MIGUEL ÂNGELO PARDAL JOÃO CARLOS MARQUES MANUEL AUGUSTO GRAÇA Scientific Editors

Aquatic Ecology of the Mondego River Basin Global Importance of Local Experience





Coimbra • Imprensa da Universidade

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THE ROLE OF Spartina maritima AND Scirpus maritimus TO SEDIMENT PORE-WATER PROFILES, AND POSSIBLE IMPLICATIONS TO THE MONDEGO ESTUARY NUTRIENT DYNAMICS

Abstract

Previous studies concerning the concentrations of inorganic nutrients in the south arm of the Mondego estuary showed a consistent yearly pattern, with an increase of nitrogen (nitrite, nitrate and ammonia) from summer until early winter, and higher phosphorus concentrations from late spring until summer. In Sportino and Scirpus salt marshes the nutrients concentrations in low water pools were monitored, and results suggested that Scirbus primarily contributes with the nitrate form of nitrogen to the sediment/water phase dynamics, and that Sporting had a stronger contribution of ammonia to the nitrogen dynamics. The aim of the present study was to compare the pore-water profiles of the two emergent macrophytes in the south arm of the Mondego estuary, and relate it to the nutrient concentrations in the two salt marshes low water pools. Our results showed statistically significance differences between Spartina and Scirpus sediment nutrient profiles (nitrate, ammonia and phosphate) (Mann-Whitney test, p<0.05), during day and night situations, suggesting that coupling between plant and sediment are species-specific processes. Although the ability to transport oxygen to the belowground parts has been described for both species, where it is used for root respiration and oxidation of the rhizosphere, it seems that the Scirpus rhizosphere had higher phosphorus adsorption capacity. Moreover, when comparing the two nutrient profiles Scirpus rhizosphere presented higher concentrations of the nitrate form of nitrogen, while Spartina rhizosphere presented higher concentrations of the ammonia form of nitrogen. In addition, the specificity of these processes will have repercussions on the sediment/water interface nutrient dynamics, which may be reflected in the entire system nutrient dynamics.

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Introduction

In the south arm of the Mondego estuary (western Portugal) the Scirpus maritimus population occupies the inner areas, while Spartina maritima occurs in the downstream areas (Fig. 1) following the salinity gradient (Lillebø 2000). These two species differ in their annual dynamics: Spartina maritima is a rhizomatous grass, forming extensive monotypic stands (Castellanos et al. 1994, Sanchéz et al. 1997), with a continuous but very slow growth (Pierce 1983 in Adams and Bate 1995); Scirpus maritimus is a stoutly rhizomatous perennial sedge (Karagatzides and Hutchinson 1991) which usually forms similar dense monospecific stands in shallow brackish marshes (Lieffers and Shay 1982 in Charpentier and Stuefer 1999). Moreover, in this species, ramets produce photosynthetic shoots that are active for a single growing season, and only belowground parts persist into the next year (Charpentier and Stuefer 1999, Lillebø 2000). In the Mondego estuary mature phase, with maximum aboveground biomass, occurs in April/May (Lillebø 2000).



Fig. 1. The location of the Spartina maritima and Scirpus maritimus salt marshes in the Mondego estuary.

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During the last decade the south arm of the Mondego estuary has been almost continuously monitored with respect to inorganic nutrients in the water column (Flindt et al. 1997, Marques et al. 1997, Pardal 1998, Martins 2000, Martins et al. 2001). Throughout a four years study period, from January 93 to January 97, the variation of nitrite and nitrate in the water column followed a similar yearly pattern, usually with higher concentrations in winter and lower concentrations in spring and summer (Fig. 2). Moreover, ammonia concentration represented an important contribution to the total inorganic nitrogen concentration in the system, and tended to increase from summer until autumn and early winter (Fig. 2). Furthermore, during the same study period, the highest concentration of dissolved inorganic phosphorus occurred mostly during summer (Fig. 2). So, these may be considered as the general pattern for inorganic nutrients concentrations in the south arm of the Mondego estuary (Martins et al. 2000).





Salt marshes have been characterised as efficient sinks for nutrients, and buffering of the effects of nutrients inputs (e.g. Anderson et al. 1997, Andersen and Rins 1999). The interaction of roots with the surrounding sediments is exceedingly complex, covering a wide range of biogeochemical processes (Caçador et al. 1996, Wigand et al. 1997). Vegetation may act as sediment traps playing an important role in the settling of suspended matter, and also, plant roots interact with the surrounding sediment (Caçador et al. 1996, 2000, Andersen and Rins 1999, Flindt et al. 1999). Several papers have reported chemical changes in the rhizosphere of several salt marsh plants, including the redox potential (Eh), organic matter, metal availability and also the nutrient profiles (e.g. Kamp-Nielsen and Flindt 1993, Caçador et al. 1996, 2000, Anderson et al. 1997, Wigand et al. 1997, Cartaxana and Lloyd 1999, Flindt et al. 1999). Moreover, it is known, that submersed rooted macrophytes link the nutrients in sediments with the overlying water which may have important implications for nutrient

cycling within such systems (e.g. Kamp-Nilsen and Flindt 1993, Valiela 1995, Anderson et al. 1997, Flindt et al. 1999).

The first objective of the present study was to compare the dissolved inorganic nutrients in the low water pools formed in the two salt marsh areas (*Spartina maritima* and *Scirpus maritimus*), with the general yearly pattern described for the system. Furthermore, we also compared the importance of the two salt marsh species to the sediment nutrient profiles, and relate it with the concentrations in the low water polls, in a typical temperate intertidal estuary (Mondego estuary).

Material and methods

In the scope of a field-monitoring program focusing on the nutrient dynamics in the Mondego estuary salt marshes (Fig I), water and sediment samples were collected during thirteen months, from March 97 to June 98, at monthly intervals (Lillebø 2000). Water samples for nutrient analyses (dissolved inorganic phosphate, ammonia, nitrate and nitrite) were collected in low water pools. All water samples were filtered (GF/F) and kept frozen until analysis. Analyses of dissolved reactive phosphate, ammonia, nitrate and nitrite were also performed according to Standard Methods (1995). Sediment triplicate sub-samples were analysed for dry weight, loss on ignition (8 h, 450 °C), total nitrogen and phosphorus. The granulometry was analysed seasonally and classified according to the nomenclature proposed by Brown and McLachlan (1990). Analyses of sediment total nitrogen and phosphorous were performed according to Standard Methods (1995).

Sediment profiles were studied by placing vertically dialysis chambers in the plants rhizosphere in May because this corresponds to the time where *Scirpus maritimus* reaches the mature phase in the Mondego estuary (for a more detailed description of the technique see Kamp-Nielsen and Flindt 1993). In our case, the water samples were collected with a syringe (2,5 ml, corresponding to each chamber volume), and simultaneously the chamber was filled up with distilled water. To evaluate the effect of plants, samples were taken after a 12 hours exposure under dark conditions (night period) and 12 hours under light conditions (day). Water samples were analysed for dissolved inorganic phosphate, ammonia and nitrate in a rapid flow autoanalyser (RFA 300 Alpkem) and performed according to Alpkem methodologies (Alpkem 1990). A non-parametric Mann-Whitney test was applied to determine the significance of differences (95% confidence level) between the sediment nutrient profiles (Zar 1996).

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Results

Sediment properties

In these two salt marshes, sediments consisted mainly of fine particles between 63µm and 125µm in size, corresponding to silt and clay, and do not show a significant

seasonal variation (Table I). Sediment water content, during low tide, did not show a clear seasonal variation although it slightly increased during the winter period, probably as a result of higher precipitation, and also lower evaporation due to lower temperatures. Moreover, results do not evidence a spatial variation. The mean percentage of sediment water content (\pm std) during low tide, at the *Spartina* salt marsh was 60.68 \pm 3.5% and 61.12 \pm 3.0% at *Scirpus* salt marsh (Lillebø 2000).

Classes (mm)	>0.500	>0.250	>0.125	>0.063	>0.063	
	<1.0	<0.500	<0.250	<0.125		
Spartina	A-97	1.2	8.1	30.1	57.2	3.5
	J-97	0.1	14.1	24.9	54.9	5.9
	O-97	2.0	39.5	28.1	28.6	1.7
	J-98	0.2	4.5	16.0	67.7	11.5
	A-98	0.7	5.1	19.2	69.5	5.5
Scirpus	A-97	0.9	8.5	37.0	50.4	3.2
	J-97	2.0	9.6	27.4	54.9	6.1
	O-97	2.2	27.9	25.1	41.4	3.4
	J-98	1.3	4.8	26.7	60.3	6.9
	A-98	2.0	24.3	21.7	49.0	3.0

Table I. Relative frequency of sediment granulometry classes determined seasonally in *Spartina* and *Scirpus* salt marshes (April, July and October 97, and in January and April, 1998).

The sediment organic matter content in the Spartina and Scirpus salt marshes was statistically different (Mann-Whitney test, p=0.0047), with lower organic matter content in the Spartina salt marsh (Mann-Whitney test, p=0.0023). The Scirpus salt marsh did not show a clear seasonal variation (Fig. 3). In the Spartina salt marsh there was a slight increase during summer, probably due to the decomposition of green macroalgae (Enteromorpha spp. and Ulva sp.) that usually occurs in the downstream areas of the estuary (Pardal 1998, Martins et al. 2001).



Fig. 3. Seasonal variation of sediment organic matter content in Sportino and Scirpus salt marshes.

Water nutrient dynamics

As general pattern of dissolved inorganic nutrients in the water column (Martins et al. 2001), phosphorus concentration in the salt marshes low water pools showed an inverse seasonal pattern of nitrogen. In the low water pools nitrate concentrations were much higher than the nitrite concentrations (Fig. 4A). Both study sites showed a clear seasonal variation with an increase on nitrate and nitrite concentrations during winter, following the general pattern for dissolved inorganic nitrogen in the Mondego estuary. Nevertheless, the low water pools formed in *Scirpus* salt marshes presented higher nitrate concentrations than the pools at *Spartina* salt marshes (Fig. 4A), which may reflect the importance of plant coverage to the efflux of nutrients from the sediment to overlaying water.

Ammonia concentrations in the low water pools were plotted together with the total nitrogen in the sediment (mg.g' sediment dWt) (Fig 4B) in order to compare the dynamics between these two compartments. In this comparison we did not use the total nitrogen in the water (ammonia, nitrate and nitrite), because ammonia is the most representative form of nitrogen in the water column (Fig. 2), Results show that the total nitrogen in the sediment is guite stable all over the study period. Sparting salt marsh presented slightly higher nitrogen concentrations in the sediment, but generally lower ammonia concentration in the water (Fig. 4B). Furthermore, the seasonal variation of ammonia concentration in the water is much more evident in the Sparting salt marsh, with a higher increase during fall and winter, while the total nitrogen in the sediment increases during late winter and early spring. In the Scirpus salt marsh, the ammonia concentration in the water is much more constant, which is not in agreement with the general pattern for ammonia concentrations in the south arm of the Mondego estuary. The total nitrogen in the sediment decreased in November and in March, and was probably related to the plant annual dynamics. New shoots started to emerge in December/January and the plant reaches the mature phase in April/May (Lillebø 2000).



Fig. 4. Variation of nutrients in the low water pools and in the sediment between March 97 and March 98 in *Spartina* and *Scirpus* salt marshes. A: nitrate and nitrite concentrations in the low water pools; B: Nitrogen dynamics in sediment (total N) and in the low water pools (ammonia); C: Phosphorus dynamics in sediment (total P) and in the low water pools (phosphate).

The concentration of dissolved inorganic phosphate concentration in the low water pools was plotted together with the total phosphorus in the sediment (mg.gl⁻¹ sediment dWt) in order to compare the dynamics between the plant rhizosphere and the low water pools (Fig. 4C). The downstream areas of the estuary show lower phosphorus content in the sediment, which was quite stable during the study period. In the low water pools phosphate concentration showed a clear seasonal variation, with higher concentrations during summer, which is in agreement with the general pattern for dissolved inorganic phosphate in the south arm of the Mondego estuary. During the summer period, July and August, the low water pools in *Scirpus* salt marsh showed higher phosphate concentration when compared with *Spartino* salt marsh. This increase is probably related to *Scirpus* annual dynamics, due the plants enter the senescent phase in June/July (Lillebø 2000), corresponding to the mineralisation period of the above ground part of the plants.

Sediment nutrient profiles

As hypothesised, the sediment pore-water profiles showed that plant coverage influences differently the nutrient profiles. The non-parametric Mann-Whitney test show statistically significance differences between *Spartina* and *Scirpus* sediment nutrient profiles, namely concerning the NO₃-N profile during the day (p=0.0000) and night period (p=0.0000), the NH₄-N profiles during day (p=0.0007) and night period (p=0.0016), and PO₄-P profile during day (p=0.0000) and night period (p=0.0000).

The nitrate concentration in pore-water is much higher in the *Scirpus* salt marsh, and it is particularly higher during the day and in the first 6 cm of sediment (Fig. 5), below this depth nitrate concentration decreases especially during the night period. This difference between day and night period is statistically significant (p=0.0017). In *Spartina* sediments there were no evident differences between day and night situations (p=0.5591), and the higher concentration corresponded to the first millimetres during the day period. Moreover, in the *Scirpus* rhizosphere, the nitrate concentration in the first 0.3 millimetres in depth (which correspond to the sediment/water interface) was in the same range as the concentrations recorded in the low water pools. On the other hand, in *Spartina* rhizosphere the nitrate concentration was ten times lower.

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The sediment pore-water profiles for ammonia concentration in *Spartina* and *Scirpus* marshes showed a different dynamics, which is evident in the first 4-5 cm in depth (Fig. 6). *Spartina* rhizosphere had much higher ammonia concentration in the first 10 cm. From the 10 cm to 20 cm, *Scirpus* rhizosphere showed an increase of ammonia concentration, although *Spartina* rhizosphere seems more stable (Fig. 6). Furthermore, in *Spartina* rhizosphere, ammonia concentration in the first 0.3 millimetres in depth was much higher than in the low water pools, while in *Scirpus* rhizosphere ammonia concentration is much lower. There were no statistically differences between the ammonia profiles in day and night situations in *Spartina* rhizosphere (p=0.5591) or in *Scirpus* rhizosphere (p=0.6785).



Fig. 5. Nitrate concentration in sediment pore-water profiles in Sportino and Scirpus salt marshes.



Fig. 6. Ammonia concentration in sediment pore-water profiles in Sporting and Scirpus salt marshes.



Fig 7. Phosphate concentration in sediment pore-water profiles in Sportino and Scirpus salt marshes.

Phosphate concentration in *Scirpus* pore-water rhizosphere was lower than the *Spartina*, and very constant during the night period (Fig. 7). During the day, phosphate concentrations in the *Scirpus* pore-water increases, especially between 10 and 20 cm in depth, although day and night situations are not statistically different (p=0.1092), and were always much lower than in *Spartina* rhizosphere. The *Spartina* rhizosphere showed a more dynamic phosphate profile, with an increase concentration with depth, especially after the first 10 cm. Phosphate concentrations were always higher during the night period, although day and night situations were not statistically different (p=0.1689). Moreover, in the *Spartina* rhizosphere, phosphate concentrations in the first 0.3 millimetres in depth was in the same range as concentration was much lower.

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Discussion

Results concerning the field-monitoring program in the Mondego estuary showed that *Scirpus maritimus* salt marsh presented higher organic matter content in the sediment when compared to the *Spartina maritima* salt marsh. This may result from differences in particulate organic matter settling rates within the estuary, because water residence time is higher in the inner areas of the estuary (Duarte et al. in press). The Spartina salt marshes occur in the downstream areas while Scirpus in the inner areas of the estuary. These may also explain why the total phosphorus concentration in the sediment is higher in the Scirpus salt marsh (Day et al. 1989). The sediment total nitrogen is lower in Scirpus salt marsh, and especially during Scirpus growing season, which corresponds to the period from December/January until April/May (Lillebø 2000). In salt marshes plants rhizosphere bacteria fix part of the total nitrogen, but the nitrogenase activity tends to be suppressed by the presence of exogenic nitrates and oxygen (Carter 1988), like in the Scirpus rhizosphere.

Differences in nutrient concentrations in the pore-water profiles seem to be related to the plants dynamics, and generally the interaction between plants and the surrounding sediment increases during the growing season, and decreases during winter (Ernst 1990, Otte 1991 *all in* Caçador et al. 2000). Due to that, the uptake of nutrients is coupled to the photosynthethic rate, and follows the same pattern as photosynthesis at different light intensities (Valiela 1995).

Sparting is an alternative type (C4) of photosynthetic mechanism (Carter 1988), or just a (C4) type (Benito and Onaindia 1991), while Scirpus is a C3 type (Boschker et al. 1999). It has been discussed that plants with C4 photosynthetic pathway have, at least theoretically, a number of competitive advantages over C3 species (Adam 1990), namely a higher potential productivity, higher water-use efficiency and also a more efficient use of available nitrogen (Adam 1990). The form of inorganic nitrogen will be dependent upon the oxic state of the sediment (e.g. Nixon and Pilson 1983, Valiela 1995, Cowan et al. 1996). According to Adam's review (1990), although there is a likely predominance of ammonium over much of the marshes, measurements of nitrate reductase in several species indicated that nitrate was the major available nitrogen source. The same author identified two possibilities, either the heterogeneity of the environment provided aerobic micro sites with available nitrate, or rhizosphere oxidation mitigated the prevailing ammonium. Moreover, it was found a declining gradient from seaward to landward in both nitrogen redutase and tissue nitrogen concentrations in Spartina, as well as in other species (Adam 1990). These may explain the fact that Scirpus rhizosphere presented higher concentrations of the nitrate form of nitrogen, while Spartina rhizosphere presented higher concentrations of the ammonia form of nitrogen. Furthermore, in the Scirpus rhizosphere, nitrate concentrations in the first millimetres in depth, was in the same range as the concentrations recorded in the low water pools, while in the Spartina rhizosphere it was ten times lower. In addition, the concentration of ammonia was much higher in the Sparting pore-water profiles and was in the same range as the concentrations recorded in the low water pools.

The yearly pattern of dissolved inorganic nutrients in the water column, in the south arm of the Mondego estuary, showed an increased concentration of nitrogen (nitrite, nitrate and ammonia) from summer until early winter, in which ammonia was the dominant form of nitrogen (Martins et al. 2001), which is also the pattern frequently found in temperate estuaries (Nixon and Pilson 1993). Our results concerning the nutrients concentrations in the *Spartina* and *Scirpus* salt marshes low water pools showed differences in nitrate and ammonia dynamics, which may

represent a different contribution from each type of salt marsh sediment/water phase to the overlaying water. In fact these results suggest that the *Spartina* salt marsh may contribute to the nitrogen pool in the water column by ammonia efflux process, while *Scirpus* salt marshes may contribute by nitrate efflux process.

Both species have the ability to transport oxygen to the belowground parts, where it is used for root respiration and oxidation of the rhizosphere (Teal and Kanwisher 1966, Bertness 1991 *all in* Adams and Bate 1995, Armstrong and Armstrong 1988, Laan and Blom 1990 *all in* Cleavering et al. 1995). This process may lead to the precipitation of iron oxides around the roots (Vale et al. 1990), and eventually increase the adsorption capacity of the sediment. In our results, although, *Scirpus* sediment rhizosphere had higher total phosphorus concentration, the pore-water profiles show that in May the phosphate concentration was much lower than in *Spartina* salt marsh. Moreover, in *Spartina* rhizosphere, phosphate concentration in the first millimetres in depth was in the same range of concentration was much lower. These results suggest that the *Scirpus* rhizosphere may have a stronger adsorption capacity, at least during the mature phase.

Vale et al. (1990) described the formation of metal-enriched concretions around the roots of Spartina maritima in the Tagus estuary, and suggests that this process is probably related to the increased oxygen in the rhizosphere. In the Mondego estuary salt marshes, we observe a thin layer of iron oxides surrounding only the Scirpus maritimus rhizomes (personal observation). Besides, under anoxic conditions, Fe3* hydroxides are reduced to Fer* ions and phosphate is released to solution, while under more oxygenated conditions, like the ones surrounding plants rhizosphere, the ferrous iron is precipitated again as ferric hydroxide, which removes dissolved phosphate by readsorption (Berner and Berner 1996). This chemical reaction may explain the differences between phosphate concentrations in Sportino and Scirpus rhizosphere. Additionally, in May, Scirpus was still in the growing season, and so phosphate uptake from the sediment pore-water could also be more intense. Therefore, this may also be the result of modifying the chemistry of the rhizosphere during Scirpus growing season. Moreover, during the summer period, which corresponds to the senescent phase of the plant, the efflux of phosphorus from the sediment seems to be an important contribution to the concentrations in the low water pools. Also, a study performed in Chesapeak Bay (USA) (Wigand et al. 1997), showed that macrophyte species composition influence the pore-water phosphate and solid phase phosphorus and metal levels. One of the possible explanations, pointed out by these authors, were the differences in root oxygenation capabilities.

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Our results reinforce the general idea that salt marsh plants regulates the fluxes of dissolved inorganic nutrients between the sediment surface and overlying water, suggesting that coupling between plant and sediment is a species-specific process.

Results obtained from this study can conduct to a more comprehensive and environmentally correct understand of estuarine systems functioning. The knowledge acquired may be of particularly importance on management programs due to excess of nutrient inputs into estuarine systems.

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