration</td>
<td>1.024</td>
<td>-</td>
</tr>
<tr>
<td>K&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Benthic oxygen uptake</td>
<td>0</td>
<td>mg-O/ft&lt;sup&gt;2&lt;/sup&gt;/day</td>
</tr>
<tr>
<td>θ&lt;sub&gt;K&lt;sub&gt;4&lt;/sub&gt;&lt;/sub&gt;</td>
<td>Temperature correction for SOD uptake</td>
<td>1.060</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 5.6 QUAL2E Reaction Coefficients for the Loxahatchee Estuary

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_0$</td>
<td>Ration of chlorophyll-a to algae biomass</td>
<td>55</td>
<td>$\mu$g-Chla / mg-A</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>Fraction of algae mass that is nitrogen</td>
<td>0.08</td>
<td>mg-N / mg-A</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>Fraction of algae mass that is phosphorus</td>
<td>0.015</td>
<td>mg-P / mg-A</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>O$_2$ production per unit of algae growth</td>
<td>1.6</td>
<td>mg-O / mg-A</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>O$_2$ uptake per unit of algae respired</td>
<td>1.95</td>
<td>mg-O / mg-A</td>
</tr>
<tr>
<td>$\alpha_5$</td>
<td>O$_2$ uptake per unit of NH$_3$ oxidation</td>
<td>3.5</td>
<td>mg-O / mg-N</td>
</tr>
<tr>
<td>$\alpha_6$</td>
<td>O$_2$ uptake per unit of NO$_2$ oxidation</td>
<td>1.0</td>
<td>mg-O / mg-N</td>
</tr>
</tbody>
</table>

5.2 Study Area Description

The Loxahatchee estuary and its watershed are located on the east coast of Florida within northern Palm Beach and southern Martin Counties. The Loxahatchee River connects to the Atlantic Ocean via the Jupiter Inlet near the city of Jupiter, Florida. The main water body consists of the estuary and several major tributaries of the river, including the North Fork, Southwest Fork, the Northwest Fork, and the North and South Intracoastal Waterways.

The Northwest Fork of the Loxahatchee River originates in natural wetlands – the Loxahatchee Slough. The slough receives discharges from C-18 Canal and runoff and groundwater inflow from adjacent uplands. Downstream from the slough, the Northwest Fork receives additional
input from three major tributaries – Cypress Creek, which drains Ranch Colony, Pal Mar and a portion of the Groves subbasin; Hobe Grove Ditch, which drains a portion the Groves subbasin, and Kitching Creek, which drains wetlands north of the river. Passing through cypress swamp, mangrove forest, historical and archeological sites, and JD State Park to the saline waters of the estuary, the Loxahatchee River has often been referred to as the “last free flowing river in southeast Florida”. The Northwest Fork also represents one of the largest vestiges of native cypress river-swamp within southeast Florida. In May 1985, a 7.5 miles reach of the Northwest Fork of the Loxahatchee River was federally designated as Florida's first Wild and Scenic River.

The attractiveness of the estuary has helped to spur large population increases over the past century. The increasing populations have spurred a dramatic increase in land development and alteration in the natural hydrologic regime of this area, which have created coastal water quality impacts. Currently the flow in the river and estuary is under the influence of tide from the Atlantic Ocean. Salt water has been pushing to upstream of the river by rising tide.

South Florida Water Management District (SFWMD) has been developing management program for this unique, “wild and scenic river” to preserve and enhance the outstanding natural and cultural values in this area (Shan, 2005). One of the primary goals is to maintain existing water quality in the river by eliminating identified water quality problems and to protect the irreplaceable watershed to the extent feasible from further human encroachment.

The computational domain in the study area includes the Loxahatchee estuary, Intracoastal Waterways, and three major tributaries of the river – the South Fork, North Fork, and Northwest
Fork. An aerial picture of the study area is shown in Figure 5.1. The top view of the model mesh is also shown in the same figure. A part of the Atlantic Ocean to the east of Florida coastal line is included in the computational domain to model the flow near the river inlet more precisely. The river miles of the major reaches of the river in the model domain are listed in Table 5.7. The upstream boundary of the South Fork in model domain is structure S-46 – a gated spillway located on C-18 Canal just north of Indiantown Road. The water delivered to the Southwest Fork through S-46 from the C-18 Canal is controlled by the automatic operation of the structure’s gates to maintain an optimum headwater elevation. The Northwest Fork has three small tributaries: the Kitching Creek, the Hobe Grove Ditch, and the Cypress Creek. The upstream boundary of the Northwest Fork in this model located at the Florida Turnpike and can be extended further upstream to Lainhart Dam which is a small weir structure located on the C-14 Canal upstream of the Northwest Fork. The C-14 Canal connects with C-18 Canal via structure G-92.

<table>
<thead>
<tr>
<th>Table 5.7 River Miles for Different Reach of the Loxahatchee Estuary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reach</td>
</tr>
<tr>
<td>North Intracoastal Waterway</td>
</tr>
<tr>
<td>South Intracoastal Waterway</td>
</tr>
<tr>
<td>North Fork</td>
</tr>
<tr>
<td>Southwest Fork</td>
</tr>
<tr>
<td>Northwest Fork (up to Florida Turnpike)</td>
</tr>
<tr>
<td>Loxahatchee River (from Jupiter Inlet to Junction of Northwest and Southwest Fork)</td>
</tr>
</tbody>
</table>
The three-dimension mesh was generated based on the two-dimensional mesh (the base mesh). Four layers of three-dimensional mesh lay over the base mesh and the grid nodes distributed uniformly in the vertical direction. The three-dimensional domain is discretized with 4,936 quadratic, triangular prism elements resulting in 30,664 nodes. Element size is ranging from 3500 ft in the Atlantic Ocean to 15 ft near the Kitching Creek. A perspective view of the three-dimensional mesh is given in Figure 5.2. It should be pointed out that for the most part of the computational domain the aspect ratio of the three-dimensional element is in the order of $O(10\sim 100)$ due to the large difference in length scale in the vertical and horizontal direction.
Figure 5.2 Computation Domain and Finite Element Discretization

5.3 Simulation and Results

This example demonstrates the capability of the model in simulating biogeochemical transport related to eutrophication kinetics. Several physical-chemical processes can affect the transport and interaction among the nutrients, algae, carbonaceous material, and dissolved oxygen in the aquatic environment. QUAL2E (Brown and Barnwell, 1987) simulates the transport and transformation reactions of up to 16 constituents. Here we focus on nine interacting non-conservative biogeochemical constituents (Table 5.8) excluding temperature, coliforms, one non-reacting non-conservative constituent, and three conservative constituents. These constituents
result from four interacting systems: algae kinetics, nitrogen cycle, phosphorus cycle, and dissolved oxygen balance (Table 5.2).

<table>
<thead>
<tr>
<th>Species</th>
<th>Initial Concentration</th>
<th>Concentration in freshwater</th>
<th>Concentration in seawater</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>5.00</td>
<td>5.00</td>
<td>0.50</td>
<td>Mg-O₂/Liter</td>
</tr>
<tr>
<td>BOD</td>
<td>0.80</td>
<td>0.80</td>
<td>0.08</td>
<td>Mg-O₂/Liter</td>
</tr>
<tr>
<td>Chla</td>
<td>20.00</td>
<td>20.00</td>
<td>2.00</td>
<td>µg-Chla/Liter</td>
</tr>
<tr>
<td>NH₄</td>
<td>2.00</td>
<td>2.00</td>
<td>0.20</td>
<td>Mg-N/Liter</td>
</tr>
<tr>
<td>ON</td>
<td>1.00</td>
<td>1.00</td>
<td>0.10</td>
<td>Mg-N/Liter</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.10</td>
<td>0.10</td>
<td>0.01</td>
<td>Mg-N/Liter</td>
</tr>
<tr>
<td>NO₃</td>
<td>1.00</td>
<td>1.00</td>
<td>0.10</td>
<td>Mg-N/Liter</td>
</tr>
<tr>
<td>OP</td>
<td>0.50</td>
<td>0.50</td>
<td>0.05</td>
<td>Mg-P/Liter</td>
</tr>
<tr>
<td>OPO₄</td>
<td>0.10</td>
<td>0.10</td>
<td>0.01</td>
<td>Mg-P/Liter</td>
</tr>
</tbody>
</table>

Our simulation is to apply Qaul2e to the Loxahatchee estuary to study its response to a hypothetical biogeochemical loading (e.g., TMDL) from its surrounding drainage (Table 5.8). BEST3D Version 1.0 (Yeh et al., 2005) was used to generate hydrodynamics including currents, tides, salinity, and temperature distributions. The flow boundary condition was implemented on the open drainage boundary sides and with the rest of the boundary treated as closed. Figure 5.3 depicts the vectors of flow velocity at initial time.

To focus on transport, we assume that the temperature is 15°C throughout the simulation region. Variable boundary conditions are applied to the open boundary sides.
Figure 5.3 Initial Flow Velocity Distributions

One size of noncohesive sediment is taken into account with settling velocity of $1.2 \times 10^{-6}$ m/s, critical friction velocity for deposition of 0.348 g/m/s$^2$, critical friction velocity for erosion of 0.345 g/m/s$^2$, and erodibility of 0.1 g/m$^2$/s. Density of the considered sediment is 1010.00 kg/m$^3$. We used the following equations to estimate the deposition and erosion rates using the different equations.

$$ D_n = \min \left( W_{sn} S_n N_{Dn}, S_n h/\Delta t \right) \quad \text{where} \quad N_{Dn} = \max \left( 0, 1 - \left( V_{cDn}/V_{cRn} \right)^2 \right) \quad (5.6) $$

$$ R_n = \min \left( E_{0n} N_{Rn}, DMA_n/\Delta t \right) \quad \text{where} \quad N_{Rn} = \max \left( 0, 1 - \left( V_{cDn}/V_{cRn} \right) \right) \quad (5.7) $$

where $W_{sn}$ is the settling velocity of the $n$-th sediment [L/T]; $S_n$ is the suspended concentration of $n$-th sediment [M/L$^3$]; $h$ is the water depth [L]; $\Delta t$ is simulation time step size [T]; $V_{cDn}$ and $V_{cRn}$ represent the critical friction velocities [L/T] for the onset of deposition and erosion, respectively; $E_{0n}$ is the erodibility of the $n$-th sediment [M/L$^2$/T]; $DMA_n$ is the amount of locally
available dry matter of $n$-th sediment, expressed as dry weight per unit area [M/L^2]. No erosion or sedimentation occurs if the bed friction does not meet the specified limits.

Initially, both bed sediment BS and suspended sediment SS exist in the domain of interest. The initial concentration is 500 g/m² for the bed sediment. The initial concentration is 10 g/m² for the suspended sediment. The variable boundary incoming concentration of suspended sediment is 0. Initial and variable boundary incoming concentrations of the 9 simulated chemical species are listed in Table 5.8.

As the simulation starts, variable boundary conditions are applied to the open boundary sides, where all chemical species have constant incoming concentrations for the freshwater boundary and sea water boundary separately and suspended sediment, SS, have zero concentration. The longitudinal dispersivity is 10.0 m. The dispersion coefficient is 5.0 m²/s. A 96-hour simulation is performed with a fixed time step size of 100 seconds. A relative error of $10^{-4}$ is used to determine the convergence for iterations involved in the computation.

Figures 5.4 and Figure 5.5 plot the concentration contour for suspended sediment at 1 hour and 96 hour respectively. They show trend of increasing concentration of the suspended sediment within the estuary. It indicates that deposition is less than erosion under the condition set for this example.
Figure 5.4 Distribution of Suspended Sediment at $t = 1$ h

Figure 5.5 Distribution of Suspended Sediment at $t = 96$ h
Figures 5.6 and 5.7 plot the concentration contour for bed sediment at 1 hour and 96 hour respectively. They show trend of decreasing concentration of the bedsediment within the estuary. It also indicates that deposition is less than erosion under the condition set for this example.
The simulation results for algae as chlorophyll a (Chla) at \( t = 1 \) h and 96h are shown in Figures 5.8 and 5.9. According to the reaction network, the source of Chla is algae growth. The sink of Chla
includes algae respiration and settling. The Chla concentration increase shown in above two figures indicates that the source is greater than the sink.
The source of organic nitrogen in water column includes algae respiration. The sink includes the mineralization of its dissolved fraction and the settlement of its particular fraction. Figure 5.10 and Figure 11 show a decreasing concentration of organic nitrogen with time.

Figure 5.12 Distribution of BOD at t =1 h

Figure 5.13 Distribution of BOD at t =96 h
Based on QUAL2E reaction network, there is no source for BOD. However, its sink includes oxidation of its dissolved fraction and the settlement of its particular fraction. Figure 5.12 and Figure 5.13 show a decreasing concentration of BOD with time.

Figure 5.14 Distribution of Dissolved Oxygen at $t=1\ h$

Figure 5.15 Distribution of Dissolved Oxygen at $t=96\ h$
The source of dissolved oxygen is the algae growth and re-aeration from the air. The sink includes algae respiration and oxidation of ammonia, nitrite, and BOD as well as the sediment oxidation demand. Figure 5.14 and 5.15 show an increasing concentration of dissolved oxygen with time, signaling that the source is greater than the sink.

5.4 Discussion

Above simulation results show that our model can simulate a reaction system reasonably. The next key step is to calibrate the model using the field measurement. In general, we can calibrate the model in three ways. First option is to optimize the rate parameters characterizing the reaction rate equations using current optimization software. The option will abuse the model and ignore the physics involved in the reaction system. The other option is to adjust part of the reaction rate parameters or find new rate equations according to the new understanding of the reaction. The third option is to reconsider and investigate the reaction system. There could be new biogeochemical processes occurring in the estuary system that QUAL2E ignores. We need to add new reaction process or change the current reaction network for solving this problem. However, the number of state variables included and biogeochemical and physical processes considered in QUAL2E are hardwired. When there are more water quality parameters and biogeochemical processes in receiving water under studies, we have to considerably modify the codes. We need derive a new reactive transport equation with its production rate for every additional water
quality. Therefore the modification of the codes would not be straightforward. Clearly, there is a
need to develop a model with sufficient generality that would allow the inclusion of any number
of biogeochemical and physical processes and any number of state variables. There is also a need
to come up with a paradigm that would automatically generate reactive transport equations under
mixed slow/kinetic and fast/equilibrium reactions.

In section 5.1, we transform physical and biogeochemical processes in QUAL2E into a reaction
network and formulate reaction rates. The Original rate equations (Table 5.1) are formulated as
functions of the total concentrations to reduce to

\[
\frac{\partial S_i}{\partial t} + L(S_i) = F_i(S_i,...,S_{Ma},p_1,...,i \in M_a)
\]

where \( S_i \) is sum of dissolved and particulate concentrations; \( p_N \) is number of species that have
both the dissolved and particulate phases. This paradigm does not enforce to maintain mass
conservation of all species with respective to reactions. How to maintain mass conservation
would probably be important factors in controlling reaction rates and inducing additional
biogeochemical processes. Under such circumstances, one probably has to revisit the rate
equations and to conduct research to uncover additional reaction networks for the system under
investigations.

Comparing with the original working rate equations in QUAL2E, our new model employs
diagonalization paradigm. Our initial species transport equations are formulated as the evolution
of one species is due to the combination of reaction rates (Equation 5.4). After decomposition,
kinetic variable transport equations can be formulated as the evolution of the combination of species is due to multi-rates or even one reaction rate (Equation 5.5).

\[ \frac{dC_i}{dt} + \alpha_i L(C_i) = \sum_{k \in N} (v_{i,k} - \mu_{i,k}) r_k, \ i \in M \]  

(5.8)

\[ \frac{\partial E_i}{\partial t} + L(E_i) = \sum_{j=1}^{N_k} K_{ij} r_j, \ k \in N \]  

(5.9)

This paradigm allows us model fast reactions with thermodynamic approaches or with users’ defined algebraic equations and mechanistically model slow reactions with users’ defined rate equations. If using original QUAL2E paradigm, we may not formulate all rate equations independently when linearly dependent reactions are present in the system. To do so, we has to design an experimental system such that only linearly independent reactions are present to individually and mechanistically formulate rate equations. Diagonalization paradigm allows us formulate reaction rates one by one and explicitly enforces mass conservation of all species.
Current widely used water quality models for receiving waters are mechanistically similar. The differences among them are the number of state variables included and the number of biogeochemical processes considered. Their Rate equations were mechanistically determined and reaction parameters were obtained through years of research for specific reaction system by the original authors. It is not possible for these models to handle any number of state variables and any number of reactions naturally, which makes them the target of abuse. Practitioners usually optimize the reaction parameters without considering whether the model is applicable to the system or not while the simulation results cannot reproduce field measurement. The other option is to adjust part of the reaction rate parameters or reconsider and investigate the reaction system to see if there are new biogeoprocesses occurring in the system that applied model ignores. We need to transform these new biogeoprocesses into a new larger reaction network and formulate each reaction rate. However, it is a heavy time-consuming work to implement a new understanding within the framework of current models. Clearly, there is a need to develop a model with sufficient generality that would allow the inclusion of any number of biogeochemical and physical processes and any number of state variables. There is also a need to come up with a paradigm that would automatically generate reactive transport equations under mixed slow/kinetic and fast/equilibrium reactions.
In thesis, we present the development of a numerical model to simulate sediment and biogeochemical transformation of chemical species as they are transported in estuary. Transport equations based on the principle of mass balance are used to describe temporal-spatial distributions of sediments and water qualities. Biochemical and geochemical processes are completely defined with reaction network and dealt with reaction-based approaches. The models are enabled to virtually include any type of equilibrium expressions and kinetic rates users want to specify. A suite of biogeochemical reactions are take into account, including aqueous complexation reactions, adsorption/desorption reactions, ion-exchange reactions, precipitation/dissolution reactions, volatilization reactions, diffusion reactions, sedimentation reactions, et al. Any individual reaction representing any of these chemical processes may be simulated as kinetic or as equilibrium, which makes the code extremely flexible for application to a wide range of geochemical transport problems.

Through the decomposition of the system of species transport equations via Gauss-Jordan column reduction of the reaction network, fast reactions and slow reactions are decoupled, which enables robust numerical integrations. Species reactive transport equations are transformed into two sets: reactive transport equations of kinetic-variables and algebraic equations of equilibrium variables. As a result, the model uses kinetic-variables instead of biogeochemical species as primary dependent variables, which reduces the number of transport equations and simplifies reaction terms in these equations. For each time step in the simulation, we first solve the advective-dispersive transport equations for kinetic-variables. We then solve the reactive biogeochemical equations node by node to yield individual species concentration. The
diagonalization method also enables the formulation and parameterization of the individual linearly independent kinetic reactions one by one.

In our model, in order to improve the efficiency and robustness of the computation, two numerical options, finite element method and Lagrangian-Eulerian method, are provided to solve the advective-dispersive transport equations, and three coupling strategies are given to deal with reactive chemistry. The three coupling strategies are fully-implicit scheme, mixed predictor-corrector/operator-splitting method, and operator-splitting approach.

In general, this thesis presents a generic paradigm that allows users to include any number of state variables with ease and the framework is applicable to receiving waters. The key of the paradigm is the reaction-based approach and the decomposition of reaction networks. The reaction-based approach allows us to include any number of reactions, thus any number of state variables. The decomposition allows the formulation of rate equations one reaction at a time with a proper design of experimental systems. The paradigm will provide an easy way to achieve the objective of incorporating new findings. To demonstrate the general paradigm, QAUL2E was recasted in the mode of a reaction network. The model then was applied to the Loxahatchee estuary to study its response to a hypothetical biogeochemical loading from its surrounding drainage. Preliminary results indicated that the model can simulate four interacting biogeochemical processes: algae kinetics, nitrogen cycle, phosphorus cycle, and Dissolved Oxygen Balance.
6.2 Future Work

This thesis presents a water quality model for an estuary. Currently the model is not linked with a hydrodynamic model directly. We need to obtain the flow fields and temperature distributions required to simulate sediment and reactive chemical transport through separated flow and thermal transport models and imported for use. In the model, we ignore the dynamic feedback effect of sediment and reactive chemical transport processes on hydrological flow field and thermal transport. This dynamic feedback may be important in some real-world systems.

The model presented in this thesis has been applied to the Loxahatchee estuary to study its response to a biogeochemical loading (e.g., TMDL) from its surrounding drainage studies. However, we only use a hypothetical biogeochemical loading. Proper simulation and prediction of a watershed water quality requires gathering existing data from past or ongoing watershed water quality studies. The approach to using these collected data is to validate the predicted water quality against the collected data and calibrate the model.

In the future, as the models are calibrated and validated for the Loxahatchee estuary, a better assessment of the impact of the limitations in design scope will be made. This will establish priorities for focusing future development efforts.

The calibration and validation will focus on hydrology, sediment and chemical transport related to eutrophication. The model will incorporate over 20 years of data. Included in the model calibration and validation will be the establishment of the sediment and chemical transport
predictor occurring throughout the bay/estuary. Beyond the model calibration and validation, an extensive sensitivity and uncertainty analysis will also be performed to investigate the impact of model uncertainties on simulation results. The information gained from this sensitivity and uncertainty analysis will be incorporated into future management decisions on the watershed.
REFERENCES


West Consultants. 1996. Evaluation hydrodynamic and contaminant transport computer models for application to Duwamish River and Elliott Bay, prepared for King Country Department of Natural Resources, Seattle, WA.


Yeh, G.T., Siegel, M.D., and M.H. Li, Numerical modeling of coupled fluid flows and reactive transport including fast and slow chemical reactions, J. Contam. Hydrol., 47, 379-390, 2001b.


