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On the Influence of the Nearbed Sediments in the Oxygen Budget of a Lagunar System: The Ria de Aveiro - Portugal

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1. Introduction

The filtering capacity of an estuary for both heavy metals and organic micropollutants is largely due to sedimentation. Because sedimentation occurs only for the fraction of contaminant that is adsorbed to particulate matter, the process of sorption (adsorption and desorption) is an essential process. Sediments constitute by far the most important reservoir of nitrogen in shallow systems (Billen & Lancelot, 1988). They play two key roles with respect to the plankton system: They act as regenerators of mineral nutrients for the water column, often supplying between 30-70% of nitrogen requirements by phytoplankton. On the other hand, being the only site in coastal marine ecosystems where anaerobic conditions exist, it is, therefore, the local of denitrification, allowing eliminating a large amount of the nitrogen mineralized in the benthos.

Sedimentary organic matter is composed of many different size fractions with different degradability (Wijsman, 1999; 2002). Due to the depletion of the degradable organic matter with depth and the preferential degradation of the labile compounds, benthic mineralization rate usually decreases rapidly with depth in the sediment. Consequently, most of the biological activity is restricted to the upper decimetres of the sediment column. Benthic macrofauna plays an important role in early diagenesis. Filter feeding organisms, for example, can selectively filter food particles from the water column and thus increase the flux of high quality organic matter to the sediment (e.g. Heip et al., 1995). Additionally, bioturbating and bio-irrigating activity of the macrofauna can increase the transport processes within the sediment (Black, 1997). Conversely, the carbon loading and the effects of benthic mineralization, such as the production of reduced substances and depletion of oxygen, can influence the activity and composition of the benthic community (e.g. Pearson & Rosenberg, 1978).

Diagenesis characterises any chemical, physical, or biological changes undergone by sediments after their initial deposition and during and after their lithification (Wijsman, 1999; 2002).

Since only a limited number of mathematically formulated problems of organic matter and nutrient diagenesis in sediments can be solved analytically, there has been a shift over the years from a focus on analytical models to numerical models (Berg, 2003). These models are commonly based on mass conservation approaches expressing balances between vertical transport contributions of selected species and biogeochemical interactions between them.
Many researchers consider the classic book by Berner (1980) on early diagenesis to be a turning point in the use of modeling in the field. Berg (2003) has reviewed a number of state of the art of mathematically models focused on the organic matter and nutrient diagenesis processes in marine sediments. Examples of these models are the detailed transport-reaction models of Boudreau (1997), Dhakar & Burdige (1996), Soetaert et al (1996), Van Cappellen et al. (1993) and Van Cappellen & Wang (1996) based on a vertical one-dimensional description of the sediment column, accounting for molecular diffusion, burial, and bioturbation. Although similar, each model is particular, namely, in describing the carbon cycle. Meysman et al. (2003a,b) developed a new object-based software package for early diagenesis modeling. Several applications with simplifications or improvements of the above models have been performed since then (Boudreau, 1996, 1997; Herman et al., 2001 Luff et al., 2000; Archer et al., 2002; Wijsman et al., 2002). The bentic sediment diagenesis processes included in the Mike3 eutrophication model (Mike3, 2005b) have a simple description of sediment release of nitrogen and phosphorus, which returns a fraction of the settled P to the sediment, back into the water column. The sediment module is, therefore, an add-on module to the main standard eutrophication module and, therefore, uses the state variables and some of the processes as input.

The main objective of this study is to assess the influence, of the main physical and biogeochemical processes occurring in the near bed sediments, on the oxygen conditions in Ria de Aveiro lagoon, focusing on the low trophic state of the water column, as well as on the organic matter and the nutrients processes associated to the sediments. It will be performed with the help of a couple hydrodynamic and ecological/eutrofication model, in order to simulate simultaneously, the hydrodynamic, the transport and dispersion as well as the Main biochemical processes within the water column. The eutrofication model (Mike3, 2005b) is focused on the lower trophic status of the water column, and it is able to describe the nutrient cycling, including, organic matter (detritus), organic and inorganic nutrients, phytoplankton and zooplankton growth, primary production and dissolved oxygen. It includes as well the nutrient diagenesis in the bottom sediments and the benthic vegetation processes. Although the model in not focused on the sediment transport, sedimentary processes for organic and inorganic matter are taken into account, namely, particles deposition into the bed.

Previous studies (Lopes & Silva, 2006) have shown that the dissolved oxygen (DO) distribution for the main areas of the lagoon is characterized by high concentration values (in general greater than 7 mg O$_2$ l$^{-1}$), which evidences the influence of the exchange of high oxygenated waters with the ocean, as well as the high productivity inside the lagoon. Hypoxic situations are not usual but reflect biogeochemical processes occurring at very limited areas, namely the far end and shallow areas, which are characterized by low flushing rates, high residence times and low residual currents. This study is focused on the relationship between the nitrogen processes, occurring in the nearbed sediments, and the biogeochemical condition within the water column. In particular, the study integrates the oxygen cycle associated to the phytoplankton processes, the nitrogen cycles, the fluxes between the water column and the sediments bed, and among other processes, nitrification and denitrification in the sediment processes.

2. The study area

Ria de Aveiro (Fig. 1) is a lagoon situated on the Northwest Atlantic coast of Portugal (40º38’ N, 8º45’ W), 45 km long and 10 km large, covering an area of 66-83 km$^2$, respectively, at low
and high tide (Dias et al., 2000). It is characterised by several branching channels, the most important of which are S. Jacinto, Ovar, Espinheiro, Mira and Ilhavo that are directly connected to the lagoon mouth and the ocean by a single tidal channel. The central areas of the lagoon is constituted by a myriad of other small channels dominated by shallow and tidal flat areas, contributing to a strong damping of the currents and an increase of the phase delay of the tidal wave (Dias, 2001). The bathymetry (Fig. 1) shows that Ria de Aveiro is a very shallow lagoon (average depth of 1 m).

Fig. 1. The study area: The Ria de Aveiro Lagoon, with the location of the stations (S).

The deepest areas of the lagoon are confined to the inlet channel and to small areas close to the lagoon mouth, at the western boundary of the lagoon. In those areas, the depth may be of the order or greater than 10 m, whereas elsewhere, at the inner parts of the lagoon, the depth barely reaches values beyond 3 m. The hydrological characterisation of the lagoon (Dias et al., 1999; Dias et al., 2000; Dias, 2001) reveals that, excluding the areas close to the lagoon mouth, the salinity and the temperature vertical profiles have very well mixed structures. Tides, which are semi-diurnal, are the main forcing of the circulation in the Ria de Aveiro lagoon. The tidal range varies between 3.2 and 0.6 m, and the estimated freshwater input is very small (about $1.8 \times 10^6$ m$^3$ during a tidal cycle) when compared with the mean tidal prism at the mouth (about $70 \times 10^6$ m$^3$). In general, fluvial input to the lagoon occurs at small steady flow alternated by intense pulses due to the sudden increase of the river’s tributaries flows. Two main rivers, the Antuã river ($5$ m$^3$ s$^{-1}$ average flow) and the Vouga river ($50$ m$^3$ s$^{-1}$) located at eastern side of the lagoon, contribute with almost 90% of the freshwater input to the lagoon. Other small rivers situated at the far end of the lagoon, namely Caster located at the far end of the Ovar channel, may contribute substantially to the salinity patterns of the lagoon, during the rainy period. Therefore, in normal situation, as the...
lagoon is dominated by tides, the freshwater flows only affects restricted areas, close to the river mouth, along the main channels (Dias et al., 1999; Dias, 2001). The salinity is an important physical variable for the understanding of the dynamic inside the lagoon, which is dominated by tides (Dias et al., 2001). During the dry season, generally coinciding with summer, the river’s flow is very low, high salinity values (30-34) which are typical for the lagoon mouth, are observed inside the lagoon and even at its far ends, namely during the flood tide. These locations are close to the river mouths, present, in general, extremely low salinity values, between 0 and 5, during the wet season (autumn and spring).

From the biogeochemical point of view Ria de Aveiro lagoon may be considered as a mesotrophic shallow estuarine system (Almeida et al., 2005). It is characterised by a rich biodiversity as well as by an increasing pressure of the anthropogenic activities near its margins, namely building and land occupation, agricultural and industrial activities. This has resulted in a significant change of the lagoon morphology, and in a constant input of a large volume of anthropogenic nutrients and contaminant loads, with negative impact in the water circulation and the water quality of the lagoon. It is subjected to considerable inputs of industrial and domestic discharges which occur mainly at its periphery, currently receiving a mean annual influxes of total nitrogen (N) and total phosphorus (P) of 6118 t y^{-1} and 779 t y^{-1}, respectively, from its influent rivers (Silva et al, 2002). The assessment of the lagoon ecological state is given, for example, by assessing its dissolved oxygen distribution. DO (dissolved oxygen concentration) inside the lagoon vary in general between 8 to 12 mg O$_2$ l$^{-1}$. Given the salinity and the temperature distribution inside the lagoon, the last value correspond to a near oxygen saturation condition (Almeida et al., 2005). The far end of the lagoon, namely at the Ovar channel and near the Vouga river mouth, may show extreme DO values, the highest ones (12 mg O$_2$ l$^{-1}$ or greater), as well as the lowest ones (below 5 mg O$_2$ l$^{-1}$).

The bottom sediments distribution of the Ria de Aveiro consists of a mixture of mud and sand. The granulometric composition of sediments contains about 2 to 90% of sands, 10 to 80% of silts and 0 to 30% of clays. Meanwhile, there are significant differences in the bed composition between north and south areas of the lagoon. Fine cohesive particles and sands, mainly, compose the northern channels, whereas the southern channels are almost composed by coarse particles and sands (Lopes et al., 2006). A gradient of the bed composition has been observed at each channel of the Ria de Aveiro, with sand near the mouth and a mixture of sand and mud near its far extremity. Dias (2001) has calculated, from measured vertical profiles of currents, the bottom roughness length of different channels. Typical values, varying from 0.02 cm at the far end of the channels, corresponding to a bed predominantly composed by mud or a mixture of mud and sands, to 0.07 cm near the mouth, corresponding to a bed composed mainly by sand, have been found. The presence of a mixture of sands, gravel, shells and mud in the main channels of the Ria de Aveiro denotes the ocean influence in the lagoon. The bottom sediments distribution of the Ria de Aveiro lagoon bed has a cohesive behaviour. Following Torfs (Torfs, 1995; Mitchener & Torfs, 1996) the cohesiveness behaviour of a sediment bed depends on the ratio of non-cohesive and cohesive particles. Above a critical mud content of 4%, and a critical clay (Kaolinite) content of 3%, as the ripples and dunes are increasingly suppressed and the bed behaved cohesively. Dyer (1986;1995) gave a transition range for non-cohesive to cohesive behavior from 5-10% clay content by dry weight.

Ria de Aveiro is a tidal dominated system well connected to the ocean, which contributes to a constant oxygen renewal of its water (Dias & Lopes, 2003; 2006). Lopes et al., (2006; 2008)
have characterized the lagoon in two main areas: (1) the central area under the influence of the tide, are characterized by strong currents, along the S. Jacinto and the Espinheiro channels, particularly close to the mouth where the intensity may reach values as high as 2 m s\(^{-1}\) (Fig. 3), which progressively decreases toward the inner areas of the channels; (2) the far end areas, which are mainly intertidal very shallow areas, (Fig. 1), where the currents may reach low values 0.1 m s\(^{-1}\) (Fig. 2), and the residence time two weeks (Dias et al., 2001, 2003).

3. The model description

3.1 The main features of the model

The physical model solves the hydrodynamic and the transport equations, and includes the main physical processes occurring in the water column, as well as the exchanges at the interface air-water between the atmosphere and the water system. The hydrodynamic model is the Hydrostatic Version of Mike3 FLOW MODEL (Mike3, 2005a), solves the continuity and the momentum equations. It is based on the solution of the three-dimensional incompressible Reynolds averaged Navier-Stokes equations, subjected to the assumptions of Boussinesq and hydrostatic pressure, therefore, the vertical accelerations are assumed to be negligible. The transport-diffusion equation is coupled to the hydrodynamic model, solves the temperature, \( T \), and salinity, \( S \), and any scalar quantity (biogeochemical variables), the turbulent kinetic energy per unit mass, \( k \), and the dissipation of the turbulent kinetic energy, \( \varepsilon \). It integrates radiative exchanges between the atmosphere and the water system, including solar and non solar radiation (Gill, A.E., 1982). The hydrodynamic and the transport models are described in Dias & Lopes (2006) and Lopes et al., (2005; 2006). The model domain covers a rectangular area corresponding to 266 \( \times \) 654 points, with a grid size of 60 m \( \times \) 60 m. It makes use of the so-called alternating direction implicit technique (ADI) to integrate the mass and the momentum equations in the space-time domain. The equation matrices, which result for each direction and each individual grid, are resolved by a Double Sweep (DS) algorithm. It results in a third-order convective matricial equation that is solved for each direction and each grid line by a double sweep algorithm (Leendertse & Gritton, 1971; Abbott et al., 1981; Casuli, 1999). The time step for the hydrodynamic and the transport model has been chosen small, 2 seconds, in order to assure stable solutions for the transport equation. The transport model makes use of the ULTIMATE-QUICKEST scheme (Leonard, 1979) for the integration of the advection-diffusion equation in the space-time domain, extended to the third dimension. The scheme ensures mass conservation through the control volume formulation of the transport terms. It is simple and computationally fast and, thus, well suited for coupling to the three-dimensional hydrodynamic model in order to simulate density-driven flows. It results in a very efficient, stable and third-order accurate explicit algorithm (Vested et al., 1992). The validation of the 3D hydrodynamic and transport models was performed with the help of the same data set and periods as those used to validate the 2D models, as those described in Dias & Lopes (2006), Lopes & Silva (2006) and Lopes et al., (2008), the hydrodynamic model is setup by spinning up the lagoon from rest. The sea surface elevation is specified at the western open boundary at each time step. The lateral boundary conditions correspond to no slip velocity and insulation for temperature and salinity on the side-walls. Initial and boundaries conditions for the transport models were obtained from Almeida et al., (2005). During the simulation period, while the biogeochemical variables were kept constant at the river boundaries, the salinity
Fig. 2. Maps of U and V currents field, during flooding (a) and ebbing (b) tide at the mouth.
and the temperature were allowed to vary at each time step, as a year time series were defined based on typical seasonality and historical data for these variables. Concerning the ocean open boundary, the von Newmann boundary conditions were imposed. The atmospheric parameters needed to compute the latent and sensible heat fluxes, as well as the radiation fluxes (relative humidity, air temperature, wind speed and cloudiness) were specified at each time step.

The ecological model, which is an eutrophication biogeochemical module, Mike3-EU (Mike3 (2005b), dealing with the basic aspects of the lower trophic status of the water column, has been applied to the study area (Lopes et al. 2010). The model includes a diagenesis sub-model, which deals with the nitrogen and the phosphorus cycles in the sediment bed.

It is coupled to the 3D hydrodynamic model described above, through the transport equation and require the definition of the concentrations at the model boundaries, flow and concentrations from pollution sources, water temperature and irradiance.

### 3.2 The ecological/eutrofication model

The ecological/eutrofication model describes the nutrient cycling, the phytoplankton and the zooplankton growth, the growth and the distribution of rooted vegetation and macroalgae. In addition it simulates the concentrations of phytoplankton, chlorophyll-a, zooplankton, organic matter (detritus), organic and inorganic nutrients, dissolved oxygen and the area-based biomass of benthic vegetation over time, as well as several derived variables, such as the primary production, the total nitrogen and phosphorus concentrations, the sediment oxygen demand and the secchi disc depth.

The model, which is described by Lessin & Raudsepp (2006) and Erichsen & Rasch (2001) consists of thirteen state variables represented by four functional groups (phytoplankton, zooplankton, benthic vegetation and detritus), nutrients and oxygen (Tab.1). Fig. 3 summarizes the conceptual diagram of the model (Mike3, 2005b). The model is based on nitrogen and phosphorus processes, but for the Ria de Aveiro lagoon, nitrogen is generally the only limiting nutrient (Almeida et al., 2005). Tab. 2 presents the parameter representing the main biochemical processes for the eutrophication model.

The mathematical formulations of the biological and chemical processes and transformations for each state variable are described by a 1st order ordinary differential equation. Phytoplankton is represented by one functional group and three state variables $PX$ representing: phytoplankton carbon ($PC$), phytoplankton nitrogen ($PN$) and phytoplankton phosphorus ($PP$). The time evolution of each state variable $X$ is related to its mass balance within the water column:

$$\frac{\partial X}{\partial t} = \text{PRODUCTION} - \text{RESPIRATION} - \text{GRAZING} - \text{SEDIMENTATION} - \text{DEATH} \quad (1)$$

Once the advection-dispersion terms as well as the sources and sinks terms of the transport equation are evaluated, the model makes an explicit time-integration of (1), then calculating the concentrations to the next time step, following a Runge-Kutta 4 integration method. Although each variable is characterized by specific processes, the mass balance is similar to (1). For instance, concerning $CH$ (Chlorophyll-a) the following processes are considered: production, death and sedimentation, whereas for $ZC$, representing important grazers, such as copepods and various microzooplankters. Detritus are defined in the model as particles of dead organic material in the water, and its pool receives the dead primary producers, dead zooplankton grazers and unassimilated material left over after grazing. Sedimentation...
and mineralisation are the only processes draining the detritus pools. The mass balance for detritus \((DC, DN \text{ and } DP)\) includes instead, regeneration, mineralisation and sedimentation processes. The inorganic nitrogen is represented by two state variables, namely oxidised forms (sum of nitrate and nitrite) and reduced forms (sum of ammonia, \(NH\), and urea). The main balance for the inorganic nitrogen and phosphorus includes the inputs from mineralisation and the uptake. The primary source of ammonia is the input from respiration and mineralisation processes, whereas the sinks include uptake by primary producers: phytoplankton and benthic vegetation, and nitrification from nitrate. The mineralization of \(NH\) is expressed as a fraction of the sedimentation of organic matter. Under anoxic conditions, the release of nutrients is not only a result of recently sedimented material, but also a zero order function, where large amounts of nutrient buried in the sediment will be released. Mineralization of organic matter is the main input of inorganic phosphorus \((IP)\), and corresponds to the sum of mineralization of detritus, zooplankton and phytoplankton phosphorus as well as the release from the sediment, the last one being only relevant for the bottom layer. The benthic vegetation, \(BC\), is assumed to be rooted and/or attached to stones etc. Fixed ratios of nitrogen to carbon and phosphorus to carbon are assumed. The mass balance for the benthic vegetation includes production and losses.

Hereafter the attention will be focused on the \(DO\) and \(PC\) related processes, as well as on the diagenesis processes, that is the nitrogen and the phosphorus cycles in the sediment bed.
The mass balances for PN and PP are similar to the mass balance of PC, as described in Lessin and Raudsepp (2006), and are not discussed here.

The net production of PC depends on light intensity, nutrient availability and ambient temperature. The gross production is computed with a multiplicative approach, considering the maximal rate of production ($\mu$), the influence of light ($F(I)$) (Jassby & Platt (1976)), a temperature Arrhenius function ($F(T)$) and the internal concentrations of nitrogen and phosphorus ($F(N,P)$) calculated from the relative saturation of the internal N and P pools, following Droop (1973, 1975), Nyholm (1976), Mommaerts (1978), Tett et al. (1986) and Lancelot & Rousseau (1987).

Loss due to respiration is represented by a basal metabolic expenditure to maintain life processes, is considered a constant fraction of biomass PC, with a dependence on temperature represented by the Arrhenius function.

Loss of phytoplankton due to grazing by zooplankton depends on zooplankton carbon, is regulated by zooplankton grazing function modified by a temperature function. The grazing rate of phytoplankton carbon by zooplankton is represented by a saturation equation relating food concentration to grazing rate, a threshold food concentration below which no grazing takes place (Kiørboe and Nielsen 1994), the Arrhenius temperature function and a function of dissolved oxygen suppression grazing at low DO (Roman et al. 1993).

The sedimentation rate of PC is described by a 1st order equation depending on the internal nutrient status and a 2nd order equation representing coagulation.

Natural mortality of phytoplankton, or autolysis, has been shown to be a significant phenomenon in the marine ecosystem (Jassby & Goldman, 1974) and this decay of blooms is partly mineralized in the water column (Lancelot et al., 1987). The mortality of phytoplankton is described by a 1st order equation, with a dependence on temperature represented by the Arrhenius function.

### 3.2.1 Oxygen processes in the water column

Dissolved oxygen mass balance plays a crucial role in the water column oxygen budget. It includes the photosynthesis, the respiration and the mineralization processes. The oxygen balance (DO) includes the production of oxygen by the primary producers and the benthic vegetation, the consumption oxygen and the exchange of oxygen between water and air i.e. re-aeration. The oxygen consumption is due to mineralization of organic matter in water and sediment, oxidation of ammonia (nitrification), respiration of zooplankton and phytoplankton, and mineralization of the part of the phytoplankton, which is mineralized immediately without entering the detritus pool. The oxygen balance (DO) follows a similar equation as (1) and includes the production of oxygen by primary producers and benthic vegetation, the consumption of oxygen and the exchange of oxygen between water and air. The production of phytoplankton is expressed by the same function as the gross production of PC. The oxygen consumption by respiration of zooplankton is considered a constant fraction of the zooplankton biomass and depends on temperature through an Arrhenius temperature dependence function for the phytoplankton respiration. The oxygen consumption in the mineralization of dead phytoplankton resulting from the natural mortality of phytoplankton, or autolysis, which is a significant phenomenon in the marine ecosystem is supposed proportional to the fraction of dead phytoplankton, undergoing...
immediate mineralization as well as on the phytoplankton concentration, and depends on temperature through an Arrhenius temperature dependence function for the phytoplankton respiration. The oxygen consumption involving the oxygen demand by the nitrification process, deals with transformation of ammonia into nitrate and nitrite into nitrate. These processes are expressed by a mathematical formula that expresses a proportionality on the ammonia and the nitrate concentrations. The sediment oxygen demand, $SOD$, is related to the carbon mineralization in the sediment which again is related to the sedimentation of organic matter (detritus and phytoplankton). It is supposed proportional to sedimentation rates of phytoplankton and detritus, on a temperature Arrhenius dependence function for the sediment oxygen demand and on a Michaelis–Menten oxygen function for the sediment oxygen. Finally the exchanges with the atmosphere, the reaeration, is supposed proportional to the difference between the water oxygen concentration and the oxygen saturation concentration.

3.3 The nitrogen cycles in the sediment bed
The $N$ cycle in the sediment is a dynamic process (Williams, 1975). The diagenic model describes the changes and the fluxes between state variables, e.g. nitrification of $NH_4$ to $NO_3$ in the sediment. Fig. 4 summarizes the conceptual diagram of the diagenesis model (Mike3, 2005b), where the state variables and the processes for the nitrogen cycle are presented. As estuaries and lagoons tend to be more nitrogen limited than phosphorus, although its cycles and processes are as well included in the model, the phosphorus influence was not considered in the experiments.

Together with the state variables the processes may be regarded as the cornerstones in a dynamic model. The processes involved in the nitrogen cycle are described in connection with the state variables (Blackburn & Henriksen, 1983; Ruadij & Raaphorst, 1995; Windolf et al., 1996). The nitrogen cycle in sediments consists of three state variables, the organic $N$ ($SON$), the total $NH_4$ ($SNH$) and the $NO_3$ ($SN03$). A sink of nitrogen is as well included in the model, as immobile nitrogen ($SNIM$). The sedimentation of organic $N$ or flux of $NH_4$ and $NO_3$ across the sediment surface connects the state variables to plankton $N$, detritus $N$ and inorganic $N$ in the water. The organic $N$ in the sediment is mineralised producing $NH_4$, which enters the $SNH$ pool. $NH_4$ in the sediment may either be exchanged with $IN$, in the water or nitrified into $NO_3$ in the uppermost layer of the sediment, with the help of $O_2$. (Sweerts 1990; Sweerts et al., 1989; Sweerts et al., 1991). The $NO_3$ entering the $SN03$ pool may either be denitrified or exchanged with inorganic $N$ in the water.

3.3.1 The organic $N$ in sediment ($SON$)
The input of new organic $N$ to the sediment is mediated by sedimentation of living algae or dead organic matter from the overlying water column. When the organic matter reaches the sediment surface, it often forms a loose layer of material, which is easily resuspended. Degradation of material, in this thin layer is fast compared to the underlying sediment layer. In the sediment, the organic material will degrade, releasing nitrogen as $NH_4$ to the pore water. However, as the $C:N$ ratio in the remaining organic matter increases, the degradation decreases because the organic matter do not fulfill the needs of nitrogen for bacteria and other organisms involved in this mineralization. At a molar $C:N$ ratio 1 of about 11, the net mineralization of $NH_4$ seems to stop (Blackburn, 1983).
Fig. 4. The conceptual diagram for the N cycle in sediments, for the diagenesis model.

In the model the input of organic N to the sediment is calculated by the standard EU as sedimentation of algae N and detritus N. A fraction of the settled organic N is assumed to be degraded returning to inorganic N in the water. This process is temperature dependent and should account for the relative fast mineralization of organic material in the surface layer. The remaining organic N, RSON, is put into the pool of organic N in the sediment, SON.

A fraction of the settled nitrogen is assumed to be buried in the sediment. This fraction (RSNIM) is defined as the part of the settled nitrogen of the settled organic matter with a C:N ratio about 11. The pool of organic N is mineralised with NH₄ as an end product, this process (RSONNH) is set to be a temperature dependent fraction of SON.

The change with time of organic N in sediment is, therefore, calculated by adding all the processes together in a differential equation set up for SON:

\[
\frac{d \text{SON}}{dt} = \text{RSON} - \text{RSONNH} - \text{RSNIM}
\]

### 3.3.2 The total NH₄ in the sediment

A part, and sometimes a major part, of this NH₄ is loosely sorbed to particles in the sediment. In the model it is assumed that fraction is available for nitrification and flux across the sediment surface. Three processes are connected to this state variable, mineralization of SON, nitrification, and flux of NH₄ across the sediment water surface. Bacteria in the sediment, mediate nitrification by oxidising NH₄ to NO₂ and NO₃, using O₂. In the model, nitrification is calculated by multiplying a potential nitrification capacity with a Monod kinetics for NH₄ in the sediment and a Monod kinetics for squared O₂ concentration in the water. As nitrification is an aerobic process, it will be restricted to the sediment layer with O₂. The flux of NH₄ between sediment and water is a process dependent on the
concentration difference between water and sediment and the total diffusion for $NH_4$. In the standard EU model, $NH_4$ and $NO_3$ are lumped together as inorganic N, IN. It is, therefore, necessary to assume that the ratio of $NH_4$ and $NO_3$ in the water just above the sediment surface has the same ratio as in the sediment. The changes with time of the total $NH_4$ in the sediment, is calculated by the fraction of organic N, $SON$, which is mineralised as $NH_4$, $RSONNH$, the nitrification of total $NH_4$ in sediment, $RSNIT$, the $NH4$ total flux between sediment and water, $FNH$, the mass ($in$ grams) of dry matter of sediment per gram of water, $DM$, the specific gravity, $VF$, and the layer of O2 in the sediment layer, $KDO2$, as represented in Fig. 4:

$$\frac{d SNH}{dt} = \frac{RSONNH - RSNIT - FNH}{(1 - DM) * VF * KDO2}$$

(3)

The $NO3$ concentration in the sediment depends on three processes: nitrification, $RSNIT$, (previously defined under $SNH$), denitrification, $RDENIT$, and the flux of $NO_3$ across the sediment surface, $FNO3$, which is calculated in the same way as the flux of $NH_4$ (g N/m²/day). The changes with time of the total $NO_3$ in the sediment, is calculated by adding all the processes together in the differential equation:

$$\frac{d SNO3}{dt} = \frac{RSNIT - RDENIT - FNO3}{(1 - DM) * VF * KDO2}$$

(4)

The immobilisation of N, $SNIM$, may occur either as burial of slowly degradable organic N or as denitrification of $NO_3$. The changes with time of the total $SNIM$ in the sediment is calculated by adding two processes together, previously described, the nitrification $RSNIT$ and denitrification, $RDENIT$, in a differential equation set up for each state variable:

$$\frac{d SNIM}{dt} = RSNIM + RDENIT$$

(5)

Each one of the different terms presented in the above equations represent specific processes associated to the nitrogen cycles in the sediment, are described and detailed in Mike3 (2005b).

4. Results

In order to investigate the interplay between the biogeochemical conditions associated to the near bottom sediment processes and the dissolved oxygen mass balance in the water column, as well as on the organic matter and the nutrients processes associated to the sediments, the model described in the previous sections were applied to the Ria de Aveiro lagoon. In all the simulations it was considered a normal summer situation, corresponding to the mean river flow for this season (Lopes et al. 2010). For the simulation period, while the biogeochemical variables at the river boundaries were kept constant and their values chosen in accordance to the observations (Almeida et al. 2005), the salinity and the temperature were allowed to vary. Concerning the ocean open boundary, the von Neumann boundary conditions were imposed. The atmospheric parameters (relative humidity, air temperature, wind speed and cloudiness) needed to compute the latent and sensible heat fluxes, as well as the radiation fluxes were specified at each time step.
The next sections present the results concerning the influence of the near bottom sediment processes on the biogeochemical state of the water column. All the simulations are compared to the reference simulation, which was performed considering the reference value for all the parameters of the model and a low background sediment concentration, 5 mg l\(^{-1}\), representing a typical summer simulations, as adopted by Lopes et al. (2010).

4.1 The influence of the suspended sediment concentration

Fig. 5 presents monthly time series of the main ecological model variables for two experiments: (1) the reference simulation (named RS); (2) simulation corresponding to a high background sediment concentration, 45 mg l\(^{-1}\) (named SI1). It can be observed that concerning RS, DO, although tidally oscillate during the day between maximum and minimum values, remains quite high for all the stations. It varies within a range of 8-10 mg O\(_2\) l\(^{-1}\), excepting for station 1 where it falls below 8 mg O\(_2\) l\(^{-1}\).

![Fig. 5. The monthly time series for the main ecological model variables and for two experiments: (a) the reference simulation (RS); (b) the simulation (SI1) corresponding to a high background sediment concentration (45 mg l\(^{-1}\))](www.intechopen.com)
Fig. 6. The surface horizontal distributions for the main ecological model variables, for the reference simulation (RS).

The semi-diurnal pattern for the time evolution, evidences the influence of the tide. On the other hand, $SI1$ show significant low $DO$ values, varying within a range of 7-8 mg O$_2$ l$^{-1}$. This situation, when compared to $RS$, evidences a significant consumption of oxygen within the water column. $Chl-a$ and $PP$ (Primary Production) present similar behaviour as $DO$. 

www.intechopen.com
While for RS, Chl-a concentrations tidally oscillate around 3 µg l⁻¹, for S11 the concentrations fall below 2 µg l⁻¹ and reach minimum values, close to 0.1 µg l⁻¹. PP values daily oscillate between the minimum value during night (0 g C m⁻² day⁻¹) and the maximum values at noon. Excepting station 1 and 2, relatively high concentration values, greater than 2 g C m⁻² day⁻¹, are observed during the day for RS. On the other hand, S11 always shows very low values for PP, well below 1 g C m⁻² day⁻¹. IN presents relatively high concentrations values for S11, reaching values as high as 0.3 mg l⁻¹, when compared to low values, below 0.05 mg l⁻¹, for RS. The strong values for IN concerning S11, suggest a release of nitrogen into the water column. N-total, which includes organic and inorganic nitrogen, excepting station 3, shows greater concentration values for S11, within the range 0.03-04 mg l⁻¹, even though of the same order of those for RS. Finally, Od-Det (the oxygen demand by detritus) shows extremely low concentration values, of the order of 0.04 mg O₂ l⁻¹, for S11, when compared to the maximum values, of the order of 0.4 mg O₂ l⁻¹, for RS.

![Fig. 7. Vertical distributions for the main ecological model variables, for the reference simulation, for station 2](www.intechopen.com)
The horizontal DO distributions for RS of Fig. 6, confirm that in the normal conditions, the concentration values remain quite high inside the lagoon, varying within the range of 8.9 mg l\(^{-1}\). DO steadily increased from the early morning low values, below 8 mg l\(^{-1}\), to maximum values at noon, of the order of 9 mg l\(^{-1}\), and decreased again towards the minimum values, at the end of the day. The maximum values are observed at the far end shallow areas. In the inner areas of the lagoon, DO values are slightly above 8 mg l\(^{-1}\), reflecting a condition of a strong influence of the ocean water. Between the central and the far end areas of the lagoon, namely those situated between the northermost part of the S. Jacinto and the Ovar channel, DO shows maximum values (close 9 mg/l). On the other hand, the DO horizontal distributions for SI1 show significantly lower values, varying within the range of 7-8 mg l\(^{-1}\). The central areas of the lagoon show, inclusively, values closely to 7 mg l\(^{-1}\). Concerning Chl-a, the horizontal distribution for RS, shows maximum values of the order of 5 \(\mu\)g l\(^{-1}\) at the central area of the lagoon and at Laranjo, but not for the far end areas of Ovar, whereas for SI1, values below 2 \(\mu\)g l\(^{-1}\) are observed, namely at the far end shallow areas. The IN horizontal distributions for SI1 show high concentration values, of the order of 0.3 mg l\(^{-1}\), for the main lagoon areas, whereas RS shows values well below 0.1 mg l\(^{-1}\). N-total distributions did not show significant differences between the two simulations. Fig. 7 presents the vertical profiles of the main model variables and for several sections for RS. Due to the shallowness of the lagoon, the distributions evidence a horizontal distribution, but no vertical stratification pattern. These results are in agreement with the physical characterisation of the lagoon by Dias et al. (1999), as a well mixed system.

4.2 The influence of the nearbed sediment processes

Fig. 8 presents monthly time series of the main ecological model variables for two experiments: a simulation corresponding to a high value of the sediment organic nitrogen mineralization rate 0.05 day\(^{-1}\) (named SI2) and the reference simulation (RS) for which the reference value for the parameter is 0.002 day\(^{-1}\). Fig. 9 presents monthly time series of the main ecological model variables for two experiments: a simulation corresponding to a high value of the depth of the oxygen penetration into sediments, 0.012 m (named SI3), and the reference simulation (RS) for which the reference value for the parameter is 0.0012 m. As previously referred, the reference simulation was performed with the default value for all the model parameters, that is, their lowest values, as no interaction with the sediment processes (Lopes et al. 2010) were taken into consideration. The value of the nitrogen mineralization rate for the SI2 is considerably lower than 0.075 day\(^{-1}\), a value taken by Ambrose et al. (1993) and Zheng & Zhang (2004) for the Satilla River Estuary. The value for the depth of the oxygen penetration into sediments is in agreement with those referred by Revsbech (1983), Revsbech & Jorgensen (1986), Sorensen et al. (1984), Booij et al. (1994), Cai & Sayles (1996). According to the authors, the oxygen penetration of the sediment goes down to between few mm and few cm in estuarine and coastal sediments. It can be observed in Fig. 8 that the DO values for SI2 remain within the range of 8-10 mg O\(_2\) l\(^{-1}\), but slightly increase from RS, reflecting an increase of Chl-a. N-total, shows some concentration increases for SI2, but the values remain within the range 0.3-04 mg l\(^{-1}\), whereas IN slightly increases from RS, even though the values stay below 0.2 mg l\(^{-1}\). Again, the increase of both N-total and IN for SI2, suggests a release of nitrogen into the water column. The Chl-a concentration increase may be attributed to the increase of nutrients availability within the water column. The most striking result corresponds the increase of Od_Det, from low
values, below 0.05 mg O$_2$ l$^{-1}$ day$^{-1}$, for RS, to extreme high values for SI1, reflecting an increase of the detritus within the water column. Concerning SI3 it can be observed (Fig. 9) that DO values are, in general, lower than those for RS, namely at station 1, where the minimum values reach 6 mg O$_2$ l$^{-1}$. N-total and IN show small concentration increases, which suggests a small amount of the nitrogen being released into the water column. Likewise, Chl-a shows small increases. Od$_{Det}$, when compared to RS, shows extreme high values for SI3, varying within the range of 0.1-0.2 mg O$_2$ l$^{-1}$ day$^{-1}$, reflecting, again, an increase of the detritus within the water column. In overall, the results show that the oxygen consumption due to the increase of the depth of the oxygen penetration layer and, therefore, the increase of the rate of the oxygen burial into sediment is only a small fraction of the oxygen budget within the water column. This lead to conclude that the DO distribution within the water column is dependent on the global transport, local production and advection by the currents, as well the exchanges with the atmosphere.

Fig. 8. The monthly time series for the main ecological model variables and for two different values of the sediment organic nitrogen mineralization rate: (a) 0.002 day$^{-1}$ for the reference simulation (RS); (b) 0.05 day$^{-1}$ for the simulation (SI2).
In the following section it will be discussed several other experiments, not presented here. A simulation corresponding to the proportionality factor for the sediment respiration of 2 (named $SI_4$), compared to the reference simulation ($RS$) for which the value for the parameter is 1. The $DO$ values for $SI_4$ are slightly sensitive to the sediment respiration, with values ranging within the interval, 7-10 mg O$_2$ l$^{-1}$. Stations 1 and 3 show the lowest minimum values, reflecting an increase of oxygen consumption by this process and the influence of shallow areas. Concerning the other variables, it was observed, for some stations, unexpected concentration changes when compared to $RS$, which may not be directly attributable to the specific process and location, but rather a consequence of the advective transport. $Od_{Det}$ has shown similar results, namely, extreme high values for $SI_5$, varying within the range of 0.1-0.2 mg O$_2$ l$^{-1}$ day $^{-1}$, were observed, which reflects the increase of the detritus within the water column.

Fig. 9. Monthly time series for the main ecological model variables, for two different values of the depth of the oxygen penetration into sediments: (a) 0.0012m for the reference simulation ($RS$); (b) 0.012 m for the simulation ($SI_3$).
In order to complement the above simulations, two other experiments have been performed: (1) a simulation corresponding to the proportionality factor for the sediment respiration, which value was chosen equal to 2 (named SI4) compared to the reference simulation (RS) for which the reference value for the parameter is 1; (2) a simulation corresponding to a high value of the nitrification rate, which was chosen equal to 9 (named SI5) compared to the reference simulation (RS) for which the reference value for the parameter is 4.8. Since the results are not very different from those presented in Fig. 9, no figure are presented concerning those cases. Concerning SI4, DO is slightly sensitive to the sediment respiration, with the concentration values ranging within the interval, 7-10 mg O$_2$ l$^{-1}$, and stations 1 and 3 showing the lowest values, reflecting an increase of the oxygen consumption and the influence of shallow areas. Concerning the other variables, unexpected concentration changes, even though small were observed. On the other hand, Od$_{Det}$, shows extreme high values for SI4, of the same range of that of Fig. 9, which reflects again, an increase of the detritus within the water column. These results may not be directly attributable to the specific process and location, but rather as direct consequence of the advective transport. Concerning SI5 it was observed that DO shows some significant amplitude fluctuations for the shallow stations, 1 and 2, which varies within the range of 6-10 mg O$_2$ l$^{-1}$, but remains quite unchanged for the deeper stations, 3 and 4. As expected no significant variations were observed for the other variables, even tough, small but significant Chl-a increase are observed for all the stations. This last result may be attributed to the increase of nutrients availability within the water column.

5. Discussion and conclusions

It is generally accepted that one of the main criteria for the assessment of the water quality of a given aquatic system is its oxygen content, as hypoxia or anoxia conditions reflect potential conditions chemical or biological contaminations. Dissolved oxygen in natural systems, as coastal and estuarine waters, reflects the state of these ecosystems and the influence of several physical, chemical and biological processes occurring in it, and is one of the most important indicators of their water quality state. Oxygen is involved in the main processes occurring in the water column, namely, photosynthesis, organic matter degradation and bacterial nitrification.

Sediments play, as well, an important role in the biogeochemical processes occurring in natural systems, namely coastal and estuarine waters, and affect the dissolved oxygen budget within the water column. During the transport and deposition, sediments may undergo many changes resulting from several chemical and biological processes. The biology of a sediment system might mediate the response of the bed to physical forcing. Accretion of sediment in intertidal areas can be influenced by vegetation: the role of vegetation is complex and is site specific, affected by a variety of physical factors as local topography, wave climate, sediment supply and vegetation patch size. The contribution of living root volume occupied by the different plant species may be important by the addition of the volume itself, as well as by binding sediments and minimising re-suspension (Wijsmann, 1999; 2002; Brown et al, 1998).

Oxygen is involved in the main processes occurring in the upper layer of the bottom sediments, namely, oxygen penetration into the bottom sediments, sediment respiration, nitrification processes (Henriksen et al., 1981; Henriksen and Kemp, 1988) and denitrification processes (Kaspar, 1982) in sediments. In the presence of the oxygen, the ammonium
nitrogen can be converted into nitrate nitrogen (called nitrification). This process is affected by pH, flow condition, salinity, and turbidity. Under low dissolved oxygen condition, nitrate nitrogen can be converted into nitrite (called denitrification). Its particulate fraction will settle and deposit on the bottom sediment when the water body is calm. Also, the organic nitrogen can be converted into ammonium nitrogen by bacterial decomposition or mineralization before it can be taken up by phytoplankton (Zheng et al., 2004). Sediment respiration, which is directly linked to the flux of degradable organic matter to the sea floor, is the key factor for many early diagenesis processes in the sediment. Situations of low oxygen concentration of the bottom water and high rates of organic matter sedimentation increase the importance of the anaerobic degradation (Wijsman, 2002).

Ria de Aveiro is a temperate lagoon and a well oxygenated system due to its hydrodynamic feature of a very shallow and tidal dominated system (Dias et al., 2003; Lopes & Dias, 2007). Although some episodic hypoxia situations, have been observed during dry seasons, in situations of high oxygen demand waters at the far end areas (Alcântara et al., 1992; 1994; Almeida et al., 2005), the lagoon state, in overall, is characterised by a high content of dissolved oxygen, even reaching saturation levels for high phytoplankton productivity season. This feature evidences the influence of the physical and the biogeochemical processes. Previous applications of the water quality and ecological models have provided some understanding about the influence of these processes in the DO distribution of the lagoon (Lopes & Silva 2006; Lopes et al., 2008; 2010). It was shown that the lagoon may be divided into two areas: the main area where the dissolved oxygen concentrations are relatively high, due to the influence of the local production and of the dynamic processes induced by tides, which allows a constant interaction between the ocean and the lagoon and a renewal of the dissolved oxygen; the far end areas, under the influence of weak tidal currents, where the bio-geochemical processes may become dominant and the dissolved oxygen concentrations may reach extreme values: (1) very low ones, corresponding to hypoxia conditions, as they may occur in situations of episodic organic contamination; (2) extremely high values, even oversaturation conditions, if favourable situations of high phytoplankton productivity, light availability and high nutrient concentration are met (Lopes & Silva, 2006; Lopes et al., 2008 2010). Indeed, the far end areas are characterized by low flushing rates, low residual currents and high residence time (Dias et al., 2003; Lopes & Dias, 2007). Therefore, in a particular situation, when the oxygen budget is negative, that is, when its consumption or degradation exceeds the production by the phytoplankton or the advection by tidal flow, hypoxic situations can be set up. Nevertheless, even considering the worst scenario, this condition tends to remain confined to the far end areas. In this situation, tidal transport, mixing and dilution between high and low oxygenated water occurs, contributing, therefore to a DO drop to values of the order of 7 mg O₂ l⁻¹ in the central area (Lopes & Silva 2006; Lopes et al., 2008; 2010). Otherwise, DO tends to remain quite high, as under the influence of the tidal transport, ocean waters bring oxygenated waters to the central areas of the lagoon. Therefore, the high DO values for the central areas of the lagoon reflect, in general, the influence of the ocean waters and the role of the lagoon hydrodynamic in the dissolved oxygen distribution. On the other hand, states of very high dissolved oxygen within the water column, occurring far from the lagoon mouth, reflect conditions of high phytoplankton growth and productivity as well as high oxygen production. Plus et al. (2003) have shown for the Thau lagoon (France) that during winter,
the oxygen concentrations remain rather high in the central areas of the lagoon, due to the phytoplankton production and water mixing by the wind, but in summer the oxygen concentrations are lower due to several factors leading to oxygen depletion: faster mineralization processes, lower solubility in warm waters and accumulation of dead organic material, coupled with higher oxygen consumption due to high temperatures. They showed that the influence of the macrophyte populations and of the mineralization of organic matter change significantly the dissolved oxygen distribution in the Thau lagoon (Denis & Grez, 2003). They found that the far end areas of the lagoon have potential risks of oxygen depletion and anoxic crisis, whereas the central and the southern areas of the lagoon may exhibit higher oxygen concentrations due the influence of marine oxygenated waters. Their results confirm that the oxygen concentrations not only depend on the in-situ biogeochemical processes, but also on the hydrodynamics of the lagoon. Malmgren-Hansen et al. (1984) modelled the oxygen depletion in the Limfjord, Denmark. They showed that the bottom oxygen concentration was sensitive to two main factors: The vertical mixing and the biological processes producing and consuming oxygen. They also demonstrated that the number of periods with oxygen depletion will increase exponentially with the rates of the oxygen consuming processes. Zeng et al., (2004) studying the water quality model for the Satilla River Estuary, Georgia, showed that the intertidal salt marsh has high sediment oxygen demand and acts as a major consumer of DO and is, therefore, the major responsible for the low DO values. They emphasised, as well, the importance of the heterotrophic bacterial respiration process in the DO distribution inside the estuary. Lianyuan et al. (2004) used the same approach as Zeng et al., (2004) and showed a DO distribution with a high-spatial variability, with high concentration values (7 mg/l) in the inner shelf and mouth of the estuary, and lower values (below 4 mg/l) in the upstream end of the estuary. They pointed out that DO balance is dominantly controlled by the SOD, reflecting the nature of an estuarine-salt marsh ecosystem, with low anthropogenic influence. Until now, no modeling studies for the Ria de Aveiro lagoon have focused on the relationship between the biogeochemical states of the water column and the biogeochemical processes occurring in the upper layers of the bottom sediments. Assessing the influence of these processes is crucial to improve the understanding of the influence of the near bottom processes in the water column biogeochemical state, and, therefore, the role of the intertidal shallow areas in the biogeochemical budget inside the lagoon. The results show that increasing suspended sediment (SPS) concentration contributes to a significant decay of the dissolved oxygen concentration, as well as of the chlorophyll-a concentrations and the primary production. This can be explained by the fact that in a situation of high background sediment concentrations, the light attenuation within the water column increases, and as less light is available for the photosynthesis, the mortality outpaces the growth of phytoplankton, which generates less oxygen production. On the other, an increase of the phytoplankton mortality may generate additional inorganic matter, which can be mineralised into nitrogen. The excess of nitrogen for the simulation, should, therefore, be attributed to the regeneration process. Furthermore, the concentration of organic substrates for the nitrifier bacterias, increases with the SPS concentration, leading to the rising of the heterotrophic nitrification rate. Therefore, increasing of the SPS concentration within the water column may generate low phytoplankton production and high consumption of oxygen. The results show, as well, that increasing the mineralisation
rate of the sediment, induces a rise of of the \( N_{\text{total}} \) and \( \text{IN} \) within the water column, which is not surprising, as this process is responsible for the nutrient regeneration from the sediments. In this situation, an increase of \( \text{Chl-a} \) reflects the condition associated to the nitrogen availability within the water column.

Xinghui et al., 2009 showed that increase of \( \text{SPS} \) concentration, caused by the erosion, resuspension and sediment transport, generate the nitrification in aquatic systems. They showed that the nitrification rate increases with \( \text{SPS} \) concentration as a power function of the concentration. For the Yellow River, when \( \text{SPS} \) concentration increases from 0.001 g l\(^{-1}\) to 1, 5, 50, and 100 g l\(^{-1}\), the nitrification rate increases about 1.1, 1.4, 2.1, and 2.3 times, respectively. On the other hand, Plus et al. (2003) showed that while during wet season, nutrient inputs from the watershed of the Thau lagoon support the uptake of macrophytes and phytoplankton, during dry periods, mineralisation processes, through mortality and decomposition, become dominant, allowing a primary production based mostly on nutrient regeneration. Part of this nitrogen stock can be released in the water and, even, feed phytoplankton growth.

When quantifying the nitrogen budget within the water column, nitrification process is not the only process to be taken into account. Denitrification, which is an inverse process by which combined nitrogen (nitrate, ammonium or organic forms) is reduced anaerobically to gaseous end products form of nitrogen (\( \text{NO}, \text{N}_2\text{O} \) or \( \text{N}_2 \)) by heterotrophic bacteria (Devol et al, 1997; Devol 2008, Fenel et al., 2009, Kaspar, 1982), should be, as well, considered in the nitrogen budget of a given water body, even though its effect in sediments containing ample labile organic matter is often limited by the availability of nitrate or nitrite (Fenel et al., 2009). Trimmer et al. (1998) discussed the role of the bottom sediments in the \( N \) budget of the upper estuary of the Great Ouse, and showed that, although a fractional loss of riverine nutrient loads via either denitrification, primary production or sediment burial, within an estuary, seems to be, in part, related to the estuary flushing time or residence time (Balls 1994, Nixon et al. 1996), estuarine sediments may also add fixed available \( N \) (primarily \( \text{NH}_4^+ \) to the overlying water via \( \text{NO}_3^- \) and organic ammonifications. They showed, as well, that more than 90% of the total sedimentary \( N \) flux removing \( \text{NO}_3^- \) from the water column was due to \( N \) gases and the sediments of the upper estuary. Billen & Lancelot (1988) showed that estuarine sediments may constitute substantial source of \( N \) for pelagic primary production. Examining the nitrogen balance during spring bloom, they showed that microheterotrophic activity could play an important role in food-web dynamics by partly satisfying the nitrogen needs of phytoplankton, which represents about twice the mineral nitrogen stock initially present in the water column.

The results presented in the previous section concerning the Ria de Aveiro lagoon have emphasized the influence of the biogeochemical processes in the \( DO \) distribution of the lagoon. They have shown that the hydrodynamic is the dominant process defining the \( DO \) distribution of the lagoon. The good connection between Ria de Aveiro lagoon and the sea and the circulation pattern inside the lagoon, the exchanges with the atmosphere, as well as the primary productivity are, therefore, responsible for the relatively high level of oxygen content within the water column. Furthermore, even, in situation of intensification of the residual circulation toward the lagoon mouth (Dias et al., 2001; Dias & Lopes, 2007), and the export of low oxygenated waters from the river flows toward the lagoon central areas, there is no severe impact in \( DO \) distribution. Biogeochemical conditions associated to near bottom sediment processes influence the dissolved oxygen mass balance through the nutrients.
On the Influence of the Nearbed Sediments in the Oxygen Budget of a Lagunar System: The Ria de Aveiro - Portugal

| State variables          | Symbol | Unit         |
|--------------------------|--------|--------------|
| Phytoplankton carbon     | PC     | gC/m³        |
| Phytoplankton nitrogen   | PN     | gN/m³        |
| Phytoplankton phosphorus | PP     | gP/m³        |
| Chlorophyll-a            | CH     | g/µm²        |
| Zooplankton              | ZC     | gC/m³        |
| Detritus carbon          | DC     | gC/m³        |
| Detritus nitrogen        | DN     | gN/m³        |
| Detritus phosphorus      | DP     | gP/m³        |
| Ammonium                 | NH     | gN/m³        |
| Nitrate                  | N³     | gN/l         |
| Inorganic phosphorus     | IP     | gP/m³        |
| Dissolved oxygen         | DO     | g/l          |
| Benthic vegetation carbon| BC     | gC/m³        |

Table 1. The ecological/eutrophication model state variable

| Phytoplankton Parameters | Values                                      |
|--------------------------|---------------------------------------------|
| Phytoplankton C growth rate | 4.2 day⁻¹                                    |
| Settling rate             | 0.1 day⁻¹                                    |
| Settling velocity         | 0.2 m²day⁻¹                                  |
| Coagulation induced settling at high phytoplankton concentration | 0.02 mg² day⁻¹ |
| 1st order death rate      | 0.07 day⁻¹                                   |
| Temperature growth rate coefficient | 1.07                                      |
| Coefficient for min. chlorophyll-a production | 0.4                                       |
| Coefficient for max. chlorophyll-a production | 1.1                                       |
| Min. intracellular concentration of nitrogen | 0.07 g N (g C)⁻¹                            |
| Max. intracellular concentration of nitrogen | 0.17 g N/g C                                 |
| Min. intracellular concentration of phosphorus | 0.003 g P/g C                               |
| Max. intracellular concentration of phosphorus | 0.02 g P/g C                                |
| Shape factor for sigmoide for nitrate uptake function | 0.01                                      |
| Half-saturation constant for NH4 uptake | 0.05 mg N l⁻¹                               |
| Half-saturation constant for NO3 uptake | 0.1 mg N l⁻¹                               |
| Half-saturation constant for P uptake | 0.2 mg P l⁻¹                                |
| Maximum N uptake          | 0.3 g N(g C)⁻³                               |
| P uptake under limiting conditions | 0.05 mg P l⁻¹                             |
| Fraction of nutrients release a phyto. death | 0.1                                       |
| Light saturation intensity at 20°C | 200 µmole (m² s⁻¹)                           |
| Temperature dependency for light saturation intensity | 1.04                                      |
| Algae respiration rate    | 0.06 day⁻¹                                   |
| Coefficient for nitrate dark uptake by phytoplankton | 0.6                                       |
| N release coefficient for N mineralisation | 1                                        |

| Zooplankton Parameters   |                                            |
|--------------------------|---------------------------------------------|
| Maximum grazing rate     | 1 day⁻¹                                     |
| Death rate (1st order) (2nd order) | 0.05 day⁻¹ 0.002 day⁻¹                   |
| Grazing threshold        | 0.02 mg l⁻¹                                  |
| Halfsaturation concentration for grazing PC | 0.5 mg l⁻¹                              |
Temperature dependency for maximum grazing rate 1.1
Temperature dependency for C mineralisation 1.14
N:C ratio 0.17 gN/gC
P:C ratio 0.03 gP/gC
Respiration due to specific dynamic 0.2
Basal metabolism 0.04 day⁻¹
Assimilation factor 0.28
Detritus c mineralization rate 0.05 day⁻¹
Detritus c settling rate <depth 2m 0.05 day⁻¹
Detritus c settling velocity >depth 2m 0.1 m day⁻¹
N release coefficient for N mineralisation 1
N release coefficient for N mineralisation 1

**Macrotelmec Parameters**

| Parameter | Value |
|-----------|-------|
| Sloughing rate at 20º | 0.01 day⁻¹ |
| Production rate at 20º | 0.25 day⁻¹ |
| Temperature dependency sloughing rate | 1.07 |
| Temperature dependency production rate | 1.05 |
| N:C ratios | 0.137 gN/gC |
| P:C ratios | 0.016 gP/gC |
| Halfsaturation concentration for N uptake | 0.5 mg l⁻¹ |
| Halfsaturation concentration for P uptake | 0.01 mg l⁻¹ |
| Light saturation intensity at 20ºC | 180 µEinstein m⁻³s⁻¹ |
| Temperature dependency for light saturation | 1.04 |

**Macroalgae Parameters**

| Parameter | Value |
|-----------|-------|
| Proportional factor for sediment respiration | 1 |
| Proportional factor for N release from sediment | 1 |
| Proportional factor for P release from sediment | 1 |
| Temperature dependency for N release from sediment | 1.1 |
| Temperature dependency for P release from sediment | 1.1 |
| N-release from anoxic conditions | 0.05 gNm⁻²day⁻¹ |
| P-release from anoxic conditions | 0.01 gPm⁻²day⁻¹ |
| Temperature factor for sediment respiration | 1.07 |
| Diffusion between coef. for NO₃ and NH₄ between sediment and water | 0.002 m²day⁻¹ |
| Max. Denitrification in sediment an 20ºC | 0.2 mg N l⁻³ day⁻¹ |
| First constant for DO penetration into sediment | 0.000124 m |
| Second constant for DO penetration into sediment | 0.0000030 m⁴/gO₂ |
| Third constant for DO penetration into sediment | 0.0000473 m³*day/gO₂ |
| Half-saturation conc. DO, for NH₄ or NO₃ release from sediment | 3 |
| Specific nitrication rate pelagic water, 20ºC | 0.05 day⁻¹ |
| Teta value, nitriﬁcation | 1.04 |
| Half-saturation conc. NO₃ for denitrification | 0.2 mg N l⁻¹ |
| Half-saturation conc. for DC denitrification | 0.2 mg C l⁻¹ |
| Half-saturation conc. DO denitrification | 0.5 mg O₂ l⁻¹ |
| g O₂ used to oxidize 1 g NH₄ to 1 g NO₃ | 4.3 g O₂/ g NH₄-N |

Table 2. Main parameter values for the ecological/eutrophication model.
processes within sediments, namely at the lagoon far end, but as the transport by tidal flow is a very effective process, the DO status seems not very affected by these processes. Therefore, in a scenario where the geomorphodynamical and the hydrodynamical conditions of the Ria de Aveiro remain unchanged, the setup of hypoxic situation inside the lagoon is unlikely to occur, even in the worst scenarios. Changes in the lagoon morphodynamics resulting from the anthropogenic activities inside the lagoon and near its border, the infilling of the lagoon mouth or channels, may induce changes in the hydrodynamic regime, altering the lagoon flushing and residence times. Therefore, it is expected in this situation a negative impact of the biogeochemical processes in the DO distribution of the water column.

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