



Research article

Climatic and anthropogenic factors driving water quality variability in a shallow coastal lagoon (Aveiro lagoon, Portugal): 1985–2010 data analysis

**Marta Rodrigues^{1,*}, Henrique Queiroga², Anabela Oliveira³, Vanda Brotas⁴
and Maria D. Manso⁵**

¹ National Laboratory for Civil Engineering, Hydraulics and Environment Department, Estuaries and Coastal Zones Unit, Lisbon, Portugal

² University of Aveiro, CESAM & Biology Department, Aveiro, Portugal

³ National Laboratory for Civil Engineering, Hydraulics and Environment Department, Information Technology in Water and Environment Group, Lisbon, Portugal

⁴ University of Lisbon, Faculty of Sciences, MARE, Lisbon, Portugal

⁵ University of Aveiro, Physics Department, Aveiro, Portugal

* **Correspondence:** Email: mfrodrigues@lnec.pt; Tel: +00351-218-443-613.

Abstract: Understanding the natural variability of coastal ecosystems, and in particular distinguishing between the natural fluctuations and the ones that are caused by anthropogenic interventions and long-term climatic variability, is a major concern for establishing adequate management and adaptation strategies. The Aveiro lagoon, a shallow coastal lagoon (Portugal), holds one of the largest saltmarshes and saltpans in Europe and is a very important ecosystem from both economic and ecological viewpoints, making the protection of its water masses a requirement. To better understand the variability of its ecosystem, the factors controlling seasonal, inter-annual and long-term variability of the water quality in the Aveiro lagoon were thus analyzed. The statistical analysis was based on a set of climatic, hydrological and water quality observations undertaken between 1985 and 2010. Seasonal variations were mostly related with the seasonal variation of the main climatic and hydrological drivers, while long-term shifts were typically driven by the anthropogenic interventions in the lagoon. After the adoption of secondary treatment for industrial effluents on 1992, a recovery from hypoxia conditions occurred in the upstream area of the lagoon. After 2000 lower concentrations of silicates occurred downstream, and may also derive from some anthropogenic modifications (e.g., shunting of river water to the sewage system, deepening of the inlet) that may have affected the physical dynamics. In the downstream area of the lagoon, chlorophyll *a* presented a downward trend between 1985 and 2010 and lower concentrations after

2000, which were probably associated with the lower concentrations of silicates. Results from the data analysis showed that the seasonal, inter-annual and long-term trends observed in the Aveiro lagoon depend on the influence of both anthropogenic and climate drivers, putting in evidence the need to combine these different drivers when evaluating and developing management strategies for estuarine ecosystems.

Keywords: Long-term variability; Chlorophyll *a*; dissolved oxygen; nutrients; estuaries

1. Introduction

The need for protection and conservation of estuaries has been recognized worldwide, as these systems harbor invaluable habitats and provide multiple ecosystem services [1]. The large diversity of activities developed in estuaries causes, in many cases, threats and pressures over their ecosystems, which may lead to a loss of ecological health and, consequently, to the degradation of their quality. One of these threats is the nutrients enrichment (e.g., due to domestic and industrial wastewater discharges) that may potentiate eutrophication. Although periodical episodes of eutrophication are natural in estuarine ecosystems [2], cultural eutrophication is increasing worldwide [3] with potentially negative consequences, such as the loss of biodiversity and replacement by opportunistic species, or local hypoxic and anoxic conditions [4,5].

Estuarine ecosystems present a natural variability dependent on several physical-chemical characteristics. Hydrodynamics and morphology combined with the freshwater runoff affect the residence times, the water column stratification, the sediments in the water column, the light penetration and the nutrients availability [2,6] in temporal scales that vary from daily to seasonal. Water temperature, influenced by heat exchanges with the atmosphere, and vertical mixing, influenced by wind and tides, may also affect the dynamics of estuarine ecosystems [7,8]. However the relative importance of these several drivers in the estuarine ecosystems dynamics, and, in particular, in the lower trophic levels, is not consensual and is still a matter of discussion [9]. The actual concern about climate change, which may induce modifications in air temperature, hydrological regimes and mean sea level, also enhances the need to deeply understand the system response to these forcings [10]. In addition, in order to fully understand the role of the main drivers in the estuarine ecosystem dynamics and to develop sustainable management strategies, there is a need to integrate both the system response to the physical drivers and the anthropogenic pressures [11]. This goal can be achieved through long-term comprehensive studies [6] that allow the understanding of the system natural variability. Although numerous studies aimed at evaluating the estuarine water masses and ecosystems quality based on a set of indicators [12], long-term integrated studies about the estuarine water quality are still scarce [6,13].

The Aveiro lagoon, located in the northwest coast of Portugal (Figure 1), holds one of the largest saltmarshes and salt pans in Europe, harboring several ecologically relevant species of flora and fauna, in particular migratory birds. The lagoon is classified as a special area of conservation. As many other coastal lagoons and estuaries, due to its privileged location at the interface sea-land, it supports several human activities (aquaculture, artisan fishing, tourism, nautical and port facilities, salt collection and industries). The lagoon was classified with moderate low overall eutrophic condition [14], but the quality status of different areas within the system can vary [15]. The untreated

or poorly treated industrial and domestic effluents that were discharged directly into the lagoon in the past were one of the pressures that contributed to a degradation of its quality [16]. Some efforts have been made to reduce this pressure in the Aveiro lagoon and an integrated wastewater treatment and disposal system was constructed, which discharges most of the treated domestic and industrial effluents in the Atlantic Ocean.

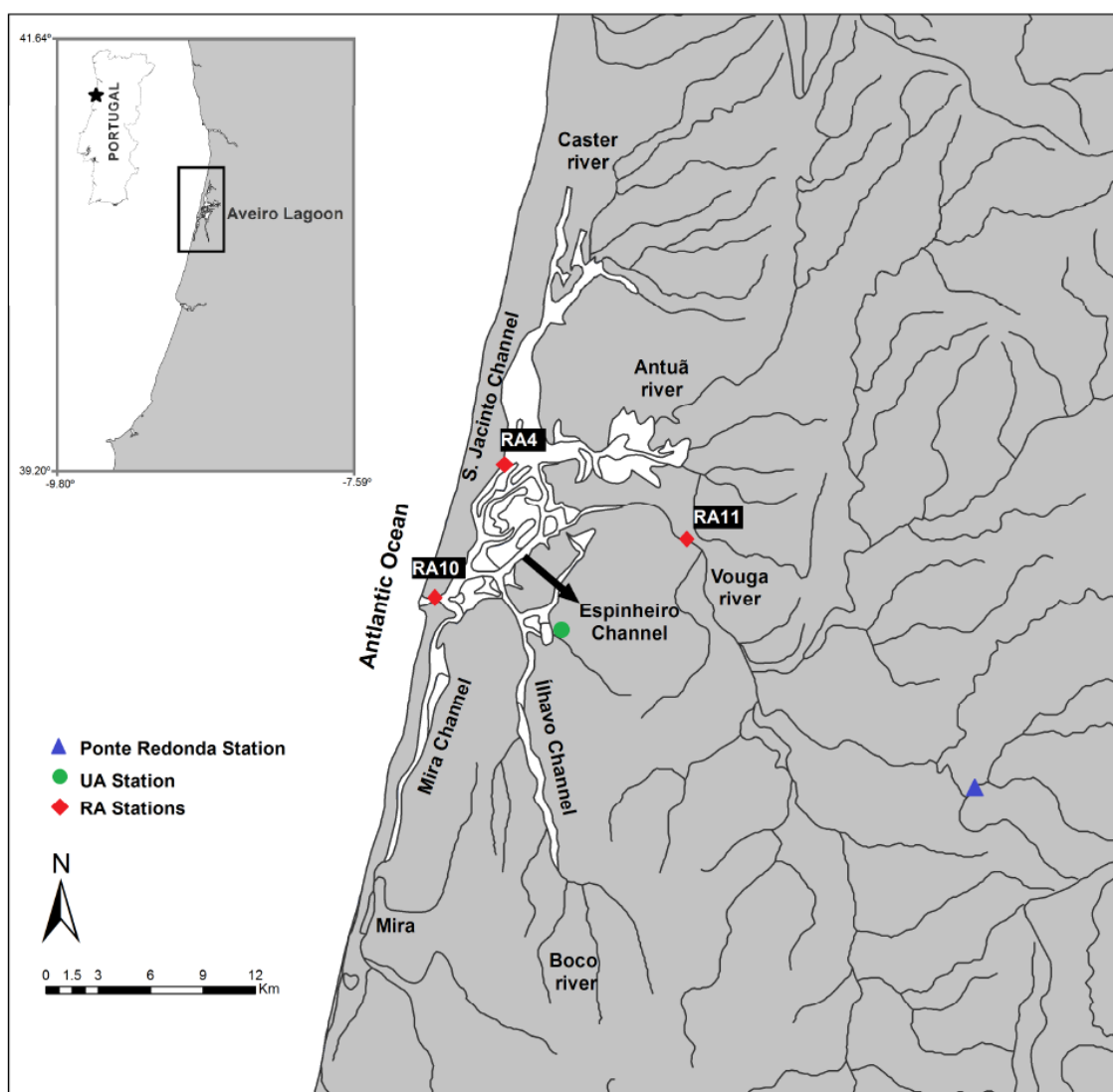


Figure 1. Schematic overview of the Aveiro lagoon and location of the water quality stations (RA stations), University of Aveiro meteorological station (UA station) and Ponte Redonda hydrometric station.

Several studies aimed at characterizing the water quality and ecological dynamics in the Aveiro lagoon. They looked for establishing and evaluating the relationships between these dynamics and the main climatic or hydrological forcings [15,17-19] or, to a smaller extent, the anthropogenic pressures [20], contributing thus significantly for the knowledge about the lagoon dynamics. However, these studies were severely limited by the short duration of the datasets used and most of them did not considered simultaneously the influence of anthropogenic and climatic forcings.

This study aimed thus at evaluating the water quality dynamics in the Aveiro lagoon relative to the climate variability and the anthropogenic interventions in this lagoon. The analysis was performed over a period of 25 years (1985–2010) and aims at contributing to the knowledge about the system's natural variability, the impacts of the management measures undertaken in the past and, ultimately, to provide information that allows the development of sustainable management strategies for the Aveiro lagoon in a climate change context. Results show that the seasonal, inter-annual and long-term trends observed in the water quality of the lagoon depend on the influence of both anthropogenic and climate forcings and stress the need to use integrated approaches in the development of management strategies that consider these drivers.

2. Materials and methods

2.1. Study area

The Ria de Aveiro is a coastal lagoon located in the northwest coast of Portugal (40°38'N, 8°45'W), about 45 km long, from Ovar to Mira, and up to 10 km wide. It spreads over four main channels (Mira, Ílhavo, Espinheiro and S. Jacinto channels), with several branches, and connects to the sea through one artificial channel of about 1.3 km (Figure 1). The lagoon is very shallow with exception of the navigation channels, where the depths range from 7 to 20 m and are maintained artificially. The circulation in the lagoon is mainly driven by tide and its area varies from 66 km² at low tide to 83 km² at high spring tide [21]. The lagoon is mesotidal and tides are semi-diurnal. The tidal range at the inlet mouth varies between 0.6 and 3.2 m, with an average of 2 m [22]. The mean tidal prism is of about 70×10^6 m³ [21]. Comparatively to tide, the annual mean freshwater input during a tidal cycle is relatively small, of about 1.8×10^6 m³ [23]. The main sources of freshwater in the lagoon are the rivers Vouga and Antuã, which flow through the Espinheiro channel [22]. Some uncertainty remains about the mean flows of these rivers, mainly due to the lack of recent data.

2.2. Data description

The datasets used in this study included atmospheric, hydrological and water quality variables and come from different sources. The analysis is conducted for the period from 1985 to 2010.

Atmospheric data were obtained from the University of Aveiro meteorological station, including daily values of air temperature, total solar radiation, rainfall and wind intensity (monthly values are presented in Figure 2).

River flow data from the Ponte Redonda station were used—available at the SNIRH database (<http://snirh.pt>). This station only covers part (ca. 10%) of the water catchment area of the Vouga River (approximately 2350 km²). However, the data available for the Angeja station, which covers the whole water catchment area of the Vouga River, is limited in time, and the Ponte Redonda station is the only one with data available throughout the period under analysis. Preliminary evaluation showed that the water levels at the two stations have a significant positive correlation, with Pearson correlation coefficient of $r_P = 0.86$ ($N = 1235$, $p < 0.0001$). Thus, the Ponte Redonda data represents the main patterns of variation and was considered adequate for the aims of the present study, regarding the evaluation of the trends and relations between the water quality variables and the main physical forcing. Mean monthly values of river flow in the Ponte Redonda station are presented in

Figure 2. Daily and monthly values of North Atlantic Oscillation (NAO) index were obtained from the NOAA website (<http://www.cpc.ncep.noaa.gov>, Figure 3).

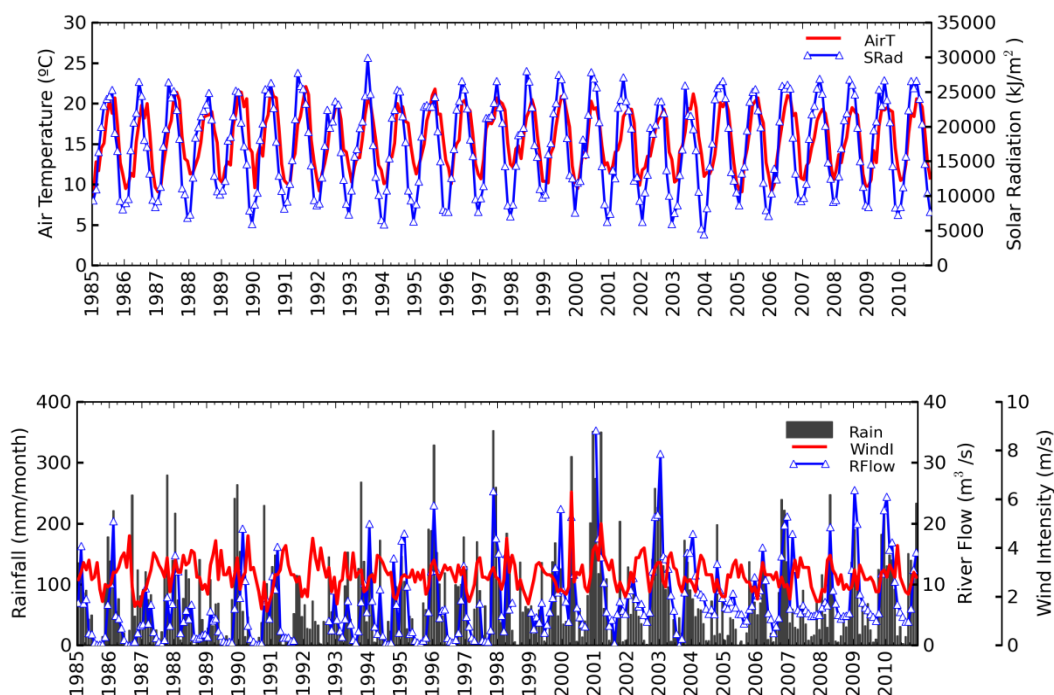


Figure 2. Monthly values of the time series of atmospheric parameters measured at the University of Aveiro meteorological station (Rain—total monthly rainfall, WindI—monthly mean wind intensity, AirT—monthly mean air temperature, SRad—monthly mean total solar radiation) and of monthly mean river flow measured at Ponte Redonda, from 1985 to 2010.

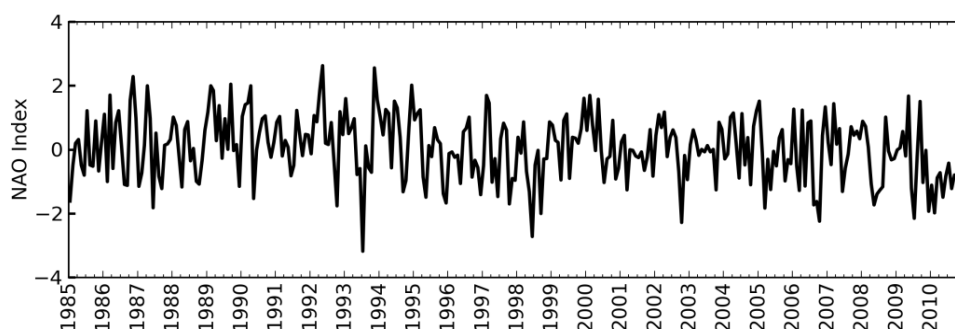


Figure 3. Monthly NAO index from 1985 to 2010.

Water quality parameters were obtained from the monitoring program POL-Aveiro developed by the Instituto Hidrográfico [24]. This program started in 1981 and the periodicity of sampling changed through time, presently occurring twice a year, in summer and winter [24,25]. All samples were collected during ebb conditions. Additional details from the sampling strategy and laboratorial analyses can be found in [25]. The data obtained in the late winter (late January, February or March)

and late summer (late August, September or October) was used in the present study. The following variables were selected (Figure 4): salinity, water temperature, chlorophyll *a* (used as a proxy for phytoplankton), dissolved oxygen and nutrients (ammonium, nitrates + nitrites, phosphates and silicates). To represent the spatial variability along the Aveiro lagoon the data from three sampling stations (RA) were acquired (Figure 1): (i) station RA10, located near the mouth of the lagoon, aims to represent the oceanic/marine influence; (ii) station RA4, located in the intermediate zone of the lagoon, in the S. Jacinto channel, which has the largest tidal prism, aims to represent an area of mixture between the freshwater and the marine water; and (iii) station RA11, which is located near the riverine boundary of the lagoon, under the influence of the main river flowing to the lagoon—the Vouga river [21,22]. Given the spatial variability of the water quality variables during the sampling period [25], these stations are representative of the main patterns observed in the lagoon.

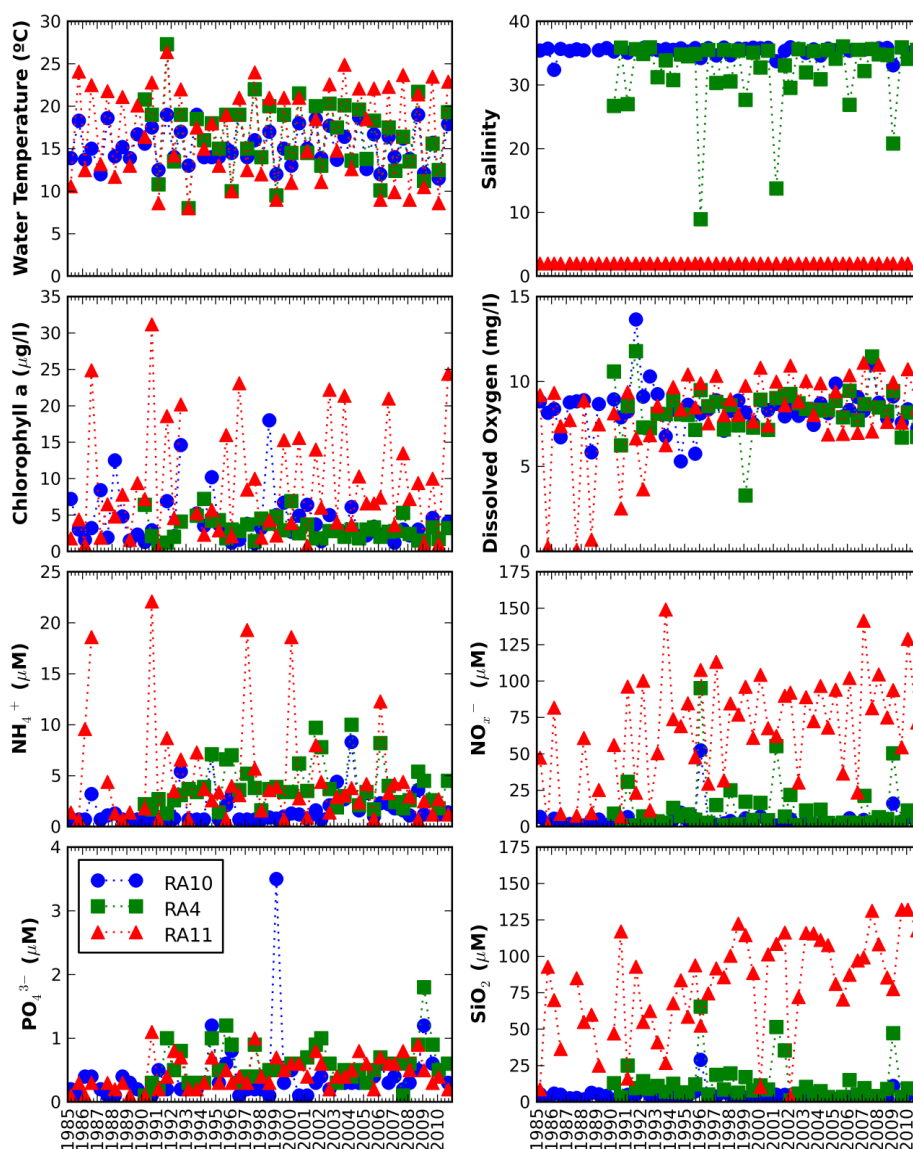


Figure 4. Time series of physical and bio-chemical parameters measured at three stations along the Ria de Aveiro (RA10, RA4 and RA11) from 1985 to 2010 (NH_4^+ —ammonium, NO_x^- —nitrates+nitrites, PO_4^{3-} —phosphates, SiO_2 —silicates).

2.3. Data analyses

The data analyses performed here aimed (1) to identify the main spatial and temporal patterns of the water quality along the Aveiro lagoon over the past 25-years, and (2) to understand its variations in the scope of the variability of climatic and hydrological drivers and of the anthropogenic interventions in the lagoon. The datasets were summarized over the period 1985–2010 through basic statistics, including the determination of mean, median, minimum, maximum, standard deviation and percentile 90 of each variable.

To evaluate the temporal variations at different scales (seasonal and long-term) autocorrelation and standardized anomalies were calculated. The stationarity of the water quality time series used in the autocorrelation analysis was achieved by differencing the series by a lag of 1. The standardized anomalies were computed at three temporal scales [26]:

(i) the standardized monthly (atmospheric and river flow data) or seasonal (water quality data) anomaly (z_{mt}),

$$z_{mt} = \frac{x_{m_25y} - \bar{x}_{25y}}{\sigma_{25y}}$$

where x_{m_25y} is the long-term mean of each month or season, \bar{x}_{25y} is the 25-years mean and σ_{25y} is the 25-years standard deviation;

(ii) the standardized inter-annual anomaly (z_y),

$$z_y = \frac{x_y - \bar{x}_{25y}}{\sigma_{25y}}$$

where x_y is the yearly mean of each year available;

and iii) the standardized individual monthly (atmospheric and river flow data) or seasonal (water quality data) anomaly (z_{m_y}),

$$z_{m_y} = \frac{x_{m_y} - \bar{x}_{m_25y}}{\sigma_{m_25y}}$$

where x_{m_y} is the mean of each month or season of each year, \bar{x}_{m_25y} is the 25-years mean of each month and σ_{m_25y} is the standard deviation of each month or season over the 25-years period.

The major changes in the atmospheric and river flow data over the 1985 to 2010 period were summarized with the cumulative sums method (CUSUM). The major long-term variations of the water quality variables were evaluated using an automatic sequential algorithm proposed by [27]. The STARS (sequential t-test analysis of regime shifts) algorithm detects regime shifts based on the mean of consecutive regimes of the time series that are statistically significant according to the Student's t-test and computes a regime shift index (RSI). The sign of the RSI indicates the variation of the regime relative to the mean, while its absolute value specifies the magnitude of the shift [26,28]. Due to the use of a sequential data processing technique, STARS has the ability to detect regime shifts relatively early and allows monitoring how their magnitude changes in time [27]. A detailed description of the STARS algorithm can be found in [27]. In the present analysis a minimum regime length of 10 years was considered and two probability levels were evaluated ($p = 0.05$ and $p = 0.10$). The long-term trend of each variable was also assessed. Linear regression over the standardized individual monthly

(atmospheric and river flow data) or seasonal (water quality data) anomalies was used, which correspond to the deseasonalized time series.

To evaluate the main relations between the variables, Spearman rank (r_s) correlations were calculated. This correlation coefficient was chosen because it evaluates the relationship between the variables without making any assumptions about the nature of this relationship. The correlations among the atmospheric, river flow and NAO index data were based on the monthly values. For these variables, cross-correlation was performed over the monthly data to estimate the degree to which the time series correlate. Autocorrelation and trend were removed from the time series used in the cross-correlation analysis. For the correlations among the water quality and climatic variables, four different periods of integration were considered for the climatic and hydrological variables specification. These periods were the 8 days [6], 1 month, 3 months and 6 months before the sampling date of the water quality variables, and aimed to evaluate the degree to which the previous climatic and hydrological variations influence the water quality, over time windows of different length. For each one of these periods mean values of air temperature, solar radiation, wind intensity and river flow, and accumulated rainfall were calculated. For the NAO index the daily value of the date of sampling was used. As multiple comparisons were performed in the correlation analysis, the Bonferroni correction [29] was used.

Principal components analysis (PCA) was also used to investigate the relative importance of the water quality parameters, the similarities between years and the relations of each principal component with the climatic and hydrological variables, following an approach similar to the one described by [30]. The results of this analysis revealed only trivial (seasonal) or redundant patterns relative to the ones evidenced by the other analyses performed and are not presented here.

3. Results

3.1. Climatic characterization

Air temperature and solar radiation exhibited an expected seasonal pattern (Figure 2), characterized by maximum standardized monthly anomalies during August and July, and minimum standardized monthly anomalies in January and December. A positive correlation was found between these two variables (Table 1), which was maximal with a time lag of 1 month. In the 25-years period, 1989, 1995 and 1997 were the warmest years (Figure 5). A detailed analysis of the CUSUM results (Figure 5) puts in evidence a global tendency for lower air temperatures between 1990 and 1995, followed by significantly warmer years until 1998 and alternations between colder and warmer years between 1998 and 2010.

Rainfall also varied seasonally (Figure 2), as expected, with maximum standardized monthly anomalies occurring in late autumn and winter. The lowest rainfall was observed in 2004–2005, while 1996–1997 and 2000–2001 were rainy years (Figure 5). Three distinct periods were observed regarding the trend (Figure 5): a period marked by decreasing rainfall until 1992, followed by a period of rainiest years until 2003 and then a period of drier years (2004–2008). A positive correlation was found between the river flow and rainfall (Table 1), which was maximal without any time lag.

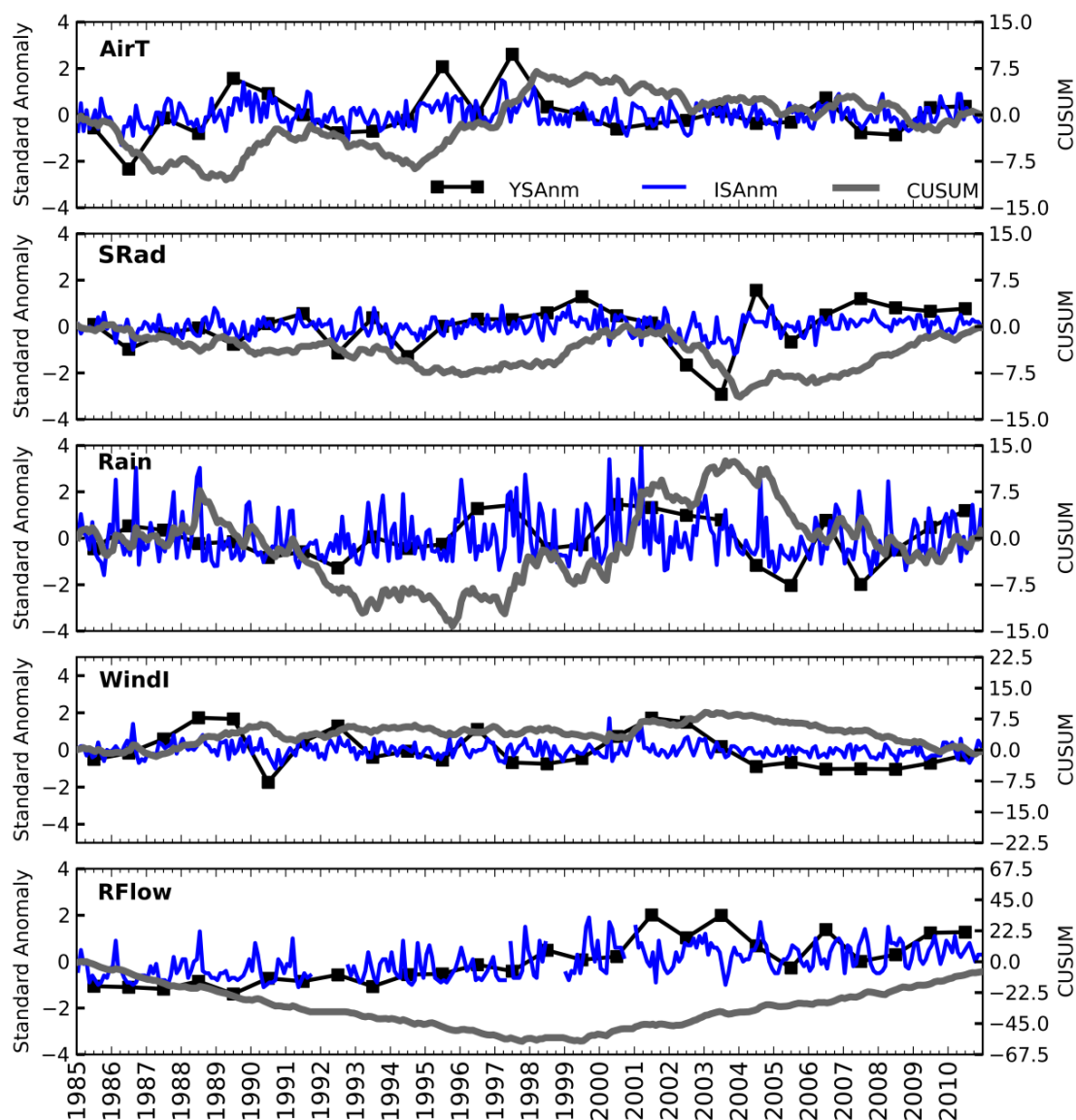


Figure 5. Standardized year anomaly (YSAnm), standardized individual monthly anomaly (ISAnm) and CUSUM for the atmospheric parameters and river flow from 1985 to 2010 (AirT—air temperature, SRad—solar radiation, Rain—rainfall, WindI—wind intensity, RFlow—river flow).

During the analyzed period, linear regression of the deseasonalised time series suggests a slight decrease in wind intensity, which is more evident after 2003 (Table 1).

The NAO index also presented a slight downward trend during the 1985 to 2010 period (Figure 3). Although significant correlations were found between this variable and the other climatic and hydrological variables, their magnitude is low (Table 1).

Table 1. Spearman rank correlations between atmospheric data (AirT—air temperature, SRad—solar radiation, Rain—rainfall, WindI—wind intensity), river flow (RFlow) and NAO index based on discrete data with no time lag (significant correlations with Bonferroni corrections are marked for $*p < 0.05$, $p < 0.01$ and $***p < 0.001$).**

	AirT	SRad	Rain	WindI	RFlow	NAO
AirT	1					
SRad	0.754***	1				
Rain	-0.481***	-0.640***	1			
WindI	0.171*	0.399***	-0.004	1		
RFlow	-0.594***	-0.515***	0.652***	0.075	1	
NAO	-0.173*	-0.092	-0.219**	-0.176**	-0.081	1

3.2. Water quality variables characterization

Salinity presented a marked seasonal pattern at both stations RA10 and RA4 (Figure 4). No significant variability was observed at station RA11, which presents clear freshwater characteristics. Water temperature also presented a seasonal variation, the larger temperatures occurring during summer, as expected.

Chlorophyll *a* presented seasonal variations throughout all the stations, with larger concentrations during summer (Figure 6). A downward trend was observed at stations RA10 and RA4 (Figure 6, Figure 7 and Figure 8), while at station RA11 a slightly upward trend occurred (Figure 6). A regime shift was predicted in 2004 at station RA10 (Figure 7), the mean concentration decreasing to 2.4 $\mu\text{g/L}$, and in 2001 at station RA4 (Figure 8). At station RA11 chlorophyll *a* correlated negatively with nitrates + nitrites and dissolved oxygen, while no significant correlations were found at the other stations (Table 2, Table 3 and Table 4).

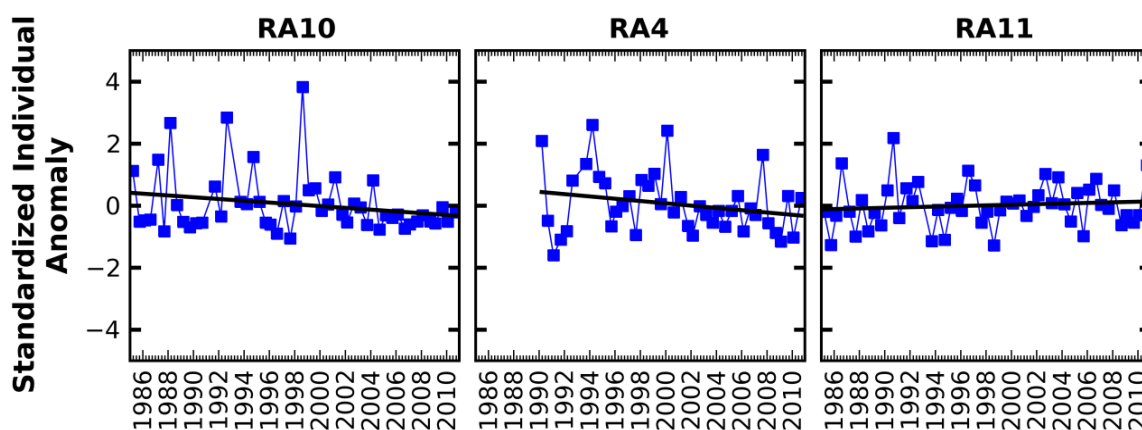


Figure 6. Chlorophyll *a* standardized individual seasonal anomalies (squared line) and linear correlation (solid line) at stations RA10, RA4 and RA11.

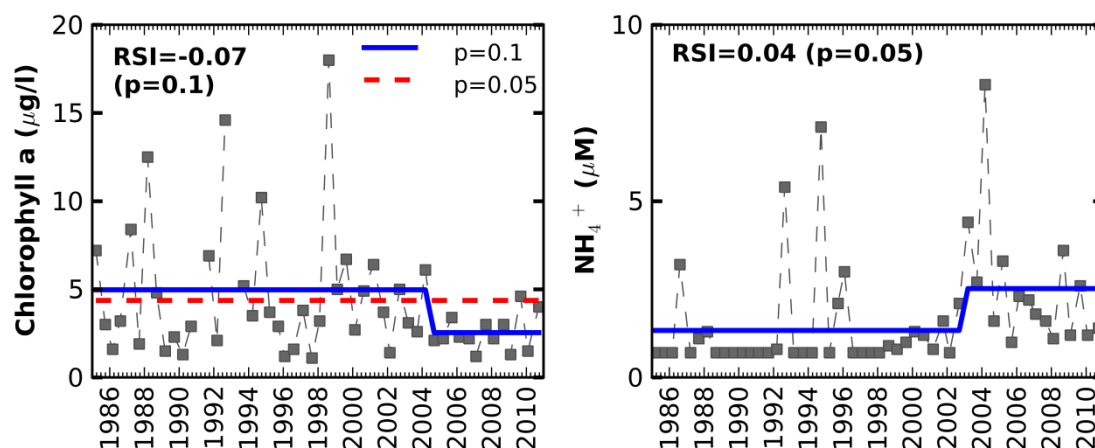


Figure 7. Shifts in chlorophyll *a* and ammonium (NH_4^+) concentrations at station RA10 (filled squares—variables concentration, solid and dashed line—regime mean, RSI—Regime Shift Index).

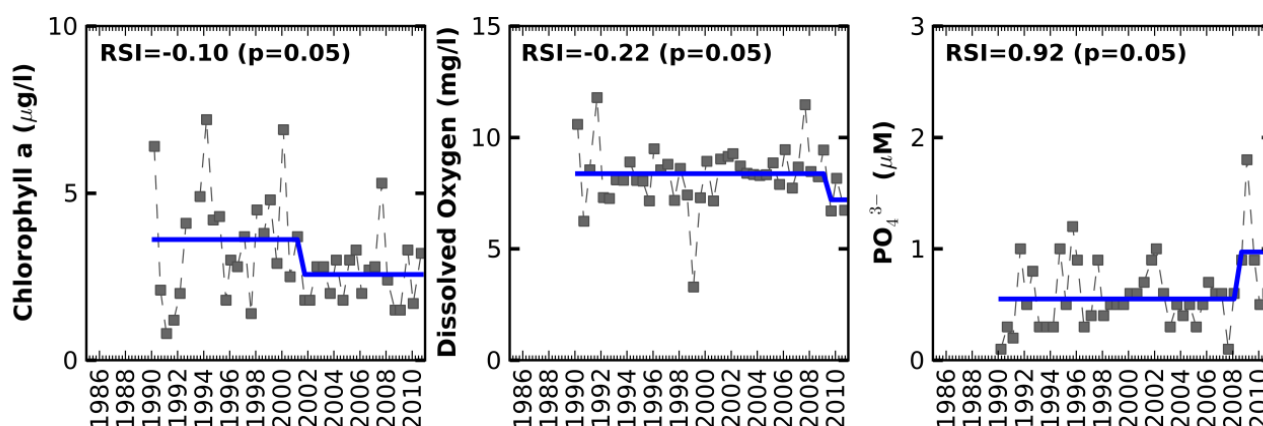


Figure 8. Shifts in chlorophyll *a*, dissolved oxygen and phosphates (PO_4^{3-}) concentrations at station RA4 (filled squares—variables concentration, solid line—regime mean, RSI—Regime Shift Index).

Mean dissolved oxygen concentrations were similar at all stations, of about 8 mg/L. Until 1993 dissolved oxygen remained relatively low at station RA11 and a regime shift occurred in 1994 (Figure 9), with an increase in the regime mean to 9.0 mg/L. At this station dissolved oxygen correlated negatively with water temperature and positively with nitrates + nitrites (Table 4). At station RA4 a regime shift was predicted in 2009 (Figure 8).

Nitrates + nitrites and silicates presented marked seasonal patterns, with larger concentrations during winter. These two variables were positively correlated (Table 2 and Table 3). Seasonal variations of ammonium were also observed at stations RA10 and RA11. Phosphates did not present a defined seasonal pattern throughout all stations. At stations RA10 and RA4, ammonium and phosphates presented an upward trend, while silicates presented a downward trend. Regime shifts were predicted for ammonium in 2003 at station RA10 (Figure 7) and for phosphates in 2008 at station RA4 (Figure 8). At station RA11 regimes shifts were observed for nitrates + nitrites (1993

and 2010) and silicates (1997 and 2009), both characterized by an increase of the concentrations of these nutrients (Figure 9). At this station, two regime shifts were also observed for phosphates: a first increasing shift in 1997 and an inverse shift in 2009 (Figure 9).

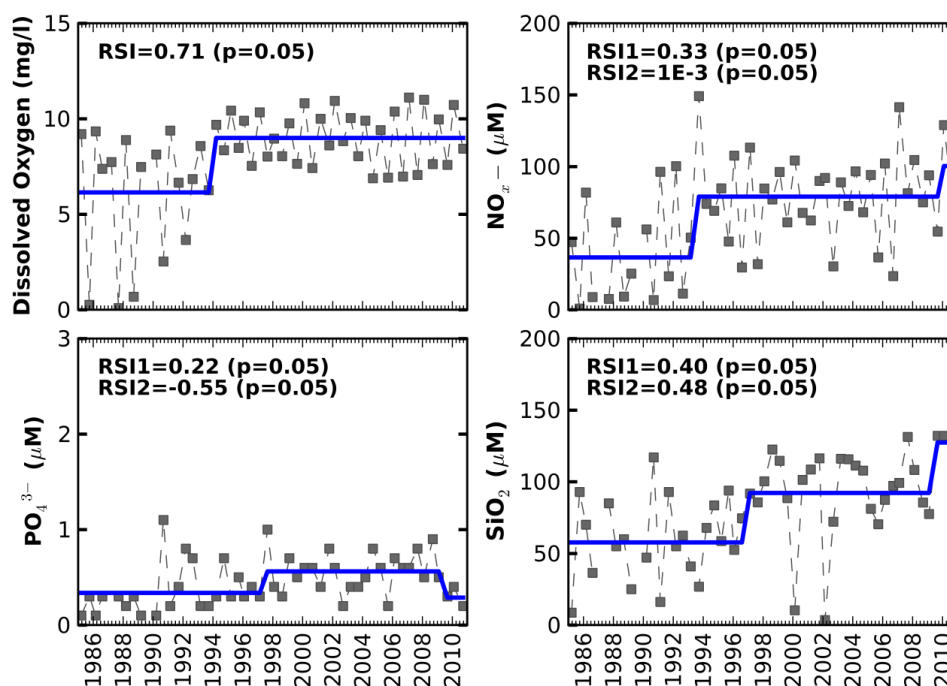


Figure 9. Shifts in dissolved oxygen, nitrates + nitrites (NO_x⁻), phosphates (PO₄³⁻) and silicates (SiO₂) concentrations at station RA11 (filled squares—variables concentration, solid line—regime mean, RSI—Regime Shift Index).

3.3. Relationships between water quality and climatic and hydrological variables

Relationships between the water quality and the climatic and hydrological variables are presented in Table 2, Table 3 and Table 4. Since four integration periods were considered for the climatic and hydrological variables (8 days, 1 month, 3 months or 6 months before the sampling of the water quality variables), only the maximum correlation obtained between each pair of variables is given.

Salinity, at the downstream stations, and water temperature, at all stations, were significantly correlated with the atmospheric and river flow variables, showing the marked seasonal pattern of these variables and the influence of the climatic and hydrological drivers in establishing these properties.

No significant correlations were found between chlorophyll *a* and the physical parameters at stations RA10 and RA4. At station RA11, chlorophyll *a* correlated positively with air temperature, solar radiation and wind intensity, and negatively with rainfall and river discharge, putting in evidence the seasonal variation of the biological activity. At this station, the correlations found between dissolved oxygen and the physical variables were opposite of those observed for chlorophyll *a* (Table 4). The maximum correlations were found when considering the climatic and hydrological data integrated over 1 or 3 months prior to the sampling date of the water quality variables, suggesting different “time lags” between the bio-chemical and the physical processes.

Table 2. Spearman rank correlations between water quality variables at station RA10 (Salt—salinity, WTemp—water temperature, Chl a—chlorophyll *a*, DO—dissolved oxygen, NH₄⁺—ammonium, NO_x[−]—nitrates + nitrites, PO₄^{3−}—phosphates, SiO₂—silicates) and climatic and hydrological variables (AirT—air temperature, SRad—solar radiation, Rain—rainfall, WindI—wind intensity, RFlow—river flow, NAO—NAO index). Significant correlations for $p < 0.05$ with Bonferroni correction are marked with *.

	Salt	WTemp	Chl a	DO	NH ₄ ⁺	NO _x [−]	PO ₄ ^{3−}	SiO ₂
Salt	1							
WTemp	0.459	1						
Chl a	0.036	0.143	1					
DO	−0.357	−0.274	−0.036	1				
NH ₄ ⁺	0.049	0.019	0.064	−0.144	1			
NO _x [−]	−0.159	−0.668*	−0.199	−0.112	0.026	1		
PO ₄ ^{3−}	0.022	−0.492*	−0.251	−0.294	0.374	0.739*	1	
SiO ₂	−0.278	−0.170	−0.077	−0.073	−0.144	0.516*	0.261	1
AirT	0.626* (1 m)	0.850* (3 m)	0.195 (8 d)	−0.506* (6 m)	0.147 (6 m)	−0.555* (8 d)	−0.439 (1 m)	−0.129 (8 d)
SRad	0.660* (3 m)	0.746* (3 m)	0.324 (1 m)	−0.359 (6 m)	0.175 (6 m)	−0.554* (1 m)	−0.385 (1 m)	−0.286 (8 d)
Rain	−0.658* (3 m)	−0.620* (3 m)	−0.225 (1 m)	0.187 (3 m)	−0.164 (3 m)	0.464 (1 m)	0.365 (1 m)	0.336 (3 m)
WindI	0.282 (6 m)	0.759* (6 m)	0.383 (6 m)	−0.265 (6 m)	−0.198 (8 d)	−0.487* (6 m)	−0.433 (6 m)	0.268 (8 d)
RFlow	−0.632* (3 m)	−0.564* (1 m)	−0.204 (1 m)	0.435 (3 m)	0.319 (6 m)	0.374 (1 m)	0.266 (8 d)	0.205 (1 m)
NAO	0.195	0.170	−0.134	0.106	−0.407	−0.085	−0.193	0.148

Table 3. Spearman rank correlations between water quality variables at station RA4 (Salt—salinity, WTemp—water temperature, Chl a—chlorophyll a, DO—dissolved oxygen, NH_4^+ —ammonium, NO_x^- —nitrates + nitrites, PO_4^{3-} —phosphates, SiO_2 —silicates) and climatic and hydrological variables (AirT—air temperature, SRad—solar radiation, Rain—rainfall, WindI—wind intensity, RFlow—river flow, NAO—NAO index). Significant correlations for $p < 0.05$ with Bonferroni correction are marked with *.

	Salt	WTemp	Chl a	DO	NH_4^+	NO_x^-	PO_4^{3-}	SiO_2
Salt	1							
WTemp	0.607*	1						
Chl a	-0.086	-0.102	1					
DO	-0.499	-0.197	0.002	1				
NH_4^+	-0.330	-0.067	-0.114	0.022	1			
NO_x^-	-0.788*	-0.612*	0.185	0.310	0.187	1		
PO_4^{3-}	0.074	0.109	-0.398	-0.023	0.427	0.065	1	
SiO_2	-0.683*	-0.307	-0.012	0.271	0.241	0.639*	0.133	1
AirT	0.810* (8 d)	0.857* (8 d)	-0.212 (6 m)	-0.405 (3 m)	-0.196 (8 d)	-0.710* (8 d)	0.333 (6 m)	-0.497 (8 d)
SRad	0.799* (1 m)	0.730* (1 m)	-0.215 (6 m)	-0.469 (1 m)	-0.173 (8 d)	-0.757* (1 m)	0.299 (6 m)	-0.569* (8 d)
Rain	-0.809* (6 m)	-0.557* (3 m)	-0.252 (1 m)	0.417 (3 m)	0.329 (8 d)	0.777* (3 m)	0.294 (8 d)	0.606* (3 m)
WindI	0.515* (6 m)	0.723* (6 m)	-0.171 (8 d)	0.196 (8 d)	0.272 (8 d)	-0.433 (6 m)	0.382 (8 d)	0.449 (8 d)
RFlow	-0.664* (3 m)	-0.543* (1 m)	0.195 (3 m)	0.487 (3 m)	-0.096 (3 m)	0.711* (3 m)	0.006 (8 d)	0.434 (3 m)
NAO	0.123	0.322	-0.055	-0.012	-0.129	-0.089	-0.197	-0.038

Table 4. Spearman rank correlations between water quality variables at station RA11 (Salt—salinity, WTemp—water temperature, Chl a—chlorophyll a, DO—dissolved oxygen, NH_4^+ —ammonium, NO_x^- —nitrates + nitrites, PO_4^{3-} —phosphates, SiO_2 —silicates) and climatic and hydrological variables (AirT—air temperature, SRad—solar radiation, Rain—rainfall, WindI—wind intensity, RFlow—river flow, NAO—NAO index). Significant correlations for $p < 0.05$ with Bonferroni correction are marked with *.

	Salt	WTemp	Chl a	DO	NH_4^+	NO_x^-	PO_4^{3-}	SiO_2
Salt	1							
WTemp	-	1						
Chl a	-	0.740*	1					
DO	-	-0.733*	-0.484*	1				
NH_4^+	-	-0.002	0.131	0.106	1			
NO_x^-	-	-0.657*	-0.480*	0.692*	0.264	1		
PO_4^{3-}	-	0.136	0.294	-0.02	0.338	0.164	1	
SiO_2	-	0.312	0.246	-0.008	0.012	0.07	0.393	1
AirT	-	0.924* (8 d)	0.690* (8 d)	-0.722* (1 m)	-0.131 (3 m)	-0.670* (1 m)	0.229 (6 m)	0.402 (6 m)
SRad	-	0.800* (1 m)	0.724* (1 m)	-0.745* (3 m)	-0.245 (8 d)	-0.674* (8 d)	0.325 (6 m)	0.420 (6 m)
Rain	-	-0.732* (3 m)	-0.698* (3 m)	0.706* (3 m)	-0.065 (1 m)	0.601* (3 m)	-0.204 (3 m)	-0.214 (6 m)
WindI	-	0.670* (6 m)	0.530* (6 m)	-0.600* (6 m)	-0.158 (8 d)	-0.601* (6 m)	-0.189 (3 m)	-0.390 (8 d)
RFlow	-	-0.642* (3 m)	-0.646* (1 m)	0.764* (3 m)	0.025 (3 m)	0.683* (8 d)	-0.092 (3 m)	0.101 (6 m)
NAO	-	0.111	0.115	-0.082	0.216	-0.035	0.029	-0.074

Regarding nutrients, only nitrates + nitrites and silicates were significantly correlated ($p < 0.05$, with Bonferroni correction) with some climatic and hydrological variables. Nitrates + nitrites were positively correlated with rainfall and river flow at stations RA4 and RA11. Silicates were positively correlated with rainfall, at station RA4. At this station, the maximum correlations occurred when considering the data from 3 months before the water quality sampling date. These results suggest that these variables are significantly influenced by the physical processes and, consequently, by anthropogenic interventions that may affect these processes (e.g., retention of freshwater). The occurrence of the predicted regime shifts in the Aveiro lagoon, particularly in the middle 1990s and after 2000, may thus be related with changes in these processes.

4. Discussion

Between 1985 and 2010 the ecological dynamics of Aveiro lagoon underwent several modifications due to the development of economic activities, the implementation of management measures or even occurring naturally (Figure 10). The construction of an integrated domestic and industrial wastewater treatment and disposal system, which started operating in 2000, is an example of a management intervention that envisioned the improvement of the water quality in the lagoon. Previously, the wastewater treatment plants were scarce and during several years untreated or poorly treated domestic and industrial effluents were discharged directly into the lagoon. Wastewater treatment systems are designed to achieve improvements in the quality of the domestic and industrial effluents and, consequently, reduce their negative impacts in the receiving water bodies. Some major changes also occurred near the inlet, namely the construction of the North pierhead and the dredging of the channels for navigation, which affected the circulation in the lagoon. As a consequence of these modifications, changes in the ecosystem and water quality dynamics were expected to occur. A long-term analysis of water quality indicators in the Aveiro lagoon, covering a period of anthropogenic modifications and different climatic and hydrological conditions contributes to the understanding of the relative role of these drivers in this type of estuarine systems.

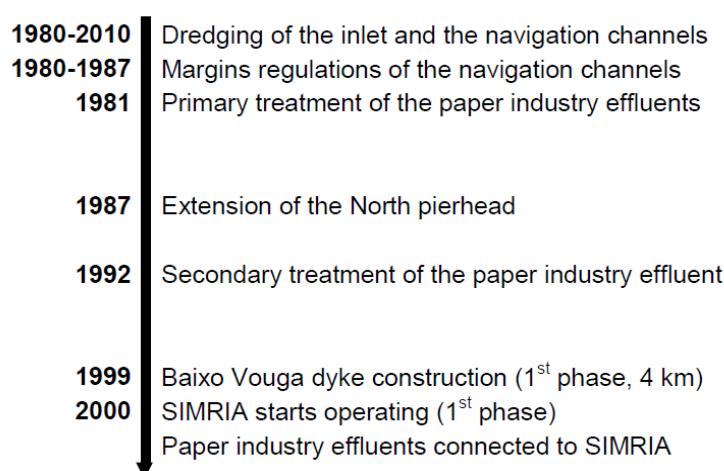


Figure 10. Timeline of some anthropogenic interventions in the Aveiro lagoon in the past 30 years.

4.1. Hypoxia

The riverine station (station RA11) experienced some hypoxia episodes until 1993 and a regime shift was predicted in 1994, characterized by an increase of the dissolved oxygen concentrations. These episodes were characterized by concentrations lower than 3 mg/L [31] and occurred mainly during summer. Most of the hypoxia episodes were not associated with increased primary productivity, although a negative correlation was found between dissolved oxygen and chlorophyll *a* at the riverine station. The paper mill that operates near this site started the primary treatment of its effluents in 1981, while the secondary treatment, with the removal of organic matter from the effluent, only started in 1992 (personal communication). A direct relation is apparent between the beginning of the secondary treatment of the paper mill effluent and the improvement of the dissolved oxygen concentrations. The effects of lower dissolved oxygen concentrations that occurred in the upstream area of the lagoon until 1993 were not observed in the downstream areas, revealing that tide promotes an effective water renewal in these areas. The occurrence of these conditions only during summer also put in evidence the role of the freshwater discharge in promoting the water renewal in the upstream area of the lagoon.

4.2. Nutrients

Inorganic nutrients concentrations in the Aveiro lagoon were within the range of variation observed in other estuaries [13,32-35]. The main sources of nutrients in the Aveiro lagoon were the wastewater discharged into the lagoon and diffuse sources from the surrounding catchments [36], namely agricultural activities [37,38]. Changes in the nutrients concentrations were expected to occur with the operation of the Aveiro wastewater treatment system [36], whose first stage started in 2000.

Ammonium and phosphates were not significantly related to the climatic and hydrological drivers, namely rainfall or the freshwater discharge, which suggests that these nutrients may come from anthropogenic sources (e.g., domestic or industrial effluents discharges) or sediments resuspension. The long-term variation of these two nutrients in the downstream area of the lagoon was characterized by an upward trend and increasing shifts after 2000, which were not expected due to the beginning of operation of the wastewater treatment system. In the upstream area of the lagoon, ammonium presented a slightly downward trend in the analyzed 25-years period, while alternations occurred in phosphates. [36] suggested that the disposal of the treated effluents in the adjacent coastal area could contribute to an increase of nutrients from oceanic sources entering the Aveiro lagoon. Numerical modelling studies suggest a strong dilution of these effluents and a reduced contribution for the tracers' concentrations in the coastal areas [39,40], although some wind conditions (West and Northwest winds) tend to promote the mass transport from the submarine outfall into the lagoon through the inlet [39]. The shifts observed in the present study may suggest an increase of ammonium and phosphates inputs from the ocean and require further monitoring. Nitrates + nitrites concentrations in the Aveiro lagoon were mainly controlled by climatic drivers, namely by rainfall and river discharge. Larger concentrations of nitrates + nitrites downstream occurred during intense rainfall periods (e.g., 1996, 2001 and 2009), putting in evidence the role of the freshwater discharge in controlling their downstream transport. Agricultural activities (including the application of effluent from livestock production on land) are the main sources of nitrogen in the Vouga catchment, with estimated loads of about 6000 ton N per year [37]. The increasing trend of nitrates + nitrites

observed in the upper limit of the Aveiro lagoon was probably related with the simultaneous increase in the dissolved oxygen in this area (section 4.1), which provided the aerobic conditions needed for nitrification.

Silicates presented an inverse trend relative to ammonium and phosphates in the downstream area of the lagoon. Freshwater discharges from upstream rivers are the major sources of silica to estuaries [41] and this pattern was also observed in the Aveiro lagoon. Larger concentrations of silicates downstream occurred during the rainier periods (winter of 1996, 2001 and 2009), and positive correlations were found with rainfall. As silicates in the water bodies come from the weathering of terrestrial rocks [10], the intense rainfall winter of 2001 followed by very wet years in 2004, 2005 and 2007 could be associated with the decrease in silicates in the downstream area of the lagoon. However, in the upstream area of the lagoon silicates presented an upward trend between 1985 and 2010 and two increasing shifts occurred (1997 and 2009), which suggests that some retention may be happening upstream. The construction of infrastructures that retain freshwater upstream (e.g., dams, dykes) may influence the volume of freshwater reaching the downstream area of the estuary and, consequently, silicates concentrations [42,43]. In the upstream area of the Aveiro lagoon two dykes used during the dry season to prevent the saltwater intrusion, allowing agricultural activities and the operation of a paper mill in the margins of the Vouga river [44]. These dykes limit partly the freshwater progression downstream: the first dyke influences the Antuã river discharge, while the paper mill dyke influences the Vouga river discharge. The paper mill, in particular, pumps water from the Vouga river and, until the connection to the sewage system in 2000 [45], also discharged its treated effluents in the river. This shunting of river water to the sewage system reduces the river flow, which has been previously identified as a risk [44], and may also be contributing for the decrease of silicates transported downstream. Another potential cause affecting silicates concentrations downstream may be deepening of the inlet of the Aveiro lagoon (maintained artificially through dredging) that occurred between 1987 and 2001 [46]. This deepening led to an increase in the tidal prism [46] and in the tidal amplitude [47], which may promote a larger transport offshore of silicates and more dilution by seawater [48,49]. It also suggested an offshore transport of silicates in the Aveiro lagoon [50].

4.3. *Phytoplankton dynamics*

Nutrient enrichment related with human disturbances has been pointed as one of the main causes of cultural eutrophication in estuaries [3].

Chlorophyll *a* concentrations in the Aveiro lagoon were within the range of variation observed in other Portuguese estuaries [13,33,34]. Some episodes with chlorophyll *a* concentrations larger than 10 µg/L were associated with blooms [6]. These blooms occurred mainly in the upstream area during summer (16 bloom episodes). Four blooms were observed near the inlet, which were probably associated with upwelling events. The seasonal pattern of chlorophyll *a* was related with rainfall and water temperature, in particular in the upstream area of the lagoon, suggesting that chlorophyll *a* was mostly driven by the climatic variability. The higher temperature observed during summer combined with the lower river discharges and, consequently, higher residence times promote hydrodynamic conditions that potentiate phytoplankton growth [51]). Some of the lower concentrations of chlorophyll *a* occurred during the rainier periods, namely in the winter of 2001 and 2009. Maximum correlations were found with the climatic and hydrological data integrated over periods of 1 to 3

months, putting in evidence a time lag between the physical forcing and the bio-chemical processes and the need to evaluate different temporal scales when performing this type of analyses.

Chlorophyll *a* presented a downward trend downstream and regime shifts occurred in 2004 (inlet station) and 2001 (transition station). Taking into account the role of nutrients to limit phytoplankton growth [52,53], the approach described by [54] and the half-saturation constants estimations by [55] were considered to evaluate nutrients limitation. Dissolved inorganic nitrogen (DIN—sum of ammonium, nitrates and nitrites) limitation ($\text{DIN} < 1 \mu\text{M}$, $\text{N/P} < 10$ and $\text{Si/N} > 1$) was never observed at the downstream stations during the analyzed period. At the inlet station, phosphates limiting conditions ($\text{PO}_4^{3-} < 0.2 \mu\text{M}$, $\text{N/P} > 30$ and $\text{Si/P} > 3$) were found four times (three of them before 2000), while at the transition station these conditions were found three times (February 1990, February 1991, and September 2007). Silicates presented a downward trend at these two stations and concentrations below the reported half-saturation constant of $5 \mu\text{M}$ were observed. In the transition station the low silicate concentrations occurred mostly after 2000, while near the inlet they were observed from 1985 to 2010. Silicates limiting conditions ($\text{SiO}_2 < 2.0 \mu\text{M}$, $\text{Si/N} < 1$, $\text{Si/P} < 3$) were found three times at these stations, all of them after 2000. Silicates concentrations and the nutrient ratios downstream, suggest that the downward trend observed in chlorophyll *a* was probably associated with the similar trend observed in silicates.

Although silicates availability seems to be the main factor affecting the decrease of phytoplankton in the downstream area of the Aveiro lagoon, the deepening that occurred between 1987 and 2001 near the inlet may have contributed for a larger transport offshore. This deepening may also have contributed for sediment resuspension and, consequently, promoted a decrease in the light availability in the water column, limiting the phytoplankton growth [56,57]. Mean suspended particulate matter in the inlet of the Aveiro lagoon after 2000 was close ($18\text{--}23 \text{ mg/L}$, [58]) to those observed in the light limited Tagus estuary (30 mg/L ; [13]). Additionally, a possible influence of zooplankton grazing cannot be discarded, but there are not enough in-situ data to confirm this hypothesis.

Upstream silicates and nitrates + nitrites were below the half-saturation constants only once, while phosphates concentrations were below $0.5 \mu\text{M}$ several times. The nutrient ratios also show minor availability of phosphorus, when compared with nitrogen and silica, suggesting a phosphorus limited-growth in the upper area of the Aveiro lagoon.

The seasonal and spatial variations of nutrients will also influence the phytoplankton species composition and distribution. A seasonal pattern of phytoplankton assemblages in the Aveiro lagoon was proposed by [19], dominated by diatoms from late autumn to spring and by chlorophytes from late spring to summer. The seasonal silicates variation observed between 1985 and 2010, with lower concentrations of silicates during summer, is consistent with this pattern. A spatial gradient of phytoplankton species is also expected to occur. At the transition station N/P and Si/P tend to be lower during summer and larger during winter. This suggests that during winter the freshwater phytoplankton species tend to be located further downstream in the lagoon, while during summer the marine phytoplankton species tend to move further upstream. Two distinct communities of phytoplankton had already been identified in the Mira channel of the Aveiro lagoon by [18]: one near the downstream area of the Mira channel and dominated by marine species (e.g., *Auliscus sculptus*, *Chaetoceros densus*, *Surirella comis*), while further upstream freshwater species were dominant (e.g., *Caloneis permagna*, *Cymbella tumida*, *Pinnularia stommatophora*).

5. Conclusions

Several anthropogenic modifications and different climatic and hydrological conditions occurred in the Aveiro lagoon between 1985 and 2010, which influenced the seasonal, inter-annual and long-term trends observed in the water quality of this coastal lagoon.

Seasonal variations were mostly associated with the seasonal variation of the main climatic and hydrological forcings. This seasonal pattern was particularly evident on nitrates + nitrites and silicates, which are transported downstream by the freshwater flow. The major shifts observed between 1985 and 2010, on the contrary, were most probably related with the anthropogenic interventions undertaken in the lagoon. The adoption of some management measures, as the use of secondary treatment of industrial effluents, allowed the system recovery from hypoxia conditions upstream. Silicates presented a downward trend in the downstream area of the lagoon, which was probably related with some anthropogenic modifications that may have affected the circulation in the lagoon, namely the shunting of river water to the sewage system that started operating in 2000 or the deepening of the inlet between 1987 and 2001. Chlorophyll *a* presented a downward trend in the downstream areas of the lagoon, with lower concentrations after 2000, which was probably related with the lower silicates concentrations. Future monitoring of this situation is needed, since the combined decrease of silicates with the observed increase of ammonium and phosphates in these areas may cause a shift in phytoplankton community, where diatom dominance is replaced by a dominance of flagellates and cyanobacteria [3], representing a potential threat for the ecosystem health. Since some of the predicted shifts are close to the end of the analyzed period, future monitoring is also essential for their validation. The significant influence on the water quality of some of the adopted management measures suggests that past anthropogenic interventions may have had a larger influence in the water quality and ecological dynamics of the lagoon, when compared with the system natural variability.

The analysis performed in this study puts in evidence the need for long-term monitoring of estuarine ecosystems and to integrate both anthropogenic and climate drivers when assessing their water and ecological quality, in order to effectively support the sustainable development and management of these systems. The present analysis contributes to an enhanced understanding of the water quality time scales of variability, as well as the identification of the main driving processes in the several regions of the Aveiro lagoon. Its conclusions set the base line for an assessment of the impacts of climate change in this system and the reference situation for future anthropogenic actions.

Acknowledgements

The first author was partly funded by Fundação para a Ciência e Tecnologia (FCT) grants SFRH/BD/41033/2007 and SFRH/BPD/87512/2012. This work was partly funded by the Fundação para a Ciência e Tecnologia project LTER (LTER/BIA-BEC/0063/2009) and by the Fundação Luso Americana para o Desenvolvimento project BGEM. Two anonymous reviewers are also acknowledged for their suggestions and comments.

Conflict of interest

The authors declare there is no conflict of interest.

References

1. Barbier EB, Hacker SD, Kennedy C, et al. (2011) The value of estuarine and coastal ecosystem services. *Ecol Monogr* 81: 169-193.
2. Pickney JL, Paerl HW, Tester P, et al. (2001) The role of nutrient loading and eutrophication in estuarine ecology. *Environ Health Persp* 109: 699-706.
3. Cloern JE (2001) Our evolving conceptual model of the coastal eutrophication problem. *Mar Ecol Prog Ser* 210: 223-253.
4. Paerl HW, Dyble J, Moisander PH, et al. (2003) Microbial indicators of aquatic ecosystem change: current applications to eutrophication studies. *FEMS Microbiol Ecol* 46: 233-246.
5. Burkholder JM, Tomasko DA, Touchette BW (2007) Seagrasses and eutrophication. *J Exp Mar Biol Ecol* 350: 46-72.
6. Gameiro C, Cartaxana P, Brotas V (2007) Environmental drivers of phytoplankton distribution and composition in Tagus Estuary, Portugal. *Estuar Coast Shelf S* 75: 21-34.
7. Yin K, Qian PY, Chen JC, et al. (2004) Dynamics of nutrients and phytoplankton biomass in the Pearl River estuary and adjacent waters of Hong Kong during summer: preliminary evidence for phosphorus and silicon limitation. *Mar Ecol Prog Ser* 194: 295-305.
8. Queiroga H, Almeida MJ, Alpuim T, et al. (2006) Wind and tide control of megalopal supply to estuarine crab populations on the Portuguese west coast. *Mar Ecol Prog Ser* 307: 21-36.
9. Baumert HZ, Petzoldt T (2008) The role of temperature, cellular quota and nutrient concentrations for photosynthesis, growth and light-dark acclimation in phytoplankton. *Limnologica* 38: 313-326.
10. Statham PJ (2012) Nutrients in estuaries—An overview and the potential impacts of climate change. *Sci Total Environ* 434: 213-227.
11. Kotta I, Simm M, Põllupüü M (2009) Separate and interactive effects of eutrophication and climate variables on the ecosystems elements of the Gulf of Riga. *Estuar Coast Shelf S* 84: 509-518.
12. Scanes P, Coade G, Doherty M, et al. (2007) Evaluation of the utility of water quality based indicators of estuarine lagoon condition in NSW, Australia. *Estuar Coast Shelf S* 74: 306-319.
13. Gameiro C, Brotas V (2010) Patterns of phytoplankton variability in the Tagus Estuary. *Estuar Coast* 33: 311-323.
14. Ferreira JG, Simas T, Nobre A, et al. (2003) Identification of sensitive areas and vulnerable zones in transitional and coastal portuguese systems, INAG, Lisbon, Portugal, 151 pp.
15. Lopes CB, Pereira ME, Vale C, et al. (2007) Assessment of spatial environmental quality status in Ria de Aveiro. *Sci Mar* 71: 293-304.
16. Rebelo JE (1992) The ichthyofauna and abiotic hydrological environment of the Ria de Aveiro, Portugal. *Estuar Coast* 15: 403-413.
17. Almeida MA, Cunha MA, Alcântara F (2005) Relationship of bacterioplankton production with primary production and respiration in a shallow estuarine system (Ria de Aveiro, NW Portugal). *Microbiol Res* 160: 315-328.
18. Resende P, Azeiteiro U, Pereira MJ (2005) Diatom ecological preferences in a shallow temperate estuary (Ria de Aveiro, Western Portugal). *Hydrobiologia* 544: 77-88.
19. Lopes CB, Lillebø AI, Dias JM, et al. (2007) Nutrient dynamics and seasonal succession of phytoplankton assemblages in a Southern European Estuary: Ria de Aveiro, Portugal. *Estuar Coast Shelf S* 71: 480-490.

20. Sampaio L (2001) Processo sucessional de recolonização dos fundos dragados da Ria de Aveiro após o desassoreamento: comunidades macrobentônicas. MsC Thesis, University of Aveiro, 2001, Aveiro, Portugal, 87 pp.
21. Dias JM, Lopes JF (2006) Implementation and assessment of hydrodynamic, salt and heat transport models: the case of Ria de Aveiro Lagoon (Portugal). *Environ Modell Softw* 21: 1-15.
22. Dias JM, Lopes JF, Dekeyser I (2000) Tidal propagation in Ria de Aveiro Lagoon, Portugal. *Phys Chem Earth Pt B* 25: 369-374.
23. Moreira MH, Queiroga H, Machado MM, et al. (1993) Environmental gradients in a southern europe estuarine system: Ria de Aveiro, Portugal. Implications for soft bottom macrofauna colonization. *Netherlands J Aquat Ecol* 27: 465-482.
24. Palma C, Valença M, Silva PP, et al. (2000) Monitoring the quality of the marine environment. *J Environ Monit* 2: 512-516.
25. Borges C, Valença M, Palma C, et al. (2011) Monitorização da qualidade ambiental das águas da Ria de Aveiro. In: Almeida A, Alves FL, Bernardes C, Dias JM, Gomes NCM, Pereira E, Queiroga H, Serôdio J, Vaz N (Eds.), *Actas das Jornadas da Ria de Aveiro*, 265-273.
26. McQuarters-Gollop A, Mee LD, Raitsos DE, et al. (2008) Non-linearities, regime shifts and recovery: the recent influence of climate on Black Sea chlorophyll. *J Marine Syst* 74: 649-658.
27. Rodionov SN (2004) A sequential algorithm for testing climate regime shifts. *Geophys Res Lett* 31: 1-4.
28. Rodionov SN, Overland JE (2005) Application of a sequential regime shift detection method to the Bering Sea ecosystem. *ICES J Mar Sci* 62: 328-332.
29. Morrison DF (1976) *Multivariate statistical methods*. McGraw-Hill, NY, USA, 415 pp.
30. Beaugrand G, Reid PC, Ibañez F, et al. (2002) Reorganization of North Atlantic marine copepod biodiversity and climate. *Science* 296: 1692-1694.
31. Nezlin NP, Kamer K, Hyde J, et al. (2009) Dissolved oxygen dynamics in a eutrophic estuary, Upper Newport Bay, California. *Estuar Coast Shelf S* 82: 139-151.
32. Harding Jr LW (1994) Long-term trends in the distribution of phytoplankton in Chesapeake Bay: roles of light, nutrients and streamflow. *Mar Ecol Prog Ser* 104: 267-291.
33. Cabeçadas G, Nogueira M, Brogueira MJ (1999) Nutrient dynamics and productivity in three European estuaries. *Mar Pollut Bull* 38: 1092-1096.
34. Barbosa AB, Domingues RB, Galvão HM (2010) Environmental forcing of phytoplankton in a Mediterranean Estuary (Guadiana Estuary, South-western Iberia): a decadal study of anthropogenic and climatic influences. *Estuar Coast* 33: 324-341.
35. Caetano M, Raimundo J, Nogueira M, et al. (2016) Defining benchmark values for nutrients under the Water Framework Directive: Application in twelve Portuguese estuaries. *Mar Chem* 185: 27-37.
36. Da Silva JF, Duck RW, Hopkins TS, et al., Evaluation of the nutrient inputs to a coastal lagoon: the case of the Ria de Aveiro, Portugal. *Nutrients and Eutrophication in Estuaries and Coastal Waters*. Springer Netherlands, 2002: 379-385.
37. Plano de Gestão das Bacias Hidrográficas dos rios Vouga, Mondego e Lis integrados na Região Hidrográfica 4 (2012) Parte 2—Caracterização Geral e Diagnóstico, Parte 2.2—Poluição difusa. Administração da Região Hidrográfica do Centro, IP: Ministério da Agricultura, Mar, Ambiente e Ordenamento de Território, 63 pp.

38. Clemêncio C, Viegas M, Nadai H (2014) Nitrogen and phosphorus discharge of animal origin in the Baixo Vouga: A spatial data analysis. *Sci Total Environ* 490: 1091-1098.
39. Ramos M, Almeida M, Silva PA, et al. (2003) Modelling study of the dispersal of pollutants at São Jacinto submarine outfall (Aveiro, Portugal), In: Brebbia CA, Almorza D, Lopez-Aguayo F (Eds.), Coastal Engineering VI, WITPRESS, 133-141.
40. Sobrinho JL, Nutrient balance in the continental shelf along the Aveiro region. MsC Thesis Thesis, Instituto Superior Técnico, University of Lisbon, Lisbon, Portugal.
41. Ji ZG (2008) Hydrodynamics and water quality—Modeling rivers, lakes and estuaries. Wiley, USA, 2008.
42. Rocha C, Galvão H, Barbosa A (2002) Role of transient silicon limitation in the development of cyanobacteria blooms in the Guadiana estuary, south-western Iberia. *Mar Ecol Prog Ser* 228: 35-45.
43. Li M, Xu K, Watanabe M, et al. (2007) Long-term variations in dissolved silicate, nitrogen, and phosphorus flux from the Yangtze River into the East China Sea and impacts on estuarine ecosystem. *Estuar Coast Shelf S* 71: 3-12.
44. Plano de Bacia Hidrográfica do Rio Vouga (1999) Plano de Bacia Hidrográfica do Rio Vouga. Anexo 10, Qualidade dos Meios Hídricos. Consórcio: Ambio, CHIRON, Agri.Pro, Drena, HCL, FBO Consultores, 160 pp.
45. Portucel Soporcel (2009) Monografia da fábrica de Cacia—2009. Portocel-Soporcel, 2009.
46. Silva A, Leitão P (2011) Simulação das condições hidromorfológicas da barra da Ria de Aveiro e respectivos impactes nos prismas de maré. In: Almeida A, Alves FL, Bernardes C, Dias JM, Gomes NCM, Pereira E, Queiroga H, Serôdio J, Vaz N (Eds.), Actas das Jornadas da Ria de Aveiro, 30-36.
47. Araújo IB, Dias JM, Pugh DT (2008) Model simulations of tidal changes in a coastal lagoon, the Ria de Aveiro (Portugal). *Cont Shelf Res* 28: 1010-1025.
48. Valiela I, Costa JE (1988) Eutrophication of Buttermilk Bay, a cape cod coastal embayment: Concentrations of nutrients and watershed nutrient budgets. *EnvironManage* 12: 539-553.
49. Ruiz A, Franco J, Villate F (1998) Microzooplankton grazing in the Estuary of Mundaka, Spain, and its impact on phytoplankton distribution along the salinity gradient. *Aquat Microb Ecol* 14: 281-288.
50. Pereira E, Lopes CB, Duarte AC (2011) Monitorização do estado trófico da Ria de Aveiro no intervalo temporal entre 2000 e 2004: implicações na evolução da qualidade da água. In: Almeida A, Alves FL, Bernardes C, Dias JM, Gomes NCM, Pereira E, Queiroga H, Serôdio J, Vaz N (Eds.), Actas das Jornadas da Ria de Aveiro, 258-264.
51. Ferreira JG, Wolff WJ, Simas TC, et al. (2005) Does biodiversity of estuarine phytoplankton depend on hydrology? *Ecol Model* 187: 513-523.
52. Padersen MF, Borum J (1996) Nutrient control of algal growth in estuarine waters. Nutrient limitation and the importance of nitrogen requirements and nitrogen storage among phytoplankton and species of macroalgae. *Mar Ecol Prog Ser* 142: 261-272.
53. Yin K, Qian PY, Chen JC, et al. (2000) Dynamics of nutrients and phytoplankton biomass in the Pearl River estuary and adjacent waters of Hong Kong during summer: preliminary evidence for phosphorus and silicon limitation. *Mar Ecol Prog Ser* 194: 295-305.
54. Dortch Q, Whittedge TE (1992) Does nitrogen or silicon limit phytoplankton production in the Mississippi River plume and nearby regions? *Cont Shelf Res* 12: 1293-1309.

55. Fisher TR, Harding Jr. LW, Stanley DW, et al. (1988) Phytoplankton, nutrients, and turbidity in the Chesapeake, Delaware, and Hudson estuaries. *Estuar Coast Shelf S* 27: 61-93.
56. Alpine AE, Cloern JE (1988) Phytoplankton growth rates in a light-limited environment, San Francisco Bay. *Mar Ecol-Prog Ser* 44: 167-173.
57. Gameiro C, Zwolinski J, Brotas V (2011) Light control on phytoplankton production in a shallow and turbid estuarine system. *Hydrobiologia* 669: 249-263.
58. Martins V, Jesus CC, Abrantes I, et al. (2009) Suspended particulate matter vs. bottom sediments in a mesotidal lagoon (Ria de Aveiro, Portugal). *J Coastal Res* 56: 1370-1374.



AIMS Press

© 2016 Marta Rodrigues et al., licensee AIMS Press. This is an open access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>)