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ORIGINAL ARTICLE

The role of *Sarcocornia perennis* and tidal flooding on sediment biogeochemistry in a South American wetland

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Abstract

The roles of *Sarcocornia perennis* and tidal flooding on sediment biogeochemistry were evaluated within a wetland in the Bahía Blanca estuary. pH and Eh were measured in sediments while particulate organic carbon (POC) and dissolved inorganic nutrient concentrations were determined in porewater, at three sites with different conditions according to vegetation and flooding. Grain size was also analysed. pH varied in a narrow range (7–8.2) and was lower in the vegetated site. Eh values (50–250 mV) imply that sediment conditions were moderately reduced, in agreement with the relatively high percentage of sand; it was influenced by both factors. POC concentration was high (26.24 ± 1.62 mg/l), especially at the vegetated site. The concentrations of ammonium and nitrate were similar (21.30 ± 1.83 and 18.77 ± 3.06 $\mu\text{mol/l}$, respectively) and not affected by flooding; only nitrate was affected by vegetation. Phosphate was rather constant (13.43 ± 1.19 $\mu\text{mol/l}$) and affected mainly by flooding. Silicate was high (566.45 ± 76.06 $\mu\text{mol/l}$) and not affected by either factor. These results suggest that the sediment biogeochemistry of this environment is significantly influenced by flooding and, especially, by *S. perennis*, as vegetation affected a higher number of parameters.

Key words: *Sarcocornia perennis*, tidal flooding, porewater, sediment conditions, nutrients, organic matter

Introduction

Coastal wetlands are naturally dynamic systems with significant ecological roles in the biogeochemical cycle of elements and in ecosystem functioning (Reddy & DeLaune 2008). For instance, they constitute large global carbon sinks, storing at least 42.6 ± 4.0 Tg C year⁻¹ and probably more, as detailed inventories are not available for China and South America (Chmura et al. 2003). One of the most studied and widely distributed types of wetland are tidal salt marshes, which are characterized by their vegetation (Adam 1993). The halophytic plants found in these systems are adapted to high salinity levels and waterlogged soils (Pezeshki 2001; Colmer & Flowers 2008; Flowers & Colmer 2008). One of the main adaptations is ‘radial oxygen loss’, which is

the release of oxygen by the roots to the surrounding sediments (Colmer 2003; Frederiksen & Glud 2006). This process has significant impacts on biogeochemical characteristics of the vegetated sediments, including pH, redox potential (Eh) and mineralization of organic matter as well as nutrient concentrations (see Reddy & DeLaune 2008 and references therein). In addition, the nutrient uptake by plants for growth is another important way the vegetation impacts on nutrient distribution.

The effect of salt marsh plants on sediment conditions and nutrient concentration in porewater has been extensively studied in *Spartina* species as well as in other grasses (e.g. Lillebø et al. 2006, 2007; Koretsky & Miller 2008). However, species from the family Chenopodiaceae, the largest group of halophytes (Flowers & Colmer 2008), have received much

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less attention. *Sarcocornia perennis* (Miller, A.J. Scott) is globally distributed, with records in Europe, Africa and South and North America (Davy et al. 2006), but information about its influence on wetland sediments is scarce and only from Mediterranean estuaries (Palomo et al. 2004; Caçador et al. 2009; Sousa et al. 2010). Although these papers deal with different aspects of sediment biogeochemistry, none studied the effect of this species on nutrient concentrations in porewater, an important source for the exchange of elements with estuarine water.

Sarcocornia perennis is the halophyte with the highest coverage ($\sim 204 \text{ km}^2$; Isacch et al. 2006) in the Bahía Blanca Estuary, in Argentina. Recently, the role of *Spartina alterniflora* ($\sim 131 \text{ km}^2$; Isacch et al. 2006), as well as tidal flooding, have been evaluated in relation to carbon, nitrogen and phosphorus dynamics in the intermediate zone of the estuary (Negrin et al. 2011), but a study of the effect of *S.*

perennis on sediment biogeochemistry is lacking. As the two species have different photosynthetic pathways (C_4 in *S. alterniflora* versus C_3 in *S. perennis*), different influences on sediment biogeochemistry could be expected (Cronk & Fennessy 2001). Therefore, the main aim of this study is to assess the roles of *S. perennis* and tidal flooding on sediment biogeochemical conditions in wetlands, taking the Bahía Blanca estuary as the study case. With this in mind, the differences in pH and Eh as well as organic matter and inorganic nutrient concentrations in different zones within the wetland were studied.

Materials and methods

Study area

Bahía Blanca is a coastal plain and mesotidal estuary with a semidiurnal tidal regime (Figure 1a). Tides are

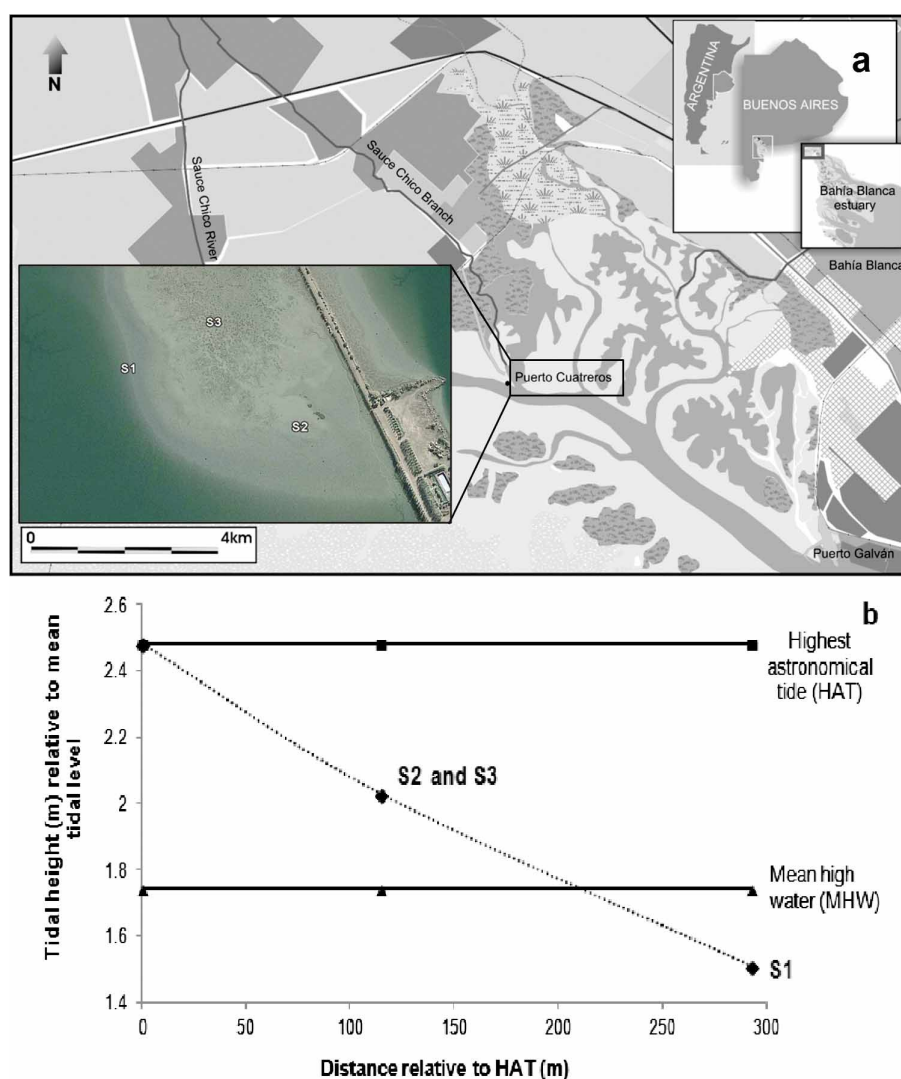


Figure 1. The study area and sites: (a) general map showing the study area and the three sites selected (source: Google Earth 5.2.1.1588) and (b) position of the sites in the tidal range.

the main energy source of the system; the mean tidal amplitude ranges from 2.2 to 3.5 m and the spring tidal amplitude ranges from 3 to 4 m (Perillo & Piccolo 1991). This system is part of the partly submerged Late Pleistocene–Early Holocene delta of the Colorado River (Piccolo et al. 2008) and is characterized by a temperate climate with variable annual precipitation. The maximum annual rainfall recorded is 712 mm and the minimum is 540 mm. Strong northwest and northern winds dominate the typical weather pattern of the region, with a mean velocity of 6.25 m/s and strong winds of over 11.9 m/s blowing across the estuary 54% of the year (Piccolo 2008).

The estuary is formed by a series of northwest to southeast oriented tidal channels separated by extensive tidal flats, salt marsh patches and islands. The total surface of the system is approximately 2300 km², including ~1150 km² of intertidal and ~740 km² of subtidal zones and ~410 km² of islands (Piccolo et al. 2008). The freshwater input to the estuary is weak and comes mainly from two tributaries, with flow rates of 1.72 m³/s (Sauce Chico River) and 1.05 m³/s (Napostá Grande Creek), average values measured for the period 2006–2007 (Carbone et al. 2008). Several ports, towns and industries are located on the northern boundaries of the estuary, discharging their residues into streams or directly into the estuary.

pH and salinity in surface seawater are quite stable on a seasonal as well as on a spatial (along the main channel of the estuary) basis, although a clear variation in these parameters is observed in the inner zone, with values as high as 9 and 41.3, respectively, in summer (Freije et al. 2008). This system maintains high levels of organic matter and inorganic nutrients in seawater (Freije et al. 2008) as well as phytoplanktonic biomass (Guinder et al. 2010) during most of the year. High concentrations of nutrients and organic matter are also found in porewater (Spetter 2006; Marcovecchio et al. 2009; Negrin et al. 2011).

The present study was conducted in a wetland adjacent to Puerto Cuatrerros, a small harbour in the inner zone of this extensive estuary (Figure 1a). The mean tidal amplitude there is 3.5 m while the spring tidal amplitude is 4 m (Perillo & Piccolo 1991). Tidal flats are dominant in this area, dissected by tidal courses of different characteristics. The high marsh is also dominated by *Sarcocornia perennis*, the most abundant halophytic species in the estuary, which is usually found forming unique rings around dense concentrations of burrows made by the crab *Neohelice granulata* (Perillo & Iribarne 2003).

Sampling

Sediment samples were collected every two months between November 2007 and November 2008 in

Puerto Cuatrerros wetland. Three sampling sites were chosen to represent different vegetation and flooding characteristics, according to their position in the tidal range (Figure 1b): Site 1 (S1): non-vegetated zone flooded daily by tidewater (tidal flat); Site 2 (S2): non-vegetated zone at a higher elevation point and, hence, flooded only during very high tides; and Site 3 (S3): zone vegetated by *Sarcocornia perennis*, flooded only during very high tides (high marsh). During the studied period, the mean above-ground biomass in S3 was ~600 g dw/m² and the mean belowground biomass was ~380 g dw/m² (Negrin 2011).

Six 10-cm long (11-cm diameter) sediment cores were randomly collected at low tide, with no overlying water over the surface, with a PVC pipe, at each site and sampling date in order to obtain porewater samples. The cores were hermetically closed with lids (top and bottom) after collection and immediately transported to the laboratory in refrigerated boxes.

Sediment pH and Eh (mV) were measured *in situ* at 1, 2 and 10 cm depth using a pH/mV meter (Oakton, USA). The Eh was measured with a WD-35805-15 (Oakton, USA) combination electrode whereas the pH was measured with a HI 8424 (Hanna, Romania) combination electrode, both properly calibrated before each sampling date. Four measurements were taken on each sampling date at each depth. Using a mini-corer (with the same diameter as the electrode), sediment was extracted at the different depths and the electrodes were immediately inserted to avoid carrying down sediments from shallower zones. Between measurements the electrodes were cleaned with distilled water. On one of the sampling dates, two surface-layer (10 cm) sediment samples were taken from each site for grain-size analysis.

Laboratory analysis

Immediately after collection, to minimize redox reactions, porewater was extracted by centrifuging the whole bulk of sediment of the samples at 3200 r/min for 40 min under ambient conditions (Adams 1994; Marchand et al. 2006). The supernatant – the volume which was quite variable and sometimes small (< 100 ml) – was filtered using a Whatman GF/C filter (1.2 µm pore size) previously muffled (450–500°C, 30 min), under controlled vacuum pressure, stored in plastic bottles and immediately frozen (–20°C) for later analysis of nutrients (Grasshoff 1976; APHA-AWWA-WEF 1998).

The corresponding filters with the retained suspended matter were stored at –4°C for the later determination of particulate organic carbon (POC)

(APHA-AWWA-WEF 1998). Nutrients were analysed with a Technicon II Autoanalyzer (Technicon Instruments Corporation, USA) expanded to five channels, following internationally standardized methods: Richards & Kletsch (1964), as modified by Treguer & Le Corre (1975), for ammonium; Treguer & Le Corre (1975) for nitrate; Eberlein & Kattner (1987) for phosphate; and Technicon® (1973) for silicate. POC was determined according to Strickland & Parsons (1968) using a spectrophotometer (DU-2 UV-Vis, Beckman, USA).

Samples for sediment characterization were dried (60°C, 24 h), weighed and analysed for particle size. First, the samples were passed through a sieve (63 µm mesh size) to separate the fine and the coarse fraction. Then, the fine particles were analysed by a laser diffractometer (Masterziser 2000).

Statistical analysis

To determine the effects of the presence of vegetation and flooding on the parameters considered, all the data for the whole study period (i.e. ignoring seasonal differences) were analysed. Two-way ANOVA tests were applied, with sites and depths as factors, to analyse differences in pH and Eh. As there was no depth factor for the measurements of POC and nutrients, one-way ANOVA and Tukey tests or non-parametric ones were used to determine differences between sites. Data were transformed to meet the required assumptions (homogeneity and normality) for the parametric tests.

Principal component analysis (PCA) was conducted with the means of each sampling date to examine the correlation among variables and the clustering of sites and sampling dates. We used seven variables in the PCA: concentration of POC, ammonium, nitrate, phosphate and silicate, and pH and Eh at 10 cm depth. The first two principal components were retained as they explained a meaningful part of the total variation according to the Kaiser–Guttman criterion.

All statistical analyses were carried out with STATISTICA 7.0 (StatSoft, Inc.), following Legendre & Legendre (1998). The acceptable level of statistical significance was 5%. Error values represent \pm SE.

Results

Grain size, pH and Eh

The sediments from the studied area were mostly silt, with more than 70% of silt at each site but with relatively high percentages of sand (Table I). In addition, approximately half of the silt is coarse silt (particles larger than 16 µm).

Table I. Composition of sediments at the studied sites (%).

Site	Clay	Silt	Sand
S1	9.35	71.73	18.92
S2	14.17	72.75	13.10
S3	8.84	70.84	20.33

pH values varied between 7 and 8.2. The temporal dynamics in both non-vegetated sites (S1 and S2) were similar at all depths, with lower values at the deepest one (10 cm) (Figure 2a,b). In S3, a clear trend was not identified at the different depths (Figure 2c).

Two-way ANOVA results showed that there is an interaction effect between sites and depths regarding pH. The values at S3 were significantly lower than at the other two sites ($p < 0.05$ in all cases) and, only in the case of the values at 10 cm, pH at S2 was significantly lower than at S1 ($p < 0.05$). Regarding depths, lower values were found at 10 cm than at 1 cm; however, the differences were only significant for S1 and S2 ($p < 0.05$) (Figure 3).

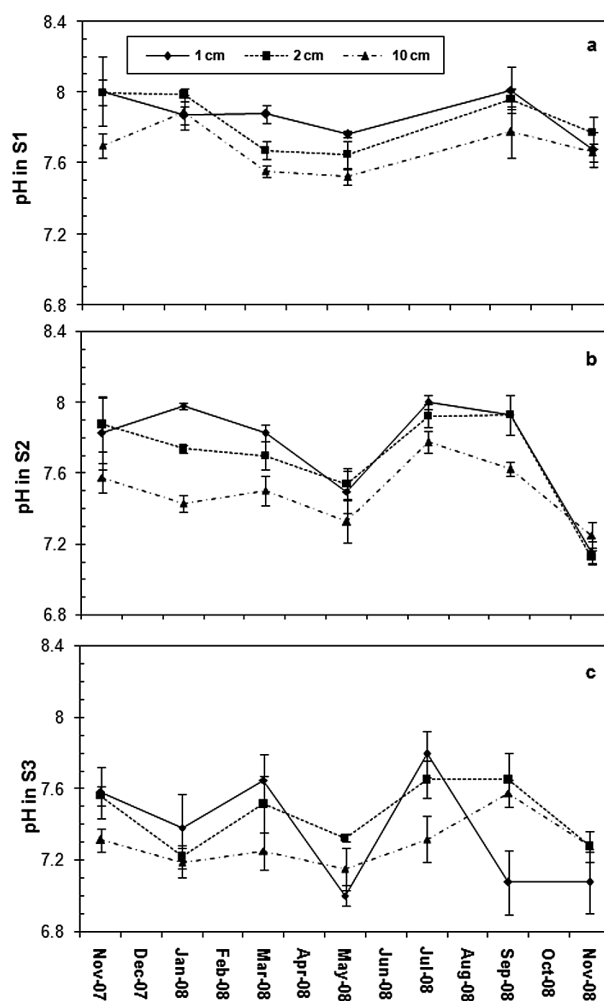


Figure 2. pH in sediment at all the analysed depths at all sites through the year (mean \pm SE; $n = 4$).

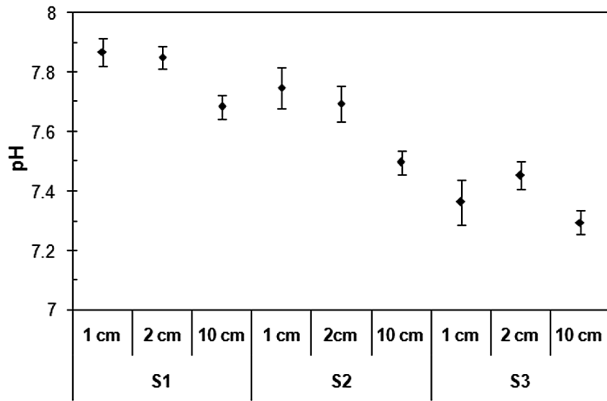


Figure 3. Average pH in sediment for the whole year at all depths and sites (mean \pm ES; 23 < n < 28).

Eh values were always positive, with levels ranging from 50 to 250 mV. The temporal pattern at all depths was similar within each site (Figure 4a–c). At S1, there was a slight decrease of Eh values in

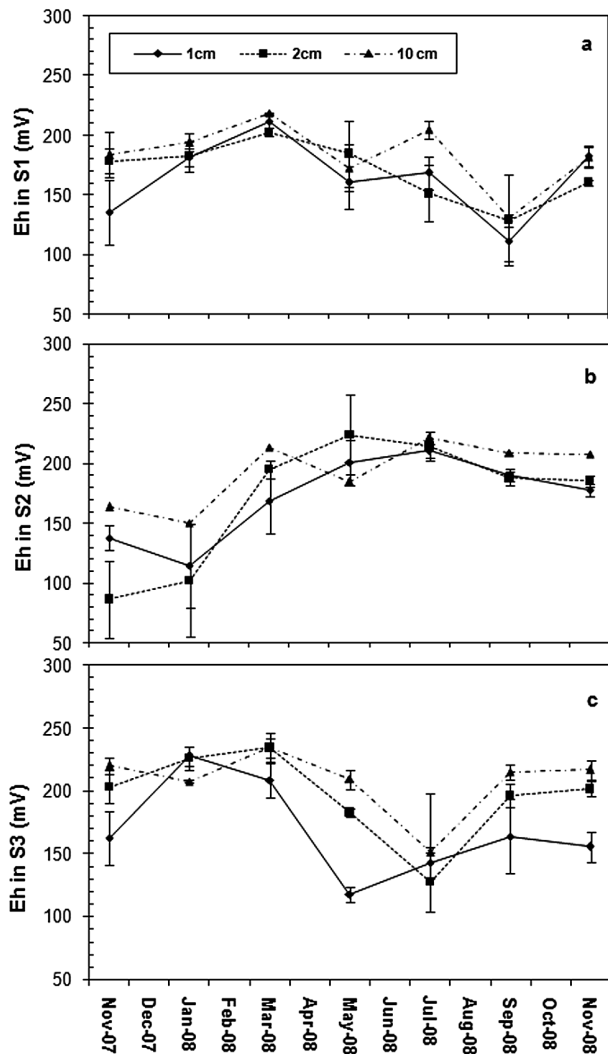


Figure 4. Redox potential (Eh) in sediment at all depths analysed for all sites throughout the year (mean \pm ES; n = 4).

September, but in general there was not a pronounced variability (Figure 4a). On the other hand, at both sites less influenced by tide (S2 and S3) changes through the year were greater (Figure 4b,c).

There was no significant interaction between sites and depths for Eh; hence, the values at all depths at each site as well as at all sites at each depth were averaged (Figure 5a,b). Eh was significantly higher at S3 than at S1 at all depths ($p < 0.05$) (Figure 5a). Regarding depths, Eh was significantly higher at 10 cm than at 1 cm at all sites ($p < 0.05$) (Figure 5b).

Particulate organic carbon and dissolved inorganic nutrients

POC

The average concentration for all the analysed sites was 7.85 ± 1.14 mg/l, with a maximum of 26.24 ± 1.62 mg/l at S3 in May and a minimum at the same site in September, with no detectable values. The three sites showed similar seasonal dynamics, usually with highest values in May and lowest ones in September (Figure 6a). POC concentration was significantly higher at the vegetated site (S3) than at the other two sites ($p = 0.000083$) (Figure 7a); the content at S3 was almost three times higher than at the other two sites averaged (14.10 ± 2.74 versus 4.98 ± 0.77 mg/l).

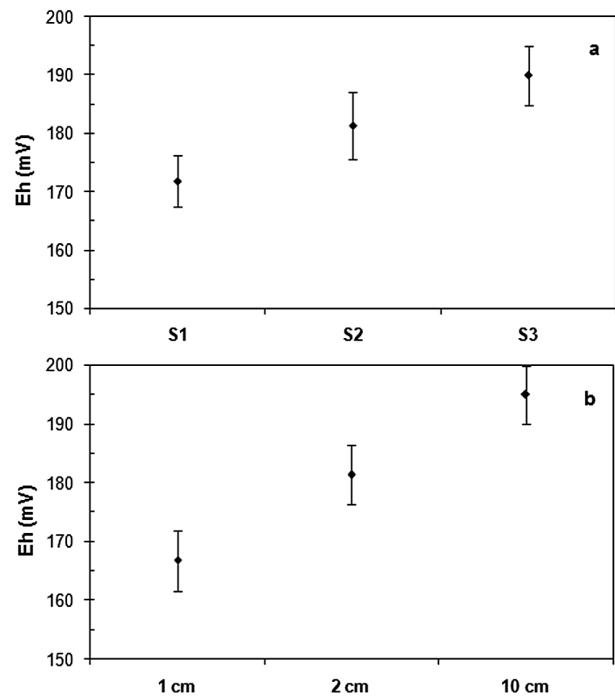


Figure 5. Redox potential (Eh) in the sediment: average for the whole year (a) at each site (80 < n < 83) and (b) at all depths analysed (78 < n < 84) (mean \pm ES).

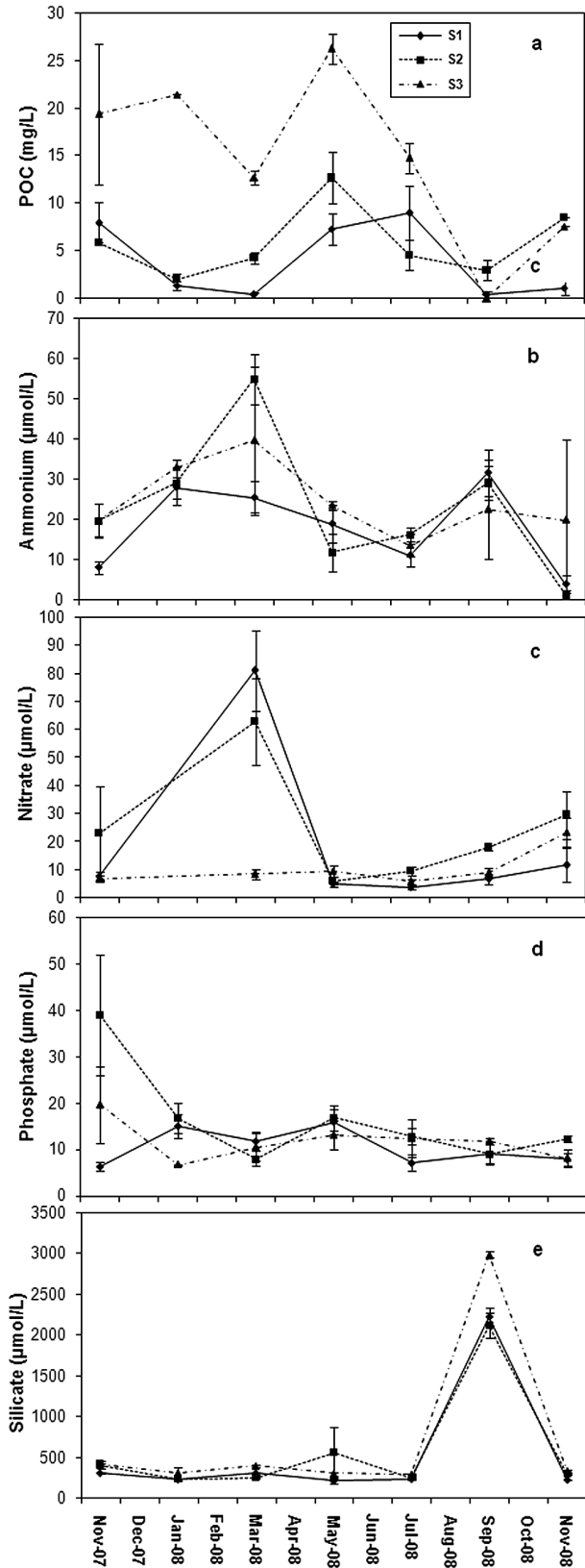


Figure 6. Seasonal dynamics of POC and nutrient concentration in porewater at the three sites ($1 < n < 6$).

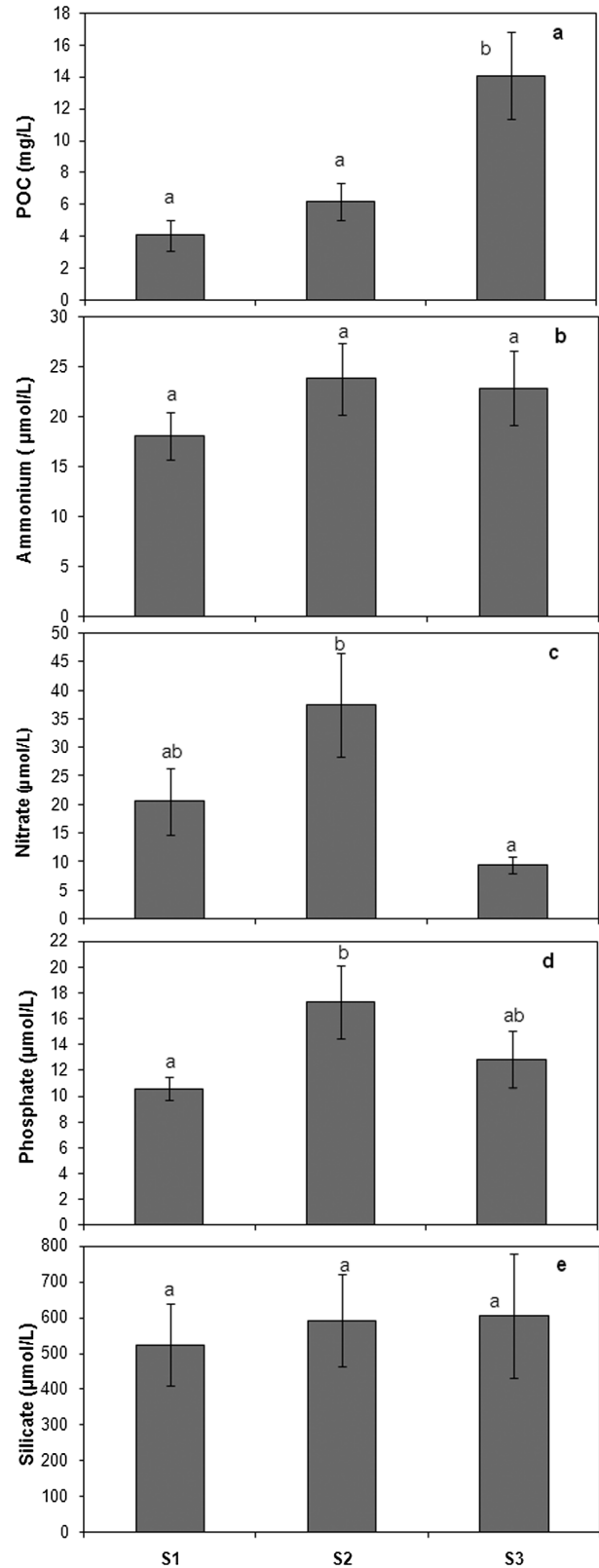


Figure 7. Concentration of POC and nutrients in porewater for the whole study period at each site ($12 < n < 37$).

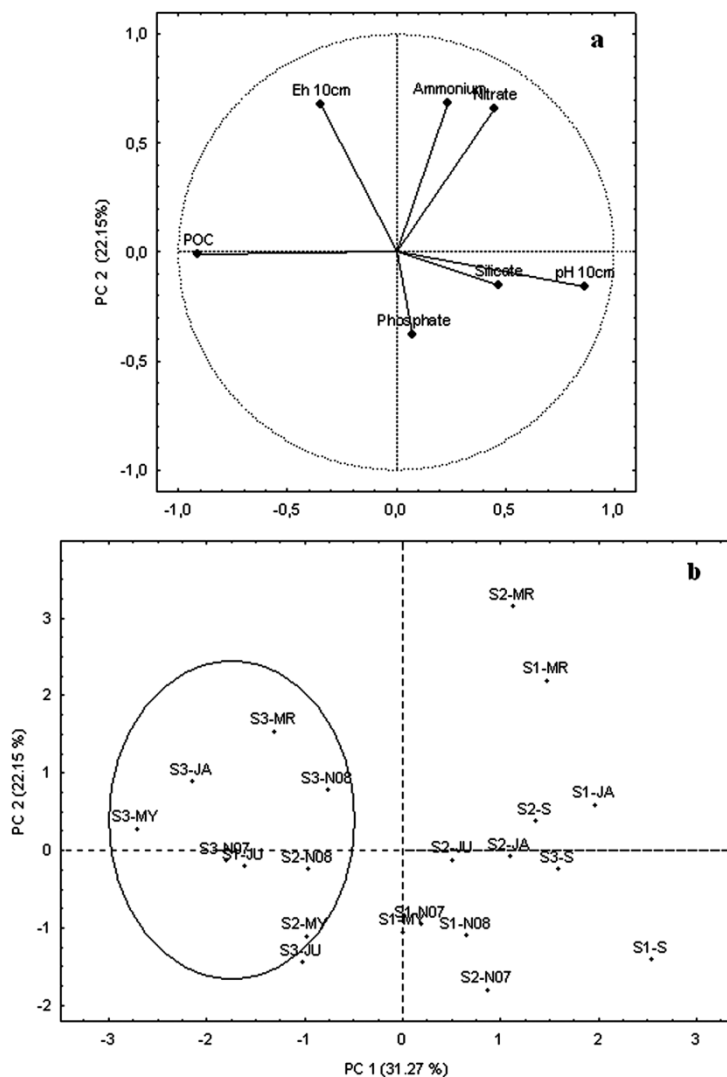


Figure 8. Two-dimensional plots of principal component (PC 1 and PC 2) loadings of (a) the variables analysed and (b) sites and sampling dates.

Ammonium

The average concentration for all the analysed sites was $21.30 \pm 1.83 \mu\text{mol/l}$, with a maximum of $54.82 \pm 6.31 \mu\text{mol/l}$ in March and a minimum of $\sim 1 \mu\text{mol/l}$ in November (2008), both at S2. All sites showed a similar seasonal dynamics, with highest values in March and September (Figure 6b). The concentra-

tion of ammonium showed no significant differences between sites ($p = 0.35$) (Figure 7b).

Nitrate

The average concentration for all the analysed sites was $18.77 \pm 3.06 \mu\text{mol/l}$, with a maximum of

Table II. Correlation matrix of the PCA ($n = 21$). Significant correlation values in bold ($p < 0.05$).

	POC	Ammonium	Nitrate	Phosphate	Silicate	pH 10 cm	Eh 10 cm
POC	1						
Ammonium	-0.045	1					
Nitrate	-0.437	0.404	1				
Phosphate	0.021	-0.088	0.045	1			
Silicate	-0.357	0.164	-0.205	-0.116	1		
pH 10 cm	-0.732	0.055	0.217	0.085	0.304	1	
Eh 10 cm	0.224	0.165	0.150	-0.271	-0.090	-0.288	1

81.03 ± 14.33 $\mu\text{mol/l}$ in March and a minimum of 3.69 ± 0.81 $\mu\text{mol/l}$ in July, both at S1. Unlike S3, the unvegetated sites had a peak in March, but since May all sites showed a similar behaviour. The concentration of nitrate was significantly higher at S2 than at S3 ($p = 0.012$) (Figure 7c).

Phosphate

The concentration for all the analysed sites was 13.43 ± 1.19 $\mu\text{mol/l}$, with a maximum of 38.9 ± 13.03 $\mu\text{mol/l}$ at S2 in November (2007) and a minimum of 6.37 ± 1.00 $\mu\text{mol/l}$ at S1 on the same date. The phosphate concentration was detectable in all the analysed samples. The seasonal dynamics for all sites were similar, but with somewhat high values in November 2007 at S2 and S3 (Figure 6d). The concentration of phosphate was significantly higher at S2 than at S1 ($p = 0.041$) (Figure 7d).

Silicate

The annual concentration for all the analysed sites was 566.45 ± 76.06 $\mu\text{mol/l}$, with a maximum of 2986.18 ± 36.87 $\mu\text{mol/l}$ in September at S3 and a minimum of 215.96 ± 35.18 $\mu\text{mol/l}$ in May at S1. The concentration of this nutrient was always detectable. All sites showed a similar seasonal dynamics with a high peak in September (Figure 6e). The concentration of silicate showed no significant differences between sites ($p = 0.89$) (Figure 7e).

PCA

Of the total variability, 53.4% was explained by PC 1 and PC 2 (Figure 8). Except for phosphate and silicate, the rest of the variables presented a percentage of reconstruction over 50% in the two-dimensional plot. PC 1, which accounted for 31.21% of the total variance, was mainly influenced by POC and pH. POC was highly correlated with the negative axis and pH with the positive axis, meaning that both variables are significantly negatively correlated (Table II; Figure 8a). PC 2 accounted for 22.1% of the total variance and was mainly influenced by ammonium, nitrate and Eh, all of which were correlated with the positive axis (Figure 8a). Site 3, except in September, was separated from S1 and S2 along the PC1, whereas there was not an evident separation between the latter sites (Figure 8b). Regarding sampling dates, there was not a very clear pattern, but a separation of March along the PC 2 was evident, especially for S1 and S2 (Figure 8b).

Discussion

In coastal wetlands, sediment conditions such as pH and Eh are dependent on a wide variety of different factors, such as presence of vegetation, tidal flooding, benthic primary productivity, the dominating respiratory pathway/s, sediment composition, etc. (Reddy & DeLaune 2008). In this article, we focused on vegetation and flooding given their significance in this kind of environment. On one hand, vegetation is a defining feature in salt marshes and, hence, highly relevant in wetland physiognomy; on the other hand, tidal flooding is also a structuring factor in these systems (Adam 1993), especially where tides are the main source of energy, as in the Bahía Blanca estuary. Moreover, both factors have significant implications in element cycling and distribution by themselves as well as by their indirect influence on sediment conditions, which are key parameters controlling the availability of nutrients and organic matter in porewater (Reddy & DeLaune 2008). The results presented here show that most of the parameters analysed (pH, Eh, POC, nitrate and phosphate) were affected by either the presence of *Sarcocornia perennis* or by tidal flooding, and in the case of Eh, by both. The influence of vegetation was greater than that of flooding since more parameters were affected by it; furthermore, the PCA showed that *S. perennis* was the most important factor given its organic matter production.

Grain size, pH and Eh

pH varied within the range of 7–8 for all the sites, but was confined to a narrower range in the vegetated sediments (~ 7.3 – 7.5). In salt marsh sediments, pH usually varies from 5 to 7 (Reddy & DeLaune 2008), and in the ones vegetated by *Sarcocornia perennis* or the related *S. fruticosa* could vary between approximately 6.3 and 8 (Caçador et al. 2009; María-Cervantes et al. 2010). Therefore, the values reported here are in agreement with those found in the literature.

For all the analysed depths, pH was lower in the vegetated site than in the non-vegetated ones, regardless the degree of flooding on them, which means that the presence of *S. perennis* but not flooding affects this parameter. Moreover, PCA showed that the vegetated site was well-separated from the other two in PC 1, which was highly correlated with pH, reinforcing the effect of plant activity in this parameter. This agrees with that observed in relation to *S. alterniflora* in another area of the same estuary (Negrin et al. 2011) and to *S. fruticosa* in the Marina del Carmolí salt marsh, Spain (María-Cervantes et al. 2010). The lower

values of pH in vegetated sediments could be associated with several factors, including oxidation of sulphides to sulphate and the consequent production of protons (Otero et al. 2009), the exudation of organic acids by roots (Dakora & Phillips 2002) and the release of protons in order to compensate for the higher rate of absorption of cations over anions (Begg et al. 1994). pH was only influenced by depth in non-vegetated sites, being significantly lower at 10 cm, which is consistent with the general trend of decreasing pH with depth in wetland soils (Reddy & DeLaune 2008).

The Eh values in the studied area were always positive and varying over a quite narrow range (approximately 50–250 mV); these redox conditions mean that the sediment was moderately reduced (Pezeshki 2001; Reddy & DeLaune 2008). Specifically in the vegetated site, the redox potential was 190 ± 5 mV, which is in agreement with the conditions required by this species for its growth (Davy et al. 2006). Similar values to the ones reported here (43–125 mV) were found in a European *S. perennis* salt marsh (Caçador et al. 2009).

Although mineralization of organic matter could be affected by several factors (temperature, pH, etc.), Eh values of a sediment could be a good indicator of the reaction(s) involved in this process, which in turn is related to the available electron acceptors. When oxygen is present, this is the main electron acceptor, at an Eh between 400 and 600 mV. However, when oxygen is depleted, other acceptors are used, at different Eh values, in this sequence: nitrate (at 250 mV), manganese (at 225 mV), iron (at 120 mV), sulphate (between –75 and –150 mV) or carbon dioxide (between –250 and –350 mV) (Cronk & Fennessy 2001; Reddy & DeLaune 2008). As a consequence, the values reported here would indicate that the oxidation of the organic matter is being performed by the reduction of nitrate, manganese and/or iron, and not of sulphate, as usually found in this kind of environment (Reddy & DeLaune 2008) and as previously reported for a *S. alterniflora* dominated wetland (Negrin et al. 2011). This fact also agrees with the sulphate concentration found in the porewater, which varied between 24.04 and 82.85 mmol/l (Negrin 2011), being usually higher than the values commonly reported for seawater (~ 28 mmol/l; Reddy & DeLaune 2008). In addition, these redox values imply that important processes such as denitrification and manganese and iron reduction are taking place in this wetland and, therefore, redox measurements may be considered as a useful tool to infer the processes that are occurring in the system. Eh at the vegetated site (S3) was higher than for the non-vegetated ones, although the difference was only significant regarding S1. This might

suggest that a combined effect (synergism) of vegetation and shorter flooding periods are needed for a measurable increase of Eh values. The effect of flooding on Eh may be simply related to the relative importance of inundation and exposure during the tidal cycle: the longer the marsh surface is exposed to the air, the more time is available for oxygen to penetrate into the porewater and the less reduced the sediment (Reddy & DeLaune 2008). The effect of plants could be associated to radial oxygen loss through their roots, which usually increase Eh (e.g. Pezeshki 2001; Otero et al. 2009; María-Cervantes et al. 2010), and also by soil aeration favoured by the cracks and macropores that develop in the presence of plants (María-Cervantes et al. 2010). In the previous work about *S. alterniflora*, Negrin et al. (2011) found that flooding was the main factor affecting Eh and that the influence of vegetation was subordinate to it. In the *S. perennis* area, where redox conditions are not so reducing, the influence of the presence of plants could be better appreciated. These differences between areas are related with the particular conditions of them as well as with the requirements of the different plant species to grow.

The sediment in the studied area is silt and mainly coarse silt, with relative large percentages of sand, which improves the permeability of the soil and helps the development of *S. perennis* since this species needs well-drained conditions (Davy et al. 2006). Moreover, the good drainage of the sediments allows an adequate porewater migration with the consequent movement of solutes, which might be an important way for exporting of nutrients and other dissolved constituents to the estuarine waters (Weston et al. 2010; Łukawska-Matuszewska & Burska 2011).

Particulate organic carbon and dissolved inorganic nutrients

The values of POC in porewater were high, being on average ~8 mg/l for the three sites. Although there are no reports of POC in porewater in other regions of the world, values are expected to be higher than in seawater since the capacity of wetlands to accumulate organic matter in the sediment is well documented (Chmura et al. 2003; Reddy & DeLaune 2008). With this in mind, and considering that values in the seawater from de Bahía Blanca estuary (1.1–2.5 mg/l; Freije et al. 2008; Marcovecchio et al. 2009) are high compared with other similar systems (0.02–0.3 mg/l; Hata et al. 2002; Flores-Cervantes et al. 2009), the reported values in porewater were very high. Furthermore, these values are higher than the ones reported in another (non-vegetated) zone of the same study area (Marcovecchio et al. 2009) and

in a wetland in the intermediate zone of the estuary partially vegetated by *Spartina alterniflora* (Negrin et al. 2011). The higher values of POC in this work with respect to the previous ones reported in the same estuary may be related to the presence of vegetation and/or its production, since the values of biomass reported for *S. alterniflora* were lower than the ones for *S. perennis* (Negrin 2011). Finally, it is worth noting that in relation with the levels of DOC in porewater (which are usually two orders of magnitude higher than POC (Reddy & DeLaune 2008)) in other wetlands ($\sim 10.5\text{--}25.0$ mg/l; Bally et al. 2004; Marchand et al. 2006), our values of POC are still considered elevated.

The concentration of POC was higher in the vegetated site than in the other two sites, suggesting that, of the factors considered here, only the presence of *S. perennis* plays a key role in organic matter distribution. These differences were noted despite the great variability that POC concentration showed at S3 throughout the year, as both the maximum and minimum for the whole area were found there. The minimum value, reported in September, corresponded to a unique sample where POC was under the limit of detection, due to the scarce volume of porewater obtained, which was a difficulty found on all the sampling dates. This point was also the only one found to the right side of the PCA plot (Figure 8b), in agreement with its absence of POC. Moreover, the concentration of POC for all the sites was at minimum in September and at maximum in May. The explanation of such temporal dynamics could rely on factors such as the abundance of benthic algae, the rate of mineralization of organic matter, the tidal energy, among others, which were not evaluated here.

Considering the whole study area, the average concentration of both nitrogen compounds analysed, ammonium and nitrate, were similar, with values of ~ 21 and ~ 19 $\mu\text{mol/l}$, respectively. With the exception of nitrate at S3, both nutrients showed a similar behavior during the year at all sites, with maximum values in March. This is consistent with the arrangement of the PCA plot along PC 2 (Figure 8b). The reason for such behaviour is not clear with the information presented here and may be associated with the dynamics of nutrient uptake by benthic microalgae during photosynthesis (Sullivan & Currin 2000) as well as with the concentration of nutrients in seawater, which is usually high during autumn in the Bahía Blanca estuary (Marcovecchio & Freije 2004; Spetter 2006).

Ammonium was not the dominant nitrogen compound, as is usually found in this kind of environment (e.g. Windham-Myers 2005; Lillebø et al. 2006; Negrin et al. 2011), and this is

presumably related to the redox conditions of the sediments, which were only moderately reduced and hence there was not an accumulation of reduced nutrients forms as ammonium (Reddy & DeLaune 2008). Ammonium values in porewater recorded here are similar to those found in the international literature (Windham-Myers 2005; Lillebø et al. 2006) as well as in other works from the Bahía Blanca estuary (Spetter 2006; Marcovecchio et al. 2009; Negrin et al. 2011). Nevertheless, our nitrate values were higher than the ones usually found in this kind of environment worldwide (Windham-Myers 2005; Lillebø et al. 2006) and in the same study area (Spetter 2006; Marcovecchio et al. 2009). The high nitrate values could be associated with oxidation of ammonium (nitrification), which has already been proven to occur in Puerto Cuatros (Spetter 2006), and/or the possible input from groundwater (Gallaway 2005), which has not been studied in the area so far. However, in order to assess the nitrate budget within this wetland, denitrification, which is very variable with particular sediment conditions (Piña-Ochoa & Álvarez-Cobelas 2006; Sirivedhin & Gray 2006), should also be taken into account.

Neither the effect of vegetation nor flooding was observed on ammonium concentration. The lack of vegetation effect on this nitrogen nutrient, one of the main required elements for plant growth, may be associated with the higher organic matter content found in the vegetated site, because ammonium is released through its mineralization. In this sense, it should be considered that organic matter concentration is higher in the vegetated sites and, thus, the ammonium produced could be quickly used by plants masking any possible difference regarding plant absorption. Nitrogen mineralization proved to be an important source of available nitrogen for plant uptake and growth in salt marshes in Portugal (Cartaxana et al. 1999). On the other hand, plants may be using nitrate as well. This in agreement with the lower values of this nutrient observed in the vegetated site. The lower values of nitrate in the area with *S. perennis* (S3) are only significant regarding S2, the site non-vegetated and less influenced by flooding. This may be related to a higher nitrate production through nitrification due to the greater temperature, light, salinity, oxygen availability, etc., in more exposed, bare sediments (S2) (Herbert 1999).

Phosphate was always present in porewater at all the three sites throughout the year and the values reported here are in the range observed in this kind of system (Lillebø et al. 2007; Koretsky & Miller 2008; Negrin et al. 2011). Unlike the nitrogen compounds, the concentration range was rather

narrow ($\sim 13 \pm 1 \mu\text{mol/l}$). This suggests that the sediment may buffer the phosphate concentration against changes caused by differential rates of production and consumption (Sundby et al. 1992). Spetter (2006) and Marcovecchio et al. (2009) found phosphate values an order of magnitude lower in bare tidal flats, showing the importance of vegetation and particular sediment conditions in the distribution of this nutrient (Palmer-Felgate et al. 2011).

The only significant difference regarding phosphate was the higher concentration found at S2 with respect to S1, which means that, of the factors considered here, flooding is the only one that affects its concentration in this wetland. In the *S. alterniflora* wetland, vegetation plays the major role in phosphate distribution (Negrin et al. 2011), showing that both flooding and vegetation consumption influence this nutrient, but varying under different sediment conditions (Palmer-Felgate et al. 2011). The concentration of phosphorus in estuarine sediment porewater is highly influenced by the ability of this element to be bound to soil particles containing aluminium, iron or calcium and a lower frequency of flooding allows the enrichment of sediments with phosphorus. Changes in sediment conditions related to flooding, such as increase of pH, decrease of Eh or depletion of oxygen concentration, induce the release of phosphate from the soil particles increasing the levels in porewater (e.g. Coelho et al. 2004; Palmer-Felgate et al. 2011). This may be occurring at S2. At S3, values are also high, but not as high as at S2, possibly due to the uptake of phosphate by plants and/or the low pH that prevent a high release from sediment particles to porewater. However, the influence of vegetation seems not to be of great importance for this element, as no significant difference between the vegetated (S3) and the unvegetated areas was found, as observed by Palomo et al. (2004).

Silicate was always present in porewater throughout the study period and in high concentration (in average $\sim 566 \mu\text{mol/l}$), which is an order of magnitude higher than values reported in other coastal environments (Jahnke et al. 2005). Nevertheless, our values are in agreement with those reported in previous studies in Puerto Cuatros (Spetter 2006; Marcovecchio et al. 2009). This might suggest that there is a high rate of dissolution of primary minerals and/or high rate of weathering in the region, as these are the main sources of dissolved silicate in coastal systems (Joye et al. 2009). In addition, the reported values may indicate the availability of this nutrient for the production of benthic diatoms, which are abundant in the area (Parodi & Barría de Cao 2003). The concentration

of silicate was not affected by flooding or by vegetation, which means that it is a rather stable nutrient, perhaps due to its continental origin. Furthermore, this element is not essential for vegetal growth and thus a lack of its effect on plants was expected.

Conclusions

As most parameters analysed were modified by either of the factors considered here, or by both of them in the case of redox potential, we conclude that the presence of *Sarcocornia perennis* and tidal flooding are significant determinants in sediment biogeochemistry in this environment. Four of the studied parameters (pH, Eh, POC and nitrate) were affected by the presence of vegetation, whereas tidal flooding was only important for two of them (Eh and phosphate). The main impact of vegetation seems to be related with the concentration of POC in the vegetated site, which was much higher than in the non-vegetated ones, and to the acidification of the sediment generated by the roots, as these are the main variables responsible of the separation of this site from the other two in the PCA. As a consequence, tidal flooding and, especially, the presence of *S. perennis* should be considered in future studies of sediment biogeochemistry in wetlands.

This study was conducted in a representative area of the inner zone of the estuary that has been well studied with regard to nutrients, organic matter, phytoplankton, physico-chemical parameters and pollutants in seawater. However, research on wetlands is scarce and this work adds valuable information for a more complete interpretation of the system as a whole. In addition, this study highlights the role of *S. perennis* on biogeochemical conditions in wetlands sediments, which has been previously overlooked. Nevertheless, for a better understanding of the mechanisms involved, processes such as nitrification/denitrification, iron reduction, phosphate speciation, among others, should be taken into account and, therefore, research regarding this species is highly advisable.

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