Ecological Modelling 320 (2016) 393–406

Contents lists available at ScienceDirect

Ecological Modelling

journal homepage: www.elsevier.com/locate/ecolmodel

Evaluation of ecological effects of anthropogenic nutrient loading scenarios in Los Molinos reservoir through a mathematical model

S.B. Rodriguez Reartes[a,*], V. Estrada[a], R. Bazán[b,c], N. Larrosa[c], A. Cossavella[c,d], A. López[c,d], F. Busso[e], M.S. Diaz[a]

[a] Planta Piloto de Ingeniería Química (Universidad Nacional del Sur—CONICET), Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina
[b] ISEA, Instituto Sup. de Estudios Ambientales, Córdoba, Argentina
[c] Dpto. Qca. Industrial y Aplicada, Fac. Cs. Exactas, Físicas y Naturales—UNC, Av. Vélez Sarsfield 1611, 5000 Córdoba, Argentina
[d] ICTA, Instituto de Ciencia y Tecnología de Alimentos, FCEFyN - UNC - Córdoba, Argentina
[e] Aguas Cordobesas S.A., Córdoba, Argentina

ARTICLE INFO

Article history:
Received 22 April 2015
Received in revised form 12 October 2015
Accepted 13 October 2015

Keywords:
Ecological model
Scenario development
Prospections
Dynamic parameter estimation
Validation
Water planning

ABSTRACT

In this paper we perform a scenario analysis to assess the likely ecosystem structural shifts that might be induced by seven alternative management scenarios relative to current simulated lake dynamics of Los Molinos reservoir, a monomictic lake located in Argentina. To carry out the scenario analysis, first, we formulate, calibrate and validate a mechanistic biogeochemical model to characterize the nutrients and phytoplankton dynamics of the reservoir under study. The model includes a set of partial differential algebraic equations, which results from dynamic mass balances on main phytoplankton groups, nutrients, dissolved oxygen and biochemical demand of oxygen. We consider the main sources of nutrient loading and the dominant phytoplankton groups. The parameter estimation model is a constrained dynamic optimization problem that has been formulated within an equation oriented control vector parameterization environment. We estimated sixteen parameters, previously identified as the most influential ones. Numerical results for calibration and validation phases show good agreement with field data, and then, we use the proposed model as a prospective tool. The obtained results for the designed nutrient loading scenarios indicate the importance of the impacts of current livestock practices and sewage/collective septic tanks discharges on the water quality. Model predictions indicate that the combination of reduction in nutrient loading from the sewage of residential areas in the lake shore, and implementation of measures to mitigate nutrient exports from livestock production will render the most beneficial effects over the studied ecosystem, thus promoting the improvement of the current ecological state of the reservoir. This is the first time such an approach has been applied to the study of Los Molinos catchment. Thus, the proposed ecological model constitutes a management tool to assess the anthropogenic impacts over this freshwater resource.

1. Introduction

Mechanistic biogeochemical models represent the biological, chemical and physical processes taking place in aquatic ecosystems. These models are formulated as a complex set of differential algebraic equations with rate coefficients that must be tuned to the specific conditions of the site under study (Jørgensen and Bendoricchio, 2001). After determining the most influential parameters into the model, dynamic parameter estimation must be performed and the model performance to represent the real ecosystem has to be validated with an independent data set from the site (Bennett et al., 2013; Jørgensen and Bendoricchio, 2001).

In a previous work, we have formulated a first principle based eutrophication model (Estrada et al., 2009), and we have also performed sensitivity analysis (Estrada and Diaz, 2010). The latter model was posed for Paso de las Piedras Reservoir and considered the dominant phytoplankton groups and nutrients present in this water body (Estrada et al., 2009). In the current work we extend Paso de las Piedras model to take into account the particular phytoplankton community, nutrient loading and hydrodynamic regimes and forcing functions existing in Los Molinos Reservoir. Los Molinos Reservoir is a multipurpose freshwater resource providing water for domestic supply, irrigation, energy generation, fishing and recreational activities, located in the Central Region of Argentina (Bazán, 2011). Field data collected between 2002 and

* Corresponding author. Tel.: +54 291 4861700.
E-mail address: brodriguez@plapiqui.edu.ar (S.B.R. Reartes).

http://dx.doi.org/10.1016/j.ecolmodel.2015.10.028
0304-3800/

2005 have allowed classification of the water body as mesotrophic. However, during the last decade, periodic monitoring of the water body allows to detect algal blooms, fish kill events and nutrient enrichment (Bazán, 2011; Cossavella, 2003). These facts evidence the shift of the reservoir state towards eutrophic, unless management measures are undertaken. Moreover, it is a well known fact that phytoplankton blooms in the fresh water source may affect the water treatment process, both physically (e.g. filter clogging) and chemically (e.g. production of harmful cyanotoxins, taste and odour compounds and disinfection by-products). In short, high phytoplankton concentrations in the source water increase the complexity and cost of the raw water treatment process (Ewerts et al., 2013).

Mechanistic biogeochemical models have been widely used for understanding aquatic ecosystems, predicting biotic responses to shifts in the driving forces (nutrient enrichment scenarios, climate change) and assessing restoration strategies for water bodies (Osidele and Beck, 2004; Zhang et al., 2004). Moreover, water quality modelling provides a range of approaches to support water resource management. One approach is to apply physically-based models for assessing water quality in catchments (Matias et al., 2008). These models produce results with limited input requirements allowing catchment assessment and management (Matias and Johnes, 2012). Provided that enough site-specific input data is available, such as to enable model parameter tuning, mechanistic models can also be applied for management purposes. The idea behind using these more complex models as management tools is the possibility of evaluating different nutrient loading scenarios over algae growth, nutrient concentrations and the entire ecological structure. In other words, the use of models in environmental management allows predicting the effect of a given change on the ecosystem under study in a wider extent.

In this context, the aim of this work is to assess the likely impact of a range of alternative management scenarios on nutrient loading in the short and middle term over Los Molinos reservoir ecosystem. The effects of each considered scenario over the trophic state and phytoplankton dynamics is analyzed. To achieve this goal, we formulate a water quality model that fits site-specific conditions of Los Molinos Reservoir. Then, we evaluate the model performance through qualitative and quantitative diagnostic measures (Bennett et al., 2013). Based on field data, we also determine the reservoir current trophic state.

2. Materials and methods

2.1. Case study

Los Molinos Reservoir is an artificial water body located at 65 km SW of Córdoba city in Argentina (31°43′30″S y 64°32′20″W). It was constructed between 1948 and 1953 for drinking water supply, hydro electrical energy generation, irrigation and flood attenuation. The reservoir has a mean depth of 14 m, a maximum depth of 52 m, an area of 21.1 km^2 at spillway level and a maximum volume of 400 hm^3. Its retention time has been estimated in 451 days. Its main tributaries are: San Pedro River, Los Espinillos River, del Medio River and Los Reartes River. Its effluent is Los Molinos River (see Fig. 1). Los Molinos is a monomictic lake, thermally stratified during summer (Bazán, 2011).

The power plant Los Molinos I generates 148 MW for the Central Region of Argentina. The reservoir supplies drinking water to half a million people of Córdoba city (one third of the population of that city). Currently, this water body represents a major tourist attraction for the region and is also used for recreational activities like fishing and water sports. The main activities performed in the basin are related to agriculture and livestock.

The watershed of Los Molinos Reservoir extends over an area of 978 km^2. In the last decade there has been an important urban development in the lakeshore area, as well as tourism increase. According to a census made in 2008 (Censo Provincial de Población, 2008—Provincia de Córdoba), there are 3500 people that permanently inhabite in the four main lakeshore villages: Potrero de Garay, Villa Ciudad de América, Los Reartes and Ciudad Parque Los Reartes. Census data also reveal that the treatment of domestic wastewater in the region is made through septic tanks and cesspools, which result inefficient due to soil characteristics of the area, and to the proximity of the dwellings to the reservoir (less than 50 m from the coast for some buildings) (Nadal et al., 2012). Moreover, in some cases, the direct discharge of the domestic effluents, i.e. without previous treatment, is performed. Additionally, a great number of tourists visit the area every year; and during summertime the population doubles in the area (Molinero Rodríguez, 2008). Around 300 animals (cows and horses) graze in the west coast of the reservoir and use it as drinking trough (Nadal et al., 2012) providing a direct discharge of their manure into the water body.

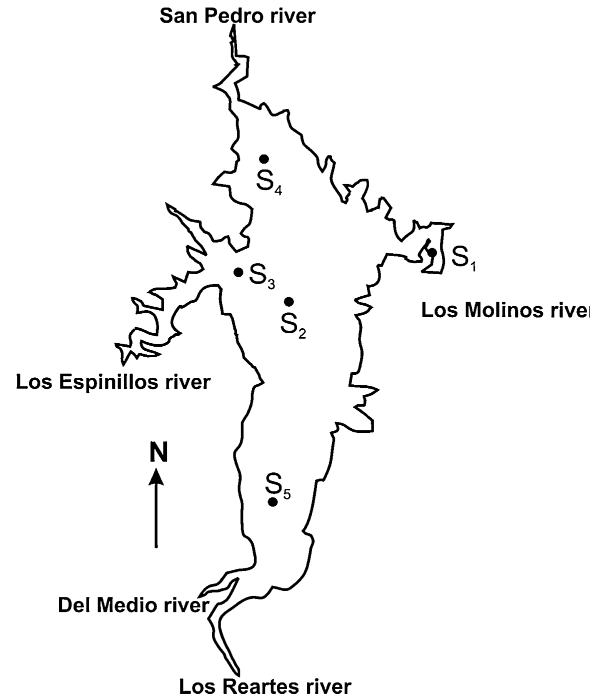

Fig. 1. Los Molinos Reservoir location. S1, S2, S3, S4 and S5: sampling stations.

The lack of land-use policies related to urbanistic development in the area, together with the inappropriate household wastewater treatment, promote nutrient enrichment of the water body (Nadal et al., 2012), especially phosphorus, which constitutes one of the essential factors for phytoplankton growth. Therefore, having a tool to assess the impact of human activities over this ecosystem is critical to the management of the water resource.

2.2. Sampling and experimental procedures

Physico-chemical and biological data have been monthly collected from January to December of 2007 and 2008 at different depths in five sampling stations (Bazán, 2011): S_1 (in the dam of the reservoir), S_2 (in the center of the water body), S_3 (in the mouth of Los Espinillos River), S_4 and S_5 in coastal zones (in the mouth of San Pedro and Los Reartes River, respectively), see Fig. 1. Sampling was performed at different depths considering the mixing and stratified periods. During the mixing regime, samples were taken at 0.2 m, at the limit o photic zone (considered as twice the Secchi disk depth), and 1 m from the lake bottom. When a thermocline was detected, samples were taken at 0.2 m, 1 m above the thermocline, 1 m below the thermocline and 1 m from the lake bottom. Tributaries flows and their nutrient concentrations were also determined.

In situ measurements of physical variables, including temperature, pH, dissolved oxygen, electrical conductivity and water turbidity have been taken with multisensors Horiba U-10, U-23 and W-22XD. Moreover, air temperature and Secchi disk depth have also been recorded.

Water samples have been taken with Van Dorn and Ninsky bottles. Nutrient determinations include phosphate (SRP), total phosphorus (TP), nitrate (NO_3), nitrite (NO_2), ammonium (NH_4), total organic nitrogen (ON), organic carbon, total iron, manganese, calcium, magnesium, potassium, sodium, chloride, fluoride and sulfate concentrations and alkalinity. For sampling, storage, preservation and sample analysis we follow the guidelines and techniques of APHA, AWWA and WEF (Clesceri et al., 1998); and the international standards ISO 5667/2 and ISO 5667/3.

Samples for quantitative analysis have been fixed immediately with Lugol's solution. The Utermöhl method (Utermöhl, 1958) was used for the quantitative phytoplankton analysis in an inverted microscope (in Cells/ml). Chlorophyll concentration has also been determined according to APHA, AWWA and WEF standards (Clesceri et al., 1998).

Biovolume has been calculated based on cell counts and their size and geometric form (Hillebrand et al., 1999; Olenina et al., 2006; Reynolds, 2006; Sun and Liu, 2003). Carbon content of phytoplankton cells has been calculated through correlations (Smayda, 1978). In the appendix II we present a detailed description (see Table II.A) with the Individual biovolumes of each phytoplankton specie considered in this work and it related geometric form.

Furthermore, water sampling and level determination of the four major tributaries has been carried out. The methodology used for sampling, storage, preservation and analysis was identical to that applied to samples collected in the reservoir.

Data on reservoir water level and volume was provided by the provincial power company: EPEC (Empresa Provincial de Energía de Córdoba), responsible for operating the power energy plant.

During 2007, thermal stratification was only detected at S_1 station on December between 19 and 20 m depth. For year 2008, a thermocline was detected on January at S_2 (between 13 and 14 m); on February at S_1 and at S_2 (between 10 and 11 m) and at S_5 (between 4 and 5 m); and on December at S_1 (between 13 and 14 m) and at S_2 (between 10 and 11 m). Then, not strong stratification was determined for the studied period.

In this study, we consider experimental data from S_1 station because the raw water abstraction point for the treatment process is located there. Even though a single sampling site would not represent in detail the conditions of a large impoundment, the emerging results of the present study would clearly assist in determining the trends of the variables for management purposes, as it is close to the water intake (van Ginkel et al., 2001).

3. Ecological model description

We propose an ecological water quality model, based on (Estrada et al., 2009). We have extended the model to take into account specific conditions of our case study. A short description of the model structure is given in this section. A conceptual diagram of the model and additional information are presented in Appendix I (Fig. AI).

We formulate dynamic mass balances for the main components of the reservoir ecosystem, rendering a set of partial differential algebraic equations (PDAE). We consider the main taxonomical phytoplankton groups in the reservoir (dinophyta, cryptophyta and cyanobacteria), nutrients (nitrate, nitrite, ammonium, organic nitrogen, phosphate and organic phosphorus), dissolved oxygen and biochemical demand of oxygen. Dinophyta and cryptophyta were considered because they represent the dominant phytoplankton groups observed in the water body and they can also produce severe problems in treatment processes, promoting filter clogging and unpleasant odors and flavors in the water. We have also included cyanobacteria by considering the potential damage they can cause on human health. Toxins synthesized by cyanobacteria would turn the resource inappropriate for human and animal consumption, and for recreational activities (Brandalise et al., 2012; Ewerts et al., 2013). For more details on the selection of the taxonomical groups included in the model, see Section 5.1.

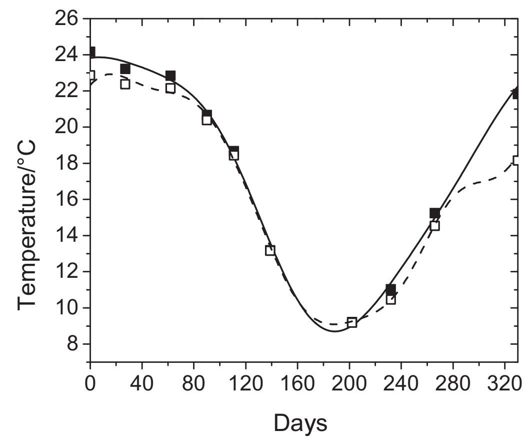

Fig. 2. Temperature profiles for the lower layer (■,—–) and the upper layer (□,– – –) as a function of time.

The formulated PDAE system is transformed into an ordinary differential-algebraic system (DAE) through spatial discretization of the water body in two horizontal layers. As Los Molinos Reservoir is a monomictic lake, thermally stratified during summer, the physical segmentation considered in this work is consistent with the observed epilimnetic and hypolimnetic depths. Moreover, different temperatures have been considered for each layer (see Fig. 2). Two layers discretization has also been applied in other ecological models for stratified lakes (Arhonditsis and Brett, 2005; Arhonditsis et al., 2001; Osidele and Beck, 2004; Zhang et al., 2004). A simplified flux diagram of Los Molinos reservoir model is presented in Fig. 3, where we observe the physical segmentation adopted, the inputs/outputs from/to terrestrial and aerial ecosystems and the interchange between layers and sediment.

The main simplifying assumptions of our model are: water constant density, constant transversal area for the upper layer, and horizontally averaged concentrations (only spatial gradients in vertical direction are considered). Phosphate is considered as the limiting nutrient in our model (Schindler et al., 2008). Although the N:P ratio is used to determine the limiting nutrient in aquatic ecosystems, some authors point out that it is most important to establish the concentration values of phosphorus and nitrogen biologically available, i.e., inorganic nitrogen ($NO_2 + NO_3 + NH_4$) and SRP (Rast and Lee, 1983; Ryding and Rast, 1992). Ryding and Rast (1992) determine a weight ratio of 8 N:1P as a reasonable one to establish the biological available limiting nutrient. A N:P ratio less than 8 suggests that nitrogen could limit the growth; and for ratios greater than 8, phosphorus is the potential limiting nutrient. Moreover, concentrations below 0.005 mg/l of phosphate and 0.02 mg/l of total inorganic nitrogen (TIN) have been signaled as limiting of the primary productivity (Rast and Lee, 1983). Other authors (Sas, 1989) indicate 0.01 and 0.1 mg/l for SRP and TIN limitation, respectively, as threshold values. In Los Molinos Reservoir, for the studied period, the ratio N:P was always above 8, indicating a phosphorus

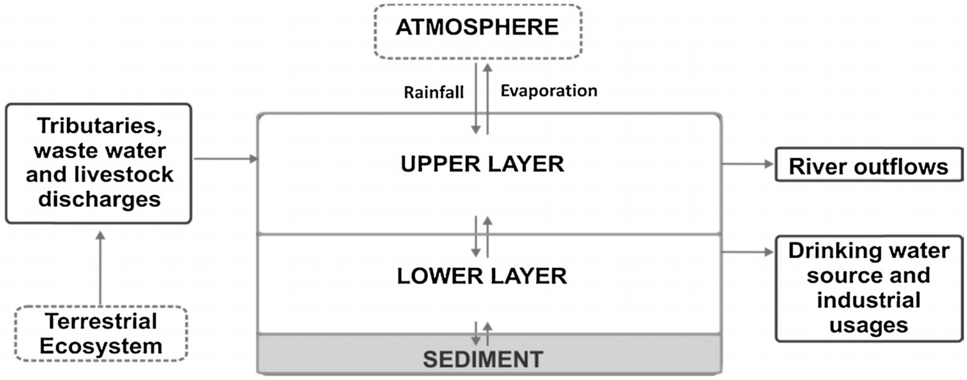

Fig. 3. Simplified flux diagram of Los Molinos reservoir model.

limitation, except for February, 2007. Furthermore, TIN and SRP have never been below the mentioned critical values (Rast and Lee, 1983; Sas, 1989), in any sampling station. Therefore, phosphorus appears as the potential limiting nutrient during the studied period and its kinetics are Monod type in the proposed model (see Ec. A.4 in Appendix I).

The global mass balance considers inputs from tributaries and discharges of domestic wastewater (Q_{IN}), inputs from rains (Q_{rain}), outputs from Los Molinos River (Q_{OUT}), and from evaporation (Q_{evap}), see the following equation:

$$\frac{dh}{dt} = \frac{1}{A}\left[\sum_k Q_{IN_k} - \sum_m Q_{OUT_m} + Q_{rain} - Q_{evap}\right] \tag{1}$$

k corresponds to the inputs from tributaries (rivers: San Pedro, Los Espinillos, Del Medio and Los Reartes), domestic wastewater discharges (in upper layer, U); m corresponds to the outputs for water treatment (in lower layer, L) and Los Molinos River (in U).

Component mass balances in each layer include the previously mentioned input (Q_{IN}) and output flow rates (Q_{OUT}), the generation/consumption terms (r_j) and terms that account for transference between layers (Fick's law), and reservoir volume variability (through upper layer height change), Eqs. (2) and (3).

Upper layer (U):

$$\frac{dC_{Uj}}{dt} = \sum_K \frac{Q_{IN,U,k}}{V_U} C_{IN,Ujk} - \frac{Q_{OUT,U}}{V_U} C_{Uj} + r_{Uj} - \frac{k_d A}{\Delta h V_U}\left(C_{Uj} - C_{Lj}\right) - \frac{C_{Uj}}{h_U}\frac{dh}{dt} \tag{2}$$

Lower layer (L):

$$\frac{dC_{Lj}}{dt} = -\frac{Q_{OUT,L}}{V_L} C_{Lj} + r_{Lj} + \frac{k_d A}{\Delta h V_L}\left(C_{Uj} - C_{Lj}\right) \tag{3}$$

j corresponds to dinophyta, cryptophyta, cyanobacteria, nitrate, nitrite, ammonium, organic nitrogen, phosphate, organic phosphorus, dissolved oxygen, biochemical demand of oxygen.

Additional algebraic equations stand for rate equations for each component (generation/consumption terms, r_j) and forcing functions, these latter ones approximated through sinusoidal functions for temperature (in each layer, see Fig. 2), solar radiation, rainfall, evaporation, river inflows/outflows and their associated nutrient profiles (in nitrogen and phosphorus). Furthermore, the model includes sewage effluents and manure animal discharges and their associated nutrient contents (in nitrogen and phosphorus), as input data. As previously mentioned, the inhabitants of the four main lakeshore villages contribute to sewage inputs throughout the year and, during summer time, these inputs rise up to 25% due to tourism activities in the region. For this reason, the effluent flow is represented with a step function (see Section 4.2.). The loadings per capita were estimated in 300 l/dy/inhab, according to ENHOSA rules, from the Ministry of Infrastructure and Housing of Argentina (Norma ENOHSA, 1993). The content of organic nitrogen, ammonium and nitrate were taken from the general characterization of sewage in (Normas para la, 1999), and the phosphate and organic phosphorus contents from (Metclaf and Eddy, 2003) (see Appendix I, Table I.D). Regarding livestock loadings, we consider that their water content is negligible (taking into account the number of animals and dimensions of the lake). The manure production and its nutrient content are taken from ASAE Standards (ASAE D384.1 Manure Production and Characteristics. American Society of Agricultural Engineers FEB03) for horses and cows, the livestock in the zone. In this latter case, ammonium and phosphate are considered (see, Table I.D in Appendix I).

Appendix I shows the rate equations that describe phytoplankton, nutrients and dissolved oxygen dynamics (Table I.A) and the input flow rates related to wastewater and livestock discharges for mass balance equation, Eq. (2), (Table I.B). Furthermore, a portrayal of the biogeochemical processes and state variables in the model has been included in Appendix I (Fig. AI). For readers interested in more details of the ecological model, we recommend the work of (Estrada et al., 2009). Initial conditions for differential equations are taken from field collected data.

4. Dynamic parameter estimation and model validation

The parameter estimation problem is formulated within a dynamic optimization framework in gPROMS (PSEnterprise, 2014), with a maximum likelihood objective function subject to the proposed ecological water quality model. Assuming constant variance for measurements, the objective function results a weighted least squares one, and the resulting DAE constrained optimization problem (P1) formulated is as follows:

$$\Phi = \frac{N}{2}\ln(2\pi) + \frac{1}{2}\min_p \sum_{j=1}^{NV}\sum_{k=1}^{NT_j}\left[\ln\left(\sigma_{jk}^2\right) + \frac{\left(C_{jk}^* - C_{jk}\right)^2}{\sigma_{jk}^2}\right]$$

st.

Water quality DAE model from Los Molinos Reservoir (Eqs. 1 to 3 and Eqs. A.1 to A.47) (P1)

$$\boldsymbol{c}(0) = \boldsymbol{c}^0$$

$$\boldsymbol{c}_L \le \boldsymbol{c} \le \boldsymbol{c}_U$$

$$\boldsymbol{p}_L \le \boldsymbol{p} \le \boldsymbol{p}_U$$

where N is the total number of measurements, the summations are over NV measured state variables (j), and NT_j data points for each j th measured variable, σ^2_{jk} is the variance of the kth measurement of variable j, c^*_{jk} is the kth measured concentration of variable j, and c_{jk} is the kth model-predicted concentration of variable j. Vectors $\boldsymbol{c}(0)$ and $\boldsymbol{p}$ contain the component concentrations at time zero, and the set of model parameters to be estimated, respectively. The optimization algorithm determines both the values of the model parameters to be estimated, i.e. the elements of vector $\boldsymbol{p}$, and the variance model parameters (σ). The component concentrations, i.e. vector $\boldsymbol{c}$, may vary between established lower and upper limits ($\boldsymbol{c}_L$ and $\boldsymbol{c}_U$). Moreover, values of the estimated parameters are within given lower and upper bounds ($\boldsymbol{p}_L$ and $\boldsymbol{p}_U$) according to data from the literature (Arhonditsis and Brett, 2005; Bruno and McLaughlin, 1977; Cerco and Cole, 1994; Cloern, 1977, 1978; Grigorszky et al., 2006; Gurung, 2007; Hamilton and Schladow, 1997; Harris et al., 1979; Hedger et al., 2004; Lindström, 1984; Morgan and Kalff, 1979; Ojala, 1993; Padisák, 1985; Pérez-Martínez and Sánchez-Castillo, 2002; Renaud et al., 2002; Reynolds, 1984, 2006; Rigosi et al., 2011; Romero et al., 2004). Water quality models have a large number of parameters, which depend on the environmental conditions of the place under study, and must be tuned considering field data of the water body. Based on a previously performed global sensitivity analysis of the ecological model (Estrada and Diaz, 2010), we have selected sixteen parameters to be estimated ($\boldsymbol{p}$).

Physical, chemical and biological data monthly collected from January to December of 2007 have been used for model calibration. The values for the estimated parameters are listed in Table 2. The remaining model parameter values are listed in Appendix I (see Table I.D). Model validation has been carried out with an additional independent data set collected monthly between January and December 2008.

4.1. Evaluation of model performance

Model performance has been evaluated through qualitative and quantitative methods (Bennett et al., 2013). Qualitative metrics assess the ability of the model to represent biogeochemical processes observed in the studied reservoir. For qualitative testing, we compare our results to field data and we analyze the outputs taking into account conceptual aspects, and the ability of the model to sketch out trends and system behaviour. Three quantitative testing, measures are calculated based on seasonal average values of the main state variables (SRP, nitrate, dissolved oxygen and phytoplankton groups). Bias or mean error, (ME, Eq. (5)) calculates the mean of the residuals, indicating model's tendency to under- or over estimate a variable. Index of agreement (d, Eq. (6)) varies between 0 and 1 with values close to unity indicating better agreement of model simulations to field data (Willmott, 1981). Root mean squared error (RMSE, Eq. (7)) calculates a mean error in data units, and it is not affected by cancelation (as could be in the case of ME).

$$\mathrm{ME} = \frac{\sum_{n}^{i=1}\left(y_i^* - y_i\right)}{n} \tag{5}$$

$$d = \frac{\sum_{n}^{i=1}\left(y_i^* - y_i\right)^2}{\sum_{n}^{i=1}\left(\left|(y_i - \bar{y})\right| + \left|(y_i^* - \bar{y})\right|\right)^2} \tag{6}$$

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{n}^{i=1}\left(y_i^* - y_i\right)^2}{n}} \tag{7}$$

where y_i^* and y_i are the measured and model predicted values, respectively; $\bar{y}$ is the mean of the measured values, and n is the total number of measurements for the analyzed variable.

4.2. Management scenarios description

Ecological water quality models can be efficiently used as tools to evaluate the impact of different nutrient loading scenarios (Matias and Johnes, 2012; Olsson and Andersson, 2007). After calibration and validation, we use Los Molinos Reservoir water quality model, to explore potential structural shifts of the ecosystem relative to the current simulated lake dynamics. We simulate the changes of ecosystem dynamics induced by seven alternative management scenarios for the catchment (Table 1, Scenarios 1 to 7). These scenarios are modeled related to the catchment state in 2007. In this way, Scenario 0 in Table 1 is considered as the "base case" for the present analysis. There are two main issues explored in this study: (1) supply of nutrients into the system from livestock, and (2)

Table 1
Scenarios run for Los Molinos bassin[a].

Scenario	Dimension	Trends	Modelled change
0	"Base case"	Catchment status for 2007	
1	Land use	Intensification of livestock production in the area	Gradual increase in livestock by 20% each year that promote the increase of ammonium and SRP discharges
2	Land use	Implementation of good farming practices by avoiding livestock entrance to the reservoir from lakeshore	Reduction to zero of ammonium and SRP discharges from livestock
3	Human population	Implementation of an efficient sewage treatment with the current resident population and land use	All sewers connected to treatment plants (removal of NO_3, NO, NH_4, PO and SRP up to allowable limits for liquid effluent discharge to surface waterways)[b]
4	Human population and land use	Implementation of an efficient sewage treatment with the current resident population and avoiding livestock entrance to the reservoir	Changes of Scenarios 2 and 3
5	Human population	Increase of resident population with the current deficient sewage treatments	Gradual increase of untreated sewage (from direct discharge of wastewater or deficient sewage treatment)
6	Human population	Increase of resident population with the implementation of an efficient sewage treatment	Gradual increase of discharges with NO_3, NO, NH_4, PO and SRP concentrations into allowable limits for liquid effluent discharge to surface waterways[b]
7	Human population and land use	Increase of resident population (with the implementation of an efficient sewage treatment) and avoidance of livestock entrance to the reservoir	Changes of the scenarios 2 and 5

[a] Each scenario considered in this work was run for a 6 year time horizon.
[b] Normas para la protección de los recursos hídricos superficiales y subterráneos de la Provincia de Córdoba (1999).

nutrient contributions from the unsewered population. The objective of the designed scenarios for this study is to determine the shifts that might be induced in the ecosystem by modification of the nutrient discharge in the reservoir; and, at the same time, to evaluate the scale of the change that might be necessary to reduce phosphorus loading to a level which could, potentially, sustain a good ecological state in the reservoir. In this context, the analyzed scenarios are designed based on: (a) detected tendencies from previous studies and field surveys; and (b) hypothetical managerial policies for the watershed. Item (a) means that we consider the local census and previous Argentinean population statistics to propose a reasonable forecast of population growth in the area under study. Item (b) is related to the possible implementation of policies and legislations regarding land use in the area; more specifically those that prevent direct access of livestock to the reservoir. Additionally, we test the possible use of proper sewage treatments for the inhabitants in the area. The last, is a hypothesis but could be achieve provided that stakeholders get involved on this specific issue.

Through scenarios 1 to 7 we want to evaluate the prospects of change of the trophic state of Los Molinos Reservoir, and the conditions that would support the generation of good ecological status in the lake. These issues are discussed in Section 5.3. A complete description of each designed scenario is presented in this section; and they are summarized in Table 1.

Scenario 1 considers intensification of livestock production in the area. This possibility is analyzed taking into account that cows and horses have currently free access to the lakeshore (Bazán, 2011; Nadal et al., 2012).

Scenario 2 is designed for preservation of the reservoir as drinking water source; therefore, preventing the direct access of animals to the lake constitutes a practice that avoids this contamination source.

Reducing point sources of discharge with large population in the catchment can be achieved through the installation of conventional sewage treatment units. However, in rugged geography areas with low population density, as in our case study, septic tank systems are widely used (Johnes et al., 1996). It should be pointed out that the type of septic tank used in the studied area are collective systems with direct drains to soil. The proximity between dwellings and the lake (less than 50 m from lake coast for some buildings), together with soil characteristics, makes this sewage treatment inadequate (Nadal et al., 2012). Furthermore, there are cases in which direct discharge to the reservoir is performed. These findings, together with field surveys, evidence the need for mitigation of point source discharges to waters and also the need of further treatment of effluents from septic tanks. In this sense, Scenario 3 contemplates performing an adequate sewage treatment with the current resident population and land use. At the end of the treatment, we consider the nutrient concentration in the effluent would fulfill the current standards for the protection of surface and groundwater resources of Córdoba Province (Normas para la protección de los recursos hídricos superficiales y subterráneos de la Provincia de Córdoba, 1999). This means that it is assumed that the effluent will be discharged to the water body, after treatment. The local standards point out that total phosphorus and total nitrogen concentrations must be below 0.5 mg/l and 10 mg/l, respectively, for direct discharge to a reservoir. As our model considers phosphorus in fractions of organic phosphorus and phosphate; and nitrogen in fractions of nitrate, organic nitrogen an ammonium, we express P and N in those terms. According to (Metclaf and Eddy, 2003) and (Norma ENOHSA, 1993), domestic wastewater organic nitrogen and ammonium content is almost 40% and 60%, respectively; while organic phosphorus and phosphate content are approximately 30% and 70%, respectively. Based on these values, we estimate the concentrations of the treated

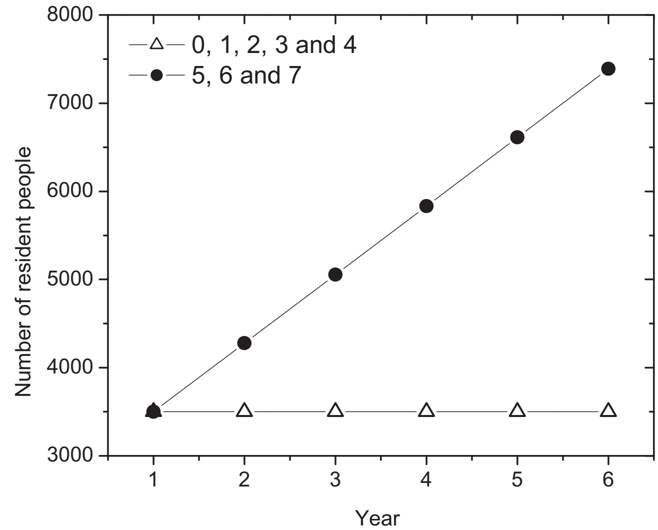

Fig. 4. Number of resident people for scenarios run (from 0 to 7) (Table 1).

effluent for organic nitrogen, ammonium, organic phosphorus and phosphate as 4 mg/l, 6 mg/l, 0.15 mg/l and 0.35 mg/l, respectively. Moreover, we consider other scenarios with efficient treatment facilities and additional factors: Scenario 4 contemplates removing livestock from the lake shore; Scenario 6 considers the increase of the resident population (according to Fig. 4) and associated effluent discharges. Scenario 7 accounts for the increase in the resident production with proper wastewater treatment and the removal of livestock. Scenario 5 contemplates the possibility of increase in the resident population (see Fig. 4), but continuing with the current deficient sewage treatments. It is worth noting that the rapid urban development is a tendency detected in the region through the provincial census (Censo Provincial de Población, 2008—Provincia de Córdoba), and also through field surveys (Bazán, 2011; Nadal et al., 2012). Moreover, during summertime tourism activities contribute to increase nutrient loadings to the lake. This effect is also considered for all the cases through a 25% increase in population (and effluent flow), with respect to the permanent resident population and consequently in the nutrient loadings (see Figs. 4 and 5).

A complete description of the characteristics of each designed scenario is presented in Table 1.

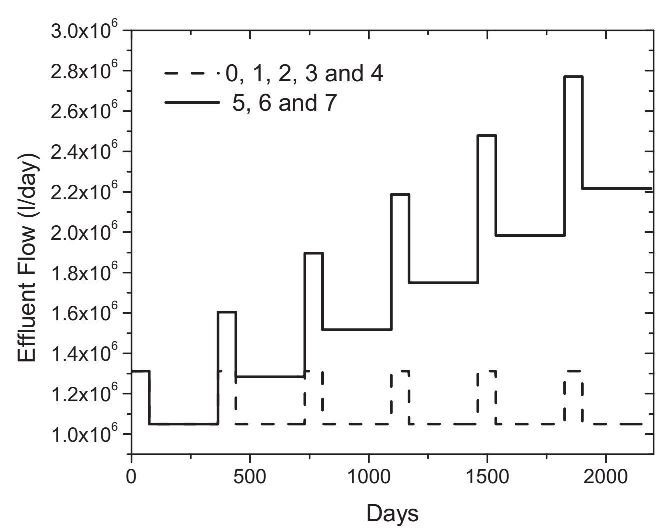

Fig. 5. Effluent flow for scenarios run (from 0 to 7) (Table 1).

5. Results and discussion

5.1. Phytoplankton succession

During the studied period the phytoplankton community was composed by 37 genera of 6 taxonomical groups: Chlorophyceae (15), Dinophyceae (2), Bacillariophyceae (14), Cyanophyceae (3), Cryptophyceae (2), and Euglenophyceae (1). Among these groups, Dinophyceae and Cryptophyceae dominate the phytoplankton community with an annual mean concentration of 0.166 mgC/l and 0.024 mgC/l, respectively. The maximum concentrations throughout the year for these groups were 0.784 mgC/l for Dinophyceae in summer (2007) and 0.070 mgC/l for Cryptophyceae in winter (2007).

Class Dinophyceaein Los Molinos Reservoir was represented by two taxa, *Ceratium hirundinella* and *Peridinium* sp. *C. hirundinella* is known to clog filters during treatment processes due to their large size and thick cell walls, and also to produce by-products that cause taste and odour problems in the final water supply (Ewerts et al., 2013; van Ginkel et al., 2001). Then, the extensive presence of *C. hirundinella* in the raw water have a negative impact over the treatment operations and their costs.

The Cryptophyceae population included the genera *Cryptomonas* and *Croomonas*. *Croomonas* dominate thought the entire year, except in spring, where *Cryptomonas* prevails.

Anabaena and *Microcystis* composed the Cyanophyceae group, with dominance of the first one. Cyanophyceae group was not dominant during the studied period, with an annual mean concentration of 0.0012 mgC/l and a maximum concentration of 0.0052 mgC/l in spring. Even though, we include this taxonomic group into our ecological model by considering the widespread evidence of their potential to produce harmful (even lethal) hepato-, neuro- and cytotoxins as well as odour organic compounds (e.g. geosmin) (Ewerts et al., 2013). Conventional treatment processes (including coagulation, flocculation, sedimentation, sand filtration) may remove quite efficiently the cyanobacterial cells, but they are not enough to eliminate toxins and geosmin, which may be present as the result of cell lysis during the operations. Cyanotoxins and geosmin, like other organic compounds present in raw water, cannot be removed without advanced treatment options (e.g. activated carbon adsorption or ozone oxidation), which increase the operational costs in water treatment. Moreover, the presence of cyanobacteria and their toxins turn the reservoir inappropriate for recreational activities (Brandalise et al., 2012). Finally, the magnitude and frequency of cyanobacterial blooms may be enhanced by nutrient enrichment of water bodies induced by human activities, and/or by climate warming (Rigosi et al., 2014). During the studied period, the concentration of soluble phosphorus on average was 0.0140 mg/l, with peaks up to 0.0470 mg/l in summer (see Fig. 7). Then, the phosphorus concentration remains low in relation to nutrient-rich conditions preferred by cyanobacteria (i.e. eutrophic or hypereutrophic environments). However, an increase of nutrient concentration could be an important driver for the development of blooms. We consider that all the previously mentioned risks associated to cyanobacteria blooms justify the inclusion of this group into our ecological model.

The three taxonomic groups included in the model, i.e. Dinophyceae, Cryptophyceae and Cyanophyceae, explain between 70% and 98% of total phytoplankton biomass except in June, August, November and December. In June and August when a peak of diatoms was detected with 32% and 27% of total biomass, respectively. And in spring, a peak of chlorophytes was registered with 51% and 54% of total biomass, respectively. However, diatoms and chlorophytes have not been included in the model because their contribution to total biomass was significant only in those months, and their annual mean biomass only reached 5.4% and 4.9%, respectively.

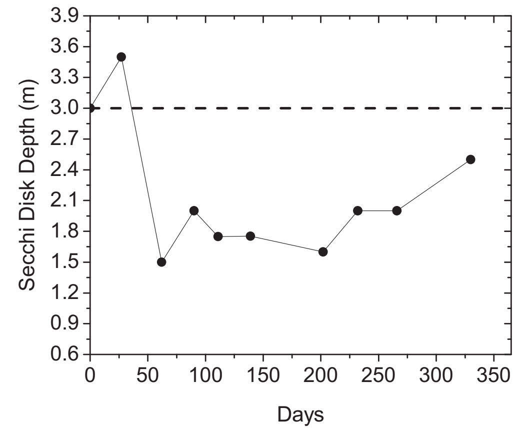

Fig. 6. Observed Secchi disk depth (eutrophic between 1 and 3 m, Wetzel, 1983).

5.2. Current trophic state

Algal blooms in Los Molinos Reservoir of *C. hirundinella* (division *Pyrrhophyta* class *Dinophyceae*) have been detected, with dominance in summer and early autumn (Bazán, 2011). Moreover, fish kill events associated to the presence of *C. hirundinella* have been registered in 1999, 2005 and 2006. The current trophic state of this reservoir is mesotrophic or eutrophic depending on the analyzed variable. Regarding Secchi disk depth (see Fig. 6), most of the year it is below the eutrophic value limit, at 3 m (Wetzel, 1983) (horizontal line in Fig. 6).

Figs. 7–9 show the concentration profiles for soluble reactive phosphorus (SRP), nitrate and total phytoplankton, respectively, and the corresponding eutrophication levels for each variable (horizontal lines at 0.02 mg/l for SRP, 0.3 mg/l for nitrate, and 5000 cells/ml for algae). Regarding SRP, it is beyond eutrophication limit for almost a half of samples considered. Nitrate is always below eutrophication level but is beyond mesotrophic limit (0.15 mg/l of nitrate) during two months. Phytoplankton remains always below the eutrophication limit but, after prior observed algal blooms and nutrient enrichment detected, phytoplankton dynamics could change and management measures should be considered to avoid undesired effects over this ecosystem (Bazán, 2011; Cossavella, 2003). Up to now, periodic monitoring of Los Molinos Reservoir has been performed and preliminary studies of

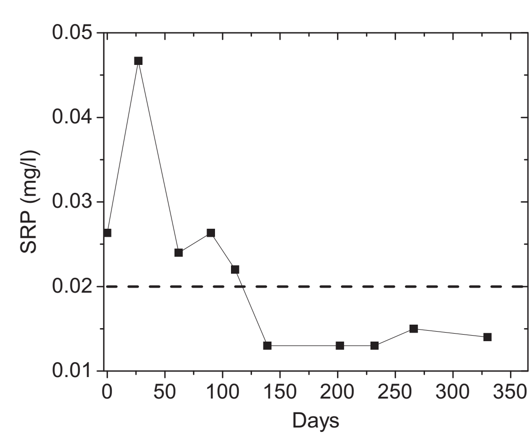

Fig. 7. Observed SRP concentration and eutrophic level (above 0.03 mg/l, Wetzel, 1983).

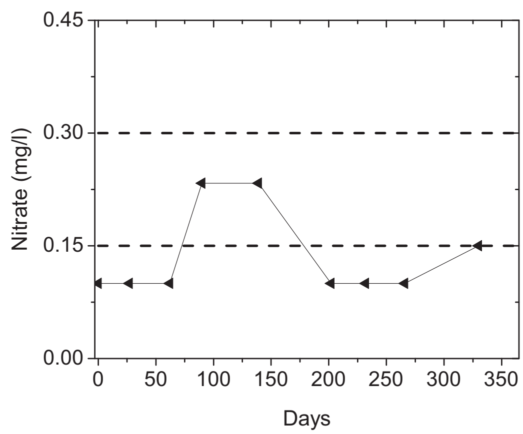

Fig. 8. Observed nitrate concentration (mesotrophic between 0.30 mg/l and 0.15 mg/l, Wetzel, 1983).

its physical parameters have been made (Corral et al., 2002, 2004). However, ecological models have not been developed and calibrated to fit local conditions for the evaluation of the effects of environmental disturbances over the dynamics of main components in the reservoir.

5.3. Model calibration and validation

Problem P1 has been implemented in gPROMS (PSEnterprise, 2014), a vector parameterization (CVP) dynamic optimization environment, with a maximum likelihood objective function, to estimate sixteen parameters. Field data collected monthly between January 2007 and December 2007 were considered for the calibration process. Optimal parameter values are listed in Table 2. (Values for the parameters not included in the calibration procedure are presented in Table I.D, Appendix I). Calibration (also referred to as "replicative validation" in the classification of Arhonditsis and Brett, 2004) results are presented in graphical and numeric form (with statistical metrics). Fig. 10 shows the observed data and the simulated profiles along the considered calibration period, for the main state variables of the model, including phytoplankton groups (dinophyta, cryptophyta, cyanobacteria) and nutrients (nitrate, ammonium, SRP and dissolved oxygen). The model displays an acceptable agreement with field data according to the visual screening of simulated time series.

Table 3 shows statistical metrics for model calibration, based on seasonal average values for the main state variables. To evaluate

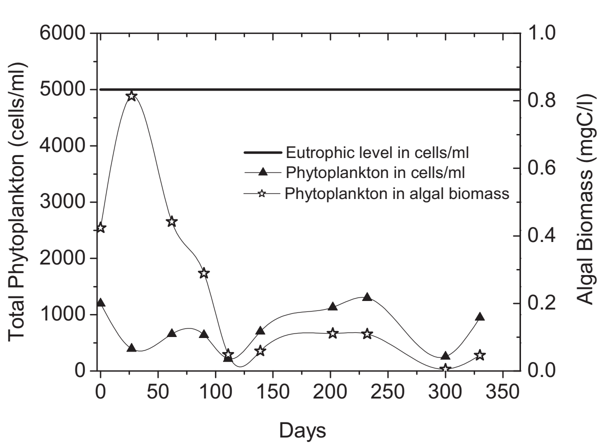

Fig. 9. Observed total phytoplakton concentration and eutrophic level (above 5000 cells/ml, Wetzel, 1983).

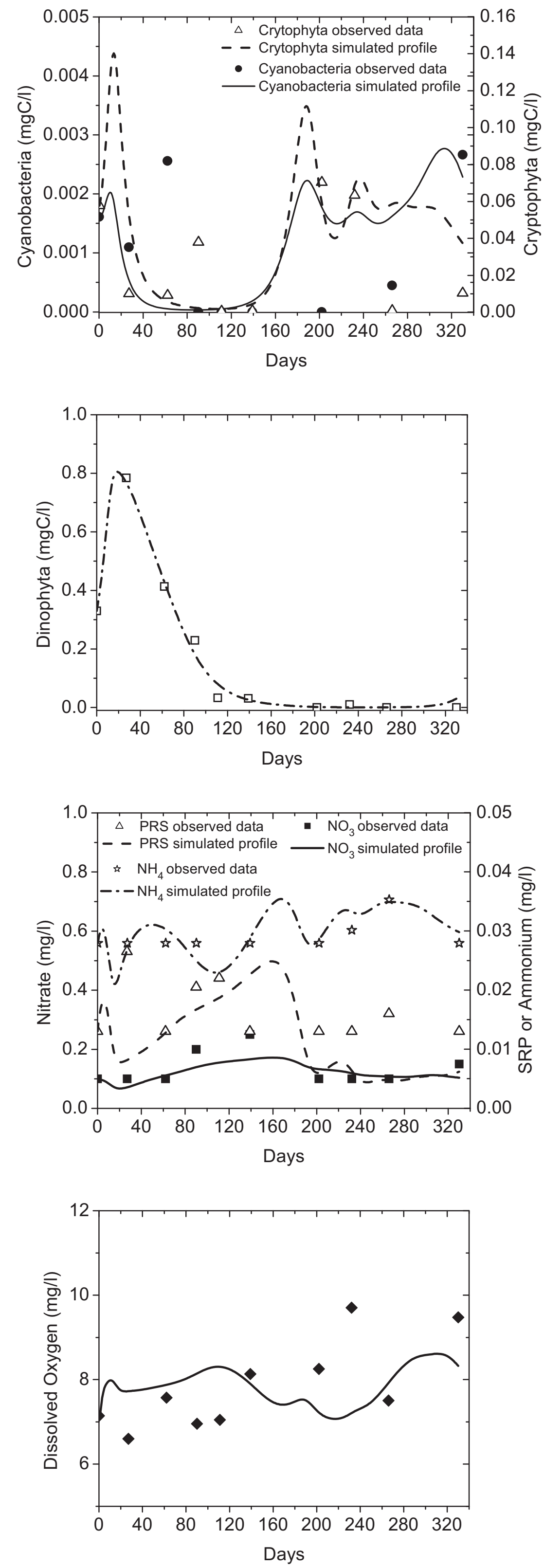

Fig. 10. Calibration results: Observed data and simulation profiles for the main state variables of Los Molinos Reservoir model (model: Eqs. 1 to 3 and Eqs. A1 to A.47; parameters: Table 2 and I.C).

the model performance, we compute the mean error, (ME)), the index of agreement (d) and the root mean squared error (RMSE), Eqs. (5)–(7). Statistical metrics reveal that dinophyta dynamics has the most accurate fit (ME = 0.0043, d = 0.9971, RMSE = 0.0237).

Table 2
Optimal parameters for water quality model of Los Molinos Reservoir (Appendix I).

Parameter	Description	Value	Unit
$k_{\text{growth,Crip}}$	Maximum growth rate for Cryptophyta	0.948609	d^{-1}
$k_{\text{growth,Dy}}$	Maximum growth rate for Dinophyta	0.649506	d^{-1}
$k_{\text{growth,Cyan}}$	Maximum growth rate for Cyanophyta	1.41899	d^{-1}
$k_{\text{death,Crip}}$	Mortality rate for Cryptophyta	0.347124	d^{-1}
$k_{\text{death,Dy}}$	Mortality rate for Dinophyta	0.149688	d^{-1}
$k_{\text{death,Cyan}}$	Mortality rate for Cyanophyta	0.046925	d^{-1}
$I_{\text{opt}_{\text{Crip}}}$	Optimal light intensity for Cryptophyta	52.0766	ly/d
$I_{\text{opt}_{\text{Dy}}}$	Optimal light intensity for Dinophyta	126.696	ly/d
$I_{\text{opt}_{\text{Cyan}}}$	Optimal light intensity for Cyanophyta	101.94	ly/d
K_{PCrip}	Half-saturation const. for P uptake by Cryptophyta	0.00768117	mg/l
K_{PDy}	Half-saturation const. for P uptake by Dinophyta	0.0048309	mg/l
K_{PCyan}	Half-saturation const. for P uptake by Cyanophyta	0.0359664	mg/l
α_{nc}	Nitrogen to carbon ratio	0.096	mgN/mgC
K_{nit}	Half-sat. const. for O_2 limitation of nitrification	0.1	mg/l
K_1	background light attenuation	1	m^{-1}
θ_m	temperature adjustment for phytoplankton respiration rate	1.00804	–
θ_r	temperature adjustment for phytoplankton mortality rate	1.36866	–
θ_{mn}	temperature adjustment for organic nitrogen mineralization rate	1.64916	–
θ_{mp}	temperature adjustment for organic phosphorus mineralization rate	1.38738	–

Table 3
Statistical metrics for the main state variables of Los Molinos Reservoir model in calibration and validation.

Variable	Statistical metric					
	Mean error (mg/l)		d (dimensionless)		RMSE (mg/l)	
	Calibration	Validation	Calibration	Validation	Calibration	Validation
Dinophyta*	−0.00434	0.02629	0.99705	0.87781	0.023727	0.09037
Cryptophyta*	−0.01380	−0.01189	0.73273	0.17113	0.02577	0.01825
Cyanobacteria*	0.00035	−0.00003	0.76915	0.96626	0.00081	0.00215
Nitrate**	0.01253	−0.01939	0.71138	0.43892	0.03902	0.06011
Ammonium**	0.00323	−0.00524	0.28920	0.51107	0.00996	0.01837
SRP**	0.00389	0.00583	0.56970	0.17829	0.00569	0.00706
Dissolved Oxygen**	0.14246	−0.79861	0.22677	0.22471	0.97530	1.92120

* mgC/l.
** mg/l.

The model properly reproduces the main biomass peaks for cryptophyta and cyanobacteria dynamics, with a less accurate performance in predicting their succession patterns, as reflected on the statistical metrics. Nutrient dynamics are satisfactorily represented as shown by the goodness-of-fit of statistics in Table 3 and Fig. 10. The annual average phosphate and inorganic nitrogen concentrations, predicted by the model, corresponds to a mesotrophic water body (Wetzel, 1983), with 0.0140 mg/l and 0.1676 mg/l, respectively (see Table 4); and deviate in a 13.9% and 0.48% with respect to field data. Phosphorus limits the primary productivity in Los Molinos Reservoir, as it is usual in freshwater ecosystems (Schindler et al., 2008). Therefore, an accurate representation of phosphate dynamics is one of the main aims of our model. The annual average concentration of dissolved oxygen simulated by the model deviates in a 0.11% with respect to observed data.

Model validation is carried out based on an independent data set of the water body, collected monthly throughout 2008. Notice that we perform validation task in a "predictive" way according to the classification proposed by Arhonditsis and Brett (2004). The field data used in the validation procedure were provided by Universidad Nacional de Córdoba and were taken within a project that only supported data collection with a monthly frequency.

Table 4
Annual average for inorganic nutrients in model calibration and validation.

Variable	Calibration (Annual average)	Validation (Annual average)
SRP (mg/l)	0.01404	0.01037
Inorganic Nitrogen (mg/l)	0.16760	0.27230

Unfortunately, we do not have access to a more complete, or an additional, data set.

Fig. 11 shows good agreement between data and predicted values for the main state variables: nutrients and phytoplankton dynamics. Statistical metrics are shown in Table 3. The annual average concentration biases with respect to field data obtained during the validation process were 30.3%, 19.3% and 6.57% for phosphate; inorganic nitrogen and dissolved oxygen, respectively (see Table 4).

The validation results here presented prove that the combination of the proposed model along with the optimized parameters are able to properly reproduce the ecosystem dynamics of Los Molinos reservoir. Then, the proposed model is an adequate tool for prospective forecasts of lake dynamics, always taking into account that the model is a bounded representation of the real natural system.

5.4. *Scenario analysis*

5.4.1. *Impact on nutrient and phytoplankton concentration*

The calibration and validation results indicate the suitability of the water quality model for representing the dynamics of the ecosystem under study. In this Section, we explore possible ecosystem structural shifts that might be induced by seven alternative management scenarios relative to current simulated lake dynamics. The analysis considers intra- and interannual variability, by introducing perturbations to the values of the model forcing functions. Table 1 depicts the proposed changes in the model forcing functions, through the design of seven different scenarios, as described in Section 4.2. Each scenario is run for a six year time horizon, with a daily time step (Fig. 13). However, as we are

Table 5
Average percentage change on nutrient and phytoplankton concentrations with respect to the base case (Scenario 0) for the main state variables in the seven analyzed scenarios (see Table 1).

	Scenario						
Variable	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	6 (%)	7 (%)
SRP	4.2	−6.2	−16.9	−31.8	7.2	−16.4	−30.9
Inorganic nitrogen	−6.1	10.6	44.6	50.0	−21.9	47.2	52.8
Total phytoplankton	14.4	−19.0	−44.3	−62.8	31.8	−45.2	−62.4
Cyanobacteria	65.0	−64.1	−87.3	−94.2	146.7	−87.2	−94.2
Dinophyta	6.8	−12.8	−36.1	−55.2	16.2	−37.6	−54.7
Cryptophyta	0.1	−18.3	−64.1	−90.3	−0.4	−61.1	−90.2

Every value was obtained as the average of the annual relative percentage change (with respect to the base case) for the analyzed variable.

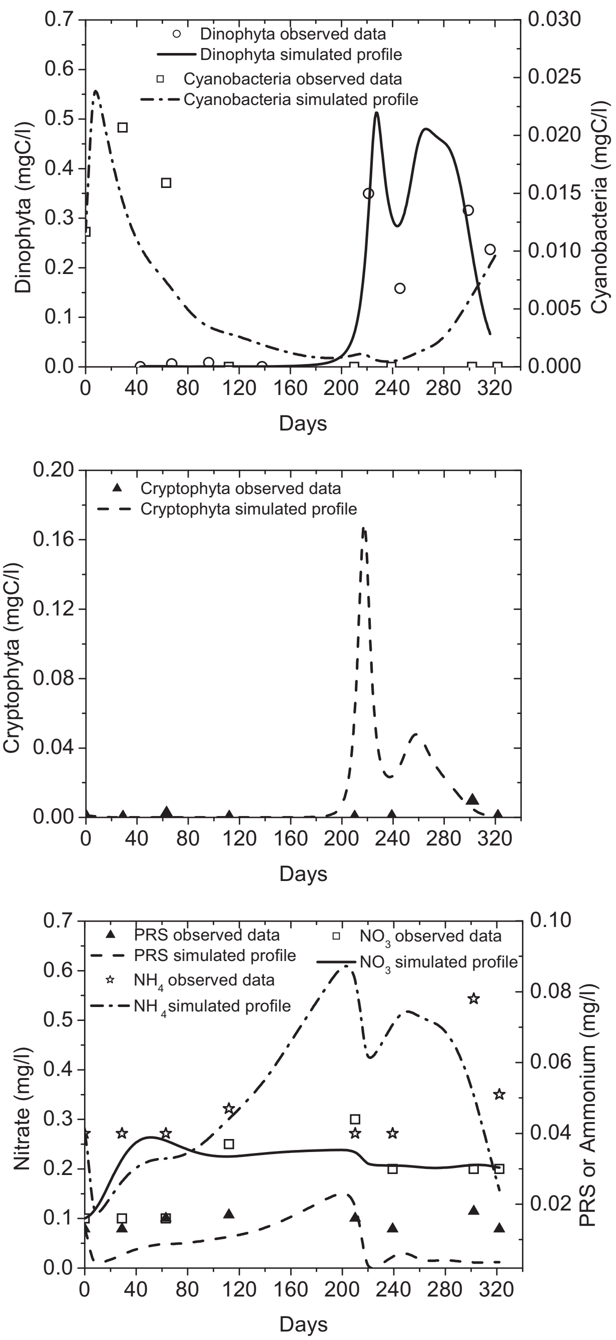

Fig. 11. Validation results: Observed data and simulation profiles for Dinophyta, Cyanobacteria and inorganic nutrients of Los Molinos Reservoir model (model: Eqs. 1 to 3 and Eqs. A1 to A.47; parameters: Table 2 and I.C).

interested in prospective results at the middle term, we analyze model predictions within an average annual basis (Fig. 12 and Table 5). Fig. 12 shows annual average values corresponding to inorganic nutrients, total phytoplankton and cyanobacteria for a six year horizon. For the sake of clarity, we also analyze the average percentage change for concentrations of the main state variables throughout the six year period under analysis. Numerical results are presented in Table 5.

As it was previously mentioned, Scenario 0 simulates current conditions, and it is considered as "base case".

The intensification of livestock production (Scenario 1 in Table 1) results in an increase of SRP (Eq. A.23 in Appendix I), and consequently, in total phytoplankton population. It is important to remark that phosphorus is the limiting nutrient of the ecosystem under study. A reduction of total dissolved nitrogen is also produced, associated to the increase of primary productivity of the water body. It is also worth noting that a sharp rise, of about 65%, in cyanobacteria population is detected (see Table 5, and Eq. A.1 in Appendix I). As was previously mentioned, the proliferation of cyanobacteria in a drinkable water source, increase the risk of harmful blooms whose toxins directly affect human and animal health (Brandalise et al., 2012; Ewerts et al., 2013).

Scenario 2 produces a slight reduction on the SRP concentration, of about 6.2% for the whole period under study, but with a significant reduction on phytoplankton concentration of 19%, and more than 64% in cyanobacteria concentration (see Table 5). This scenario illustrates that preventing livestock access to the reservoir would result in an associated improvement of the ecosystem quality. This practice requires stakeholders compromise to adhere to environmental schemes (Straton et al., 2011), and it is the less expensive option to implement. Moreover, the introduced changes in the current production scheme, would not affect the local economy provided that suitable measures are taken to allow animals to drink water in livestock farms (and not directly from the lake).

Scenario 3 induces a greater reduction in SRP concentration (16.9%) and phytoplankton production (44.3%). This scenario reflects the effect of performing proper sewage treatment works (STWs) with current resident population. The decay in primary productivity associated to the reduction of the limiting nutrient (phosphorus) also promotes a rise in the inorganic nitrogen concentration.

Scenario 4 has the most important effect on SRP concentration, with a reduction of 31.8% with respect to the base case. Nutrient concentration decrease also produces a drop of 62.8% in total phytoplankton concentration, and of 94.2% in cyanobacteria production (see Table 5).

The increase in resident population with current STWs and livestock practices (Scenario 5, Table 1) results in the largest increase in SRP and phytoplankton concentrations, about 7.2% and 31.8%, respectively, with respect to the base case. This scenario clearly evidences the need for suitable land use and urban planning policies that involve social, economic and environmental considerations,

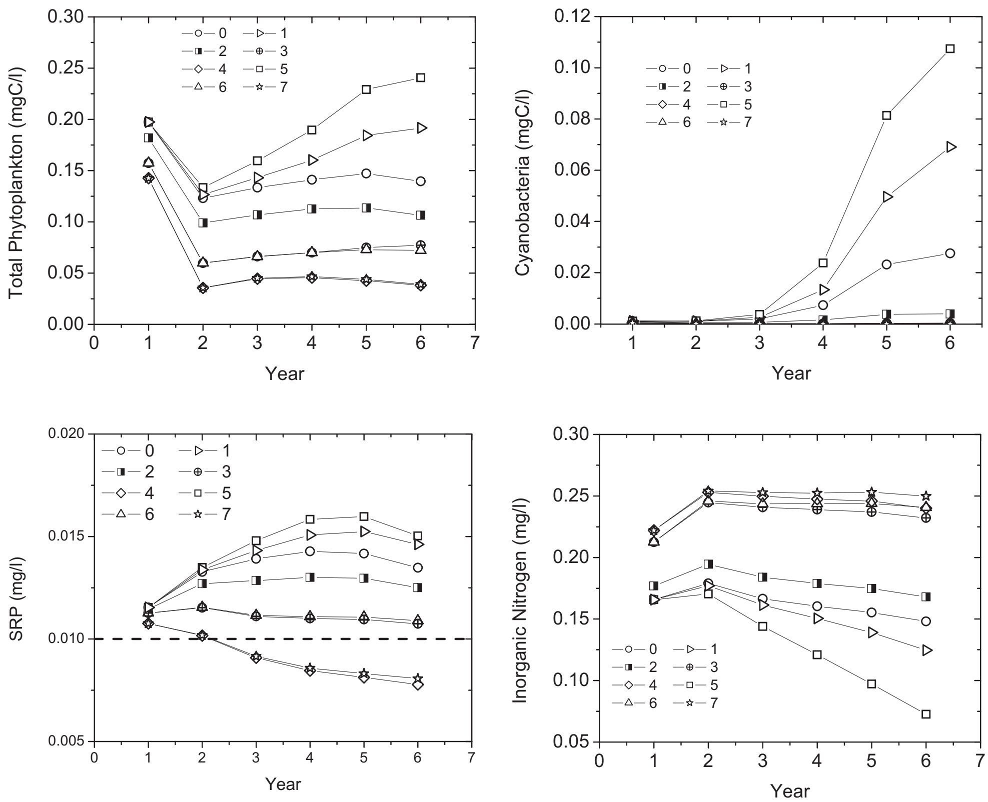

Fig. 12. Prospection results: Annual averages of inorganic nutrients, total phytoplankton and cyanobacteria for a six year time horizon (model: Eqs. 1 to 3 and Eqs. A1 to A.47; parameters: Table 2 and I.C). Scenarios 0 to 7 are depicted in Table 1. Horizontal line in SRP vs Time graph: oligotrophic level for SRP (Wetzel, 1983).

specially taking into account that the tendency of population growth during the last decade and the increase of tourism in the area has been clearly shown through local census 2008 (Censo Provincial de Población, 2008—Provincia de Córdoba) and field surveys (Bazán, 2011; Nadal et al., 2012). Moreover, a significant rise of cyanobacteria concentration is also predicted (146.7%) by our simulations; and this fact represents a rise on the potential risks over human health related to water quality (Brandalise et al., 2012; Ewerts et al., 2013; Reynolds, 2006). Increased nutrient concentrations have been proved as one of the most important factors controlling cyanobacteria blooms development in field studies (Rigosi et al., 2014). In this context, Scenario 5 results support these findings. Moreover, an increase in dinophyta population (Eq. A.1 in Appendix I), of about 16.2%, is observed for this scenario. This could produce severe problems during drinkable water treatment processes, promoting filter clogging and unpleasant odors and flavors in the water supply (Ewerts et al., 2013; van Ginkel et al., 2001). It is also worth noting that for years 4 to 6, nitrogen becomes the limiting nutrient. According to Ryding and Rast (1992), when the N:P ratio is less than 8 nitrogen could limit algae growth. This is the case for Scenario 5. Currently, nitrogen may become limiting in lakes as a result of the great increase in the phosphorus concentration caused by waste water discharges (Jørgensen and Bendoricchio, 2001).

Scenario 6 assesses the effect of increasing resident population with proper STWs over water quality of Los Molinos Reservoir. Significant reductions on SRP and phytoplankton concentrations are predicted of 16.4% and 45.2%, respectively. These values are quite similar to the obtained for Scenario 3, as well as the forecasted reduction in cyanobacteria concentration (see Table 5).

Scenario 7 results in a significant impact on predicted SRP and phytoplankton concentrations, with drops similar to the calculated for Scenario 4 (Table 5). Both scenarios consider the implementation of proper sewage treatment and good livestock practices, but Scenario 7 also takes into account the rise on resident population (see Fig. 4).

For the sake of clarity, Fig. 13 shows numerical results for three analyzed scenarios on a daily time basis, as obtained with our ecological water quality model. Cyanobacteria, Dynophyta and SRP profiles correspond to Scenarios 0, 5 and 7, as depicted in Table 1. Regarding cyanobacteria concentration profiles, is worth noting that, for Scenario 5 some peaks are predicted with maximum concentration of 0.6083 mgC/l. Moreover, cyanobacteria concentration peaks take place related to SRP peaks. At the same time, our numerical results show that nutrient enrichment, promoted in Scenario 5 (see SRP profile in Fig. 1) is positively related to cyanobacteria concentration increase. Moreover, nutrient depletion simulated in Scenario 7, can produce a drastic reduction of cyanobacteria population. Therefore, it is clear that an increase in SRP concentration in the water body, can stimulate phytoplankton production; and special attention must be taken in the case of cyanobacteria concentration increase, considering their potential to produce taste and odour compounds and even toxic compounds, which may be lethal to consumers.

5.4.2. Shifts in the trophic state of the reservoir

For the baseline simulation (Scenario 0), the model predicts mesotrophic conditions according to Wetzel standards (Wetzel, 1983). Scenarios 1 and 5 promote the largest increase in SRP and phytoplankton concentrations, and a reduction of inorganic nitrogen, associated to primary productivity increase. In these scenarios, our predictions show that the water body trophic state is still mesotrophic. However, these results should not be misunderstood because our simulations also predict a significant increase in phytoplankton concentration, in particular in cyanobacteria population (Figs. 1 and 12, Table 5). Additionally, the reduction of inorganic

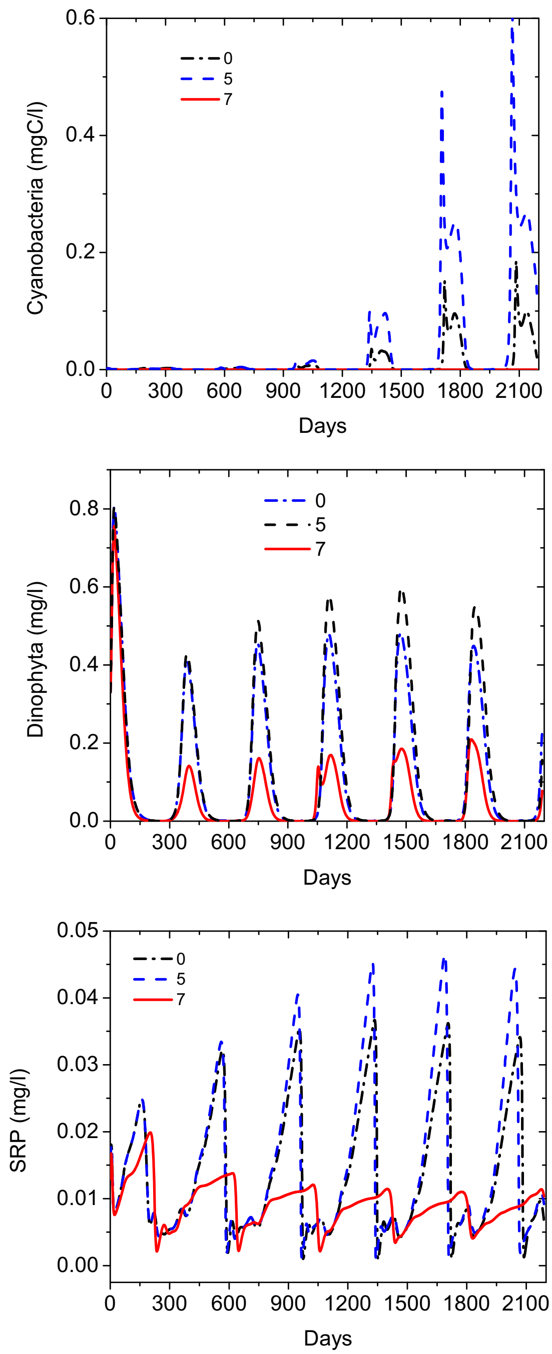

Fig. 13. Prospection results: Cyanobacteria, Dinophyta and SRP profiles on a daily basis, for a six year time horizon (model: Eqs. 1 to 3 and Eqs. A1 to A.47; parameters: Table 2 and I.C). Scenarios 0, 5 and 7 are depicted in Table 1.

nitrogen concentration, of about 6% and 22% for Scenarios 1 and 5, respectively, can be related to the simulated increase in sewages discharges in the lake under study (Jørgensen and Bendoricchio, 2001). While algae use four to ten times more nitrogen than phosphorus to growth, wastewater generally has only three times as much nitrogen as phosphorus. Consequently, nitrogen can remain less abundant than phosphorus regarding phytoplankton needs, and eventually, nitrogen can limit the algal growth (Ryding and Rast, 1992). Even so, as cyanobacteria can fix atmospheric nitrogen, and produce an input of nitrogen into the lake (Jørgensen and Bendoricchio, 2001), the best management policy remains to remove phosphorus from sewage. Furthermore, the bacterial content associated to sewage discharges should also be a matter of concern to water treatment managers and local authorities when a reservoir is used for drinking water supply, fishing and recreational purposes; as in Los Molinos Reservoir case. Even though bacterial dynamics is not included in the actual version of our model, this issue will be taken into account in future work, for a most effective water resource management.

Scenarios 2, 3 and 6 contribute to the improvement of Los Molinos Reservoir trophic state by promoting the reduction on SRP and phytoplankton concentrations (i.e. on primary productivity), and mesotrophic phosphorus levels will still stand for these cases.

Scenarios 4 and 7 promote the highest reductions in SRP and phytoplankton concentrations, and lead to oligotrophic conditions for the water body, in relation to SRP, in about 3 years. Accordingly, measures to reduce phosphorous loading to the reservoir should focus on reducing effluent concentration by proper STWs of wastewaters from residential areas, in combination with the implementation of measures to mitigate phosphorous loading from livestock production in the lakeshore.

The trophic state of a reservoir is based on its biological productivity and nutrient conditions. In this work, Los Molinos reservoir was set as a mesotrophic which implies that it generally has medium biological activity and good water quality. A water body in these conditions supports small augments in nutrient supply with a rise in production without serious damaging the ecosystem, but further increases in nutrient loads render in more serious impacts on water and sediment quality. These effects were captured by our model in scenarios 1 and 5, where a marked rise of nutrient loads (see SRP augments of 4.2% and 7.2% in Table 5, respectively) promote a pronounced augment of phytoplankton community, especially of cyanobacteria population (65% and 146.7%, respectively, Table 5) whose growth is very dependent on phosphorus concentration, with respect to the other two phytoplankton groups considered in this study. Special attention should be paid to the increase of cyanobacteria population, as they can have harmful effects over human and animal health (Brandalise et al., 2012; Ewerts et al., 2013; Reynolds, 2006).

Furthermore, these results evidence the "lability" of mesotrophic environments and its possibility of turning eutrophic, which means that the excessive concentration of nutrients in the water column could promote the development of harmful algae blooms related to the following several problems: (1) turbidity due to high suspended solids and organic matter, with low light penetration; (2) changes in species composition promoting a reduction in the ecosystem biodiversity; (3) dominance of potentially toxic cyanobacteria species, (4) low DO concentrations in deepest waters which can promote sediment nutrient release and fish kill; (5) a thick sediment layer laden with organic matters; and (6) odors from algae and muds.

6. Remarks and conclusions

We propose an ecological water quality model based on first principles for a freshwater reservoir and we formulate a constrained dynamic optimization problem to estimate the model main parameters, based on field data collected monthly from January to December 2007. The problem is formulated within an equation oriented control vector parameterization framework (PSEnterprise, 2014). The dynamic parameter estimation problem has 16 parameters, previously identified as the most influential ones within the model (Estrada and Diaz, 2010). We also perform model validation with an independent field data set of the water body, collected monthly during 2008. Qualitative and quantitative assessment of the model performance, in the calibration and validation tasks, shows a good agreement with observed data.

Once calibrated and validated, the model has proved to be a useful tool to evaluate the possible ecosystem structural shifts under seven alternative management scenarios. Numerical results show that the combination of nutrient loading reduction from the sewage of residential areas, with implementation of measures to mitigate nutrient loadings from livestock production can render the most beneficial effects over the studied ecosystem. These management practices can promote important decrease in nutrients and phytoplankton concentrations within the water body, promoting an improvement in its current trophic state and, at the same time, decreasing cyanobacteria concentration. On the other hand, some alternative analyzed scenarios boost the increase in nutrients and phytoplankton concentrations. In this case, it is important to mention that, according to our results, the intensification of livestock production (with access to lake shore); and the growth of resident population (with deficient sewage treatment works) can produce the largest increases in SRP and phytoplankton concentrations, and a reduction on inorganic nitrogen associated to the rise of the primary productivity. These effects can also be associated to a significant increase in cyanobacteria population, even though the mesotrophic state of the water body is still kept.

The present study shows the ability of water quality models to predict ecosystem dynamic trends induced by different nutrient loading regimes. Even though the prospective results must be considered as hypothetical, accounting for the model limitations, they can provide a tool to catchment managers for determining the optimal options to reduce phosphorus concentration in freshwater bodies.

Acknowledgements

The authors gratefully acknowledge the financial support from: the National Research Council (CONICET, grant number: PIP 11220110101078), Universidad Nacional del Sur (grant number: 24/M125), Universidad Nacional de Córdoba (grant numbers: 162/2012, 124/2013 and 214/10) and Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT, grant number: PICT 2012-2469), Argentina.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.landurbplan.2015.07.003.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.landurbplan.2015.07.003.

References

Arhonditsis, G.B., Brett, M.T., 2004. Evaluation of the current state of mechanistic aquatic biogeochemical modelling. Mar. Ecol.-Prog. Ser. 271, 13–26.

Arhonditsis, G.B., Brett, M.T., 2005. Eutrophication model for Lake Washington (USA): Part I. Model description and sensitivity analysis. Ecol. Modell. 187, 140–178, http://dx.doi.org/10.1016/j.ecolmodel.2005.01.040.

Arhonditsis, G.B., Stremilov, S., Gudimov, A., Ramin, M., Zhang, W., 2001. Integration of Bayesian inference techniques with mathematical modeling. In: Press, W.A. (Ed.), Treatise on estuarine and coastal science. Elsevier Inc., Amsterdam, pp. 173–192.

ASAE D384.1 Manure Production and Characteristics. American Society of Agricultural Engineers (FEB03). USA.

Bazán, R., 2011. Evaluación de la calidad del aguanivel de eutroficación y sus consecuencias en el Embalse Los Molinos (Córdoba). Universidad Nacional de Córdoba, Córdoba, Argentina.

Bennett, N.D., Croke, B.F.W., Guariso, G., Guillaume, J.H.A., Hamilton, S.H., Jakeman, A.J., Marsili-Libelli, S., Newham, L.T.H., Norton, J.P., Perrin, C., Pierce, S.A., Robson, B., Seppelt, R., Voinov, A.A., Fath, B.D., Andreassian, V., 2013. Characterising performance of environmental models. Environ. Modell. Softw. 40, 1–20.

Brandalise, M.V., Nadal, A.F., Rodríguez, M.I., Larrosa, N., Ruiz, M., Halac, S., Olivera, P., Licera, L., 2012. Índice de Calidad de Agua para uso Recreativo en Ambientes con Cianobacterias. In: Paper presented in the 1er Encuentro de Investigadores en Formación en Recursos Hídricos, 14–15 June, Ezeiza, Buenos Aires.

Bruno, S.F., McLaughlin, J.J.A., 1977. The nutrition of the freshwater dinoflagellate *Ceratium hirundinella*. J. Protozool. 24, 548–553.

Censo Provincial de Población, 2008. Provincia de Córdoba. Direccción General de Estadística y Censos Córdoba. Censo Provincial de Población.

Cerco, C.F., Cole, T.M., 1994. Three-dimensional eutrophication model of Chesapeake Bay. In: Technical Report EL-94-4. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Clesceri, L.S., Greenberg, A.E., Eaton, A.D., 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. APHA American Public Health Association, Baltimore, Maryland, USA.

Cloern, J.E., 1977. Effects of light intensity and temperature on cryptomonas ovata (cryptophyceae) growth and nutrient uptake rates. J. Phycol. 13, 389–395, http://dx.doi.org/10.1111/j.1529-8817.1977.tb02947.x.

Cloern, J.E., 1978. Simulation model of *Cryptomonas ovata* population dynamics in southern Kootenay Lake, British Columbia. Ecol. Modell. 4, 133–149, http://dx.doi.org/10.1016/0304-3800(78)90004-2.

Corral, M., Helmbrecht, J., Rodríguez, A., Avena, M., Rodríguez, M.I., Cossavella, A., Alonso, F., 2002. Modelado de parámetros físicos en el Embalse los Molinos, Córdoba, Argentina. In: Paper Presented at the XIX Congreso Argentino del Agua.

Corral, M., Rodríguez, A., Oroná, C., Bazán, R., Cossavella, A., Del Olmo, S., Rodríguez, M.I., Larrosa, N., Bonfanti, E., Busso, F., 2004. Simulación numérica de procesos de transporte y de calidad del agua en el Embalse los Molinos. Mecánica Computacional XXIII.

Cossavella, A., 2003. Influencia de efectos antrópicos y naturales en el proceso de eutroficación de las aguas del embalse Los Molinos. Universidad Tecnológica Nacional, Córdoba, Argentina.

Estrada, V., Diaz, M.S., 2010. Global sensitivity analysis in the development of first principle-based eutrophication models. Environ. Modell. Softw. 25, 1539–1551, http://dx.doi.org/10.1016/j.envsoft.2010.06.009.

Estrada, V., Parodi, E.R., Diaz, M.S., 2009. Determination of biogeochemical parameters in eutrophication models with simultaneous dynamic optimization approaches. Comput. Chem. Eng. 33, 1760–1769, http://dx.doi.org/10.1016/j.compchemeng.2009.01.007.

Ewerts, H., Swanepoel, A., du Preez, H., 2013. Efficacy of conventional drinking water treatment processes in removing problem-causing phytoplankton and associated organic compounds. Water SA 39, 739–750, http://dx.doi.org/10.4314/wsa.v39i5.19.

Grigorszky, I., et al., 2006. The Effects of Temperature, Nitrogen, and Phosphorus on the Encystment of Peridinium cinctum, Stein (Dinophyta). Hydrobiologia 563, 527–535, http://dx.doi.org/10.1007/s10750-006-0037-z.

Gurung, R.P., 2007. Modelling of Eutrophication in Roxo Reservoir, Alentejo, Portugal—A System Dynamic Based Approach. International Institute for Geo-information Science and Earth Observation (ITC), Enschede, The Netherlands.

Hamilton, D.P., Schladow, S.G., 1997. Prediction of water quality in lakes and reservoirs. Part I—Model description. Ecol. Modell. 96, 91–110, http://dx.doi.org/10.1016/S0304-3800(96)00062-2.

Harris, G.P., Heaney, S.I., Talling, J.F., 1979. Physiological and environmental constraints in the ecology of the planktonic dinoflagellate *Ceratium hirundinella*. Freshwater Biol. 9, 413–428, http://dx.doi.org/10.1111/j.1365-2427.1979.tb01526.x.

Hedger, R., Olsen, N., George, D., Malthus, T., Atkinson, P., 2004. Modelling spatial distributions of *Ceratium hirundnella* and Microcystis. In a small productive British lake. Hydrobiologia 528, 217–227, http://dx.doi.org/10.1007/s10750-004-2349-1.

Hillebrand, H., Dürselen, C.-D., Kirschtel, D., Pollingher, U., Zohary, T., 1999. Biovolume calculation for pelagic and benthic microalgae. J. Phycol. 35, 403–424, http://dx.doi.org/10.1046/j.1529-8817.1999.3520403.x.

Johnes, P., Moss, B., Phillips, G., 1996. The determination of total nitrogen and total phosphorus concentrations in freshwaters from land use, stock headage and population data: testing of a model for use in conservation and water quality management. Freshwater Biol. 36, 451–473, http://dx.doi.org/10.1046/j.1365-2427.1996.00099.x.

Jørgensen, S.E., Bendoricchio, G., 2001. Fundamentals of ecological modelling, Chapter 7: Dynamic biogeochemical models. In: Volume 21. Developments in Environmental Modelling. Elsevier, http://dx.doi.org/10.1016/S0167-8892(01)80009-9.

Lindström, K., 1984. Effect of temperature, light and ph on growth, photosynthesis and respiration of the dinoflagellate peridinium cinctum FA. WESTII in laboratory cultures. J. Phycol. 20, 212–220, http://dx.doi.org/10.1111/j.0022-3646.1984.00212.x.

Matias, N.-G., Johnes, P., 2012. Catchment phosphorous losses: an export coefficient modelling approach with scenario analysis for water management. Water Resour. Manage. 26, 1041–1064, http://dx.doi.org/10.1007/s11269-011-9946-3.

Matias, N.G., Gago, J., Boavida, M.J., 2008. Catchment consultation for water management: the case of two Portuguese reservoirs with different water quality. Int. J. Environ. Stud. 65, 737–754, http://dx.doi.org/10.1080/00207230701783577.

Metclaf, Eddy, 2003. Wastewater Engineering: Treatment and Reuse, fourth ed. McGraw Hill, New York, NY.

Molinero Rodríguez, A., 2008. Impacto del turismo en la cuenca del embalse Los Molinos. Universidad Politécnica de Valencia, Valencia, España.

Morgan, K.C., Kalff, J., 1979. Effect of light and temperature interactions on growth of cryptomonas erosa (Cryptophyceae). J. Phycol. 15, 127–134, http://dx.doi.org/10.1111/j.1529-8817.1979.tb02975.x.

Nadal, A.F., Larrosa, N., Alasino, N., Gutiérrez, C., Severini, H., Hillman, G., 2012. Propuestas de sistemas de remediación sanitaria para Potrero de Garay, Córdoba, Argentina. In: Paper Presented at the 1er Encuentro de Investigadores en Formación en Recursos Hídricos, 14–15 June, 2012, Ezeiza, Buenos Aires.

Norma ENOHSA, 1993. Ente Nacional de Obras Hídricas de Saneamiento. Ministerio de Infraestructura y Vivienda—Rep, Argentina.

1999. Normas para la protección de los recursos hídricos superficiales y subterráneos de la Provincia de Córdoba.

Ojala, A., 1993. Effects of temperature and irradiance on the growth of two freshwater photosynthetic cryptophytes. J. Phycol. 29, 278–284, http://dx.doi.org/10.1111/j.0022-3646.1993.00278.x.

Olenina, I., et al., 2006. Biovolumes and size-classes of phytoplankton in the Baltic Sea. In: HELCOM Balt. Sea Environ. Proc. vol. 106.

Olsson, J., Andersson, L., 2007. Possibilities and problems with the use of models as a communication tool in water resource management. Water Resour. Manage. 21, 97–110, http://dx.doi.org/10.1007/s11269-006-9043-1.

Osidele, O.O., Beck, M.B., 2004. Food web modelling for investigating ecosystem behaviour in large reservoirs of the south-eastern United States: lessons from Lake Lanier, Georgia. Ecol. Modell. 173, 129–158, http://dx.doi.org/10.1016/j.ecolmodel.2003.06.003.

Padisák, J., 1985. Population dynamics of the freshwater dinoflagellate *Ceratium hirundinella* in the largest shallow lake of Central Europe, Lake Balaton, Hungary. Freshwater Biol. 15, 43–52, http://dx.doi.org/10.1111/j.1365-2427.1985.tb00695.x.

Pérez-Martínez, C., Sánchez-Castillo, P., 2002. Winter dominance of Ceratiumhirundinella in a southernnorth-temperate reservoir. J. Plankton Res. 24, 89–96, http://dx.doi.org/10.1093/plankt/24.2.89.

PSEnterprise, 2014. gPROMS Advanced User Guide-Release 2.3. Process Systems Enterprise Ltd, London.

Rast, W., Lee, G., 1983. Nutrient loading estimates for lakes. J. Environ. Eng. 109, 502–517, http://dx.doi.org/10.1061/(ASCE)0733-9372(1983)109:2(502).

Renaud, S.M., Thinh, L.-V., Lambrinidis, G., Parry, D.L., 2002. Effect of temperature on growth, chemical composition and fatty acid composition of tropical Australian microalgae grown in batch cultures. Aquaculture 211, 195–214, http://dx.doi.org/10.1016/S0044-8486(01)00875-4.

Reynolds, C.S., 1984. The Ecology of Freshwater Phytoplankton. Cambridge University Press, Cambridge.

Reynolds, C.S., 2006. The Ecology of Phytoplankton. Cambridge University Press, New York, NY.

Rigosi, A., Carey, C.C., Ibelings, B.W., Brookes, J.D., 2014. The interaction between climate warming and eutrophication to promote cyanobacteria is dependent on trophic state and varies among taxa. J. Limnol. Oceanogr. 59, 99–114.

Rigosi, A., Marcé, R., Escot, C., Rueda, F.J., 2011. A calibration strategy for dynamic succession models including several phytoplankton groups. Environ. Modell. Softw. 26, 697–710, http://dx.doi.org/10.1016/j.envsoft.2011.01.007.

Romero, J.R., Antenucci, J.P., Imberger, J., 2004. One- and three-dimensional biogeochemical simulations of two differing reservoirs. Ecol. Modell. 174, 143–160, http://dx.doi.org/10.1016/j.ecolmodel.2004.01.005.

Ryding, S., Rast, W., 1992. In: Pirámide (Ed.), El Control de la Eutrofización en Lagos y Pantanos. Pirámide, Madrid, España.

Sas, H., 1989. Lake Restoration by Reduction of Nutrient Loading: Expectations, Experiences, Extrapolations. Academia Verlag Richarz, Weinheim, Germany.

Schindler, D.W., et al., 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. Proc. Natl. Acad. Sci. U.S.A. 105, 11254–11258, http://dx.doi.org/10.1073/pnas.0805108105.

Smayda, T.J., 1978. From phytoplankters to biomass. In: Sournia, A.E. (Ed.), Phytoplankton Manual. Paris, Oxford UNESCO, pp. 273–280.

Straton, A., Jackson, S., Marinoni, O., Proctor, W., Woodward, E., 2011. Exploring and evaluating scenarios for a river catchment in northern australia using scenario development, multi-criteria analysis and a deliberative process as a tool for water planning. Water Resour. Manage. 25, 141–164, http://dx.doi.org/10.1007/s11269-010-9691-z.

Sun, J., Liu, D., 2003. Geometric models for calculating cell biovolume and surface area for phytoplankton. J. Plankton Res. 25, 1331–1346, http://dx.doi.org/10.1093/plankt/fbg096.

Utermöhl, H., 1958. Zur Vervollkommmung der quantitative Phytoplankton-Methodik. Mitt. Int. Verein. Theor. Angew. Limnol. 5, 567–596.

van Ginkel, C., Hohls, B., Vermaak, E., 2001. A *Ceratium hirundinella* (O.F. Müller) bloom in Hartbeespoort Dam, South Africa. Water SA 27, 269–276.

Wetzel, R.G., 1983. Limnology, second edn. Saunders College Publishing, Philadelphia, USA.

Willmott, C.J., 1981. On the validation of models. Phys. Geogr. 2, 184–194, http://dx.doi.org/10.1080/02723646.1981.10642213.

Zhang, J., Jørgensen, S.E., Mahler, H., 2004. Examination of structurally dynamic eutrophication model. Ecol. Modell. 173, 313–333, http://dx.doi.org/10.1016/j.ecolmodel.2003.09.021.