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## Prospective scenarios for water quality and ecological status in Lake Sete Cidades (Portugal): The integration of mathematical modelling in decision processes

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### ABSTRACT

The design of alternative strategies for water and ecological quality protection at the Lake Verde of Sete Cidades should be coupled with the assessment of future trophic states. Therefore, a mathematical model was developed to make prospective scenarios to reduce the risk of environmental degradation of the lake, and a modified Psenner scheme was used to characterize P distribution in the sediments. The model was able to describe thermal stratification, nutrient cycling (P, NH<sub>4</sub> and NO<sub>3</sub>), dissolved O<sub>2</sub>, and phytoplankton dynamics in the water column and adjacent sediment layers. Internal P recycling, resulting from thermal stratification and sediment anoxia, was identified as the main cause for the increase of P concentration in the hypolimnion followed by slow transfer to the epilimnion (about 20 µg/L annual average). Cyanobacteria blooms during spring were explained by the availability of P and increased water temperature verified during this season. The most sensitive model parameter was sediment porosity. This parameter has a direct effect in dissolved O<sub>2</sub> and P profiles and also in phytoplankton biomass. Finally, different water quality restoration scenarios were identified and their effectiveness assessed. Without the adoption of remediation measures (scenario *control*), Lake Verde water quality would deteriorate with annual average concentrations of total P and phytoplankton biomass (dry matter) reaching 34 µg/L and 2 mg/L, respectively, after 10 a of simulation. The reduction of P loads (scenario *PORAL*) into the lake would improve water quality comparatively to the scenario *control*, reducing the annual average concentrations of total P from 34 µg/L to 26 µg/L and of phytoplankton from 2 mg/L down to 1.4 mg/L after 10 a of simulation. In scenario *sediments*, corresponding to a decrease in the organic content of the sediments, a reduction in the concentrations of total P and phytoplankton is expected in the first two a of simulation, but this effect, would be attenuated throughout the years due to organic matter sedimentation. The best strategy is obtained by combining external and internal measures for P remediation. Finally, it is recommended that the model be used to integrate the results of water quality monitoring and watershed management plans.

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52 **1. Introduction**

53 Eutrophication of surface water bodies results mainly  
54 from anthropogenic activities occurring in their water-  
55 sheds and constitutes one of the most serious water qual-  
56 ity problems, with repercussions on lake chemical and  
57 biological characteristics. Nutrient loads from intensive  
58 fertilization and livestock manure are difficult to control  
59 and have increased in recent times. This human environ-  
60 mental disturbance has become a major problem, particu-  
61 larly during intense precipitation due to the transport of  
62 nutrients through the watershed lotic system and ulti-  
63 mately into downstream water bodies. As a result of in-  
64 creased nutrient availability, increased phytoplankton  
65 and cyanobacteria can form blooms, causing the release  
66 of cyanotoxins, and thus affect multiple water uses. An-  
67 other measure of eutrophication is the content of P in lake  
68 sediments. Indeed, when the external nutrient sources are  
69 controlled, the sediments can act as a source of P and such  
70 mobility along the sediment/water column interface is a  
71 well known problem for remediation success (Zhou et al.,  
72 2001).

73 Water quality conditions of Lake Verde in the Azores is-  
74 lands (Portugal) are influenced by local agricultural wa-  
75 tershed activities. Algae blooms and the release of P from  
76 the sediments during the summer are recurrent events in  
77 the lake (Santos et al., 2004; Medeiros et al., 2004). In order  
78 to reduce the external input of nutrients, the Regional Gov-  
79 ernment has designated eight Azorean lake watersheds as  
80 "vulnerable areas" complying with Nitrates Directive 91/  
81 676/EEC and a watershed management plan for the Lake  
82 Verde was approved in 2005.

83 Biological processes in aquatic ecosystems are complex.  
84 The application of mathematical modelling is necessary in  
85 order to design management strategies, test functional  
86 hypotheses and simulate future states for the system in re-  
87 sponse to environmental alteration. Several models have  
88 been developed in past years for the modelling of different  
89 restoration measures in lake ecosystems. For example,  
90 PAMOLARE I, a structurally dynamic model based on the  
91 UNEP software (Jørgensen et al., 2003), was developed for  
92 examining the effects of an ongoing restoration project in  
93 Lake Fure by testing different prognosis scenarios (Gurkan  
94 et al., 2006). Possible management strategies to improve  
95 water quality in an eutrophic water supply reservoir in  
96 Argentina were also evaluated using the one-dimensional  
97 coupled hydrodynamics and water quality model DY-  
98 RESM-CAEDYM (Antenucci et al., 2003). Burger et al.  
99 (2007) also used DYRESM-CAEDYM to model the relative  
100 importance of internal and external nutrient loads on  
101 water column nutrient concentrations and phytoplankton  
102 biomass. AQUASIM, a computer program designed for the  
103 analysis of aquatic systems (Reichert, 1994), was used by  
104 Omlin et al. (2001a,b) to model Lake Zürich, and by Frisk  
105 et al. (1999) to assess the effect of nutrient loading and  
106 water level regulation of water quality in Lake Vörtsjärv.  
107 AQUASIM has also been used to model wastewater treat-  
108 ment systems (Nogueira et al., 2005) and soil contamina-  
109 tion (Vera et al., 2006). AQUASIM is a reasonable  
110 compromise between model simplicity and fundamental

111 process description, basically due to the open structure of  
112 biogeochemical processes description that allow modifica-  
113 tions and the integration of new processes. Furthermore,  
114 the required core experimental data can be easily  
115 collected.

116 The design of alternative strategies for water and eco-  
117 logical quality protection at Lake Verde should be coupled  
118 with the assessment of future trophic states. Therefore, the  
119 goal of this research was to evaluate the response of the  
120 Lake Verde ecosystem to different environmental protec-  
121 tion measures.

122 **2. Materials and methods**123 **2.1. Study site**

124 Lake Sete Cidades is located in the Western part of São  
125 Miguel Island, in the archipelago of Azores (Portugal). The  
126 lake occurs inside a volcanic crater and has an area of  
127 4.5 km<sup>2</sup> representing 23% of the watershed basin and is di-  
128 vided into two interconnected sub-units: Lagoa Azul (Lake  
129 Azul) and Lagoa Verde (Lake Verde). Lake Azul is the largest  
130 one, with a surface of approximately 3.6 km<sup>2</sup>, a water vol-  
131 ume of 40 × 10<sup>6</sup> m<sup>3</sup> and a maximum depth of 24 m. Lake  
132 Verde has an extension of 0.9 km<sup>2</sup> and a volume of  
133 8 × 10<sup>6</sup> m<sup>3</sup>, with a maximum depth of 21 m. The drainage  
134 basin is 13.7 km<sup>2</sup> and is composed of permanent grass-  
135 lands (4.6 km<sup>2</sup>), forest (8.3 km<sup>2</sup>), agricultural zones  
136 (0.4 km<sup>2</sup>) and urban areas (0.3 km<sup>2</sup>) (Santos et al., 2004).  
137 This work will focus on Lake Verde because of its eutrophic  
138 condition. Indeed, whereas Lake Azul is still regarded as  
139 meso-eutrophic, Lake Verde is considered eutrophic (San-  
140 tos et al., 2004).

141 **2.2. Data collection**

142 Water quality data used in the present work was ob-  
143 tained in 2004 during quarterly sampling field campaigns.  
144 Water samples were collected, at surface, 2.5 m, 5.0 m,  
145 10.0 m, 15.0 m and 20.5 m, at a sampling point located in  
146 the middle of Lake Verde, in the deepest zone, using a  
147 Van Dorn bottle with 6 L capacity. Water samples were  
148 analyzed for chemical parameters, such as PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>  
149 and NH<sub>4</sub><sup>+</sup>. Chemical analyses were performed according to  
150 Standard Methods (APHA, 1998). Phosphate was analyzed  
151 using the spectrophotometric molybdenum blue/stannous  
152 chloride method (SMEWW 4500-P), NO<sub>3</sub><sup>-</sup> by the ultraviolet  
153 spectrophotometric screening method (SMEWW  
154 4500-NO<sub>3</sub><sup>-</sup>), and NH<sub>4</sub><sup>+</sup> by the visible spectrophotometric  
155 screening method (SMEWW 4500-NH<sub>3</sub> C). Temperature  
156 and dissolved O<sub>2</sub> were determined *in situ* at several water  
157 depths (previously described), with a portable multipa-  
158 rameter meter.

159 Phytoplankton cell counting was performed in water  
160 samples collected at the surface of the lake, after settling,  
161 using the inverted microscope method (Utermöhl, 1958).  
162 At least 100 specimens of the dominant species were  
163 counted (Lund et al., 1958). For biomass determination  
164 the mean cell volume of each species was calculated  
165 according to Hillebrand et al. (1999).



Sediment samples were collected at the deepest location of Lake Verde using a gravity Uwitec-corer. The Uwitec-corer tubes, with a diameter of 6 cm and 60 cm length, penetrated about 40 cm into the sediments, collecting the overlaying water as well. The composite sediment/water samples were sealed *in situ*, inside the core tubes. Later, in the laboratory, the water from the sampling core tubes was removed and placed in glass flasks that were preserved at 4 °C. The sediment of each core was later cut in five slices with an Uwitec mechanical cutting apparatus and each slice was homogenized and frozen in sealed Petri dishes for further analysis. The sediment density was measured with a He pycnometer (Micromeritics, Pycnometer 1305). To determine the organic fraction and water fraction, 2 g of sediment were weighed, dried at 105 °C and re-weighed. Next, the sediments were burned at 550 °C and weighed a final time.

For P speciation in the sediments, a modified scheme from Psenner and Pucsko (1988) was used, as proposed by Romero-Gonzalez et al. (2001). This procedure allows the separation of the phosphorus Fe- and Al-bound fractions from the Ca-bound fraction. The extraction process comprises five steps and allows the fractionation of labile P (using NH<sub>4</sub>Cl as solvent at room temperature), redox-sensitive P (using bicarbonate-dithionite as solvent at 40 °C), metal oxide bound P and organically bound P (using NaOH as solvent at room temperature), Ca-bound P (using HCl as solvent at room temperature) and refractory/residual P (using NaOH as solvent at 85 °C).

### 2.3. Mathematical modelling

The use of mathematical models in environmental management should lead to the development of lake management policies to reduce the risk of environmental degradation. The model used in the present study is based on the one developed by Omlin et al. (2001a,b) and includes two coupled submodels, one for the water column and another for the adjacent sediment layers. All processes are active in both submodels, but different conversion rates were used. The model was then implemented in AQUASIM simulation and data analysis software (Reichert, 1994).

The present model is based on horizontal average changes in nutrient concentrations (PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>), O<sub>2</sub> and organism concentration that are transported in the water column by vertical mixing, sedimentation, in- and out-flows and on biogeochemical conversion processes in the water column and in the adjacent sediment layers. Vertical mixing was described as a diffusion process and different values for the diffusion coefficient in summer and winter periods in the epilimnion, metalimnion and upper and lower hypolimnion were defined. The time dependent boundaries between these zones were taken from temperature data. Particulate components are assumed to have a constant sedimentation velocity, which is different for different types of particles. Suspended particles interact with the sediment layers by sedimentation and the diffusive exchange with the sediment pore water affects the concentrations of dissolved substances (Omlin et al., 2001a). The light intensity

was assumed to decrease with water depth and the light extinction coefficient depends linearly on the concentration of suspended particles.

The model state variables were O<sub>2</sub> (S<sub>O<sub>2</sub></sub>), NH<sub>4</sub><sup>+</sup> (S<sub>NH<sub>4</sub></sub>), NO<sub>3</sub><sup>-</sup> (S<sub>NO<sub>3</sub></sub>) and PO<sub>4</sub><sup>3-</sup> (S<sub>HPO<sub>4</sub></sub>), as dissolved components. As particulate components inert organic matter (non-degradable) (X<sub>I</sub>), degradable organic matter (summarizes organic particles resulting from allochthonous sources, from death of phytoplankton and zooplankton, and from zooplankton excretion as fecal pellets) and organic P (X<sub>P,phyto</sub>, X<sub>P,I</sub> and X<sub>P,S</sub>) were considered. The P contents of phytoplankton classes and organic matter are separate state variables because the variable stoichiometry of primary production leads to a variable P content of these particles (Omlin et al., 2001a). In addition, the P content resulting from PO<sub>4</sub><sup>3-</sup> uptake by sinking particles is considered as a state variable (X<sub>P,I,S</sub>). The biological part of the model is represented by three plankton classes, diatoms (X<sub>Diat</sub>) and cyanobacteria (X<sub>Cyan</sub>) as phytoplankton groups, and zooplankton (X<sub>Zoo</sub>). The major input variables driving the model are presented in Table 1.

Table 2 illustrates the biogeochemical processes considered in the model and the interactions with the different state variables, namely: aerobic, anaerobic and anoxic mineralization of degradable organic matter, carried out by bacteria; growth, respiration, and mortality of cyanobacteria; growth, respiration and mortality of diatoms; growth, respiration and mortality of zooplankton; bacterial nitrification and lastly P uptake by sinking particles. The rate equations and the respective stoichiometric coefficients are presented in Omlin et al. (2001a). Nutrient and O<sub>2</sub> conversion rates were formulated with Monod-type expressions for the transition from unlimited to limited rates.

Model calibration was carried out using a heuristic method; the temperature profile was adjusted firstly, followed by dissolved O<sub>2</sub> and P profiles, in the water column. Phytoplankton biomass, expressed as dry matter concentration of diatoms and cyanobacteria, was calibrated finally. Table 3 shows initial and final values of the major

**Table 1**  
Input variables of the model

Description	Value	Units
Annual inflow	7.9 × 10 <sup>6</sup>	m <sup>3</sup> /yr
Input phosphorus concentration	20	µg/L P
Initial phosphorus	5	µg/L P
Initial ammonium	0.08	µg/L N
Initial nitrate	0.20	µg/L N
Initial dissolved oxygen	10	mg/L
Initial biomass of diatoms (dry mass without P)	1.0	mg/L DM <sup>a</sup>
Initial biomass of cyanobacteria (dry mass without P)	0.1	mg/L DM <sup>a</sup>
Initial inert organic material (dry mass without P)	0.01	mg/L DM <sup>a</sup>
Initial biodegradable organic material (dry mass without P)	0.01	mg/L DM <sup>a</sup>
Maximum water temperature	22	°C
Minimum water temperature	13	°C

<sup>a</sup> Dry matter.



**Table 2**

Biogeochemical processes considered in the model and the respective interactions with the state variables

State variables	Consumption processes	Production processes
Ammonium ( $S_{NH_4}$ )/mg/L N	Bacterial nitrification	Aerobic, anaerobic and anoxic mineralization Respiration of diatoms Respiration of cyanobacteria Growth and respiration of zooplankton Bacterial nitrification
Nitrate ( $S_{NO_3}$ )/mg/L N	Anoxic mineralization Growth of diatoms Growth of cyanobacteria Growth of diatoms	Aerobic, anaerobic and anoxic mineralization Respiration of diatoms Respiration of cyanobacteria Growth and respiration of zooplankton Mortality of cyanobacteria Bacterial nitrification
Phosphate ( $S_{HPO_4}$ )/mg/L P	Growth of cyanobacteria Phosphorus uptake by sinking particles	Aerobic, anaerobic and anoxic mineralization Respiration of diatoms Respiration of cyanobacteria Growth and respiration of zooplankton Mortality of cyanobacteria Mortality of diatoms Growth and mortality of zooplankton Mortality of cyanobacteria Mortality of diatoms Mortality of zooplankton Growth of diatoms Growth of cyanobacteria
Organic phosphorus in biodegradable organic materia ( $X_{P,S}$ )/mg/L P	Aerobic, anaerobic and anoxic mineralization	Mortality of diatoms Mortality of cyanobacteria Mortality of zooplankton Growth of diatoms Growth of cyanobacteria
Organic phosphorus in inert organic material ( $X_{P,I}$ )/mg/L P	–	Mortality of diatoms Mortality of cyanobacteria Mortality of zooplankton Growth of diatoms Growth of cyanobacteria
Organic phosphorus in phytoplankton ( $X_{P,phyto}$ )/mg/L P	Respiration and mortality of diatoms Respiration and mortality of cyanobacteria Growth of zooplankton	Phosphorus uptake by sinking particles
Phosphate attached to biodegradable organic material ( $X_{P1}$ )/mg/L P	Aerobic, anaerobic and anoxic mineralization	Growth of diatoms Growth of cyanobacteria
Dissolved oxygen ( $S_{O_2}$ )/mg/L	Aerobic mineralization Respiration of diatoms Respiration of cyanobacteria Growth and respiration of zooplankton Bacterial nitrification	Mortality of diatoms Mortality of cyanobacteria Growth and Mortality of zooplankton Mortality of diatoms Mortality of cyanobacteria Mortality of zooplankton Growth of diatoms
Degradable organic matter ( $X_S$ )/mg/L DM <sup>a</sup>	Aerobic, anaerobic and anoxic mineralization	Mortality of diatoms Mortality of cyanobacteria Growth and Mortality of zooplankton Mortality of diatoms Mortality of cyanobacteria Mortality of zooplankton Growth of diatoms
Inert organic matter ( $X_I$ )/mg/L DM <sup>a</sup>	–	Mortality of diatoms Mortality of cyanobacteria Mortality of zooplankton Growth of diatoms
Diatoms ( $X_{Diat}$ )/mg/L DM <sup>a</sup>	Respiration and mortality of diatoms Growth of zooplankton	Growth of cyanobacteria
Cyanobacteria ( $X_{Cyan}$ )/mg/L DM <sup>a</sup>	Respiration and mortality of cyanobacteria	Growth of zooplankton
Zooplankton ( $X_{Zoo}$ )/mg/L DM <sup>a</sup>	Respiration and mortality of zooplankton	Growth of zooplankton

<sup>a</sup> Dry matter.

265 calibrated parameters. The values of the remaining model  
266 parameters were taken from Omlin et al. (2001a).

#### 267 2.4. Scenarios design

268 Eutrophication caused by P loads into surface water  
269 bodies can be minimized by the implementation of external  
270 measures (reduction of incoming loads) and internal  
271 measures (reduction of organic content of sediments).  
272 Therefore, in order to carry out an evaluation of policies  
273 based on external and internal measures, four scenarios  
274 for the next 10 a were developed for the Lake Verde. The  
275 scenario *control* was based on actual conditions; the sce-  
276 nario *PORAL* (Operational Program for Lake Requalification)  
277 is associated with a reduction of the P input to Lake Verde  
278 (the P load was reduced 50%, from 432 g/d to 216 g/d of P);  
279 the scenario *sediments* foresees a reduction in the organic  
280 fraction of sediments from 18% to 9% to simulate the effect  
281 of changing sediment composition on P release and, finally,  
282 the scenario *PORAL + sediments* combines the previous  
283 scenarios.

#### 284 2.5. Sensitivity analysis

285 A sensitivity analysis of the model parameters was car-  
286 ried out using the absolute-relative sensitivity function  
287 (Sens AR). The Sens AR measures the absolute change in  
288 a state variable for a 100% change in a model parameter  
289 and does not depend on the parameter units (Reichert,  
290 1998). The parameters are varied independently to assess  
291 how these changes affect the model results. The calcula-  
292 tions were performed with AQUASIM.

293 A sensitivity analysis was conducted for all model  
294 parameters (Table 3) and was focused only on the water  
295 column. The parameters were grouped in three classes of  
296 standard deviation, according to their accuracy (Omlin  
297 et al., 2001b): accurately known parameters (5%), very  
298 poorly known parameters (50%), and an intermediate class  
299 of moderately inaccurate parameters (20%). A general cri-  
300 terion was used in order to classify stoichiometric and spe-  
301 cific growth rate parameters as moderately inaccurate  
302 parameters and the other kinetic parameters as very  
303 poorly known parameters. Input-related parameters were



**Table 3**

Values of the major calibrated parameters

Description	Initial value	Final value	Units
Fraction of degradable organic matter in the sediment ( $a_{deg, sed, ini}$ )	0.40	0.18	–
Parameter for switching to production with reduced P content ( $\Delta S_{HPO_4}$ )	0.0013	0.0030	mg/L P
Thickness of sediment layers ( $h_{sed}$ )	0.0036	0.01	m
Maximum solar radiation ( $I_{max}$ )	200	250	W/m <sup>2</sup>
Minimum solar radiation ( $I_{min}$ )	40	50	W/m <sup>2</sup>
Light extinction coefficient in the absence of particles ( $k_1$ )	0.31	0.50	1/m
Diatoms maximum specific growth rate at 20 °C ( $k_{gro, Diat, 20}$ )	1.10	1.14	1/d
Cyanobacteria maximum specific growth rate at 20 °C ( $k_{gro, Cyan, 20}$ )	1.10	1.00	1/d
Diatoms Monod coefficient for HPO <sub>4</sub> ( $K_{HPO_4, Diat}$ )	0.0019	0.0020	mg/L
Cyanobacteria Monod coefficient for HPO <sub>4</sub> ( $K_{HPO_4, Cyan}$ )	0.0019	0.0020	mg/L
Diatoms half saturation rate for light intensity ( $K_{I, diat}$ )	34	5	W/m <sup>2</sup>
Cyanobacteria half saturation rate for light intensity ( $K_{I, cyan}$ )	20	5	W/m <sup>2</sup>
Diatoms half saturation rate for NO <sub>3</sub> ( $K_{NO_3, Diat}$ )	0.040	0.050	mg/L
Cyanobacteria half saturation rate for NO <sub>3</sub> ( $K_{NO_3, Cyan}$ )	0.040	0.045	mg/L
Cyanobacteria maximum specific respiration rate at 20 °C ( $k_{resp, Cyan, 20}$ )	0.05	0.10	1/d
Diffusion coefficient for epilimnion ( $Kz_{epi}$ )	200	5.0	m <sup>2</sup> /d
Diffusion coefficient for metalimnion ( $Kz_{met}$ )	0.2	0.3	m <sup>2</sup> /d
Diffusion coefficient for hypolimnion ( $Kz_{hyp}$ )	2.0	0.3	m <sup>2</sup> /d
Sediments porosity ( $\theta$ )	0.95	0.90	–
Time of minimum temperature ( $t_{min, temp}$ )	30	15	d

304 typically classified as moderately inaccurate parameters.  
 305 Physical parameters, like sediment porosity, thickness of  
 306 sediment layer, light extinction coefficient and maximum  
 307 and minimum solar radiation, were classified as accurately  
 308 known parameters. To estimate the uncertainty of the pro-  
 309 spective scenarios, standard deviations of the model re-  
 310 sults were determined using the error propagation  
 311 method as described by Reichert (1998).

### 312 3. Results and discussion

#### 313 3.1. Sediments characterization

314 The sediments of Lake Verde have a density of 2.44 kg/L  
 315 and an organic content of 18%. Fig. 1 shows the results of P  
 316 speciation in the lake sediments. The distribution of P frac-  
 317 tions in the different sediment layers is fairly homoge-  
 318 neous with the exception of the fraction extracted by  
 319 NH<sub>4</sub>Cl that decreased from 17% in the top layer to 4% in  
 320 the bottom layer. The NH<sub>4</sub>Cl–P fraction corresponds to P  
 321 in the interstitial water and to PO<sub>4</sub> weakly adsorbed onto  
 322 the sediment surfaces. It can be released to the water col-  
 323 umn by a decrease in pH verified during anoxic conditions  
 324 in the hypolimnion contributing to the occurrence of algae  
 325 blooms (Gonsiorczyk et al., 1998). The NaOH extraction (at  
 326 room temperature) resulted in the highest amount of P

(49%) that is both bound to metal oxides (25%) and incor-  
 327 porated into biomass and detritus (24%). The presence of  
 328 P bound to Al and Fe oxides in sediments from Lake Verde  
 329 was reported by Cruz et al. (2006). This fraction can be re-  
 330 leased to the water column under reductive conditions in  
 331 the hypolimnion due to low O<sub>2</sub> concentrations (Wang  
 332 et al., 2006). It is important to note that 46% of the P ex-  
 333 tracted in all steps was bound to organic material and that  
 334 was the only P-fraction considered in the model described  
 335 above.  
 336

Lake water quality models often describe the processes  
 337 occurring in the sediments in less detail than the ones  
 338 occurring in the water column. Usually, only the minerali-  
 339 zation process is considered in the sediments (Omlin et al.,  
 340 2001a) as is the case for the present model. However, other  
 341 significant P-fractions present in the sediments, as re-  
 342 ported in the present work, might be released to the water  
 343 column by several biological and physic-chemical pro-  
 344 cesses (Kim et al., 2003) that need to be included in the  
 345 model in the near future.  
 346

#### 347 3.2. Model calibration

##### 348 3.2.1. Physical-chemical quality

349 Temperature, dissolved O<sub>2</sub> and PO<sub>4</sub><sup>3-</sup> concentration pro-  
 350 files along the water column experimentally observed and  
 351 simulated are shown in Figs. 2–4. Lake Verde undergoes  
 352 seasonal thermal stratification that extends between May  
 353 and November (Fig. 2) otherwise the lake is completely  
 354 mixed. The surface water temperature varies from 14 °C  
 355 in February to 22 °C in July. During stratification, the tem-  
 356 perature difference between the surface and bottom of the  
 357 lake is around 4 °C in May and 7 °C in July. The dissolved O<sub>2</sub>  
 358 profiles (Fig. 3) show that O<sub>2</sub> concentration at the lake bot-  
 359 tom was very low in July due to stratification. At the lake  
 360 surface the lowest value of O<sub>2</sub> concentration (7.8 mg/L)  
 361 was recorded in November with the highest one (9.7 mg/  
 362 L) in February. During summer, both temperature and dis-  
 363 solved O<sub>2</sub> values (Figs. 2 and 3) simulated at the lake bot-  
 364 tom (approximately 15 °C and less than 1 mg/L) were  
 365 lower than those at the surface (approximately 22 °C and  
 366 9 mg/L), consistent with the stratification conditions  
 367 occurring during this period. Concerning temperature and  
 368 O<sub>2</sub> profiles, there was no significant difference in the sim-  
 369 ulated profiles and the experimental data. However, in  
 370 November, the simulated profile for dissolved O<sub>2</sub> showed  
 371 a deviation from the experimental data. Under anoxic con-  
 372 ditions at the lake bottom, P was released from sediments  
 373 into the hypolimnion and accumulated there due to mass  
 374 transfer limitations between the epilimnion and hypolim-  
 375 nion (Fig. 4). Phosphate concentration at the lake bottom  
 376 was 88 µg/L P in November compared to 7 µg/L P in May.  
 377 The model predicted experimental PO<sub>4</sub><sup>3-</sup> profiles (Fig. 4)  
 378 and flux of PO<sub>4</sub><sup>3-</sup> from the sediments quite well. However,  
 379 PO<sub>4</sub><sup>3-</sup> concentrations at the lake bottom in May and in  
 380 November are exceptions. In May, the concentration was  
 381 higher than expected while in November the opposite hap-  
 382 pened. These differences might be due to the low number  
 383 of experimental data points available for calibration. To  
 384 calibrate temperature and O<sub>2</sub> profiles lake destratification



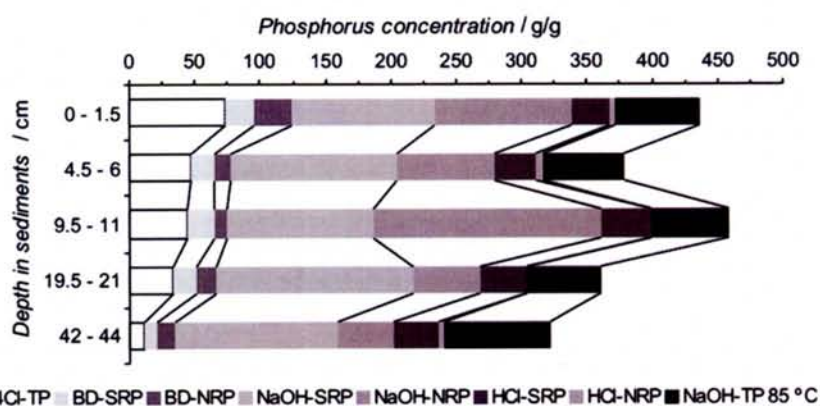


Fig. 1. Phosphorus fractionation at different sediment depths from Lake Verde expressed as mass of P per mass of sediment. (SRP – soluble reactive P; TP – total P; NRP – non-reactive P).

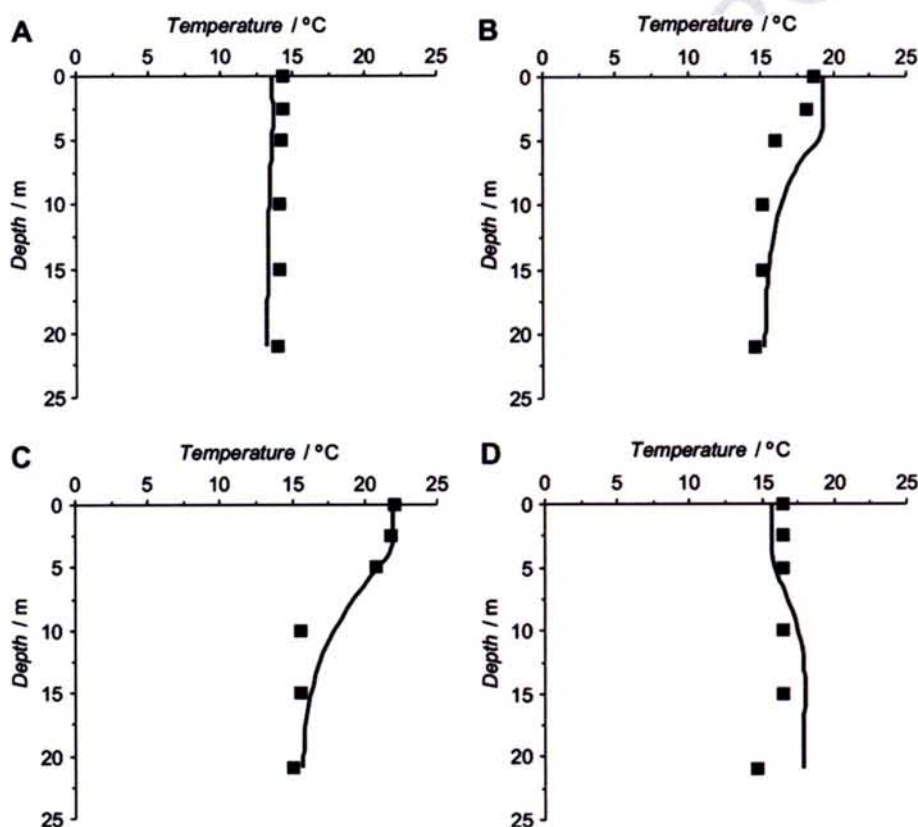


Fig. 2. Temperature profiles: (A) February 17; (B) May 11; (C) July 7; (D) November 10. Markers (■) represent experimental data and lines (—) predicted values.

385 was imposed sooner than was expected with regard of the  
386  $\text{PO}_4^{3-}$  profiles.

387 To assess the organic P fraction in the sediments, the  
388 maximum concentration of P predicted at the lake bottom  
389 was compared with the one obtained by the maximum sol-  
390 ubilisation potential (MSP) assessment test described in  
391 Ribeiro et al. (2008). The MSP was calculated for each or-  
392 ganic P fraction, respectively, 29  $\mu\text{g/L}$  for BD–NRP, 102  $\mu\text{g/L}$

393 L for NaOH–NRP at room temperature, 3  $\mu\text{g/L}$  for HCl–  
394 NRP and 64  $\mu\text{g/L}$  for NaOH–TP at 80 °C. In the calculations  
395 a 10 mm thick sediment layer was considered as well as a  
396 water column of 2.5 m corresponding to the upper hypo-  
397 limnion bound. Interestingly, the maximum P concentra-  
398 tion predicted in the lake bottom, 105  $\mu\text{g/L}$ , was similar  
399 to the MSP of the NaOH–NRP (P in microorganisms and  
400 detritus plus phosphates bound to humic material),

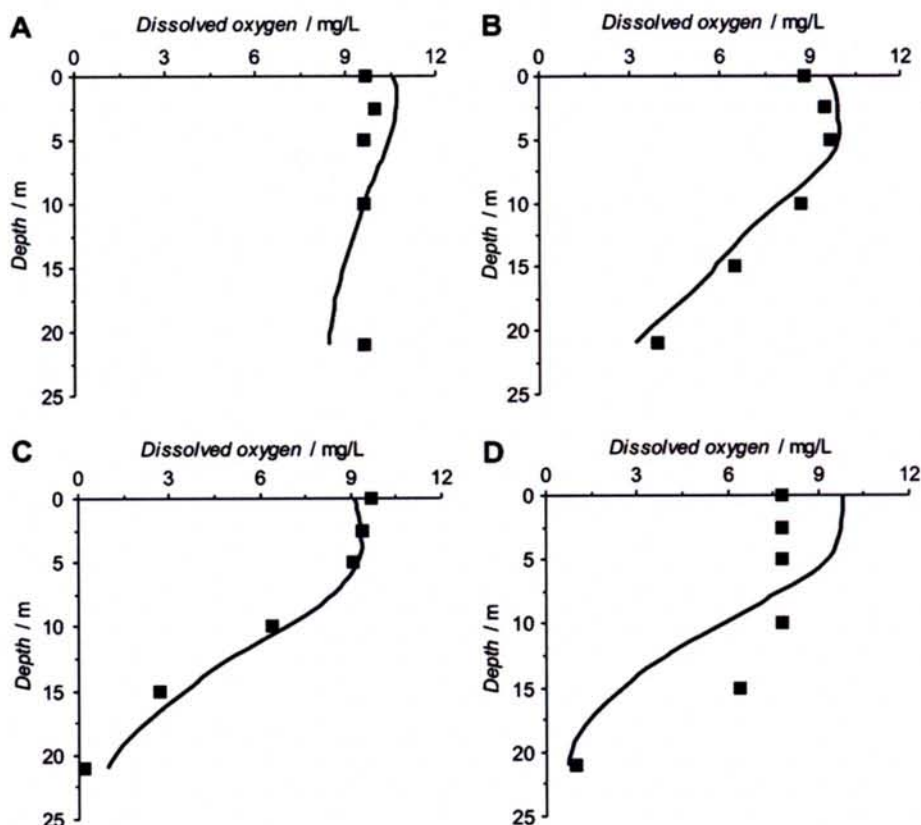


Fig. 3. Dissolved O<sub>2</sub> profiles: (A) February 17; (B) May 11; (C) July 7; (D) November 10. Markers (■) represent experimental data and lines (—) predicted values.

401 102 µg/L. The sum of all organic fractions has a MSP of  
 402 200 µg/L that is higher than the predicted P concentration  
 403 in the lake bottom. Considering that the P present in the  
 404 fractions HCl-NRP and NaOH-TP at 80 °C might not be re-  
 405 leased to the water column under pH and temperature  
 406 conditions present in the lake, the MSP of the NaOH-NRP  
 407 fraction is a reasonably good approximation of the pre-  
 408 dicted value.

### 409 3.2.2. Ecological quality

410 In general, species belonging to the diatom and cyano-  
 411 bacteria groups dominate the Lake Verde phytoplankton.  
 412 The community was mostly composed of *Asterionella for-*  
 413 *mosa*, *Fragilaria delicatissima*, *Fragilaria crotonensis* as dia-  
 414 tom species and by *Woronichinea naegeliana*, *Microcystis*  
 415 *flos-aquae* and *Aphanizomenon flos-aquae* as cyanobacteria  
 416 species. The experimental observations and the predicted  
 417 values of phytoplankton biomass at the surface of Lake  
 418 Verde are depicted in Fig. 5. Diatom biomass concentration  
 419 remained approximately constant throughout the year,  
 420 varying between 0.96 mg/L in June and 1.60 mg/L in  
 421 March. The concentration of cyanobacteria was lower than  
 422 that of diatoms during autumn and winter (between  
 423 0.33 mg/L and 0.46 mg/L) but increased later reaching a  
 424 maximum value of 1.78 mg/L after June and dominated  
 425 the phytoplanktonic biomass. The cyanobacteria bloom  
 426 was probably provoked by both an increase of water tem-

perature and availability of P at the lake surface (Mukho-  
 427 padhyay and Bhattacharyya, 2006). 428

429 The predicted results of phytoplankton dynamics indi-  
 430 cated that diatoms were the predominant group in the lake  
 431 during autumn and winter, while cyanobacteria dominated  
 432 during spring and summer, with the exception of Septem-  
 433 ber. The cyanobacteria bloom was simulated in late March,  
 434 beginning of April, and occurred when P concentration at  
 435 the lake surface reached its highest value (4.4 µg/L). The  
 436 predicted maximum cyanobacteria biomass concentration  
 437 occurred before the observed result, a discrepancy that  
 438 could be mitigated if more experimental data points were  
 439 available to calibrate the ecological model component, de-  
 440 spite the fact that many authors have reported deviations  
 441 in the order of 45% between predicted and observed results  
 442 for phytoplankton dynamics (Jørgensen et al., 2002; Gur-  
 443 kan et al., 2006).

### 444 3.3. Sensitivity analysis

445 The results of the sensitivity analysis carried out to as-  
 446 sess the effect of the different parameters on state vari-  
 447 ables are presented in Table 4.

448 As depicted in Table 4, the parameters that significantly  
 449 affect the state variables considered in the sensitivity anal-  
 450 ysis are sediment porosity ( $\theta$ ), light extinction coefficient  
 451 ( $k_1$ ), maximum specific growth rate of cyanobacteria



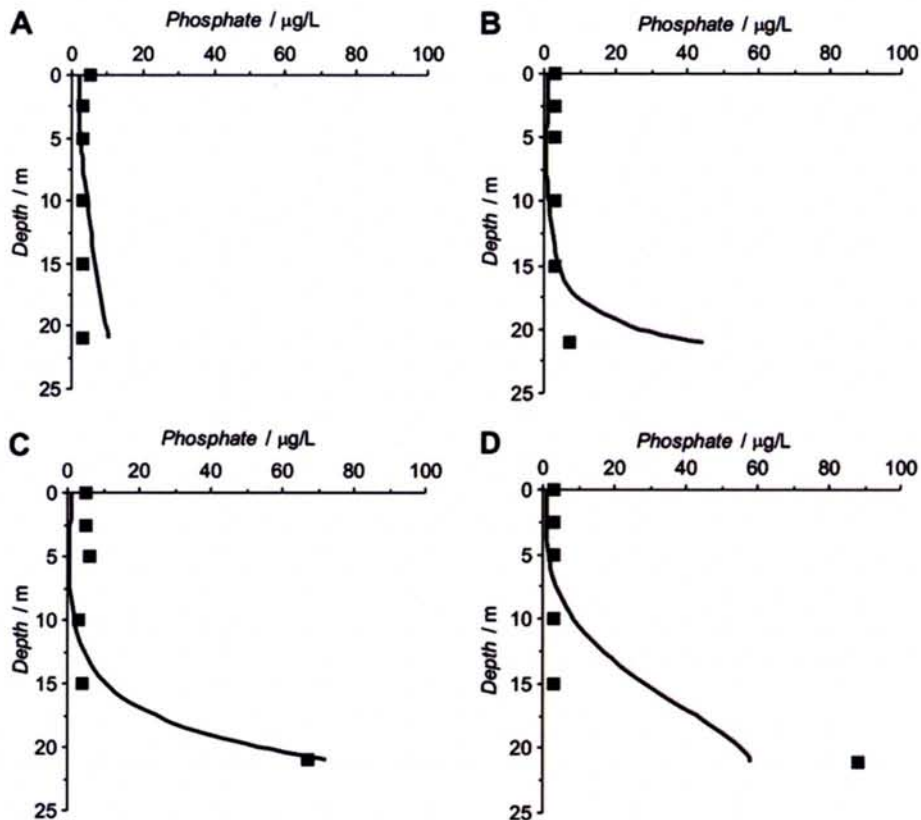


Fig. 4. Phosphate concentration profiles: (A) February 17; (B) May 11; (C) July 7; (D) November 10. Markers (■) represent experimental data and lines (—) predicted values.

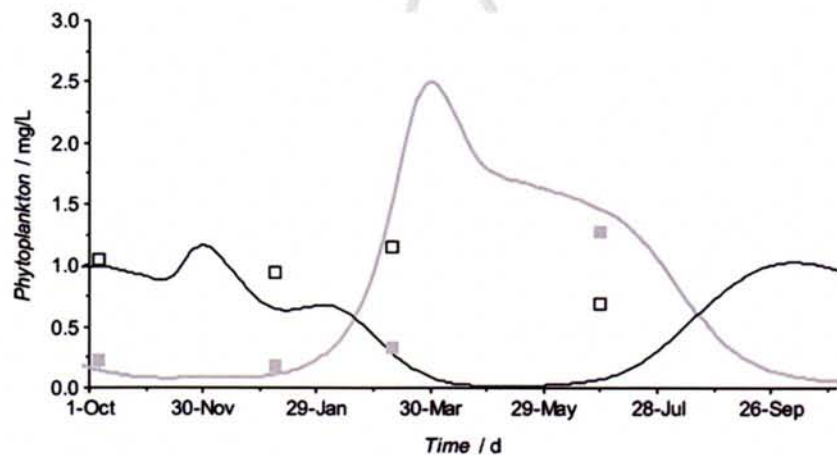


Fig. 5. Phytoplankton dynamics on the surface of Lake Verde during the hydrologic year of 2003/2004. The black line (—) and marker (□) represent predicted and observed values of diatom biomass; the gray line (—) and marker (■) predicted and observed values of cyanobacteria biomass.

452 ( $k_{gro,Cyan,20C}$ ), maximum specific growth rate of diatoms  
 453 ( $k_{gro,Diat,20C}$ ), maximum specific growth rate of zooplank-  
 454 ton ( $K_{gro,ZOO,20C}$ ), temperature dependence coefficient for  
 455 bacteria ( $\beta_{BAC}$ ), and sediment anaerobic specific mineraliza-  
 456 tion rate ( $k_{miner,anae,sed,20C}$ ). The increase in sediment  
 457 porosity positively affects the degradation of organic mat-

ter leading to both an increase in sediment  $O_2$  consumption and in P release from sediments. The resulting  
 458 increase of P in the water column favours phytoplankton  
 459 growth. The temperature dependence coefficient for bacte-  
 460 ria and the sediment anaerobic specific mineralization rate  
 461 also influence the mineralization process in sediments,  
 462  
 463



**Table 4**

Absolute-relative sensitivity (Sens AR) values of model parameters for water column

Parameter	State variables [effect <sup>a</sup> , (absolute value)]			
	Oxygen/ mg/L	Phosphate/ μg/L P	Diatoms/ mg/L WM	Cyanobacteria/ mg/L WM
$a_{deg, sed, ini}$	– (0.00)	– (0.00)	– (0.00)	– (0.00)
$\Delta S_{HPO_4}$	+ (0.68)	– (4.05)	+ (1.34)	++ (2.57)
$h_{sed}$	+ (0.68)	– (3.59)	+ (0.77)	+ (1.51)
$I_{max}$	– (0.28)	– (2.02)	– (0.21)	– (0.54)
$I_{min}$	– (0.13)	– (1.13)	– (0.33)	– (0.44)
$k_1$	+ (1.56)	+ (10.24)	+ (1.00)	+ (2.31)
$k_{gro, Diat, 20\text{ }^\circ\text{C}}$	+ (1.39)	+ (7.37)	++ (4.84)	++ (5.90)
$k_{gro, Cyan, 20\text{ }^\circ\text{C}}$	+ (1.53)	+ (8.09)	++ (5.81)	++ (7.15)
$K_{HPO_4, Diat}$	+ (0.80)	+ (4.66)	++ (4.28)	++ (4.41)
$K_{HPO_4, Cyan}$	+ (0.79)	+ (4.82)	++ (3.10)	++ (3.76)
$K_{L, diat}$	+ (0.56)	– (1.55)	+ (0.47)	+ (1.69)
$K_{L, cyan}$	– (0.30)	– (2.51)	+ (0.45)	+ (1.62)
$K_{NO_3, Diat}$	+ (1.08)	+ (4.64)	++ (4.32)	++ (5.75)
$K_{NO_3, Cyan}$	+ (0.95)	– (4.44)	++ (3.63)	++ (5.43)
$k_{resp, Cyan, 20\text{ }^\circ\text{C}}$	+ (0.96)	+ (5.81)	++ (3.62)	++ (5.07)
$\theta$	++ (5.82)	++ (51.98)	++ (6.55)	++ (19.14)
$k_{gro, ZOO, 20\text{ }^\circ\text{C}}$	+ (1.53)	– (3.85)	++ (2.74)	++ (5.41)
$k_{miner, anaer, sed, 20\text{ }^\circ\text{C}}$	+ (0.95)	+ (12.37)	+ (1.12)	++ (2.97)
$\beta_{BAC}$	+ (1.05)	+ (11.83)	+ (1.21)	++ (3.20)

<sup>a</sup> Insignificant effect; + moderate effect; ++ significant effect.

464 although the effect is less significant than the one of sedi-  
465 ment porosity. The light extinction coefficient influences  
466 the time at which the cyanobacteria peak concentration  
467 occurs and its intensity. Parameters related to phytoplank-  
468 ton growth all have a high sensitivity. Finally, it was also  
469 observed that the model did not reveal sensitivity to the  
470 fraction of degradable organic matter in the sediment. This  
471 result might be explained by the fact that this parameter  
472 influences only the initial concentration of organic matter  
473 in sediments.

#### 474 3.4. Prospective scenarios

475 In order to achieve the goal of the present work, four  
476 prospective scenarios for water and ecological quality  
477 assessment of Lake Verde during the next 10 a were devel-

oped: the scenario *control*, the scenario *PORAL*, the scenario  
478 *sediments* and the scenario *PORAL + sediments*. It can be ob-  
479 served in Fig. 6 that water quality will deteriorate without  
480 the adoption of remediation measures (scenario *control*),  
481 the annual average concentration of total P increases from  
482 19 μg/L at present to 34 μg/L in 10 a. As a consequence, the  
483 intensity of cyanobacteria blooms will increase, as depic-  
484 ted in Fig. 7A. The adoption of external remediation  
485 measures foreseen in scenario *PORAL*, consisting in the  
486 reduction to half of P loads into the lake, lead to a smaller  
487 increase of total P than in *scenario control*, from 19 μg/L at  
488 present to 26 μg/L in 10 a. The effect of the reduction in the  
489 organic fraction of sediments (scenario *sediments*) from  
490 18% to 9% is transitory. During the first 2 a, the concentra-  
491 tion of total P decreases from 19 μg/L to 14 μg/L. After-  
492 wards it increases steadily due to deposition of organic  
493 matter that gradually reaches sediments and mineralizes  
494 with the consequent release of P. As expected, the best  
495 remediation strategy was achieved by the combination of  
496 scenarios *PORAL and sediments* (Fig. 6D), the annual aver-  
497 age concentration of total P decreases from 19 μg/L at pres-  
498 ent to 16 μg/L in 10 a. As can be seen, both strategies *PORAL*  
499 and *PORAL + sediments* will improve water quality. The pre-  
500 dicted results show a significant reduction in the peak va-  
501 lue of total P from 190 μg/L, in scenario *control*, to 138 μg/L,  
502 in scenario *PORAL*, and 131 μg/L, in scenario *PORAL + sedi-*  
503 *ments*, in a 10-a horizon. In *scenario sediment* although a  
504 significant reduction in the peak value of total P occurs in  
505 the first 5 a (155 μg/L) comparatively to scenario *control*  
506 (171 μg/L), by the end of 10 a the two peak values are no  
507 longer significantly different.

Regarding the dynamics of phytoplankton growth  
509 (Fig. 7), the simulated results for scenarios *PORAL* and  
510 *PORAL + sediments* show that the reduction of P loads into  
511 the lake did not have a significant effect on the intensity  
512 of cyanobacteria peaks. In the extreme situation, where  
513 the external P load was completely eliminated, the amount  
514 of P released from the sediments was not sufficient to pro-  
515 mote cyanobacteria blooms. In scenarios *control* and *sed-*  
516 *iments* the annual average concentration of diatoms is  
517 lower than in scenarios *PORAL* and *PORAL + sediments*  
518

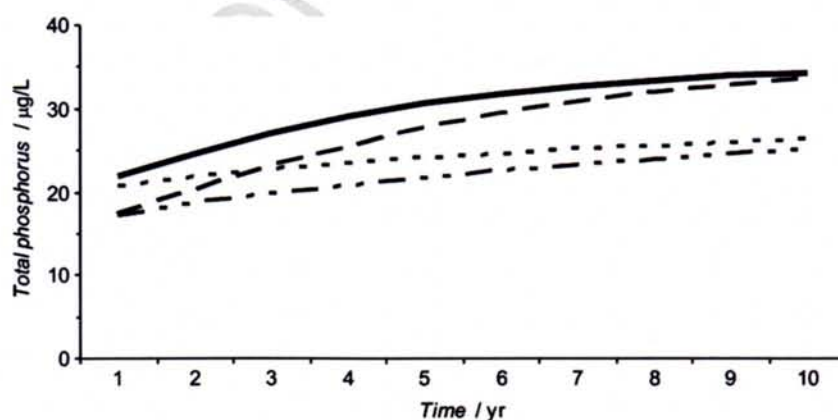


Fig. 6. Predicted average values of total P concentration in Lake Verde for scenario *control* (—), scenario *PORAL* (- - -), scenario *sediments* (- · - ·) and for scenario *PORAL + sediments* (· · · ·).



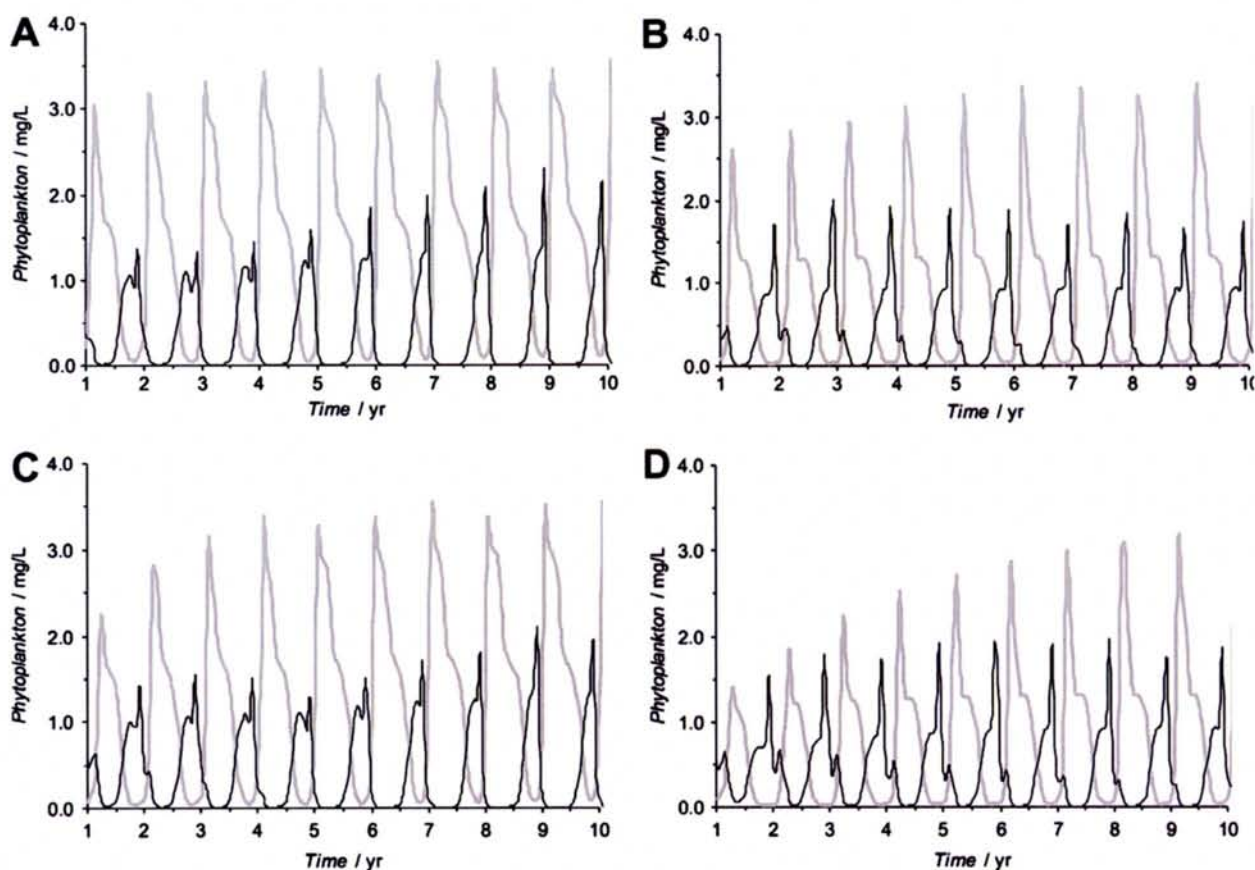


Fig. 7. Predicted phytoplankton dynamics in Lake Verde for scenario control (A), scenario *PORAL* (B), scenario *sediments* (C) and for scenario *PORAL + sediments* (D). The black line (—) represents the diatoms and the gray line (—) represents the cyanobacteria.

519 which is due to the lower intensity of the cyanobacteria  
 520 blooms verified in the first years of simulation. The pre-  
 521 dicted results show a reduction of the annual average con-  
 522 centration of phytoplankton from 2 mg/L, in scenario  
 523 control, to 1.4 mg/L, in both scenarios *PORAL* and  
 524 *PORAL + sediments*, in a 10-a horizon. The initial differ-  
 525 ences between observed between scenario control and scenario  
 526 *sediments* vanished in a 10-a horizon. The predicted  
 527 dynamics of phytoplankton biomass is well correlated with  
 528 the evolution of P availability in the water column.

529 Briefly, the reduction of P external load into Lake Verde  
 530 as put in perspective by scenario *PORAL* may not be suffi-  
 531 cient to improve water quality to a mesotrophic state. Con-  
 532 sidering the economical difficulties in the implementation  
 533 of the nutrients load reduction program, a concomitant  
 534 reduction of internal loading (scenario *sediments*) would  
 535 be advisable.

#### 536 4. Conclusions

537 A mathematical model of Lake Verde was developed to  
 538 make prospective scenarios of water quality and ecological  
 539 status. The present study has shown how a calibrated  
 540 mathematical model can be used to support the decision-  
 541 making processes in aquatic restoration programmes. The  
 542 following conclusions can be drawn:

- 543 – The water quality tends to deteriorate unless a strong  
 544 policy of environmental protection is adopted: annual  
 545 average values of 34  $\mu\text{g/L}$  total P and 2.0 mg/L of phyto-  
 546 plankton biomass can be reached in a 10-a horizon;  
 547
- 548 – A reduction of P load into the lake to half of the actual  
 549 value will improve water quality: an average concentra-  
 550 tion of total P of 26  $\mu\text{g/L}$  and phytoplankton biomass of  
 551 1.4 mg/L could be reached in a 10-a horizon;  
 552
- 553 – The reduction of both internal P loads from sediments  
 554 and external P load into the lake will lead to significant  
 555 improvements in water quality.  
 556

557 Finally, it is recommended that the present mathemat-  
 558 ical model is used to integrate the results of future water  
 559 quality monitoring programmes and to assess the effi-  
 560 ciency of the current Lake Verde watershed management  
 561 plan.  
 562

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 566



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