


Effects of External Nutrient Sources and Extreme Weather Events on the Nutrient Budget of a Southern European Coastal Lagoon

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Abstract The seasonal and annual nitrogen (N), phosphorus (P), and carbon (C) budgets of the mesotidal Ria Formosa lagoon, southern Portugal, were estimated to reveal the main inputs and outputs, the seasonal patterns, and how they may influence the ecological functioning of the system. The effects of extreme weather events such as long-lasting strong winds causing upwelling and strong rainfall were assessed. External nutrient inputs were quantified; ocean exchange was assessed in 24-h sampling campaigns, and final calculations were made using a hydrodynamic model of the lagoon. Rain and stream inputs were the main freshwater sources to the lagoon. However, wastewater treatment plant and groundwater discharges dominated nutrient input, together accounting for 98, 96, and 88 % of total C, N, and P input, respectively. Organic matter and nutrients were continuously exported to

the ocean. This pattern was reversed following extreme events, such as strong winds in early summer that caused upwelling and after a period of heavy rainfall in late autumn. A principal component analysis (PCA) revealed that ammonium and organic N and C exchange were positively associated with temperature as opposed to pH and nitrate. These variables reflected mostly the benthic lagoon metabolism, whereas particulate P exchange was correlated to Chl *a*, indicating that this was more related to phytoplankton dynamics. The increase of stochastic events, as expected in climate change scenarios, may have strong effects on the ecological functioning of coastal lagoons, altering the C and nutrient budgets.

Keywords Coastal lagoon · Groundwater · Wastewater treatment plants · Nutrient budget · Climate change · Ria Formosa

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Introduction

Coastal lagoons are shallow coastal water bodies, separated from the ocean by sand barriers and connected to it by one or more inlets. They occupy 13 % of the coastal areas worldwide (Kjerfve 1994). They are complex, highly dynamic environments located at the interface between drainage basins and the coastal ocean, often hosting a wide range of habitats and communities such as saltmarshes, seagrass beds, intertidal and subtidal flats, and oyster reefs. Because of this, they are generally highly productive systems, providing a range of ecosystem services of great environmental and economical values (e.g., fisheries, aquaculture, and tourism; Newton et al. 2014). Coastal lagoons sustain complex biogeochemical cycles, intercepting, transforming, and recycling the fluxes of nutrients and organic matter from the land to the ocean (and

vice versa) (McGlathery 2008; Valiela and Cole 2002). Ultimately, they control the magnitude of nutrient export from the land to the ocean (Makings et al. 2014). Their setting within the coastal landscape, generally supporting large human populations, and their restricted exchange with the ocean make these systems especially vulnerable to anthropogenic pressures such as freshwater withdrawal from groundwater and surface water, eutrophication and pollution, overfishing, and climate change (Newton et al. 2014).

Lagoon nutrient budgets are simple mass balances of the dominant nutrients (in this case carbon, nitrogen, and phosphorus (C, N, and P) over a defined period that describes the rates of matter delivery and removal to the system and its change within the system (Artioli et al. 2008). Budgets are powerful tools to analyze threats as eutrophication because they enable the assessment of the absolute and relative importance of the external nutrient sources (and consequently the underlying causes), internal biogeochemical processes, and water exchange (Gordon et al. 1996). Despite this, annual budgets of complete systems are still quite scarce (Boynton and Kemp 2008) and mainly based on exchange of dissolved inorganic nutrients following Land-Ocean Interactions in the Coastal Zone (LOICZ) program budget methods for estuaries (Gordon et al. 1996). According to these, lagoons can both be a sink and a source of dissolved nutrients for the adjacent coastal zone, and this may be different for N and P as found for various temperate (Boynton et al. 1995; Giordani et al. 2008; Krasakopoulou and Pagou 2011), subtropical (Miyajima et al. 2007), and tropical lagoons (Cerdeira et al. 2013). In some cases, lagoons were found to be exclusive sinks (Sfriso et al. 1994) or sources (Falco et al. 2010; McGuirk Flynn 2008) on an annual basis. In general, it appears that with increasing nutrient loads, either of anthropogenic or natural origin, at some point lagoons will shift from sink to source, as was found in a LOICZ budget exercise of 17 Italian lagoons (Giordani et al. 2008). A similar pattern emerged in a study of 24 Mexican and Central American lagoons (Smith et al. 1999), although here in some cases a lack of data did not allow for specific conclusions. Even though on an annual basis there might be nutrient export, the capacity of lagoons for intercepting nutrient fluxes from watersheds thereby diminishing the release of (dissolved inorganic) nutrients to the coastal zone is eminent; for example, for West Falmouth Harbor (Cape Cod, USA), it was calculated that from spring to autumn, on average, 60 % of the N loading from the watershed were intercepted, despite a recent three-fold increase in loading (Hayn et al. 2014). In summer, this even amounted to 100 % (no data for winter are given).

The case of West Falmouth Harbor also illustrates the finding that budgets vary greatly on a seasonal basis, related to activity of primary producers, bacteria (nitrifiers, denitrifiers), and other organisms, stressing the need for frequent and year-long sampling. Logically, increased nutrient assimilation

related to higher primary production in the main growth season, generally late spring and summer, turns the lagoon from nutrient source to sink, although not necessarily for both N and P simultaneously (Giordani et al. 2008; Hayn et al. 2014; Krasakopoulou and Pagou 2011). Extreme meteorological events, such as storm and heavy rainfall, can have profound impacts on nutrient concentrations and thus on budgets, although on an annual basis, the impact may be minimal (Burkholder et al. 2006). This is particularly true for tropical systems that are often affected by typhoons or hurricanes with associated heavy rainfall (Wetz and Yoskowitz 2013), but storm-driven alterations of relative availabilities of C, N, and P and stoichiometric ratios also occur in Mediterranean systems (Lipizer et al. 2012). However, their effects on annual budgets to our knowledge have not yet been quantified. Additionally, specific strong wind conditions can bring upwelled nutrient-enriched waters to systems outside traditional upwelling areas that can also impact the nutrient budget (Nieblas et al. 2009; Relvas and Barton 2005). The occurrence of these stochastic events is difficult to predict; high-frequency sampling with high temporal resolution might be instrumental in analyzing their effects.

The aim of this work was to estimate the annual nutrient budgets (N, P, and organic C) of the mesotidal Ria Formosa lagoon, southern Portugal, considering all inputs and outputs. The seasonal changes on the water input and output fluxes were analyzed to reveal how they may influence the ecological functioning of the system as a sink or source of nutrients and the potential contribution of organic matter and nutrients to the adjacent coastal zone. These may feed important local coastal fisheries of bivalves (Vânia et al. 2014) or contribute to noxious summer blooms of green macroalgae (Malta et al. 2007; Stigter et al. 2013). The sources of nutrients to the lagoon are the rainwater, the surface, and groundwater inputs from the watershed and the effluents of the wastewater treatment plants (WWTPs; Fig. 1). The nutrient exchanges between the lagoon and the adjacent coastal zone were also considered.

In addition, we describe how this budget is affected by extreme weather events such as a heavy rain period that occurred in winter and a summer upwelling event caused by an extended period of strong NW winds. Even though these events may not occur every year, they are relatively common and their frequency is expected to increase as a result of climatic changes. Regarding rainfall, though long-term climate change scenarios (2070–2100), foresee an overall decrease in Mediterranean regions (Giorgi and Lionello 2008), predicting also an enhanced torrential character of seasonal rains (Sánchez et al. 2004). For the south of Portugal in particular, short-term predictions (2020–2050) show a possible increase in winter rainfall volume and intensity (Stigter et al. 2014). Less can be said for wind, since regional climate models vary strongly with respect to predicted changes in velocity in the

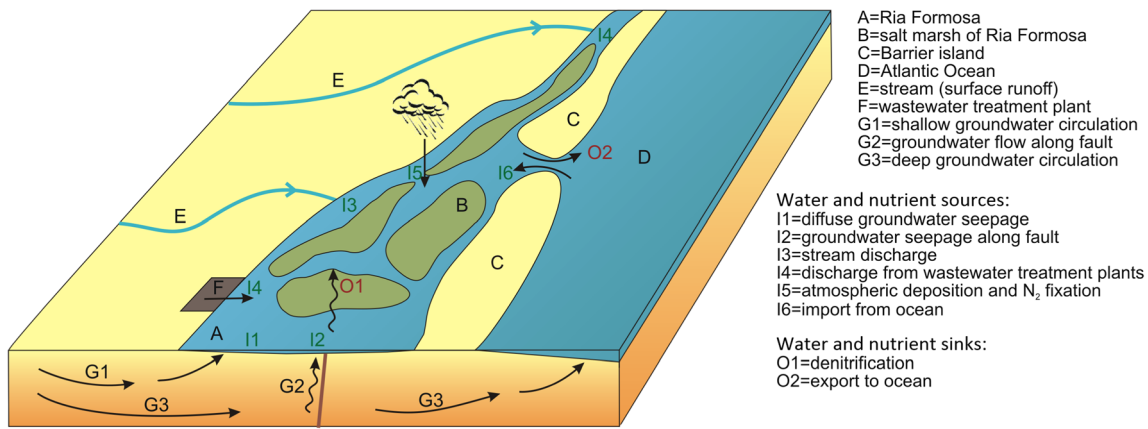


Fig. 1 Schematic diagram of water and nutrient sources and sinks in the Ria Formosa lagoon

Mediterranean, as well as in many other regions in Europe (Rockel and Woth 2007). We will discuss the effect of potential increases of extreme events on the nutrient fluxes of coastal lagoons, on their interaction with the coastal ocean, and how the results of this study can be used to implement policy measures to improve the water quality of Ria Formosa lagoon.

Materials and Methods

Study Site

The study was carried out at the Ria Formosa lagoon in the south of Portugal, including its drainage basin (Fig. 2). The

total area of the drainage basin is 844 km², with a maximum and mean altitude of 512 m and 112 m, respectively, and an average slope of 11 %. The two most important subbasins are of the rivers Rio Séqua/Gilão and Ribeira do Almagem, which together cover 39 % of the area and account for approximately 80 % of total runoff. These two rivers have an intermittent behavior and discharge directly to the ocean through the Tavira inlet, whereas all other streams are ephemeral, discharging only during and slightly after significant rainfall events.

The hydrogeology of the drainage basin is summarized in Fig. 2, details from Stigter et al. (2009). The area is dominated by surface runoff. Recharge is estimated to be 10 to 15 % of rainfall in sandy aquifers and up to 50 % in limestone aquifers

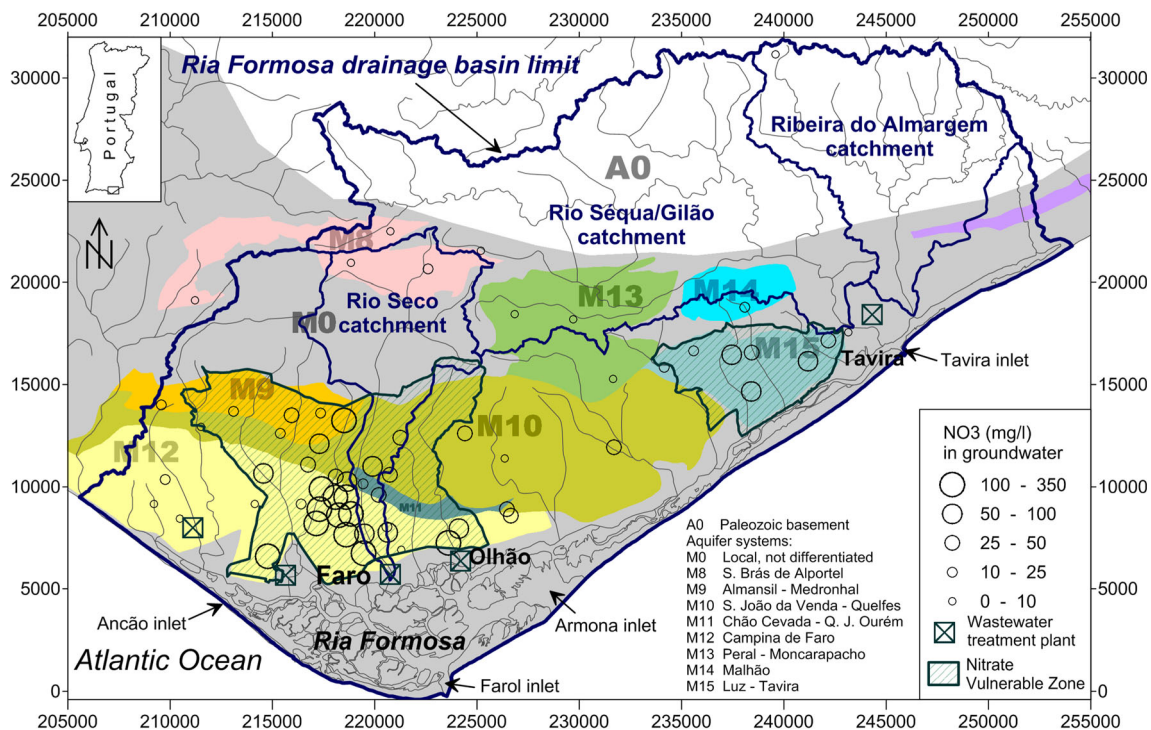


Fig. 2 Location of Ria Formosa lagoon (South Portugal), its drainage basin and the three major stream catchments, defined aquifer systems, nitrate concentrations in groundwater (mg/l), the designated nitrate vulnerable zones, and wastewater treatment plants

(Stigter et al. 2009). Intensive irrigated citrus and horticultures characterize land use, particularly in two areas of the basin-designated nitrate vulnerable zones (Fig. 2). Together with losses from septic tanks, these cause high nitrate concentrations in groundwater, which are well above the guideline value for drinking water (50 mg/l NO_3) and can locally exceed 300 mg/l.

The Ria Formosa is a mesotidal lagoon (average depth <2 m), extending for approximately 55 km along the south coast of Portugal. Water exchange with the ocean ranges from 52 to 80 % between neap and spring tides (see Andrade et al. 2004 for details on geography and morphology). Water temperature varies between 12 °C in winter and 27 °C in summer (Falcão and Vale 1990). The Ria Formosa lagoon receives secondarily treated sewage inputs from five WWTPs (Fig. 2) that flow into the main navigation channels.

Two hydrodynamic subsystems can be distinguished in Ria Formosa (Pacheco et al. 2010), with limited connection between them, the larger western sector that develops up to the Armona inlet and the narrow eastern sector that develops easterly from Armona. In this study, we focused only on the western sector of the lagoon as 93 % of the total water exchange between the whole lagoon and the ocean take place through the three inlets of this sector (Pacheco et al. 2010). The two major and opposing interconnected inlets of the system, which are the main stabilized inlet of Farol and the natural inlet of Armona, represent almost 90 % of the total prism of the Ria Formosa system. Farol inlet is flood dominated (more water enters at high tide than goes out at low tide) and Armona inlet ebb dominated; i.e., the exceeding flood prism of Farol inlet ebbs through the Armona inlet.

Inputs to the Lagoon

To obtain a complete nutrient budget for the Ria Formosa lagoon, all inputs from both the watershed and from rain were estimated from October 2005 to April 2007 as well as the exchanges between the lagoon and the Atlantic Ocean through the Farol and Armona inlets (March 2006 to March 2007) as schematized in Fig. 1.

Rain Input

The total amount of rain was obtained from data of the meteorological stations of Faro airport (at the border of the lagoon) and Quelfes that is situated a few kilometers more inland. The spatial distribution of mean annual rainfall was obtained from Nicolau (2002), who applied a kriging interpolation with external drift, using elevation as auxiliary variable, to map the spatial distribution of rainfall with a resolution of 1 km². By entering these data into a GIS, the ratio of mean annual rainfall into the lagoon to that of the meteorological stations was calculated. To determine nutrient concentrations in the rain, water samples

were collected during two rain events with a funnel mounted on a polypropylene (PolyP) 100-ml bottle (Kartell, Italy). The rainwater was collected during the first 15 to 20 min, filtered over a 0.45- μm filter (Whatman) in a PolyP bottle, and frozen for nutrient analysis. Nutrient (and major ion) concentrations in coastal rainwater are highly variable, depending on the atmospheric conditions, such as wind speed and direction, as well as duration, intensity, and time of year of the rainfall event (e.g., Neal and Kirchner 2000; Koçak et al. 2007). To account for variability, average values of collected rain samples, past rainwater samples, and minimum observed nutrient concentrations in runoff water (presenting minimum contribution of soil N during runoff) from the rivers Gilão and Almargem were used to estimate the nutrient contribution of rain. Total annual nutrient input from precipitation was then calculated as the product between rain volume and average nutrient concentration. To validate the representativeness of the obtained results, they were compared to existing (older) data for Faro, available through the Chemical Coordinating Centre of the European Monitoring and Evaluation Programme (EMEP; see <http://www.nilu.no/projects/ccc/sitedescriptions/pt/index.html>).

Riverine Input, WWTP, and Groundwater Discharge

The methodology for quantification of water and nutrient discharges from river discharge and WWTPs is presented by Stigter et al. (2006a). These values were updated and slight adjustments were made to the river discharge calculations as indicated below. As WWTPs do not provide data on particulate and dissolved organic carbon contents, we used the levels measured by Santos et al. (2004) at the outlets of the two WWTPs of Faro and multiplied them by total discharge.

Total runoff into the Ria Formosa lagoon was determined for the two largest and most important rivers and for the Rio Seco stream (Fig. 2). Despite the ephemeral nature of the latter, its high nutrient content, linked to agricultural and residential areas, justified its inclusion in the budget calculations. Recorded water levels and available rating curves were provided by the Regional Water Basin Authority (RWBA) and used to calculate runoff. Runoff of the unmonitored stream reaches (downstream) was extrapolated based on geology, considering proportionally equal runoff in areas of Paleozoic rock and zero runoff in areas of outcropping detritic and limestone formations. Water samples for particulate and dissolved nutrient (C, N, and P) analysis were gathered from the main streams during runoff periods (see “Analytical procedures” section for analytical procedures). Data resulting from continuous recording of the electrical conductivity (EC) by the RWBA were used to detect and account for the dilution effects in the calculations caused by runoff peaks.

A water balance approach was used as detailed in Stigter et al. (2013) to assess the annual groundwater discharge from land into the lagoon. The N load on groundwater mainly originates from fertilization and domestic effluents (septic tanks) and dry and wet deposition. Localized groundwater outflow into the lagoon along geological faults was studied with the help of electromagnetic surveys (Stigter et al. 2013). The method proved adequate for the detection of freshwater outflow into the lagoon, but its direct quantification was not possible. In order to assess the spatial distribution of groundwater and corresponding N discharges, the water and mass balances were performed in a GIS environment for N-S oriented, 200-m-wide “bands.” The relative contribution of shallow groundwater outflow into the lagoon and deep circulation passing below the lagoon and discharging into the ocean is particularly important in the east (Stigter et al. 2013). This estimate was quantified by defining a “groundwater divide” separating the shallow and deep flow components. In other words, only aquifer recharge occurring south of the groundwater divide is believed to result in direct discharge into the lagoon. An important exception occurs in the westernmost sector, where groundwater inflow from the north occurs due to high extractions for irrigation in the south.

The N content in groundwater was considered constant throughout the year. Monthly averages of groundwater flow were obtained from existing transient numerical simulations for a large aquifer bordering the region to the west (Stigter et al. 2009). As for N, P content of groundwater was considered constant throughout the year. The average observed concentration in the coastal groundwater of the area (0.01 mg/l) was multiplied by monthly flow estimates to quantify P discharges into the lagoon.

Lagoon–Ocean Exchange

Water exchange volumes were obtained from Pacheco et al. (2010). Average velocities and discharge volumes in the channel cross section due to the ocean tide and tidal elevation change in the bay were used to determine the tidal prism discharge for different tidal amplitudes using the linear method approach (see Dean and Dalrymple 2002). To apply this approach, inlet morphology parameters were obtained from a 2006 bathymetric chart for the Farol inlet, following the recommendations of Seabergh (2006). The same procedure could not be applied to Armona inlet, due to the lack of a detailed bathymetry. To estimate flows at this inlet, an exponential equation was obtained relating the mean tidal prism and the tidal range for Farol inlet. Assuming the two inlets as an interconnected subsystem, where Ancão inlet contribution is negligible (Pacheco et al. 2010), the percentage of water flowing through each inlet was determined. We assumed a linear relation between that percentage and tidal range and

estimated the discharge at Armona inlet as a function of Farol inlet discharge. Because the inlets are an interconnected hydrodynamic cell system, with a clear circulation pattern from Farol to Armona inlets, it was also necessary to correct for the difference between flood and ebb between the inlets. This method allowed estimating velocity and discharge at each inlet for any specific tidal amplitude.

Continuous data on sea surface temperature (SST) measured on a buoy approximately 2 nm off the coast were obtained from the Hydrographical Institute (Lisbon). Exchange of nutrients, chlorophyll *a* (Chl *a*), and particulate matter between the Ria Formosa and the Atlantic Ocean were measured every 2 h during full tidal cycles (24 h) from March 2006 to March 2007. Neap and spring tidal cycles were sampled every other month, but due to technical problems, the July spring tide could only be sampled during daytime and the November 2006 neap tide campaign had to be canceled. In total, 12 full tidal cycles and 1 half (12 h) cycle were sampled. Samples were taken from the far end of the jetty in the Farol inlet (Fig. 2) using a bucket attached to a 20-m-long rope to collect water that was transported in insulated bags to a provisional field laboratory within 5 min time, where they were processed as described in “Analytical procedures” section. To test for potential differences of water parameters between Farol and Armona inlets, additional samples were taken in the months of April, June, August, October, and December 2006 and February 2007, at 3 h from the turn of tides during daytime neap and spring tides. As no significant differences between the inlets were found, the calculations of the inlet budgets were based only on the concentrations measured in the Farol inlet.

Analytical Procedures

Duplicate water samples for both riverine and seawater were collected in 2-l PolyP bottles. Temperature, EC (rivers) or salinity (ocean), and pH of the two water samples were measured on the spot using a multiparametric sonde (WTW, Weilheim, Germany). All samples were analyzed for suspended particulate matter (SPM); particulate C, N, and P (POC, PON, and PP); dissolved organic carbon (DOC); and dissolved inorganic nutrients. In addition, seawater samples were analyzed for Chl *a* concentrations.

For SPM and POC, PON, and PP analyses, 500 ml of water was taken from each bottle after vigorous shaking and filtered over precombusted (450 °C, 2 h), preweighed filters (Whatman GF/F). Filters were dried at 60 °C for 2–3 days and weighed to calculate SPM. POC and PON were analyzed at the University of Málaga (Spain) using a 2400 CHN elemental analyzer (Perkin-Elmer, USA). PP was analyzed as orthophosphate as indicated below after acid persulfate

digestion of the filters (Sommer and Nelson 1972). For seawater samples, another 500 ml was filtered over untreated filters after which these were stored frozen wrapped in aluminum foil. Chl *a* was analyzed spectrophotometrically (Beckman Coulter DU 650, USA) on these filters after overnight extraction in the dark at 4 °C (Lorenzen 1967).

For DOC analyses, 20 ml of the sample was filtered with precombusted filters in a glass ampoule to which 10 μ l, 85 % H_3PO_4 was added after which the ampoules were sealed. Samples were analyzed at the Mediterranean Institute for Advanced Studies (IMEDEA-CSIC, Spain) using a Shimadzu TOC-5000 A (seawater sample) and at the University of La Coruña, Spain, on a Shimadzu TOC-V CSN analyzer (freshwater samples). For nutrient (ammonium, nitrite + nitrate, and orthophosphate) analyses, 200 ml water was filtered over 0.45- μ m cellulose acetate filters (Whatman) and frozen. Nutrients were later analyzed on a portable loop flow analyzer (Micromac-1000 MP, Systea, Italy) based on traditional colorimetric analyses (APHA 2005).

Data Analysis and Budget Calculation

A principal component analysis (PCA) was performed on a correlation matrix of 11 variables (listed in “Results” section) to assess multivariate relationships among variables and to reveal hydroecological processes occurring during the sampling period. To calculate the nutrient and particulate matter exchange between Ria Formosa lagoon and the adjacent coastal zone, the average of the initial and final concentrations was calculated for each 2-h period and multiplied with the volume of water exchanged during this period. The amounts of nutrients or particulate matter exchanged in each 2-h period were summed to obtain tidal and daily exchange totals. Based on PCA results, the cycles were separated in spring-summer (May, July, and September) and autumn-winter cycles. To detect whether cycles were deviating significantly from the average in a season, a Dixon’s *Q* test was performed for all nutrients (Rorabacher 1991), using the outlier package (Komsta 2011) in R version 3.1 (R Core Team 2014). Seasonal exchange budgets were calculated by averaging the daily exchanges per season, multiplied with 183 and 182 days for summer and winter, respectively, and summed to obtain annual exchange. Based on the results of the outlier analyses, two annual budgets were calculated, one including the July and November cycles and one excluding those, to assess the importance of short-lasting, isolated events (in this case wind induced upwelling and torrential rain, respectively) on the annual budgets of Ria Formosa lagoon.

Results

Freshwater Nutrient Inputs

The main contributors to the total freshwater discharge into Ria Formosa lagoon between October 2005 and April 2007 were rainfall and stream runoff, which peaked in November in both years, followed by groundwater and WWTP discharge, respectively (Fig. 3a). Rain and stream discharges showed considerable intraannual and interannual variations, which albeit less pronounced were also observed in groundwater discharge. Discharge was minimum in August and September and maximum in February to April. In contrast, WWTP discharge was highest in summer and lowest in winter (December to February), although variation was generally small.

Contrasting to water volumes, nutrient discharge for rain and riverine runoff was much more modest (Fig. 3b–d). WWTPs and groundwater were the main nutrient contributors because their concentrations are orders of magnitude higher, together accounting for 88.3 and 96.0 % of the total P and N annual loading into the lagoon, respectively (Table 1). Dissolved inorganic nitrogen (DIN) was the major N component of stream runoff, with PON contributing with up 6.0 ± 3.9 % to the total N load. In contrast, the particulate form of P is much more abundant in stream runoff, on average responsible for 43 % of the total input. WWTPs are the main source of organic carbon, although during the months of highest rainfall, riverine contribution can be significant (Fig. 3d). Stream carbon discharge was mainly in the form of DOC (average DOC/POC ratio 6.3), whereas POC was the dominant form discharged by WWTPs (average DOC/POC of 0.2). A considerable spatial variation of inputs into the Ria Formosa lagoon was observed with the larger western/central sector of the Ria Formosa receiving most of the rain input, whereas the narrower eastern sector received most of the riverine inputs (Fig. 2). Discharge from the WWTPs is mostly concentrated in the western/central sector.

The spatial distribution of groundwater outflow from Ria Formosa watershed is shown in Figs. 4 and 5. The total groundwater discharge from land was estimated as 57×10^6 m³ for an average year, corresponding to approximately 70 % of natural recharge. The remaining fraction is consumed by agriculture, pumped mainly from the aquifer systems located in the west (Stigter et al. 2013). These aquifers are therefore characterized by a significant negative contribution to outflow (white and very light gray areas of Fig. 4); i.e., there is no groundwater and thus no N contribution to the lagoon (Fig. 5a). These negative values are mostly compensated by positive water balances in neighboring areas, but cumulative outflow in this area is close to zero. The areas with highest recharge are located in the north (Fig. 5a). In the western sector of Ria Formosa lagoon, even though N load in

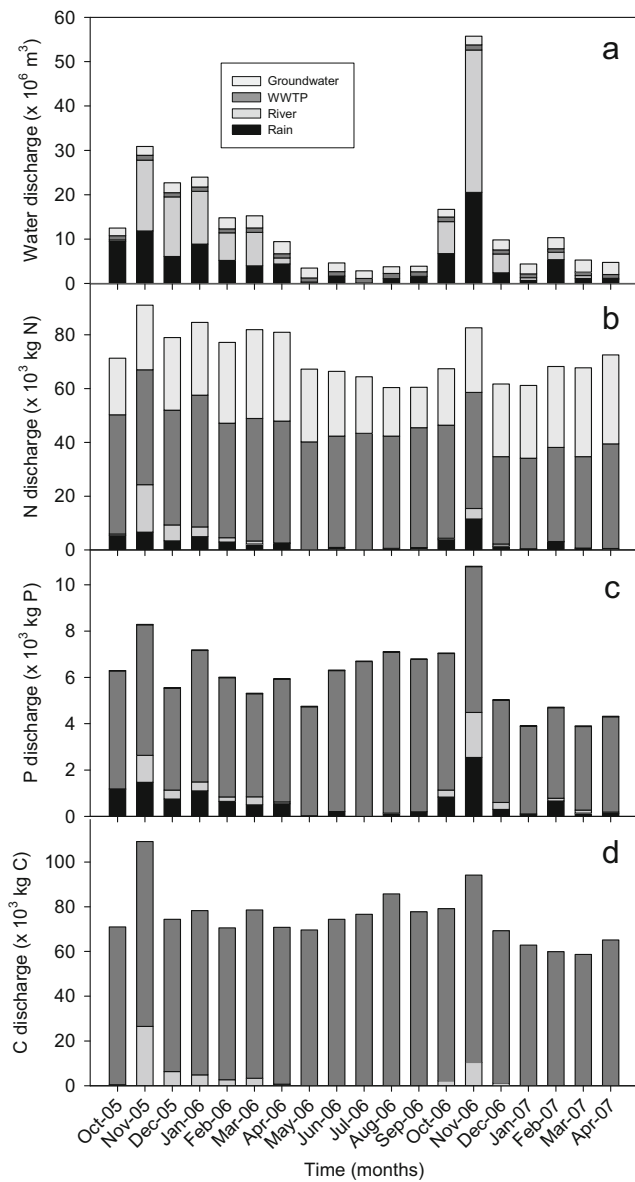


Fig. 3 a–d Monthly discharges of water, N, P, and C from rain, streams, wastewater treatment plants (WWTPs), and groundwater into the Ria Formosa lagoon

groundwater is high, N transport into the lagoon hardly occurs (Fig. 5b). The annual N load on the basin was 570 t yr⁻¹, from which 430 t yr⁻¹ was transported from land via groundwater. Only part of this N enters the lagoon (300 t yr⁻¹), corresponding

Table 1 Absolute (tonnes) and relative (percent of total) annual contribution of freshwater sources to the nutrient (C, N, and P) load of Ria Formosa lagoon in the period of April 2006 to March 2007

Input	Organic C (t)	N (t)	P (t)	C (percent total)	N (percent total)	P (percent total)
Rain	–	25.5	5.6	–	3.1	7.7
Stream runoff	15.1	5.8	2.9	1.7	0.7	4.0
WWTP	863.6	476.9	64.3	98.3	59.0	88.0
Groundwater	–	300.5	0.2	–	37.2	0.3
Total	878.7	808.7	73.1	100.0	100.0	100.0

WWTPs wastewater treatment plants

to a groundwater discharge of $25 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ (Fig. 5b). The remaining fraction is considered to discharge directly into the Atlantic Ocean.

Exchanges with Ocean

Water temperature monitored at the main inlet of Ria Formosa (Farol inlet) showed normal seasonal variation, reaching a maximum of 25 °C in September (Table 2) and a minimum of 14 °C in March. SST measurements obtained from the Hydrographical Institute showed a similar pattern (Fig. 6). A striking, strong SST drop that lasted from 25 June to 9 July 2006 indicates an upwelling event that preceded the Jul06-1 sampling. The diurnal variation in water temperature was generally small, presenting patterns with afternoon maxima and night to early morning minima without any clear differences between incoming and outgoing tides (not shown).

Average pH values were higher from late September to March and lower from late March to early September (Table 2). No distinct day-night or tidal patterns were observed. Salinity was practically constant all year round with little variation both between and within cycles, with a notable exception at the Nov06-1 sampling cycle. This cycle was sampled in the last day of a period of several days of heavy rainfall. Outflowing river water caused a decrease in salinity, which influence reached the Farol inlet as salinity dropped to lowest values of below 33 at two consecutive low tides (Fig. 7a). During this event, pH showed strong positive correlations with salinity (Pearson $r = 0.89$; Fig. 7a), as opposed to the negative correlations found between salinity and DIN and phosphate (Pearson $r = -0.94$ and -0.62 , respectively; Fig. 7b), all showing the influence of the watershed freshwater runoff.

The variables seston, PON, DOC, and POC, measured over tidal cycles at the Farol inlet showed a seasonal pattern with higher values in summer and lower in winter (Fig. 8a–h). In general, these variables did not show any clear diurnal or tidal patterns of variability. Chl *a* concentration was relatively constant year-round except for two distinct peaks in the first half of May 2006 and March 2007 (Fig. 8b). In both cases, concentrations tended to increase with outgoing and decreased again with incoming tides, whereas no clear tidal or day-night pattern could be discerned for the other cycles.

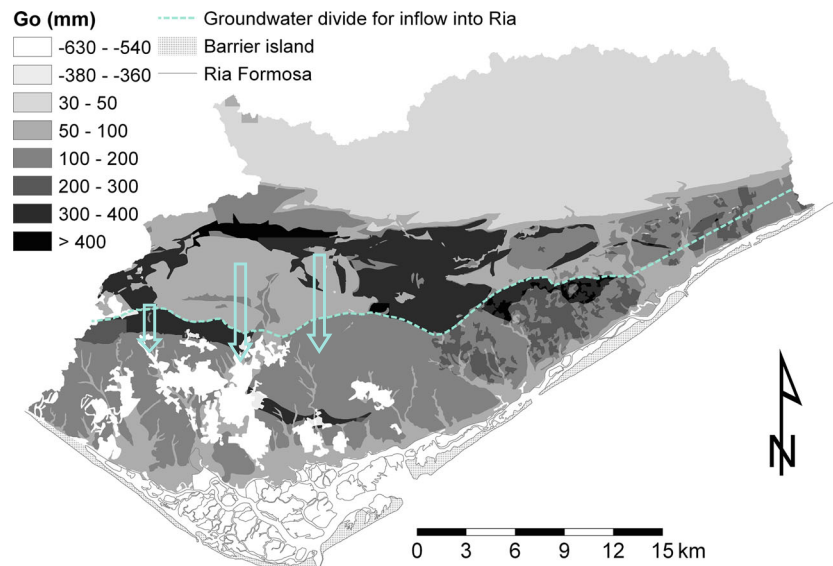


Fig. 4 Map showing the spatial distribution of the average annual contribution to groundwater outflow from Ria Formosa watershed (G_o , in mm); also shown is the estimated divide (*dashed line*) separating groundwater inflow into the lagoon (to the south) from direct outflow

into the Atlantic Ocean (area north of the divide). Exception is the area with *arrows* that indicate inflow from the northern to the southern area to compensate high irrigation deficits in the south

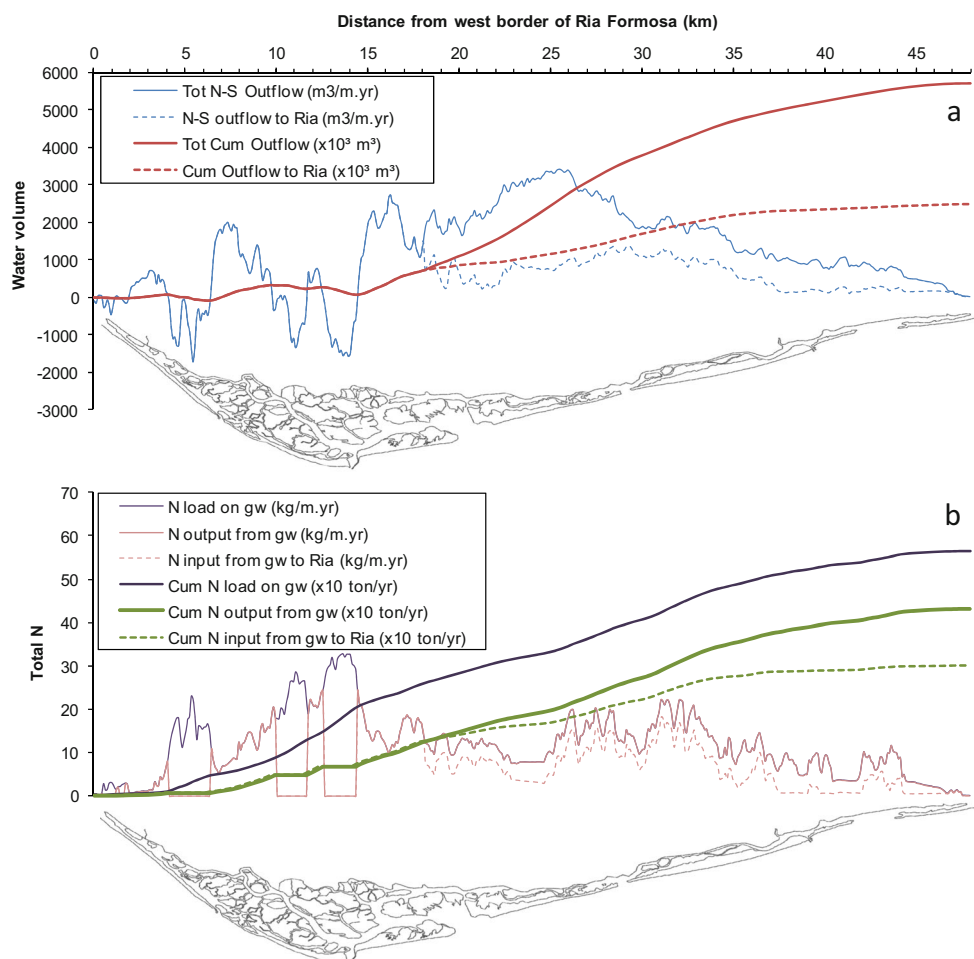


Fig. 5 Spatial distribution of the groundwater contribution to Ria Formosa lagoon quantified from west to east along the coastline. **a** Annual and cumulative water export and **b** N export

Table 2 Characterization of water sampling campaigns over a full tidal cycle with samples taken every 2 h in the Faro-Olhão inlet of the Ria Formosa lagoon in the period of April 2006 to March 2007

Code	Starting date	Starting time	A (m)	T (°C)	Salinity	pH
Mar6-1	23/03/2006	9:30 (H)	1.06 (N)	15.9 ± 0.7	35.9 ± 0.1	7.80 ± 0.05
Mar6-2	30/03/2006	9:00 (L)	3.26 (S)	16.1 ± 0.5	36.1 ± 0.1	7.78 ± 0.04
May6-1	18/05/2006	8:00 (H)	1.73 (N)	20.3 ± 1.0	36.4 ± 0.1	7.92 ± 0.04
May6-2	25/05/2006	8:00 (L)	2.60 (S)	17.9 ± 0.8	36.2 ± 0.1	7.93 ± 0.03
Jul6-1	12/07/2006	10:30 (L)	2.68 (S)	21.8 ± 0.5	35.9 ± 0.2	7.92 ± 0.04
Jul6-2	19/07/2006	10:30 (H)	1.58 (N)	23.5 ± 0.8	36.0 ± 0.1	7.91 ± 0.05
Sep6-1 ^a	07/09/2006	9:00 (L)	2.37 (S)	25.4 ± 0.5	35.9 ± 0.1	7.91 ± 0.05
Sep6-2	18/09/2006	14:00 (H)	1.74 (N)	19.9 ± 1.1	35.8 ± 0.1	7.99 ± 0.04
Nov6-1	07/11/2006	11:00 (L)	3.03 (S)	19.8 ± 1.3	34.4 ± 1.0	8.18 ± 0.07
Jan7-1	11/01/2007	8:00 (H)	1.16 (N)	15.9 ± 0.6	36.0 ± 0.1	8.25 ± 0.04
Jan7-2	22/01/2007	12:00 (L)	2.83 (S)	15.2 ± 0.6	36.0 ± 0.2	8.10 ± 0.03
Mar7-1	13/03/2007	10:00 (H)	0.97 (N)	15.4 ± 0.4	35.9 ± 0.1	8.15 ± 0.02
Mar7-2	20/03/2007	10:00 (L)	3.45 (S)	14.1 ± 0.7	35.8 ± 0.1	8.11 ± 0.04

Name of campaign (code), starting time of campaign at high (H) or low (L) tide, tidal amplitude (A) indicating neap (N) or spring (S) cycle, average temperature (T), salinity (S), and pH. Averages ± 1 SD

^a Twelve-hour cycle only

Total DIN was also relatively constant year-round except for peak values in winter (first March cycle 2006 and January cycles 2007) and considerably lower values during the rest of the year (Fig. 8c). Lowest values (1–3 $\mu\text{M N}$) were recorded during the Jul6-2 cycle. High DIN values in winter were mostly due to increases in nitrate ($\text{NH}_4^+/\text{NO}_3^- = 0.34 \pm 0.29$), whereas in summer, a considerable decrease in nitrate was accompanied by a slight increase in ammonium ($\text{NH}_4^+/\text{NO}_3^- = 3.59 \pm 2.80$). In general, DIN was the main component of total nitrogen ($\text{DIN}/\text{PON} = 2.25 \pm 1.22$); however, during summer, PON was slightly dominant ($\text{DIN}/\text{PON} = 0.82 \pm 0.10$).

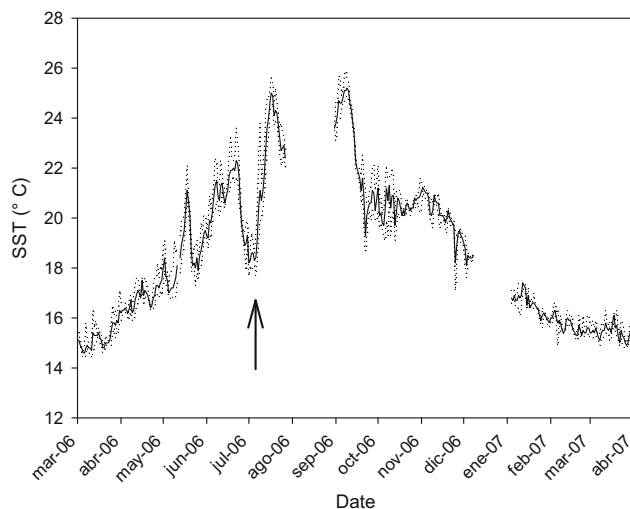


Fig. 6 Sea surface temperature (SST, °C) variation throughout the study period, obtained by a hydrographic buoy of the Hydrographical Institute of Portugal located 5 nm offshore the Farol inlet of Ria Formosa lagoon. The gaps represent the periods where no data were available; the arrow marks an upwelling event coincident with a sampling cycle

Phosphate and particulate phosphorus (PP) concentrations showed little variation along the year. Phosphate peaked in March 2006 (Fig. 8e), whereas PP showed minima in

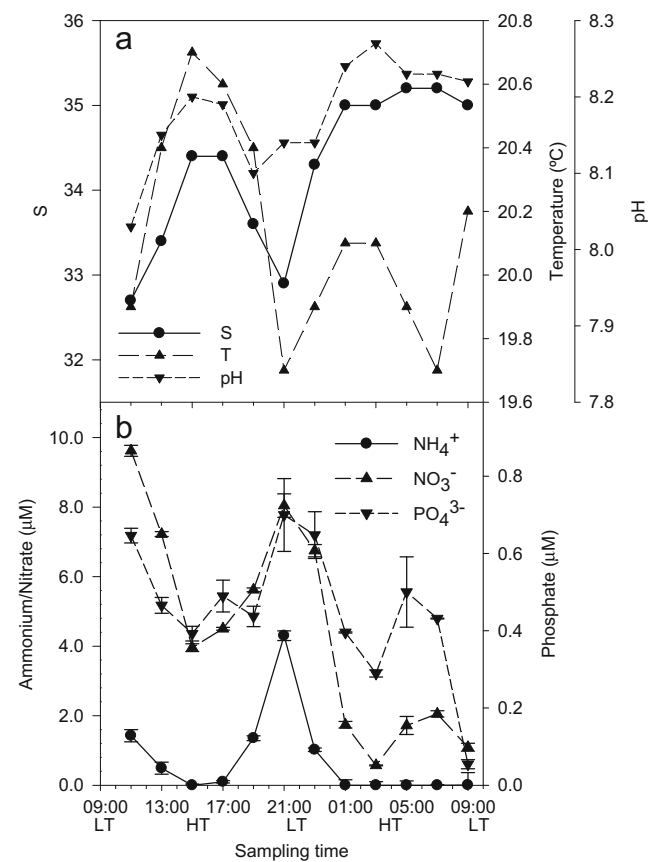


Fig. 7 **a** Water salinity, temperature (°C), and pH. **b** Ammonium (NH_4^+), nitrate (NO_3^-), and orthophosphate (PO_4^{3-}) concentrations (μM) in the Farol inlet of Ria Formosa lagoon during the November 2006, 24-h sampling cycle. LT and HT indicate low and high tides, respectively

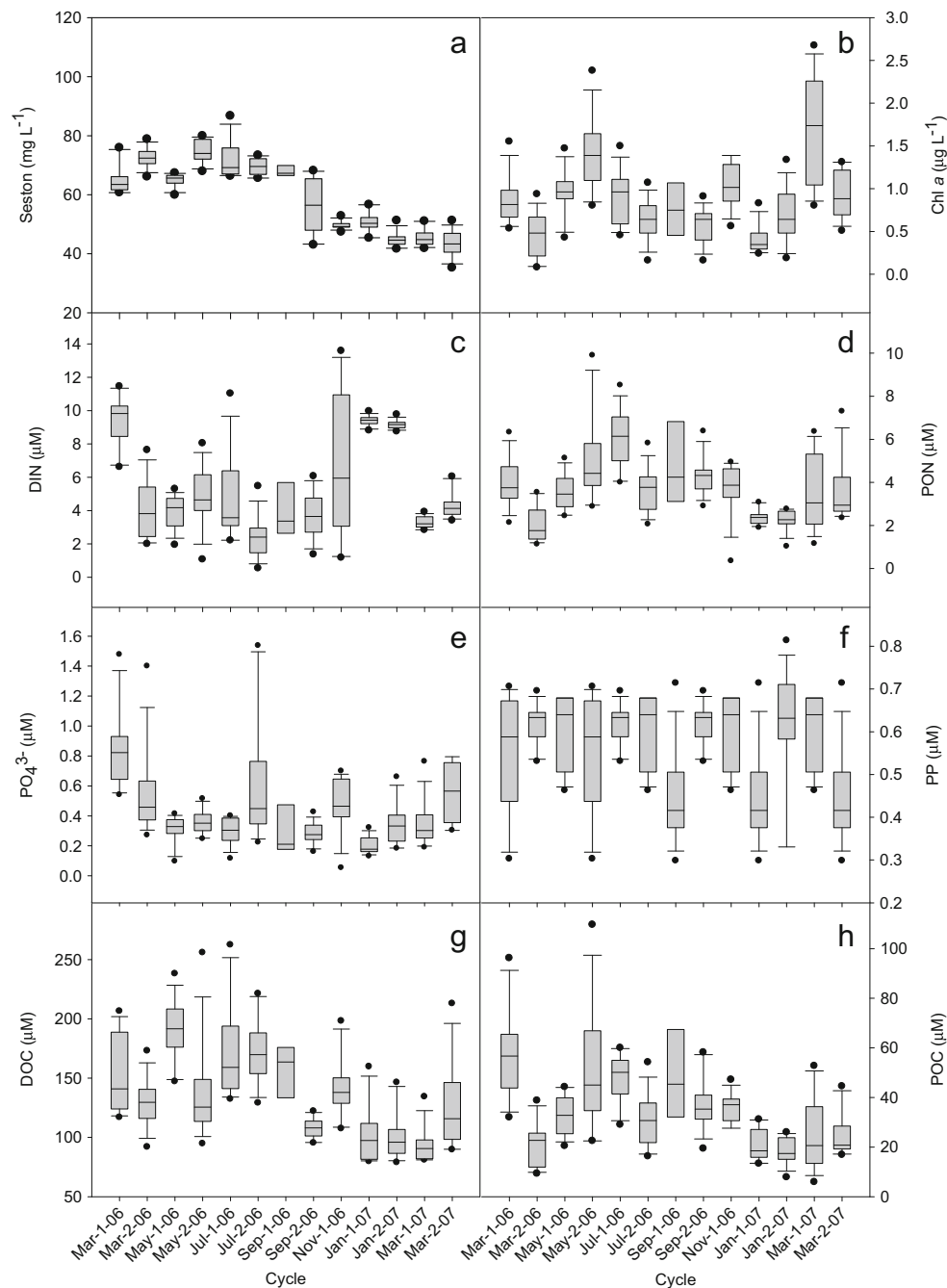


Fig. 8 Box-and-whisker plots showing the time variation of concentrations of seston (mg l^{-1}), Chl *a* ($\mu\text{g l}^{-1}$), DIN, PON, PO_4^{3-} , PP, DOC, and POC (all μM) between March 2006 and March 2007 in the Faro inlet of Ria Formosa lagoon. Each box-and-whisker plot represents

two tidal cycles (spring and neap) per month. The central line in each box indicates the median concentrations, the ends of the boxes are the 25th and 75th percentiles, error bars are the 10th and 90th percentiles, and points are the 5th and 95th percentiles

September, January, and March 2007 (Fig. 8f). On average, PO_4^{3-} and PP contributed equally to total phosphorus (TP) levels (average $\text{PO}_4^{3-}/\text{PP}$ ratio of 1.00 ± 0.51). Annual TP evolution (not shown) showed a V-shaped pattern with maximum values in both winters and minimum in summer. DOC was by far the major component of total carbon (TC), with a maximum observed DOC/POC ratio of 22.8; average DOC/POC ratio for all cycles was 4.76 ± 1.46 .

The first three principal components of the PCAs explained 66 % of total data variance (Fig. 9 and Table 3). The first component, which explains 37 % of the data variance, represents positive correlations with seston, ammonium, DOC, POC, PON, and temperature and negative correlations to pH and nitrate. The second component explains 16 % of the variance and represents the positive relationship between chlorophyll *a* and particulate phosphorus. The third component is

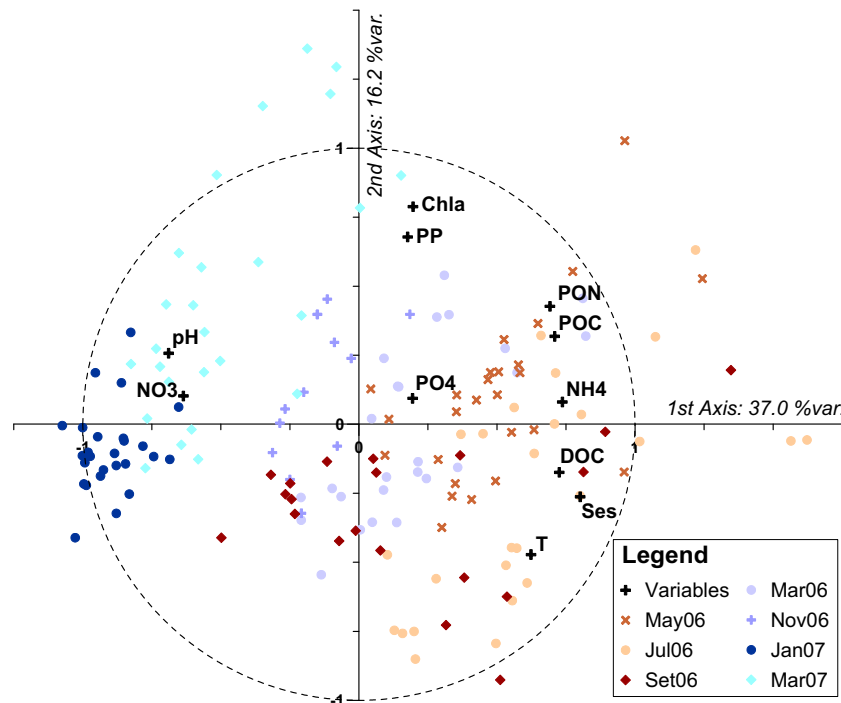


Fig. 9 Primary factorial plane (explaining 53.2 % of data variance), resulting from the PCA of data from 13 sampling campaigns between March 2006 and March 2007 in the Farol inlet of Ria Formosa lagoon.

Both the variable loadings and the sample scores are shown; the *different symbols and colors* show the monthly sampling times. For variable description and abbreviations, see Table 3

basically attributed to phosphate variability. The PCA plot reveals a clear seasonal gradient along the first component, from winter samples on the left side when high values of nitrates and pH contrasted with the other variables to the summer samples on the right side when high levels of PON, POC, ammonium, DOC, seston, and temperature contrasted with lower nitrates and pH values (Fig. 9). The shifting of the data along the negative side of component 2 indicates the reduced

loadings of chlorophyll *a* and particulate phosphorus during summer.

Net Exchange Budgets

Graphs for net matter exchange for all cycles between the Ria Formosa lagoon and the Atlantic Ocean are attached as supplementary material (S1), except for nitrogen (Fig. 10). Both

Table 3 PCA of seawater parameters of 13 diurnal sampling campaigns in the Ria Formosa in the period of April 2006 to March 2007

Variable	Description	First factor	Second factor	Third factor
λ	Eigen value	4.07	1.78	1.41
CEDV	Cumulative explained data variance	37.0	53.2	66.0
<i>T</i>	Temperature	<i>0.62</i>	-0.47	0.43
pH	$-\log[H^+]$	-0.69	0.26	0.49
Ses	Seston	0.80	-0.26	-0.17
Chl <i>a</i>	Chlorophyll <i>a</i>	0.20	0.79	0.17
NH ₄	Ammonium	0.74	0.08	-0.08
NO ₃	Nitrate	-0.64	0.10	-0.28
PON	Particulate organic nitrogen	0.69	0.43	0.34
PO ₄	Phosphate	0.19	0.09	-0.78
PP	Particulate phosphorus	0.18	0.68	-0.29
POC	Particulate organic carbon	0.71	0.32	0.13
DOC	Dissolved organic carbon	0.73	-0.17	-0.11

Eigenvalues, explained variance, and variable loadings of the first three components. Loadings higher than ± 0.60 are in italics

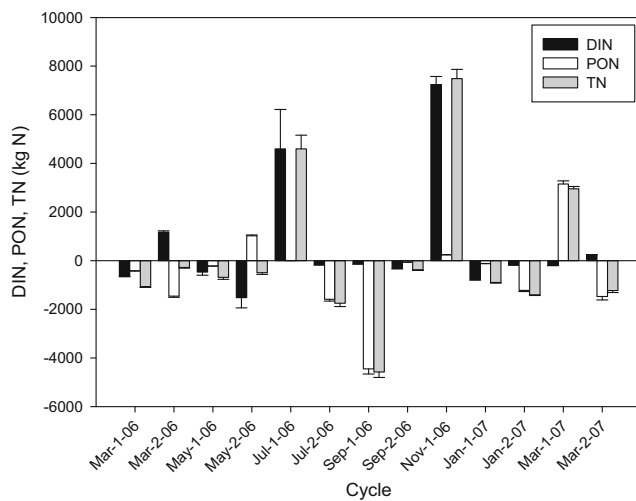


Fig. 10 Net daily exchange budgets of nitrogen (dissolved inorganic (DIN), particulate (PON), and total nitrogen (TN); kg N), between Ria Formosa lagoon and the coastal ocean between March 2006 and March 2007. The values represent the exchange averages observed in each sampling cycle, i.e., including spring and neap full tidal cycles; the negative numbers indicate the export from the lagoon to the ocean

import and export of plankton was observed without a clear seasonal pattern. Seston was exported from May to the first cycle of January 2007 with maximum values in summer, except for the Jul06-1 cycle. Nitrogen was exported from the lagoon during the whole year, except for the Jul06-1 and the Nov06-1 cycles when a high import of DIN resulted in net N import and during the Mar07-1 cycle, where important PON import was observed (Fig. 10). Phosphorus showed a general pattern of export in summer and autumn (May–November) and import in winter, with the exception of the Nov06-1 cycle and the Mar07-2 cycle. For carbon, the pattern was less clear, although again, net import was observed during the Jul06-1 and the Nov06-1 cycles.

Two budgets of annual oceanic exchange through the inlets either including or excluding the two cycles of extreme stochastic events, the upwelling event (Jul06-1) and the heavy rainfall (Nov06-1), are presented in Table 4. On annual basis, Ria Formosa is a source of plankton, seston, and phosphorus

Table 4 Net budgets of matter exchange (t = tonnes, kt = kilotonnes) between Ria Formosa lagoon and the ocean (average \pm standard error): summer (April to September 2006), winter (October 2006 to March 2007), and annual

	Chl <i>a</i> (t)	Seston (kt)	C (kt)	N (t)	P (t)
Summer ^a	-2.96 \pm 4.84	-35.31 \pm 71.77	1.62 \pm 4.82	-100.28 \pm 496.88	-47.61 \pm 31.49
Winter ^a	1.21 \pm 5.30	15.15 \pm 44.07	-0.39 \pm 4.08	252.00 \pm 628.05	-16.83 \pm 98.09
Total ^a	-1.75	-20.16	1.24	151.72	-64.45
Summer	-3.96 \pm 4.77	-62.50 \pm 41.77	0.64 \pm 4.70	-288.59 \pm 288.99	-52.70 \pm 32.16
Winter	0.85 \pm 5.87	19.68 \pm 48.21	-1.82 \pm 3.25	-25.78 \pm 327.51	-34.51 \pm 101.96
Total	-3.11	-42.82	-1.17	-314.36	-87.60

The negative numbers indicate the export of matter from the lagoon to the ocean

^a Nov6-1 cycle (with rain) and the Jul6-1 cycle (upwelling) included in the calculations

to the ocean, but the total amounts were reduced due to stochastic events. In contrast, the effects of extreme events on the exchange of nitrogen and carbon were particularly strong, converting the role of the lagoon from a source to a sink of N and C.

Table 5 presents the annual nutrient (C, N, and P) budget for the Ria Formosa lagoon, obtained from the sum of the different sources minus the output to the ocean. A budget was calculated both excluding and including the extreme, stochastic events. This again shows the strong effect of these events on the total annual budget in the cases of C and P, completely reversing the flow of matter. For P, the effect was relatively small.

Discussion

Freshwater Nutrient Inputs

WWTPs were the most important sources of nutrients to Ria Formosa lagoon and consequently stand as the most important driver of the ecosystem metabolism, fuelling both the ecosystem respiration (DOC and particulate matter) and the ecosystem primary production (inorganic N and P). The pronounced seasonality in WWTP discharge is driven by the seasonal fluctuation of population fuelled by tourism, which peaks in the summer. Groundwater appeared as the second major freshwater source of nutrients to Ria Formosa lagoon, contributing with about 300 t of N. This estimate is 1 order of magnitude higher than a previous estimate by Leote et al. (2008), which was based on in situ measurements made at only one site. Our estimate reveals the importance of this component in the N loading of Ria Formosa as it has been shown for coastal systems elsewhere, where groundwater discharge compares with riverine inputs (Niencheski et al. 2007).

The input of nutrients, through atmospheric deposition and riverine discharge, was strongly coupled to the periods of rainfall, i.e., in autumn and winter, rapidly decreasing in the following months, a characteristic of Mediterranean climate (e.g., Ludwig et al. 2003). Total contribution of nitrogen

Table 5 Net annual budgets of nutrients (C, N, and P) of Ria Formosa lagoon in the period of April 2006 to March 2007

	Input	Exchange 1	Exchange 2	Difference 1	Percent	Difference 2	Percent
Organic C (t)	878.7	-1174.9	1239.8	-296.2	-133.7	2118.5	141.1
N (t)	808.7	-314.4	151.7	494.3	38.9	960.4	18.8
P (t)	73.1	-87.6	-64.5	-14.5	-119.8	8.6	88.2

Input is the sum of freshwater input sources, exchange 1 is the exchange with the ocean excluding the Nov6-1 cycle (with rain) and the Jul6-1 cycle (upwelling), exchange 2 is the exchange including these cycles, difference is the input + exchange 1 or 2, and percent is the exchange as percentage of input. The negative numbers indicate the export of matter from the lagoon to the ocean

through dry and wet depositions to the lagoon (51.4 t) was 1 order of magnitude lower than that of groundwater or WWTP. This relatively low value was confirmed with data from EMEP and is also seen to occur in moderately industrialized areas of the USA (e.g., NADP 2000). Industrial activities and emissions are low in the area of Faro, and during the touristic summer season when emissions could be slightly higher, precipitation is very scarce. The nutrient contributions of riverine discharge to the lagoon are also relatively modest, mainly because water discharge is low. Larger rivers flowing into the Mediterranean and Black Sea show higher nutrient contributions to coastal systems (Ludwig et al. 2009). The most important riverine contributions to Ria Formosa lagoon originate from agricultural runoffs and, to a lesser extent, from domestic effluents. During the period of heavy rainfall in November, the effects of agricultural runoff were particularly notable in the high nitrate concentration of the water flowing into the lagoon.

Groundwater outflow occurred throughout the year, with higher flow rates in winter and early spring, as confirmed by transient flow simulations in a bordering aquifer (Stigter et al. 2009). Groundwater outflow in the western sector is highly restricted, as large volumes of groundwater are extracted for irrigation. This is evident in Fig. 5, where sectors with negative outflow indicate potential seawater intrusion. Negative outflow is compensated by positive water discharge in neighboring areas, resulting in a cumulative outflow close to zero. Consequently, the N export into Ria Formosa lagoon from the western sector is very low. The reduced outflow of N combined with the water pumping for agriculture, fertilization, and irrigation tend to increase the storage of N in the western aquifers. Stigter et al. (2006b) also show that the groundwater discharge in this sector is indeed very limited and that the long residence times promote groundwater salinization and increased nitrate contamination. In the eastern sector, N loads of groundwater are lower but are completely exported into Ria Formosa lagoon. Localized groundwater outflow along geological faults was also revealed by electromagnetic surveys (Stigter et al. 2013), but the N export along these pathways is believed to be limited,

as it originates from deeper, less contaminated groundwater.

More than 60 % of the freshwater N load into Ria Formosa lagoon is consumed internally. Highly productive saltmarsh and seagrass communities that occupy up to 65 % of the lagoon area (Santos, unpublished) and the low residence times of water that is flushed to the ocean every tide (Andrade 1990) explain why no eutrophic symptoms have been detected in the water column of the system (Nobre et al. 2005). The nutrient loading reported here, about $100 \text{ kg ha}^{-1} \text{ yr}^{-1}$, lay on the declining trends of seagrass response to N loading in the conceptual model of Valiela et al. (1997) for systems with low residence times. Interestingly, the mathematical model of seagrass habitat loss in relation to N loading presented by Short and Burdick (1996) previews a seagrass surface area of 21 % in Waquoit Bay, MA, with the N loading observed in Ria Formosa lagoon, which compares very well with the actual seagrass area cover of 23 % in Ria Formosa lagoon (recalculated based on Guimarães et al. 2012). Both models suggest that increasing N loading of Ria Formosa lagoon will have a strong effect in the area covered by seagrasses within this system. Worrying benthic symptoms of excessive macroalgal growth occur sporadically in Ria Formosa lagoon both in winter and summer (Stigter et al. 2013) with the later being exported to the adjacent coastal beaches, where they become an important nuisance (Malta et al. 2007). It is expected that the increasing population of surrounding urban centers will result in increasing WWTP nutrient discharges into the lagoon and thus into the risk of the system to become eutrophic.

Ocean Exchange: Seasonal Dynamics and Effects of Stochastic Events

Nutrient loading into Ria Formosa lagoon showed a strong seasonal variation fuelling within lagoon metabolic processes that are apparent in the variables measured. The data on the carbon budget, with C being exported to the ocean in winter and retained in the lagoon in summer, suggest that the whole system metabolism is autotrophic in winter and heterotrophic in summer. This is supported by the seasonal variation of pH in the water column showing higher values in winter and

lower in summer. In winter, the net consumption of CO₂ by the whole system will be positive, increasing the pH. As temperature increases during summer, a higher relative importance of the system respiration versus production is expected, lowering the pH, as observed here. Santos et al. (2004) estimated the metabolic contributions of the main biological communities in a section of Ria Formosa lagoon in the summer, concluding that the whole ecosystem was in metabolic balance.

Temperature is probably the main driver of the summer nutrient dynamics as it increases remineralization (Serpa et al. 2007), thereby increasing the availability of ammonium. In addition, WWTP discharges of ammonium increase in summer due to increased visiting population loadings (Cabaço et al. 2008). Higher temperature and ammonium levels enhance activity of benthic producers (seagrasses, saltmarsh plants, and macroalgae; Asmus et al. 2000), leading to higher particle (seston) production (McGuirk Flynn 2008) as observed in Ria Formosa lagoon. Macrophytes are the dominant primary producers in the system and the major contributors to water column POM, with a minor contribution from microalgae (Machás et al. 2003), thereby explaining the positive associations found between temperature, seston, POC, DOC, and PON in this study. The increase of DOC in the summer is supported by the results of Santos et al. (2004) that showed that the benthic communities are net producers of DOC during this season in spite of the higher temperatures and consequent higher metabolism of microbes.

Our results suggest that P exchange is controlled by different processes than those that drive C and N fluxes. The strong, positive relation between PP and phytoplankton (Chl *a*) but not to other variables was evidenced by the second factor of PCA that explained 16 % of the variation of the whole data set. This probably reflects the much higher P content of microalgae compared to the benthic primary producers (Atkinson and Smith 1983). The phytoplankton population in the lagoon was found to be a mixture of lagoon and coastal zone algae (Brito et al. 2013), which is hence influenced both by an interaction of coastal zone and lagoon processes (e.g., currents, upwelling, and water mixing). This is probably why they do not correlate with the other variables.

Suggestions of P limitation of plankton production for part of the year were made by Falcão and Vale (1990). However, later studies failed to confirm this (e.g., Loureiro et al. 2005), in agreement with the results presented here that on an annual basis, P export to the ocean surpassed input. Phosphate showed a weak negative correlation with temperature and pH, indicating some role of metabolic processes in the dynamics of DIP. Sedimentary consumption was found to be positively correlated to phosphate concentration in the water in Ria Formosa lagoon, leading to higher sediment uptake rates in winter (Asmus et al. 2000). In contrast, sedimentary releases of phosphate were found in summer (Falcão and Vale

1990), mainly due to increases in remineralization rate (Serpa et al. 2007). This in agreement with our exchange data that generally show higher P export in summer and indicates the importance of benthic processes in the regulation of P exchange between Ria Formosa and the ocean, as has been observed in other coastal sediments (Serpa et al. 2007; Slomp 2011).

The nitrate levels were higher in winter than in the summer, responding to the higher groundwater and stream inputs in winter. These observations agreed with the long-term seasonal pattern of nitrate variation in the system (Barbosa et al. 2010). However, the N exchange results of both the first July cycle and the November cycle (Fig. 8) suggest a strong disruption of the general exchange pattern, driven by the extreme stochastic events that occurred at the time of sampling. The large drop observed in the water temperature in July indicates upwelling of deep oceanic nutrient-rich waters. This is supported by wind data from that period where a dominance of strong (north)western winds during several days preceding the sampling occurred, complying with the main upwelling conditions for this area (Relvas and Barton 2005). As a result, during this period, the system changed from a net nutrient exporter to a nutrient importer, as also reported recently by Cravo et al. (2014) under upwelling conditions. Conditions that cause upwelling currents to reach the Ria Formosa are relatively rare (Brito et al. 2012). Analyses of the available water temperature data of the period 2005–2008 show that on average, 15.7 ± 7.2 days of summer had temperatures compatible with upwelling events, i.e., 8.6 % of the summer period. The impact of summer upwelling on the annual nutrient budget of Ria Formosa lagoon may be considered low under current meteorological conditions but may become important if the number of upwelling events increases due to climate change.

The November anomaly coincided with heavy rainfall in the days prior to and during sampling, which resulted in important atmospheric and fluvial water inputs into the lagoon. Contrary to expectations, a net nutrient import from the ocean was found in this period. A likely explanation for this may be incomplete mixing of outflowing stream freshwater above the higher-density oceanic water, leading to reimport of the nutrient-rich water with the next incoming tide. This hypothesis is supported by the high-nutrient concentrations and reduced salinity of incoming ocean water during the morning flood as shown in Fig. 7. As the mouths of the main rivers (Gilão/Sequa and Almargem) are located in the narrow eastern sector of the Ria Formosa and discharge directly through the small Tavira inlet (Fig. 2), the majority of the water discharged by those rivers goes straight to the ocean, especially at ebb tide. Near-coastal currents in the area depend on the dominant wind direction (Relvas and Barton 2005). Wind data extracted from the Windguru (www.windguru.cz) archive showed that moderate to strong eastern winds prevailed in the week preceding the November cycle. Thus, most likely, nutrient-rich stream water that flows into the ocean through the

Tavira inlet was imported again with flood tides through the westerly Farol and Armona inlets, explaining the net import during this cycle.

It must be noted that some underestimation of the export may be expected due to an artifact caused by the exchange model, which considers tidal water flow, assuming equilibrium (i.e., all water entering with flood leaves again with ebb) and does not take into account water inputs from land and rainfall or losses due to evaporation. We estimated that for November 2006, the month with the highest freshwater input in the sampling period, the export would be approximately 2 % higher than in our exchange calculations but still an order of magnitude lower than the estimated import during the November cycle. Consequently, the net result would still be that there is a net import of nitrogen.

Budget

The differences in the calculated annual budget, including and excluding the extreme stochastic events, clearly demonstrate their importance on connectivity of Ria Formosa lagoon with the ocean, stressing the need for high-resolution sampling taking into account all potentially relevant processes. As these are still short-living and relatively rare events, we consider the annual budget excluding these cycles from the calculations as the most realistic estimate of the real budget under current conditions. Obviously, if the frequency of these events increases, their impact on total annual C, N, and P budgets will be more important.

The uncertainty surrounding the groundwater component may be relatively large, particularly in terms of N-leaching estimates. Nevertheless, our estimate of the average nitrate (NO_3^-) concentration of discharging groundwater is similar to the median nitrate concentration of observation wells in the groundwater of Ria Formosa watershed. Groundwater discharges of P are more difficult to assess but less important. P is much less mobile, due to the tendency to sorb on solids (e.g., iron oxides) or, in its ionized form, precipitate with dissolved cations such as calcium (Ca^{2+}) (e.g., Griffioen 2007). For these reasons, we used the average concentration of the monitoring wells of the area and the monthly flow estimates to quantify P discharge into the lagoon. With respect to C, the role of groundwater is still largely unknown. DOC concentrations can be important in groundwater (see review by Bauer and Bianchi 2011), but in general, inorganic carbon is the dominant component (Maher et al. 2013). Part of the DOC in groundwater may also originate from overlying seawater (Goñi and Gardner 2003).

Nutrient removal due to export of litter and plant parts (seagrasses and macroalgae) is generally not included in budgets due to difficulties of setting up representative sampling protocols, but they may represent a considerable sink (Flindt et al. 2007; McGlathery 2008). Nutrient export data in

1999/2000 in the form of litter were available for the small Barra inlet in the westernmost part of the Ria Formosa (Santos et al. unpublished data). Linearly extrapolating these values to the scale of the lagoon indicates that for C, litter export might be a relevant sink that could account for nearly 11 % of import, whereas for N and P, it is probably much less relevant (around 1 % of import). It must be said however that leaf litter export is highly variable and can be especially high during storms (Flindt et al. 2007); increased storm activity as predicted under climate change scenarios (Gastineau and Soden 2009), particularly when combined with high spring tides, may increase significantly the export to the ocean.

Shellfish harvest is being increasingly considered a potential mitigating measure for nutrient extraction in eutrophicated systems (Beseres Pollack et al. 2013). Ria Formosa lagoon is the main producer of shellfish in Portugal; about 10,000 t of bivalves are harvested annually (Santos et al. 2004). Taking into account published shellfish C, N, and P contents (Beseres Pollack et al. 2013; Smaal and Vonck 1997), this roughly corresponds to 1260.5, 7.3, and 0.8 t of C, N, and P, respectively. This is approximately 1.5 times the input of organic carbon; according to Santos et al. (2004), it accounts for nearly all organic carbon stored in the lagoon. For N and P, it represents approximately 1 % of the estimated input. Thus, we conclude that shellfish harvesting probably plays a large role on the C budget of the lagoon but that impacts on the N and P budgets are small.

Dissolved organic N and P analyses are often not included in budget studies mainly due to methodological problems (Aluwihare and Meador 2008). Recently, it has become clear that dissolved organic nutrients can form a very important fraction of total dissolved nutrients in temperate systems (Makings et al. 2014; McGuirk Flynn 2008). Dissolved organic nutrients have not been measured during this study. A limited number of data on both inorganic and total dissolved nitrogen and phosphorus is available online through SNIRH (the database of the Portuguese Water Institute INAG; <http://snirh.pt>), indicating that this might be quite important, although highly variable. However, the lack of detail on the precise nature of these samplings and their scarcity does not allow for straight conclusions at this moment, stressing the need for further studies on this subject.

Combining the above considerations for the general carbon budget, seafood harvest and to a much lesser degree litter export are important sinks as discussed above. Seafood harvest is in the same order of magnitude as export of DOC and POC to the ocean. Adding these to the measured export to the ocean, this means that in total, more than 2500 t C per year is exported from the lagoon. According to our data (Table 5), 34.9 % of this can be accounted for by the observed import of DOC and POC through streams and the WWTPs. Net primary production should be responsible for the remaining part, which should hence be in the order of 1600 t per year, minus

the groundwater contribution. Organic carbon in groundwater was not considered in this work, but in general, its concentration is low (Goñi and Gardner 2003), whereas groundwater can be an important source for inorganic carbon (Goñi and Gardner 2003; Santos et al. 2012).

In relation to the N budget with the outcome of the net annual exchange budget presented in Table 5, there is a missing sink of N of around 500 t N. This may be accounted for by the outcome of nitrogen fixation and denitrification processes that were not measured here. In temperate lagoons and estuaries, except for the Baltic Sea, the role of N fixation is generally modest in comparison to loadings from external sources (Herbert 1999). On the other hand, denitrification (including canonical denitrification and anammox) is recognized as one of the most important processes of N removal in coastal zones (Devol 2008). To close the N budget, the annual denitrification should be $\geq 47.9 \mu\text{mol m}^{-2} \text{h}^{-1}$. Published (canonical) denitrification rates for lagoons vary widely, depending on the environment in which it is measured and the measuring technique applied (Boynton and Kemp 2008). Nevertheless, the rate estimated here is close to the averages listed for lagoons, seagrass beds, mudflats, and coastal wetlands (21, 29, 71, and $94 \mu\text{mol m}^{-2} \text{h}^{-1}$, respectively; Boynton and Kemp 2008). We conclude that denitrification can be a major nitrogen removal process (as N_2) from Ria Formosa lagoon, of the same order of magnitude as the export to the ocean.

Considering the P budget, and similarly to the N budget, there might be relevant inputs of DOP in the form of probably wastewater and agricultural runoff (McGuirk Flynn 2008; Slomp 2011). Inputs from the ocean are only relevant in oligotrophic zones as total concentrations are generally low (Miyajima et al. 2007; Slomp 2011). To obtain better estimates of the P budget, it is important to assess the DOP dynamics of the system.

Concluding Remarks

On an annual basis, nutrient (C, N, and P) input in the Ria Formosa is dominated by WWTP discharge and groundwater outflow. In general, there is a continuous export of particulate and dissolved organic (C) and inorganic (N and P) nutrients, fertilizing the coastal ocean. Extreme stochastic events, such as strong rainfall and oceanic upwelling, strongly disrupt the general pattern. If the frequency of these events will increase, as predicted under global climate change, this will have great consequences on the annual nutrient budget and consequently on the ecological functioning of Ria Formosa lagoon. This study was initiated as part of a project on macroalgal blooms growing both in the lagoon in winter and in spring/summer in the adjacent coastal ocean in order to try to identify major nutrient sources for these algae. Although nutrient concentrations in the coastal zone are low, the continuous nutrient

outflow displayed in this study may support these blooms. Management policies should firstly be focused on the development of more advanced wastewater treatment plants as a first step to reduce the nutrient loads to Ria Formosa and to the coastal ocean. Furthermore, changes in irrigation practices will have to be critically considered as they strongly effect groundwater flow and through that the nutrient budget of the lagoon.

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