Biogeochemistry (2005) 75: 289–304
DOI 10.1007/s10533-004-7587-9

Dissolved inorganic nitrogen pools and surface flux under different brackish marsh vegetation types, common reed (*Phragmites australis*) and salt hay (*Spartina patens*)

LISAMARIE WINDHAM-MYERS
Department of Earth and Environmental Sciences, United States Geological Survey, Mailstop 480, 345 Middlefield Road, Menlo Park, CA 94025; (e-mail: lwindham@usgs.gov; phone: 650-329-4447; fax: 650-329-4463)

Received 14 August 2003; accepted in revised form 14 December 2004

Key words: Ammonium, Diffusion, Estuary, Invasion, Macrophyte, National Estuarine Research Reserve, Porewater

Abstract. The current expansion of *Phragmites australis* into the high marsh shortgrass (*Spartina patens*, *Distichlis spicata*) communities of eastern U.S. salt marshes provided an opportunity to identify the influence of vegetation types on pools and fluxes of dissolved inorganic nitrogen (DIN). Two brackish tidal marshes of the National Estuarine Research Reserve system were examined, Piermont Marsh of the Hudson River NERR in New York and Hog Island in the Jacques Coustaeu NERR of New Jersey. Pools of DIN in porewater and rates of DIN surface flux were compared in replicated pairs of recently-expanded *P. australis* and neighboring *S. patens*-dominated patches on the high marsh surface. Both marshes generally imported nitrate (NO_3^-) and exported ammonium (NH_4^+), such that overall DIN was exported. No differences in surface exchange of NO_3^- or NH_4^+ were observed between vegetation types. Depth-averaged porewater NH_4^+ concentrations over the entire growing season were 56% lower under *P. australis* than under *S. patens* (average 1.4 vs. 3.2 mg NH_4^+ L^{-1}) with the most profound differences in November. Porewater profiles showed an accumulation of NH_4^+ at depth in *S. patens* and constant low concentrations in *P. australis* from the soil surface to 50 cm depth, with no significant differences in porewater salinity. Despite these profound differences in porewater, NH_4^+ diffusion from soils of *P. australis* and *S. patens* were not measurably different, were similar to other published rates, and were well below estimated rates based on passive diffusion alone. Rapid adsorption and uptake by litter and microbes in surface soils of both communities may buffer NH_4^+ loss to flooding tides in both communities, thereby reducing the impact of *P. australis* invasion on NH_4^+ flux to flooding waters.

Introduction

In addition to hydrological and morphological differences (Childers 2000) seasonal, site and successional differences in vegetative cover within and between salt marshes have been correlated repeatedly with tidal exchanges of dissolved inorganic nitrogen (DIN). Several researchers have demonstrated that marsh-estuarine fluxes of DIN follow the seasonality of macrophyte growth, with greater DIN import during the summer than during the spring

and fall, when DIN may be exported (Jordan et al. 1983; Wolaver et al. 1988; Jordan and Correll 1991; Childers et al. 1993). Additionally, different vegetation zones within marshes (high marsh, low marsh, unvegetated) often exhibit different dynamics of nutrient-exchange (Jordan et al. 1983; Wolaver and Ziemann 1983). In comparisons between marshes, Childers and Day (1990) demonstrated that marsh maturity decreased nutrient exchange rates, and Childers (1994) found that macrophyte biomass was positively correlated with ammonium import in summer months.

Although spatial and temporal patterns of vegetation appear to influence DIN flux, studies isolating the effects of vegetation types on DIN flux have historically been confounded by the strong hydrological zonation of plant species within marshes. The distribution of plant species and aboveground biomass is largely constrained by porewater turnover rates, a consequence of distance from tidal creeks and patterns of tidal flooding (Howes et al. 1981; Dame and Kenny 1986). Terrestrial ecologists have consistently demonstrated that individual plant species can profoundly alter rates of nitrogen cycling in surrounding soils (see Hobbie 1992; Wedin and Tilman 1994; Hooper and Vitousek 1998). Salt marsh plants of different morphologies (e.g. rooting biomass and distribution, aboveground stature and biomass) and physiologies (nutrient uptake, salt exclusion, gas transport, transpiration rates, photosynthetic pathways) may not only differ in plant uptake of DIN, but also affect microbial, physical and chemical processes within the soil and vegetation (e.g. Howes et al. 1981).

Over the past century, populations of *Phragmites australis* (common reed) have been expanding throughout high marshes of the eastern U.S., rapidly replacing the short tussock-forming grass *Spartina patens*, with tall deep-rooted, sod-forming monotypic reed beds (see Chambers et al. 1999). Temporal correlations and manipulative experiments demonstrate that *P. australis* invasions can greatly increase biomass and alter soil properties, such as increased reduction–oxidation potentials, decreased interstitial water levels, less variable microtopography, and lower sulfide concentrations, in less than 15 years (Windham and Lathrop 1999; Bart and Hartman 2000). Windham and Ehrenfeld (2003). Demonstrated that fluxes of N between internal pools were generally increased when *P. australis* replaces *S. patens*, but that due to compensatory responses, the net effect on N availability was only marginal. They suggested, however, that the greater magnitude of N cycling under *P. australis* may reduce the mobility of N pools, thus reducing the hydrologic export of DIN.

In this study, seasonal DIN dynamics were compared between replicate paired plots of neighboring populations of *P. australis* and *S. patens* in two undisturbed brackish tidal marshes. Measured rates of DIN flux from soils to the water column are compared to modeled rates of DIN flux based on porewater concentrations and soil porosity. These data are discussed in relation to concurrent measurements of nitrogen cycling processes among plants and microbial communities (Windham and Ehrenfeld 2003).

Site description

Data were collected within two brackish tidal marshes of the National Estuarine Research Reserve (NERR) system – Piermont Marsh, NY of the Hudson River NERR and Hog Island, NJ of the Jacques Cousteau-Mullica River NERR. All research sites within these marshes were historically dominated by *S. patens* with recently expansive populations of *P. australis* (Ferren et al. 1981; Winogrond et al. 1997). All sites had similar elevations and hydroperiods, with flooding during approximately 20% of annual high tides, with tidal amplitudes of 1–1.2 m, and with water of low salinity (maximum 6–8 ppt; Windham 1999). In regards to establishment patterns, *P. australis* has invaded Piermont Marsh primarily from creek banks toward high marsh surfaces (Winogrond et al. 1997; Lathrop et al. 2003), whereas the invasion of *P. australis* on Hog Island has originated from randomly scattered patches throughout the island Ferren et al. 1981; Windham and Lathrop 1999; Lathrop et al. 2003).

At each marsh, neighboring paired plots (which included 1 plot in a 15–20-year-old *P. australis* population and 1 plot in a neighboring uninvaded *S. patens*-dominated community, less than 2 m apart) were chosen and established at 3 replicate sites in which both species were present at the same elevation ($n = 12$). All plots were located more than 15 m away from tidal creeks to reduce the influence of horizontal advective flows of porewater (Howes and Goehringer 1994). Measurements with replicate PVC wells at each site ($n = 12$) in May 1995 confirmed that the depth (10–13 cm) and source (surface flow) of flooding at spring high tides were similar between sites.

Methods

Porewater pools

Pools of DIN in soil porewater were measured in 3 consecutive years using porewater equilibrators (peepers; Harvey et al. 1995) to measure DIN concentrations and soil cores to measure soil moisture content before, during and after the growing season (August and November in 1995 and 1996; April, August and November in 1997). In 1995 and 1996, I used 30-cm long peepers ($n = 12$) with 14 wells (7 pairs at 4 cm depth increments). Due to interesting patterns observed along the 30 cm porewater profile, I built and deployed 50 cm-long peepers to capture additional variability with depth. The 50 cm depth peepers consisted of a single row of 5 wells at 10 cm depth increments ($n = 24$) and were deployed as pairs. Wells were filled with 15 ml of deionized water and covered with cellulose dialysis tubing (0.6 μm; Spectrapor) that was clamped down with a fitted sheet of PVC. Prior to deployment, the peepers were submerged in buckets of deionized water through which N_2 gas was bubbled continuously for 24 h, bringing dissolved oxygen below detection levels (< 0.1 mg l^{-1} O_2).

Peepers were inserted into saturated marsh soils during neap tides. The well water in the peepers was allowed to equilibrate for 10–12 days with surrounding porewater across the cellulose membrane, after which the peepers were removed and the porewater samples were collected from each well with disposable syringes.

All water samples were filtered immediately upon collection (0.45 μm Millipore HA). Approximately 1–2 ml were analyzed immediately for porewater salinity on a Reichert-Jung refractometer. The remaining volume was acidified with 100 μl of 6 N HCl, and refrigerated until chemical analyses were performed. All water samples were analyzed for concentrations of NH_4^+ and $NO_3^- + NO_2^-$ (hereafter referred to as NO_3^-) by colorimetric analyses on a continuous flow analyzer (Alpkem RFP2, Oregon Scientific). Lower limits of detection were 0.01 mg l^{-1} for both NH_4^+ and NO_3^-. Although porewater pools of dissolved organic nitrogen (DON) are often greater than DIN pools (Childers et al. 2000), this study focused on DIN as it is directly available for plant assimilation.

Soil cores (0–50 cm depth) were collected in August 1996 and April, August, and November of 1997. Subsamples (approximately 20 g wet weight) from each 10 cm depth increment were oven-dried to a constant weight to determine moisture content. Water volume, as estimated by water weight, was multiplied by porewater concentrations of N to estimate pools of $N–NH_4^+$, $N–NO_3^-$, and N–DIN. Belowground biomass was also collected in 1997, as reported in Windham (2001).

Soil–water exchanges of DIN during tidal periods

Short-term surficial tidal flux of DIN was measured at each site with a permanently installed, fluctuating tidal chamber (36 cm diam) in each of the 12 plots, modified from Chambers (1992). Each chamber contained live stems of the target species only. After installing the chambers in the early summer of 1995, the marsh plots remained undisturbed until the following spring when the seal of each chamber was tested with a bromide tracer (KBr) in April 1996. Control 'chambers' ($n = 3$) were 20 l acid-washed polypropylene basins (Rubbermaid) that received the same flooding treatments as the vegetated chambers. Control basins were used to calculate DIN transformations in the water column alone and thus separate these from DIN transformations due to soil–water exchange.

Soil–water exchanges of DIN were measured from June–October in 1996 and May–October in 1997 during weeks of spring tide. To insure our ability to capture a 'first flush' event, sampling was conducted 3–4 days before the highest predicted spring tides each month. During the growing season of 1996, 20 l of river water were pumped into a collapsible vinyl reservoir and carried onto the marsh surface to 'actively flood' the chambers. The tidal chambers were sealed with rubber stoppers and the enclosed marsh surface was slowly

flooded (13–16 cm depth) with the river water over a period of 1 h. A 20 ml sample of the pre-incubated river water was collected immediately and when the reservoir had emptied entirely into the chamber, the depth of flooding in the chamber was measured to the nearest cm. When the natural flood tide had completely receded (6–12 h later), the post-incubation water was stirred, a sample collected, and the depth of flooding in the chambers was re-measured. The chambers were allowed to drain, and this procedure was repeated over 3 consecutive tidal cycles each month, to determine differences in DIN flux rates over consecutive flood events.

To reduce the drainage of surface water into the soil in our experimental chambers, the sampling procedure was modified in 1997, toward the 'passive flooding' described in Anderson et al. (1997). On 1 day of spring tide each month (May–October) in 1997, the chambers were allowed to flood naturally and were sealed at the time of peak flooding. After stirring the water columns inside the chambers, a 20 ml sample of enclosed water was collected and the depth of flooding within and outside of the chambers was measured. When the tide had completely receded from the marsh surface, a second sample from the enclosed water was collected and the depth of flooding inside the chambers was measured again. This passive flooding method was more successful than the active flooding method in retaining the majority of the surface water but it yielded no results in June and July 1997, when both marshes failed to flood during spring tides.

All water samples were preserved and analyzed as previously described for porewater samples. Pools of $N–NH_4^+$ and $N–NO_3^-$ in the surface water of chamber were calculated as mg N m^{-2}. The differences between initial and final pools were used to calculate rates of $N–NH_4^+$, $N–NO_3^-$, and N–DIN flux in mg N m^{-2} h^{-1}.

In June 1996 and May 1997, DIN pools within the control and experimental chambers were monitored in hourly increments for 12 and 6 h periods, respectively. In those months, DIN flux rates were calculated for hourly time periods. For the remainder of the growing seasons, in which measurements were only taken at the beginning and end of the 6–12 h incubation period, a single integrated rate was calculated over the tidal period.

Modeled rates NH_4^+ flux through soil–water exchange

NH_4^+ diffusion rates were estimated using Fick's first law of diffusion. Rates of NH_4^+ diffusion from porewater to the surface were estimated using depth-averaged porewater concentrations of NH_4^+ to 30 cm depth, and a conservative diffusion coefficient for NH_4^+ ($D_s = 5.9*10^6$ cm^2 s^{-1}, Bolalek and Garca 1996). Diffusion rates were calculated for each site and species ($n = 12$) in August 1996 and 1997, as paired concentrations of porewater and surface water were only available for the month of August.

Statistical analyses

All statistical analyses were performed with Statview (Abacus Concepts 1996). In June 1996 and May 1997, pools of $N–NH_4^+$ and $N–NO_3^-$ pools in surface water were analyzed with a repeated measures 2-way analysis of variance (ANOVA) testing for effects of vegetation treatment (*P. australis*, *S. patens*, and control) and time under incubation (0, 1, 2, 4, 6, and 12 h). For all months, rates of DIN flux were compared using a factorial 3-way ANOVA that tested for effects of vegetation, month and marsh. The data from each month of 1996 were also analyzed for effects of 3 consecutive tidal cycles crossed with vegetation type by a 2-way ANOVA. A single factor correlation analysis was performed to compare $N–NO_3^-$ import with $N–NO_3^-$ supply in all treatments.

Porewater concentrations of $N–NH_4^+$, $N\text{-}NO_3^-$, and N–DIN were compared for each year using factorial 4-way ANOVA's that tested for effects of species, depth, month and site. A regression between predicted and measured rates of NH_4^+ diffusion from each site in August 1996 and 1997 was compared to a 1:1 regression relationship using an *F*-test to test for deviance between two regression slopes (Sokal and Rohlf 1981). Significance for all statistical tests was recognized at $\alpha < 0.05$. Differences between treatments were determined with Fisher's LSD post-hoc tests where appropriate.

Results

Porewater pools

NO_3^- concentrations in porewater were consistently below detection for each species. In contrast, NH_4^+ was found in each porewater sample of both *P. australis* and *S. patens*. For all 14 sampling events from 1995–1997, depth-averaged (0–30 cm) $N–NH_4^+$ concentrations were lower under *P. australis* than under *S. patens* ($F_{1,662} = 19.177$, $p < 0.0001$; Figure 1). Further, for *S. patens* $N–NH_4^+$ concentrations were higher during November than during August ($F_{2,72} = 16.163$, $p < 0.0001$). Concentrations of NH_4^+ under *S. patens* rose by 24% ± 3%SE after the growing season at all sites in all years except Hog Island in 1996. In contrast, seasonal concentrations of $N–NH_4^+$ remained constant under *P. australis* ($F_{2,72} = 1.41$, $p = 0.2429$) at all sites in all years.

NH_4^+ concentrations generally increased with depth in *S. patens* in August, and to a lesser extent in November (e.g. in 1997, $F_{4,120} = 12.31$, $p < 0.0001$, Figure 2a; Table 1). In contrast, NH_4^+ concentrations under *P. australis* remained consistently low throughout the porewater profile ($F_{4,120} = 1.69$, $p = 0.267$; Figure 2b, Table 1). No correlation was observed between salinity and NH_4^+ concentrations (Figure 3a and b, $p = 0.318$), suggesting that hydrology alone could not account for the observed differences in DIN concentrations.

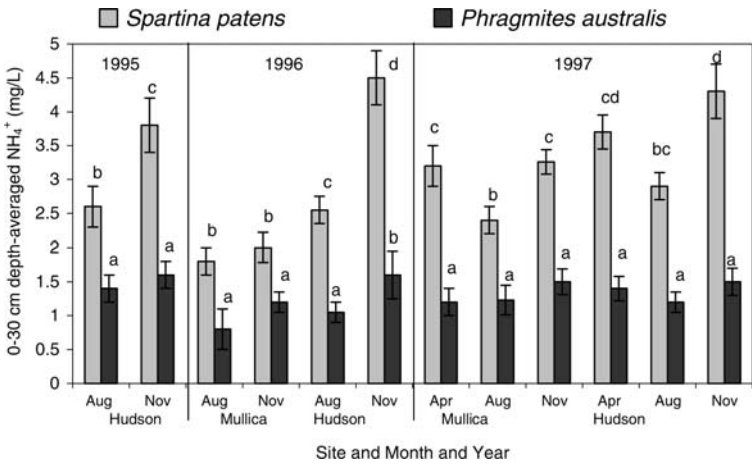

Figure 1. Depth-averaged porewater ammonium (NH_4^+) concentrations for 1995–1997, in *P. australis* and *S. patens* communities at both the Hudson River and Mullica River marshes. Error bars denote a 95% confidence interval (2 standard errors). $n = 12$ for combination of plant species, site and date.

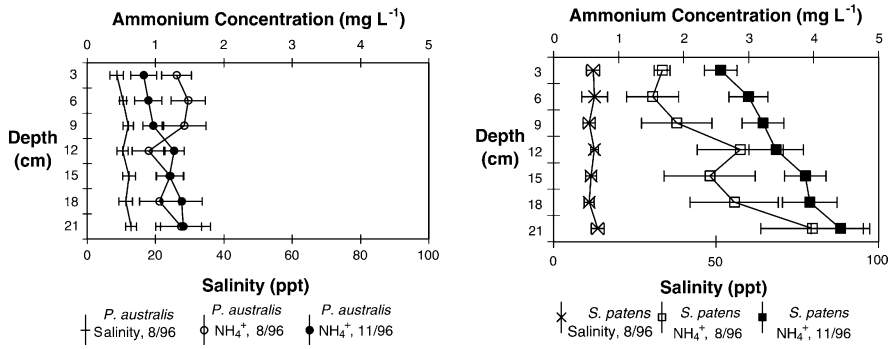

Figure 2. (a and b) Diagram of depth profiles of porewater ammonium (NH_4^+) concentrations and salinity within *S. patens* and *P. australis* from the surface to 30 cm depth for August and November of 1996. Error bars denote a 95% confidence interval (2 standard errors). Figure taken from Windham and Ehrenfeld (2003), courtesy of Ecological Applications and Allen Press.

When compared with the distribution of belowground biomass to 50 cm depth, porewater profiles from August 1997 demonstrate a strong inverse relationship between root and rhizome mass and porewater concentrations in *S. patens* (Table 1; $r^2 = 0.912$, $p = 0.001$). In contrast, both porewater N–NH_4^+ concentrations and belowground biomass remain relatively constant under *P. australis* yielding a much weaker correlation Table 1; $r^2 = 0.271$, $p = 0.048$).

The soils in both sites were saturated with water (82% + 2.3 SE) at all times measured, suggesting that differences in porewater DIN pools are driven primarily by differences in DIN concentrations.

Table 1. Average soil moisture, bulk density, organic content, porosity, porewater salinity and NH_4^+ concentrations for plots of *P. australis* and *S. patens* at Piermont Marsh, Hudson River, NY. Soil characteristics and belowground biomass pools are reported from soil cores collected in August 1997 ($n = 9$ for each plant species at each depth). Standard error indicated in parentheses.

	Soil moisture % wet wt.	Bulk density g cm^{-3}	Porosity ϕ	Belowground biomass (g m^{-2})	Porewater Salinity	Porewater NH_4^+ concentration mg NH_4^+ l^{-1}
P. australis						
0–10 cm	77.6 (2.42)	0.24 (0.045)	0.91	349 (29)	8.7 (0.8)	1.20 (0.23)
10–20 cm	68.7 (4.70)	0.27 (0.054)	0.90	297 (19)	10.5 (1.5)	1.77 (0.49)
20–30 cm	81.2 (1.23)	0.28 (0.106)	0.89	231 (27)	10.3 (1.7)	1.41 (0.34)
30–40 cm	82.3 (1.89)	0.28 (0.049)	0.89	175 (37)	11.3 (2.4)	1.91 (0.87)
40–50 cm	89.0 (1.77)	0.34 (0.057)	0.77	141 (42)	12.8 (1.4)	1.88 (0.98)
S. patens						
0–10 cm	83.1 (2.98)	0.15 (0.024)	0.94	545 (24)	12.2 (1.2)	1.54 (0.81)
10–20 cm	78.9 (1.45)	0.22 (0.052)	0.92	239 (38)	12.6 (1.5)	2.76 (0.59)
20–30 cm	83.4 (1.92)	0.27 (0.076)	0.90	78 (35)	12.4 (2.2)	4.18 (0.69)
30–40 cm	88.5 (0.98)	0.31 (0.095)	0.88	0	10.9 (1.4)	4.89 (1.70)
40–50 cm	93.8 (1.27)	0.36 (0.045)	0.86	0	13.6 (2.7)	5.65 (1.67)

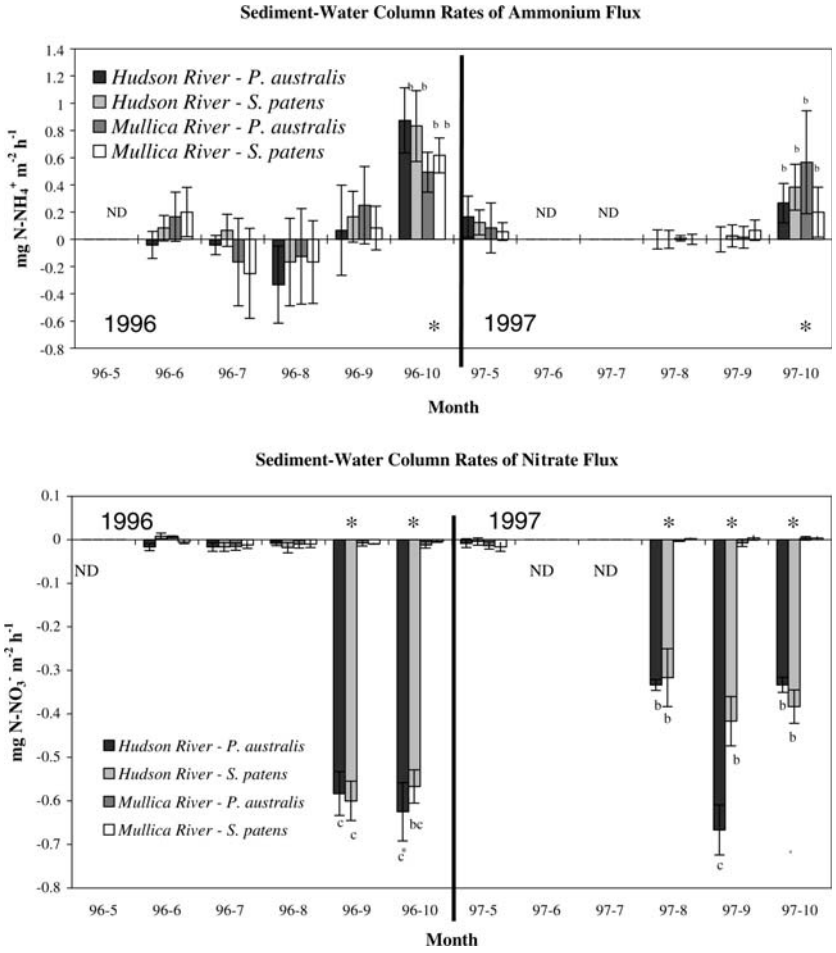

Figure 3. (a and b) Net (a) ammonium ($N–NH_4^+$) and (b) nitrate (NO_3^-) flux (mg N m^{-2} h^{-1}) within plots of each plant species across the growing season (May–October). Positive values are increases of DIN within the water column, and negative values are decreases of DIN within the water column. Error bars denote a 95% confidence interval (2 standard errors).

Soil–water exchanges of DIN during tidal periods

Changes in the DIN pools of the water column occurred quickly in all treatments at both locations (Table 2). Pools of both $N–NH_4^+$ and $N–NO_3^-$ in the surface water of vegetated treatments were altered within 2 h of incubation during each year (1996: $F_{5,108} = 3.78$ $p = 0.019$; 1997 $F_{4,108} = 2.21$, $p = 0.032$). $N–NO_3^-$ pools decreased over the incubation in all treatments, although the decrease occurred more slowly in control treatments. After 4 h, $N–NO_3^-$ pools reached a plateau in all treatments and did not change for the

Table 2. Flux rates of ammonium and nitrate over 1–12 h incubations in June 1996 and May 1997 at Piermont Marsh NY, in vegetated chambers (*P. australis* and *S. patens*) and in control basin. Fisher's LSD characters denote significant differences between hourly flux rates between both time of incubation and marsh treatment.

Year	Time (h)	Ammonium flux (mg $N–NH_4^+$ m^{-2} h^{-1})			Nitrate flux (mg $N–NO_3^-$ m^{-2} h^{-1})		
		P. australis	*S. patens*	Control	*P. australis*	*S. patens*	Control
1996	1	-0.05^{a}	0.06^{a}	0.05^{a}	-0.77^{a}	-0.71^{a}	-0.57^{a}
	2	0.42^{b}	0.13^{ab}	0.02^{a}	-1.60^{ab}	-1.33^{ab}	-0.88^{ab}
	4	0.18^{b}	0.15^{ab}	0.25^{a}	-2.25^{b}	-1.93^{b}	-1.41^{b}
	6	0.22^{ab}	0.19^{b}	0.06^{ab}	-4.30^{c}	-3.45^{c}	-2.19^{bc}
	12	0.24^{b}	0.28^{b}	0.22^{b}	-7.30^{d}	-6.60^{d}	-5.80^{cd}
1997	1	-0.20^{a}	0.20^{a}	0.35^{ab}	0.05^{a}	-0.69^{a}	0.30^{a}
	2	0.21^{ab}	0.32^{b}	0.37^{b}	-1.94^{b}	-2.10^{b}	-1.05^{ab}
	4	0.43^{b}	0.42^{b}	0.31^{ab}	-1.20^{ab}	-2.34^{b}	-1.8^{b}
	6	0.47^{a}	0.43^{b}	0.54^{b}	-0.97^{ab}	-1.50^{ab}	-0.23^{ab}

remainder of the experiment in either year. $N–NH_4^+$ pools were more variable within treatments over the full course of the incubations, but the increases in $N–NH_4^+$ pools that were observed over the first 6 h persisted until the end of the incubation (Table 2). Because $N–NH_4^+$ pools increased more than $N–NO_3^-$ pools decreased, N–DIN overall increased within water columns in vegetated treatments (e.g. in contact with soil), suggesting that soil–water flux was positive (i.e. N–DIN was exported).

Sequential flooding events had similar flux rates (there was no decay in nutrient flux over consecutive tides; $F_{2,36} < 5.06$, $p > 0.05$ for June–October 1996) and were thus analyzed as independent events. When water column transformations were removed from soil–water interactions, in most months, hourly rates of surficial N–DIN flux were not significantly different than zero (Figure 3a and b). When fluxes of DIN were observed (such as in October 1996 and 1997), the directions were relatively consistent; $N–NO_3^-$ was removed from the water column and $N–NH_4^+$ was added (Figure 3a and b). $N–NH_4^+$ export was commonly greater than $N–NO_3^-$ import, generating an overall export of N–DIN.

Surprisingly, no major differences in DIN flux were observed between chambers vegetated with *P. australis* or *S. patens* (Figure 3a and b). In the only case where a difference was found between chambers of different plant species, $N–NO_3^-$ flux was greater in *P. australis* plots in September 1997 at Piermont Marsh ($F_{1,6} = 7.12$, $p = 0.006$).

For all treatments, the magnitude of $N–NO_3^-$ import was strongly influenced by the river NO_3^- concentrations (Figure 4). Across both years, $N–NO_3^-$ consumption by soils and the water column was positively correlated with $N–NO_3^-$ concentrations in flooding water ($r^2 = 0.949$; $p < 0.0001$). In 1996 for example, NO_3^- concentrations doubled over the growing season in the Hudson River, rising from 0.07 to 0.15 mg $N–NO_3^-$ l^{-1}, with $N–NO_3^-$

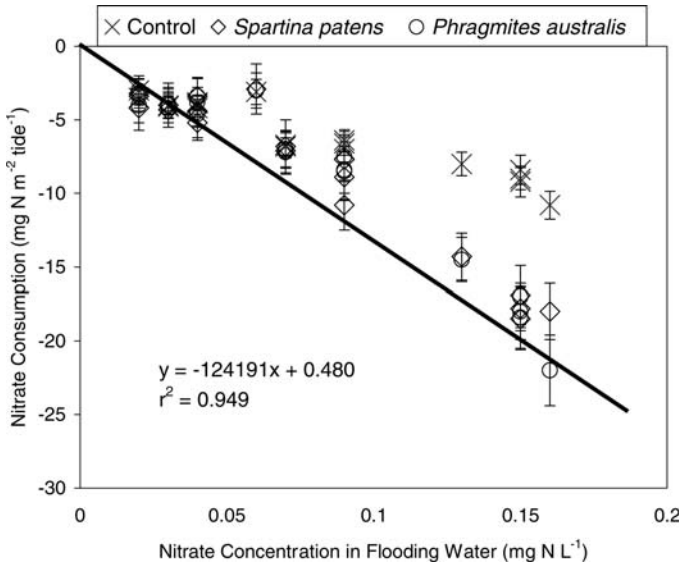

Figure 4. Nitrate consumption increases with increasing nitrate concentration in flooding water, in both *P. australis*-dominated and *S. patens*-dominated plots, as well as in control basins. Note that at higher concentrations of nitrate in flooding water (as measured at the Hudson River – Piermont Marsh site), nitrate consumption by vegetated plots becomes significantly greater than nitrate consumption by the water column alone (control). Error bars denote a 95% confidence interval (2 standard errors), with sample sizes of 6 for nitrate concentration, and 3 for nitrate consumption

consumption increasing in turn. The consistently small amounts of NO_3^- present in flooding water along the Mullica River (0.02–0.06 mg N–NO_3^- l^{-1}) were quickly removed within the water columns, preventing a net flux into the soils at the Hog Island marsh. Net fluxes of N–NO_3^- were found at Piermont Marsh when Hudson River concentrations of NO_3^- were >0.12 mg N–NO_3^- l^{-1} (Figure 4).

Predicted rates of soil–water exchange of NH_4^+

Predicted rates of NH_4^+ diffusive flux in *P. australis* and *S. patens* communities (7.4 and 20.6 mg NH_4^+ m^2 h^{-1}) were consistently greater than measured rates of NH_4^+ flux (0–1 mg NH_4^+ m^2 h^{-1} ; $F_{(1,11)} = 16.67$, $p < 0.0001$; Figure 5). Although the diffusion model overestimated measured rates of NH_4^+ flux, predicted and measured rates were correlated for both *P. australis* ($r^2 = 0.19$; $p < 0.001$) and *S. patens* ($r^2 = 0.30$ $p = 0.029$). The regression slope ($m = 9.07$) for *S. patens* of predicted rates vs. measured rates indicates that measured rates of diffusion were much less than estimated rates (Figure 5), and thus significantly different than a 1:1 slope ($F_{(1,5)} = 4.66$, $p = 0.021$). For

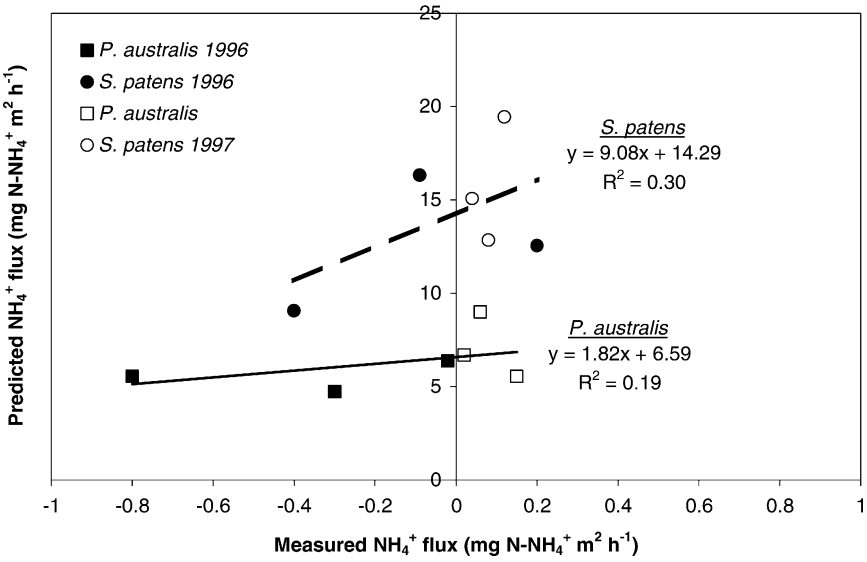

Figure 5. Scatterplot of measured vs. predicted rates of ammonium export from the sediment to the water column for each plant species, *P. australis* and *S. patens*. The correlation coefficient (r^2) and linear equation of significant correlations between measured and predicted rates are reported individually for each species.

P. australis, measured rates were also less than estimated rates ($m = 1.8$) but the relationship was not significantly different than a 1:1 slope ($F_{(1,5)} = 2.12$, $p > 0.05$).

Discussion

The soil under *P. australis* exhibited a 3-fold reduction in NH_4^+ pools as compared to the soil under *S. patens*. Given the similar elevation, hydrology and salinity among paired plots of both vegetation types, in two sites of different invasion patterns, it is likely that the recent establishment of *P. australis* generates these differences in porewater pools of NH_4^+. A similar pattern was observed by Chambers (1997), whereby NH_4^+ concentrations were 5-fold greater in *Spartina alterniflora (*cordgrass) than in *P. australis* plots. Whereas porewater concentrations of NH_4^+ under *S. patens* are high at the surface and increase significantly with depth, *P. australis* reduces porewater concentrations of NH_4^+ from the soil surface to at least 50 cm depth, generating a porewater profile of consistently low NH_4^+ concentrations.

Despite the differences between these vegetation types in porewater NH_4^+ pools, soil–water exchanges of NH_4^+ were similar under *P. australis* and *S. patens* throughout the growing season. When soil–water exchanges of DIN were observed, NH_4^+ was exported and NO_3^- was imported equally under

each vegetation type, except in 1 sampling event. In that unique case (September 1997 at Piermont Marsh), *P. australis*-dominated marsh plots imported 48% more NO_3^- than *S. patens*-dominated plots.

The lack of significant flux rates of NH_4^+ and a lack of differences between the vegetation types in surficial tidal exchange suggest that during most of the growing season, DIN pools in overlying surface waters do not interact strongly with porewater. The distance of these sites (>15 m) from tidal creeks suggests that horizontal advective flow is minimal and unlikely to explain the lack of surface diffusion (Agosta 1985; Howes and Goehringer 1994). Further, although the subsurface hydrology of this marsh is poorly understood, interstitial salinities are similar both between communities and with depth (Figure 2a and b), implying that drainage rates are similar in the paired plots of *P. australis* and *S. patens*.

Significant NH_4^+ export is only observed near the end of the growing season, and then, even the greater differences in porewater NH_4^+ between species does not generate any difference in flux. Modeled diffusion rates, which accounted only for physical and chemical soil properties, grossly overestimated measured rates of NH_4^+ flux in both communities, as well as NH_4^+ flux measured in most other published studies (see Childers 1999). Although porewater concentrations of NH_4^+ are much higher in this study, the low rates of NH_4^+ export are similar in magnitude to those reported by Jordan and Correll (1985) from a surface flume study in a brackish marsh of Chesapeake Bay (1.2 g N–NH_4^+ m^{-2} $year^{-1}$). Assuming 12 flooding tides each month, the small fluxes of NH_4^+ measured at my sites generate an annual load of 2.16 g N–NH_4^+ m^2 $year^{-1}$ to overlying marsh water. This liberal calculation is surprisingly low, particularly considering the strong NH_4^+ gradient present in *S. patens* communities.

Several studies have demonstrated that subsurface–surface exchange may be strongly mediated by soil and litter adsorption (Bowden 1986) and/or microbial immobilization (White and Howes 1994). Using a process-based nitrogen mass balance model, Anderson et al. (1997) also observed high rates of NH_4^+ supply (mineralization rates) but low rates of export from *S. alterniflora*-dominated salt marsh. They suggested that NH_4^+ is rapidly immobilized into a readily remineralizable microbial N pool which prevents the advective and/or diffusive loss of N to overlying water. In a companion study to the results reported here, Windham and Ehrenfeld (2003) found that NH_4^+ immobilization on fresh litter of both communities can account for more than twice the entire estimated annual flux of NH_4^+ from surficial exchange. Rapid, temporary microbial uptake may also play a role but was not measured in this study. Finally, NH_4^+ flux in the marsh interior may be reduced if the marsh surface is not saturated at the time of flooding, as the front of interaction between surface and subsurface water pools may be far below the surface (Hemond et al. 1984),thereby limiting diffusive, upward flux of DIN.

Why were NH_4^+ surficial flux rates so similar between species, and what processes were inhibiting ammonium diffusion, especially from the *S. patens*

community? One possible reason is that during the growing season, NH_4^+ concentrations in the 0–5 cm depth were relatively similar between species. This implies that differences at depth do not directly influence NH_4^+ flux at the soil surface. However, this shallow depth (0–5 cm) did show differences between communities in November of both 1996 (Figure 2) and 1997 (Figure 1). Whereas we did not measure NH_4^+ surficial flux rates after October, it is possible that significant differences might have been observed. It is unlikely that the *S. patens* community has a substantially more rapid rate of litter adsorption and uptake. As demonstrated in Windham and Ehrenfeld (2003), *S. patens* litter adsorbed NH_4^+ at a marginally faster rate than *P. australis*, but *P. australis* generated nearly 5-times the litter mass (Windham 2001). A ^{15}N tracer study by White and Howes (1994) and a process-based model by Anderson et al. (1997) both suggest that microbial immobilization is likely to be an important process limiting soil–water exchange of DIN, and while this is likely important in this site as well, it was not directly measured.

As has been observed for *P. australis* (Meyerson 2000; Windham and Ehrenfeld 2003), DIN uptake by litter, plants and microbes can be increased substantially when smaller macrophytes are replaced by monocultures of larger macrophytes. These increased rates of N retention and removal, however, are only likely to influence marsh-estuary DIN relations in sites subject to horizontal advective flow (e.g. creekbank). The interior marsh sites examined in this study are dominated by a vertical hydrology, and thus, differences in porewater ions could accumulate in situ between infrequent flushings. As discussed by Lathrop et al. (2003), the spatial location of *P. australis* may be more important than total coverage in estimating its effects on marsh-estuary DIN relations. In direct contrast to the lack of surficial differences observed in this study, it is likely that the subsurface tidal flux of NH_4^+ from the marsh to tidal creeks will be substantially reduced by the invasion of *P. australis* near salt marsh creekbanks.

Conclusion

When *P. australis* replaces *S. patens* in high marsh sites, porewater pools of NH_4^+ were strongly reduced but surface water DIN dynamics remained similar in direction, magnitude, and seasonality. Low rates of NH_4^+ export and NO_3^- import to the marsh were not affected by vegetation types, despite the greater porewater pools under *S. patens*. The incongruity between measured and modeled rates of NH_4^+ flux suggests that adsorption and immobilization in the upper soils and marsh surface restrict the export of NH_4^+ to overlying water during tidal flooding. Therefore, although the replacement of *S. patens* with *P. australis* reduces NH_4^+ pools within the marsh, this shift in plant species did not affect tidal exchanges of DIN on the marsh surface.

Acknowledgements

This research was conducted with funding from New York Sea Grant (NOAA) and the Hudson River National Estuarine Research Reserve, and through a NASA Earth System Science Fellowship. My deepest thanks go to Joan Ehrenfeld, Stuart Findlay, Jean Marie Hartman, Rick Lathrop and Sybil Seitzinger, as well as Chuck Nieder and Randy Chambers, for help with experimental design and interpretation. Mark Pekosz, Andre Cantelmo, Jeff Lambe, Mark Laska, and Jack Paxton provided outstanding field and/or laboratory assistance.

References

Abacus Concepts 1996. Statview 4.1. Abacus Concepts, Inc. Berkeley, CA.

Agosta K. 1985. The effect of tidally induced changes in the creekbank water table on porewater chemistry. Estuar. Coast. Shelf Sci. 2: 389–400.

Anderson I.C., Tobias C.T., Neikirk B.B. and Wetzel R.L. 1997. Development of a process-based nitrogen mass balance model for a Virginia (USA) *Spartina alterniflora* salt marsh: implications for net DIN flux. Mar. Ecol. Prog. Ser. 159: 13–27.

Bart D.J. and Hartman J.M. 2000. Environmental determinants of *Phragmites australis* expansion in a New Jersey salt marsh: an experimental approach. Oikos 89: 59–69.

Bolalek J. and Graca B. 1996. Ammonium flux at the sediment-water interface in Puck Bay, Baltic Sea. Estuar. Coast. Shelf Sci. 43: 767–779.

Chambers R.M. 1992. A fluctuating water-level chamber for biogeochemical experiments in tidal marshes. Estuaries 15: 53–58.

Chambers R.M. 1997. Porewater chemistry associated with *Phragmites* and *Spartina* in a Connecticut tidal marsh. Wetlands 17: 360–367.

Chambers R.M., Meyerson L.A. and Saltonstall K. 1999. Expansion of *Phragmites australis* into tidal wetlands of North America. Aquat. Bot. 64: 261–273.

Childers D., Day J.W. and McKellar H.N. 2000. Twenty (more) years of marsh and estuarine flux studies – Nixon (1980) revisited. In: Weinstein M. and Kreeger D. (eds), Concepts and Controversies in Tidal Marsh Ecology. Kluwer Academic Publishing, Dordrecht, The Netherlands, pp. 391–424.

Childers D.L. 1994. Fifteen years of marsh flumes: a review of marsh-column interactions in southeastern U.S.A. estuaries. In: Mitsch W.J. (ed.), Global Wetlands: Old World and New. Elsevier Publishing: Amsterdam, The Netherlands, pp. 277–294.

Childers D.L. and Day J.W.Jr. 1990. Marsh-water column interaction in two Louisiana estuaries: II. Nutr. Dynam. Estuar. 13: 393–403.

Childers D.L., McKellar H.N., Dame R.F., Sklar F.H. and Blood E.R. 1993. A dynamic nutrient budget of subsystem interactions in a salt marsh estuary. Estuar. Coast. Shelf Sci. 36: 105–131.

Dame R.F. and Kenny P.D. 1986. Variability of *Spartina alterniflora* primary production in the euhaline North Inlet estuary. Mar. Ecol. Prog. Ser. 32: 71–80.

Ferren W.R.Jr., Good R.E., Walker R. and Arsenault J. 1981. Vegetation and flora of Hog Island, a brackish wetland in the Mullica River, New Jersey. Bartonia 48: 1–10.

Harvey J.W., Chambers R.M. and Hoelscher J.R. 1995. Preferential flow and segregation of porewater solutes in wetland sediment. Estuaries 18: 568–578.

Hemond H.F., Nuttle W.K., Burke R.W. and Stolzenbach K.D. 1984. Surface infiltration in salt marshes: theory, measurement, and biogeochemical implications. Water Resour. Res. 20: 591–600.

Hobbie S. 1992. Effects of plant species on nutrient cycling. Trends in Ecology and Evolution 7: 213–216.

Hooper D.U. and Vitousek P.M. 1998. Effects of plant composition and diversity on nutrient cycling. Ecological Monographs 68: 121–149.

Howes B., Howarth R.W., Teal J.M. and Valiela I. 1981. Oxidation–reduction potentials in a salt marsh: spatial patterns and interactions with primary productivity. Limnol. Oceanogr. 26: 350–360.

Howes B.L. and Goehringer D.D. 1994. Porewater drainage and dissolved organic carbon and nutrient losses through intertidal creekbanks of a New England salt marsh. Mar. Ecol. Prog. Ser. 114: 289–301.

Jordan T.E. and Correll D.L. 1985. Nutrient chemistry and hydrology of interstitial water in brackish tidal marshes of Chesapeake Bay. Estuar. Coast. Shelf Sci. 21: 45–55.

Jordan T.E. and Correll D.L. 1991. Continuous automated sampling of tidal exchanges of nutrients by brackish marshes. Estuar. Coast. Shelf Sci. 32: 527–545.

Jordan T.E., Whigham D.F. and Correll D.L. 1983. Nutrient flux in the Rhode River: tidal exchange of nutrients by brackish marshes. Estuar. Coast. Shelf Sci. 17: 651–677.

Lathrop R.G., Whindham L. and Montesano P. 2003. Does Phragmites expansion after the structure and function of marsh landscapes? Patterns and processess revisited. Estuaries 26: 423–435.

Meyerson L. 2000. Ecosystem level effects of invasive species: A Phragmites case study in two freshwater tidal marsh ecosystems on the Connecticut River. Doctoral Thesis, Yale University, New Haven, Connecticut.

Sokal R.R. and Rohlf F.J. 1981. Biometry: the principles and practice of statistics in biological research. W.H. Freeman: New York, NY.

Wedin D.A. and Tilman D. 1994. Species effects on nitrogen cycling: a test with perennial grasses. Oecologia 84: 433–441.

White D.S. and Howes B.L. 1994. Long-term ^{15}N-nitrogen retention in the vegetated sediments of a New England salt marsh. Limnol. Oceanogr. 39: 1878–1892.

Windham L. 1999. Effects of an invasive reedgrass, *Phragmites australis*, on nitrogen cycling in brackish tidal marshes of New York and New Jersey. Ph.D. Thesis., Rutgers University, New Brunswick, New Jersey. 182, pp.

Windham L. and Ehrenfeld J.G. 2003. Net impact of a plant invasion on nitrogen cycling processes within a brackish tidal marsh. Ecological Applications 13: 883–897.

Windham L. and Lathrop R.G.Jr. 1999. Effects of *Phragmites australis* on aboveground biomass and soil properties in brackish tidal marsh. Estuaries 22: 927–935.

Winogrond H.G. and Kiviat E. 1997. Invasion of *Phragmites australis* in the tidal marshes of the Hudson River. Section VI: 29 pp. In: Nieder W.C. and Waldman J.R. (eds), Final Reports of the Tibor T. Polgar Fellowship Program, 1996. Hudson River Foundation, NY.

Wolaver T.G. and Zieman J. 1983. The role of tall and medium *Spartina alterniflora* zones in the processing of nutrients in tidal water. Estuar. Coast. Shelf Sci. 19: 1–13.

Wolaver T.G., Spurrier J.D., Wetzel R. and Webb K.L. 1988. Tidal exchange of nitrogen and phosphorus between a mesohaline vegetated marsh and the surrounding estuary in the lower Chesapeake Bay. Estuar. Coast. Shelf Sci. 16: 321–332.