

# Nitrogen Cycling and Ecosystem Exchanges in a Virginia Tidal Freshwater Marsh

SCOTT C. NEUBAUER<sup>1,2,\*</sup>, IRIS C. ANDERSON<sup>1</sup>, and BETTY B. NEIKIRK<sup>1</sup>

<sup>1</sup> College of William and Mary, School of Marine Science, Virginia Institute of Marine Science, Gloucester Point, Virginia 23062

<sup>2</sup> Villanova University, Department of Biology, Villanova, Pennsylvania 19085

**ABSTRACT:** Tidal freshwater marshes are diverse habitats that differ both within and between marshes in terms of plant community composition, sediment type, marsh elevation, and nutrient status. Because our knowledge of the nitrogen (N) biogeochemistry of tidal freshwater systems is limited, it is difficult to assess how these marshes will respond to long-term progressive nutrient loading due to watershed development and urbanization. We present a process-based mass balance model of N cycling in Sweet Hall marsh, a pristine (i.e., low nutrient) *Peltandra virginica*-*Pontederia cordata* dominated tidal freshwater marsh in the York River estuary, Virginia. The model, which was based on a combination of field and literature data, revealed that N cycling in the system was largely conservative. The mineralization of organic N to  $\text{NH}_4^+$  provided almost twice as much inorganic N as was needed to support marsh macrophyte and benthic microalgal primary production. Efficient utilization of porewater  $\text{NH}_4^+$  by nitrifiers and other microbes resulted in low rates of tidal  $\text{NH}_4^+$  export from the marsh and little accumulation of  $\text{NH}_4^+$  in marsh porewaters. Inputs of N from the estuary and atmosphere were not critical in supporting marsh primary production, and served to balance N losses due to denitrification and burial. A comparison of these results with the literature suggests that the relative importance of tidal freshwater marsh N cycling processes, including plant productivity, organic matter mineralization, microbial immobilization, and coupled nitrification-denitrification, are largely independent of small changes in water column N loading. Although very high (millimolar) concentrations of dissolved inorganic N can affect processes including denitrification and plant productivity, the factors that cause the switch from efficient N recycling to a more open N cycle have not yet been identified.

## Introduction

Tidal freshwater marshes lie at the upper end of the tidal zone but beyond the limit of salt water intrusion and have characteristics that resemble both nontidal freshwater wetlands and tidal brackish and salt marshes. These ecologically valuable wetlands are often found in densely populated and heavily industrialized regions and can be exposed to increased sediment, nutrient, and pollutant runoff associated with land clearing and the replacement of natural ecosystems with development. Despite the environmental stresses to which tidal freshwater marshes are exposed, they provide a range of ecosystem services including acting as water quality filters, serving as nursery habitats for juvenile fishes, and buffering storm and flood waters (Odum et al. 1984; Mitsch and Gosselink 2000).

In their role as water quality filters, tidal freshwater marshes can remove water column nutrients including nitrogen (N) and phosphorus (P) through denitrification, plant uptake, and burial. Tidal freshwater marshes are often seasonal sinks for P and inorganic N (as nitrate [ $\text{NO}_3^-$ ] and

ammonium [ $\text{NH}_4^+$ ]; Grant and Patrick 1970; Simpson et al. 1978; Bowden et al. 1991; Chambers 1992; Ziegler et al. 1999). With few exceptions (Chambers 1992; Anderson et al. 1998; Campana 1998), tidal freshwater marsh nutrient studies have been conducted in marshes affected by sewage effluent or urban runoff. The concentration of N in tidal waters may affect the strength of nutrient uptake (or release) and other processes including denitrification, organic matter decomposition, and plant productivity (Whigham and Simpson 1978; Valiela et al. 1985; Jordan et al. 1989; Gale et al. 1992; Cornwell et al. 1999). The availability of P can also affect rates of marsh N cycling (Sundareshwar et al. 2003).

Tidal freshwater marshes are typically characterized by significant variability both within and between marshes in plant community composition, sediment type (mineral versus organic), and marsh elevation (high versus low marsh) that can affect marsh nutrient cycling and marsh-estuarine exchanges. Despite their ecological significance, tidal freshwater marshes have not been studied nearly as well as their brackish and salt marsh counterparts. Only limited data are available to assess how these wetlands will respond to long-term nutrient loading resulting from watershed development. We constructed a comprehensive process-based N cycling

\* Corresponding author; current address: Baruch Marine Field Laboratory, P. O. Box 1630, Georgetown, South Carolina 29442; tele: 843/546-3623; fax: 843/546-1632; e-mail: scott@belle.baruch.sc.edu

model for a relatively pristine tidal freshwater marsh. The model was based on field and literature data, and included the uptake of N by marsh autotrophs, marsh-estuary and marsh-atmosphere N exchanges, and N transformations within marsh sediments. By comparing results from this study with data from more eutrophic systems, we can begin to understand which N cycling processes are most affected by the supply of allochthonous nutrients.

#### SITE DESCRIPTION

The Pamunkey River drains 3,768 km<sup>2</sup> in southeastern Virginia before merging with the Mattaponi River at the town of West Point to form the York River, which drains into Chesapeake Bay. The Pamunkey River watershed is primarily undeveloped (65% forested, 6% tidal + nontidal wetlands), with 27% as grass and croplands and <2% urbanized areas (USEPA 1996). As a result, tidal fresh and oligohaline waters of the Pamunkey River generally have dissolved inorganic nitrogen (DIN) concentrations that are low relative to more urbanized Chesapeake Bay watersheds (e.g., Potomac and Patuxent Rivers; USEPA 2002; Chesapeake Bay Program water quality data base, accessed March 11, 2004, at <http://www.chesapeakebay.net>).

Sweet Hall marsh is a microtidal freshwater wetland located on the Pamunkey River, approximately 35 km (by river) from West Point, Virginia, and 69 km from the mouth of the York River. Between 1996 and 1999, we measured rates of N cycling at Sweet Hall marsh near the western branch of Hill's Ditch, a small tidal creek that drains the southern portion of the marsh. Our study site, and the majority of the marsh, are separated from the mainland by the Pamunkey River and a relatively deep tidal channel (>2 m). The marsh does not receive direct land-derived nutrients from a shallow aquifer. To minimize sampling effects, three 30-m long boardwalks were constructed perpendicular to the tidal creek at the beginning of the study.

Salinities at the marsh are typically <0.5‰ (except during drought years), so large portions of the marsh (including our study site) are seasonally dominated by freshwater herbaceous vegetation including *Peltandra virginica* (arrow arum), *Pontederia cordata* (pickerel weed), and *Zizania aquatica* (northern wild rice). Based on our previous work at Sweet Hall, we defined seasons based on vegetation processes. During the early growth season (61 d), aboveground macrophyte biomass (AGB) rises from near 0 in March to approximately 100 g dry weight (gdw) m<sup>-2</sup> in April. The AGB increases to 600 gdw m<sup>-2</sup> by May and reaches maximum biomass in June (640 gdw m<sup>-2</sup>; Neubauer et al. 2000). May and June were classified as the late

growth season (61 d). In mid Atlantic tidal freshwater marshes, the AGB of *P. virginica* and *P. cordata* begins to die in July and continues to decline through the end of the growing season in October. Other species, notably *Z. aquatica*, reach peak biomass later in the season but the period of senescence (July to October, 123 d) is characterized by a large decrease in total AGB. From November to February (winter, 120 d), AGB is low, with a large fraction of dead biomass. These vegetation-based seasons were used to extrapolate discrete samples to annual rates.

Concurrent with the research reported herein, we studied carbon (C) dynamics at Sweet Hall marsh including marsh primary production and respiration rates (Neubauer et al. 2000), sediment deposition and burial processes (Neubauer et al. 2002), and exchanges of dissolved inorganic carbon (DIC) between the marsh and adjacent estuary (Neubauer and Anderson 2003). The C flux data from these studies were used in constructing the N mass balance model for Sweet Hall marsh. Scientists working in other parts of Sweet Hall marsh have focused individually on plant nutrient cycling (Wohlgemuth 1988; Booth 1989), sediment dynamics (Ledwin 1988), porewater nutrient turnover (Reay 1989), and marsh-water column nutrient exchanges (Campana 1998).

### Materials and Methods

#### TIDAL EXCHANGES

Sediment-water exchanges of DIN (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and nitrite [NO<sub>2</sub><sup>-</sup>]) by the marsh community were measured in May–June 1996, August 1996, November 1996, and April–May 1997 using replicate in situ flux chambers (n = 5) placed on the marsh surface (after Neikirk 1996). A second set of chambers with bottoms (n = 4) was used so that marsh-mediated DIN uptake and release could be distinguished from water column processes. Complete inundation of the study transect did not always occur (e.g., the creekside levee was periodically dry at high tide due to wind-induced ebbing or low amplitude tides), so sediment-water exchange measurements were not made near the creek bank. In each season, experiments were performed under light and dark conditions (chambers covered with double layer of black plastic). During sampling events, water samples were collected from each chamber every 30–45 min over a 2-h period, filtered in the field (0.45 μm Gelman supor acrodiscs), and analyzed for NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and NO<sub>2</sub><sup>-</sup>.

#### SEDIMENT NITROGEN CYCLING PROCESSES

Gross NH<sub>4</sub><sup>+</sup> production and nitrification were measured on intact sediment cores using an isotope

pool dilution technique as described by Anderson et al. (1997) and Neubauer et al. (2000). Briefly, triplicate cores were collected from 5 locations along 3 creek bank to marsh interior transects in September and November 1996 and April 1997 ( $n = 45$  cores per N cycling process per sampling date). Cores for gross  $\text{NH}_4^+$  production were collected at 9–12 cm depth; those for nitrification were to a depth of 3–4 cm. In the lab, the cores were injected with  $^{15}\text{N}$ -labeled product [ $(^{15}\text{NH}_4)_2\text{SO}_4$  for  $\text{NH}_4^+$  production,  $\text{K}^{15}\text{NO}_3$  for nitrification] to a final concentration of 1 mM at 20 to 30 atom %  $^{15}\text{N}$  enrichment. Incubations for gross  $\text{NH}_4^+$  production (24–48 h) and nitrification (3–6 h) were conducted at ambient temperatures (September: 28.5°C; November: 9°C; April: 14°C). KCl-extractable N was volatilized to  $\text{NH}_3$ , trapped on acidified paper filters, and analyzed for % N and  $^{15}\text{N}$  enrichment using an elemental analyzer connected to an isotope ratio mass spectrometer at the University of California at Davis, California. N cycling rates were calculated using the models of Wessel and Tietema (1992). The  $\text{NH}_4^+$  production rates obtained using this technique will overestimate gross mineralization to the extent that dissimilatory  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$  (DNRA) is a source of unlabelled  $\text{NH}_4^+$ .

#### POREWATER NUTRIENTS

In August 1996, porewater samplers (sippers) were installed along one transect in the marsh. Each sipper had a 5-cm interval of porous sintered plastic centered at a depth of 5, 15, or 25 cm. Clusters of 3 sippers (one per depth) were installed at 1, 15, and 30 m from the creek bank. During sampling, care was taken to avoid introducing  $\text{O}_2$  to subsurface sediments (see Neubauer and Anderson 2003). All porewater samples were filtered (0.45  $\mu\text{m}$ ) and frozen until DIN analysis. On several sampling dates, part of each filtered sample was stored with no air headspace in a gas-tight Hungate tube for DIC analysis.

#### ANALYTICAL METHODS

Dissolved inorganic nutrients were measured spectrophotometrically using the phenolhypochlorite method (for  $\text{NH}_4^+$ ; Solorzano 1969) or on an Alpkem nutrient autoanalyzer (for  $\text{NO}_3^-$  and  $\text{NO}_2^-$ ). Water column  $\text{NH}_4^+$  samples were analyzed immediately upon return to the lab. Samples for  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , as well as all porewater samples and extracts from the mineralization and nitrification experiments, were frozen prior to analysis. The DIC concentration of porewater samples was determined within 2 d of sample collection by injecting a 50  $\mu\text{l}$  sample into a 0.05 M  $\text{H}_2\text{SO}_4$  acid bath

that was constantly sparged with  $\text{CO}_2$ -free  $\text{N}_2$  into a LI-COR 6252 infrared gas analyzer (Neubauer and Anderson 2003).

#### MASS BALANCE MODEL

##### *Framework*

Our process-based mass balance model to describe N cycling at Sweet Hall marsh considered exchanges of N between the marsh, tidal waters, and atmosphere, as well as internal N cycling. The spatial extent of the model was limited to the upper 30 cm of marsh sediments; the model does not explicitly address N transformations occurring in the tidal waters of the marsh creeks or the Pamunkey River. Many of the processes we studied involved transformations of N within the marsh so we did not set up the model in terms of whole-marsh sources and sinks of N. We conceptually divided the marsh into four compartments—autotrophic biomass (aboveground and belowground macrophytes and microalgae), dissolved  $\text{NH}_4^+$ , dissolved  $\text{NO}_3^-$ , and sediment particulate N (including microbial biomass, microinfauna and macroinfauna)—and determined inputs and outputs to each compartment. Most annual fluxes were based on measured short-term rates (presented herein and in previous publications by our research group) and literature values, although several rates were calculated to force the model to steady state conditions.

We ran 500 iterations of our mass balance model to assess variability around each flux using a bootstrap resampling technique where we defined an original set of data points (e.g., all nitrification measurements within a particular month) as a sample population. This population was resampled with replacement and the average of the resampled values calculated to give a bootstrapped mean value. This bootstrapped value represents an average that we could expect to see if we repeated our field measurements, assuming that our original set of data points encompassed the range in variability within our study site. In our model, this resampling process was repeated 500 times to give a distribution of values that was directly derived from field samples and rate measurements. The grand mean of the 500 bootstrapped mean values was the final rate presented in this paper. Additional iterations did not significantly change calculated flux rates or the variability around the rates. For literature-derived values, the input data for the N model were in the form of a range (with minimum and maximum values) or were described by a mean and standard deviation. In these cases, each model iteration involved independently and randomly selecting a value from a distribution described by the input

TABLE 1. Nitrogen transformations at Sweet Hall marsh. Fluxes are in units of  $\text{g N m}^{-2} \text{yr}^{-1}$  (modeled means [ $\pm$  standard deviation]). Letters before each pathway correspond to fluxes on Fig. 3. AGB = aboveground macrophyte biomass, DIC = dissolved inorganic carbon, DIN = dissolved inorganic nitrogen, DNRA = dissimilatory  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$ , DOC = dissolved organic carbon, PN = particulate nitrogen, and PON = particulate organic nitrogen.

Pathway	Flux	Comments
Autotrophic N demand and fates of primary production		
(a) Total macrophyte N demand	72.0 (6.3)	Net macrophyte production (Neubauer et al. 2000) $\div$ macrophyte $\text{g C (g N)}^{-1}$
(b) Rhizome to AGB (recycled N)	22.2 (3.2)	Spring translocation (Neubauer et al. 2000) $\div$ macrophyte $\text{g C (g N)}^{-1}$
(c) Fall translocation	26.9 (1.3)	Based on carbon translocation (Neubauer et al. 2000) and peak biomass
(d) "New" $\text{NH}_4^+$ -N for macrophytes	36.9 (4.4)	Calculated to fulfill macrophyte N demand; $d + e = a - c$ . Assume that plant uptake
(e) "New" $\text{NO}_3^-$ -N for macrophytes	12.9 (2.3)	of $\text{NH}_4^+$ and $\text{NO}_3^-$ is proportional to the abundance of each DIN species
(f) Microalgal $\text{NH}_4^+$ -N uptake	4.7 (0.8)	Net algal primary production (Neubauer et al. 2000) $\div$ microalgal $\text{g C (g N)}^{-1}$ . Assume
(g) Microalgal $\text{NO}_3^-$ -N uptake	1.7 (0.3)	uptake is proportional to the abundance of each DIN species
(h) Reincorporated into sediments	27.1 (16.8)	Calculated to balance PN pool; $h = (u + x) - (r + v + w)$
(i) Macrophyte leaching	4.1 (1.0)	DOC leaching rate (Neubauer et al. 2000) $\div$ macrophyte $\text{g C (g N)}^{-1}$
(j) Herbivory and export as PON	25.0 (16.0)	Calculated to balance autotroph pools; $j = (d + e + f + g) - (h + i)$
Marsh-creek exchanges		
(k) $\text{NO}_3^-$ uptake (diffusive)	8.3 (1.8)	Sediment-water exchange chambers, this study; Fig. 1
(l) $\text{NO}_3^-$ release (advective)	0.1 (0.04)	From DIC export (Neubauer and Anderson 2003) and DIC : DIN stoichiometry
(m) $\text{NH}_4^+$ release (diffusive)	1.0 (2.0)	Sediment-water exchange chambers, this study; Fig. 1
(n) $\text{NH}_4^+$ release (advective)	0.2 (0.1)	Calculated as for flux (l). Average of 74% of advective export as $\text{NH}_4^+$
Marsh-atmosphere fluxes		
(o) Atmospheric $\text{NH}_4^+$ deposition	0.2 (0.01)	Bootstrapped from measured Virginia $\text{NH}_4^+$ atmospheric deposition
(p) Atmospheric $\text{NO}_3^-$ deposition	0.3 (0.08)	Bootstrapped from measured Virginia $\text{NO}_3^-$ atmospheric deposition
(q) Denitrification	14.4 (3.5)	Gross denitrification = net denitrification (from Kana et al. 1998) + $\text{N}_2$ fixation (r)
(r) $\text{N}_2$ fixation	6.1 (3.5)	Estimated from literature sources. See text for citations
Sediment N cycling		
(s) Nitrification	36.3 (3.8)	Isotope pool dilution; this study; Table 3
(t) Dissimilatory $\text{NO}_3^-$ reduction to $\text{NH}_4^+$	15.7 (6.2)	Calculated to balance $\text{NO}_3^-$ pool; $t = (k + p + s) - (e + g + l + q)$
(u) Gross mineralization	141.9 (43.9)	Table 3; isotope pool dilution gross $\text{NH}_4^+$ production rate - DNRA (t)
(v) Microbial immobilization	78.7 (43.7)	Calculated to balance $\text{NH}_4^+$ pool; $v = (o + t + u) - (d + f + m + n + s)$
(w) Sediment deposition	48.1 (15.5)	Spatially-variable deposition rates (Neubauer et al. 2002) $\div$ sediment C : N ratio
(x) Sediment burial	18.1 (3.1)	224 $\text{g C m}^{-2} \text{yr}^{-1}$ burial (Neubauer et al. 2002) $\div$ depth-varying sediment C : N ratio

data. All model calculations were done using Microsoft Excel.

## Results

### AUTOTROPHIC NITROGEN DEMAND

#### Macrophyte Nitrogen Demand and Translocation

The net primary production rate of marsh macrophytes (in C units) was used to calculate the annual plant N demand. Using a net macrophyte production rate of  $1129.3 \pm 54.3 \text{ g C m}^{-2} \text{yr}^{-1}$  (mean  $\pm$  standard deviation; recalculated from Neubauer et al. 2000) and a measured C : N ratio of  $15.8 \pm 1.2 \text{ g C (g N)}^{-1}$  for aboveground *P. virginica* and *P. cordata* (the biomass-dominant species at the marsh), we calculated that  $72.0 \pm 6.3 \text{ g N m}^{-2} \text{yr}^{-1}$  are required to support aboveground macrophyte production (Table 1). Spring translocation provides  $22.2 \pm 3.2 \text{ g N m}^{-2} \text{yr}^{-1}$  of recycled N to support aboveground production (based on the C translocation rate of  $347.9 \pm 42.6 \text{ g C m}^{-2} \text{yr}^{-1}$  in Neubauer et al. 2000). By difference, the remaining  $49.8 \pm 5.5 \text{ g N m}^{-2} \text{yr}^{-1}$

must be new N. We assumed that these DIN species were assimilated from marsh sediments in proportion to their abundance in the porewater (annual average =  $74.0\% \pm 3.4 \text{ NH}_4^+$ ). Foliar uptake of DIN from tidal floodwater is a potential source of N to satisfy plant demand, but this uptake pathway may not be significant in tidal marsh plants (Bouma et al. 2002).

The autumn translocation of N to belowground biomass was estimated using 2 independent calculations. An autumn translocation rate of  $460 \text{ g C m}^{-2} \text{yr}^{-1}$  (Neubauer et al. 2000) was converted to N using the AGB C : N ratio to yield a translocation rate of  $29.2 \text{ g N m}^{-2} \text{yr}^{-1}$ . We also used peak biomass ( $845 \text{ g C m}^{-1} \text{yr}^{-1}$ ) and Smalley harvest estimates ( $776 \text{ g C m}^{-2} \text{yr}^{-1}$ ) of aboveground production and assumed that half of the N in AGB was translocated belowground in the fall (after Hopkinson and Schubauer 1984; Anderson et al. 1997) to generate estimates of  $24.6\text{--}26.8 \text{ g N m}^{-2} \text{yr}^{-1}$ . By randomly generating 500 values between the extremes of 24.6 and  $29.2 \text{ g N m}^{-2} \text{yr}^{-1}$  (assuming a uniform distribu-

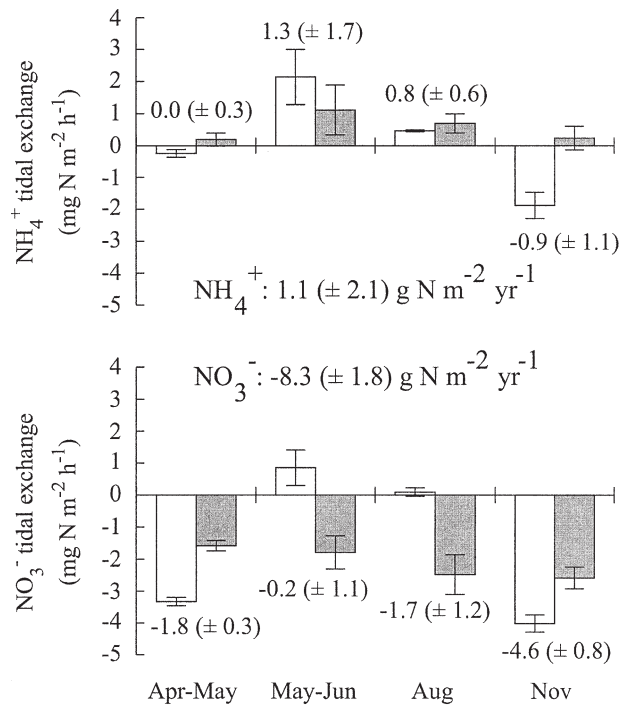


Fig. 1. Sediment-water exchanges of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the light (open bars) and dark (filled bars). Negative values indicate uptake of nutrients by the marsh. Values are means ( $\pm$  SD;  $n = 5$ ). Seasonal and annual rates ( $\pm$  SD) were modeled as described in the text. Seasonal rates (adjacent to data bars) are in  $\text{g N m}^{-2}$  season<sup>-1</sup>; annual rates are in  $\text{g N m}^{-2}$  yr<sup>-1</sup>.

tion), our model estimated a fall translocation rate of  $26.9 \pm 1.3 \text{ g N m}^{-2} \text{ yr}^{-1}$  (Table 1).

#### Microalgal Nitrogen Demand

The net benthic microalgal production rate of  $59 \pm 10 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Neubauer et al. 2000) was converted to a N demand of  $6.4 \pm 1.1 \text{ g N m}^{-2} \text{ yr}^{-1}$  using measured algal C : N ratios of  $9.3 \pm 0.3 \text{ g C (g N)}^{-1}$  (Neubauer unpublished data). We assumed that  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were assimilated in proportion to their abundance in marsh porewater.

#### Fate of Autotrophic Production

N in macrophyte and benthic microalgal biomass can be retained in the marsh (as sediment particulate organic matter or standing dead tissues) or exported from the marsh as dissolved or particulate matter. We estimated that  $4.1 \pm 1.0 \text{ g N m}^{-2} \text{ yr}^{-1}$  were leached from the plant biomass (from calculations in Booth 1989 and Neubauer et al. 2000). These leaching calculations did not differentiate between organic and inorganic N and assumed that N was leached into tidal waters and not into marsh porewater. A negligible amount of N ( $<0.5 \text{ g N m}^{-2}$ ) is left as standing dead biomass at the end of the growing season

( $25.3 \text{ g dw m}^{-2}$  in November  $\times$  0.9% N in dead biomass). We calculated the reincorporation of macrophyte and microalgae N into the sediments ( $27.1 \pm 16.8 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) to balance the sediment particulate N pool (assuming steady state on an annual scale). By difference, the remaining  $25.0 \pm 16.0 \text{ g N m}^{-2} \text{ yr}^{-1}$  of autotroph N were exported as particulate organic N or removed via herbivory.

#### MARSH-CREEK EXCHANGES

Diffusive marsh-water exchanges of  $\text{NH}_4^+$  in the light followed a seasonal pattern with highest release rates during the May–June sampling period ( $2.14 \text{ mg N m}^{-2} \text{ h}^{-1}$ ) and greatest uptake of  $-1.89 \text{ mg N m}^{-2} \text{ h}^{-1}$  in November (Fig. 1). In all seasons,  $\text{NH}_4^+$  was released from the marsh in the dark. There was significant marsh uptake of  $\text{NO}_3^-$  in all seasons in the dark with rates ranging from  $-2.58$  to  $-1.58 \text{ mg N m}^{-2} \text{ h}^{-1}$  (Fig. 1). The marsh was also a sink for water column  $\text{NO}_3^-$  in the light during the April–May and November sampling periods. Light and dark flux rates in each season (e.g., early growth, senescence) were multiplied by the average hours of daylight (sunrise to sunset) or night in that season, the number of days per season, and then by 0.5 (since the marsh is flooded for  $12 \text{ h d}^{-1}$ ) to give seasonal  $\text{NH}_4^+$  and  $\text{NO}_3^-$  fluxes. Seasonal rates were summed to calculate annual fluxes. There was a net release of  $\text{NH}_4^+$  from the marsh to the overlying water column during the late growth ( $1.3 \pm 1.7 \text{ g N m}^{-2} \text{ season}^{-1}$ ) and senescence ( $0.8 \pm 0.6 \text{ g N m}^{-2} \text{ season}^{-1}$ ) seasons and a slight uptake of  $\text{NH}_4^+$  during winter ( $-0.9 \pm 1.1 \text{ g N m}^{-2} \text{ season}^{-1}$ ; Fig. 1). Annually, the marsh was a source of  $\text{NH}_4^+$  ( $1.1 \pm 2.1 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) to water flooding the marsh around high tide. The marsh was a net sink for water column  $\text{NO}_3^-$ . The  $\text{NO}_3^-$  uptake rates were greatest in winter ( $-4.6 \pm 0.8 \text{ g N m}^{-2} \text{ season}^{-1}$ ) and lowest in the late growth season ( $-0.2 \pm 1.1 \text{ g N m}^{-2} \text{ season}^{-1}$ ; Fig. 1). The annual diffusive flux of  $\text{NO}_3^-$  from tidal waters into the marsh sediments was  $-8.3 \pm 1.8 \text{ g N m}^{-2} \text{ yr}^{-1}$  (Table 1).

In addition to DIN fluxes across the marsh-water interface (measured above as diffusive exchanges), DIN can be removed from the marsh at low tide due to drainage of porewater into tidal creeks. Across all samples, porewater  $\text{NH}_4^+$  concentrations ranged from 0.2 to  $41.2 \mu\text{M}$  (Table 2); the range for  $\text{NO}_2^- + \text{NO}_3^-$  was considerably lower (0.1– $5.1 \mu\text{M}$ ). We used whole-marsh DIC export rates ( $16.4 \text{ mol C m}^{-2} \text{ yr}^{-1}$ ; Neubauer and Anderson 2003) and porewater DIC : DIN stoichiometry to estimate DIN export from the marsh due to porewater drainage. The median porewater DIC : DIN ratio ranged from 398 to 1071 (Table 2) and was generally lower at the surface, reflecting lower DIC

TABLE 2. Porewater nutrients. Median concentrations (ranges in parentheses) for all sippers sampled on each sampling date. Samples for a given date are pooled across all sampled depths.  $n = 5$  to 9 sippers per date for each measurement.  $\Sigma\text{DIN} = [\text{NH}_4^+] + [\text{NO}_3^-] + [\text{NO}_2^-]$ . nd = not determined.

Date	$\text{NO}_3^- + \text{NO}_2^-$ ( $\mu\text{M}$ )	$\text{NH}_4^+$ ( $\mu\text{M}$ )	DIC ( $\mu\text{M}$ )	DIC : $\Sigma\text{DIN}$
September 1996	0.50 (0.26–1.48)	3.66 (0.99–13.47)	nd	nd
May 1997 (early)	0.20 (0.10–1.64)	3.15 (1.22–33.37)	3109 (1080–6494)	1013 (31–2338)
May 1997 (late)	0.46 (0.28–1.10)	0.40 (0.24–2.46)	nd	nd
July 1997	1.94 (0.68–2.30)	3.54 (2.16–8.25)	4695 (2916–5787)	782 (439–1764)
June 1999	2.87 (0.72–5.06)	7.84 (2.13–16.63)	3608 (1137–4685)	424 (60–803)
August 1999	1.14 (0.34–2.05)	9.98 (3.06–41.19)	4687 (2150–6735)	398 (81–1237)
November 1999	1.28 (0.81–3.49)	1.88 (1.48–11.33)	3655 (2097–5452)	1071 (300–2012)

at shallower depths. There were no consistent spatial patterns (either by depth or distance from creek) for any of the DIN species. Porewater drainage estimates were generated using DIC : DIN ratios for all samples, regardless of depth or distance from the creek bank and took into account that 68% of the DIC flux occurred when the surface of the marsh was exposed to air. Based on a bootstrapped DIC : DIN ratio of  $771 \pm 124$  and the measured partitioning between porewater  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , we estimated an advective  $\text{NH}_4^+$  flux of  $0.2 \pm 0.1 \text{ g N m}^{-2} \text{ yr}^{-1}$  and a  $\text{NO}_3^- + \text{NO}_2^-$  flux of  $0.1 \pm 0.04 \text{ g N m}^{-2} \text{ yr}^{-1}$ .

#### MARSH-ATMOSPHERE FLUXES

Rates of  $\text{N}_2$  fixation, denitrification, and atmospheric deposition were not directly measured but were calculated using a combination of existing data and literature sources. Our model randomly selected  $\text{N}_2$  fixation rates between literature extremes of 0 and  $12 \text{ g N m}^{-2} \text{ yr}^{-1}$  for mature tidal freshwater and salt marshes (e.g., Bowden 1987 as cited in Bowden et al. 1991; DeLaune and Patrick 1990; Currin and Paerl 1998; Sutula et al. 2001; Tyler et al. 2003) to estimate a  $\text{N}_2$  fixation rate of  $6.1 \pm 3.5 \text{ g N m}^{-2} \text{ yr}^{-1}$  (Table 1). To estimate denitrification, we used the denitrification versus water column  $[\text{NO}_3^-]$  relationship from Kana et al. (1998). Using an average water column  $[\text{NO}_3^-]$  of  $6.0 \pm 0.4 \mu\text{M}$ , we calculated an annual net denitrification rate of  $8.3 \pm 0.4 \text{ g N m}^{-2} \text{ yr}^{-1}$ . The  $\text{N}_2$  : Ar technique used by Kana et al. (1998) measures net  $\text{N}_2$  production (i.e., the balance

TABLE 3. Seasonal and annual sediment gross mineralization and nitrification rates ( $\text{g N m}^{-2} \text{ season}^{-1}$ ). Nitrification rates were measured in the upper 3–4 cm of marsh sediments. Mineralization rates, calculated as gross  $\text{NH}_4^+$  production – DNRA, were scaled to 30 cm depth. Standard deviations of modeled seasonal and annual rates are in parentheses.

Season	Days	Nitrification	Mineralization
Growth (March–June)	122	5.7 (1.1)	61.0 (28.6)
Senescence (July–October)	123	27.1 (3.5)	71.4 (30.4)
Winter (November–February)	120	3.5 (1.0)	9.5 (3.7)
Annual totals ( $\text{g N m}^{-2} \text{ yr}^{-1}$ )		36.3 (3.8)	141.9 (43.9)

between denitrification and  $\text{N}_2$  fixation); we estimated a gross denitrification rate of  $14.4 \pm 3.5 \text{ g N m}^{-2} \text{ yr}^{-1}$  by adding our estimated  $\text{N}_2$  fixation rate to the calculated net denitrification rate. This will underestimate denitrification to the extent that  $\text{NO}_3^-$  is supplied via nitrification rather than diffusive  $\text{NO}_3^-$  inputs. Atmospheric deposition of  $\text{NH}_4^+$  ( $0.2 \pm 0.01 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) and  $\text{NO}_3^-$  ( $0.3 \pm 0.01 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) were estimated from wetfall deposition rates reported for 8 stations in Virginia between 1979 and 2002 (National Atmospheric Deposition Program, accessed March 11, 2004, at <http://nadp.sws.uiuc.edu>).

#### SEDIMENT NITROGEN CYCLING

Median nitrification rates in the sample cores were 5–10 times greater in September ( $8.9 \text{ mg N m}^{-2} \text{ h}^{-1}$ ) than in April ( $1.9 \text{ mg N m}^{-2} \text{ h}^{-1}$ ) or November ( $0.9 \text{ mg N m}^{-2} \text{ h}^{-1}$ ; Fig. 2). These short-term measurements of nitrification were extrapolated to an annual scale using the seasons defined above for tidal DIN exchanges, with the exception that the early growth and late growth seasons were combined into a single growth season. Seasonal nitrification rates were greater during marsh senescence (July–October;  $27.1 \text{ g N m}^{-2} \text{ season}^{-1}$ ; Table 3) than during the winter (November–February;  $3.5 \text{ g N m}^{-2} \text{ season}^{-1}$ ) and growth seasons (March–June;  $5.7 \text{ g N m}^{-2} \text{ season}^{-1}$ ). Annually, there was a gross conversion of  $36.3 \pm 3.8 \text{ g N m}^{-2}$  from  $\text{NH}_4^+$  to  $\text{NO}_3^-$  (Table 1).

Within a season,  $\text{NH}_4^+$  production rates were generally more variable than nitrification rates. Short-term rates of gross  $\text{NH}_4^+$  production (integrated over the core depth) were greater in September ( $4.6 \text{ mg N m}^{-2} \text{ h}^{-1}$ ) and April ( $4.4 \text{ mg N m}^{-2} \text{ h}^{-1}$ ) than in November ( $0.9 \text{ mg N m}^{-2} \text{ h}^{-1}$ ; Fig. 2). Seasonal and annual  $\text{NH}_4^+$  production rates were extrapolated to 30 cm depth since mineralization needs an organic substrate and this depth interval contains the highest concentrations of live roots and organic matter in *P. virginica* marshes (Booth 1989; Chambers and Fourqurean 1991; Hussey and Odum 1992; Harvey et al. 1995). Because the isotope pool dilution mineralization technique measures gross

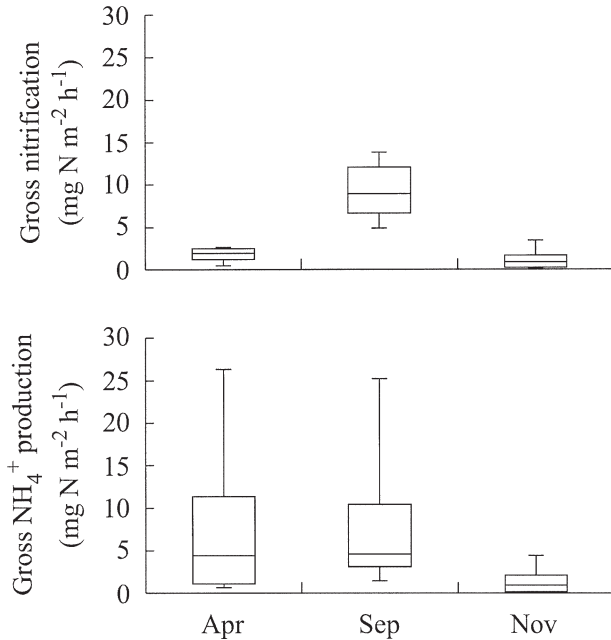


Fig. 2. Isotope-pool dilution measurements of nitrification and gross  $\text{NH}_4^+$  production. The horizontal line within each shaded bar is the median, the ends of the shaded bars represent 25th and 75th percentiles, and the lines extending from each bar indicate the 10th and 90th percentiles for the monthly rate measurements;  $n = 13$  to 20 measurements per rate per month. Rates are integrated to the total depth of the cores (3–4 cm for nitrification; 9–12 cm for gross  $\text{NH}_4^+$  production).

$\text{NH}_4^+$  production (rather than gross mineralization, per se), we calculated gross mineralization by subtracting DNRA rates from the isotope-based  $\text{NH}_4^+$  production rates. The DNRA rates ( $15.7 \pm 6.2 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) were calculated to balance the  $\text{NO}_3^-$  pool. Gross mineralization rates were similar during growth ( $61.0 \text{ g N m}^{-2} \text{ season}^{-1}$ ; Table 3) and senescence ( $71.4 \text{ g N m}^{-2} \text{ season}^{-1}$ ) and were considerably lower during winter ( $9.5 \text{ g N m}^{-2} \text{ season}^{-1}$ ). Annual gross mineralization ( $141.9 \pm 43.9 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) was 4 times greater than nitrification. Microbial  $\text{NH}_4^+$  immobilization ( $78.7 \pm 43.7 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) was calculated to balance the  $\text{NH}_4^+$  pool (Table 1).

#### SEDIMENT DEPOSITION AND BURIAL

Net rates of marsh sediment deposition were measured over a 1.5-yr period (February 1998 to August 1999) using ceramic sedimentation tiles (Neubauer et al. 2002) deployed along a creek bank to marsh interior transect. Annual N inputs via sediment deposition were calculated using measured mass sedimentation rates and sediment N content ( $0.57\% \pm 0.10$ ) and ranged from  $19.2 \pm 9.7 \text{ g N m}^{-2} \text{ yr}^{-1}$  in the marsh interior to  $114.5 \pm 59.5 \text{ g N m}^{-2} \text{ yr}^{-1}$  at the creek bank. Across our site,

the annual N inputs due to sediment deposition averaged  $48.1 \pm 15.5 \text{ g N m}^{-2} \text{ yr}^{-1}$  (Table 1).

The  $^{137}\text{Cs}$  profile ( $t_{1/2} = 30.17 \text{ yr}$ ) in a 1.3-m deep core was used to estimate decadal accretion rates of 8.4 to  $8.5 \text{ mm yr}^{-1}$  (Neubauer et al. 2002). The vertical accretion rate since the 1963  $^{137}\text{Cs}$  activity peak was converted to a N accretion rate of  $18.1 \pm 3.1 \text{ g N m}^{-2} \text{ yr}^{-1}$  (Table 1) using depth-varying sediment bulk densities and N contents (after Neubauer et al. 2002) and was used to estimate N removal (burial) from the upper 30 cm of the marsh.

#### Discussion

The process-based N mass balance model described herein (Fig. 3) is a useful tool for quantifying annual N fluxes and transformations within a tidal freshwater marsh ecosystem. Despite several detailed N models for tidal salt marshes (White and Howes 1994; Anderson et al. 1997; Thomas and Christian 2001), there are few N cycling models for tidal freshwater wetlands. Several input-output models have looked at tidal freshwater marshes as net sources-sinks for DIN (e.g., Simpson et al. 1978; Jordan et al. 1983; Academy 1998) and Morris and Bowden (1986) modeled marsh sedimentation and mineralization, but we know of only one comprehensive N budget for a tidal freshwater marsh system (Bowden et al. 1991). Like the model of Bowden and colleagues, our model incorporates data collected seasonally and from different locations within the marsh but as a whole is not seasonally or spatially explicit.

From an ecosystem perspective, the most active N cycling at Sweet Hall marsh occurs internally and the exchanges of N between the marsh, river, and atmosphere are relatively small (Fig. 3). The largest annual N transformation is the mineralization of organic N to  $\text{NH}_4^+$ . The importance of internal N recycling may be a common theme in both tidal freshwater and salt marshes since internal remineralization can supply the majority (or more than enough) N to support all autotrophic N requirements (e.g., Bowden et al. 1991; White and Howes 1994; Anderson et al. 1997; Thomas and Christian 2001; this study). Although the exchanges of dissolved and particulate N between the marsh and estuary are quantitatively less important in a marsh N budget, these ecosystem exchanges may be ecologically significant with respect to estuarine nutrient cycling. This is especially true in the Pamunkey River where the area of tidal marshes is about 4 times greater than the area of open water (Neubauer and Anderson 2003).

At Sweet Hall marsh, the largest exchange of N between the marsh and the estuary is the deposition of sediment-associated N onto the marsh surface. Although sediment deposition and accretion have

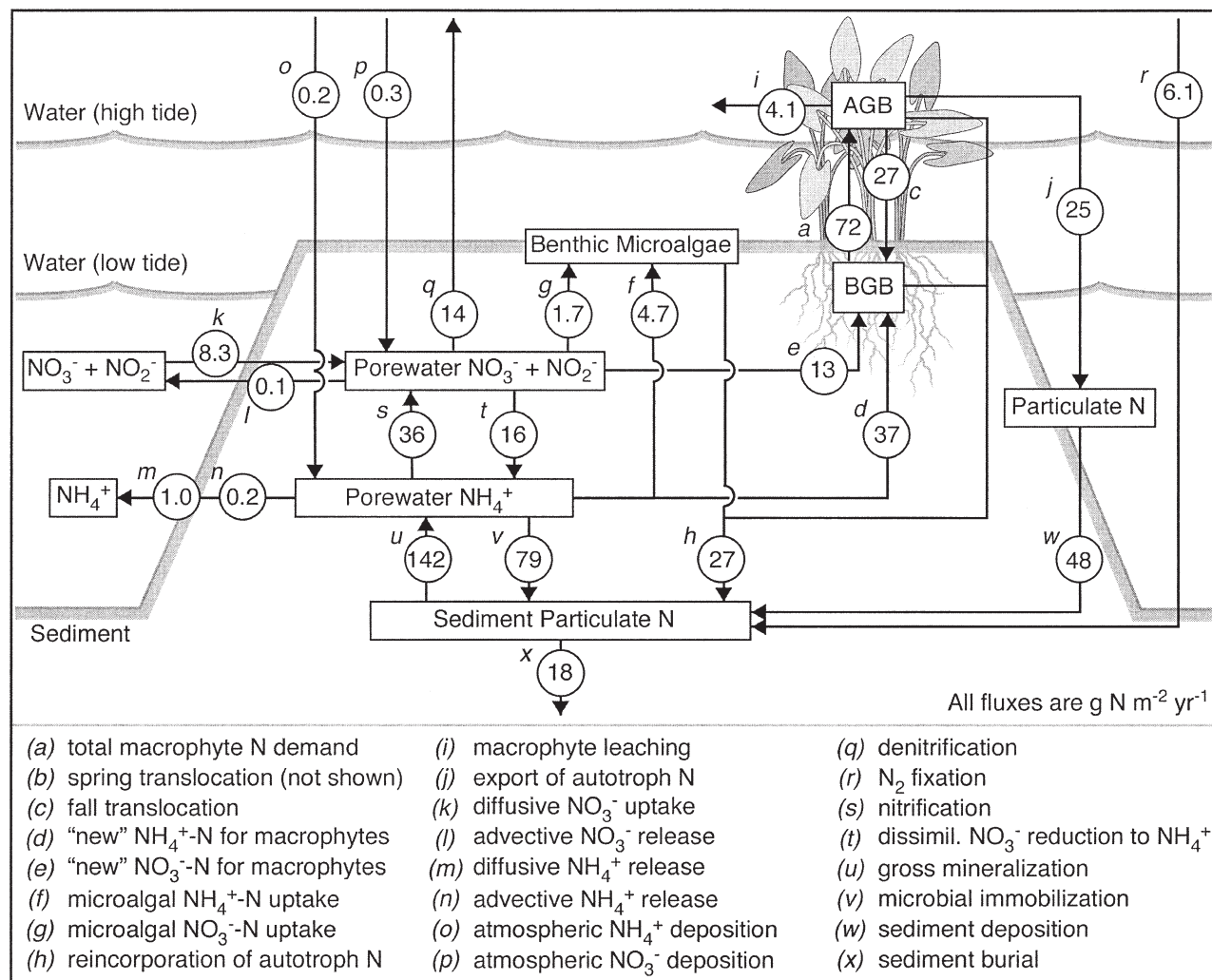


Fig. 3. Nitrogen mass balance for Sweet Hall marsh. All fluxes are in  $\text{g N m}^{-2} \text{ yr}^{-1}$  and are based on measured rates, literature values, or calculated by difference (assuming steady state) as detailed in the text. Standard deviations for each flux are omitted for visual clarity but can be found in Table 1 and in the text. AGB = aboveground macrophyte biomass; BGB = belowground macrophyte biomass.

been measured in several tidal freshwater marshes along the Atlantic coast of North America (Bowden et al. 1991; Childers et al. 1993; Pasternack and Brush 1998; Neubauer et al. 2002; Darke and Megoignil 2003), few of these studies also reported the N content of the deposited sediments. Still, it appears that sediment-associated N deposition rates measured at Sweet Hall marsh are similar to those in other tidal freshwater marshes in Maryland and Virginia (Pasternack and Brush 1998; Darke and Megoignil 2003). Bowden and coworkers studied a North River, Massachusetts, tidal freshwater marsh with a plant community dominated by *Typha latifolia* (broad-leaved cattail), *Carex lacustris* (hairy sedge), and *Calamagrostis canadensis* (bluejoint). In that system, which was very different from many Chesapeake Bay marshes, sediment-associated N deposi-

tion onto the marsh ranged from 0 to  $9 \text{ g N m}^{-2} \text{ yr}^{-1}$  (Bowden et al. 1991). This range is much lower than we measured at Sweet Hall ( $48.1 \pm 15.5 \text{ g N m}^{-2} \text{ yr}^{-1}$ ), and is reflected in the relative organic content of surface sediments at Sweet Hall (20%, Neubauer et al. 2002) and the North River marsh (60%, Bowden 1984b).

Ultimately, the burial of sediments and organic detritus can result in long-term N sequestration. Rates of N burial in Atlantic coast tidal freshwater marshes range from  $5.8$  to  $23.4 \text{ g N m}^{-2} \text{ yr}^{-1}$  (Bowden et al. 1991; Academy 1998 and references therein). Our N burial rate of  $18.1 \pm 3.1 \text{ g N m}^{-2} \text{ yr}^{-1}$  is about three times greater than that reported by Bowden et al. (1991). The burial rate at Sweet Hall is at the upper end of the range for all tidal freshwater marshes, presumably due to a com-

bination of high sediment availability, frequent tidal flooding, and the effect of plants in promoting the deposition and retention of sediments on the marsh.

The assimilation of N into autotrophic biomass represents a temporary N sink. Rates of DIN uptake into autotrophic biomass were about 3 times greater at Sweet Hall than in Bowden's North River marsh. These differences resulted from a combination of higher AGB and a higher N content in the biomass at Sweet Hall (Bowden et al. 1991; Neubauer et al. 2000), even though average riverine nutrient concentrations were 4 times greater in the North River marsh. At Sweet Hall marsh, we calculated that 30% of annual macrophyte and microalgal production was exported to tidal waters as dissolved or particulate matter; Bowden et al. (1991) did not report an export of organic material from the North River marsh, despite litter accumulation in that system. Low marsh vegetation is more easily fragmented (Odum and Heywood 1978; Webster and Benfield 1986) and can be exported by the tides. High marsh vegetation is more recalcitrant and, because of the position of the high marsh relative to the tidal prism, there is less physical energy to export detritus from the high marsh. The export of microalgal N from Sweet Hall may also be important. We periodically (but not consistently) measured peaks in tidal creek chlorophyll *a* near low tide and have seen a microalgal scum suspended from the marsh surface by the rising tide. Rates of both N burial and detritus export appear to be roughly correlated with rates of primary production in each marsh, but other factors including marsh elevation, tidal energy, and sediment supply may also be important.

In addition to receiving (and potentially sequestering) sediment-associated N, tidal freshwater marshes can actively exchange DIN with the adjacent estuary. Annually, Sweet Hall marsh is a net sink for riverine  $\text{NO}_3^-$  and a net source (exporter) of  $\text{NH}_4^+$ . We did not quantify the exchanges of dissolved organic nitrogen (DON) between the marsh and tidal waters at Sweet Hall, but studies at brackish water sites 30–55 km downriver from Sweet Hall (salinities of 7–12‰) have shown an annual DON export ranging from 2 to 9 g N  $\text{m}^{-2} \text{yr}^{-1}$  (Axelrad et al. 1976). At Sweet Hall, tidal creek DON concentrations were typically greater than DIN concentrations and showed large seasonal variability (June:  $<20 \mu\text{M}$ ; August:  $>100 \mu\text{M}$ ; Neubauer 2000), indicating the dynamic nature of the DON and suggesting that additional study is required.

Many tidal freshwater marshes show similar patterns of DIN exchange to those measured in this study ( $\text{NH}_4^+$  release and  $\text{NO}_3^-$  uptake; Grosz-

kowski 1995; Campana 1998; Zeigler et al. 1999), but other studies have demonstrated the opposite pattern ( $\text{NH}_4^+$  uptake and  $\text{NO}_3^-$  release; Seitzinger 1987; Zeigler et al. 1999). Still other marshes show net uptake of both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (Heinle and Flemer 1976; Bowden 1986; Bowden et al. 1991) or sometimes both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  release (Velinsky et al. unpublished, as cited in Academy 1998). In general, diffusive DIN fluxes occur due to a concentration gradient between tidal waters and marsh porewater. Bowden (1986) observed a net uptake of  $\text{NH}_4^+$  from tidal waters to the marsh, despite nearly 100 times greater  $\text{NH}_4^+$  in the porewater relative to tidal waters. This  $\text{NH}_4^+$  uptake was attributed to microbial immobilization of  $\text{NH}_4^+$  onto a layer of litter overlying the sediment surface (Bowden 1986).  $\text{NH}_4^+$  exchange dynamics can differ within elevation zones (i.e., plant communities) within a wetland, depending on the production and persistence of litter. The strength of tidal DIN exchanges may also be related to the nutrient status (e.g., eutrophic versus oligotrophic) of the adjacent river. Average  $\text{NH}_4^+$  release rates from low marsh cores at Jug Bay, a tidal freshwater system on the more nutrient enriched Patuxent River, Maryland, were up to 4.5 times higher than the maximum rate at Sweet Hall, despite similar plant communities and sediment characteristics (e.g., texture) in both marshes (Groszkowski 1995; Zeigler et al. 1999). N cycling may be more conservative (i.e., lower marsh-estuary DIN exchanges) when nutrients are less abundant in tidal waters. Alternately, the differences in  $\text{NH}_4^+$  export between these marshes may be related to methodology; the Jug Bay  $\text{NH}_4^+$  fluxes were measured on cores removed from the marsh, whereas we used in situ chambers.

There is typically a diffusive flux of  $\text{NO}_3^-$  from the water column into tidal freshwater marsh sediments (this study and above citations) where  $\text{NO}_3^-$  can act as a substrate for denitrification and DNRA. Reported denitrification rates in tidal freshwater wetlands range from  $-0.088$  (i.e., net  $\text{N}_2$  fixation) to  $0.088 \text{ g N m}^{-2} \text{d}^{-1}$  (rates measured using a variety of techniques; Academy 1998 and references therein) and are generally of similar magnitude to  $\text{NO}_3^-$  uptake rates on both daily and annual scales (e.g., Bowden et al. 1991). Increasing concentrations of  $\text{NO}_3^-$  in tidal waters can increase rates of sediment denitrification (e.g., Kana et al. 1998), but nitrification is often the dominant  $\text{NO}_3^-$  source for denitrification in many lake, riverine, and estuarine sediments (Seitzinger 1988). Kana et al. (1998) demonstrated that denitrification rates in estuarine sediments were related to water column  $\text{NO}_3^-$  concentrations, but also showed that denitrification was not solely supported by water column  $\text{NO}_3^-$ . Because water column  $\text{NO}_3^-$  con-

centrations are relatively low at Sweet Hall ( $\bar{x} = 6.0 \mu\text{M}$ ) and nitrification rates are high, we probably underestimated denitrification since our calculations did not account for coupled nitrification-denitrification. Still, our calculated denitrification rate is similar to the  $19.6 \text{ g N m}^{-2} \text{ yr}^{-1}$  estimated for the Jug Bay tidal freshwater marsh (Merrill 1998, as cited by Zeigler et al. 1999) and is also comparable to reported rates in other eastern United States tidal freshwater wetlands (Bowden et al. 1991; Academy 1998 and references therein).

We may have also underestimated nitrification since our isotope pool dilution measurements of nitrification included only the top 3–4 cm of the sediment profile. We did not integrate to a deeper depth to include nitrification that could be occurring in the rhizosphere of wetland plants. That calculation would require data about the spatial distribution of roots within the marsh, rates of radial  $\text{O}_2$  loss from roots, and the fate of the  $\text{O}_2$  in the sediment (e.g., heterotrophic uptake versus nitrification versus Fe(II) oxidation). Although such a robust modeling approach has been applied in other wetland systems (e.g., van Bodegom et al. [2001a] for a flooded rice soil), a similar analysis was beyond the scope of our data and objectives. It is probably safe to say that a consideration of radial  $\text{O}_2$  loss would increase rates of both nitrification and denitrification (coupled nitrification-denitrification, e.g., Reddy et al. 1989; Eriksson and Weisner 1999), unless nitrifiers are out-competed for  $\text{O}_2$  within the rhizosphere (van Bodegom et al. 2001b).

As modeled, denitrification and DNRA each account for 50% of the  $\text{NO}_3^-$  reduced within the sediments (not counting that which is assimilated by plants and benthic microalgae). From an ecosystem perspective, denitrification represents a loss of N from the system whereas DNRA retains N within the marsh in a biologically available form. One of the major uncertainties in this study (and other wetland N cycling models) is the relative importance of denitrification, DNRA, and assimilatory  $\text{NO}_3^-$  reduction. To our knowledge, the only study to report rates of each of these three processes in a tidal freshwater system was that by Bowden et al. (1991). Despite the paucity of data on these processes in tidal freshwater marshes, the pathways of  $\text{NO}_3^-$  reduction have been studied in other aquatic sedimentary environments. As summarized in Megonigal et al. (2004), the percentage of total  $\text{NO}_3^-$  reduction due to DNRA ranged from 0% to 100% ( $\% \text{ DNRA} = \text{DNRA}/(\text{denitrification} + \text{DNRA})$ ; assimilatory  $\text{NO}_3^-$  reduction not considered). Despite this range, it is clear that several factors, including organic C availability and the concentrations of  $\text{O}_2$  and reduced sulfur compounds, affect the partitioning between DNRA and denitrification.

Of these factors, the availability of labile C relative to  $\text{NO}_3^-$  (i.e., electron donor : electron acceptor ratio) seems to be of primary importance. Working in nonmarsh soils and sediments, Fazzolari et al. (1998) and Christensen et al. (2000) showed that the importance of DNRA increased as a function of organic C availability; denitrification tends to dominate at higher concentrations of  $\text{NO}_3^-$  (Nijburg et al. 1997; Tobias et al. 2001a,b). Across the estuarine gradient, DNRA is generally more important (relative to denitrification) in estuarine and marine systems whereas denitrification increases in importance in freshwater systems (Tobias et al. 2001b) and may be related to sulfide inhibition of denitrification (e.g., Brunet and Garcia-Gil 1996; An and Gardner 2002). We can speculate that DNRA rates will be higher in vegetated than unvegetated sediments due to labile C inputs from the roots (Nijburg and Laanbroek 1997), but the partitioning between DNRA and denitrification in freshwater wetlands is highly uncertain due to limited empirical data. Several studies in freshwater environments have suggested that 24–60% of  $\text{NO}_3^-$  reduction could be attributed to assimilatory  $\text{NO}_3^-$  reduction (Jones 1979, as cited in Bowden et al. 1991; Matheson et al. 2003). We did not include assimilatory  $\text{NO}_3^-$  reduction in our mass balance model because high sediment water content (Rückauf et al. 2004) and even low concentrations of  $\text{NH}_4^+$  ( $>0.5 \mu\text{M}$ ; Bengtsson and Annadotter 1989) can inhibit assimilatory  $\text{NO}_3^-$  reduction.

The availability and composition of organic matter can exert a strong influence on N mineralization rates. The average Sweet Hall sediment organic content is fairly constant over the first 30 cm of the marsh (16–21%; Neubauer et al. 2002), but we occasionally measured high organic matter concentrations (50–80%) in the upper 2 cm of the marsh that may drive the high spatial variability in gross mineralization rates (Neubauer et al. 2000). The quality (or lability) of organic matter also can influence mineralization rates (Bowden 1984a; Tobias et al. 2001a). At Sweet Hall marsh, there were temporal changes in the C : N ratio of surface sediments (Neubauer et al. 2002), but no consistent patterns that could explain the seasonal differences in gross  $\text{NH}_4^+$  production. The bulk C : N ratio is only a coarse indicator of organic matter quality. Labile organic matter inputs (e.g., root leachates, microalgal biomass) may drive seasonal cycles of gross mineralization, even if these materials are not reflected in bulk sediment characteristics. N mineralization rates also can be affected by temperature (e.g., Bowden 1984a), but we did not observe a standard Arrhenius-type mineralization versus temperature relationship across seasons (data not shown). We also observed

high variability in  $\text{NH}_4^+$  production rates within a season (i.e., all incubations at same temperature; Fig. 2), suggesting that organic matter quality has a stronger effect on mineralization than does temperature.

The major fates of  $\text{NH}_4^+$  produced via organic matter mineralization were autotrophic and microbial uptake. Over the course of the year, the competition between plants and nitrifiers for  $\text{NH}_4^+$  may have affected nitrification rates. The ratio of mineralization to nitrification was similar during senescence ( $2.7 \pm 1.2$ ) and winter ( $3.0 \pm 1.7$ ) but substantially higher during the growth season ( $11.2 \pm 5.9$ ), indicating proportionally lower nitrification rates during the time of plant growth. We suggest that high mineralization rates between March and June resulted in considerable  $\text{NH}_4^+$  production, but the  $\text{NH}_4^+$  was not available to nitrifiers due to rapid plant uptake. Supporting this hypothesis, the cores for the April–May mineralization and nitrification measurements were taken during the rapid 6-fold increase in AGB reported by Neubauer et al. (2000) and corresponding decrease in porewater  $\text{NH}_4^+$  from 3.2 to 0.4  $\mu\text{M}$  (Table 2). Reduced autotrophic N demand later in the summer may also explain why porewater  $\text{NH}_4^+$  concentrations were typically greatest toward the end of the growing season (Table 2). We observed large spikes in tidal creek [ $\text{NH}_4^+$ ] during the early growing season (low tide: 25–30  $\mu\text{M}$ ; high tide: <2  $\mu\text{M}$ ; Anderson et al. 1998), but total  $\text{NH}_4^+$  export from the marsh was at least an order of magnitude lower than either plant or microbial  $\text{NH}_4^+$  uptake (Fig. 3). High rates of mineralization and nitrification, in combination with relatively low porewater  $\text{NH}_4^+$  during most of the year, suggest a coupling between these microbial processes that is influenced by seasonal patterns of plant N demand.

In addition to nitrification and plant uptake, microbial immobilization represents a third strong sink for porewater  $\text{NH}_4^+$ . On an annual basis, immobilization in the sediments of Sweet Hall marsh results in the (temporary) sequestration of  $\text{NH}_4^+$  in the particulate N pool and accounts for an average of  $52.2\% \pm 14.8$  of the  $\text{NH}_4^+$  released via mineralization. The relative importance of  $\text{NH}_4^+$  immobilization at Sweet Hall is similar to that reported by Bowden et al. (1991) and Anderson et al. (1997), despite differences in marsh type, experimental methods, and modeling approaches between these studies. For a North River, Massachusetts, tidal freshwater marsh, Bowden et al. (1991) calculated that the  $\text{NH}_4^+$  immobilization rate into fresh litter and peat was 57% of the mineralization rate of these substrates. Working in a *Spartina alterniflora* dominated tidal salt marsh in Virginia, Anderson et al. (1997) used a mass balance

approach to determine that 50% of the mineralized N was temporarily immobilized as microbial biomass and exopolymer materials and suggested that these relatively labile organic products could be rapidly mineralized to support plant DIN demand. Our model calculations further support the idea that microbial  $\text{NH}_4^+$  immobilization is an important mechanism for recycling N within the marsh.

## CONCLUSIONS

The lack of comprehensive N cycling models for tidal freshwater marshes has hindered our efforts to completely understand how these systems, which are often located in watersheds that are either urbanized or threatened by development, interact with estuarine waters. The great variability between tidal freshwater marshes in terms of plant community composition, sediment characteristics, tidal water nutrient concentrations, and the frequency and duration of tidal flooding further complicates our efforts to make generalizations about N cycling in these systems. Based on the existing (albeit limited) data, it appears that many processes such as plant productivity, mineralization of organic matter, microbial immobilization, and coupled nitrification-denitrification may be largely independent of small changes in water column DIN loading and are instead dependent on internal (and largely conservative) cycling of N within marsh sediments. Some processes such as marsh-estuarine nutrient exchanges and denitrification rates can be influenced by water column DIN concentrations. At very high DIN loadings (> millimolar concentrations) due to wastewater or groundwater inputs, denitrification rates are often enhanced due to the increased availability of  $\text{NO}_3^-$  (e.g., Nijburg et al. 1997; Xue et al. 1999; Tobias et al. 2001b). It is possible that plant productivity will be similarly affected although macrophyte biomass in freshwater wetlands does not always respond to nutrient fertilization (Whigham and Simpson 1978 as cited in Bowden 1986; Bowden et al. 1991; Chambers and Fourqurean 1991). At present, the factors that cause a marsh to switch from being supported primarily by internal N recycling (oligotrophic end of gradient) to being supported by allochthonous nutrients (eutrophic end of gradient) are poorly understood.

## ACKNOWLEDGMENTS

We thank everyone who helped with this research, especially Britt Anderson, Eva Bailey, José Constantine, David Miller, Craig Tobias, and Dick Wetzel. This research was supported in part by National Science Foundation grant DEB-9411974 to the University of Virginia, and the Virginia Department of Environmental Quality through National Oceanic and Atmospheric Administration grants NA570Z0561-01 and NA670Z0360-01. S. C. Neubauer was supported by the National Estuarine Research Reserve system through a Graduate Research Fellowship, and expresses gratitude

to Villanova University for financial support during the writing of this manuscript. This is contribution number 2699 of the Virginia Institute of Marine Science, School of Marine Science, College of William and Mary.

#### LITERATURE CITED

- ACADEMY. 1998. Impact of aquatic vegetation on water quality of the Delaware River Estuary. Submitted to Delaware River Basin Commission by the Academy of Natural Sciences, Patrick Center for Environmental Research final report 98-5F. Philadelphia, Pennsylvania.
- AN, S. AND W. S. GARDNER. 2002. Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). *Marine Ecology Progress Series* 237:41–50.
- ANDERSON, I. C., S. C. NEUBAUER, B. B. NEIKIRK, AND R. L. WETZEL. 1998. Exchanges of carbon and nitrogen between tidal freshwater wetlands and adjacent tributaries. Final report to Virginia Coastal Resources Management Program, Virginia Department of Environmental Quality. Richmond, Virginia.
- ANDERSON, I. C., C. R. TOBIAS, B. B. NEIKIRK, AND R. L. WETZEL. 1997. Development of a process-based nitrogen mass balance model for a Virginia (USA) *Spartina alterniflora* salt marsh: Implications for net DIN flux. *Marine Ecology Progress Series* 159:13–27.
- AXELRAD, D. M., K. A. MOORE, AND M. E. BENDER. 1976. Nitrogen, phosphorus, and carbon flux in Chesapeake Bay marshes. Virginia Water Resources Research Center. VPI-VWRR-C-BULL 79. Blacksburg, Virginia.
- BENGTSSON, G. AND H. ANNADOTTER. 1989. Nitrate reduction in a groundwater microcosm determined by  $^{15}\text{N}$  gas chromatography-mass spectrometry. *Applied and Environmental Microbiology* 55:2861–2870.
- BOOTH, P. M. 1989. Nitrogen and phosphorus cycling strategies in two tidal freshwater macrophytes, *Peltandra virginica* and *Spartina cynosuroides*. Ph.D. Dissertation, College of William and Mary, Virginia Institute of Marine Science, Gloucester Point, Virginia.
- BOUMA, T. J., J. STAPEL, J. VAN DER HEIDEN., B. KOUTSTAAL, J. VAN SOELEN, AND L. VAN IJZERLOO. 2002. Relative importance of macrophyte leaves for nitrogen uptake from flood water in tidal salt marshes. *Marine Ecology Progress Series* 240:93–104.
- BOWDEN, W. B. 1984a. A nitrogen-15 isotope dilution study of ammonium production and consumption in a marsh sediment. *Limnology and Oceanography* 29:1004–1015.
- BOWDEN, W. B. 1984b. Nitrogen and phosphorus in the sediments of a tidal, freshwater marsh in Massachusetts. *Estuaries* 7:108–118.
- BOWDEN, W. B. 1986. Nitrification, nitrate reduction, and nitrogen immobilization in a tidal freshwater marsh sediment. *Ecology* 67:88–99.
- BOWDEN, W. B. 1987. The biogeochemistry of nitrogen in freshwater wetlands. *Biogeochemistry* 4:313–348.
- BOWDEN, W. B., C. J. VÖRÖSMARTY, J. T. MORRIS, B. J. PETERSON, J. E. HOBBI, P. A. STEUDLER, AND B. MOORE, III. 1991. Transport and processing of nitrogen in a tidal freshwater wetland. *Water Resources Research* 27:389–408.
- BRUNET, R. C. AND L. J. GARCIA-GIL. 1996. Sulfide-induced dissimilatory nitrate reduction to ammonia in anaerobic freshwater sediments. *FEMS Microbiology Ecology* 21:131–138.
- CAMPANA, M. L. 1998. The effect of *Phragmites australis* invasion on community processes in a tidal freshwater marsh. M.S. Thesis, College of William and Mary, Virginia Institute of Marine Science, Gloucester Point, Virginia.
- CHAMBERS, R. M. 1992. A fluctuating water-level chamber for biogeochemical experiments in tidal marshes. *Estuaries* 15: 53–58.
- CHAMBERS, R. M. AND J. W. FOURQUREAN. 1991. Alternative criteria for assessing nutrient limitation of a wetland macrophyte (*Peltandra virginica* (L) Kunth). *Aquatic Botany* 40:305–320.
- CHILDERS, D. L., F. H. SKLAR, B. DRAKE, AND T. E. JORDAN. 1993. Seasonal measurements of sediment elevation in three mid-Atlantic estuaries. *Journal of Coastal Research* 9:986–1003.
- CHRISTENSEN, P. B., S. RYSGAARD, N. P. SLOTH, T. DALSGAARD, AND S. SCHWAERTER. 2000. Sediment mineralization, nutrient fluxes, denitrification, and dissimilatory nitrate reduction to ammonium in an estuarine fjord with sea cage trout farms. *Aquatic Microbial Ecology* 21:73–84.
- CORNWELL, J. C., W. M. KEMP, AND T. M. KANA. 1999. Denitrification in coastal ecosystems: Methods, environmental controls, and ecosystem level controls, a review. *Aquatic Ecology* 33:41–54.
- CURRIN, C. A. AND H. W. PAERL. 1998. Epiphytic nitrogen fixation associated with standing dead shoots of smooth cordgrass, *Spartina alterniflora*. *Estuaries* 21:108–117.
- DARKE, A. K. AND J. P. MEGONIGAL. 2003. Control of sediment deposition rates in two mid-Atlantic Coast tidal freshwater wetlands. *Estuarine, Coastal and Shelf Science* 57:255–268.
- DELAUNE, R. D. AND W. H. PATRICK, JR. 1990. Nitrogen cycling in Louisiana Gulf Coast USA brackish marshes. *Hydrobiologia* 199:73–79.
- ERIKSSON, P. G. AND S. E. B. WEISNER. 1999. An experimental study on effects of submersed macrophytes on nitrification and denitrification in ammonium-rich aquatic systems. *Limnology and Oceanography* 44:1993–1999.
- FAZZOLARI, E., B. NICOLARDOT, AND J. C. GERMON. 1998. Simultaneous effects of increasing levels of glucose and oxygen partial pressures on denitrification and dissimilatory nitrate reduction to ammonium in repacked soil cores. *European Journal of Soil Biology* 34:47–52.
- GALE, P. M., K. R. REDDY, AND D. A. GRAETZ. 1992. Mineralization of sediment organic matter under anoxic conditions. *Journal of Environmental Quality* 21:394–400.
- GRANT, JR., R. R. AND R. PATRICK. 1970. Tincum marsh as a water purifier, p. 105–123. In *Two Studies of Tincum Marsh*. The Conservation Foundation, Washington, D.C.
- GROSKOWSKI, K. M. 1995. Denitrification in a tidal freshwater marsh. Senior Thesis, Harvard College, Cambridge, Massachusetts.
- HARVEY, J. W., R. M. CHAMBERS, AND J. R. HOELSCHER. 1995. Preferential flow and segregation of porewater solutes in wetland sediment. *Estuaries* 18:568–578.
- HEINLE, D. R. AND D. A. FLEMER. 1976. Flows of material between poorly flooded tidal marshes and an estuary. *Marine Biology* 35:359–373.
- HOPKINSON, C. S. AND J. P. SCHUBAUER. 1984. Static and dynamic aspects of nitrogen cycling in the salt marsh graminoid *Spartina alterniflora*. *Ecology* 65:961–969.
- HUSSEY, B. H. AND W. E. ODUM. 1992. Evapotranspiration in tidal marshes. *Estuaries* 15:59–67.
- JONES, J. G. 1979. Microbial nitrate reduction in freshwater sediments. *Journal of General Microbiology* 115:27–35.
- JORDAN, T. E., D. L. CORRELL, AND D. F. WHIGHAM. 1983. Nutrient flux in the Rhode River: Tidal exchange of nutrients by brackish marshes. *Estuarine Coastal and Shelf Science* 17:651–668.
- JORDAN, T. E., D. F. WHIGHAM, AND D. L. CORRELL. 1989. The role of litter in nutrient cycling in a brackish tidal marsh. *Ecology* 70:1906–1915.
- KANA, T. M., M. B. SULLIVAN, J. C. CORNWELL, AND K. M. GROSKOWSKI. 1998. Denitrification in estuarine sediments determined by membrane inlet mass spectrometry. *Limnology and Oceanography* 43:334–339.
- LEDWIN, J. M. 1988. Sedimentation and its role in the nutrient dynamics of a tidal freshwater marsh. M.A. Thesis, College of William and Mary, Virginia Institute of Marine Science, Gloucester Point, Virginia.

- MATHESON, F. E., M. L. NGUYEN, A. B. COOPER, AND T. P. BURT. 2003. Short-term nitrogen transformation rates in riparian wetland soil determined with nitrogen-15. *Biology and Fertility of Soils* 38:129–136.
- MEGONIGAL, J. P., M. E. HINES, AND P. T. VISSCHER. 2004. Anaerobic metabolism: Linkages to trace gases and aerobic processes, p. 317–424. *In* W. H. Schlesinger (ed.), *Biogeochemistry*, Volume 8. Elsevier-Pergamon, Oxford, U. K.
- MERRILL, J. Z. 1998. Denitrification in the Maryland National Estuarine Research Reserves. Final report to National Oceanic and Atmospheric Administration #NA77OR0251. Silver Spring, Maryland.
- MITSCH, W. J. AND J. G. GOSSELINK. 2000. *Wetlands*, 3rd edition. Van Nostrand and Reinhold, New York.
- MORRIS, J. T. AND W. B. BOWDEN. 1986. A mechanistic, numerical model of sedimentation, mineralization and decomposition for marsh sediments. *Soil Science Society of America Journal* 50:96–105.
- NEIKIRK, B. B. 1996. Exchanges of dissolved inorganic nitrogen and dissolved organic carbon between salt marsh sediments and overlying tidal water. M.A. Thesis, College of William and Mary, Virginia Institute of Marine Science, Gloucester Point, Virginia.
- NEUBAUER, S. C. 2000. Carbon dynamics in a tidal freshwater marsh. Ph.D. Dissertation, College of William and Mary, Virginia Institute of Marine Science, Gloucester Point, Virginia.
- NEUBAUER, S. C. AND I. C. ANDERSON. 2003. Transport of dissolved inorganic carbon from a tidal freshwater marsh to the York River estuary. *Limnology and Oceanography* 48:299–307.
- NEUBAUER, S. C., I. C. ANDERSON, J. A. CONSTANTINE, AND S. A. KUEHL. 2002. Sediment deposition and accretion in a mid-Atlantic (U.S.A.) tidal freshwater marsh. *Estuarine Coastal and Shelf Science* 54:713–727.
- NEUBAUER, S. C., W. D. MILLER, AND I. C. ANDERSON. 2000. Carbon cycling in a tidal freshwater marsh ecosystem: A carbon gas flux study. *Marine Ecology Progress Series* 199:13–31.
- NIJBURG, J. W., M. J. L. COOLEN, S. GERARDS, P. J. A. KLEIN GUNNEWIEK, AND H. J. LAANBROEK. 1997. Effects of nitrate availability and the presence of *Glyceria maxima* on the composition and activity of the dissimilatory nitrate-reducing bacterial community. *Applied and Environmental Microbiology* 63:931–937.
- NIJBURG, J. W. AND H. J. LAANBROEK. 1997. The fate of <sup>15</sup>N-nitrate in healthy and declining *Phragmites australis* stands. *Microbial Ecology* 34:254–262.
- ODUM, W. E. AND M. A. HEYWOOD. 1978. Decomposition of intertidal freshwater marsh plants, p. 89–98. *In* R. E. Good, D. F. Whigham, and R. L. Simpson (eds.), *Freshwater Wetlands: Ecological Processes and Management Potential*. Academic Press, New York.
- ODUM, W. E., T. J. SMITH, III, J. K. HOOVER, AND C. C. MCIVOR. 1984. The ecology of tidal freshwater marshes of the United States East Coast: A community profile. U.S. Department of the Interior, Fish and Wildlife Service FWS/OBS-83-17, Washington, D.C.
- PASTERNAK, G. B. AND G. S. BRUSH. Sedimentation cycles in a river-mouth tidal freshwater marsh. *Estuaries* 21:407–415.
- REAY, W. G. 1989. Subsurface hydrodynamics and nutrient exchange within an extensive tidal freshwater wetland. M.A. Thesis, College of William and Mary, Virginia Institute of Marine Science, Gloucester Point, Virginia.
- REDDY, K. R., W. H. PATRICK, JR., AND C. W. LINDAU. 1989. Nitrification-denitrification at the plant root-sediment interface in wetlands. *Limnology and Oceanography* 34:1004–1024.
- RÜCKAUF, U., J. AUGUSTIN, R. RUSSOW, AND W. MERBACH. 2004. Nitrate removal from drained and flooded fen soils affected by soil N transformation processes and plant uptake. *Soil Biology and Biochemistry* 36:77–90.
- SEITZINGER, S. P. 1987. The effect of pH on the release of phosphorus from Potomac River sediments. U.S. Environmental Protection Agency, Chesapeake Bay Program, CBP/TRS 15. Annapolis, Maryland.
- SEITZINGER, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. *Limnology and Oceanography* 33:702–724.
- SIMPSON, R. L., D. F. WHIGHAM, AND R. WALKER. 1978. Seasonal patterns of nutrient movement in a freshwater tidal marsh, p. 243–257. *In* R. E. Good, D. F. Whigham, and R. L. Simpson (eds.), *Freshwater Wetlands: Ecological Processes and Management Potential*. Academic Press, New York.
- SOLORZANO, L. 1969. Determination of ammonium in natural waters by the phenylhypochlorite method. *Limnology and Oceanography* 14:799–801.
- SUNDARESHWAR, P. V., J. T. MORRIS, E. K. KOEPLER, AND B. FORNWALT. 2003. Phosphorus limitation of coastal ecosystem processes. *Science* 299:563–565.
- SUTULA, M., J. W. DAY, J. CABLE, AND D. RUDNICK. 2001. Hydrological and nutrient budgets of freshwater and estuarine wetlands of Taylor Slough in Southern Everglades, Florida (U.S.A.). *Biogeochemistry* 56:287–310.
- THOMAS, C. R. AND R. R. CHRISTIAN. 2001. Comparison of nitrogen cycling in salt marsh zones related to sea-level rise. *Marine Ecology Progress Series* 221:1–16.
- TOBIAS, C. R., I. C. ANDERSON, E. A. CANUEL, AND S. A. MACKO. 2001a. Nitrogen cycling through a fringing marsh-aquifer ecotone. *Marine Ecology Progress Series* 210:25–39.
- TOBIAS, C. R., S. A. MACKO, I. C. ANDERSON, E. A. CANUEL, AND J. W. HARVEY. 2001b. Tracking the fate of a high concentration groundwater nitrate plume through a fringing marsh: A combined groundwater tracer and in situ isotope enrichment study. *Limnology and Oceanography* 46:1977–1989.
- TYLER, A. C., T. A. MASTRONICOLA, AND K. J. MCGLATHERY. 2003. Nitrogen fixation and nitrogen limitation of primary production along a natural marsh chronosequence. *Oecologia* 136:431–438.
- U. S. Environmental Protection Agency (USEPA). 1996. Region III land cover data set. U.S. Environmental Protection Agency, Washington, D.C.
- U. S. Environmental Protection Agency (USEPA). 2002. Mid-Atlantic Integrated Assessment 1997–98 Summary Report. U.S. Environmental Protection Agency, Atlantic Ecology Division EPA/620/R-02/003. Narragansett, Rhode Island.
- VALIELA, I., J. WILSON, R. BUCHSBAUM, C. RIETSMAN, D. BRYANT, K. FOREMAN, AND J. TEAL. 1985. Importance of chemical composition of salt marsh litter on decay rates and feeding by detritivores. *Bulletin of Marine Science* 35:261–269.
- VAN BODEGOM, P., J. GOUDRIAAN, AND P. LEFFELAR. 2001a. A mechanistic model of methane oxidation in a rice rhizosphere. *Biogeochemistry* 55:145–177.
- VAN BODEGOM, P. J., F. STAMS, L. MOLLEMA, S. BOEKE, AND P. LEFFELAR. 2001b. Methane oxidation and the competition for oxygen in the rice rhizosphere. *Applied and Environmental Microbiology* 67:3586–3597.
- WEBSTER, J. R. AND E. F. BENFIELD. 1986. Vascular plant breakdown in freshwater ecosystems. *Annual Review of Ecology and Systematics* 17:567–594.
- WESSEL, W. W. AND A. TIETEMA. 1992. Calculating gross N transformation rates of <sup>15</sup>N pool dilution experiments with acid forest litter: Analytical and numerical approaches. *Soil Biology and Biochemistry* 24:931–942.
- WHIGHAM, D. F. AND R. L. SIMPSON. 1978. Nitrogen and phosphorus movement in a freshwater tidal wetland receiving sewage effluent, p. 2189–2203. *In* Coastal Zone 1978. Symposium on Technical, Environmental, Socioeconomic, and Regulatory Aspects of Coastal Zone Management, Volume 3. American Society of Civil Engineers, Washington, D.C.
- WHITE, D. S. AND B. L. HOWES. 1994. Long-term <sup>15</sup>N retention in the vegetated sediment of a New England salt marsh. *Limnology and Oceanography* 39:1878–1892.
- WOHLGEMUTH, M. 1988. Estimation of net aerial primary production of *Peltandra virginica* (L.) Kunth using harvest and

- tagging techniques. M.A. Thesis, College of William and Mary, Virginia Institute of Marine Science, Gloucester Point, Virginia.
- XUE, Y., D. A. KOVACIC, M. B. DAVID, L. E. GENTRY, R. L. MULVENEY, AND C. W. LINDAU. 1999. In situ measurements of denitrification in constructed wetlands. *Journal of Environmental Quality* 28: 263–269.
- ZIEGLER, S., D. J. VELINSKY, C. W. SWARTH, AND M. L. FOGEL. 1999. Sediment-water exchange of dissolved inorganic nitrogen in a freshwater tidal wetland. Technical report of the Jug Bay Wetlands Sanctuary, Lothian, Maryland.

## SOURCES OF UNPUBLISHED MATERIALS

- VELINSKY, D. J. Unpublished data. Patrick Center for Environmental Research, The Academy of Natural Sciences, 1900 Benjamin Franklin Parkway, Philadelphia, Pennsylvania 19103.

*Received, February 1, 2005*

*Revised, July 28, 2005*

*Accepted, August 31, 2005*