A biogeochemical model for metabolism and nutrient cycling in a Southeastern Piedmont impoundment

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Abstract

While non-point nutrient loads are important determinants of biological productivity in Southeastern Piedmont impoundments, productivity can be attenuated by concomitant sediment loads that reduce the biological availability of these nutrients. A biogeochemical model is proposed that explicitly accounts for the effects of sediment–nutrient interactions on multiple components of phytoplankton metabolism dynamics, including algal photosynthesis and respiration, pH, carbonate speciation, dissolved oxygen, and biochemical oxygen demand. Sediment–nutrient interactions relate nutrient uptake and release to pH, sediment oxygen demand, sediment organic matter, and iron. pH is a state variable in our model, affects sediment–nutrient adsorption, and constrains model parameters. The model replicates water quality observations in a small Southeastern Piedmont impoundment and suggests that pH-dependent sediment–nutrient adsorption dominates both orthophosphate and ammonium dynamics, with phosphate adsorption being controlled by ligand exchange to iron oxides, and ammonium adsorption being controlled by the cation exchange capacity. Sediment organic matter accumulation and decay also affects nutrient availability, and may explain the long-term increase of hypolimnetic dissolved oxygen deficit in Lake Lanier, a large Southeastern Piedmont impoundment.

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1. Introduction

Phosphorus (P) and nitrogen (N) are essential elements affecting the trophic status of lakes. At elevated concentrations, these nutrients generally lead to increased biological productivity and a tendency towards lake eutrophication (Daniel et al., 1998). The principal effects of eutrophication include increased algal growth, hypolimnetic oxygen depletion, increased pH variation, and food-chain alteration. Given that nutrients can be removed from point-source discharges — typically municipal wastewater treatment plants — increased attention has been placed on curbing non-point nutrient sources (Carpenter et al., 1998). Of special relevance to the Southeastern Piedmont, soil particles mobilized in surface runoff from erodible soils may bear significant loads of phosphorus.

The Piedmont region of the Southeastern United States has a humid, warm-temperate climate. The region’s abundant rainfall generates runoff which — when combined with the region’s deeply-weathered and highly-erodible soils — carries large amounts of
sediments to receiving waterbodies. These sediments consist of mineral soil along with abundant iron and nutrients (Zeng and Rasmussen, 2001). Both observations and models of suspended sediment dynamics and their interactions with nutrients in typical Southeastern Piedmont rivers indicate strong positive correlations between discharges and sediment concentrations and nutrients, especially phosphorus (Zeng and Beck, 2001).

Economic activities and land-use changes affect the behavior of impoundment systems in Georgia primarily through the accumulation of clay-dominated sediments (deriving from land-surface disturbances) and the accumulation of nutrients, which are strongly associated with these sediments. Hatcher (1994) estimated that 80–90% of the phosphorus load entering Lake Lanier is probably sequestered by sediment deposits and does not leave the lake. The observed record of Lanier shows that concentrations of soluble species of nitrogen and phosphorus are significantly lower than those expected from currently estimated inputs of these materials to the lake (Zeng, 2001).

In short, Lake Lanier appears to behave as a most effective trap for sequestering sediments and nutrients, thereby lessening their potential impacts on biological cycles, presumably due to their sorption onto mineral sediments, with subsequent deposition, and then burial. This hypothesis, regarding the strong association between suspended Piedmont sediments and nutrients (especially P), has indeed been substantiated through fertilization manipulations of both exclusively soluble and nutrient—slurry (soil) mixtures within an aquaculture pond, located in the Georgia Piedmont some 100-km distant from Lanier (Mayhew et al., 2001; Parker et al., in preparation; Parker, 2004).

Modeling the associated biogeochemical dynamics of the perturbed aquaculture pond based on experiment data obtained in the 1998 manipulations is the primary subject of this paper.

The ultimate goal of the present exercise is the application of the pond manipulation results to Lake Lanier. Lanier, its watershed, and the future management of associated nutrient and sediment loadings are focal issues of often contentious and acrimonious debate amongst all the many stakeholders (Beck et al., 2002). Historical data on Lanier’s water quality suggest that the hypolimnetic dissolved oxygen (DO) deficit in the lake has increased over the past 40 years or so. What detailed, complex web of interactions in the lake’s biogeochemistry, we ask, therefore, might stand behind this macroscopic trend in DO deficit? Would particulate materials, the iron (Fe) cycle, the phosphorus (P) cycle, the carbon (C) cycle, pH, algal concentrations, and bacterial levels – as in the microbial loop hypothesis of Porter (1996) and Porter et al. (1996) – suffice for the characterization of that biogeochemistry? If so, and if we could capture this biogeochemistry in a model, could we say anything about the future trajectory of hypolimnetic metabolism, as a function of changing relative loads of particulates, Fe, P, and organic C entering Lanier from its watershed? Of special significance in this last respect is the possibility of an unfortunate combination of policy-driven sediment and nutrient loadings promoting plentiful re-release of nutrients from sequestration in the bed sediments of the lake.

In this paper, we describe the results of the first step in a program of research designed to answer such questions. In particular, the novel model developed – with reference to a comprehensive database from the aquaculture pond manipulations – has subsequently been employed for making relatively short-term projections of the potential responses of Lanier to changes in future sediment and nutrient loadings (Zeng, 2001). This approach complements the accompanying development and application of a foodweb model (Osidle, 2001; Osidle and Beck, 2004), which has been designed to explore the hopes and fears of the community of stakeholders for the longer-term well-being of Lanier (Beck et al., 2002; Osidle and Beck, 2003; Fath and Beck, 2005).

Section 2 reviews the theoretical background of the proposed model, with special reference to its novel and distinctive features. Section 3 outlines the field experiments conducted in 1998 on the manipulated aquaculture pond, using a specialized real-time monitoring facility (the University of Georgia’s Environmental Process Control Laboratory, EPCL). Section 4 introduces the application of the controlled random search (CRS) procedure for model parameterization which aims at reducing model uncertainty and identifying the crucial processes and initial values of unobserved states. Section 5 presents the results of model parameterization and evaluation against the field data, along with some prospective insights into the implications of the aquaculture pond experiments and model for the future management of Lake Lanier.

2. Biogeochemical modeling approach

Our efforts toward improved management of Southeastern Piedmont lake systems require an accurate formulation of lake biogeochemical processes, without which model predictions lack the necessary degree of credibility. Since substantial progress in lake biogeochemical models during the 1970s (Harris, 1980; Beck, 1985; Reynolds and Irish, 1997) along with a few subsequent advances (Thomann and Fitzpatrick, 1982), the biogeochemical processes from these models have become standard (Reckhow and Chapra, 1999) and are embedded in most of the major management software for lakes and impoundments (e.g. Ambrose et al., 1993; Cole and Buchak, 1995; Cole and Wells, 2000; Hamilton and Schladow, 1997). On the whole, lake biogeochemical models have focused primarily on the prediction of algal
population dynamics and their effects on dissolved oxygen and conventional cycles of nitrogen and phosphorus (Kayombo et al., 2000; Chapelle et al., 2000; Omlin et al., 2001).

These models, while adequate for many systems, fail to account for important properties of Southeastern Piedmont lake ecosystems, specifically the importance of pH on biogeochemical processes, as well as the effects of sediments on nutrient uptake and release. To overcome these shortcomings, a more robust formulation of Southeastern Piedmont lake biogeochemical systems is proposed to both model pH as a state variable and model the effects of pH on lake biogeochemical processes.

pH serves as an important factor affecting algal growth, the forms of carbon and nutrient species, sediment–nutrient interactions, and many other chemical reactions. The existing widely-used lake water quality model CE-QUAL-W2 models pH by assuming carbonate alkalinity invariant with time (Cole and Buchak, 1995; Cole and Wells, 2000). In Panizzuti and Tartari’s model (1995), pH is modeled by assuming total inorganic carbon is constant with time (i.e. closed system). Ottosson and Håkansson (1997) modeled pH primarily based on statistical regressions and without including formulations for the relationship between primary production and changes in pH. In our model, pH is modeled by simulating the dynamics of both total inorganic carbon and carbonate alkalinity which are affected by carbon cycling in the system. Incorporating pH as a state variable — with its own prescribed dynamics — means that this important control on biogeochemical cycling can be explicitly incorporated during model parameterization.

A second contribution is the use of two new sediment–nutrient interactions, specifically the phosphorus—iron ligand reaction along with ammonium sorption due to cation exchange on clay surfaces caused by isomorphic substitution within the clay lattice. Coupling sediment–nutrient interactions using appropriate state variables allows us to account for pH-dependent iron–phosphorus chelation, as well as ammonium sorption to anions. We show that this approach provides improved estimates of nutrient uptake and release over time. Together, these improvements provide us the ability to simulate — in just one model — the diurnal dynamics of DO, algae, nutrients, pH, and sediment–water interactions.

The complete model structure is illustrated in Fig. 1. Individual components are described below — the full set of governing equations is provided in Appendix A.

2.1. Phytoplankton metabolism

Phytoplankton metabolism is an important ecosystem process that can be approximated using (Redfield et al., 1963):

106CO2 + 16NO3− + HPO42− + 18H+ + 122H2O
⇌ (CH2O)106(NH3)16(H2PO4)+ 138O2 (1)

The forward reaction in Eq. (1) is photosynthesis, while the reverse reaction is decay and respiration. Oxygen is produced and consumed in the water column as a result of phytoplankton growth and respiration, respectively. Stoichiometrically, 138:106 moles of oxygen are produced for every mole of phytoplankton carbon produced, and vice versa.

Eq. (1) can be modified for the pH-range typical of Southeastern Piedmont impoundments (i.e. 7 < pH < 9) in which the aqueous system is dominated by bicarbonate ions:

106HCO3− + 16NO3− + HPO42− + 124H+ + 16H2O
⇌ (CH2O)106(NH3)16(H2PO4)+ 138O2 (2)

In this form, note the strong effect on pH introduced by this reaction, with 124:106 moles of H+ consumed per mole of phytoplankton carbon produced. While pH can be substantially buffered in some systems, waters with low buffering capacity can result in substantial changes in pH as a result of photosynthesis (Stumm and Morgan, 1996). Note also the close ratio between oxygen and pH; 124:138 moles of H+ are consumed per mole of oxygen produced. This suggests that pH and DO have similar behavior under phytoplankton metabolism dynamics. Reasonably simulating both DO and pH simultaneously would provide more confidence in modeling phytoplankton metabolism dynamics.

Key to understanding the dynamics of carbon, nutrients, oxygen, and pH, therefore, is the ability to understand and quantify the rate of carbon cycling; specifically the growth, respiration, and decay of phytoplankton. We model the phytoplankton growth rate, $K_g$, as a function of light intensity, I, temperature, $T$, and the limiting nutrient (Chen and Orlob, 1975; Scavia, 1980; Ambrose et al., 1993):

$$K_g = K_g^* f(T) f(I) \text{min}$$

$$K_g^* \times \left[ \frac{[PO_4]}{[k_p + [PO_4]]} \right] \left[ \frac{[NO_3] + [NH_4]}{[k_N + [NO_3] + [NH_4]]} \right] \left[ \frac{\text{TIC}}{k_C + \text{TIC}} \right]$$

$$f(I) = \frac{I}{I_s} \exp \left[ 1 - \frac{I}{I_s} \right]$$

where $K_g^*$ is the maximum growth rate (d−1), and orthophosphate (PO4), nitrate (NO3), ammonium (NH4), and total inorganic carbon (TIC) are expressed as concentrations (mg/L). The light function is described by Steele’s (1965) equation:

$$I \leq I_s \quad \text{for } f(I) = I/I_s$$

where $I_s$ is the saturation light intensity at the maximum photosynthetic rate and $I$ is the available light intensity.
The temperature function is described using temperature-dependent coefficients, $\Theta_i$:

$$f(T) = \Theta_i^{T-20}$$  \hspace{1cm} (5)

where $T$ is the temperature, °C.

Phytoplankton death provides a source of organic carbon that can be oxidized, a process assumed independent of temperature (Bierman, 1976). The phytoplankton respiration rate is computed using:

$$K_r = K_r^* f(T)$$  \hspace{1cm} (6)

where $K_r^*$ is the maximum respiration rate of phytoplankton (Ambrose et al., 1993; Cole and Buchak, 1995; Cole and Wells, 2000). Settled phytoplankton enters the pool of sediment organic matter (SOM).

### 2.2. SOD and SOM

Oxygen consumption by bed sediments is influenced by two phenomena: (1) the rate at which oxygen diffuses into the bottom sediments and is then consumed; and (2) the rate at which reduced organic substances in the sediment are conveyed into the water column, and are then oxidized there (Bowie et al., 1985). We simulate these processes by separating the oxygen demand by bed sediments into sediment oxygen demand (SOD) and oxidation of sediment organic matter (SOM). Sources of SOM include sedimentation of phytoplankton and organic matter. Eq. (A.3) in Appendix A accounts for SOM processes.

### 2.3. DO

Dissolved oxygen concentration (DO) depends on atmospheric exchange, consumption through algal respiration, production by algal photosynthesis, BOD decay, nitrification, sediment oxygen demand, and sediment organic matter decay. Nitrification, in particular, can significantly affect DO, with a reaction that can be summarized using:

$$\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+$$  \hspace{1cm} (7)

which shows that two moles of oxygen are consumed for every mole of ammonium nitrogen oxidized. The process of nitrification in natural waters is carried out by aerobic autotrophs in a two-step process, with *Nitrosomonas* bacteria responsible for the conversion of ammonium to nitrite, while *Nitrobacter* are responsible for the conversion of nitrite to nitrate (Alexander, 1977; Van Veen and Frissel, 1981). Essential to both reactions are aerobic conditions.

However, *Nitrosomonas* growth can be inhibited at both high and low values of pH, particularly below four and greater than nine, which is exceeded in the observed aquaculture pond behavior. Darrah et al. (1986) provided experimental results that describe the influence of pH on nitrification using a fourth-order polynomial:

$$f(pH) = 35.019 - 24.538pH + 6.147pH^2 - 0.647pH^3 + 0.02435pH^4 \quad 4 \leq pH \leq 9$$  \hspace{1cm} (8)

where $f(pH) = 0$ outside this range.

### 2.4. BOD

The oxidation of carbonaceous material is assumed to occur according to conventional kinetics. A principal source of carbonaceous biochemical oxygen demand
(BOD), other than man-made sources and natural runoff, is detrital phytoplankton carbon, produced as a result of algal death. The primary loss mechanism associated with BOD is oxidation. Under low DO conditions, the denitrification reaction provides a sink for BOD, i.e. easily degradable organic material associated with BOD is oxidation. Under low DO conditions, the denitrification reaction provides a sink for BOD, i.e. easily degradable organic material provides a carbon substrate for the growth of the denitrifying bacteria:

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

(9)

thus, 5:4 moles of carbon are consumed per mole of nitrate-nitrogen reduced — thus reducing BOD by 5:4 moles as well.

2.5. Nitrogen cycle

Three nitrogen variables are used to characterize the nitrogen cycle: organic nitrogen, ammonium, and nitrate. As phytoplankton grow, dissolved inorganic nitrogen (as either ammonium or nitrate) is taken up and incorporated into their biomass. However, for physiological reasons, the preferred form is ammonium nitrogen. The ammonium preference term \( P_{\text{NH}_4} \) is given by (Thomann and Fitzpatrick, 1982; O’Connor et al., 1981; Ambrose et al., 1993):

\[
P_{\text{NH}_4} = \frac{[\text{NH}_4]}{K_{\text{mN}} + [\text{NO}_3]} \left( \frac{[\text{NO}_3]}{K_{\text{mN}} + [\text{NH}_4]} + \frac{K_{\text{mN}}}{[\text{NH}_4] + [\text{NO}_3]} \right)
\]

(10)

where \( K_{\text{mN}} \) is the saturation constant for nitrogen mineralization. As phytoplankton respire and die, living organic material is recycled to non-living organic and inorganic matter.

A key feature of this model is the sorption of ammonium by suspended sediment. This relationship is modeled using the linear relationship shown as Eq. (A.8) in Appendix A. Clay minerals normally have a negative charge due to isomorphic substitution (Stumm and Morgan, 1996). Positive ions are attracted to these surfaces, the magnitude of which is measured using the Cation Exchange Capacity, CEC. As a cation, the ammonium concentration in equilibrium with sediment is decreased as a function of sediment concentration and the CEC.

2.6. Phosphorus and iron

Phosphorus is the key element in many freshwater aquatic ecosystems because it tends to be the growth-rate limiting nutrient for phytoplankton (Carlson, 1977; Carpenter et al., 1998). Phosphorus is assumed to be completely available for uptake by phytoplankton when it is in the orthophosphate (PO₄) form, but becomes unavailable when removed through adsorption onto suspended sediment and iron, as shown in Eq. (A.10) in Appendix A.

Another key feature of this model is the inclusion of total iron, primarily because of its effect on orthophosphate concentrations through adsorption and settling. Phosphorus—iron cycling in lake systems usually causes Fe³⁺ oxides to sorb soluble reactive phosphorus via ligand exchange (Reynolds and Davies, 2000; Stumm and Morgan, 1996). These Fe³⁺—phosphate complexes can be transformed by reduction of Fe³⁺ ions to the more soluble Fe²⁺ form, which solubilizes both Fe²⁺ and phosphate ions (Wetzel, 2000; Stumm and Morgan, 1996).

Traditional models of aquatic sediment phosphorus biogeochemistry ascribe phosphorus mobilization to release of SRP from Fe³⁺ oxides as these compounds are reduced and solubilized with the onset of low redox potentials in sediments, especially in conjunction with oxygen depletion from overlying waters (Mortimer, 1941, 1942; Kamp-Nielsen, 1974; Wetzel, 1983; Caraco et al., 1991). Summer hypolimnetic anoxic conditions should promote SRP release from bed sediments, which is then available for algal production in the photic zone during subsequent mixis. Iron release from bed sediments is also accounted for using a release rate coefficient. Eq. (A.11) in Appendix A describes the mass balance of total iron in the water column.

2.7. pH and carbonates

A final key feature of this model is the explicit incorporation of pH as a state variable. pH is computed from the equilibrium among carbonate species, i.e. carbonic acid, bicarbonate, and carbonate. Carbon dioxide enters and leaves the inorganic carbon pool via two major pathways: atmospheric and biological exchange processes. Other heterogeneous reactions such as calcium carbonate dissolution and precipitation are neglected due to the lack of significant calcium in Southeastern Piedmont systems.

A local equilibrium assumption is made because the reactions between the inorganic carbon species are much faster than the gains and losses due to atmospheric and biotic exchange (DiToro, 1976; Cai et al., 1995). Therefore Eqs. (A.12), (A.13), and (A.14) in Appendix A can be combined to yield:

\[
\frac{\partial [\text{CO}_2]}{\partial t} = K_{\text{CO}_2} ([\text{CO}_2]_{aq}) - [\text{H}_2\text{CO}_3] + \frac{5 \times 12 k_{\text{DN}}}{4 \times 14} \frac{K_{\text{NO}_3}}{K_{\text{NO}_3} + \text{DO}} [\text{NO}_3^-] - (K_e - K_i) \text{PHYT} + k_{\text{BOD}} [\text{BOD}] + k_{\text{SOM}} [\text{SOM}]
\]

(11)
where \( C_T \) is the concentration of total inorganic carbon, defined using:

\[
C_T = H_2CO_3^- + HCO_3^- + CO_3^{2-}
\] (12)

and \( CO_2(aq) \) is the concentration of dissolved carbon dioxide at saturation (mol/L), given by:

\[
[CO_2(aq)]_s = K_H P_{CO_2}
\] (13)

in which \( K_H \) is Henry’s constant and \( P_{CO_2} \) is the partial pressure of \( CO_2 \) (atm). At standard conditions (1 atm, 25 °C), \( pK_H = -1.47 \). The \( \Theta_i \) terms represent temperature-dependent constants, discussed below.

Eq. (11) allows computation of the dynamics of total inorganic carbon, used to solve for the four unknowns (each time step). Eqs. (12), (14), (16), and (17) are then used to solve for the four unknowns. Consider, therefore, the alkalinity (\( A_c \)) reaction given as:

\[
A_c = HCO_3^- + 2CO_3^{2-} + OH^- - H^+
\] (14)

A differential equation for the alkalinity can be assembled as:

\[
\frac{\partial A_c}{\partial t} = \frac{18 \times 1}{106 \times 12} (K_a - K_r) \text{PHYT} - \frac{2}{14} K_{NIT} \Theta_{NIT} \left( \frac{\text{DO}}{K_{NIT} + \text{DO}} \right) [\text{NH}_4]/f(pH)
\] (15)

where \( K_1 \) is the equilibrium constant for dissociation of carbonic acid, and \( K_2 \) is the equilibrium constant for bicarbonate dissociation. At standard conditions, \( pK_1 = -6.35 \) and \( pK_2 = -10.33 \) (Langmuir, 1997).

The method of solving for the carbonate species is to dynamically recompute the total inorganic carbon, \( C_T \), and alkalinity, \( A_c \), by first using Eqs. (11) and (15) at each time step. Eqs. (12), (14), (16), and (17) are then used to solve for the four unknowns \( (H^+, H_2CO_3^-, HCO_3^-, \text{ and } CO_3^{2-}) \) at each time step using:

\[
[H^+] = \frac{K_1}{2(1 - \alpha)} \left( 1 - \sqrt{1 - 4K_2(1 - 2\alpha)/K_1(1 - \alpha)^2} \right)
\] (18)

\[
[H_2CO_3^+] = \frac{C_T[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}
\] (19)

\[
[HCO_3^-] = \frac{C_TK_1[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}
\] (20)

\[
[CO_3^{2-}] = \frac{C_TK_1K_2[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}
\] (21)

where \( \alpha = C_T/A_c \).

2.8. Temperature effects

Henry’s constant, \( K_{HI} \), the equilibrium constants, \( K_1 \) and \( K_2 \), and many other reactions are affected by temperature. The relationship between equilibrium constant and temperature is given by the van’t Hoff equation (Atkins, 1998):

\[
\frac{d(ln K)}{dT} = \frac{\Delta H^o}{RT^2}
\] (22)

where \( K \) is an equilibrium constant, \( T \) is temperature, \( R \) is the universal gas constant, and \( \Delta H^o \) is the reaction enthalpy at standard conditions. The van’t Hoff equation is easily integrated if \( \Delta H^o \) is a constant and independent of temperature:

\[
\ln K_{T_2} - \ln K_{T_1} = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\] (23)

\( \Delta H^o \) can be calculated using:

\[
\Delta H^o = \sum \nu H_i^o(\text{products}) - \sum \nu H_i^o(\text{reactants})
\] (24)

The terms on the right-hand side are the standard formation enthalpies of the products and reactants weighted by the stoichiometric coefficients, \( \nu \), in the chemical equation. The standard formation enthalpies of the considered species are shown in Table 1. From the known values of \( K_{HI} \), \( K_1 \) and \( K_2 \) under standard conditions, Eqs. (23) and (24) can be used to give \( K_{HI} \), \( K_1 \) and \( K_2 \) at different temperatures.

A second thermal effect is accounted for by using temperature-dependent coefficients, \( \Theta_s \), such that:

<table>
<thead>
<tr>
<th>Species</th>
<th>( H_i^o ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2) (g)</td>
<td>-393.51</td>
</tr>
<tr>
<td>CO(_2) (aq)</td>
<td>-413.80</td>
</tr>
<tr>
<td>H(_2)CO(_3)</td>
<td>-699.65</td>
</tr>
<tr>
<td>HCO(_3)</td>
<td>-691.99</td>
</tr>
<tr>
<td>( CO_3^{2-} )</td>
<td>-677.14</td>
</tr>
<tr>
<td>( H_2O )</td>
<td>-285.83</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>-229.99</td>
</tr>
<tr>
<td>( H^+ )</td>
<td>0</td>
</tr>
</tbody>
</table>
Throughout the following presentation, any use of the $\Theta_i$ coefficients implicitly incorporates this functional form.

3. Field experiments

Data were collected over a 95-day period (August 12 through November 14, 1998) from an impounded aquaculture pond (33.8873°N, 83.3517°W) located within the Whitehall Experimental Forest of the Warnell School of Forest Resources, near the campus of the University of Georgia in Athens, Georgia. The pond has an average depth of about 1 m, a fluid volume of some 7000 m$^3$ and a surface area of approximately 0.7 ha. Surface inflows to the pond are from a first-order perennial stream that drains wildlife pens and woodlots on the experimental forest. Water depths in the pond vary between a minimum of 0.5 m near its headwater and a maximum of 2 m near the dam.

Three nutrient-enrichment experiments were conducted using applications of 8 L of a commercially available $11\text{e}^{37\text{e}^0}(\text{N\text{e}P\text{e}K)$ liquid ammonium hypophosphate fertilizer. The dates of the experiments were August 21, September 13, and October 24, 1998. The pond was treated with a lime addition a few days prior to the first fertilization, approximately 25 days before the second fertilization.

The University of Georgia’s Environmental Process Control Laboratory (EPCL) was deployed onsite for automated sampling in real time of a comprehensive suite of variables (Liu, 2000): ammonium-N ($\text{NH}_4$); total oxidized nitrogen (TON), which is the sum of nitrite-N ($\text{NO}_2$) plus nitrate-N ($\text{NO}_3$); total oxidizable carbon (TOC); orthophosphate-P ($\text{PO}_4$); Chlorophyll-$a$ (Ch$_a$); dissolved oxygen (DO); and temperature ($T$). The real-time monitoring capability of the EPCL is useful in High-Performance Integrated Control (H-PIC) in intensively developing urban watersheds (Beck, 2005). Additional information can be obtained from our website at http://www.modeling.uga.edu/epcl/.

Construction of the EPCL was by Minworth Systems Limited (now part of Capital Controls). Most of the instrumentation, which includes two on-line respirometers (not used in this study), are products of Minworth Systems Limited, except for the TOC monitor (Pollution and Process Monitoring Protoc Model 100) and the Chlorophyll-$a$ monitor (Turner 10-AU Fluorometer). The monitors are housed in two mobile trailers, each of which is capable of receiving continuous-flow streams of pumped samples from up to three locations around the pond. Typically, samples from these streams are automatically analyzed at 15-min intervals. On this occasion sample streams were pumped from two locations within the pond: EPCL Intake 1 was stationed by the dam at a depth of 0.5 m, while EPCL Intake 2 was attached to a platform at the upstream end of the pond, also at a depth of 0.5 m (Fig. 2).

In addition, two Hydrolab multi-parameter sondes were used to monitor oxidation–reduction potential (ORP), pH, specific conductivity, photosynthetically active radiation (PAR), dissolved oxygen (DO) and temperature ($T$). These data were also collected at 15-min intervals at the EPCL intake locations (Fig. 2). Rainfall and pond stage were monitored using a data-logger connected to a tipping bucket and a pressure transducer, respectively.

The observed three-month record of pond behavior suffers from the usual difficulties of gaps over certain periods of time. While such difficulties are not insurmountable, and effective methods of interpolation and signal processing are available (Young, 1998; Beck and Lin, 2003), our preference was to select two uncompromised, complete sub-blocks of the raw data record for model evaluation, as follows: (i) September 14–24, just after the second fertilization, for model parameterization; (ii) October 25–November 6, just after the third fertilization, was then available for model evaluation — or validation, as it might be more familiarly known (Beck, 2002). It is important to note here that there was some production of duckweed on the pond surface during the model parameterization period, and the duckweed was removed at the end of September, i.e. some 25 days before the start of the evaluation period.

Time-series of the input (forcing) functions of the model, primarily PAR and water temperature, are shown in Fig. 3. For the two chosen periods, inflow and outflow of the pond were small (a sustained drought began in
Georgia in the Spring of 1998); input tributary loadings and outflows of the various state variables in the model were therefore considered negligible. Where observations were available for a given state variable, e.g. ammonium, initial conditions were determined from data.

Quality assurance procedures for the EPCL instrumentation, including calibration procedures (which are implemented automatically), can be found in Liu (2000). There were four generic components for ensuring the EPCL and its ancillary equipment performed reliably: (1) testing using standard solutions (e.g. orthophosphate concentration) supplied automatically to the monitor at regular intervals (e.g. daily); (2) accompanying automatic testing of the transmission of light through a sample cell under unambiguously defined optical conditions, i.e. no sample in cell, or cell entirely obscured; (3) comparisons with standard methods of laboratory analysis and (4) daily visual inspection of recorded signal patterns during a calibration cycle for each instrument. Where instruments are designed to utilize automated chemical methods of analysis, such as color development by titration, these methods follow standard methods of analysis. Turner fluorometers and Hydrolab multi-parameter sondes were checked and calibrated on a weekly basis according to their respective manufacturer’s specifications.

We note that subsequent manipulations of the pond were undertaken over a six-month period in 2000, primarily to test hypotheses regarding the role of Piedmont sediment in phosphorus cycling (Parker, 2004). This equally comprehensive data set has been the subject of studies in the application of advanced signal processing algorithms for identification of a model of diurnal interactions amongst Cha, DO, pH, and PAR (Lin, 2003; Beck and Lin, 2003; Lin and Beck, in press).

4. Model parameterization

Model parameterization normally encompasses the estimation of the optimal values of model parameters as well as initial values of the unobserved state variables (Beck et al., 1993). These parameters and initial states have been compiled in Table 2. At first glance, the multitude of model parameters seems to imply a large degree of freedom when fitting the observed data, leading to the inability to uniquely identify the best combination of parameter values that fit the observed data (Beck, 1987). To overcome this issue, we used the controlled random search (CRS) procedure (Price, 1979; Klepper et al., 1991) for model parameterization.

CRS is a Monte Carlo sampling-based method to efficiently calibrate a model and investigate identifiability of the model. A well-identified model is seen as a model with process parameters that lie within a relatively small region of the parameter space. A model lacking of identifiability can result in feasible model parameterizations over a wide range of the parameter space which produce equally or near equally good fits to the observed data (Beck, 1987; Beck et al., 1993). The objective of CRS is to search for sub-regions of the parameter domain that contain the best-fitting parameter values, and eventually converge an ensemble of randomly generated parameter vectors onto the global optimum parameter vector. As shown in Table 3, CRS starts with a Monte Carlo simulation, and

![Figure 3](image-url)  
**Fig. 3.** Measured photosynthetically active radiation (PAR) and temperature during Fall 1998. The pond was stimulated using 14 L of liquid fertilizer (11–37–0, N–P–K) on August 21 (not shown), September 13, and October 24, 1998.
Table 2
Model parameters and values

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
<th>Assigned</th>
<th>Parameterization</th>
<th>Evaluation</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Min</td>
<td>Max</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>Suspended sediment</td>
<td>mg/L</td>
<td>2</td>
<td>10</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>SOM</td>
<td>Sediment organic matter</td>
<td>mg(C)/L</td>
<td>0</td>
<td>10</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>cBOD</td>
<td>Dissolved BOD</td>
<td>frac. of total</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cON</td>
<td>Dissolved organic nitrogen</td>
<td>frac. of total</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cOP</td>
<td>Dissolved organic phosphorus</td>
<td>frac. of total</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dw</td>
<td>Water column depth</td>
<td>m</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qout</td>
<td>Impoundment outflow</td>
<td>m³/d</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Impoundment water volume</td>
<td>m³</td>
<td>7000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fON</td>
<td>Dead algae recycled to dissolved ON</td>
<td>frac. of total</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fOP</td>
<td>Dead algae recycled to dissolved OP</td>
<td>frac. of total</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iₘₐₓ</td>
<td>Light intensity for algal maximum growth</td>
<td>kJ/m²/h</td>
<td>400</td>
<td>1200</td>
<td>900</td>
<td>550</td>
</tr>
<tr>
<td>k₇ₐₜₖₖ</td>
<td>Maximum algal growth rate</td>
<td>1/d</td>
<td>1</td>
<td>3</td>
<td>1.70</td>
<td>(3),(8)</td>
</tr>
<tr>
<td>k₈ₐₜₖₖ</td>
<td>Maximum algal respiration rate</td>
<td>1/d</td>
<td>0.10</td>
<td>0.40</td>
<td>0.24</td>
<td>0.18</td>
</tr>
<tr>
<td>k₉ₐₜₖₖ</td>
<td>Algal death rate</td>
<td>1/d</td>
<td>0.00</td>
<td>0.10</td>
<td>0.04</td>
<td>(2),(3)</td>
</tr>
<tr>
<td>SOD</td>
<td>Sediment oxygen demand</td>
<td>g(O₂)/m³/d</td>
<td>0</td>
<td>1</td>
<td>0.5</td>
<td>(2)</td>
</tr>
<tr>
<td>kCO₂</td>
<td>CO₂ atmospheric exchange rate</td>
<td>1/d</td>
<td>0.40</td>
<td></td>
<td></td>
<td>(5),(10)</td>
</tr>
<tr>
<td>kO₂</td>
<td>O₂ atmospheric exchange rate</td>
<td>1/d</td>
<td>0.20</td>
<td></td>
<td></td>
<td>(2)</td>
</tr>
<tr>
<td>kBOD</td>
<td>BOD decay rate</td>
<td>1/d</td>
<td>0.10</td>
<td></td>
<td></td>
<td>(2)</td>
</tr>
<tr>
<td>kSOM</td>
<td>SOM decay rate</td>
<td>1/d</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kDN</td>
<td>Denitrification rate</td>
<td>1/d</td>
<td>0.10</td>
<td></td>
<td></td>
<td>(4)</td>
</tr>
<tr>
<td>kNI</td>
<td>Nitrification rate</td>
<td>1/d</td>
<td>0.10</td>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>kON</td>
<td>Organic N mineralization rate</td>
<td>1/d</td>
<td>0.10</td>
<td></td>
<td></td>
<td>(1),(3)</td>
</tr>
<tr>
<td>kOP</td>
<td>Organic P mineralization rate</td>
<td>1/d</td>
<td>0.10</td>
<td></td>
<td></td>
<td>(1),(3)</td>
</tr>
<tr>
<td>SFe</td>
<td>Iron release rate</td>
<td>g(Fe)/m³/d</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kₐₗ₉</td>
<td>Algal growth: carbon</td>
<td>mg(C)/L</td>
<td>0.70</td>
<td></td>
<td></td>
<td>(2)</td>
</tr>
<tr>
<td>kₐ₊</td>
<td>Algal growth: nitrogen</td>
<td>mg(N)/L</td>
<td>0.1</td>
<td>0.4</td>
<td>0.27</td>
<td>(2)</td>
</tr>
<tr>
<td>kₐ₎₉</td>
<td>Algal growth: phosphorus</td>
<td>mg(P)/L</td>
<td>0.05</td>
<td>0.15</td>
<td>0.10</td>
<td>(2)</td>
</tr>
<tr>
<td>kₐ₅₉</td>
<td>Nitrification</td>
<td>mg(O₂)/L</td>
<td>2</td>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>kₐ₉₉</td>
<td>Denitrification</td>
<td>mg(O₂)/L</td>
<td>0.10</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>k₉₉₉₉</td>
<td>Nitrogen mineralization constant</td>
<td>µg(N)/L</td>
<td>25</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>k₉₉₉₉</td>
<td>Carbon mineralization constant</td>
<td>mg(C)/L</td>
<td>1.00</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>kₚ₉</td>
<td>Phosphorus</td>
<td></td>
<td>0.00</td>
<td>0.10</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>kₙ₉</td>
<td>Ammonium</td>
<td></td>
<td>0.20</td>
<td>0.60</td>
<td>0.48</td>
<td>0.20</td>
</tr>
<tr>
<td>uₐ₉</td>
<td>Algae</td>
<td>m/d</td>
<td>0.20</td>
<td>0.20</td>
<td>0.10</td>
<td>(4)</td>
</tr>
<tr>
<td>u₉₉₉₉</td>
<td>Organic matter</td>
<td>m/d</td>
<td>0.20</td>
<td></td>
<td></td>
<td>(5)</td>
</tr>
<tr>
<td>u₉₉₉₉</td>
<td>Iron</td>
<td>m/d</td>
<td>0.10</td>
<td></td>
<td></td>
<td>(5)</td>
</tr>
<tr>
<td>u₉₉₉₉</td>
<td>Sediment</td>
<td>m/d</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>θₐ₉</td>
<td>Algal growth</td>
<td></td>
<td>1.047</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>θ₉₉₉₉</td>
<td>BOD</td>
<td></td>
<td>1.047</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>θ₉₉₉₉</td>
<td>Nitrification</td>
<td></td>
<td>1.080</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>θ₉₉₉₉</td>
<td>Denitrification</td>
<td></td>
<td>1.045</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>θ₉₉₉₉</td>
<td>Iron release</td>
<td></td>
<td>1.080</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>θ₉₉₉₉</td>
<td>Organic N mineralization</td>
<td></td>
<td>1.080</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>θ₉₉₉₉</td>
<td>Organic P mineralization</td>
<td></td>
<td>1.080</td>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>θ₉₉₉₉</td>
<td>SOD</td>
<td></td>
<td>1.080</td>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>θ₉₉₉₉</td>
<td>SOM</td>
<td></td>
<td>1.080</td>
<td></td>
<td></td>
<td>(5)</td>
</tr>
</tbody>
</table>

Parameterization of values constrained to indicated range. Evaluation value indicates that a different value used during evaluation period. Sources of information: (M) measured; (1) Ambrose et al., 1993; (2) Chen and Orlob, 1975; (3) Bowie et al., 1985; (4) DiToro and Matystik, 1980; (5) Cole and Buchak, 1995; (6) Lehman et al., 1975; (7) Canale et al., 1976; (8) O'Connor et al., 1976; (9) Larsen et al., 1974; (10) Stumm and Morgan, 1981.
computes the mean value of each constituent parameter in the vector \( \mathbf{q} \), \( i = 1, \ldots, Q \), where \( Q \gg p \).

4. Select a subset of \((p + 1)\) of the candidate parameters at random from the initial set of \( Q \) candidates, i.e., a set of vectors \( \{ \mathbf{a}^1, \mathbf{a}^2, \ldots, \mathbf{a}^{p+1} \} \).

5. Compute the mean value of each constituent parameter in the vector \( \mathbf{a}^i \): \( \bar{a}_i = \frac{1}{p} \sum_{j=1}^{p} a_{ij} \) for parameter \( j \).

6. Generate a new candidate value of the parameter vector \( \mathbf{a} \) using the centroid of the \( (p + 1) \) candidate vectors chosen from the \((p + 1)\) subset:
   \[ a_{ij} = 2 \bar{a}_i - a_{ij}^{p+1}. \]

7. Substitute the newly generated parameter vector \( \mathbf{a}^{p+1} \) into the model and compute the objective function \( J^p + 1 \):
   - If \( J^p + 1 < \max J^i \) for \( i = 1, \ldots, Q \), then:
     - (a) Substitute the parameter vector \( \mathbf{a}^{p+1} \) for the vector \( \mathbf{a}^i \) which generates the worst match.
     - (b) Return to Step 4.
   - If \( \max J^i > C \times \min J^i \) for \( C \in [1.05, 1.10] \), then return to Step 4.

8. Search completed.

Calculates a goodness-of-fit value or objective function for each simulation. CRS iteratively updates a stored set of randomly selected parameter vectors, by searching for and substituting a new trial parameter vector that better fits the model to available data. The trial vector is obtained by reflecting the centroid of a subset of the current set of parameter vectors about another stored parameter vector. The iteration stops when a specified minimum objective function is achieved, or until no better trial vectors can be generated.

One aim of this study is to investigate effects of sediment–nutrient interactions. Therefore, initial conditions for the unobserved states of suspended sediment and sediment organic matter were obtained by model parameterization. Initial conditions for other unobserved states were estimated mainly based on monitoring results from Lake Lanier with trial-and-error experimentation during parameterization. For the evaluation period, initial conditions for the unobserved states were primarily based on the simulated results at the end of the parameterization period.

Diurnal variations of DO and pH are presumably dominated by algal photosynthesis and respiration. The model parameters which represent the processes of algal dynamics were calibrated using the CRS. These parameters include algal maximum growth rate \( (K_g) \), algal maximum respiration rate \( (K_r) \), algal mortality rate \( (K_d) \), algal settling rate \( (\omega_s) \), optimal light intensity for algal growth \( (I) \), nitrogen half-saturation constant \( (k_N) \) for algal growth, and phosphorus half-saturation constant \( (k_P) \) for algal growth.

In addition to these parameters, sediment oxygen demand rate and sediment–nutrient adsorption coefficients for ammonium and orthophosphate were also calibrated using the CRS for the purpose of investigating effects of sediment–nutrient interactions and bed sediments. The sampling domain of the selected model parameters and initial values of the unobserved states are listed in Table 2. The boundaries were set wide enough such that any possible behavioral parameter combination is simulated.

Fig. 4 shows the parameter space for the selected parameters determined by the CRS for the parameterization period. The figure shows that the set of selected parameters satisfying the objective function are distributed as clusters of values (or zones in parameter space). The objective function of CRS is the sum of weighted square errors of mismatch between simulated and observed output responses, including phytoplankton biomass, dissolved oxygen, pH, ammonium, and orthophosphate. The weighting coefficients were chosen according to the relative scales of the selected state variables for model parameterization. The apparent clustering of acceptable estimates within the feasible parameter space indicates the model is relatively well identifiable in terms of the selected parameters.

Final estimates of the model parameters so obtained are also summarized in Table 2, with the performance of the model for the first sub-block of the observed record being shown in Figs. 5 and 6. Likewise, model performance over the second sub-block (the evaluation period) is demonstrated in Figs. 7 and 8. The data shown in these figures are from EPCL Intake 1, near the pond dam. The water depth at EPCL Intake 2 was about 0.8 m, which was too shallow to simulate settling processes, because the average water depth was assumed as 1.0 m in the model.

5. Model evaluation

We now examine how well our parameterized model reproduces the response of the aquaculture pond to two fertilization experiments. It is important to note that despite the relatively comprehensive coverage of the data available, our model includes a larger set of state variables than were actually observed in the field. Thus, model performance focuses on our ability to reproduce
Fig. 4. CRS parameter space showing scatterplots between selected parameters.

Fig. 5. Simulated results of observed state variables during the parameterization period.
Fig. 6. Simulated results of unobserved state variables during the parameterization period.

Fig. 7. Simulated results of observed state variables during the evaluation period.
a primary set of observed variables, as well as predictions for a secondary set of unobserved variables.

The logical consequences of the rather generic model structure — calibrated to the specific observed behavior of the aquaculture pond — can also be examined in the context of this secondary cluster of unobserved variables. Finally, the accompanying, implied behavior of a third cluster of (unobserved) variables having to do with features of the bed sediment, is then presented, with a view to establishing preliminary thinking about the application of our generic model in the setting of Lake Lanier.

5.1. Primary cluster of observed states

Parameterization of the model was governed essentially by a primary cluster of observed variables — dissolved oxygen, pH, phytoplankton biomass, orthophosphate-P, ammonium-N, and nitrate-N. The ability to calibrate the model using observed versus modeled pH values added a measure of confidence to our model because pH is highly sensitive to many processes, and a correct interpretation of model structure and parameterization is more likely if the model pH closely matches observations.

Simulated diurnal variations of DO and pH over both the parameterization and evaluation periods are reasonable (Fig. 5b,c, and Fig. 7b,c). This is to be expected, since this was our primary goal. We know that under these particular field conditions phytoplankton metabolism dynamics should dominate what is observed in the DO and pH records. It is therefore crucial to have some confidence in the behavior of the phytoplankton biomass, evidence for which is available in Fig. 5a and Fig. 7a, where variations in the accompanying model state variable are compared with observed variations in phytoplankton biomass.

Table 4 is a statistical summary of simulated and observed results for the primary cluster of state variables. It is fair to conclude that the general trends of the observed and estimated quantities are unbiased.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Calibration</th>
<th>Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$</td>
<td>$r^2$</td>
</tr>
<tr>
<td>PHYT</td>
<td>0.99</td>
<td>0.92</td>
</tr>
<tr>
<td>DO</td>
<td>0.99</td>
<td>0.84</td>
</tr>
<tr>
<td>pH</td>
<td>1.00</td>
<td>0.78</td>
</tr>
<tr>
<td>PO₄</td>
<td>0.97</td>
<td>0.82</td>
</tr>
<tr>
<td>NH₄</td>
<td>0.91</td>
<td>0.93</td>
</tr>
<tr>
<td>NO₃</td>
<td>1.01</td>
<td>0.10</td>
</tr>
</tbody>
</table>

$A$ is the coefficient in the linear equation $y = Ax$, where $x$ and $y$ are observed and simulated results, respectively.
over both periods, and that for both the parameterization and evaluation periods the relative amplitudes of the diurnal oscillations in simulated and observed phytoplankton biomasses are comparable when the observed biomass is greater than about 2.0 mg/L. The two observed segments of phytoplankton exhibit no diurnal variation below this level. During the evaluation period, the observed pH is close to 7, the model underestimates oscillations in pH, although the simulated phytoplankton biomass has significant diurnal oscillations. This may result from higher buffering capacity during the evaluation period than the calibration period.

Quantifying the dynamics of an algal bloom is notoriously difficult (Harris, 1980). One can speculate that this might be a function of assuming, erroneously, invariant maximum specific algal growth and respiration rates — erroneous because a change in species dominance may even occur over a short period (Reynolds, 1984; Steel, 1995). Blue-green and green algae are capable of cell division several times a day, given the relatively elevated temperature and nutrient conditions of the pond. Over the evaluation period, as Table 2 shows, it proved necessary to change the value of the phytoplankton respiration rate constant, as well as the optimal light intensity for algal growth, in order to fit the trend of the observed phytoplankton. Phytoplankton may adjust their chlorophyll composition to adapt to the changes in solar radiation, and the optimal light intensity varies for different phytoplankton groups (Jin et al., 1998). While there are other approaches to address the issue, such as including different phytoplankton functional groups as state variables (Cole and Wells, 2000) or adopting a dynamic structural approach that allows for adaptation and predicts changes in parameter values over time (Zhang et al., 2004), it would be more difficult to verify the model’s identifiability due to the dramatically increased number of model parameters.

There are several basic issues related to matching the performance of the model for the primary cluster of associated variables — PAR, DO, pH, and phytoplankton biomass — with respect to the general trend and diurnal variation of the data. Application of the model, in the context of Lake Lanier, will be such that diurnal variability does not need to be simulated (Zeng, 2001). Yet it is possible to extract information about the system using the light and dark cycles of photosynthesis and the subtleties associated with the relative phasing of diurnal cycles in the foregoing primary variables and nutrient concentrations. Subsequent observations of the pond’s behavior, under similar manipulations, were analyzed in just this manner during 2000, which was a similarly dry year (Lin, 2003).

Both simulated and observed orthophosphate results declined exponentially in the days and weeks after the fertilization in both the parameterization and evaluation periods (Fig. 5d and Fig. 7d). This results from adsorption of the orthophosphate-P onto sediment particles and its subsequent removal from the water column by particulate settling. A Langmuir isotherm describes adsorption in the model, but since orthophosphate concentrations in fresh waters are generally low, only the linear region of the isotherm is utilized, with an appropriate adsorption coefficient \( P_P \) (Eq. (A.10) in Appendix A). As sediments decline exponentially (in the model) due to settling (Fig. 6c and Fig. 8c), the decline of orthophosphate has a trend similar to that of the simulated suspended sediments concentration (for which the initial concentration in the parameterization period was determined by the CRS due to a lack of observations). However, this dominant removal mechanism is not likely to be the case in Lake Lanier, which is subject to continuous inputs of sediments from its tributaries.

Observed ammonium concentrations decline more quickly during the parameterization period (Fig. 5e) than during the evaluation period (Fig. 7e). We argue that this could result from different cation exchange capacities (CEC) for the two periods, as follows. According to Sparks (1995), soil minerals can exhibit two types of charge: one that is constant, while the other is variable, in particular, pH-dependent. Elevated pH would increase CEC on the clays (aluminum silicates, etc.) to allow for greater sorption of ammonium. Most soils have this combination of properties. The variable-charge component changes with pH, due to protonation and deprotonation of functional groups on inorganic soil minerals, such as kaolinite, amorphous materials, metal oxides, oxyhydroxides, hydroxides, layer silicates coated with metal oxides, and soil organic matter. As a result, soils with a high pH have a high CEC. Such a dependence accords with our observations: over the parameterization period pH is much higher (8.2 < pH < 9.4) than for the evaluation period (when it is pH ≈ 7.2), suggesting, therefore, that soil particulates in the aquaculture pond during the former should have a higher CEC, hence a greater capacity to adsorb ammonium ions. In the current structure of our model the process of adsorption is assumed to be independent of pH variations. However, if we relax this constraint, by allowing a different value for the adsorption coefficient of ammonium with suspended sediments to obtain over the evaluation period, the match of simulated versus observed ammonium variations of Fig. 7e is readily achieved (see also Table 2).

While the elevated pH would increase CEC in the parameterization period, the anion exchange capacity (AEC) for the same time step would be reduced because the charge balance must be maintained. Thus, there would be a reduced binding of P to the metals and/or clays, due to the change in the surface charge allowing greater sorption of cations (i.e. ammonium) than anions.
being present in
sustaining continued algal growth, especially during
consequence in the model is for nitrate-N to be taken up
ammonium monitor’s detection limits
the parameterization period
ammonium-N drops rapidly in the first two days of
nitrification of the ammonia. Both simulated and
model does not simulate such a removal of nitrate.
period offsets the influences of P
desorption under elevated pH conditions.
the parameterization
and ammonium results, it is important to note that
with PAR as the driving force, the logic of the model
demands that both phytoplankton biomass and nutrient
concentrations oscillate diurnally. The phytoplankton
observations show such fluctuations. The observed
nutrient concentrations, especially ammonium and
orthophosphate, show some oscillations during both
periods of analysis. In addition, the oscillation ampli-
tudes of these nutrients generally conform to those of
the phytoplankton observations, except that the ammo-
nium concentration falls below the instrument’s level of
detection. Nutrient uptake and release from phyto-
plankton photosynthesis and respiration are relatively
low when compared with the high nutrient background
concentrations in the manipulated pond. The diurnal
oscillations in the ammonium and orthophosphate
observations are therefore not as significant as those in
the phytoplankton observations.
Simulated and observed variations of nitrate concen-
trations differ over the parameterization and evaluation
periods, with a slight increase over the former (Fig. 5f)
yet a significant increase over the latter (Fig. 7f).
Observations of total oxidized nitrogen, and indeed
the separation of this into its nitrite and nitrate
constituents, are available. In the model, phytoplank-
tons are defined to have a preference for assimilating
ammonium-N over nitrate-N (Eq. (10)). Thus, when
ammonium-N drops rapidly in the first two days of
the parameterization period — in fact, to below the
ammonium monitor’s detection limits — the logical
consequence in the model is for nitrate-N to be taken up
in sustaining continued algal growth, especially during
the peak in the bloom. In contrast, with ammonium
being present in excess
over the evaluation period, the
model does not simulate such a removal of nitrate.
Instead, the increase in simulated nitrate is the result
of nitrification of the ammonia. Both simulated and
observed nitrate concentrations support the assumption
that phytoplankton have a preference for assimilating
ammonium-N over nitrate-N, otherwise significant
increase of nitrate concentrations during the evaluation
period would not occur.

5.2. Secondary cluster of unobserved states

Biochemical oxygen demand (BOD) is mainly affected
by phytoplankton death, oxidation, and organic matter
settling. During both periods of parameterization and
evaluation, simulated and observed BOD concentra-
tions (Fig. 6a and Fig. 8a) show a general trend of slight
decline. This may result from relatively higher loss due
to oxidation and organic matter settling than the source
produced as a result of phytoplankton death in the
system. The fact that the observed total oxidizable
carbon (TOC) oscillates diurnally, especially over the
period of evaluation (Fig. 8a), while the simulated BOD
does not oscillate diurnally, could merit further in-
vestigation, although TOC is a measure differing
significantly from that of BOD.

In natural waters, carbonic acid is theoretically very
low in concentration when pH > 8 (as it is over the
parameterization period; Fig. 5b), while carbonate
concentration is very low when pH < 8, as during the
evaluation period (Fig. 7b). Bicarbonate is the major
component of total inorganic carbon in natural waters
(Fig. 6b and Fig. 8b). In other words, in the absence
of observations for these species, Fig. 6b and Fig. 8b
merely show the logical consequences of the assumed
prior theory, albeit modulated by parameterization of
the model to the given pH conditions. During the last
two days of the parameterization period, carbonate
concentration is low, yet the concentration of carbonic
acid is relatively high, because of a relatively low pH.
At this point, following the crash of the algal bloom,
respiration generally exceeds photosynthesis and the
resulting production of excessive CO₂ lowers the pH.
The behavior of organic nitrogen and organic
phosphorus in the model are subject to similar process
mechanisms. Both components are affected by the
recycling of living organic material to non-living organic
matter, as phytoplankton respires and dies. They are
also influenced by organic matter mineralization and
organic matter settling. Simulated results of organic
5.3. Loading scenarios

The previous analysis focused on internal (autochthonous) biogeochemical cycling, and ignores external (allochthonous) inputs. Allochthonous sediment and nutrient loading to the aquaculture pond — especially from watershed inputs — were negligible during the analysis period. A hypothetical loading is now presented that demonstrates watershed loading effects. The objective of this exercise is to provide a perspective for managing other systems dominated by external loading — such as our eventual target system, Lake Lanier. External loadings can be estimated and managed using a wide range of tools (Zeng and Rasmussen, 2001; Gömann et al., 2005; Turpin et al., 2005; Zhang and Jørgensen, 2005). Assessing the impacts of these loadings on lake water quality is an important management requirement.

To demonstrate the difference between with and without external loadings, our synthetic experiment assumes a steady inflow and outflow of 0.01 m³ s⁻¹ during the parameterization period. Inflow concentrations are 50 mg/L of suspended sediment (SS), 1 mg/L of orthophosphate (PO₄), 1 mg/L of iron (Fe), and 10 mg/L of biochemical oxygen demand (BOD). The pond pH is assumed neutral and so the sediment-ammonium adsorption coefficient was assigned to be the same as for the evaluation period (i.e. 𝑃ₙ = 0.2). For the purpose of demonstrating sediment adsorption effect on orthophosphate, PO₄ inflow concentration is assumed to be close to its initial concentration in the pond. The assumed zero inflow concentration of ammonium with reduced 𝑃ₙ coefficient can demonstrate pH effect on sediment-ammonium adsorption process. The assumed inflow concentration of BOD is used to demonstrate the dynamic effect of external organic carbon on sediment organic matter in the pond.

Fig. 9 compares the results of this experiment with and without external loadings, with increased concentrations of SS, Fe, and BOD resulting from the higher influent concentrations. Yet, contrary to the other state variables, the PO₄ concentration actually decreases when external loads were increased. This is attributed to higher SS concentrations — with their attendant sorption. This is in spite of there being a continuing phosphate inflow of 1 mg/L. Elevated BOD concentrations and associated organic matter settling under the
5.4. Bed sediments: extrapolation to Lake Lanier

We now wish to provide a few prospective insights into the implications of the aquaculture pond experiments and model for Lake Lanier management of associated nutrient and sediment loadings, sediment–nutrient interactions, as well as bed sediment effects. This purpose is expected to be achieved by investigating the behaviors of suspended sediments (SS), iron (Fe), sediment oxygen demand (SOD), and sediment organic matter (SOM). There were no observations for the rate constant SOD (a model parameter) and the state variables SS, Fe, and SOM.

In the current model structure, SS is only affected by sediment settling and an exponential decline of SS is expected. Given the settling rate, the SS initial concentration is determined by the parameterization of both orthophosphate and ammonium because of its interactions (e.g. adsorption) with these nutrients. The CRS results indicate that the initial concentration of SS in the parameterization period is most likely 6 mg/L (Fig. 4c). The initial concentration of SS in the evaluation period (Fig. 8c) was set as the same value as in the parameterization period (Fig. 6c) for the purpose of examining the difference of sediment–nutrient adsorption capacity under different pH levels.

The transformation of iron and manganese are key processes in the biogeochemistry of marine and freshwater sediments (Van Cappellen and Wang, 1996). As mentioned in Section 2, the iron cycle can be coupled to phosphorus cycling in lake systems. Fe(III) oxides sorb dissolved inorganic phosphorus (DIP) via ligand exchange (Reynolds and Davies, 2000; Stumm and Morgan, 1996). These Fe(III)–phosphorus complexes can be transformed by reduction of Fe(III) ions to the more soluble Fe(II) form, which solubilizes both Fe(II) and phosphate ions (Wetzel, 2000; Stumm and Morgan, 1996).

Traditional models of aquatic sediment P biogeochemistry ascribe P mobilization to release of DIP from Fe(III) oxides as these compounds are reduced/solubilized with the onset of low redox potentials in surface sediments, especially in conjunction with oxygen depletion from overlying waters (Mortimer, 1941, 1942; Kamp-Nielsen, 1974; Wetzel, 1983; Caraco et al., 1991). However, recent cross-system comparison in Lake Lanier and other southeastern lakes failed to show a correlation between sediment DIP release and the presence or absence of bottom water anoxia (Mayhew and Mayhew, 1992; Parker, 2004; Reckhow, 1988).

Recently a hypothesis has been proposed, attributed to the iron-rich clay soils that dominate watersheds in the Southeastern United States, and observed to be present in high concentrations in surface runoff. Iron-oxide sorption reduces the bioavailability of DIP, and prevents the accumulation of DIP in the anoxic depths of lakes and reservoirs during summer stratification (Stumm and Morgan, 1996; Parker and Rasmussen, 2001; Parker, 2004). This hypothesis is believed to explain the observed pattern of phosphorus cycling in Lake Lanier better than the traditional paradigm, whereby summer anoxic conditions at the bottom of the Northern lakes promote the release of DIP from bed sediments, which is then available for algal production in the photic zone during subsequent mixis. Factor analysis on Lake Lanier water quality data by Zeng and Rasmussen (in press) lend additional support for this hypothesis.

In the current model structure, the concentration of iron in the water column is affected by settling into and release from bed sediments. There were no observations of iron in the aquaculture pond. Its initial concentration is not identifiable due to unknown release rate and dynamics. The simulated results of iron in Fig. 6c and Fig. 8c merely show the logical consequence, by adjusting iron release rate until relatively stable conditions are reached. However, given intensive observations of iron in Lake Lanier, application of the advanced computational methodology to determine iron release rate from bed sediments of the lake provides an alternative approach to test the recently proposed hypothesis. This will be our focus of application of the model, in the context of Lake Lanier.

Oxygen consumption by bed sediments can represent a large fraction of oxygen consumption in surface waters (Walker and Snodgrass, 1986). Traditional measurement techniques for oxygen consumption by bed sediments, whether they are performed in situ or in the laboratory, do not differentiate between the two processes (i.e. oxygen diffusion and oxidation of sediment organic matter) but measure, either directly or indirectly, the gross oxygen uptake. Hence in modeling dissolved oxygen, a single term in the dissolved oxygen mass balance formulation is normally used for both processes (Bowie et al., 1985; Cerco, 1989; Stefan et al., 1995; Herzfeld et al., 2001).

In our model, total oxygen consumption by bed sediments is separated into two components: sediment oxygen demand (SOD) and oxidation of sediment organic matter (SOM). The former is a rate constant which represents the oxygen diffusion process at the sediment–water interface. The latter is a state variable which reflects dynamic effects of bed sediments on dissolved oxygen in the water column.
Sediment oxygen demand (SOD) is the dissolved oxygen flux at the sediment—water interface. Fig. 4e indicates that SOD in the aquaculture pond is most likely about 0.5 g(O₂)m⁻²d⁻¹. This demonstrates that the modeling approach with advanced computational methodology makes it possible to quantify the sediment oxygen demand. Sediment organic matter (SOM) in an aquatic system is the result of the transportation and deposition of organic material. The material may be from a source outside the system such as leaf litter or wastewater particulate BOD (allochthonous) material, or it may be generated inside the system, as occurs with plant growth (autochthonous) material. The internal and external sources for SOM are included in the current model structure. The simulated results of SOM during both parameterization and evaluation periods show a general trend similar to phytoplankton biomass.

It appears that the internal cycling of SOM dominates the highly productive pond system. Unlike the aquaculture pond, however, Lake Lanier has continuous inputs of organic matter and relatively low phytoplankton productivity. Urbanization in the Lake Lanier watershed and associated increase of wastewater particulate BOD material into the lake provide an external source for SOM. Accumulation of sediment organic matter and its oxidation may explain the long-term increase of hypolimnetic dissolved oxygen deficit in Lake Lanier over the past 40 years. Reduction of organic matter entering the lake through Best Management Practices (BMP) would improve hypolimnetic water quality of the lake.

6. Summary and conclusions

A biogeochemical model is presented that predicts phytoplankton metabolism dynamics in Southeastern Piedmont impoundments. Conventional model variables (including algal photosynthesis and respiration, carbonate speciation, dissolved oxygen, and biochemical oxygen demand) are used in conjunction with an augmented set of state variables (including pH and its effects on sediment-related properties) to better identify the long-term effects of alternative watershed management strategies on regional lake ecosystems. pH is included because it interacts with other state variables and also because it facilitates the identification of the optimal model structure during model parameterization. Sediment—nutrient interactions are included because soils in Southeastern Piedmont watersheds are dominated by clay minerals which are known to bind nutrients, primarily orthophosphate and ammonium. Elevated sediments are ubiquitous because of the region’s erosive soils, high rainfall intensities, and large areas of land-disturbing activities. Also, lake sediments contain organic matter, from both allochthonous and autochthonous sources, whose accumulation and decay controls lake nutrient cycling.

Model parameterization and evaluation was performed using real-time (in situ plus onsite EPCL monitoring) water quality data from a small Southeastern Piedmont impoundment that was manipulated using a series of nutrient additions. Model parameters and the initial values of unobserved states — including water column sediments and bed sediments — were determined by the controlled random search (CRS) procedure. CRS employs a Monte Carlo technique with optimization, on the basis of comprehensive observations in the Fall 1998. Parameter values are identified based on their clustering within the CRS-determined parameter space. The outcomes of the model provide a good description of diurnal variations of phytoplankton, dissolved oxygen, pH, and nutrients of a small, manipulated Southeastern Piedmont impoundment. An initial nutrient-addition experiment was used for CRS model parameterization, while a second nutrient addition was used for CRS model evaluation. Few model parameters required modification during the evaluation stage, and these modifications can be attributed to water column changes.

Model results suggest that pH-dependent sediment—nutrient adsorption is crucial for the accurate characterization of biogeochemical cycling in the aquaculture pond, specifically orthophosphate and ammonium dynamics. Model parameterization and subsequent evaluation support our hypothesis that sediment-phosphate sorption is controlled by iron oxides that provide sites for ligand exchange. Both sediment-phosphate and sediment-ammonium adsorption are controlled by the pH-dependent charge of soils. For orthophosphate, hydroxyl ion substitution on iron oxides is the presumed mechanism, while the cation exchange capacity (CEC) is the presumed adsorption mechanism for ammonium ions. Also, simulated and observed nitrate concentrations support the assumption that phytoplankton have a preference for assimilating ammonium-N over nitrate-N.

Extrapolating our lake biogeochemical model to Lake Lanier, a regionally important impoundment serving the water supply needs of the Atlanta Metropolitan Area, indicates that sediments again affect lake biogeochemical processes, but in a different manner than the processes that affect the smaller aquaculture pond. For Lake Lanier, the accumulation of sediment organic matter and its decay can explain the long-term increase of hypolimnetic dissolved oxygen deficit in Lake Lanier over the past 40 years, and the reduction of organic matter entering the lake may improve hypolimnetic water quality of the lake. While this result cannot be confirmed without additional monitoring within the lake, it clearly suggests that sediment—nutrient interactions are an important component of lake biogeochemical cycling.
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Appendix A. Model equations

Suspended solids, SS

\[
\frac{\partial [\text{SS}]}{\partial t} = \frac{W_{\text{SS}}}{V} \frac{\omega_{\text{SS}}}{D_w} [\text{SS}] - \frac{Q_{\text{out}}}{V} [\text{SS}] 
\] (A.1)

Phytoplankton, PHYT

\[
\frac{\partial [\text{PHYT}]}{\partial t} = K_{\text{growth}} [\text{PHYT}] - K_{\text{respiration}} [\text{PHYT}] - K_{\text{death}} [\text{PHYT}] 
\] (A.2)

Sediment organic matter, SOM

\[
\frac{\partial [\text{SOM}]}{\partial t} = \frac{\omega_{\text{plankton settling}}}{D_w} [\text{PHYT}] - k_{\text{SOM decay}} [\text{SOM}] + \frac{12}{32} \frac{\omega_{\text{BOD settling}}}{D_w} (1 - c_{\text{BOD}}) [\text{BOD}] 
\] (A.3)

Dissolved oxygen, DO

\[
\frac{\partial [\text{DO}]}{\partial t} = \frac{32 \times 138}{12 \times 106} K_{\text{growth}} [\text{PHYT}] - \frac{\text{SOD}}{D_w} \Theta_{\text{SOD}} \frac{32}{12} \frac{K_{\text{respiration}}}{[\text{PHYT}]} - K_{\text{BOD}} \Theta_{\text{BOD}} [\text{BOD}] 
\] (A.4)

Carboneous biochemical oxygen demand, BOD

\[
\frac{\partial [\text{BOD}]}{\partial t} = \frac{W_{\text{BOD}}}{V} + \frac{32}{12} K_{\text{growth}} \Theta_{\text{PHYT}} - k_{\text{BOD oxidation}} [\text{BOD}] 
\] (A.5)

Organic nitrogen, ON

\[
\frac{\partial [\text{ON}]}{\partial t} = \frac{W_{\text{ON}}}{V} + \frac{16 \times 14}{106 \times 12} K_{\text{growth}} f_{\text{ON}} [\text{PHYT}] 
\] (A.6)

Nitrate nitrogen, NO₃

\[
\frac{\partial [\text{NO}_3]}{\partial t} = \frac{W_{\text{NO}_3}}{V} - \frac{Q_{\text{out}}}{V} [\text{NO}_3] 
\] (A.7)
Ammonium nitrogen, NH₄

\[
\frac{\partial [\text{NH}_4]}{\partial t} = \frac{16 \times 14}{106 \times 12} K_e (1 - f_{\text{OP}}) [\text{PHYT}] \\
+ k_{\text{ON}} \theta_{\text{ON}} \left( \frac{[\text{PHYT}]}{[\text{PHYT}] + K_{\text{mc}}} \right) [\text{ON}] \\
- k_{\text{NH}} \theta_{\text{NH}} \left( \frac{[\text{NH}_4]}{[\text{NH}_4] f(pH)} \right) \\
- \frac{16 \times 14}{106 \times 12} k_e P_{\text{NH}_4} [\text{PHYT}] \\
+ \frac{16 \times 14}{106 \times 12} k_{\text{NH},\text{NH}_4} \theta_{\text{NH}} [\text{SOM}] \frac{P_{\text{NH}_4}}{D} [\text{SS}] [\text{NH}_4] \\
- \frac{Q_{\text{out}}}{V} [\text{NH}_4] + \frac{W_{\text{NH}_4}}{V} 
\]  
(A.8)

Organic phosphorus, OP

\[
\frac{\partial [\text{OP}]}{\partial t} = \frac{W_{\text{OP}}}{V} + \frac{1 \times 31}{106 \times 12} K_e f_{\text{OP}} [\text{PHYT}] \\
- k_{\text{OP}} \theta_{\text{OP}} \left( \frac{[\text{PHYT}]}{[\text{PHYT}] + K_{\text{mc}}} \right) [\text{OP}] \\
- \frac{Q_{\text{out}}}{V} [\text{OP}] 
\]  
(A.9)

Orthophosphate, PO₄

\[
\frac{\partial [\text{PO}_4]}{\partial t} = \frac{W_{\text{PO}_4}}{V} + \frac{1 \times 31}{106 \times 12} K_e (1 - f_{\text{OP}}) [\text{PHYT}] \\
+ k_{\text{PO}} \theta_{\text{PO}} \left( \frac{[\text{PHYT}]}{[\text{PHYT}] + K_{\text{mc}}} \right) [\text{OP}] \\
- \frac{Q_{\text{out}}}{V} [\text{PO}_4] 
\]  
(A.10)

Total iron, Fe

\[
\frac{\partial [\text{Fe}]}{\partial t} = \frac{W_{\text{Fe}}}{V} + \frac{S_{\text{Fe}}}{D} \theta_{\text{Fe}} \frac{\omega_{\text{Fe}} [\text{Fe}]}{D} - \frac{Q_{\text{out}} [\text{Fe}]}{V} 
\]  
(A.11)

Carbonic acid, H₂CO₃*

\[
\frac{\partial [\text{H}_2\text{CO}_3^*]}{\partial t} = K_{\text{CO}_3} \left( [\text{CO}_2(aq)_4] - [\text{H}_2\text{CO}_3^*] \right) - K_e [\text{PHYT}] \\
+ k_e [\text{PHYT}] + k_{\text{SOM}} \theta_{\text{SOM}} [\text{SOM}] \\
+ k_{\text{BOD}} \theta_{\text{BOD}} [\text{BOD}] \\
+ 5 \times 12 \frac{4 \times 14}{K_{\text{NO}_3} [\text{DO}] + K_{\text{NO}_3}} [\text{NO}_3^-] \\
- (K_3 [\text{H}_2\text{CO}_3^*] - K_4 [\text{H}^+] [\text{HCO}_3^-]) 
\]  
(A.12)

Bicarbonate, HCO₃⁻

\[
\frac{\partial [\text{HCO}_3^-]}{\partial t} = \left( K_5 [\text{H}_2\text{CO}_3^*] - K_4 [\text{H}^+] [\text{HCO}_3^-] \right) \\
- \left( K_3 [\text{H}_2\text{CO}_3^*] - K_4 [\text{H}^+] [\text{CO}_3^{2-}] \right) 
\]  
(A.13)

Carbonate, CO₃²⁻

\[
\frac{\partial [\text{CO}_3^{2-}]}{\partial t} = K_5 [\text{HCO}_3^-] - K_6 [\text{H}^+] [\text{CO}_3^{2-}] 
\]  
(A.14)

Hydrogen ion, H⁺

\[
\frac{\partial [\text{H}^+]}{\partial t} = 18 \times 1 \left( K_3 - K_1 \right) [\text{PHYT}] \\
+ \frac{2 \times 14}{K_{\text{NH}} [\text{DO}] + K_{\text{NH}}} [\text{NH}_4] f(pH) \\
+ (K_3 [\text{H}_2\text{CO}_3^*] - K_4 [\text{H}^+] [\text{HCO}_3^-]) \\
+ (K_5 [\text{HCO}_3^-] - K_6 [\text{H}^+] [\text{CO}_3^{2-}]) 
\]  
(A.15)
Alkalinity, $A_c$

$$\frac{\partial [A_c]}{\partial t} = \frac{18 \times 1}{106 \times 12} (K_f - K_e) [\text{PHYT}]$$

net production

$$-\frac{2}{14} K_{\text{NIT}} (\frac{[\text{DO}]}{[\text{DO}] + K_{\text{NIT}}}) [\text{NH}_4] f(\text{pH})$$

(A.16)

nitrification

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