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Seasonal steady-state budgets of nutrients and stoichiometric calculations in an Eastern Mediterranean lagoon (Papagos Lagoon-Greece)

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Abstract

The Papagos Lagoon is an enclosed, small shallow water body in western Greece. The lagoon is naturally affected by eutrophication phenomena, but occasionally during the summer season, dystrophic crises occur, related to the decomposition of large beds of macroalgae. Physicochemical data collected monthly, from June 1998 to September 1999, were compiled and coupled with historical meteorological data, in order to construct seasonal water, salt and nutrients budgets using a single box-single layer LOICZ model. Nutrients and other hydrochemical parameters exhibit great spatial and temporal variations. The non-conservative dissolved inorganic phosphorus flux (Δ DIP) is always positive, thus indicating that the system acts as a net source of DIP for the adjacent coastal waters. Higher values were estimated during summer and autumn, probably due to organic matter mineralisation and release of DIP from surficial sediments in the reduced environment. In contrast to the Δ DIP, the non-conservative balance of dissolved inorganic nitrogen (Δ DIN) is negative for most of the year, except for the summer, indicating the dominance of DIN removal processes in the Papagos Lagoon. The *Ulva* growth and decomposition processes seem likely to be of essential importance for the evaluation of the non-conservative DIN fluxes. During the investigated period the amount of organic carbon respired and mineralized is greater than that produced by gross photosynthesis and the Papagos Lagoon is a net heterotrophic system. Losses of DIN via denitrification appear to dominate over its inputs through nitrogen fixation throughout the year.

Keywords: Nutrients; Non-conservative fluxes; Budgets; Coastal lagoon; Eastern Mediterranean.

Introduction

Despite the low coverage of ocean surface, coastal systems contribute to a significant portion (14%) of ocean production and play an important role in nutrient recycling and organic matter decomposition.

The functional coupling of coastal ecosystems and offshore waters may involve physical energy inputs, flows of dissolved nutrients and organic matter, net fluxes of living or dead particulate organic matter and suspended sediments (NIXON, 1981). Whether coastal systems supply carbon, nitrogen and

phosphorus to the coastal ocean remains debatable, largely because coastal systems' responses to changes of external forcing are extremely variable. Investigations of ecosystem processes and functions are relatively more effective in confined systems like coastal lagoons, as their boundary conditions can be more clearly defined.

Coastal lagoons are inshore shallow water bodies, partially isolated from the adjacent sea by a sedimentary barrier and consequently characterized by restricted water exchanges. Lagoon environments are highly dynamic environments, controlled by physical and continental influences. Due to their location between land and sea, most lagoons receive large amounts of organic and inorganic nutrients derived from urban, agricultural and industrial effluents. The nutrient inputs, in combination with shallow water depth, high incident light irradiance reaching the sediment surface, and turbulent mixing, lead to increased levels of both benthic and planktonic primary production. Eutrophication is a naturally occurring process in most lagoons, however eutrophication has dramatically increased over the last decades, due to human activity in the catchment areas. Coastal lagoons are vital spawning places for fish and shellfish and have been extensively exploited for aquaculture. Along the Mediterranean coast, more than half of the larger lagoons are used for extensive and semi-intensive aquaculture of both fish and shellfish (BARNES, 1995).

Characteristic features of these shallow ecosystems, depending on their hydrological and trophic status, are the frequent fluctuations of the environmental parameters on a daily and seasonal basis. The sharp variations of the physicochemical water properties in the lagoons are linked to the appearance of dystrophic events, mainly dur-

ing summer in temperate environments (e.g. PUGNETTI *et al.*, 1992; RINALDI *et al.*, 1992; CASTEL *et al.*, 1996; HEIJS *et al.*, 2000). The decomposition of accumulated macroalgal biomass is considered to be one of the most important factors in the occurrence of these summer dystrophic crises (e.g. VIAROLI *et al.*, 1996; DE WIT *et al.*, 2001), causing severe changes in the abundance and distribution of organisms (e.g. BACHELET *et al.*, 2000; VIAROLI *et al.*, 2008 and references therein).

During the last 20 years, the Papas Lagoon, a shallow semi-enclosed water body in western Greece, has been subject to frequent dystrophic crises followed by mass mortalities of fish and benthic fauna (REIZOPOULOU & NICOLAIDOU, 2004). Until the dystrophic event of summer 1997, the Papas Lagoon system was poorly investigated. Aiming to assess the current structure and functioning of the system, as well as to provide a basis for the development of an integrated management policy, a multidisciplinary study was carried out (NCMR, 2000) in 1998-1999. In the framework of this study, a number of hydrological, chemical and biological variables were sampled on a monthly basis (salinity, temperature, oxygen, nutrients, phytoplankton biomass and composition, zooplankton abundance and composition, zoobenthos abundance and community structure).

In the present work, physicochemical data collected from June 1998 to September 1999, combined with historical meteorological data, are used to construct seasonal water, salt and nutrients budgets according to the LOICZ biogeochemical modelling guidelines (GORDON *et al.*, 1996; <http://nest.su.se/mnode/>). This study also aims to evaluate the importance of the different nutrient inputs to the lagoon in re-

lation to their possible internal sources and sinks. Furthermore, the results of this work allow for comparison with similar budget calculations from different coastal areas obtained using the LOICZ approach, thereby enhancing knowledge concerning the role that the coastal zone plays in global biogeochemical cycles. Quantification of nutrient budgets and biogeochemical processes based on the LOICZ guidelines has been conducted in several European (<http://nest.su.se/mnode/Europe/EUROPE.H TM>) and Mediterranean coastal ecosystems (DUPRA *et al.*, 2001; GIORDANI *et al.*, 2005; KAVAKLI *et al.*, 2006; SYLAIOS, 2003; SYLAIOS *et al.*, 2005; SYLAIOS & TSIHRINTZIS, 2009), however this work is the first attempt to demonstrate this topic in a Greek lagoon.

Materials and methods

Study area

The Papas (Araxos) Lagoon is a semi-enclosed water body located on the north-western coast of the Peloponnese, in western Greece (Fig. 1). The lagoon is shallow (mean depth $\sim 1.2\text{m}$) and is connected to the neighbouring Ionian Sea via three narrow mouths; it is supplied with freshwater by a small draining stream discharging in the southeastern part only during winter. The total area of the lagoon is about $3.9 \times 10^6 \text{ m}^2$, with a volume of approximately $4.7 \times 10^6 \text{ m}^3$. The lagoon is used for the semi-intensive, and recently extensive, culture of mullet (*Mugil cephalus*) and sea bream (*Sparus aurata*). Smaller amounts of other commercial species like sea bass (*Dicentrarchus*

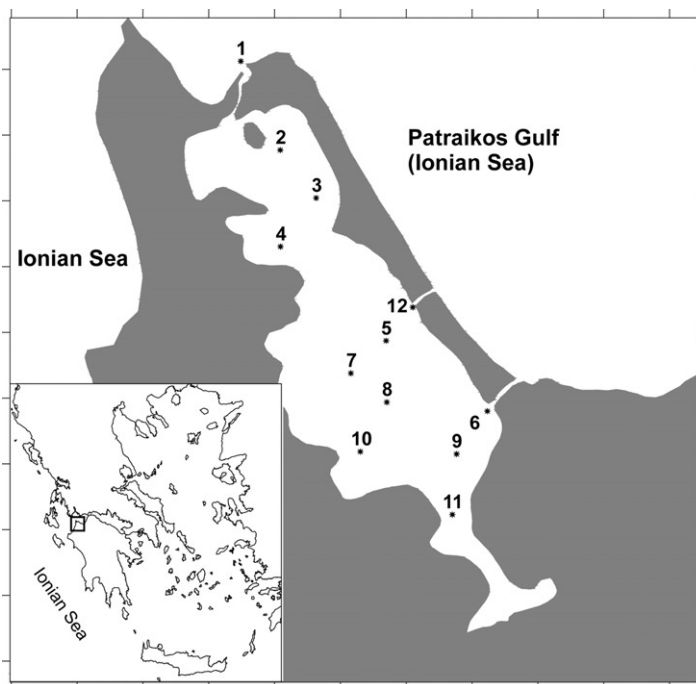


Fig. 1: Location of the Papas Lagoon and sampling sites.

labrax), eel (*Anguilla anguilla*) and the bivalve (*Tapes semidecussatus*) are also caught. During the last 20 years, recurrent dystrophic crises that cause extensive fish and benthic invertebrate mortalities and great damage to the local economy, have occurred in the lagoon during the warm summer months. In general, the crises begin in spring in the SE shallow part of the Papas Lagoon, which is in the vicinity of cultivated lands and is where the nutrient loadings are increased, with the blooming of the green macroalga *Ulva rigida*. In the summer, the algal biomass is degraded by aerobic bacteria; the oxygen concentration then decreases, leading to anoxia and the predominance of anaerobic processes.

Sampling and analytical methods

From June 1998 to September 1999 water samples were mostly collected monthly at 11 stations in the lagoon and one station in the adjacent coastal sea (Fig. 1). Water samples were collected from the upper and bottom layers using a NIO sampling bottle. Regarding the dissolved oxygen determination, samples taken from the NIO bottle were analysed immediately after collection with the Winkler method as modified by CARPENTER (1965). Samples for the determination of nutrients were collected in 100 ml polyethylene bottles, poisoned with HgCl₂, constantly maintained under deep freeze (-20° C), until further analysis in the laboratory by a Bran-Luebbe Autoanalyser II. The methods described by MULLIN & RILEY (1955) for silicate, BENDSCHNEIDER & ROBINSON (1952) and STICKLAND & PARSONS (1968) for nitrite and nitrate were employed. Phosphate and ammonium were measured by a Perkin Elmer Lambda 2S UV/VIS Spectrometer, according to the methods of MURPHY & RILEY (1962) and

KOROLEFF (1969) respectively. Salinity and temperature were recorded *in situ* using a portable thermosalinometer. In addition, the salinity measurements underwent quality control based on Autosal estimates on selected water samples.

Biogeochemical model

The biogeochemical fluxes and metabolism of nutrients in the lagoon were calculated using the LOICZ biogeochemical budget model. Details of the modelling approach can be found in GORDON *et al.* (1996) and at LOICZ Biogeochemical Modelling Node (<http://nest.su.se/mnnode/>). In brief, this biogeochemical budget model is a steady-state box model from which non-conservative nutrient and carbon budgets can be constructed from non-conservative distributions of nutrients and water budgets, which in turn are constrained by the salt balance under a steady-state assumption. The equations which describe the steady state water and salt balance for the Papas Lagoon were then formulated (Eqs. 1-2) and solved, in order to estimate the unknown water flows:

$$V_P + V_E + V_Q + V_R = 0$$

(water mass balance) (1)

$$V_P S_P + V_E S_E + V_R S_R + V_X (S_{ocn} - S_{sys}) = 0$$

(salt mass balance) (2)

where V_P and V_E are the precipitation and the evaporation, V_Q is the freshwater surface runoff and V_R is denoted as residual flow and is the amount of freshwater needed to keep the volume constant.

Precipitation data, together with other climatological data, were obtained from the Hellenic National Meteorological Service (Araxos airport meteorological station) for the period 1955-1997 and were then used

in order to calculate the evaporation losses according to the Hargreaves equation (HARGREAVES, 1975). The surface runoff was calculated by the difference between precipitation and evaporation over the entire drainage basin (about $30.7 \times 10^6 \text{ m}^2$; P. Drakopoulou personal communication) using an empirical formula developed by SHREIBER (1904). Taking salinity as nil for freshwater, the salt mass balance in the lagoon can be derived:

$$V_R S_R + V_X(S_{ocn} - S_{syst}) = 0 \quad (3),$$

where the term V_X is described as exchange or mixing flow that is necessary to match the salt exported through the residual flow: $S_R = (S_{syst} + S_{ocn})/2$ (GORDON *et al.*, 1996) and S_{syst} and S_{ocn} are the mean salinities of the lagoon and the adjacent sea. The residence time of the water in the lagoon or exchange time (τ), which is defined as the average length of time that water stays in the system (<http://nest.su.se/mnode/Methods/>), depends on both residual and exchange flows and is estimated from the ratio

$$V_{syst}/(V_X + |V_R|) \quad (4),$$

where V_{syst} is the volume of the lagoon.

In the case of single box-single layer systems such as the Papas Lagoon, the absolute value of the residual flow is equal to the net freshwater inflow volume (<http://nest.su.se/mnode/Methods/>). It should also be noted that multiple names are given to time scales with respect to mixing and flushing of natural basins in the literature, such as: ‘residence time’, ‘flushing time’, ‘transit time’, ‘turn-over time’ and ‘age’ (MONSEN *et al.*, 2002). Quite often, the same name is used for time scales which are essentially different, whereas in other cases the same time scale is given more than

one title. In this study, the definitions given by the LOICZ modelling guidelines are followed in order to allow ease of comparison with similar global systems.

Dissolved nutrient budgets are estimated from water transports and the appropriate nutrient concentrations in each box model compartment. In steady state, the non-conservative dissolved inorganic phosphorus flux (ΔDIP) can be derived from the following equation:

$$\Delta DIP = -(\Sigma DIP_{out} - \Sigma DIP_{in}) = -[V_R DIP_R + V_X DIP_X + V_Q DIP_Q + V_P DIP_P] \quad (5),$$

where $DIP_R = (DIP_{syst} + DIP_{ocn})/2$, $DIP_X = DIP_{ocn} - DIP_{syst}$ and DIP_{syst} and DIP_{ocn} are the mean DIP concentrations of the lagoon and the adjacent sea. The term ΔDIP represents the change in the concentration of DIP, due to biogeochemical processes that take place within the system and is positive in case of DIP addition and negative in case of DIP removal. DIN (sum of ammonium, nitrite and nitrate) notations are similar to those of DIP in budget derivation.

Although transport via the atmosphere is recognised as an important route through which nutrients and particles are delivered to the sea surface, unfortunately there are no available data on atmospheric inputs for the study area. The atmospheric inputs of inorganic nitrogen and phosphorus were calculated using the estimated concentrations ($DIP_p = 0.56 \text{ mmol/m}^3$; $DIN_p = 48.47 \text{ mmol/m}^3$) for a station close to the Israeli coast, away from urban activities and adjacent to agricultural areas (HERUT *et al.*, 1999). The dissolved inorganic phosphorus and nitrogen concentrations of the waters originating from the drainage basin ($DIN_Q = 38.32 \text{ mmol/m}^3$, $DIP_Q = 0.40 \text{ mmol/m}^3$) are based on the mean concentrations recorded in a nearby river assum-

ing similar soil quality and agricultural activities in both catchment areas.

Without further interpretation, the nutrient budgets do not provide information on the processes which account for the summed sources minus sinks. The net ecosystem metabolism (NEM) is a measure of the imbalance between the production (p) and respiration (r) of organic matter, providing a rough estimate of the trophic status of the system, while it is calculated as $(p-r) = -\Delta\text{DIP} (C/P)_{\text{part}}$ (GORDON *et al.*, 1996). The C/P ratio of the particulate organic matter in the Papas Lagoon was not determined and, thus, the calculations are based on the assumption that the decomposed organic matter is dominated by plankton having a Redfield composition (C:N:P = 106:16:1).

Nitrogen metabolism in the lagoon is expressed as the difference between nitrogen fixation and denitrification and is calculated as $(nfix-denit) = \Delta\text{DIN}_{\text{obs}} - \Delta\text{DIN}_{\text{exp}}$, where $\Delta\text{DIN}_{\text{obs}}$ is the observed non-conservative flux of DIN and $\Delta\text{DIN}_{\text{exp}}$ is the flux that would be expected if the only flux pathway was the production or consumption of organic matter with a Redfield N/P ratio and thus $(nfix-denit) = \Delta\text{DIN}_{\text{obs}} - (N/P)_{\text{part}} \Delta\text{DIP}$ (GORDON *et al.*, 1996).

Recently, GIORDANI *et al.* (2008) developed a new version of the LOICZ biogeochemical model that also takes into account the sediment component, based on simulations of the 0D biogeochemical model of ZALDIVAR *et al.* (2003). In the Papas Lagoon, the sampling strategy and the available datasets (e.g. oxygen and nutrients benthic fluxes were never measured) excluded the application of such an approach. Nutrient budgets and stoichiometric calculations were completed on a seasonal basis before their integration as annual values.

Results and Discussion

Water characteristics

The Papas Lagoon is very shallow and the physicochemical properties exhibit significant variation in time (Fig. 2). All measurements during each sampling period are averaged and the range bars (standard deviation) are used to indicate the spatial variability within the lagoon. Salinity exhibits wide variation between seasons, ranging from 22.7 psu (St. 11 in January 1999) to 43.0 psu (St. 5 in August 1998), coinciding with the precipitation and surface runoff fluctuations. Overall, low salinity values are recorded during the high rainfall period (late autumn-winter-early spring). Water temperature responds rapidly to the seasonal changes of atmospheric temperature and follows almost the same seasonal pattern as salinity; it presents minimum values during winter (9.7° C in January 1999) and maximum values during summer (31.8° C in August 1998).

Dissolved oxygen concentrations in the lagoon are controlled by air/sea gas exchanges, water temperature and salinity, as well as by biogeochemical processes, thus they show strong seasonal and spatial variations. The sharp decrease in oxygen concentrations observed in the summer (Fig. 2; July 1998, July 1999) indicates the large distribution of hypoxic conditions in the lagoon. Dystrophic conditions often occur in Mediterranean lagoons during summer, when large quantities of decomposed algal biomass coincide with high temperatures, scanty water circulation and reduced exchange with marine waters due to stable atmospheric conditions and the blockage of the water movements from large beds of macroalgae (PUGNETTI *et al.*, 1992; RINALDI *et al.*, 1992; CASTEL *et al.*, 1996; HEIJS *et al.*, 2000; ZALDIVAR *et al.*, 2008).

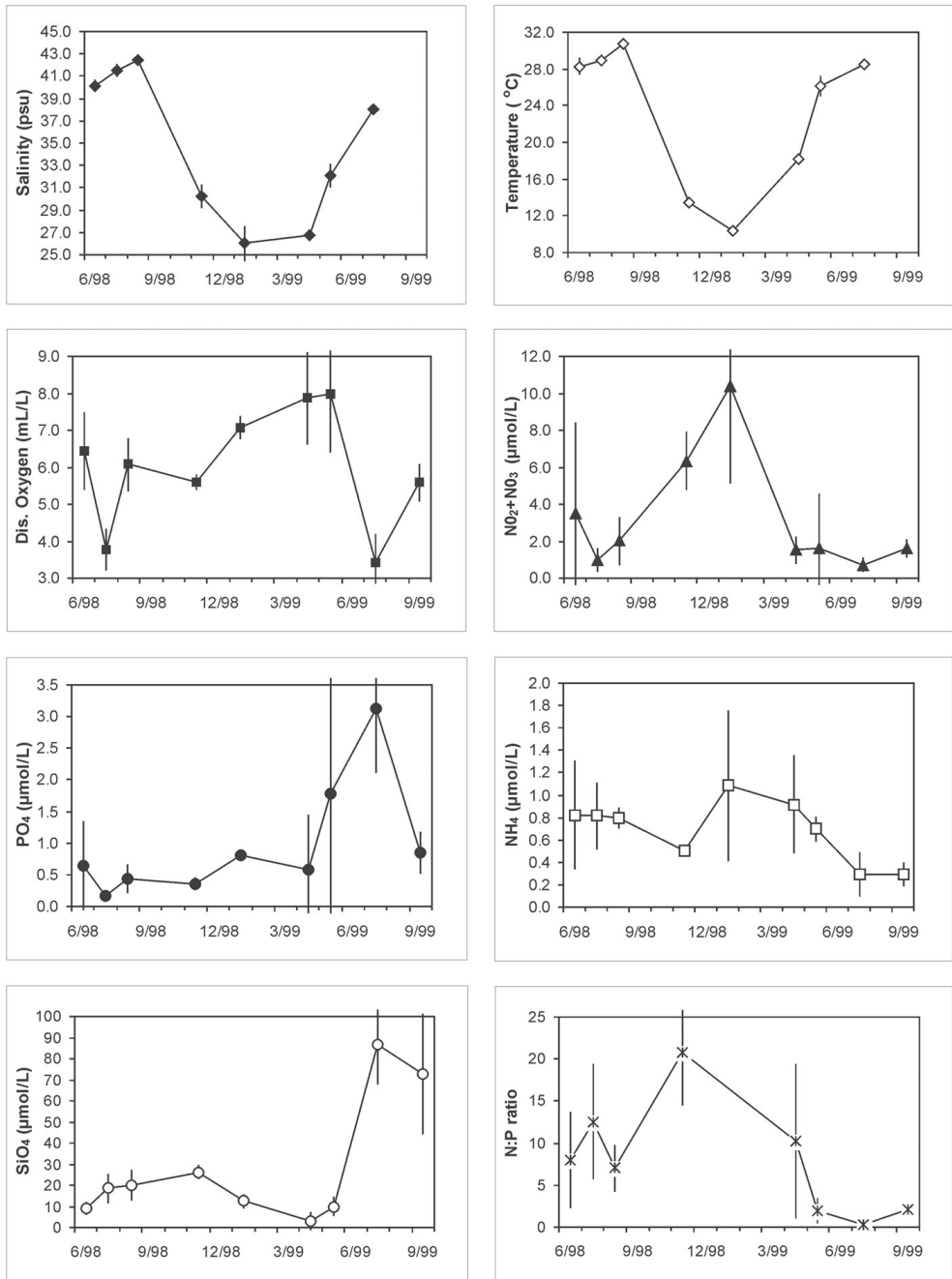


Fig. 2: Seasonal variations of averaged salinity, temperature, dissolved oxygen, nitrite + nitrate, phosphate, ammonium, silicate and N:P ratio in Papas Lagoon for the period from June 1998 to September 1999. Range bars are standard deviations.

During July 1998, an almost homogeneous bed of the green macroalga *Ulva rigida* accumulated in the sheltered, inner part of the Papas Lagoon and spread as far as the centre of the lagoon; the accumulated macroalgal biomass decomposed causing a drastic decrease in the dissolved oxygen concentrations (<2.5 mL/L), mainly in this shallow area (Fig. 3).

Regarding the trophic conditions of the lagoon, nutrients covered a wide range of concentrations seasonally and spatially. The highest nutrient concentrations were mainly observed at the innermost sampling sites and the lowest ones at the sites located closer to the communication channels with the sea. Among dissolved inorganic nitrogen (DIN) species, nitrite + nitrate concentrations were higher than those

of ammonium for all sampling periods, and ranged between 0.20 (St.11-July 1998) and 18.1 $\mu\text{mol/L}$ (St.11-January 1999). Moreover, ammonium values exhibited the smallest oscillations between stations and seasons and varied between 0.10 (St. 4-July 1999) and 2.1 $\mu\text{mol/L}$ (St. 9-January 1999) (Fig. 2). The observed increase of nitrogen species during winter is probably caused by the leaching of nitrogen-based fertilizers used in the surrounding cultivated lands and the scarce activity of the biological component.

Phosphate and silicate concentrations exhibited an reverse seasonal trend in relation to the nitrite + nitrate values; this kind of fluctuation leads to a consequent seasonal variation in the N:P ratio in the lagoon waters, where the lowest values oc-

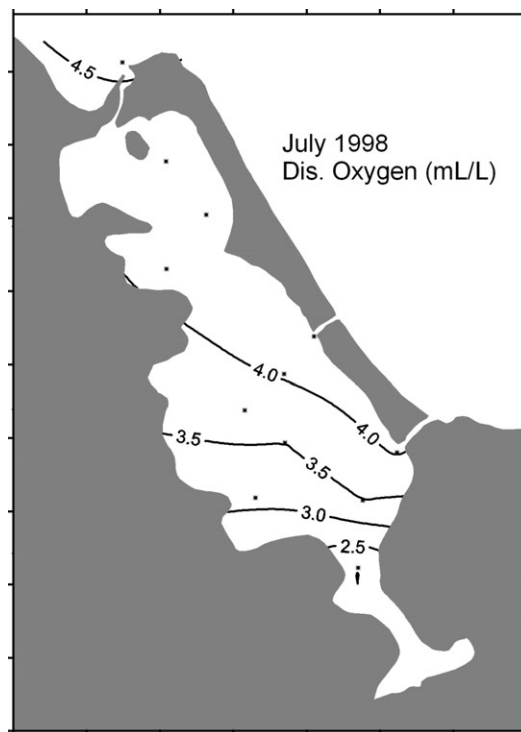


Fig. 3: Distribution of dissolved oxygen during July 1998 in Papas Lagoon.

curred in the summer of 1999, while the highest in winter-early spring (Fig. 2). Phosphate and silicate concentrations reached extremely high values during summer-early autumn 1999, when the maximum concentrations of both parameters were recorded (4.44 $\mu\text{mol/L}$, St. 11-July 1999 for phosphate; 107.0 $\mu\text{mol/L}$ St. 7-September 1999 for silicate). It is suggested that sediment regeneration was the dominant process supplying nutrients to the water column of the shallow Papas Lagoon during this period. Unlike nitrogen and phosphorus, silicon regeneration is not caused by organic matter degradation, but rather by the dissolution of opaline SiO_2 . Dead diatoms and empty siliceous frustules from diatoms and other phytoplankton and protozoan species sink to the bottom without significant dissolution, stripping silicon from the water column. Silicate originating from the slow dissolution of the accumulated siliceous debris in the sea floor is released at high rates during summer, due to the increased temperature (KAMATANI, 1982; DEGOBBIS, 1990; DEGOBBIS & GILMARTIN, 1990; BERTUZZI *et al.*, 1997). However, the relative abundance of diatoms within the total phytoplanktonic community during the preceding samplings (PAGOU & ASSIMAKOPOULOU, 2000) cannot explain the elevated silicate concentrations that were observed during summer-early autumn 1999. It is quite possible that a diatom bloom had already occurred but unfortunately was not recorded due to the monthly sampling.

The large spatial variability of the N:P ratio (high range bars; Fig. 2) is related to the particular characteristics of the different stations sampled within the lagoon e.g. proximity to the sea or the land, depth, occurrence of macroalgae, etc. The molar N:P ratio, an important index for identify-

ing the factor limiting algal growth, varied between 0.34 in July 1999 and 20.8 in November 1998. It appears lower than the optimum ratio for macrophytes (30:1; ATKINSON & SMITH, 1983) and in most cases even lower than the phytoplankton ratio (16:1; REDFIELD *et al.*, 1963), thus revealing a nitrogen deficiency relative to phosphorus occurrence in Papas Lagoon. RINALDI *et al.* (1992) assume that, in lagoon ecosystems, the algal biomass is limited by nitrogen when the N:P weight ratio is lower than 5 and by phosphate for N:P values higher than 10, while the intermediary values of the ratio indicate that both nutrients regulate algal growth. Therefore, in the Papas Lagoon, it is evident that nitrogen is the limiting factor during June and August 1998, May, July and September 1999 (Fig. 2), while during July 1998 and April 1999 the system is characterized by alternations between normal and nitrogen limitation conditions. November 1998 is the only month during which phosphorus seems to be deficient and the lagoon fluctuates between normal and phosphorus limitation conditions.

Water and salt budget

The water budget is critical in deriving the budgets of the non-conservative parameters in the lagoon. A significant difference in salinity between the lagoon and the adjacent oceanic system is required in order to reliably determine the water and salt budgets. Based on the salt balance in the box model, the freshwater inputs, the residual and the mixing flows were estimated according to Equations 1 and 2, and the results are summarized in Table 1. In addition, the annual balance model was obtained by considering the average of the input values of the seasonal models and is illustrated in Figure 4. Annually, the difference be-

tween freshwater inflows ($26.9 \times 10^3 \text{ m}^3 \text{ d}^{-1}$) and evaporative losses ($12.3 \times 10^3 \text{ m}^3 \text{ d}^{-1}$) is balanced by the residual flow ($14.6 \times 10^3 \text{ m}^3 \text{ d}^{-1}$). The required mixing volume to replace the salt loss through the residual flow is about four times the total freshwater inputs ($117 \times 10^3 \text{ m}^3 \text{ d}^{-1}$).

It is interesting to note that a net export of water from the lagoon towards the sea, indicated by the negative residual flow (V_R), was observed in autumn, winter and spring. During the summer months, a net import of water from the sea to the lagoon was observed (V_R is positive). The highest negative residual flow values were observed in winter and autumn during the high rainfall period. Over the summer months, the total freshwater inputs in the lagoon are lower than evaporative losses and a strong net inflow of seawater from the adjacent sea is required to conserve the water volume of the system. Despite the positive residual flow, the salinity values recorded in the lagoon were much higher than those of the sea and allow the reliable estimation of the mixing volume (V_X).

Assuming constant lagoon volume, the exchange time (τ) of the lagoon water was determined by the net freshwater input and the exchange flow (Eq. 4). Expected water exchange time was short during winter

and autumn, and more specifically, 21.4 and 28 days respectively. Surprisingly enough, water residence time was also short during summer (22 days) and much longer (more than 150 days) in spring. Although the lagoon salinity remains lower than the sea salinity, thus reflecting the increased freshwater inflow of the preceding winter, the reduced precipitation and surface runoff obtained during spring induced low residual and exchange flows, consequently leading to the elongation of the water's residence time in the lagoon. It should also be mentioned that the springtime salt and water budget was calculated without taking into account the precipitation, evaporation and surface runoff flows of April because their inclusion resulted in unreliable mixing volume estimates. On the other hand, in summer time the more stable meteorological conditions generate more constant monthly V_R estimates which contribute to the limited variability of V_X . The lower water exchange time estimated for summer with respect to the spring value is due to the higher evaporation rates and the high mixing volume required to compensate for evaporative losses. The annual average time that the water remains in the lagoon is estimated to be around 36 days (Table 1; Fig. 4).

Table 1
Seasonal variations of salinity, water flows and residence time in the Papas lagoon.
Abbreviations are explained in the text.

Season	S_{sys}	S_{ocn}	V_Q	V_P	V_E	V_R	V_X	τ
			(x10 ³ m ³ d ⁻¹)					(days)
winter	26.0	35	42.2	12.8	-5.0	-50.0	170	21.4
spring	29.5	36	9.14	6.9	-11	-5.0	25	157
summer	41.4	37	0	0.76	-22.4	21.6	192	22.0
autumn	30.2	36	25.3	10.5	-10.7	-25.1	143	28.0
<i>mean annual</i>	<i>31.8</i>	<i>36</i>	<i>19.2</i>	<i>7.7</i>	<i>-12.3</i>	<i>-14.6</i>	<i>117</i>	<i>35.7</i>

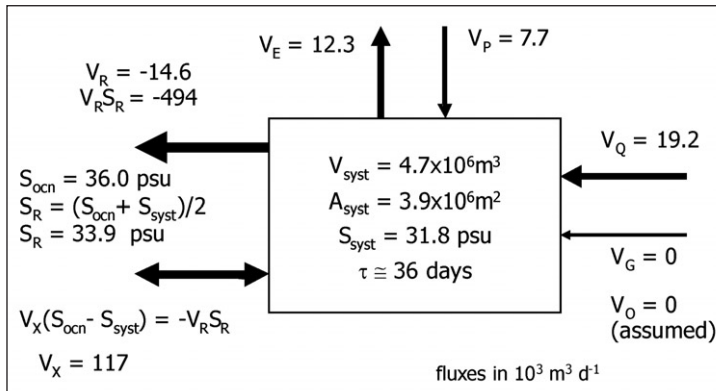


Fig. 4: Annual water and salt budget for Papas Lagoon. Abbreviated notations are explained in the text.

3.3. Budgets of non-conservative materials

Physical and biogeochemical processes are responsible for the non-conservative fluxes of DIP and DIN in the lagoon. As illustrated in Equation 5, the non-conservative nutrient flux is derived from the difference between total inputs and total outputs for each sampling event and is an indication of an existing source (inputs < outputs) or sink (inputs > outputs) within the ecosystem. This, for example, may simply mean that when the sum of inputs is algebraically smaller than the sum of outputs then some internal process other than hydrography is controlling the matter fluxes and introduces the material of interest into the system, which consequently acts as source for the adjacent marine ecosystem. The obtained DIP and DIN non-conservative fluxes are summarized in Tables 2 and 3, while Figures 5 and 6 respectively, illustrate the annual DIP and DIN budgets. The annual non-conservative fluxes of DIP and DIN were calculated by applying the average DIP and DIN input values of the seasonal models to the previously estimated annual water flows.

During winter and autumn, the DIP and DIN fluxes originating from the drainage

basin dominate the total nutrient inputs, coupled with the higher freshwater input through the stream in the southeastern part. During spring, the nutrient fluxes imported into the Papas Lagoon through atmospheric precipitation appear to be equally important to the nutrients from the drainage basin. However, during the dry season, minimal nutrient inputs in the lagoon occur only through the atmospheric pathway.

It is also worth noting that during the entire study period, the mixing volume (V_x) removes nutrients from the system, as a result of the existing differences in the nutrient concentrations between the lagoon and the adjacent Ionian Sea. In addition, the largest values of the system ΔDIP and ΔDIN during summer result primarily from a large output caused by high mixing flux.

For the duration of the study, ΔDIP is always positive, thus indicating that the system acts as a net source of DIP at a yearly rate of about $6.0 \text{ mmol m}^{-2} \text{ y}^{-1}$. Higher values were estimated during summer and autumn (6.2 and $6.8 \text{ mmol m}^{-2} \text{ y}^{-1}$ respectively) probably due to organic matter mineralisation and release of DIP from surficial sediments in the reduced environment. The release of nutrients from the sediments to

Table 2
Seasonal variations of concentrations, fluxes and non-conservative budget of DIP
in the Papas Lagoon. Abbreviations are explained in the text.

			'freshwater'	Atmospheric	Residual	Mixing	DIP budget	
Season	DIP_{sys}	DIP_{ocn}	$V_Q DIP_Q$	$V_P DIP_P$	$V_R DIP_R$	$V_X DIP_X$	ΔDIP	
	mmol m ⁻³		mol d ⁻¹	mol d ⁻¹	mol d ⁻¹	mol d ⁻¹	mol d ⁻¹	mmol m ⁻² d ⁻¹
winter	0.40	0.04	16.9	7.1	-11	-61.1	48.1	0.012
spring	1.18	0.04	3.7	3.9	-0.3	-28.4	21.2	0.005
summer	0.41	0.04	0	0.4	+4.9	-72	66.7	0.017
autumn	0.60	0.04	10.1	5.9	-8.0	-80.7	72.7	0.019
<i>mean annual</i>	<i>0.65</i>	<i>0.04</i>	<i>7.7</i>	<i>4.3</i>	<i>-5.0</i>	<i>-71.3</i>	<i>64.4</i>	<i>0.017</i>

Table 3
Seasonal variations of concentrations, fluxes and non-conservative budget of DIN
in the Papas Lagoon. Abbreviations are explained in the text.

			'freshwater'	Atmospheric	Residual	Mixing	DIN budget	
Season	DIN_{sys}	DIN_{ocn}	$V_Q DIN_Q$	$V_P DIN_P$	$V_R DIN_R$	$V_X DIN_X$	ΔDIN	
	mmol m ⁻³		mol d ⁻¹	mol d ⁻¹	mol d ⁻¹	mol d ⁻¹	mol d ⁻¹	mmol m ⁻² d ⁻¹
winter	11.46	1.50	1617	618	-324	-1690	-222	-0.06
spring	2.39	1.50	350.2	334.4	-5.0	-22.2	-658	-0.17
summer	2.98	1.50	0	36.8	48.1	-283.9	199	0.05
autumn	4.37	1.50	968	508	-73.5	-411.6	-991	-0.25
<i>mean annual</i>	<i>5.3</i>	<i>1.50</i>	<i>734</i>	<i>374.2</i>	<i>-49.6</i>	<i>-444.4</i>	<i>-614</i>	<i>-0.16</i>

the overlying waters is regulated by different processes, such as molecular diffusion, bioturbation/bioirrigation, and resuspension caused by waves and currents. In September 1999, significantly elevated concentrations of organic carbon, nitrogen and phosphorus were found in the surface sediments of the lagoon. Under the low oxygen conditions which usually prevail in the bottom waters of the lagoon, the surface sediments could act as a very important source of dissolved nutrients (KABERI *et al.*, 2005). INGALL & JAHNKE (1997)

stated that benthic fluxes of phosphate are much higher in sediments overlaid by oxygen-depleted waters, due to the release of the associated phosphate with reducible iron oxide phases. The results of experiments conducted in benthic chambers for the study of the impact of macrophyte communities on the benthic fluxes of oxygen, sulphide and nutrients in shallow eutrophic environments showed that the decay of *Ulva* thalli strongly stimulated the fluxes of phosphorus from the anoxic sediment surface to the water column (VIAROLI *et al.*,

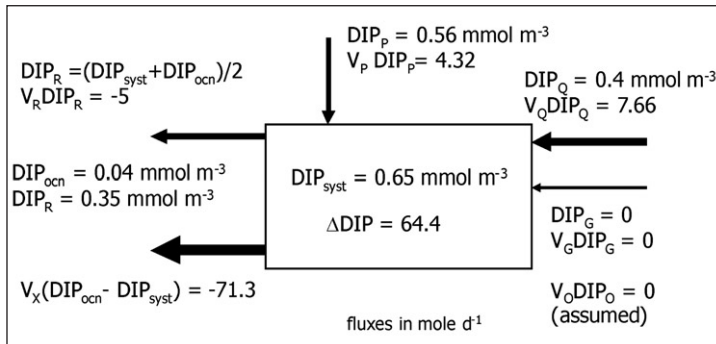


Fig. 5: Annual DIP budget for Papas Lagoon. Abbreviated notations are explained in the text.

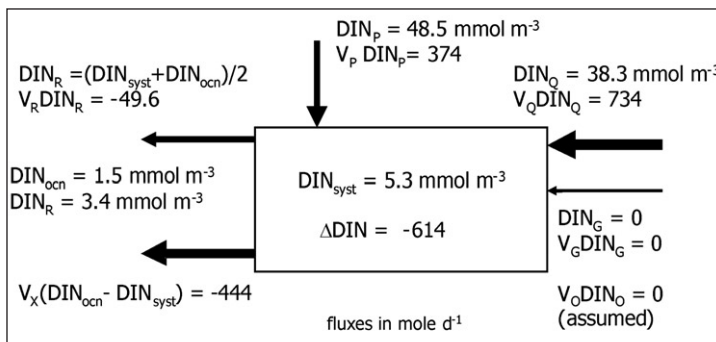


Fig. 6: Annual DIN budget for Papas Lagoon. Abbreviated notations are explained in the text.

1996). In addition, recent field and laboratory experiments have shown that under anoxic conditions, the build-up of sulphide by the bacterial sulphate reduction induces enhanced release of phosphate from coastal lagoon sediments. The interactions of sedimentary iron and sulphur cycles have implications for phosphorus cycling and its availability to macroalgae (HEIJS *et al.*, 2000; AZZONI *et al.*, 2005). Evidence to show that the sulphide metabolism is critical for the release of non-iron-bound phosphate (organic and/or Ca-bound phosphate) was also obtained however, the responsible mechanism has not yet been elucidated (HEIJS *et al.*, 2000).

In contrast to the non-conservative DIP balance, ΔDIN is negative during most of the year ($-92.8 - -20.8 \text{ mmol m}^{-2} \text{ y}^{-1}$), except in summer ($+18.6 \text{ mmol m}^{-2} \text{ y}^{-1}$). The negative annual ΔDIN ($-57.5 \text{ mmol m}^{-2} \text{ y}^{-1}$) shows the dominance of DIN removal processes (assimilation) and implies that the lagoon is a net sink for DIN during the study period. It seems likely that in the Papas Lagoon, the *Ulva* growth and decomposition processes are of essential importance for the evaluation of the non-conservative DIN fluxes. Fast growing macroalgae such as *Ulva* play a central role in controlling the nitrogen cycle in coastal lagoons; in particular, they assimilate and store ni-

trogen in excess of their growth requirements. During the active growth phase, *Ulva* out-competes the phytoplankton for available nitrogen whilst during the decomposition phase nitrogen regeneration is slow resulting in low efflux of dissolved inorganic nitrogen to the overlying water column. Experimental results have shown that nitrogen release from decomposing *Ulva* was slow and that after two months, when about 80% of the biomass was decomposed, the regeneration of nitrogen did not exceed 50% of the initial nitrogen content (PUGNETTI *et al.*, 1992), whereas a recent controlled laboratory experiment, lasting for 31 days, revealed that only 4% of the N contained in the added *Ulva lactuca* thalli material effluxed to the overlying water (LOMSTEIN *et al.*, 2006). This slow release of dissolved inorganic nitrogen to the overlying water suggests prolonged nitrogen retention in the sediment during winter; the nitrogen is then released during the following spring when macroalgal growth is again initiated. It seems quite paradoxical that nitrogen is the growth limiting nutrient in lagoonal systems which annually receive substantial nitrogen inputs from anthropogenic sources, but the major part of it is sequestered in *Ulva* thalli and is therefore unavailable (HERBERT, 1999).

It is reasonable to ask what would be the potential effect of the calculated fluxes of nutrients in the oligotrophic and phosphorus deficient eastern Mediterranean (KROM *et al.*, 1991). Comparing the amounts of phosphorus and nitrogen transported annually out of and towards the lagoon respectively (728 kg P/y and 3138 kg N/y), to the total P and N pools in the eastern Mediterranean (12606x10⁶ tons P and 119715x10⁶ tons N from BETHOUX *et al.*, 1992, 1998), it seems unlikely that these would alter the nutrient regime of the basin. Although large-

scale effects related to the Δ DIP and Δ DIN fluxes are not justified, the possibility of impairing the immediate marine environment by changing the trophic status cannot be overlooked. Since Δ DIP and Δ DIN fluxes have opposite signs, the continuous addition of P, accompanied by the concurrent removal of N, could lead to unbalanced conditions in relation to their optimum and decrease the N:P ratio of the P-deficient neighbouring Ionian Sea. In a recent experiment of P-addition to surface waters of the ultra-oligotrophic, phosphorus-starved eastern Mediterranean, unexpected ecosystem responses were revealed. The system exhibited a decline in chlorophyll and an increase in bacterial production and copepod egg abundance. Although nitrogen and phosphorus co-limitation hindered phytoplankton growth, phosphorus was transferred through the microbial food web to copepods, thus providing an indication of nutrient transfer to higher trophic levels (THINGSTAD *et al.*, 2005). The results of this experiment imply that the risk of noticeable and adverse effects induced by the Δ DIP and Δ DIN fluxes in the Ionian ecosystem adjacent to the Papas Lagoon is not obvious. Further research is needed to investigate the fate of the Δ DIP and Δ DIN fluxes and assess their role in controlling the trophic status and functioning of the nearby Ionian ecosystem.

Stoichiometric linkage

During the investigated period, the net ecosystem metabolism ($NEM = p-r$) is negative (Table 4) indicating that the amount of carbon respired and decayed is greater than the amount of organic carbon produced by gross photosynthesis. The seasonal variation of NEM is not remarkable, ranging from -0.21 to -0.72 molC m⁻² y⁻¹. However, higher mineralisation rates are estimated

Table 4
Stoichiometric calculations in the Papas lagoon.

Season	(<i>p-r</i>) molC d ⁻¹	(<i>p-r</i>) mmolC m ⁻² d ⁻¹	(<i>nfix-denit</i>) molN d ⁻¹	(<i>nfix-denit</i>) mmolN m ⁻² d ⁻¹
winter	-5090	-1.31	-991	-0.25
spring	-2250	-0.58	-997	-0.26
summer	-7070	-1.81	-868	-0.22
autumn	-7710	-1.98	-2150	-0.55
<i>mean annual</i>	-6825	-1.75	-1644	-0.42

during summer and autumn, probably in relation to the decomposition of the large amounts of algal biomass (*Ulva rigida*), while lower respiration rates are recorded in springtime, a period of vigorous algal growth. Overall, on an annual basis, the negative value of net ecosystem metabolism, -0.64 molC m⁻² y⁻¹, indicates that organic matter oxidation processes predominate and the Papas Lagoon system is a net producer of CO₂. The lagoon is considered to be a slightly net heterotrophic system, active in breaking down the organic matter produced *in situ*, as well as that which is externally imported. However, in coastal lagoons the macroalgal *U. rigida* system is usually characterized by extreme fluctuations of biomass and by alternating shifts between highly autotrophic and heterotrophic phases (DE WIT *et al.*, 2001; VIAROLI & CHRISTIAN, 2003). It is worth noting that the assumption behind the NEM calculation with the classical LOICZ guidelines is that net system production or oxidation of organic matter is the primary non-conservative uptake or release pathway for DIP within the system. This assumption does not exclude the contribution of DIP fluxes related to geochemical reactions occurring in the sediments. It has been demonstrated that the overall mass balance, and the resulting NEM in shallow

ecosystems, could be affected not only by external inputs but also by internal benthic fluxes (GIORDANI *et al.*, 2008). In any case, no direct measurements of the ecosystem metabolism are available for comparison; however, NEM data reported by GAZEAU *et al.* (2004) and derived by the LOICZ methodology for other coastal Mediterranean systems, show that the Papas Lagoon is close to a balanced status (-1.75 mmolC m⁻² d⁻¹) and lies between the net heterotrophic Sacca di Goro Lagoon (-16 mmolC m⁻² d⁻¹) and the net autotrophic Gulf of Lions (16 mmolC m⁻² d⁻¹).

In the Papas Lagoon system, losses of DIN via denitrification appear to dominate over the gains through nitrogen fixation (*nfix-denit* < 0) throughout the year (Table 4). The results of our study indicate that, annually, the lagoon was net denitrifying at a rate of -0.15 molN m⁻² y⁻¹. Denitrification is a reducing process whereby heterotrophic bacteria utilize nitrate as an electron acceptor in respiration and reduce it to either gaseous end-products (N₂ and N₂O) or ammonium (nitrate ammonification). It is a key process in the sediment nitrogen cycle since it decreases the amount of available nitrogen for primary producers, as the gaseous end-products are diffused into the atmosphere. In coastal marine systems that re-

ceive large quantities of nitrogen from anthropogenic sources, denitrification provides a mechanism for the removal of excess nitrogen and thus it helps to control the rate of eutrophication in these environments (SEITZINGER, 1988). However, the N_2O produced is one of the main, most potent, and therefore most undesirable, greenhouse gases. In coastal lagoons, the denitrification rate is further stimulated during the dystrophic crisis period. In the shallow Sacca di Goro Lagoon (northern Italy) high rates of denitrification ($\sim 1 \text{ gN m}^{-2} \text{ d}^{-1}$) have been reported to occur during the annual dystrophic period and represent a significant loss of nitrogen from this ecosystem (HERBERT, 1999). In the Papas Lagoon, a relatively higher denitrification rate ($-0.20 \text{ molN m}^{-2} \text{ y}^{-1}$) was recorded during autumn, when the *Ulva* decomposition was still in progress. Denitrification values are in the same range of those previously estimated by the LOICZ approach for the Valli di Comacchio (VIAROLI & GIORDANI, 2001) and Valle Smarlacca (GIORDANI & VIAROLI, 2001) Lagoons in the northern Adriatic.

It is clear that 'net heterotrophy' and 'net denitrification' do not impede the occurrence of autotrophy and nitrogen fixation, at least in small areas of the lagoon. One could also argue that the 'uncertainty' in the ratios used in stoichiometric relations is a possible drawback of these calculations. In fact, the original stoichiometry of the decomposed organic matter is not known, thus the assumption that the primary producer in the lagoon is phytoplankton with a Redfield composition (C:N:P = 106:16:1) was adopted. Since the lagoon is colonized by dense floating *Ulva* beds for a long period of time throughout the year, the C:N:P = 336:35:1 for macroalgae (ATKINSON & SMITH, 1983) was also applied. The results

of this approach indicate that such high ratios do not alter our initial thoughts and conclusions, since the sign of the $p-r$ and $nfix-denit$ rates remains the same. In essence, the use of the ratio C:N:P = 336:35:1 almost doubles the net denitrification rate, while leading to a $p-r$ rate which is three times as high.

Conclusions

Nutrient concentrations in the Papas Lagoon exhibit strong seasonal and spatial variation. The pattern of availability and depletion of nutrients seems to be regulated, most likely, by the temporal variability of the surface runoff, biological removals, release from sediments (bacterial degradation of organic matter and dissolution of accumulated siliceous debris) as well as exchanges with the open sea. In addition, the presence of the macroalgae seems to greatly affect the DIP and DIN seasonal cycles, as well as their non-conservative fluxes. Algal growth contributes to the spring-early summer DIN consumption, while their subsequent degradation leads to the summer DIP fast recycling and to the yearly storage of nitrogen in the sediments. Based on the nutrient budgets, the study shows that the lagoon was a slightly heterotrophic system ($p-r = -0.64 \text{ molC m}^{-2} \text{ y}^{-1}$) and was in a state of net denitrification ($nfix-denit = -0.15 \text{ molN m}^{-2} \text{ y}^{-1}$). However, coastal lagoons are highly dynamic environments and are usually subject to high temporal variations regarding inputs and outputs of nutrients. Consequently, relatively extended observations are necessary in order to reliably model carbon and nutrients budgets in the system. The DIN and DIP budgets, the NEM and the net nitrogen budget obtained with the LOICZ methodology have satisfactorily simulated the in-

ternal processes occurring in the Papas Lagoon, highlighting and proving yet again the reliability of the LOICZ modeling guidelines, as well as its efficiency and ease of application as a tool for integrated coastal zone management practices.

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