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Determination of biogeochemical parameters in eutrophication models with simultaneous dynamic optimization approaches

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ABSTRACT

This work addresses a parameter estimation problem in an ecological water quality model through a simultaneous dynamic optimization approach. The model is based on first principles and has a large number of parameters, which must be estimated based on data collected in the water body under study. Gradients of state variables are considered along the water column, rendering a partial differential equation problem, which is transformed into a differential algebraic (DAE) one by spatial discretization in several water layers. Within a simultaneous approach, the DAE constrained optimization problem is transformed into a large-scale nonlinear programming problem, with a weighted least squares objective function. Main biogeochemical parameters have been obtained, which allow a close representation of the lake dynamics, as it is shown in the numerical results.

1. Introduction

The increasing download of nutrients into lakes, rivers and costal zones throughout the world, mainly due to agricultural and industrial activities, have intensified eutrophication of water bodies, which has in turn increased the need for predictive ecological water quality modeling. Eutrophication models provide a representation of major physical, chemical and biological processes that affect the biomass of phytoplankton and nutrients. Based on first principles, they represent ecological processes through a set of complex nonlinear partial differential algebraic equations, with rate coefficients that require estimation to suit site-specific environment.

The parameter estimation problem in hybrid ecological water quality model has been addressed through different approaches. The traditional approach has been the iterative calibration of parameters by trial and error adjustment of the most important parameters derived from a sensitivity analysis (Scavia, 1980; Schladow & Hamilton, 1997). Hamilton and Schladow (1997) developed a combined hydrodynamic and ecological model (DYSREM) and they estimated main parameters through a trial and error procedure.

Shen and Kuo (1996, 1998) used the variational method for estimating the unknown kinetic parameters for an estuarine eutrophication model. This method requires running both the forward and the adjoint models in each iteration, regardless of the number of parameters to be estimated. They proposed the use of a pre-conditioner to improve ill-conditioning of the Hessian matrix. However, determination of the pre-conditioner is not trivial and the application of the variational method requires extensive model coding. Omlin, Brun, and Reitchert (2001) and Omlin, Reitchert, and Forster (2001) developed a biogeochemical model for a lake within program AQUASIM (Reichert, 1994, 1998). In this program, parameter estimation is performed by minimizing a least squares objective function. Partial derivative equations are transformed into differential equations by spatial discretization along the water column. The resulting differential algebraic system is integrated in time by applying the Backward Differentiation Formulae within DASSL (Ascher & Petzold, 1998), coupled to the Simplex (Nelder & Mead, 1965) and/or the secant method (Ralston & Jennrich, 1978). Based on the availability of observed data, Omlin et al. divided model parameters into two groups, those potentially to be estimated from the lake data and those to be estimated from other sources. They included kinetic parameters, specific for the populations in the lake, as the ones requiring estimation based on experimental data.

Jorgensen (1994, 2001) proposed a general procedure for parameter calibration in ecological modeling that includes determination of possible ranges of parameters, sensitivity analysis and calibration of the most sensitive ones. He proposed the minimization of the system exergy as the goal function when estimating model parameters. The concept is based on the fourth law of thermodynamics, describing the change in parameters when the system moves away from equilibrium (Jorgensen, Ray, Berec, & Straskraba, 2002). While minimizing exergy, these authors proposed a sequential procedure to determine model parameters by calibrating both physical and chemical parameters by trial and

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Table 1
Trophic classification of water bodies.

	Oligotrophic	Mesotrophic	Eutrophic	Hypereutrophic
Inorganic phosphorus (μg/l)	1–10	10–20	20–100	>100
Inorganic nitrogen (μg/l)	<150	150–300	>300	
Phytoplankton (cells/ml)	2000	2000–5000	>5000	
Superficial chlorophyll a (μg/l)	1–2	2–5	5–50	>50
Depth of Secchi disk (m)	5–10	3–5	1–3	<1

error and iteratively introducing size functions for phytoplankton and zooplankton parameters (Zhang, Jorgensen, & Mahler, 2004).

More recently, Shen (2006) proposed a least squares objective function and the application of a modified Gauss–Newton method for the solution of the dynamic parameter estimation problem. He has modified the algorithm to handle upper and lower bounds on parameters. Partial derivatives of state variables with respect to parameters are obtained by finite differences. The efficiency of the algorithm is proved in the same estuarine eutrophication model proposed by Shen and Kuo (1998).

Bayesian approaches have also been applied for parameter estimation in estuary and coastal zone models (Borsuk, Higdom, Stow, & Reckhow, 2001) and lake models (Arhonditsis et al., 2006), as well as genetic algorithms (Whigham & Recknagel, 2001).

Rode, Suhr, and Wriedt (2007) estimated seven kinetic and biological parameter for a river water quality model using the automatic Parameter Estimation Program (PEST, Doherty, 2004), which implements the Gauss–Marquardt–Levenberg optimization method. Furthermore, complex three-dimensional eutrophication models have been proposed for lakes with horizontal uneven distributions (Hu, Jørgensen, & Zhang, 2006). More recent work includes a water quality model considering sediment related processes (Chao, Jia, Shields, Wang, & Cooper, 2007) and detailed modeling of functional phytoplankton groups (Mieleitner & Reichert, 2008).

The main objective in the development of hybrid eutrophication models is to provide a tool for the proposal of remediation policies to improve water quality and to examine competition patterns and structural shifts under nutrient enrichment conditions (Zhao, Ramin, Cheng, & Arhonditsis, 2008).

In this work, we formulate a constrained parameter estimation problem for a water quality model, subject to a partial differential algebraic equations (PDAE) model. Partial differential equations result from temporal and spatial dynamic mass balances in the major groups of phytoplankton community, key nutrients in lake, biochemical demand of oxygen and dissolved oxygen. Algebraic equations represent profiles for temperature, solar radiation and river inflows, in addition to the calculation of most factors that affect rate equations, such as effect of solar radiation, temperature, nutrients, etc. The PDE is transformed into an ordinary differential equation system by spatially discretizing into horizontal layers. The parameter estimation problem subject to DAE constraints is solved within a simultaneous approach and the resulting large-scale nonlinear program is solved with an Interior Point method with successive quadratic programming techniques within program IPOPT (Biegler, Cervantes, & Waechter, 2002), which takes advantage of the special structure of the resulting model. The present study has been performed on Paso de las Piedras Reservoir, which is the drinking water source for two cities in Argentina and whose current state is eutrophic. Numerical results show good agreement with observed data from the lake throughout an entire year and provide values for parameters that are within ranges published in the literature. The model is currently being validated with recently obtained data from the lake.

2. Eutrophication processes

In the life cycle of water bodies, there are four stages: oligotrophic, mesotrophic, eutrophic and hypereutrophic. In an extremely clean water body, as nutrients available are minimal, there is no significant biological activity in the water column that can support sedimentation. The water body is healthy and the condition is called oligotrophic. As time passes and possible due to human activities, nutrients can build up. A water body with nutrient concentration support biological activity that is not objectionable, but above that of the oligotrophic conditions is considered mesotrophic. In the next stage of the life cycle, the water body becomes eutrophic. This is characterized by murky water with an accelerated rate of sedimentation of microorganisms. The final life stage before extinction is hypereutrophic. Table 1 shows a quantitative description of the above-mentioned trophic states.

As a result of cultural eutrophication, the one encouraged by human activities, the water body goes through an over enrichment of nutrients (mainly phosphorous and nitrogen), with an associated increase in the production levels and biomass. There is a very strong development of the phytoplankton community and a decrease in the water depth caused by sediment accumulation.

Eutrophication has both point and non-point sources. Main point sources are the discharges of agricultural, industrial and urban wastewater. Much research effort is being devoted in the chemical engineering community to address effluent treatment when dealing with point sources. However, non-point sources, which are mainly due to agricultural activities, are more difficult to deal with and have not received much attention. The application of restoration policies requires modeling and optimization of major chemical and biological processes that take place within water bodies and the first step is model calibration to the lake specific conditions.

3. Study area and input data

Paso de las Piedras Reservoir is located in the south of Buenos Aires Province (Argentina) at 38°22′S and 61°12′W. It was built 30 years ago to supply drinking water to Bahía Blanca and Punta Alta (cities whose population is above 450,000 inhabitants) and for industrial purposes at a petrochemical complex nearby. The lake has two tributaries: El Divisorio Stream and Sauce Grande River, which run through an important agricultural area. This water body has a coastline perimeter of 60 km and a mean depth of 8.2 m, so it can be considered as a shallow lake. The high content of phosphorus and nitrogen in Paso de las Piedras Reservoir is a consequence of agricultural activities. The trophic state of this water body is currently eutrophic (Parodi, Estrada, Trobbiani, & Argañaraz Bonini, 2004), as it can be clearly seen in Figs. 1 and 2. These figures show observed concentration profiles for total phytoplankton and Secchi disk depth (depth at which a white disk can be seen from outside the water body) as related to the levels beyond which the water body is considered eutrophic (horizontal lines that correspond to 5000 cells/ml and 3 m, for phytoplankton concentration and Secchi disk depth, respectively). The urgent need for application of systematic restoration strategies requires a deep knowledge of the dynamics of main components in the lake.

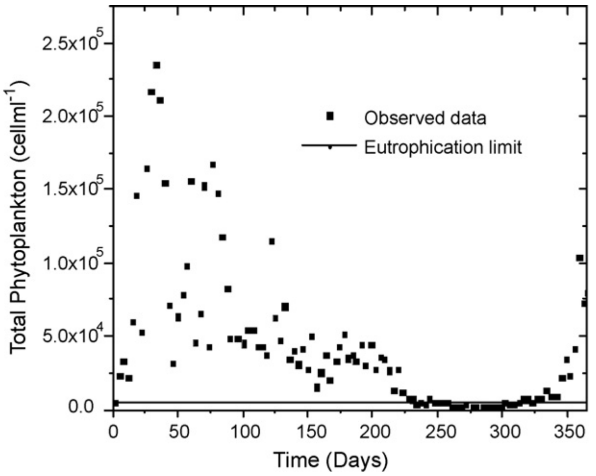

Fig. 1. Observed total phytoplankton concentration (eutrophic above 5000 cells/ml).

Biological and chemical data have been collected weekly from January to December 2004 at four sampling stations and two depths. Biological qualitative and quantitative determinations have been carried out, as well as physicochemical ones. They include the determination of concentrations of nitrate, ammonium, organic nitrogen, phosphate, organic phosphorus, dissolved oxygen and biochemical demand of oxygen, water temperature, pH and depth of Secchi disk. An important characteristic of this water body is that it does not form a thermocline in any season of the year (Intartaglia & Sala, 1989), hence there is no limitation in the nutrients circulation. One reason for the lack of thermal stratification of the water column could be that the reservoir is wind-exposed due to the low topography of the surrounding area.

Inputs for the model are of four types. They are descriptive data for the lake itself, hydrodynamic forcing data (primarily meteorological, as temperature and solar radiation profiles, and inflow and outflow profiles data), water quality known parameters, phytoplankton and nutrients profiles and initial conditions for state variables. High frequency sampling is required to properly describe the dynamics of the lake. Water temperature and solar radiation profiles were approximated with sinusoidal functions, as shown in Fig. 3, based on meteorological data and measured water temperature. River inflows and associated nutrient loading, as well as outflow data and rain and evaporation, have been approximated with polynomial functions, based on observed data.

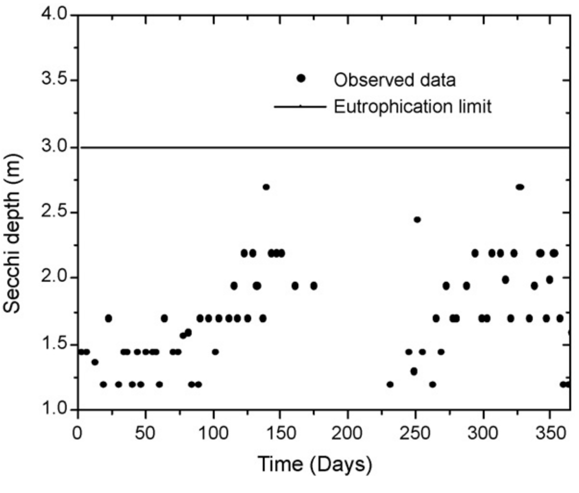

Fig. 2. Observed Secchi disk depth (eutrophic between 1 and 3 m).

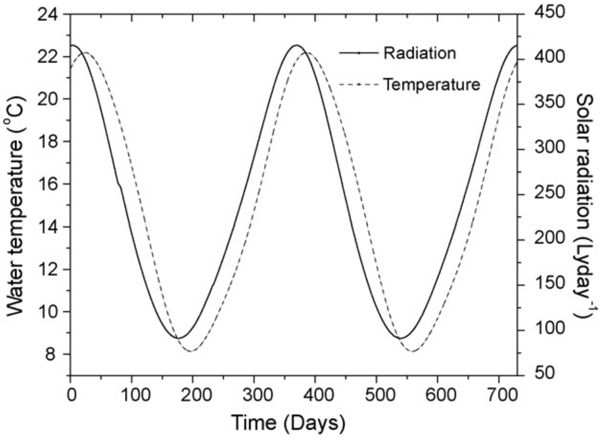

Fig. 3. Temperature (°C) and solar radiation (ly day^{-1}) profiles (2 years).

4. Parameter estimation problem

Eutrophication models comprise large sets of complex partial differential algebraic systems of equations (PDAE) that arise from dynamic mass balances for phytoplankton, nutrients and main components. Therefore, the associated parameter estimation problem is formulated as a PDAE-constrained optimization problem. The main simplifying assumption in the present model is the consideration of horizontally averaged concentrations. This assumption has been introduced in the literature in most mechanistic eutrophication models for lakes and reservoirs (Arhonditsis et al., 2006; Hamilton & Schladow, 1997; Jorgensen et al., 2002; Omlin, Brun, et al., 2001; Omlin, Reitchert, et al., 2001; Zhang et al., 2004). Arhonditsis and Brett (2005) and Arhonditsis et al. (2006) have proposed a very detailed 1D model for lake Washington, which has a surface area of 87 km^2, seven inflows and 12 surrounding cities. On the other hand, 3D eutrophication models for lakes have been developed for different situations. Hu et al. (2006) formulated a 3D model for lake Taihu (China), whose surface area is 2338 km^2, with 38 cities and 34.2 million people surrounding the lake, with the associated discharges of domestic and industrial wastewater. In our case study, Paso de las Piedras Reservoir (surface area: 36 km^2, two inflows and no discharges of wastewater), we analyzed collected data at the four existing sampling stations to decide the inclusion of the simplifying assumption. Two sampling stations are coastal and the remaining ones are in central parts of the lake. The analysis of the data collected during the bloom period, gives up to 8, 9 and 12% average relative differences in nitrate, phosphate and total phytoplankton concentrations, respectively, as related to the first sampling station. These small differences justify the assumption of horizontally averaged concentrations in our model and they could be explained with the fact that the reservoir is located in a windy area and is wind-exposed throughout the entire year due to the low topology.

Additional simplifying assumptions in the present model include constant transversal area in the lake and constant water density (Estrada, Parodi & Diaz, 2007). In this way, only gradients along the water column height are considered. Phosphorus is considered as the limiting nutrient, as it is generally the case in lakes. To transform the partial differential equations system into a set of ordinary differential equations, the column height is discretized into two layers, according to available data from the lake. The fact that the residence time in the lake is 4 years suggests that a discretization with only two horizontal layers may be enough to describe the process. In most eutrophication models, the different types of phytoplankton are lumped within one state variable; however, we have considered three state variables corresponding to diatoms, chlorophytes and cyanobacteria, which are representative of the dominating phytoplankton groups in the lake. The detailed information on each phytoplankton group is very useful to determine the potential damage they can produce in the drinking water source when an algal bloom takes place. The remaining state variables correspond to concentrations of main nutrients (nitrate, nitrite, ammonium, organic nitrogen, phosphate, and organic phosphorus), dissolved oxygen and biochemical demand of oxygen.

4.1. Process description and model equations

Algae are produced by photosynthesis. In these complex reactions and using sunlight energy, the water molecule breaks down releasing electrons for synthesis:

$$276\mathrm{H_2O} \rightarrow 138\mathrm{O_2} + 552\mathrm{H^+} + 552\mathrm{e^-} \tag{1}$$

Dissolved carbon dioxide, together with nutrients and trace elements, take the electrons to produce algae and water, according to:

$$\begin{aligned}&106\mathrm{CO_2} + 16\mathrm{NO_3}^- + \mathrm{HPO_4}^{2-} + 570\mathrm{H^+} + 552\mathrm{e^-} + \text{trace elements}\\ &\quad\rightarrow (\mathrm{CH_2O})_{106}(\mathrm{NH_3})_{16}\mathrm{H_3PO_4}.\text{traceelements} + 154\mathrm{H_2O}\end{aligned} \tag{2}$$

According to Eq. (2), algae are able to uptake nitrogen in both ammonium and nitrate form for growth. Phosphorus is also uptaken by phytoplankton in phosphate form for growth.

Dynamic mass balances in each spatial layer include component inputs from tributaries (Q_{IN}), outputs for both potabilization and industrial purposes and the river itself (Q_{OUT}), generation and consumption, and transference between layers, also accounting for lake volume variability (through upper layer height variability). A global mass balance also takes into account inputs from rains (Q_{rain}) and outputs due to evaporation (Q_{evap}). Algebraic equations stand for the generation/consumption terms, as well as for profiles in temperature, solar radiation, rain, evaporation and river inflows and corresponding concentrations. Estimated kinetic and physicochemical parameters are included within the generation/consumption terms. The objective function is a weighted least squares one.

Total mass balances:

$$\frac{dh_T}{dt} = \frac{1}{A}\left[Q_{\mathrm{rain}} - Q_{\mathrm{evap}} + \sum_{k=1}^{N_{\mathrm{IN}}} Q_{\mathrm{IN}_k} - \sum_{m=1}^{N_{\mathrm{OUT}}} Q_{\mathrm{OUT}_m}\right] \tag{3}$$

where k = Sauce Grande River, El Divisorio Stream and m = potabilization plant, industrial usage, and Sauce Grande River outflows.

Component mass balances for horizontal layers (U: upper layer; L: lower layer; j: cyanobacteria, diatoms, chlorophytes, nitrate, ammonium, organic nitrogen, phosphate, organic phosphorus, biochemical demand of oxygen, dissolved oxygen):

- Upper layer:

$$\begin{aligned}\frac{dC_{Uj}}{dt} &= \sum_{k=1}^{N_{\mathrm{IN}}} \frac{Q_{\mathrm{IN}_{U,k}}}{V_U} C_{\mathrm{IN}_{Ujk}} - \sum_{m=1}^{N_{\mathrm{OUT}}} \frac{Q_{\mathrm{OUT}_U}}{V_U} C_{Uj} + r_{Uj}\\ &\quad - \frac{kdA}{\Delta h_U h_U}(C_{Uj} - C_{Lj}) - \frac{C_{Uj}}{h_U}\frac{dh_U}{dt}\end{aligned} \tag{4}$$

- Lower layer:

$$\frac{dC_{Lj}}{dt} = \sum_{m=1}^{N_{\mathrm{OUT}}} \frac{Q_{\mathrm{OUT}_L}}{V_L} C_{Lj} + r_{Lj} + \frac{kdA}{\Delta h_L h_L}(C_{Lj} - C_{Uj}) - \frac{C_{Lj}}{h_L}\frac{dh_L}{dt}, \tag{5}$$

where r_{Uj} and r_{Lj} correspond to generation and consumption terms, h_U and h_L are height of water column and V_U and V_L correspond to lake volume in upper (U) and lower (L) water layer, respectively.

4.1.1. Rate equations for components

Phytoplankton. Rate equations for phytoplankton groups take into account production and losses due to respiration, natural death, settling, and grazing by herbivorous zooplankton.

$$\begin{aligned}&r_{ij} = R_{ij,growth} - R_{ij,resp} - R_{ij,death} - R_{ij,settling} - R_{ij,graz},\\ &i = UL, LL; \quad j = \text{cyano, diatom, chlorophyte}\end{aligned} \tag{6}$$

The growth rate of the three phytoplankton groups is a function of solar radiation, water temperature and nutrients availability. The effect of solar radiation and nutrients on phytoplankton growth rate is handled following a multiplicative model.

$$\begin{aligned}&R_{ij,growth} = k_{i,growth} f(T)_{ij} f(I)_{ij} f(N)_{ij} C_{ij},\\ &i = UL, LL; \quad j = \text{cyano, diatom, chlorophyte}\end{aligned} \tag{7}$$

The temperature limitation function for the three phytoplankton groups follows Zhang et al. (2004).

$$\begin{aligned}&f(T)_{ij} = -\frac{(T_j - T_{opt_i})^2}{T_{opt_i}^2} + 1, \qquad i = UL, LL;\\ &j = \text{cyano, diatom, chlorophyte}\end{aligned} \tag{8}$$

The Steele (1962) function is applied to take into account solar radiation control on phytoplankton growth, coupled with Beer's Law to adjust the extinction of the incoming solar radiation with depth.

$$\begin{aligned}&f(I)_{ij} = \frac{I_{oi}}{I_{opt_j}} \exp\left(1 - \frac{I_{oi}}{I_{opt_j}}\right), \qquad i = UL, LL;\\ &j = \text{cyano, diatom, chlorophyte}\end{aligned} \tag{9}$$

where

$$I_{oi} = \frac{I[1 - \exp(-K_e\,\Delta D_i)]}{K_e\,\Delta D_i} \tag{10}$$

$$K_e = K_1 + K_2\frac{\sum_{j=1}^{3} C_j}{cchl} \tag{11}$$

where I is the incoming solar radiation in ly day^{-1} and K_e is the light extinction coefficient.

Generally, phosphate is considered as the limiting nutrient for primary productivity in freshwater ecosystems (Hecky & Kilham, 1988; Vollenweider, 1975) and its control is usually the best strategy for management proposes. An important concept to determine the limiting nutrient in an aquatic ecosystem has been the N:P ratio. However, studies performed in sites with large nitrogen and phosphorus downloads has shown that the N:P ratio is not applicable to highly eutrophic systems (Paerl, Fulton, Moisander, & Dyble, 2001; Xie, Xie, Li, Tang, & Liu, 2003). Sas (1989) suggested threshold values for phosphate and inorganic nitrogen limitation of 0.01 and 0.1 mg l^{-1}, respectively. Both dissolved inorganic nitrogen ($\mathrm{NH_4} + \mathrm{NO_3} + \mathrm{NO_2}$) and phosphate in Paso de las Piedras Reservoir have never been below the threshold values. Hence, the model includes a Monod type kinetics to account for phosphate limitation as well as limitation by silica for diatoms, since it is a requirement for most of the diatoms species for cell wall formation (Thamatrakoln & Hildebrand, 2008).

$$f(N)_{ij} = \frac{C_{i,\mathrm{PO_4}}}{C_{i,\mathrm{PO_4}} + K_{\mathrm{P}_i}}, \frac{C_{\mathrm{Si}_i}}{C_{\mathrm{Si}_i} + K_{\mathrm{S}_j}}, \qquad i = UL, LL; \quad j = \text{diatom} \tag{12}$$

$$f(N)_{ij} = \frac{C_{\mathrm{PO}_{4j}}}{C_{\mathrm{PO}_{4j}} + K_{\mathrm{P}_i}}, \qquad i = UL, LL; \quad j = \text{cyano, chlorophyte} \tag{13}$$

Phytoplankton respiration and natural death rates are given as:

$$\begin{aligned}&R_{ij,resp} = k_{j,resp}\theta_r^{(T-20)} C_{ij}, \qquad i = UL, LL;\\ &j = \text{cyano, diatom, chlorophyte}\end{aligned} \tag{14}$$

$$R_{ij,death} = k_{j,death}\theta_m^{(T-20)}C_{ij}, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{15}$$

Since phytoplankton species are denser than water, a term taking into account settling of the cells is included:

$$R_{ij,settling} = k_{j,settling}\frac{C_{ij}}{h_i}, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{16}$$

The herbivorous zooplankton grazing rate is:

$$R_{ij,graz} = k_{j,graz}\frac{C_{ij}}{C_{ij}+K_{graz}}C_{Zoo_i}, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{17}$$

The differences in growth rates for the three phytoplankton groups are given by differences between their maximum growth rates, nutrients kinetics, optimal light and temperature requirements.

4.1.2. *Nutrients cycles*

Nitrogen cycle. Three state variables describe nitrogen cycle: ammonium, nitrate and organic nitrogen. Phytoplankters are able to absorb both ammonium and nitrate for growth, with ammonium preference as it is energetically less expensive to metabolize. Ammonium and nitrate concentration decrease in the water column by algal uptake. Ammonium is oxidized to nitrate in an oxygen-temperature-dependent nitrification rate and its concentration increases by organic nitrogen hydrolysis at a temperature-dependent mineralization rate. For the lower layer, the model includes a term of ammonium release from sediments (Hamilton & Schladow, 1997). Nitrate can be reduced to molecular nitrogen by a process requiring low oxygen conditions, i.e., denitrification. The organic nitrogen pool is reduced by mineralization and settling and increases with mortality of phytoplankton. The governing equations that describe the above processes are given by

$$r_{U,NH_4} = -R_{U,NH_4,uptake} - R_{iU,nit} + R_{U,NH_4,death} + R_{U,NH_4,miner} \tag{18}$$

$$r_{L,NH_4} = -R_{L,NH_4,uptake} - R_{L,i,nit} + R_{L,NH_4,death} + R_{L,NH_4,miner} + R_{L,NH_4,sediment} \tag{19}$$

$$r_{i,NO_3} = -R_{i,NO_3,uptake} + R_{i,NO_3,nit} - R_{i,NO_3,denit}, \qquad i = UL, LL \tag{20}$$

$$r_{i,ON} = R_{i,ON,death} - R_{ij,miner} - R_{i,ON,settling}, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{21}$$

$$R_{i,NH_4,uptake} = \sum_j(\alpha_{nc}R_{j,growth}P_{NH_4}), \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{22}$$

where P_{NH_4} is the preference factor for ammonium uptake (Arhonditsis & Brett, 2005).

$$P_{NH_4} = 1 - \exp(\psi_j C_{i,NH_4}), \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{23}$$

$$R_{i,NH_4,nit} = k_{nit}\theta_{nit}^{(T-20)}\frac{C_{i,DO}}{K_{nit}+C_{i,DO}}C_{i,NH_4}, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{24}$$

$$R_{i,NH_4,death} = \sum_j(C_{ij}k_{j,death}\alpha_{nc}(1-f_{ON})), \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{25}$$

$$R_{ij,miner} = k_{mn}\theta_{mn}^{(T-20)}\frac{\sum_j C_{ij}}{K_{mpc}+\sum_j C_{ij}}C_{i,ON}, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{26}$$

$$R_{L,NH_4,sediment} = S_N\left(1 - \frac{C_{L,DO}}{K_{DOS}+C_{L,DO}}\right)A \tag{27}$$

$$R_{i,NO_3,uptake} = \sum_j(\alpha_{nc}R_{j,growth}(1-P_{NH_4})), \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{28}$$

$$R_{i,NO_3,denit} = k_{denit}\theta_{denit}^{(T-20)}\frac{K_{denit}}{K_{denit}+C_{i,DO}}C_{i,NO_3}, \qquad i = UL, LL \tag{29}$$

$$R_{i,ON,death} = \sum_j(C_{ij}k_{j,death}\alpha_{nc}f_{ON}), \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{30}$$

$$R_{i,ON,settling} = \frac{k_{ON,settling}(1-f_{DON})}{D_i}C_{i,ON}, \qquad i = UL, LL \tag{31}$$

Phosphorus cycle. The state variables describing phosphorus cycle are phosphate and organic phosphorus. Processes within the phosphorus cycle are similar to those from the nitrogen ones. Phosphorus is uptaken by phytoplankton in phosphate form. Phytoplankton mortality, temperature-dependent mineralization of organic phosphorus and oxygen-dependent release from sediments (only for lower layer) increase concentration of phosphate. Organic phosphorus pool is augmented with algal dead and decline by mineralization and settling process. The following rate equations express the main processes in the phosphorus biogeochemical cycle:

$$r_{i,PO_4} = -R_{U,PO_4,uptake} + R_{U,PO_4,death} + R_{U,j,miner}, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{32}$$

$$r_{L,PO_4} = -R_{L,PO_4,uptake} + R_{L,PO_4,death} + R_{L,j,miner} + R_{L,PO_4,sediment}, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{33}$$

$$r_{i,OP} = R_{i,OP,death} - R_{ij,miner} - R_{i,OP,settling}, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{34}$$

$$R_{i,PO_4,uptake} = \sum_j(\alpha_{pc}R_{j,growth}), \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{35}$$

$$R_{i,PO_4,death} = \sum_j(C_{ij}k_{j,death}\alpha_{pc}(1-f_{OP})), \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{36}$$

$$R_{L,PO_4,sediment} = S_P\left(1 - \frac{C_{L,DO}}{K_{DOS}+C_{L,DO}}\right)A, \qquad i = UL, LL; \qquad j = \text{cyano, diatom, chlorophyte} \tag{37}$$

$$R_{i,\mathrm{OP},death} = \sum_j (C_{ij} k_{j,death} \alpha_{pc} f_{\mathrm{OP}}), \qquad i = UL, LL;$$
$$j = \text{cyano, diatom, chlorophyte} \tag{38}$$

$$R_{ij,\mathrm{miner}} = k_{mp} \theta_{mp}^{(T-20)} \frac{\sum_j C_{ij}}{K_{mpc} + \sum_j C_{ij}} C_{i,\mathrm{OP}}, \qquad i = UL, LL;$$
$$j = \text{cyano, diatom, chlorophyte} \tag{39}$$

$$R_{i,\mathrm{OP},settling} = \frac{k_{\mathrm{OP},settling}(1 - f_{\mathrm{DOP}})}{D_i} C_{i,\mathrm{OP}} \qquad i = UL, LL;$$
$$j = \text{cyano, diatom, chlorophyte} \tag{40}$$

Dissolved oxygen. The main sources of dissolved oxygen in the water column are atmospheric re-aeration, which depends on saturation concentration, and photosynthetic oxygen production. The dissolved oxygen sink are autotrophic and heterotrophic respiration, organic matter oxidation, nitrification and sediment oxygen demand. The rate equations that describe the major processes governing the dynamics of dissolved oxygen are given as Priyantha, Asaeda, Saitoh, and Gotoh (1997).

$$r_{U,\mathrm{DO}} = R_{U,\mathrm{DO},reair} - R_{U,\mathrm{DO},nitr} + R_{U,\mathrm{DO},resp/fot} - R_{U,\mathrm{DO},bod},$$
$$i = UL, LL \tag{41}$$

$$r_{L,\mathrm{DO}} = -R_{L,\mathrm{DO},nitr} - R_{L,\mathrm{DO},resp/fot} - R_{L,\mathrm{DO},bod} + R_{L,\mathrm{DO},sediment},$$
$$i = UL, LL \tag{42}$$

$$R_{U,\mathrm{DO},reair} = \frac{k_a \theta_a^{(T-20)}}{D_U} (C^* - C_S) \tag{43}$$

where C^* is the saturated oxygen concentration at the surface temperature and is given by Zhang et al. (2004).

$$C^* = 16.5 - \frac{8}{22} T \tag{44}$$

$$R_{i,\mathrm{DO},nitr} = k_{nit} \theta_{nit}^{(T-20)} \frac{C_{i,\mathrm{DO}}}{K_{nit} + C_{i,\mathrm{DO}}} C_{i,\mathrm{NH_4}} \alpha_{on}, \qquad i = UL, LL;$$
$$j = \text{cyano, diatom, chlorophyte} \tag{45}$$

$$R_{i,\mathrm{DO},resp/fot} = \left(\sum_j R_{ij,growth} - R_{ij,resp} \right) \alpha_{oc}, \qquad i = UL, LL;$$
$$j = \text{cyano, diatom, chlorophyte} \tag{46}$$

$$R_{i,\mathrm{DO},bod} = k_{bod} \theta_{bod}^{(T-20)} \frac{C_{i,\mathrm{DO}}}{K_{bod} + C_{i,\mathrm{DO}}} C_{\mathrm{BOD}_i}, \qquad i = UL, LL;$$
$$j = \text{cyano, diatom, chlorophyte} \tag{47}$$

$$R_{L,\mathrm{DO},sediment} = \frac{k_{sod} \theta_{sod}^{(T-20)}}{D_L} \frac{C_{L,\mathrm{DO}}}{K_{sod} + C_{L,\mathrm{DO}}} \tag{48}$$

Carbonaceous biochemical demand of oxygen. The main source of carbonaceous biochemical oxygen demand is phytoplankton mortality and the sink term is the sum of carbonaceous oxidation and settling processes.

$$r_{i,\mathrm{BOD}} = R_{i,\mathrm{BOD},death} - R_{i,\mathrm{BOD},oxid} - R_{i,\mathrm{BOD},denit} - R_{i,BOD,settling},$$
$$i = UL, LL \tag{49}$$

$$R_{i,\mathrm{BOD},death} = \sum_j (C_{ij} k_{j,death} \alpha_{oc}), \qquad i = UL, LL;$$
$$j = \text{cyano, diatom, chlorophyte} \tag{50}$$

$$R_{i,\mathrm{BOD},oxid} = k_{bod} \theta_{bod}^{(T-20)} \frac{C_{i,\mathrm{DO}}}{K_{bod} + C_{i,\mathrm{DO}}} C_{i,\mathrm{BOD}}, \quad i = UL, LL \tag{51}$$

$$R_{i,\mathrm{BOD},settling} = \frac{k_{bod,settling}(1 - f_{\mathrm{DBOD}})}{D_i} C_{i,\mathrm{BOD}}, \qquad i = UL, LL;$$
$$j = \text{cyano, diatom, chlorophyte} \tag{52}$$

Based on a previous global sensitivity analysis (Estrada et al., 2008; Estrada & Diaz, 2009), we have selected 15 main parameters to be estimated; they are: maximum growth rate ($k_{C,growth}$, $k_{D,growth}$, $k_{G,growth}$, Eq. (7)) and mortality rate ($k_{C,death}$, $k_{D,death}$, $k_{G,death}$, Eqs. (15), (25), (36), (38) and (50)) for the three species of phytoplankton; optimal light intensity for cyanobacteria (I_{optC}, Eq. (9)); half-saturation constant for oxygen limitation of nitrification (K_{nit}, Eqs. (24) and (45)); temperature adjustment for phytoplankton respiration and mortality rate (θ_r, θ_m, Eqs. (14) and (15)); temperature adjustment for organic nitrogen and organic phosphorus mineralization rate (θ_{mn}, θ_{mp}, Eqs. (26) and (39)); phytoplankton nitrogen to carbon ratio and phytoplankton phosphorus to carbon ratio (α_{nc}, α_{pc}, Eqs. (25), (28), (30), (35) and (38)); and background light attenuation (K_1, Eq. (11)). The remaining model parameters and their values are shown in Table A.1.

The resulting DAE constrained optimization problem is:

$$\min \ \phi = \frac{1}{2} \sum_{i=1}^{\mathrm{NI}} \sum_{j=1}^{\mathrm{NV}} \sum_{k=1}^{\mathrm{NL}} (c_{ijk}^M - c_{ijk})^T V^{-1} (c_{ijk}^M - c_{ijk}) \tag{53}$$

st

Eqs. (13)–(62)
$c(0) = c^0$
$\mathbf{c}_L \le \mathbf{c} \le \mathbf{c}_U$
$\mathbf{p}_L \le \mathbf{p} \le \mathbf{p}_U$

where the summation in the objective function is over NL layers, NV state variables and NI data points. The symbol M stands for measured values of component concentrations and V is a diagonal weighting matrix for state variables, whose elements correspond to variances of measurement errors. Vector $\mathbf{p}$ corresponds to estimated parameters.

4.2. Optimization algorithm

The resulting differential algebraic equations constrained optimization problem is formulated within a simultaneous dynamic optimization approach, in which the DAE system is transformed into a large nonlinear programming (NLP) problem by representing state variables profiles by polynomial functions over finite elements in time and discretizing the DAE by collocation over these finite elements. The NLP is then solved with an efficient reduced successive quadratic programming (rSQP) algorithm within an Interior Point program IPOPT (Biegler et al., 2002; Zabala & Biegler, 2006). As described in Cervantes, Waechter, Tutuncu, and Biegler (2000), a barrier approach is applied to convert the inequality constraints in the NLP to a logarithmic penalty term in the objective function. This leads to a parametric NLP with only equality constraints; a penalty parameter on the barrier terms is systematically forced to zero and an NLP is solved for each value of this parameter. Applying Newton's method to the KKT conditions of this equality constrained NLP leads to large, sparse linear subproblems, which are solved using a range and null space decomposition tailored to the structure of the collocation equations. Further details of this method can be found in Cervantes et al. (2000). Extensions of this approach have also been described in Kameswaran and Biegler (2006).

5. Discussion of results

The resulting parameter estimation problem in Paso de las Piedras eutrophication model has 20 differential equations and 60 algebraic ones, after spatial discretization into two horizontal water layers. Currently available observed data of concentrations at two water levels (water surface and outflow level, at 6 m depth) have rendered this discretization. The 4-year residence time in this shallow lake is large enough to enforce the validity of this discretization scheme. Phytoplankton observed data correspond only to the upper layer, as no data on phytoplankton were collected from the lower layer during the sampling period. The remaining components concentration data are available for both the upper and lower layer. Most eutrophication models from the literature use less frequent data (e.g., monthly, Arhonditsis & Brett, 2005; Omlin, Brun, et al.,

Table 2
Optimal parameter set for eutrophication model.

Parameter	Initial value	Lower bound	Upper bound	Value
$k_{C,growth}$ (day^{-1})	0.195	0.15	1.5	0.216
$k_{D,growth}$ (day^{-1})	0.653	0.6	5.0	0.640
$k_{G,growth}$ (day^{-1})	0.785	0.5	5.0	0.846
$k_{C,death}$ (day^{-1})	0.019	0.0005	0.1	0.001
$k_{D,death}$ (day^{-1})	0.100	0.001	0.1	0.074
$k_{G,death}$ (day^{-1})	0.100	0.001	0.5	0.147
I_{optC} ($\mathrm{ly\,day}^{-1}$)	99.0	70.0	150.	149.12
K_{nit} ($\mathrm{mg\,day}^{-1}$)	0.115	0.1	7.0	0.191
θ_r	1.04	0.96	2.0	1.077
θ_m	1.02	0.96	2.0	0.998
θ_{mn}	1.08	0.96	2.0	0.960
θ_{mp}	1.10	0.96	2.0	0.994
α_{nc} ($\mathrm{mg\,N\,mg\,C}^{-1}$)	0.125	0.09	3.0	0.099
α_{pc} ($\mathrm{mg\,P\,mg\,C}^{-1}$)	0.01	0.01	0.3	0.022
K_1 (m^{-1})	1.97	1.0	5.0	2.137

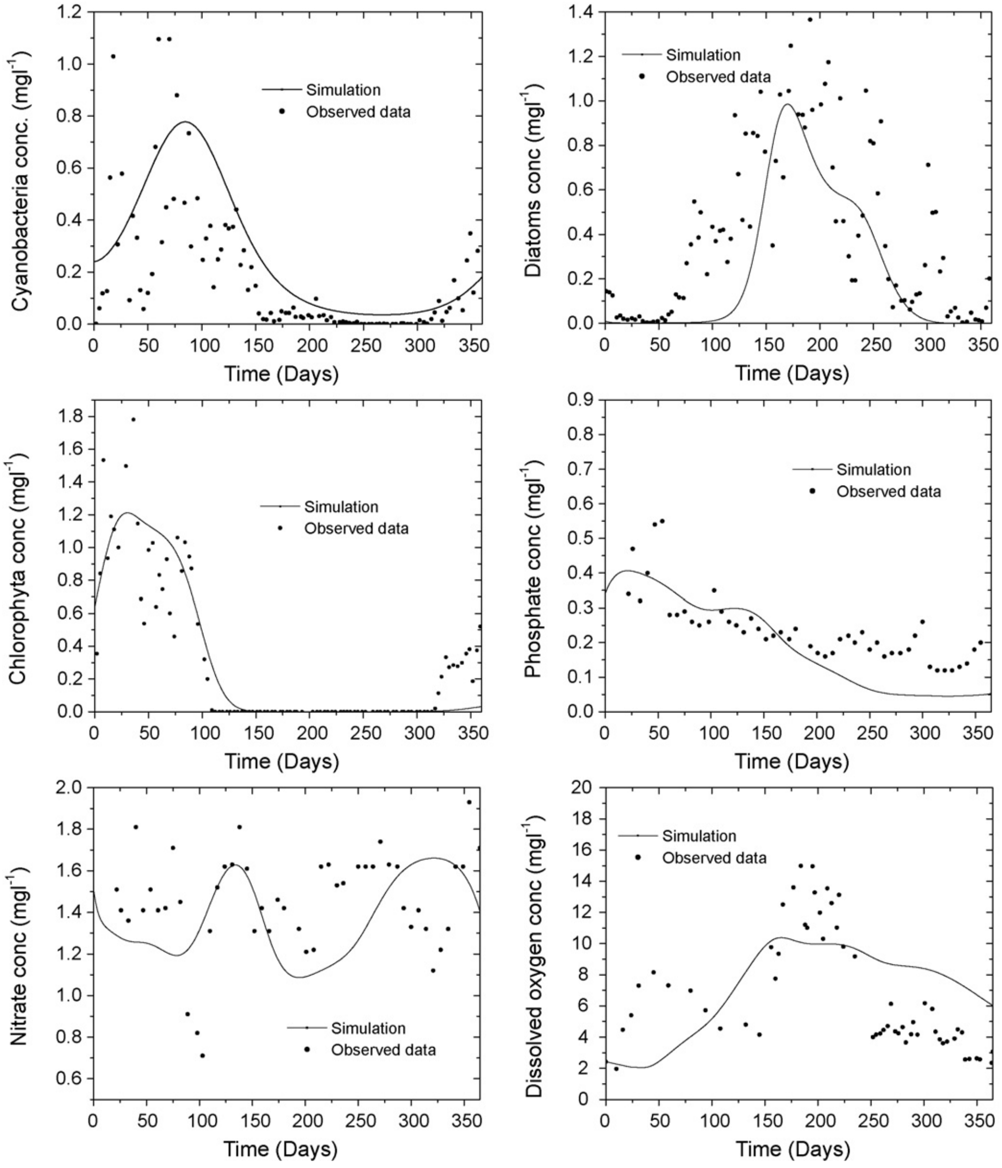

Fig. 4. Observed data and simulation profiles for cyanobacteria (mg C/l), diatoms (mg C/l), chlorophytes (mg C/l), phosphate (mg P/l), nitrate (mg N/l) and dissolved oxygen (mg O/l) concentrations in upper water layer.

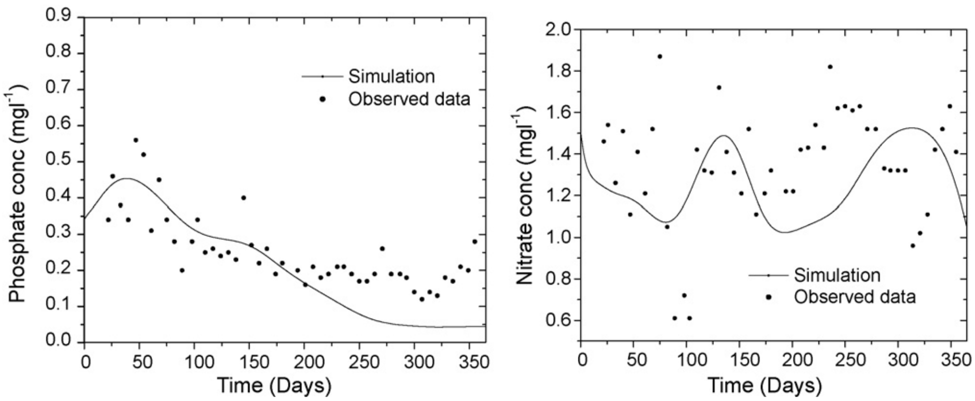

Fig. 5. Observed data and simulation profiles for phosphate (mg P/l) and nitrate (mg N/l) concentration in lower layer.

Table 3
Average deviations between observed data and model predictions and standard deviation of error for main components.

	Cyanobacteria (mg C/l)	Diatoms (mg C/l)	Chlorophyta (mg C/l)	Phosphate (mg P/l)	Nitrate (mg N/l)	Ammonium (mg N/l)	Dissolved oxygen
Average deviation (upper/lower layer)	0.115	0.223	0.285	0.041/0.040	0.121/0.122	0.657/0.601	2.763/2.560
Standard deviation of error (upper/lower layer)	0.067	0.078	0.110	0.024/0.074	0.077/0.079	0.301/0.298	1.438/1.321

2001). However, for modeling purposes, it is important to sample data with a frequency corresponding to the dynamics of the system (Jorgensen, Jorgensen, Kamp-Nielsen, & Mejer, 1981). This rule has often been neglected in modeling the eutrophication process, mainly because limnological lake data, which are not sampled for modeling purposes, are often collected with a relatively low frequency. In the present work, samples have been collected with twice a week frequency. We have considered a 1 day time unit, as well as a time horizon of 365 days, to account for a complete annual cycle, starting at January. This is another distinctive feature of the present model, as many ecological water quality models either consider a monthly time unit or shorter time horizons when using a daily basis. To transform the DAE constrained optimization problem into a nonlinear programming (NLP) problem, we have considered a time discretization with 40 finite elements and three collocation points. The resulting constrained parameter estimation problem

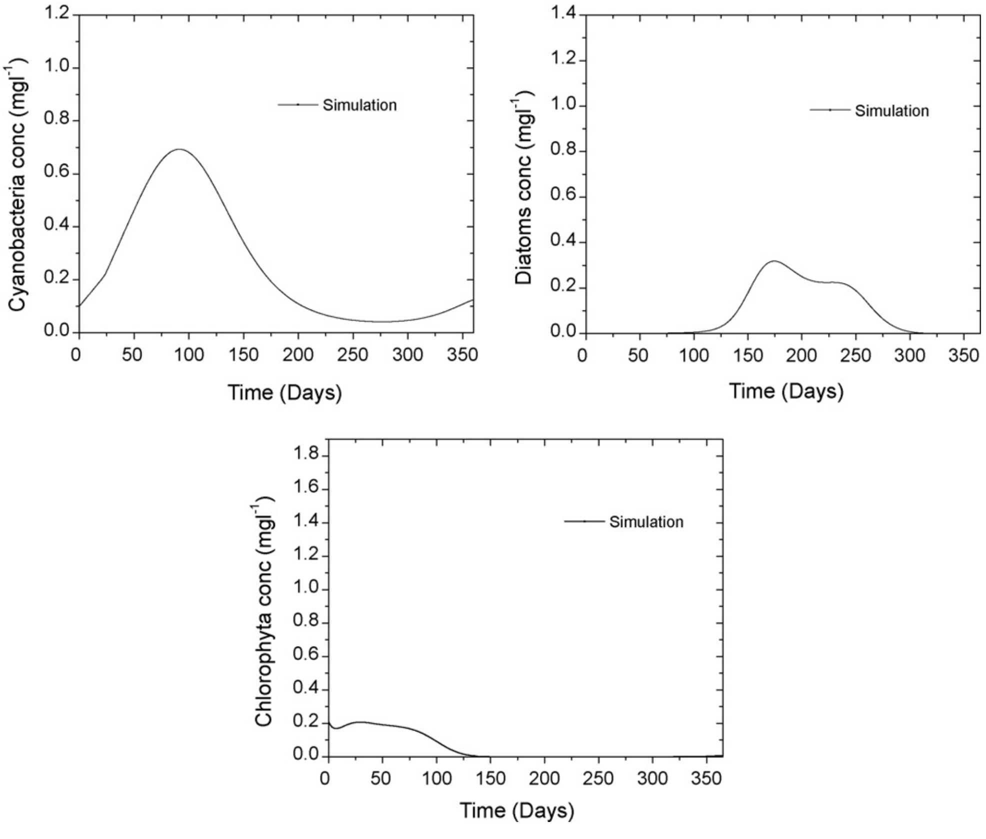

Fig. 6. Predicted profiles for cyanobacteria, diatoms and chlorophytes concentration (mg C/l) in lower layer of water body.

(Bard, 1974) has 10,436 nonlinear equations. It has been solved with an Interior Point method with reduced successive quadratic programming (rSQP) techniques within program IPOPT (Biegler et al., 2002; Raghunathan, Diaz, & Biegler, 2004), in which successive parametric NLP subproblems are solved for decreasing values of the barrier parameter. Initial barrier parameter value has been 0.01. The 15 estimated parameters are shown in Table 2, as well as their initial values and bounds, which are taken from the literature. The objective function has an initial value of 5816.45 and it has been reduced to 122.85 in the optimal solution, in 51 iterations. Figs. 4 and 5 show main state variables profiles as compared to observed data, in the upper and the lower water layers, respectively. It can be noted that a reasonable reproduction of concentration profiles for the three phytoplankton groups, cyanobacteria, diatoms and chlorophytes, and main nutrients has been obtained. Table 3 shows main components average deviation for concentrations and the standard deviation of the error. Major discrepancies between model predictions and observed data have been obtained for dissolved oxygen concentration. In this component, experimental data show a wide dispersion and, consequently, the associated standard deviation to weight in the objective function is large (5.24), rendering a low weight on errors in dissolved oxygen concentrations deviations.

The model closely reproduces cyanobacteria autumn bloom, as well as summer bloom, mainly composed of chlorophytes and cyanobacteria (80 and 20%, respectively) and spring blooms of diatoms in the lake. Fig. 6 shows predicted concentration profiles for the three main phytoplankton groups in the lower layer. It can be noted that cyanobacteria concentration reduction with respect to the upper layer is lower that the reduction in concentration corresponding to the other phytoplankton groups, as it is the case with these groups.

6. Conclusions and future work

We have formulated a partial differential equation constrained parameter estimation problem for a first principles based eutrophication model of a shallow lake, within a simultaneous dynamic optimization framework. This hybrid model includes complex relationships in the consumption-generation terms and requires a large number of experimental data for tuning biogeochemical parameters to site conditions. The problem has been solved in the water modeling literature with approaches ranging from iterative trial and error estimations to the use of variational methods. The formulation within a simultaneous dynamic optimization approach has proved to be quite efficient in the determination of model parameters and it has allowed the straightforward inclusion of bounds on both parameters and state and algebraic variables, as well as path constraints in complex nonlinear systems (Rodriguez & Diaz, 2007).

We have determined optimal values for 15 biogeochemical parameters, which have been identified as most influential through a previous global sensitivity analysis. The model provides a good representation of the main components in both upper and lower layers in the lake. A satisfactory fit was obtained between simulated and observed data throughout a time horizon of 1 year, with a sampling frequency of twice a week. The case study on a highly eutrophic reservoir that is the drinking water source for more than 450,000 inhabitants, is a challenging problem that requires a close representation of the dynamics of biogeochemical processes that take place within the water body. Currently, more data are being collected at different water levels in the lake to perform both additional model validation and model extension by considering a finer spatial discretization in the water column. The dynamic optimization model is currently being used to determine bio-restoration policies for the control of algal blooms and the reduction of nutrient loading to the lake. Such policies include tributaries derivation through a wetland for nutrient removal and the application of systematic inlake bio-restoration strategies.

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Appendix A.

See Table A.1 .

Table A.1
Model biogeochemical parameters.

Parameter	Description	Value
A (km^2)	Transversal area of the lake	36
$k_{C,resp}$ (day^{-1})	Respiration rate for cyanobacteria	0.047
$k_{D,resp}$ (day^{-1})	Respiration rate for diatoms	0.43
$k_{G,resp}$ (day^{-1})	Respiration rate for chlorophytes	0.42
$k_{C,settling}$ (m day^{-1})	Settling velocity for cyanobacteria	0.15
$k_{D,settling}$ (m day^{-1})	Settling velocity for diatoms	0.20
$k_{G,settling}$ (m day^{-1})	Settling velocity for chlorophytes	0.15
K_d (m^2 day^{-1})	Vertical eddy diffusivity rate	0.5428
T_{optC} (°C)	Optimal temperature for cyanobacteria	30
T_{optD} (°C)	Optimal temperature for diatoms	19
T_{optG} (°C)	Optimal temperature for chlorophytes	20
I_{optD} (ly day^{-1})	Optimal light intensity for diatoms	25
I_{optG} (ly day^{-1})	Optimal light intensity for chlorophytes	89.8
K_{PC} (mg P l^{-1})	Half-saturation constant for P uptake by cyanobacteria	0.0002
K_{PD} (mg P l^{-1})	Half-saturation constant for P uptake by diatoms	0.05
K_{PG} (mg P l^{-1})	Half-saturation constant for P uptake by chlorophytes	0.0009
K_S (mg Si l^{-1})	Half-saturation constant for Si uptake	0.0053
k_{nit} (day^{-1})	Nitrification rate	0.09
k_{denit} (day^{-1})	Denitrification rate	0.001
k_{mn} (day^{-1})	Organic nitrogen mineralization rate	0.032
k_{mp} (day^{-1})	Organic phosphorus mineralization rate	0.02
k_{bod} (day^{-1})	CBOD deoxygenation rate	0.5
k_{sod} (day^{-1})	Sediment oxygen demand rate	0.65
S_{N} (g N m^{-2} day^{-1})	Release rate of ammonium from the sediment	0.4
S_{P} (g P m^{-2} day^{-1})	Release rate of phosphate from the sediment	0.013
K_{denit} (mg day^{-1})	Half-saturation constant for oxygen limitation of denitrification	0.2
K_{bod} (mg day^{-1})	Half-saturation constant for oxygen limitation of CBOD oxidation	0.5
K_{sod} (mg day^{-1})	Half-saturation constant for sediment oxygen demand	0.4
K_{mpc} (mg day^{-1})	Half-saturation constant for phytoplankton limitation	1.00
K_{DOS} (mg day^{-1})	Half-saturation constant for nutrient sediment fluxes	0.4
$k_{\mathrm{ON},settling}$ (m day^{-1})	Settling velocity for organic nitrogen	0.03
$k_{\mathrm{OP},settling}$ (m day^{-1})	Settling velocity for organic phosphorus	0.03
$K_{bod,settling}$ (m day^{-1})	Settling velocity for organic CBOD	0.03
θ_{nit}	Temperature adjustment for nitrification rate	1.080
θ_{denit}	Temperature adjustment for denitrification rate	1.080
θ_{N}	Temperature adjustment for release of NH_4 sediment rate	1.080
θ_{P}	Temperature adjustment for release of PO_4 sediment rate	1.080
θ_{bod}	Temperature adjustment for CBOD deoxygenation rate	1.050
θ_{sod}	Temperature adjustment for oxygen sediment demand rate	0.4
f_{ON}	Fraction of dead and respired phytoplankton recycled to ON pool	0.5
f_{OP}	Fraction of dead and recycled phytoplankton recycled to OP pool	0.5

Table A.1 (*Continued*)

Parameter	Description	Value
f_{DON}	Fraction of dissolved organic nitrogen	1.00
f_{DOP}	Fraction of dissolved organic phosphorus	1.00
f_{DBOD}	Fraction of dissolved CBOD	1.00
α_{oc} (mg O mg C^{-1})	Oxygen to carbon ratio	2.67
cchl (mg C mg Chl^{-1})	Phytoplankton carbon to chlorophyll ratio	50
K_2 (m^2 mg^{-1})	Light attenuation coefficient for chlorophyll	0.002
$\Psi_{C,D,G}$ ((mg N m^{-3})$^{-1}$)	Strength of the ammonium preference	0.009
k_a (day^{-1})	Reaireation rate	0.38
α_{on} (mg O mg N^{-1})	Stoichiometric oxygen to nitrogen ratio for nitrification	Estimated
$k_{C,growth}$ (day^{-1})	Maximum growth rate for cyanobacteria	Estimated
$k_{D,growth}$ (day^{-1})	Maximum growth rate for diatoms	Estimated
$k_{G,growth}$ (day^{-1})	Maximum growth rate for chlorophytes	Estimated
$k_{C,death}$ (day^{-1})	Mortality rate for cyanobacteria	Estimated
$k_{D,death}$ (day^{-1})	Mortality rate for diatoms	Estimated
$k_{G,death}$ (day^{-1})	Mortality rate for chlorophytes	Estimated
I_{optC} (ly day^{-1})	Optimal light intensity for cyanobacteria	Estimated
K_{nit} (mg day^{-1})	Half-saturation constant for oxygen limitation of nitrification	Estimated
θ_r	Temperature adjustment for phytoplankton respiration rate	Estimated
θ_m	Temperature adjustment for phytoplankton mortality rate	Estimated
θ_{mn}	Temperature adjustment for ON mineralization rate	Estimated
θ_{mp}	Temperature adjustment for OP mineralization rate	Estimated
α_{nc} (mg N mg C^{-1})	Phytoplankton nitrogen to carbon ratio	Estimated
α_{pc} (mg P mg C^{-1})	Phytoplankton phosphorus to carbon ratio	Estimated
K_1 (m^{-1})	Background light attenuation	Estimated

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