ELSEVIER

Ecological Modelling 129 (2000) 209–227

ECOLOGICAL MODELLING

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Quantification of the effects of nonpoint nutrient sources to coastal marine eutrophication: applications to a semi-enclosed gulf in the Mediterranean Sea

G. Arhonditsis [a,*], G. Tsirtsis [b], M.O. Angelidis [c], M. Karydis [a]

[a] *Aquatic Ecosystems Laboratory, Department of Environmental Studies, University of the Aegean, 81100 Mytilene, Greece*
[b] *Department of Marine Sciences, University of the Aegean, 81100 Mytilene, Greece*
[c] *Air and Water Analysis Laboratory, Department of Environmental Studies, University of the Aegean, 81100 Mytilene, Greece*

Received 14 October 1998; received in revised form 7 December 1999; accepted 1 February 2000

Abstract

An integrated modelling approach is proposed for the assessment of the nutrient loading of a coastal marine ecosystem from terrestrial sources. The evaluation of the model was based on a data set collected on a monthly basis from a Greek gulf surrounded by an intensively cultivated watershed. It consisted of three interacting components, that is the terrestrial, the hydrodynamic and the biological submodels. A modification of the loading-functions approach formed the basis of the terrestrial submodel, used for the estimation of the nutrient fluxes due to agricultural run-off. Nutrient loads from the atmosphere, the domestic effluents and the industrial activity were also considered. The hydrodynamic submodel, based on the Princeton Ocean Model, was used for the estimation of the spatial transport of nutrients and organic carbon. The third component was the biological submodel that was focused on the interactions of nitrogen, phytoplankton, zooplankton, bacteria and organic carbon. The model has shown good fit to the experimental data and it was further used for the assessment of the role of various exogenous and endogenous sources of nutrients and organic carbon. It was found that nutrient loading from the agricultural run-off was remarkable during winter, the contribution being between 40 and 60% of the total nitrogen stock. The fluxes of nitrogen and organic carbon from sewerage and industrial activity were also quantified and they were estimated to be up to 10% of the total stock whereas, the contribution of the wet and dry deposition from the atmosphere was insignificant. The integrated modelling approach could also be used for the understanding of the energy flow through the marine food web and the testing of various scenaria concerning the development of the coastal zone. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Simulation modelling; Marine eutrophication; Nutrient cycling; Exogenous sources; Nonpoint pollution

1. Introduction

The role of the coastal zone as a filter between land and the open sea retaining suspended materi-

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* Corresponding author. Tel.: +30-251-36255; fax: +30-251-36099.
E-mail address: garh@env.aegean.gr (G. Arhonditsis).

PII: S0304-3800(00)00239-8

als and nutrients is very important (Nixon and Pilson, 1983; Sharp et al., 1984). The understanding and quantification of the processes related to the terrestrial input and fate of nutrients and organic matter are essential for the evaluation and prediction of coastal marine eutrophication (Borum, 1996). The sources of nutrients and organic matter for the coastal ecosystem can be classifiedinto two groups, that is, the point and nonpoint sources. Point sources, such as sewerage and industrial wastewater, flow out at discrete, identifiable locations and their impacts can be measured directly (Rossi et al., 1992). However, the largest nutrient contribution for coastal marine environments is from nonpoint sources, that are rather diffused and highly variable from year to year depending on climate and rainfall (Borum, 1996). The most important nonpoint loads include the wet and dry deposition from the atmosphere, the erosion of land, the weathering of minerals and anthropogenic sources. The latter are directly related to human activities, such as fertilizer application, accumulation of dust and litter, erosion of soil materials from agricultural farming and animal feedlots (Novotny and Chesters, 1981).

The difficulties and inaccuracies concerning the measurement of the nonpoint loads have been faced by multi-year monitoring projects and the construction of mathematical models (Spooner and Line, 1993). These models can be classified according to their level of sophistication and potential field of application and each class is efficient for a range of simulations which, in principle, cover any level of detail the user might deem necessary (Bouraoui and Dillaha, 1996). However, a significant boundary constraint for non-point source models, the so-called 'downstream' condition linking the processes of the terrestrial ecosystem to those of the receiving water body, has received less attention (Bilby, 1993; Paerl, 1997; Valiela et al., 1997). The accomplishment of such a concept requires the appropriate selection and linking of the terrestrial and biological models describing the functioning of the marine ecosystem, studied on a time scale mainly determined by the hydrodynamic regime of marine environment (Bendoricchio and Rinaldo, 1986). These modelling developments enable the partitioning of the seawater nutrient stock and the evaluation of the role of various sources of nutrients and organic matter. Furthermore, these models can be used to evaluate scenaria concerning water quality in coastal areas influenced by various human activities (Grossman, 1994).

In the present work a modelling effort has been made for the integration of terrestrial and aquatic processes. The model was evaluated in a semi-enclosed marine ecosystem in Greece, surrounded by a cultivated and inhabited watershed. The model developed consisted of three interacting components, that is the terrestrial, the hydrodynamic and the biological submodels and the emphasis was placed on linking the terrestrial and marine processes. Furthermore, the model was used for the evaluation of the role of the various exogenous and endogenous sources of nutrients and organic matter and the understanding of the microbial processes and nutrient cycling in the coastal marine ecosystem.

2. Methodology

2.1. The study area

The area that has been used for the evaluation of the model was the gulf of Gera, Island of Lesvos, Greece, a semi-enclosed water body with a mean depth of 10 m and a total volume of 0.9×10^9 m^3 (Fig. 1). This shallow marine environment is influenced by the surrounding area that is intensively cultivated mainly with olive trees and inhabited by 7000 people. Agricultural runoff from rivers and non-point sources, sewerage and wastewater from industrial activities flow into the gulf, especially from the northern and western parts whereas the terrestrial sources from the east can be characterized as insignificant. The gulf area was therefore subdivided into four spatial compartments, that is the northern, central, western and eastern compartments (Fig. 1). Hydrodynamics is another important factor for the functioning of the marine ecosystem under consideration. The exchange of material with the open sea shows a fluctuation during the year due to the morphological characteristics of the gulf (Theocharis and Georgopoulos, 1984). During the warm months of the year (April to October), the physical factors (density, temperature, salinity, wind pattern) allow the entrance of the oligotrophic water masses of the Aegean Sea into the gulf and the area is characterized by an anticyclonic circulation pattern. The hydrodynamic regime is reversed during the rest period (November to March) and the renewal time of the seawater of the gulf is between 2 and 3 months.

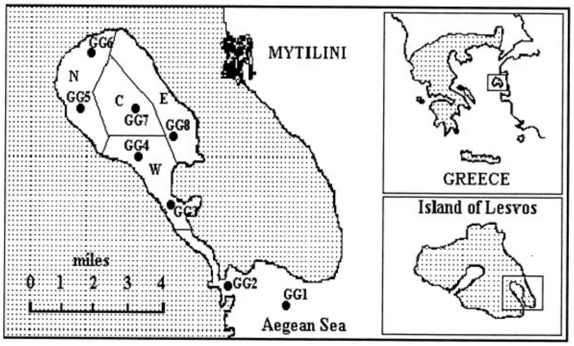

Fig. 1. The study area, the Gulf of Gera, Island of Lesvos, Greece: the four spatial compartments of the model (N: northern, C: central, E: eastern and W: western) and the station locations (GG1–GG8).

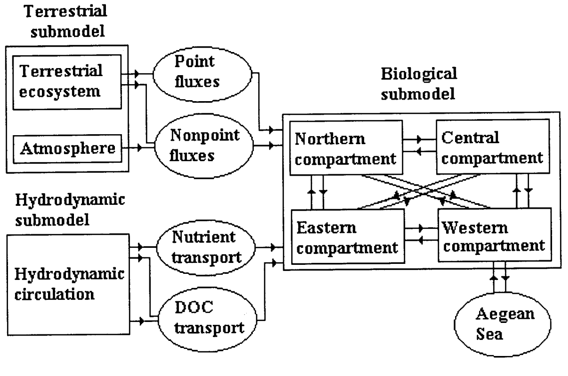

Fig. 2. The flow diagram of the model: the terrestrial submodel estimating the input of nutrients and organic carbon from point and nonpoint sources, the hydrodynamic submodel quantifying the transport of nutrients and organic carbon and the biological submodel consisting of four spatial compartments and interacting with the open sea.

2.2. Field work

Seventeen cruises have been carried out on a monthly basis from June 1996 to October 1997. Samples have been collected from eight sampling stations GG1 to GG8, that are shown in Fig. 1; six stations (GG3-GG8) were located inside the gulf whereas the rest were situated in the entrance (station GG2) and outside of the gulf (station GG1) as reference sites. The seawater samples were collected with a Van Dorn sampler from standard depths in order to determine the vertical distribution of the chemical and biological properties. Temperature, salinity and density were recorded with a CTD Seabird SBE19 profiler and the ambient and underwater solar irradiance with a Kahlsiko irradiance meter. The current velocity and speed were recorded on the upper layer and near the bottom, with a current meter, Sensordata model LTV 11402.

2.3. Analytical work

Nitrate, nitrite, phosphate, silicate and organic nitrogen were determined spectrophotometrically according to Parsons et al. (1984a) and ammonia according to Liddicoat et al. (1974). Total bacterial counts were carried out by epifluorescence microscopy (Fry, 1990). The chlorophyll α concentration was measured fluorometrically according to Neveux and Panouse (1987).

2.4. The concept of the model

The quantification and understanding of the functioning of the marine ecosystem was attempted using an integrated modelling approach. The model developed consisted of three interacting components, the terrestrial, the hydrodynamic and the biological submodels. The flow diagram of the model is shown in Fig. 2. The non-point fluxes of nutrient and organic carbon from terrestrial sources were estimated using a modification of the loading functions approach (Haith and Tubbs, 1981). Moreover, the assessment of the nutrient loads from the atmosphere and the point sources was obtained by the use of empirical formulations and experimental data from the bibliography. The hydrodynamic submodel was based on the Princeton Ocean Model (Mellor and Yamada, 1982); it was used for the estimation of the transport of nutrients and organic carbon. The third component was the biological submodel, focusing on the flow of energy through the microbial components of the marine food web (Tsirtsis, 1995). This submodel consisted of four spatial compartments shown in Fig. 2, the northern, the western, the eastern and the central compartment, related to the morphological characteristics of the surrounding area, whereas the open sea has been used for the definition of the boundary conditions. The experimental procedure and the statistical analysis of the data revealed that the effects of the stratification were insignificant and the seawater column is characterized by a vertical homogeneity (Arhonditsis, 1998). Therefore, it was assumed that the 2-D perception of the system would describe sufficiently the dynamics of its physical, chemical and biological properties.

3. The development of the simulation model

3.1. The terrestrial submodel

3.1.1. Nonpoint exogenous sources of nutrients

The model that was used for the estimation of the non-point nutrient loading from the terrestrial ecosystem is a modification of the modelling approach suggested by Haith and Tubbs (1981). The agricultural land surrounding the water body under consideration was divided into unit source areas, using a grid 1 × 1 km. It was assumed that each unit area was homogeneous with respect to soil, crop, management, topographic and weather characteristics. It was also assumed that each unit source area is independently contributing to the total nutrient export from the watershed. The discrimination of the characteristics of the unit source areas, was supported by the use of GIS (ARC/INFO, Environmental Systems Research Institute, Inc.). The dissolved and solid-phase fractions of nutrients were computed separately, reflecting the different loss mechanisms from the agricultural land (erosion and runoff). Special emphasis was placed on the soluble fraction of nutrients being directly available for biological uptake, whereas the particulate fraction is available after oxidation and decomposition processes and can therefore provide a long-term source of nutrients to the aquatic biota of a water body (Sharpley and Menzel, 1987). The nutrient losses from the unit source area k, due to a runoff event on day t, are given by:

$$\mathrm{LD}_{kt} = 10 \cdot \mathrm{Cd}_{kt} \cdot Q_{kt} \cdot \mathrm{TD}_{kt},$$

where LD_{kt} is the dissolved-phase fraction of nutrient loss in kg/km^2, Cd_{kt} is the nutrient concentration in the dissolved-phase form measured in mg/litre, TD_{kt} is a transport factor indicating the fraction of dissolved-phase nutrient that moves from the edge of the source area to the watershed outlet and Q_{kt} is the rainfall height in cm. The estimation of the runoff volume was based on a modification of the well-known algorithm of the Soil Conservation Service (S.C.S.) Curve Number that is based on the rainfall height, evaportranspiration and interim drainage losses of the watershed (Hawkins, 1978). The total dissolved nutrient export LD, for a specific time period is calculated by multiplying the losses from each source unit area by its respective area A_k (in km^2) and summing over all unit source areas and days in the time period:

$$\mathrm{LD} = 10 \sum_t \sum_k \mathrm{Cd}_{kt} \cdot Q_{kt} \cdot \mathrm{TD}_{kt} \cdot A_k$$

The concentrations of dissolved nutrients in runoff are affected mainly by the quantity of available nutrients in the soil and consequently by the crop type (Haith and Tubbs, 1981). In the present work, the calibration and verification of the various parameters of the model was obtained by its field-scale application to the characteristic vegetation types of the study area, that are olive groves, maquis, forested areas and wetlands (Arhonditsis, 1998).

The nutrient fluxes through atmospheric wet and dry deposition were also considered as exogenous sources of nutrients. The estimation of these fluxes was based on local data and the existing literature for the Mediterranean (Herut and Krom, 1996; Medinets, 1996).

3.1.2. Exogenous point sources of nutrients and organic carbon

The most important point discharges in the water body under consideration are the domestic effluents and the wastewater from the local industrial activities. This wastewater is mainly a by-product of the elaboration of oil crops by ‘centrifugal’ type oil presses and it can be characterized as ‘plant’ extract containing minor quantities of inorganic nitrogen and 0.03–0.05% of inorganic phosphorus (Michelakis and Koutsaftakis, 1989). The estimation of the nutrient loads from the domestic effluents was based on available data for the human population of the area and bibliographic information. The total human population in the area surrounding the gulf of Gera is estimated to be 7064 people according to the 1991 census. Each year during the summer (especially in July and August), the whole area hosts approximately 5000 tourists, resulting in an increase of point loading of up to 35%. On the basis of the existing literature (Smith, 1977; Marchetti and Verna, 1992; Werner and Wodsak, 1994), it was assumed that the per capita contribution of inorganic nitrogen is 6.5 g/person·per day and of inorganic phosphorus is 2 g/person·per day whereas, the per capita contributions of the organic forms of these elements are 3.5 and 1 g/person·per day, respectively.

The terrestrial submodel was run with a time step of 1 day and the nutrient and organic carbon loadings of the marine ecosystem were estimated on a daily basis. These loadings were used as an input for the biological submodel describing the flow of energy through the microbial components of the marine ecosystem.

3.2. The hydrodynamic submodel

The Princeton Ocean Model, that was developed by Mellor and Yamada (1982), was applied to simulate the hydrodynamic regime of the study area. The 2-D mode of the model was deemed sufficient due to the exposed resemblance between the circulation pattern of the upper layer and that of the bottom (Arhonditsis, 1998). The output of the hydrodynamic submodel was used as the input for the eutrophication submodel in order to estimate the nutrient and organic carbon transport due to the hydrodynamic circulation. The Princeton Ocean Model is a sigma coordinate model in that the vertical axis is scaled on the water column depth, a necessary attribute in dealing with significant topographical variability such as that encountered in estuaries or over continental shelf breaks and slopes (Mellor, 1996). This free surface model produces realistic bottom boundary layers which are important for the simulation of tidally driven coastal waters (Zavatarelli and Mellor, 1995). In the present work a rectangular grid was used with cell dimensions of 330 × 330 m and the boundary conditions between the study area and the open sea, were specified by the calculation of the tidal forces. It was assumed that the resultant tidal forces, can be considered as the sum of a number of simple harmonic constituents, each one reflecting the motions of sun and moon and having its own characteristic period, phase and amplitude. Wind stresses have been also taken into account using the Wilson’s equation (Weiyan, 1992). The hydrodynamic submodel was run with a time step of one day, forced with the prevailing wind patterns in the study area to simulate the 2-D hydrodynamic circulation. The output of the model was used for the estimation of nutrient and organic carbon transports among the spatial compartments of the biological submodel.

3.3. The biological submodel

It was assumed that the study area should be divided into four spatial compartments (Fig. 1) for the application of the biological submodel, taking into account the morphological characteristics of the surrounding area. Nutrient input from agricultural runoff, from rivers and non-point sources, sewerage and wastewater from industrial activities influence the northern compartment whereas, the terrestrial sources for the eastern compartment can be characterized as insignificant. The central compartment has been used to characterize the water masses that are not influenced by human activities in the coastal zone. The western compartment is in the vicinity of the open sea and is expected to be influenced by the mixing process with the oligotrophic waters of the

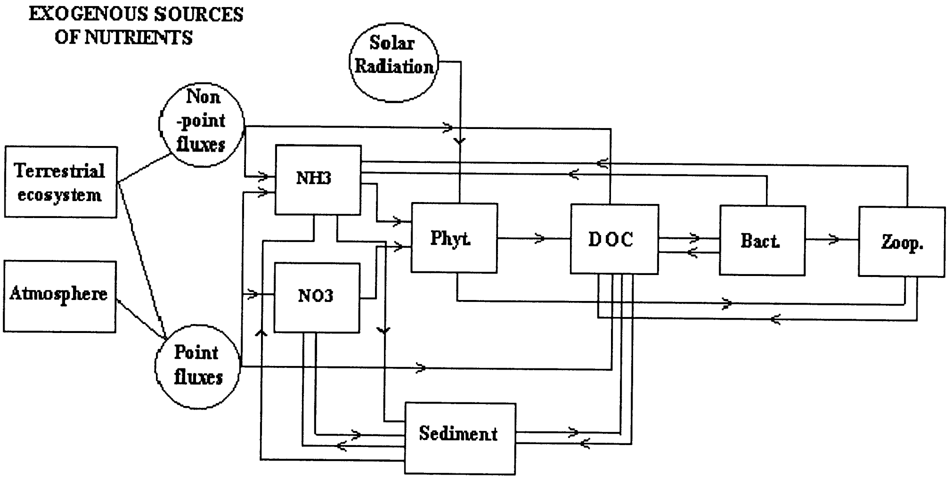

Fig. 3. The flow diagram of the biological submodel (PHYT, BACT and ZOOP, the phytoplanktonic, bacterial and zooplanktonic biomasses, respectively).

Aegean Sea. A fifth spatial compartment, the open sea, has been used for the definition of the boundary conditions.

The energy flow through the microbial food-web has been described in nitrogen terms, since it was found that this element was the limiting factor for primary production in the study area. The use of nitrogen has an additional advantage; a distinction can be made between the 'new primary production' based on nitrate and the 'regenerated primary production' based on ammonia. Therefore, it was considered that the simplest model that could be developed to describe the energy flow through the microbial food web consists of six state variables, phytoplanktonic (PHYT), zooplanktonic (ZOOP) and bacterial (BACT) biomasses, nitrate (NO_3), ammonia (NH_3) and dissolved organic carbon (DOC) concentrations (Fig. 3).

The six differential equations describing the temporal variations of the state variables are:

$$\begin{aligned}\mathrm{dPHYT}/\mathrm{d}t = {} & (\mathrm{Pro} \times \min(\phi_{\mathrm{NA}},\ \phi_{\mathrm{LT}}) \times (1-\gamma) \\ & - m_{\mathrm{p}} - k_{\mathrm{WS}}) \times \mathrm{PHYT} \\ & - G_{\mathrm{p}} \pm \mathrm{PHYT}_{\mathrm{comp}}\end{aligned}$$

$$\begin{aligned}\mathrm{dBACT}/\mathrm{d}t = {} & (U_1 + U_2 - m_{\mathrm{b}} - e_{\mathrm{b}} - k_{\mathrm{WS}}) \times \mathrm{BACT} \\ & - G_{\mathrm{b}} \pm \mathrm{BACT}_{\mathrm{comp}}\end{aligned}$$

$$\begin{aligned}\mathrm{dZOOP}/\mathrm{d}t = {} & as_{\mathrm{p}} \times G_{\mathrm{p}} + as_{\mathrm{b}} \times G_{\mathrm{b}} - (e_{\mathrm{z}} + m_{\mathrm{z}}) \\ & \times \mathrm{ZOOP} \pm \mathrm{ZOOP}_{\mathrm{comp}}\end{aligned}$$

$$\begin{aligned}\mathrm{dDOC}/\mathrm{d}t = {} & (\mathrm{Pro} \times \min(\phi_{\mathrm{NA}},\ \phi_{\mathrm{LT}}) \times \gamma + m_{\mathrm{dp}}) \\ & \times \mathrm{PHYT} + (m_{\mathrm{db}} - U_{\mathrm{l}}) \times \mathrm{BACT} \\ & + (e_{\mathrm{dz}} + m_{\mathrm{dz}}) \times \mathrm{ZOOP} + \mathrm{DOC}_{\mathrm{sed}} \\ & + \mathrm{DOC}_{\mathrm{point}} + \mathrm{DOC}_{\mathrm{npoint}} \\ & + \mathrm{DOC}_{\mathrm{atm}} \pm \mathrm{DOC}_{\mathrm{comp}}\end{aligned}$$

$$\begin{aligned}\mathrm{dNH_3}/\mathrm{d}t = {} & -(a_{\mathrm{nap}} \times \phi_{\mathrm{A}} - m_{\mathrm{ap}}) \times \mathrm{PHYT} \\ & + (m_{\mathrm{ab}} + e_{\mathrm{b}} - U_2) \times \mathrm{BACT} + (e_{\mathrm{az}} + m_{\mathrm{az}}) \\ & \times \mathrm{ZOOP} + \mathrm{NH}_{3_{\mathrm{sed}}} + \mathrm{NH}_{3_{\mathrm{point}}} \\ & + \mathrm{NH}_{3_{\mathrm{npoint}}} + \mathrm{NH}_{3_{\mathrm{atm}}} \pm \mathrm{NH}_{3_{\mathrm{comp}}}\end{aligned}$$

$$\begin{aligned}\mathrm{dNO_3}/\mathrm{d}t = {} & -a_{\mathrm{nap}} \times \phi_{\mathrm{N}} \times \mathrm{PHYT} + \mathrm{NO}_{3_{\mathrm{sed}}} \\ & + \mathrm{NO}_{3_{\mathrm{point}}} + \mathrm{NO}_{3_{\mathrm{npoint}}} \\ & + \mathrm{NO}_{3_{\mathrm{atm}}} \pm \mathrm{NO}_{3_{\mathrm{comp}}}\end{aligned}$$

The transfer coefficients and the model parameters of the equations are described in Tables 2 and 3. The subscripts sed, point, npoint, atm, indicate the fluxes from the sediment, the point, non-point terrestrial sources and the atmosphere, respectively. The subscript comp indicates the transport processes among the spatial compartments of the study area. The differential equations of the western compartment include an additional term describing the interactions of the compartment with the open sea.

3.3.1. The physical forcing

Two physical factors were taken into account for the development of the model; the solar irradiance and the exchanges of nutrients and organic carbon among the spatial compartments due to advective and diffusive transport. Methodological details about the model that has been used for the estimation of light availability have been given elsewhere (Tsirtsis, 1995). The nutrient and organic carbon transport among the spatial compartments was estimated using the multiple-box model approach (Shanahan and Harleman, 1984). The concentrations of chemical and biological parameters in each compartment are determined by simple mass balance, essentially the integration of the equation of mass conservation over the volume element (compartment). For an arbitrary configuration of elements, the differential equation for element k is:

$$V_k \times \frac{\mathrm{d}c_{\mathrm{k}}}{\mathrm{d}t} = \sum_j \left[Q_{jk} \times c_j - Q_{kj} \times c_k + \frac{E_{jk} \times A_{jk}}{l_{jk}} \times (c_j - c_k) \right] + S_k$$

where c_k the concentration in element k (μg-at/litre), V_k the volume of element k (m^3), E_{jk} the dispersion coefficient between elements j and k (m^2/day), A_{jk} the interfacial area between elements j and k (m^2), l_{jk} the distance separating the centroids of elements j and k (m), S_k the sum of all sources and sinks within element k and Q_{jk} the flow from element j to k (m^3/day) computed from the output of the hydrodynamic submodel by averaging the velocities of the grid cells that are situated on the interfacial area between elements j and k.

3.3.2. Nutrient fluxes from the sediment

The nitrogen exchange at the seawater-sediment interface was estimated according to the empirical formulation of Jacobsen and Jorgensen (1975):

$$S_{\mathrm{N}} = (k_{\mathrm{SN}} \times N_{\mathrm{sed}} + 0.13) \times \mathrm{e}^{0.134 \times T}/D \quad \text{(aerobic conditions)}$$

$$S_{\mathrm{N}} = (k_{\mathrm{SN}} \times N_{\mathrm{sed}} + 0.08) \times e^{0.151 \times T}/D \quad \text{(anaerobic conditions)}$$

where, S_{N} the daily nitrogen fluxes from the sediment per unit area (g N/day m^2), N_{sed} the concentration of nitrogen in the sediment estimated from experimental data (g/m^3), T the temperature in °C, D the average depth of the compartment (m) and k_{SN} the exchange coefficient between the sediment and the seawater column (day^{-1}). Thus, these fluxes are incorporated in the respective differential equations by the form:

$$N_{\mathrm{sed}} = 71.393 S_{\mathrm{N}}(A/V)$$

where, N_{sed} the daily nitrogen fluxes from the sediment (μg at N/day per litre), V and A the seawater volume (m^3) and the area (m^2) of the spatial compartment. Furthermore, the plankton exchanges between sediment and seawater are also incorporated in the model; they are expressed explicitly in the phytoplankton and bacterial equations by the parameter k_{WS}.

3.3.3. The phytoplankton equation

Phytoplanktonic growth depends on light and nutrient availability. The light limitation on phytoplanktonic growth was expressed by the model proposed by Taylor and Joint (1990):

$$\phi_{\mathrm{LT}} = \ln\{(1 + I/I_k)/[1 + I \exp(-k \cdot \mathrm{z})/I_k]\}/(k \cdot z),$$

where I is the surface irradiance (MJ/m^2·per day), I_k the half saturation light intensity for phytoplanktonic growth (MJ/m^2·per day), z the maximum depth (m) and k the light extinction coefficient (m^{-1}), that is related to chlorophyll concentration with the equation $k = k_{\mathrm{w}} + k_{\mathrm{c}} \times C$, where k_{w} the extinction of water without chlorophyll (m^{-1}), k_{c} a coefficient for light attenuation due to chlorophyll litre/μg per m and C the chlα concentration (μg/litre) (Tsirtsis, 1995). Phytoplanktonic growth rate is expressed by the equation $a_{\mathrm{PNA}} = \mathrm{Pro} \times \min(\phi_{\mathrm{NA}}, \phi_{\mathrm{LT}})$, where Pro is the maximum specific growth rate for phytoplankton (day^{-1}) and ϕ_{NA} the nitrogen limitation of the phytoplanktonic growth, expressed by the Michaelis–Menten equation:

$$\phi_{NA} = \phi_N + \varphi_A = \frac{NO_3 \exp(-\psi NH_3)}{NO_3 + NH} + \frac{NH_3}{NH_3 + AH},$$

where NH and AH the half saturation constants for nitrate and ammonia phytoplanktonic uptake (μg at N/litre) and ψ is a constant parameterizing the strength of the ammonium inhibition on nitrate uptake (μg at N/litre)$^{-1}$ (Wrobleski, 1977). Phytoplanktonic losses are assumed to be due to biological (exudation, mortality and zooplankton grazing) and physical factors (mixing processes caused by advection-dispersion). The chlorophyll α content of the phytoplanktonic cells is converted to carbon assuming a C/chlα ratio of 50 (Fasham et al., 1990).

3.3.4. The bacterial equation

The model proposed by Fasham et al. (1990) has been used to describe bacterial growth. According to this model, the bacterial growth depends on the availability of dissolved organic nitrogenous compounds (DON) and ammonia. In a balanced growth situation, the ratio of bacterial ammonium uptake to DON uptake should be constant so as to ensure that bacterial biomass of the required C:N ratio is produced. This concept is incorporated into a Michaelis–Menten model of bacterial uptake by defining a total bacteria nitrogenous substrate S as:

$$S = \min(NH_3,\ n \times DON),$$

where n is the ratio of bacterial ammonium uptake to DON uptake and the product $n \times DON$ represents the organic nitrogenous substrate that is being consumed for the bacterial growth. Therefore, the bacterial DON uptake (U_1) and ammonium uptake (U_2) can be written as:

$$U_1 = \frac{a_{BD} \times DON}{DH + S + DON} \quad \text{and}$$

$$U_2 = \frac{a_{BD} \times S}{DH + S + DON},$$

where a_{BD} is the maximum bacterial uptake rate (day^{-1}) and DH the half-saturation constant for bacterial uptake (mg/m^3). Bacterial losses are assumed to be due to exudation, mortality and zooplankton grazing. The bacterial biomass is calculated on the assumption of a carbon content of 20 fgr/cell (Lee and Fuhrman, 1987).

3.3.5. The zooplankton equation

The model proposed by Fasham et al. (1990) has been used for the zooplanktonic growth. According to this model, the zooplanktonic growth is based on the grazing of phytoplankton and bacteria. A Michaelis–Menten equation was used to parameterize the effect of food level on grazing rate. A measure of the total food stock F, is defined as:

$$F = p_1 PHYT + p_2 BACT,$$

where p_1 and p_2 are parameters expressing the zooplankton preferences for the two food types, phytoplanktonic and bacterial biomasses, respectively. It was assumed that these grazing preferences change dynamically as a function of the relative proportion of the two prey concentrations. For simplicity purposes, the assigned preference for phytoplankton was defined as:

$$p_1 = \frac{PHYT}{PHYT + BACT},$$

expressing the fact that zooplankton actively selects the most abundant food organism. The grazing rate on phytoplankton (G_p) is given by the equation:

$$G_p = gZOOP \frac{p_1 PHYT}{K_z + F},$$

where g is the maximum specific growth rate (day^{-1}) and K_z is the half-saturation constant for zooplankton grazing (mg/m^3). Equivalent equation can be written for bacteria and the total zooplankton grazing $G_p + G_b$ is equal to:

$$G_z = gZOOP \frac{F}{K_z + F}$$

The grazing rates G_p and G_b are multiplied by the coefficients as_p and as_b, which reflect the equivalent assimilation efficiencies. Losses of the zooplanktonic biomass are due to excretions and mortality including the grazing by higher predators of the trophic chain. Moreover, these products of the zooplankton metabolism were assumed to constitute an indirect source of ammonia and dissolved organic carbon, in order to quantify their contribution to nutrient cycling. Finally, the zooplankton was considered to be sufficiently motile to be unaffected by diffusive processes (Fasham et al., 1990).

3.3.6. The ammonia equation

Ammonia is utilized by phytoplankton and bacteria as a source of nitrogen. Endogenous sources of ammonia are the planktonic exudation and the bacterial mineralization processes, whereas significant exogenous fluxes result from the domestic effluents, the sediment and the non-point sources, that is the agricultural runoff and the atmospheric deposition.

3.3.7. The nitrate equation

The processes that have been considered were nitrate uptake by the phytoplankton, the flux from the sediment and inflows by the terrestrial sources.

3.3.8. The DOC equation

The major endogenous sources of DOC are phytoplanktonic, bacterial and zooplanktonic excretions and mortality, whereas the only biological sink is bacterial utilization. The input of organic carbon from the atmosphere, domestic effluents and industrial activity were also incorporated into the model. The dissolved organic carbon concentration is computed from the dissolved organic nitrogen data available, assuming a C:N ratio of 5.6 (Redfield et al., 1963).

The set of ordinary differential equations defining the biological and chemical processes in the four compartments of the biological submodel was integrated with a fourth-order Runge–Kutta algorithm. Different integration time steps were tested and it was found that a time step of one day was sufficient to give accurate estimates of the state variables in the 95% confidence interval. The simulation was run until a steady-state annual cycle was achieved, i.e. the state variable concentrations on a given day of the year were the same in successive years of simulation. The model is not very sensitive to initial conditions and it took 3 years to achieve a steady state. The calibration of the model was based on the 'controlled random search' method. The experimental values were smoothed by the use of a polynomial of degree 9 in order to isolate the random errors of the experimental procedure and calibrate objectively the model. The output of the terrestrial submodel describing the nutrient and organic carbon terrestrial loadings and the output of the hydrodynamic submodel estimating the transport of nutrients and organic carbon due to the hydrodynamic circulation, were used as inputs for the biological submodel.

3.4. Sensitivity analysis

The extent to which uncertainties in the values of parameters influence the equilibrium values of the state-variables was carried out by changing separately each model parameter and measuring the response to the state variables of the system such as the maxima in phytoplanktonic, bacterial and zooplanktonic biomass. The sensitivity analysis was focused on the most uncertain parameters of the model that were estimated from the calibration procedure. Each model parameter was reduced at half and then increased twofold and the percentage changes of the maxima in phytoplanktonic, bacterial and zooplanktonic biomass were estimated by the model.

4. Results and discussion

4.1. System dynamics and results of the model

Summary statistics of the chemical and biological information collected in the study area from June 1996 to October 1997 is presented in Table 1. The mean concentrations of nitrate, phosphate, organic nitrogen and chlorophyll α are rather high, being 0.55, 0.19, 7.93 μM and 0.98 μg/litre, respectively. These mean values are characteristic of a marine environment that can be classified as mesotrophic with eutrophic trends according to the scaling for the Aegean proposed in previous work (Ignatiades et al., 1992; Kitsiou and Karydis, 1998).

The quantification of the interrelations among the biological and chemical state variables of the marine ecosystem was attempted using an integrated simulation modelling approach. The hydrodynamic submodel was used to simulate the 2-D hydrodynamic circulation in the study area. The output of this submodel forced by a southeast wind (the prevailing wind pattern in the study area) is shown in Fig. 4. It was observed that the mixing processes with the open sea were remarkable in the summer characterized by current velocities of 0.04–0.06 m/s (Fig. 4a and b); during the sea rise (flood tide) an inflow of the oligotrophic water masses of the Aegean was predicted by the model (Fig. 4a) whereas, this hydrodynamic regime was reversed during the ebb tide (Fig. 4b). Conversely the winter period, the inflow of the water masses of the Aegean into the gulf is minimal (currents of 0.01–0.02 m/s) and a cyclonic pattern of circulation is predicted by the model (Fig. 4c). These simulation results are in accordance with previously published work for the study area (Theocharis and Georgopoulos, 1984) and the current direction and velocity measurements carried out during June 1996 to October 1997 at the sampling stations.

The model was calibrated in relation to the smoothed experimental data and the parameter values after the calibration are shown in Table 3. The model has shown good fit to the experimental data, since the main trends of annual variability of the state variables under consideration were predicted. The simulation was considered successful for phytoplanktonic and bacterial biomasses, nitrate and DOC concentrations, whereas minor discrepancies were observed between simulated and experimental data for ammonia. The simulated annual cycle of the six state variables of the model in the western compartment along with the experimental data are shown in Figs. 5 and 6. The western compartment was considered as the most complicated, since it is influenced both by exogenous point and nonpoint nutrient loadings and by the interactions with the open sea.

The phytoplanktonic biomass was relatively high from February until June and during

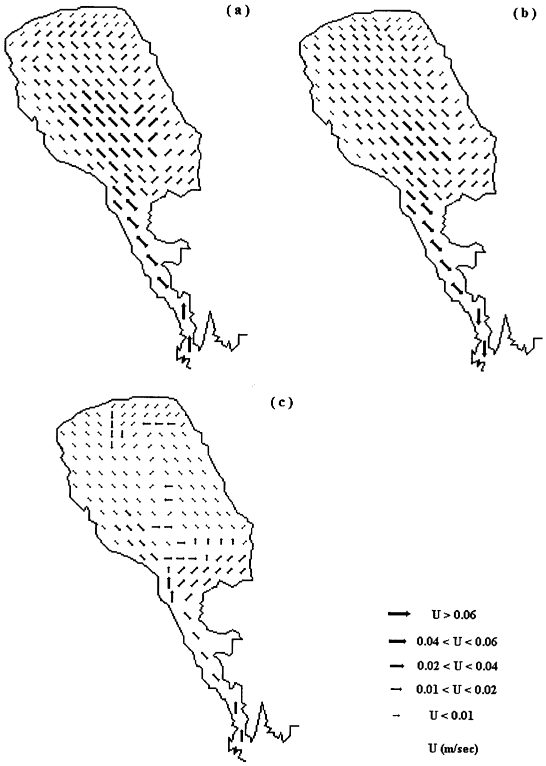

Fig. 4. The output of the hydrodynamic submodel forced by a southeast wind (the prevailing wind pattern in the study area): (a) in the summer period during the sea rise (flood tide), (b) in the summer period during the ebb tide and (c) in the winter period when the mixing processes between the study area and the open sea are limited.

Table 1
Summary statistics of nitrate, nitrite, ammonia, phosphate, silicate, organic nitrogen[a]

Parameter	Range	Mean value	Standard deviation
Nitrate	0.09–2.57	0.55	0.37
Nitrite	0.01–0.56	0.10	0.07
Ammonia	0.05–6.62	0.91	0.98
Phosphate	0.02–0.85	0.19	0.12
Silicate	3.09–10.17	7.59	1.15
Organic nitrogen	0.17–27.99	7.93	4.06
Chlorophyll α	0.03–3.07	0.98	0.59
Total bacterial number	331–1145	655.00	162.00

[a] In μM, chlorophyll α in μg/litre and total bacterial number in 10^3 cells/ml, in the gulf of Gera, from June 1996 to October 1997.

November in the study area (Fig. 5a). This annual cycle shows considerable differences from the typical seasonal trend observed in the open sea, that is a peak in phytoplanktonic biomass during early spring, low biomass during summer and a second peak during September (Harris, 1986). This seasonal trend is affected mainly by the availability of light and nutrients in the euphotic zone (Mann and Lazier, 1991). The light and nutrient availability during early spring support the first phytoplanktonic bloom. During the summer nutrients are exhausted due to the phytoplanktonic uptake and the primary production is low whereas, the physical mixing of the water column during September and the enrichment of the euphotic zone with nutrients from the deeper layers support the second bloom. The differences observed in the study area from the typical annual cycle are possibly due to the nutrient enrichment of the marine ecosystem from terrestrial sources, especially during winter and spring when strong rainfall events were observed. The bacterial biomass has shown two peaks, the first during winter and the second during early spring (Fig. 5b). These peaks were observed soon after the phytoplanktonic blooms, supporting the view that the model efficiently describes the processes related to the flow of energy through the microbial loop (Azam et al., 1983). The dissolved organic carbon resulting from phytoplanktonic exudation and mortality supports the growth of heterotrophic bacteria; this relationship of the two variables is the main reason for the observed sequence between the phytoplanktonic and bacterial blooms that has been also observed in previous work (Tsirtsis, 1995; Tsirtsis and Karydis, 1997). The zooplanktonic biomass has not shown considerable changes during the year, although higher values were predicted by the model during summer and autumn. The only factor that has been taken into account for the model of the zooplanktonic growth was the availability of food. It seems possible that the phytoplanktonic and bacterial biomass were enough to support the zooplanktonic growth, even when the prey populations were remarkably low. Furthermore, zooplankton was not affected by the seasonal changes of the circulation pattern in the study area, since it was assumed that is sufficiently motile to be unaffected by transport processes (Fasham et al., 1990).

Nitrate concentrations showed several peaks during the winter period, the concentrations being low throughout the rest of the year (Fig. 6a). These peaks are due to the inflow from exogenous sources, since strong rainfall events were observed during this period at the study area. Ammonia concentration was relatively stable during the year (Fig. 6b) whereas, a seasonal trend of high values during winter and late spring was observed for dissolved organic carbon concentration (Fig. 6c). These two variables, ammonia and dissolved organic carbon, are not related with the inputs from terrestrial sources; endogenous sources related to biological processes regulate the variability of the ammonia and organic carbon stock of the gulf.

Table 2
Description and definition of the transfer coefficients of the differential equations describing the temporal variation of the state variables in the biological submodel

Transfer coefficient	Description	Definition	Units
m_{dp}	Phytoplanktonic mortality to DOC	$m_{\mathrm{p}} \times p_4$	day^{-1}
m_{ap}	Phytoplanktonic mortality to ammonia	$m_{\mathrm{p}} \times 0.071393 \times p_5/p_1$	day^{-1}
m_{db}	Bacterial mortality to DOC	$m_{\mathrm{b}} \times p_6$	day^{-1}
m_{ab}	Bacterial mortality to ammonia	$m_{\mathrm{b}} \times 0.071393 \times p_7/p_2$	day^{-1}
m_{dz}	Zooplanktonic mortality to DOC	$m_{\mathrm{z}} \times p_8$	day^{-1}
m_{az}	Zooplanktonic mortality to ammonia	$m_{\mathrm{z}} \times 0.071393 \times p_9/p_3$	day^{-1}
e_{dz}	Zooplanktonic excretions to DOC	$e_{\mathrm{z}} \times p_{10}$	day^{-1}
e_{az}	Zooplanktonic excretions to ammonia	$e_{\mathrm{z}} \times 0.071393 \times p_{11}/p_3$	day^{-1}
a_{NAP}	Inorganic nitrogen to phytoplankton	$a_{\mathrm{PNA}} \times 0.071393/p_1$	day^{-1}

Table 3
Description and values of the biological submodel parameters after the calibration of the model

Parameter	Description	Value	Units
γ	Fraction of phytoplanktonic production exudated as DOC	0.22	dimensionless
m_p	Phytoplanktonic mortality rate	0.25	day^{-1}
m_b	Bacterial mortality rate	0.32	day^{-1}
m_z	Zooplanktonic mortality rate	0.15	day^{-1}
k_{ws}	Exchange coefficient between sediment and seawater for phytoplankton and bacteria	0.12	day^{-1}
k_{SNO_3}	Rate constant for nitrate release from sediment	0.0042	day^{-1}
k_{SNH_3}	Rate constant for ammonia release from sediment	0.0038	day^{-1}
k_{SOrgN}	Rate constant for organic nitrogen release from sediment	0.0040	day^{-1}
NH	Half saturation constant for nitrate phytoplanktonic uptake	1.00	μg-at N/litre
AH	Half saturation constant for ammonia phytoplanktonic uptake	1.00	μg-at N/litre
Pro	Maximum specific growth rate for phytoplankton	2.10	day^{-1}
e_b	Bacterial excretion rate	0.09	day^{-1}
e_z	Zooplanktonic excretion rate	0.15	day^{-1}
a_{sp}	Zooplanktonic assimilation efficiency of phytoplankton	0.75	Dimensionless
a_{sb}	Zooplanktonic assimilation efficiency of bacteria	0.75	Dimensionless
DH	Half saturation constant for bacterial uptake	135	mg/m^3
I_k	Half saturation light intensity	2.50	$MJ/m^2 \cdot day$
k_w	Light extinction coefficient for water without chlorophyll	0.16	m^{-1}
k_c	Light extinction coefficient due to chlorophyll	0.19	$l(\mu g\ m)^{-1}$
ψ	Strength of the ammonium inhibition of nitrate uptake	0.60	$(\mu g\text{-at N/litre})^{-1}$
n	Ratio of bacterial ammonium uptake to DON uptake	0.60	Dimensionless
a_{BD}	Maximum bacterial uptake rate	1.45	day^{-1}
g	Zooplanktonic maximum specific growth rate	0.55	day^{-1}
K_Z	Half-saturation constant for zooplanktonic grazing	0.95	mg/m^3
p_1	C:N for phytoplankton	5.60	Dimensionless
p_2	C:N for bacteria	4.50	Dimensionless
p_3	C:N for zooplankton	6.00	Dimensionless
p_4	Fraction of phytoplanktonic mortality becoming DOC	0.35	Dimensionless
p_5	Fraction of phytoplanktonic mortality becoming ammonia	0.15	Dimensionless
p_6	Fraction of bacterial mortality becoming DOC	0.35	Dimensionless
p_7	Fraction of bacterial mortality becoming ammonia	0.15	Dimensionless
p_8	Fraction of zooplanktonic mortality becoming DOC	0.30	Dimensionless
p_9	Fraction of zooplanktonic mortality becoming ammonia	0.15	Dimensionless
p_{10}	Fraction of zooplanktonic excretions becoming DOC	0.30	Dimensionless
p_{11}	Fraction of zooplanktonic excretions becoming ammonia	0.15	Dimensionless

4.2. Results of the sensitivity analysis

The results of the sensitivity analysis of the model to the uncertainties of the model parameters are presented in Table 4. It can be shown that the phytoplanktonic growth is more liable to rapid changes and it depends mainly on the maximum phytoplanktonic specific growth rate (Pro) and mortality (m_p), as well as on the fraction of phytoplanktonic production exudated as DOC (γ). Furthermore, the half saturation constant for bacterial uptake (DH), the maximum bacterial uptake rate (a_{BD}) and mortality rate (m_b) are the critical model parameters for bacterial biomass growth. The half-saturation constants for ammonia (AH) and nitrate uptake (NH) are related to algal species and to their cell sizes; for a given nutrient regime larger cells have higher values of K_s (Valiela, 1984). Consequently, the minor effects of their uncertainties on the state variables reflect the constancy of the system to the qualitative alterations of the phytoplankton (e.g. morphological characteristics, species composition). Similar inferences could be extracted by the independence of the primary production from the half saturation constant of light intensity (I_k); a measure of how efficiently cells use changes in light. The ratio of the change in photosynthesis with respect to the change in light is steeper for greens and diatoms than for dinoflagellates, indicating that photosynthesis is saturated at lower light intensities for the former than the later. Thus, the stability of the model to the changes of these constants indicates that the perception of the phytoplankton community as a hall stimulates the ecosystem dynamics sufficiently and further analysis with a view of detecting the effects of classes or species composition seems to be worthless. However, generalizations about the structure of the model and the sensitivity of the system from the aforementioned relationships are difficult, since the behavior of the primary producers varies substantially even within one species and may be changed by nutrient deficiencies or by cellular adaptations in the spectrum of environmental perturbations (Harris, 1986).

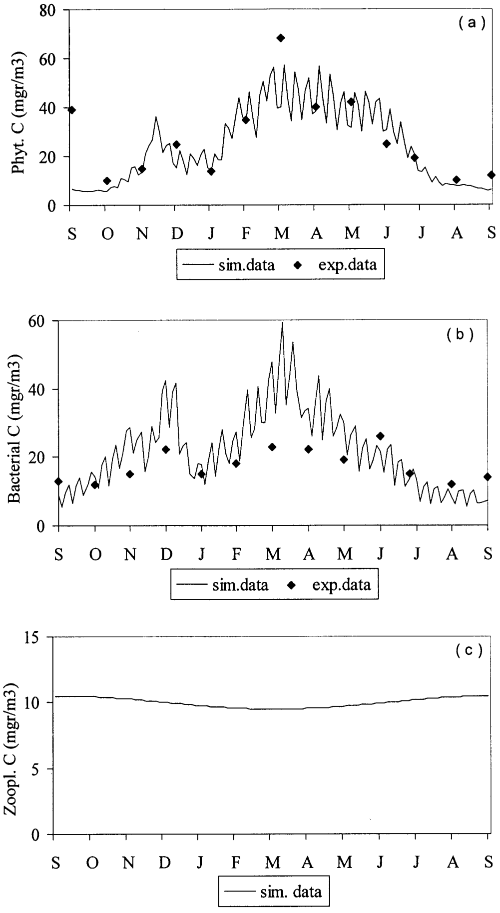

Fig. 5. Temporal variability of (a) phytoplanktonic, (b) bacterial and (c) zooplanktonic biomasses in the western compartment of the study area: simulated and experimental data.

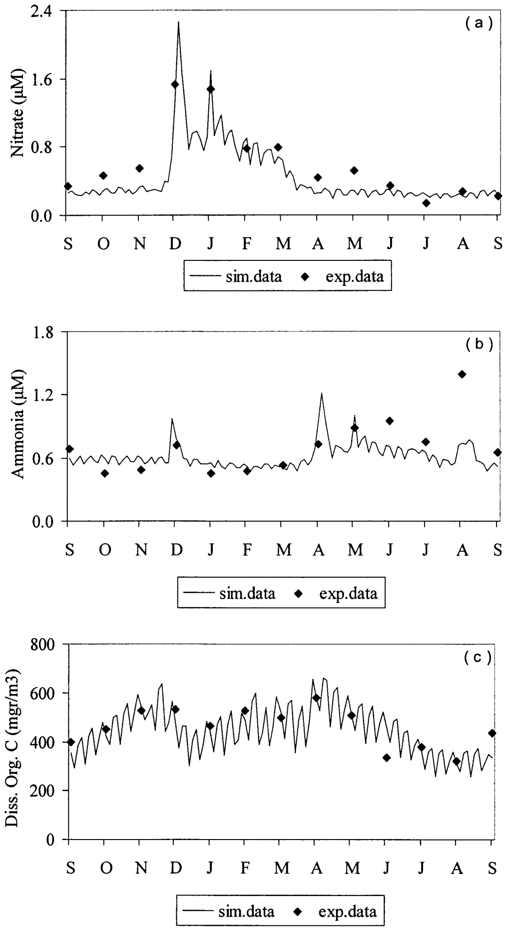

Fig. 6. Temporal variability of (a) nitrate, (b) ammonia and (c) dissolved organic carbon (DOC) concentrations in the western compartment of the study area: simulated and experimental data.

The zooplanktonic biomass is quite stable to the changes of the model parameters and it is related mostly to the mortality rate (m_z), whereas minor are the effects of the maximum zooplanktonic specific growth rate (g) and the half saturation constant for zooplanktonic grazing (K_z).

Moreover, the exposed resistance of the zooplankton to the fluctuations of the prey populations, stimulated by the uncertainties of their characteristic model parameters, verifies the aforementioned idea that the phytoplanktonic and bacterial biomasses are quantitatively adequate to sustain the zooplanktonic growth. The significance of the zooplankton mortality rate is attributed mostly to the fact that it parameterizes natural mortality and predation by higher predators which are not explicitly modeled. Contrarily, the role of the uncertainties of the maximum specific growth rate is rather ambiguous due to the fact that the zooplankton term models an aggregated entity that incorporates herbivores and bacteriovores species with different sizes and ages. In general, at some point in a zooplankter's life cycle there is a period of maximum growth efficiency when the specific metabolism per unit body weight is lowest for a maximun in growth rate; and the same general relationship applies to different species with different size. It has been shown that there is a distinct advantage for larger and older animals compared with adults and smaller animals (Parsons et al., 1984b). Thus, the stability of the state variables to the changes of this model parameter indicates that further analysis of the zooplankton term, e.g. the discrimination to taxinomic subgroups or the incorporation of different size classes of organisms, is unlikely to improve the model results. Another point of interest is that the zooplankton predates preferentially the phytoplanktonic biomass and therefore the occurrence of drastic changes on the grazing pressure (e.g. uncertainties of the mortality rate) constitutes a significant regulatory factor of its density. This result seems to be an 'artifact' of the chosen formula to describe the zooplankton preferences for the various food types in combination with the relative proportion of the phytoplankton and bacteria abundances. Therefore, the assignment of a functional expression for the feeding selectivity of predators is essential and should be considered as a matter of concern for future exploitation with a view of improving the predictive power of the model.

Table 4
Sensitivity evaluation for phytoplanktonic, bacterial and zooplanktonic biomass; percentage changes in phytoplanktonic, bacterial and zooplanktonic biomass maxima induced after the twofold increase and half reduction of the model parameters[a]

Sensitivity evaluation

Parameter	Twofold increase			Half reduction		
	Phytoplanktonic biomass	Bacterial biomass	Zooplanktonic biomass	Phytoplanktonic biomass	Bacterial biomass	Zooplanktonic biomass
γ	−17.6	2.2	−0.1	4.5	−0.8	0.5
e_b	0.3	−1.8	0.0	−0.2	2.5	0.1
e_z	3.0	1.9	−1.7	−1.3	−1.0	0.9
m_p	−32.9	3.7	−0.8	20.8	−0.2	1.3
m_b	1.2	−19.3	−0.1	−0.5	17.0	0.2
m_z	14.7	3.2	−10.2	−12.1	−2.0	6.9
Pro	25.0	−0.4	0.7	−29.7	2.9	−1.0
a_{BD}	−1.6	10.4	0.0	2.0	−9.7	0.4
g	−14.9	−2.9	3.7	11.3	4.7	−3.1
NH	−2.7	0.0	−0.1	3.0	−0.1	0.6
AH	−5.2	0.1	−0.4	4.9	−0.2	0.7
DH	1.9	−13.0	−0.3	−1.1	9.9	0.4
I_k	−5.5	0.9	−0.4	6.3	−0.2	0.5
K_Z	6.7	2.9	−2.3	−8.4	−3.1	4.2

[a] The notation is explained in Table 3

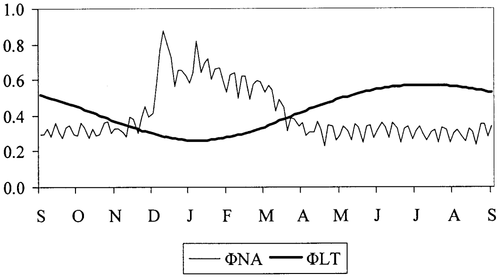

Fig. 7. Annual variability of the limiting factor for phytoplanktonic growth: the coefficient ϕ_{NA} is expressing the nitrogen limitation and the coefficient ϕ_{LT} the light limitation on phytoplanktonic growth.

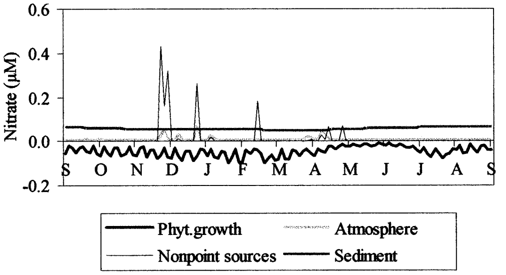

Fig. 8. Annual variability of the various sources and sinks of nitrate for the coastal marine ecosystem.

4.3. Partitioning of the nutrient stock

The simulation model was further applied for assessment of the contribution of the various exogenous and endogenous sources of nutrients and organic carbon. The following results concern the western spatial compartment that was considered as the most complicated, but similar inferences could be extracted from the other three elements. The annual variability of the limiting factor for primary production in this spatial compartment is presented in Fig. 7. It was predicted by the model that the phytoplanktonic growth was nitrogen-limited during the stratified period (May–October) whereas the light availability was the limiting factor during the mixing period (November–April). The low light availability in the water column during the winter and early spring periods may be related to the attenuation of light from suspended particulate material and the self-shading effect (Kirk, 1983), since the ambient irradiance was considerably high even in the winter time in the study area.

The daily contribution of the various sources and sinks of nitrate is shown in Fig. 8. The phytoplanktonic uptake was considered as the only sink of nitrate. The sources that have been modeled were the inflow from the non-point terrestrial sources, from the atmosphere and the diffusion process from the sediment to the water column. It was predicted by the model that the contribution of terrestrial non-point sources was significant only in the winter period. The inflows in an event-based time scale from November to March, resulted to an increase of the nitrate concentration of up to 40–60% of the total stock at the spatial compartments mostly affected by the terrestrial sources. The contribution of the wet and dry deposition of nitrate from the atmosphere was approaching zero during the year, except for a number of rainfall events during winter and spring, when the daily inflows reached the level of 0.025 μM. The regeneration of nitrate at the sediment by benthic processes seems to be an important source of nitrate throughout the year. These mineralization processes at the sediment are mainly affected by temperature, that was high throughout the year in the study area, and the availability of labile organic compounds (Blackburn and Sorensen, 1988). The organic compounds that reach the sediment are expected to be of planktonic and terrestrial origin. The planktonic exudation and mortality products are labile compounds (Buffle, 1990), mainly proteins, hydrocarbons, aminoacids and lipids (Hellebust, 1974) whereas the terrestrial fluxes consist of plant by-products and sewerage, that are also considered as labile organic compounds (Buffle, 1990).

The daily contribution of the endogenous and exogenous sources and sinks of ammonium was also assessed by the model (Fig. 9). Phytoplanktonic and bacterial mortalities were considered as the only biological sources of ammonium. The phytoplanktonic and bacterial exudation and mortality processes contribute significantly to the stock of nitrogenous organic compounds (Buffle, 1990), that is easily mineralized to ammonium by the heterotrophic bacterial cells. It was predicted by the model that the above mentioned biological processes were a continuous significant source of ammonium for the water column throughout the year (Fig. 9a). Phytoplanktonic and bacterial growth were the only sinks for ammonium. The model predicted that the phytoplanktonic uptake was rather high during winter and summer (Fig. 9a). Phytoplankton preferentially uptake ammonium as a source of nitrogen instead of nitrate, throughout the annual cycle, and this preference is mainly affected by the relative concentrations of the two forms of inorganic nitrogen (Syrett, 1981). However, the increased concentrations of nitrate during the winter period, affected the phytoplankton feeding and the 'new primary production' approached locally the mean daily concentrations (0.1 μM) that correspond to the 'regenerated primary production'. The bacterial ammonium uptake was rather high from September to January and during summer (Fig. 9a), whereas, it was relatively low during early spring when the peak in bacterial biomass was observed. The bacterial cells uptake ammonium and organic nitrogen as sources of nitrogen for the synthesis of their cell proteins (Fenchel and Blackburn, 1979; Ducklow et al., 1989). The maximum in bacterial biomass does not coincide with the maximum bacterial uptake of ammonium, supporting the view that ammonium and dissolved organic nitrogenous compounds are both utilized as alternative sources of nitrogen throughout the year; and that there is no specific trend in the preferences of bacterial cells.

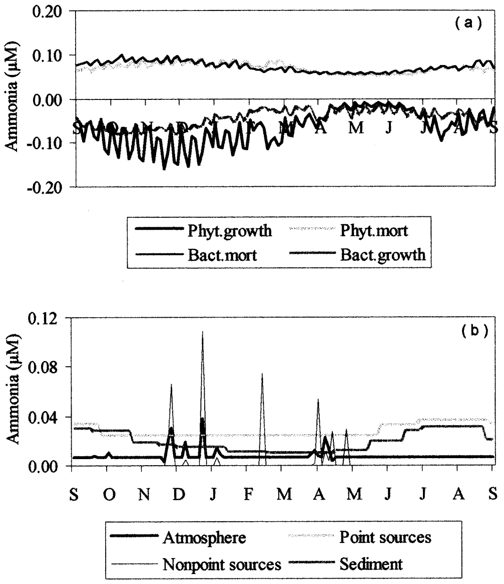

Fig. 9. Annual variability of the (a) biogenous and (b) exogenous sources and sinks of ammonia for the coastal marine ecosystem.

The annual variability of the exogenous sources of ammonium for the western spatial compartment of the marine ecosystem is presented in Fig. 9b. The contribution of the non-point sources is significant during rainfall events from November to May, being equal to that of the biological sources mentioned before. Another remarkable exogenous source of ammonium is the riverine input, that is higher in summer than in winter. Rivers end up into the water body under consideration mainly from the north and west and carry the sewerage of small towns and villages inhabited by 7000 people. The increase in the ammonium input during summer is up to 10% of the total stock at the most affected spatial compartments due to the corresponding increase in the human population by about 5000 people, since the coastal area is used as a tourist resort during summer. The diffusion process from the sediment is also a remarkable source of ammonium, especially in summer whereas the atmospheric wet and dry deposition is minimal.

The daily contribution of the various endogenous and exogenous sources and sinks of dissolved organic carbon can be shown in Fig. 10. The phytoplanktonic exudation seems to be the main source of dissolved organic carbon for the coastal ecosystem, especially during the phytoplanktonic blooms (Fig. 10a). The contribution of phytoplanktonic and bacterial mortalities is also remarkable throughout the year. The only sink for dissolved organic carbon is the bacterial uptake that is high during summer and autumn. The exogenous sources of dissolved organic carbon that have been modeled were the terrestrial input from point and non-point sources, the wet and dry deposition from the atmosphere and the diffusion process from the sediment (Fig. 10b). The contribution of the point sources is high from December to May, being up to 4 mg/m^3 whereas,

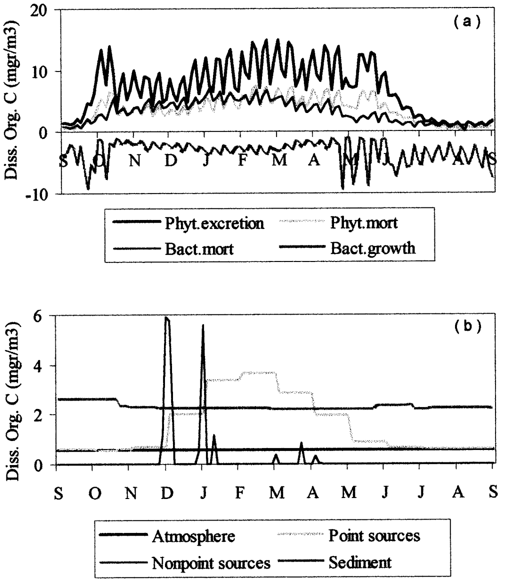

Fig. 10. Annual variability of the (a) biogenous and (b) exogenous sources and sinks of dissolved organic carbon for the coastal marine ecosystem.

the inflow of dissolved organic carbon from nonpoint sources was significant, up to 6 mg/m^3, during episodic rainfall events. The diffusion process from the sediment was also considered as a significant exogenous source of dissolved organic carbon, the contribution being 2–3 mg/m^3 throughout the year. The wet and dry deposition from the atmosphere was also assessed and it was predicted by the model that is less than 1 mg/m^3 during the year. The total contribution per day of the allochthonous sources of dissolved organic carbon is up to 10 mg/m^3 and it is less important quantitatively than that of the autochthonous sources. The importance of the autochthonous sources is further emphasized from the fact that the organic compounds of phytoplanktonic and bacterial origin are easily degradable from bacteria (Buffle, 1990) and constitute the major part of the labile fraction of dissolved organic carbon in the water column.

4.4. Future developments

The good fit of the model to the experimental data and the efficiency to quantify the dynamics of inorganic nitrogen-phytoplankton-bacteria-zooplankton and organic carbon relationships support the view that it can be proposed as a methodological tool for the assessment of the contribution of terrestrial sources to coastal marine eutrophication. Although the ecological structure of the model is highly aggregated, a significant increase in the number of biotic compartments is unlikely to improve our understanding of the system behavior with a view of interlinking terrestrial and marine processes. A possible improvement could be the incorporation into the model of the fine particulate matter resulting from soil erosion and sediment perturbation due to their ambiguous role in the water column. These soil particles provide a long-term source of nutrients to the primary producers and perform purification action by absorbing the dissolved-phase fraction (Sharpley and Menzel, 1987; Davidson, 1996).

The estimation of nitrogen fluxes from the terrestrial ecosystem and the sediment were based on empirical equations and this aspect should be a matter of concern on future developments. This model category, the so-called ‘black box’ models, reflects only what changes in the input will affect the output response whereas, it does not consider the mechanisms by which inputs are connected to states and how the states are connected to each other and to the output of the model. The disadvantages of this approach is that its application is limited to the ecosystem under consideration or at least to similar ecosystems, and that it cannot take into account changes in the system (Jorgensen, 1997). Further applicability of the model and improvement of its accuracy in the partitioning of the seawater nutrient stock will be obtained by developing ‘causal’ submodels, focused on (i) the description of internal mechanisms of various components (e.g. terrestrial ecosystem and sediment), and (ii) the representation of their continuous changes with time.

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