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Salt marsh ecosystem biogeochemical responses to nutrient enrichment: a paired ^{15}N tracer study

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Abstract. We compared processing and fate of dissolved NO_3^- in two New England salt marsh ecosystems, one receiving natural flood tide concentrations of $\sim 1\text{--}4\ \mu\text{mol NO}_3^-/\text{L}$ and the other receiving experimentally fertilized flood tides containing $\sim 70\text{--}100\ \mu\text{mol NO}_3^-/\text{L}$. We conducted simultaneous $^{15}\text{NO}_3^-$ (isotope) tracer additions from 23 to 28 July 2005 in the reference (8.4 ha) and fertilized (12.4 ha) systems to compare N dynamics and fate. Two full tidal cycles were intensively studied during the paired tracer additions. Resulting mass balances showed that essentially 100% ($0.48\text{--}0.61\ \text{mol NO}_3\text{-N}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$) of incoming NO_3^- was assimilated, dissimilated, sorbed, or sedimented (processed) within a few hours in the reference system when NO_3^- concentrations were $1.3\text{--}1.8\ \mu\text{mol/L}$. In contrast, only 50–60% of incoming NO_3^- was processed in the fertilized system when NO_3^- concentrations were $84\text{--}96\ \mu\text{mol/L}$; the remainder was exported in ebb tidewater. Gross NO_3^- processing was ~ 40 times higher in the fertilized system at $19.34\text{--}24.67\ \text{mol NO}_3\text{-N}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$. Dissimilatory nitrate reduction to ammonium was evident in both systems during the first 48 h of the tracer additions but $<1\%$ of incoming $^{15}\text{NO}_3^-$ was exported as $^{15}\text{NH}_4^+$. Nitrification rates calculated by $^{15}\text{NO}_3^-$ dilution were 6.05 and $4.46\ \text{mol}\cdot\text{ha}^{-1}\cdot\text{h}^{-1}$ in the fertilized system but could not be accurately calculated in the reference system due to rapid (<4 h) NO_3^- turnover. Over the five-day paired tracer addition, sediments sequestered a small fraction of incoming NO_3^- , although the efficiency of sequestration was 3.8% in the reference system and 0.7% in the fertilized system. Gross sediment N sequestration rates were similar at 13.5 and $12.6\ \text{mol}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$, respectively. Macrophyte NO_3^- uptake efficiency, based on tracer incorporation in aboveground tissues, was considerably higher in the reference system (16.8%) than the fertilized system (2.6%), although bulk uptake of NO_3^- by plants was lower in the reference system ($1.75\ \text{mol NO}_3^-\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$) than the fertilized system ($\sim 10\ \text{mol NO}_3^-\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$). Nitrogen processing efficiency decreased with NO_3^- load in all pools, suggesting that the nutrient processing capacity of the marsh ecosystem was exceeded in the fertilized marsh.

Key words: biogeochemistry; eutrophication; New England, USA; nitrogen processing efficiency; salt marsh; stable isotopes.

INTRODUCTION

Human activities are changing nutrient dynamics and biogeochemical cycles at a global scale. Nutrient enrichment in near-shore waters stimulates primary production and causes harmful algal blooms, shifts in food webs, increases in sedimentation, and eventually, changes in biogeochemistry and biodiversity (NRC 1994). In open-water areas, decreased light availability and decay of phytoplankton-derived organic matter has led to widespread loss of seagrass beds and hypoxia (Nixon 1995, Cloern 2001). Nitrogen is usually the

limiting nutrient in coastal waters, and flux of bioactive N as NH_4^+ and NO_3^- from New England rivers is currently 5–20 times higher than during pre-industrial times (Howarth et al. 1996, Jaworski et al. 1997).

The extensive salt marshes of eastern North America (see Plate 1) are thought to be an important landscape-scale N sink and regulator of near-shore water quality (Valiela and Cole 2002). These highly productive ecosystems buffer nutrient pollution moving from terrestrial sources into coastal water through a number of physical and biological processes. Anoxic, carbon-rich, salt marsh sediments can provide ideal conditions for denitrifying bacteria. Denitrification rates are typically high and can account for a majority of N flux in salt marshes (e.g., $420\ \mu\text{mol N}_2\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, $\sim 76\%$ of total N flux in Narragansett Bay salt marshes; Davis et al. 2004; see also Kaplan et al. 1979). Marsh vegetation is also an important nutrient sink through generation of

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plant biomass (Verhoeven et al. 2006) and persistence of plant detritus in marsh sediments with turnover rates of up to 500 years (e.g., Campbell et al. 1967). A third important sink is the uptake of N by suspended particulates (including microbial life and phytoplankton) and subsequent deposition in tidal creek and river sediments (Holmes et al. 2000) or on the marsh platform that is only flooded during spring tides (e.g., LeMay 2007). Sorption of NO_3^- is minor, although NH_4^+ adsorption to sediments can be large depending on salinity. The limits and extent of these processes, however, are difficult to quantify at ecosystem scales and against the background of increasing anthropogenic nutrient loads that threaten coastal environments.

Nutrient mass balances in tidal creeks have traditionally been used to quantify net uptake and loss from salt marsh ecosystems (e.g., Peterson et al. 1983), but mass balances cannot be used to understand the mechanisms or locations of nutrient removal. Isotopic tracer approaches have been used in combination with mass balances to calculate both gross and net N cycling in rivers (e.g., Peterson et al. 2001), but few large-scale tracer studies have been conducted in open tidal systems. Large and highly variable hydrologic throughput and tidal exchange, varying water tables, and strong gradients in salinity and redox conditions all complicate the study of nutrient dynamics in tidal systems (see Hopkinson and Giblin 2008). Prior to the work described here, ^{15}N tracer studies had been conducted in three tidal systems. Two were precursors to this study conducted within the same estuary (Plum Island Sound, Massachusetts, USA). Holmes et al. (2000) examined $^{15}\text{NO}_3^-$ cycling and fate at the upper range of tidal intrusion. Because water residence times were long in the upper estuary, short-term fate of NO_3^- was dominated ($>75\%$) by planktonic diatom uptake. Most of the tracer then quickly settled to and accumulated in channel bottom sediments. The second study examined analogous processes in the more rapidly flushed Rowley River subestuary (Tobias et al. 2003). Due to rapid tidal flushing, phytoplankton were sparse and a much smaller portion of NO_3^- was taken up, primarily by benthic diatoms leading to tidal export of 75–80% of NO_3^- as untransformed NO_3^- . Gribsholt et al. (2007) examined the fate of $^{15}\text{NH}_4^+$ tracer in tidal freshwater marshes of the Scheldt River, Belgium, a diked, high-nutrient ($\sim 400 \mu\text{mol/L}$ dissolved inorganic N) system, where over an individual tidal cycle, 69% of the tracer was exported as untransformed $^{15}\text{NH}_4^+$.

Here we examine NO_3^- processing and the effects of nutrient pollution on N dynamics in tidal salt marsh creeks of the Plum Island Sound Estuary. This study (and its local precursors) concern the fate of NO_3^- rather than NH_4^+ or a combination of the two because increasing inorganic N inputs from rivers and groundwater are dominated by NO_3^- (Fenn et al. 1998) and are linked to changes in the local watersheds (Pontius et al. 2000). We conducted simultaneous (paired) $^{15}\text{NO}_3^-$

tracer experiments in a salt marsh receiving ambient nutrient concentrations in inundating tidewater (the reference system) and an experimentally fertilized salt marsh system with at least 20 times ambient N and P concentrations. The tracer addition was conducted during the second year of the experimental fertilization. Nitrogen dynamics (e.g., net and gross NO_3^- production, NH_4^+ production, and export) were intensively studied and quantified over two individual tidal cycles of the five-day, paired $^{15}\text{NO}_3^-$ tracer addition. Sequestration by plants and sediments was quantified at the end of the five-day paired addition. Companion papers examine effects of the fertilization on salt marsh food web structure (Galván et al. 2008), plant N dynamics (Drake et al. 2008), and denitrification and dissimilatory reduction of nitrate to ammonium (Koop-Jakobsen 2008).

METHODS

TIDE, which stands for “trophic cascades and interacting control processes in a detritus-based aquatic ecosystem,” is a multiyear, ecosystem-scale, manipulative study in the extensive salt marshes of Plum Island, Massachusetts, USA (Fig. 1), a Long-term Ecological Research Site supported by the National Science Foundation. The goals of TIDE are to quantify the effects and interactions of increased nutrient loading (NO_3^- and PO_4^{3-}) and reduced abundance of a key fish species (mummichog [*Fundulus heteroclitus*]) on salt marsh ecosystems. A variety of approaches have been used to examine effects of the treatments on salt marsh flora, fauna, and physical characteristics (see Deegan et al. 2007). Here we compared N dynamics and biogeochemistry in a large, fertilized salt marsh creek shed (a tidal creek catchment of 12.4 ha, with mean tidal exchange volumes of 21 170 m^3) and a reference creek shed (8.4 ha, with an average tidal exchange volume of 10 560 m^3 ; Fig. 1). The reference and fertilized sites were paired in 2003. Pair members were selected from ~ 10 creek sheds of similar area, based on their relative position in the estuary, plant assemblages, and water column nutrient concentrations. Large-scale manipulative studies such as TIDE provide a realistic environment for examining effects and processes at an ecosystem scale. For example, our results include the effects of spatial variation and complexity, interactions between all of the species in the system, gradients across large areas, and large habitat patches. Methods relevant to the paired ^{15}N tracer studies are summarized briefly here, and a detailed description is provided in Appendix A. Portions of the methods are reproduced from Drake et al. (2008) with permission of the Inter-research Science Center.

The fertilizer addition

Dissolved NaNO_3 and KPO_4 were added to the fertilized marsh in all incoming tidal waters from approximately 15 May to 30 September in 2004 and 2005. This increased the mean NO_3^- concentrations in

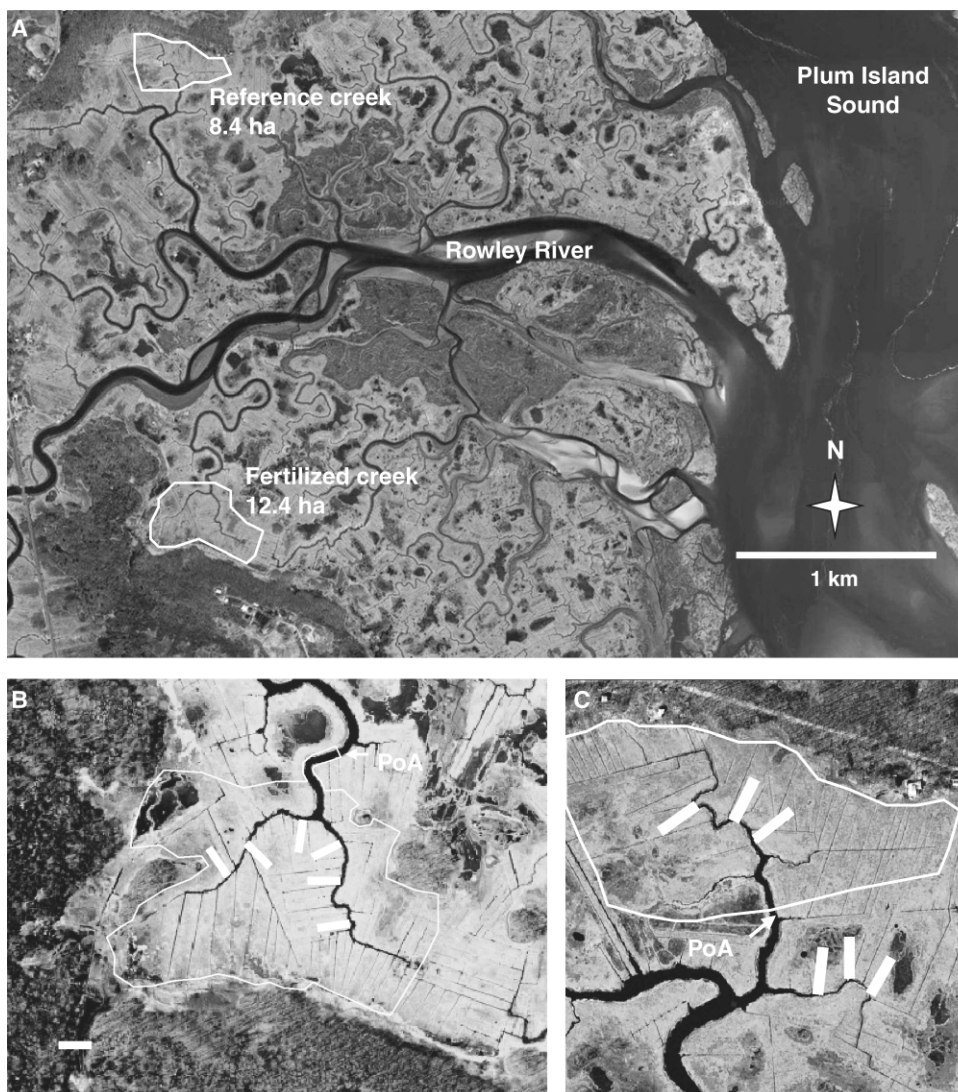


FIG. 1 (A) The paired marsh study areas in the Plum Island Sound estuary, Massachusetts, USA. Creek sheds or sub-catchments to which nutrients and the $^{15}\text{NO}_3^-$ tracer were added are outlined in white. These areas were delineated by adding tracer dye to incoming tidal water and testing for presence of dye in a grid of receiving bottles distributed over the marsh surface. Points of addition (PoA) of nutrients and $^{15}\text{NO}_3^-$ tracer are shown in (B) the fertilized creek shed and (C) the reference creek shed. The white rectangles are locations of the permanent sample plots for plant and sediment collections.

inundating water from $<4 \mu\text{mol/L}$ to $70\text{--}90 \mu\text{mol/L}$ and mean PO_4^{3-} concentrations from $\sim 1 \mu\text{mol/L}$ to $\sim 5\text{--}6 \mu\text{mol/L}$. The fertilizers were dissolved in a 2000-L tank of seawater and pumped into the creek at a rate matching tidal water influx to maintain a relatively constant enrichment throughout each tidal cycle. Flow-proportional nutrient addition mimics surface water pollution and creates a gradient of nutrient loading across the marsh that is proportional to inundation time and frequency (see Deegan et al. 2007).

Pre- $^{15}\text{NO}_3^-$ addition (baseline) data

Water quality, plant, and sediment data (constituent concentrations and standing stocks) were collected in

both creeks in 2003 and 2004 and prior to the ^{15}N additions in 2005. Concentrations of tidewater constituents (total dissolved nitrogen [TDN], NO_3^- , NH_4^+ , PO_4 , salt, chlorophyll *a*, and total suspended sediments [TSS]) were measured hourly during whole tidal cycle sampling (semidiurnally), once or twice per month during growing seasons. During each semidiurnal sampling, water samples were collected hourly by autosamplers (0.5 L at 20-min intervals, composited by hour) with intakes ~ 50 cm above the mid-channel sediment surface.

The paired ^{15}N tracer addition

We conducted simultaneous $^{15}\text{NO}_3^-$ tracer additions in the fertilized and reference systems from 23 to 28 July

2005. This was the height of the growing season during the second year of fertilization. At the fertilized site, 10 atom% $K^{15}NO_3$ was added to the $NaNO_3/KPO_4$ fertilizer solution and pumped into the creek with the regular dose of fertilizer. A total of 39.1 kg of $K^{15}NO_3$ and ~1800 kg $NaNO_3$ was added over a period of five days (nine tides), and a consistent $\delta^{15}NO_3^-$ of 650‰ in incoming creek water was maintained. Consistent $^{15}NO_3^-$ enrichment in the fertilized system was possible because the tracer was mixed directly into the fertilizer solution and the fertilizer NO_3^- overwhelmed (was at least 20 times higher than) ambient concentrations. At the reference site, tracer solution was pumped into the creek during flood tides at a rate calculated to match both water flux and estimated changes in ambient NO_3^- concentration (determined from 2003 and 2004 baseline concentrations), with a target $\delta^{15}N$ of 1000‰. The $^{15}NO_3^-$ enrichment attained in the reference system during the five-day paired addition varied from ~800‰ to 3090‰ and increased NO_3^- concentrations in the reference creek by 3–11%, depending upon ambient NO_3^- concentrations. The $^{15}NO_3^-$ addition continued for 37 days beyond the paired addition for related food web and N fate studies. In total we added 6.88 kg of $K^{15}NO_3$ to the reference system over a period of 42 days. Rhodamine WT tracer dye was added to the tank of $^{15}NO_3^-$ solution on both creeks immediately prior to each of the ^{15}N semidiurnal samplings for qualitative assessments (as an indicator of tracer solution presence that is more conservative than labeled NO_3^-).

Tidal cycle mass balances were quantified in both systems during the third and seventh tides of the paired $^{15}NO_3^-$ addition (henceforth called the ^{15}N semidiurnal samplings on 24 and 27 July). The ^{15}N semidiurnal samplings were similar to the (pre-experimental) semidiurnal samplings (summarized in Appendix A), but required collection of much larger water samples (4–5 L each hour at each location) for $^{15}NO_3^-$ and $^{15}NH_4^+$ analyses. During the ^{15}N semidiurnal samplings we collected water samples ~5 m seaward of each point of $^{15}NO_3^-$ addition (PoA) and ~100 m landward on the two main branches of the fertilized creek and at the main branch in the reference creek (i.e., at five locations).

Laboratory analyses

Water samples were filtered immediately. The $^{15}NH_4^+$ diffusions were started immediately, and the remaining filtrate was frozen for concentration analyses. Analyses included TSS, nutrient concentrations, and N isotope composition (TDN, NO_3^- , NH_4^+ , $^{15}NO_3^-$, $^{15}NH_4^+$, and particulate [P] ^{15}N) and chlorophyll *a*. Laboratory methods are described in Appendix A.

Quantitative methods

Uptake of total NO_3^- (in kilograms) into each pool was calculated from the increase in pool $\delta^{15}N$ (excess above natural abundance background $\delta^{15}N$; Eq. 1). Per mil excess $\delta^{15}N$ over the pre-experimental baseline was

multiplied by natural abundance of ^{15}N , converted to percentage (multiplied by 3.336×10^{-6}), multiplied by 10 to account for the percentage of ^{15}N in the tracer (10 atom % ^{15}N) and then multiplied by the pool N standing stock (in kilograms):

$$NO_3^- \text{ uptake} = \text{excess } ^{15}N_{\text{pool}} \times (3.663 \times 10^{-6}) \times 10 \times N \text{ standing stock}_{\text{pool}}. \quad (1)$$

Tidal mass balances were calculated from hourly concentrations (NO_3^- , TSS, etc.) and multiplied by water flux at 10-min intervals. Water flux in the reference system (dv/dt) was calculated using an exponential equation (Eq. 2) relating water height (h , in meters) in the channel at the permanent recorder. When $h > 2.71$ m, the entire marsh surface was flooded, and volume (in cubic meters) increased as a factor of the creek shed area (840 000 m²):

$$\text{if } h < 2.71\text{m}, V = b_0 \times e^{b_1 \times h}$$

$$\text{if } h > 2.71\text{m}, V = b_0 \times e^{b_1 \times h} + 84\,000 \times (h - 2.71) \quad (2)$$

where $b_0 = 45.749$ and $b_1 = 2.112$ were derived from empirical tidal flux measurements.

A related hydrological study quantified water flux in a fertilized system (C. W. Freidrichs, *unpublished data*) using a fifth-order polynomial equation based on h at a permanent recorder at the study area boundary. Area of the creek shed flooded (a) is multiplied by change in water height over the 10-min period ($\delta h/\delta t$) h , where water coverage is 100% = 3.05 m depth:

$$a = \exp(0.722 \times h^4 + -4.6274 \times h^3 + 10.2519 \times h^2 + -8.0123 \times h + 9.2541). \quad (3)$$

Eq. 3 provided the shape of the water influx curve, and water flux volumes were modified (multiplied by a factor of ~0.71) to correct for a discrepancy between known NO_3^- fertilizer addition rates and calculated water flux. The NO_3^- concentrations observed in the creek would have required addition of ~30% more fertilizer than was known to be added. This adjustment does not affect the calculation of balances (e.g., percentage of retention) and permits the most accurate mass estimates (e.g., NO_3^- -N loading rates per kilogram) based on known NO_3^- loading from the fertilizer addition.

We treated volume-weighted concentrations of TSS, nutrients, and phytoplankton N in each semidiurnal sampling (2003–2005) as an independent observation and used nonparametric *t* tests for comparisons. We use linear regression to determine whether a relationship between tidal exchange volume and TSS concentration was supported. Microsoft Office Excel 2003 was used to calculate all statistics. Differences in N fate between the two paired ^{15}N semidiurnal samplings cannot be statistically compared, but were critically examined in light of known processing rates in this and other studies. Phytoplankton N was calculated by multiplying chloro-

phyll *a* concentration by a biomass:chlorophyll *a* ratio of 50:1 and Redfield C:N (106:16).

Gross NO_3^- processing was calculated as the difference between mass flux in flood and ebb tides and converted to aerial rates for the total marsh area. System-scale nitrification rates were calculated from the dilution of $^{15}\text{NO}_3^-$ with unlabeled NO_3^- produced in the marsh between flood and ebb tides: we divided mean volume-weighted $\delta^{15}\text{NO}_3^-$ in the ebb tide by the mean volume-weighted $\delta^{15}\text{NO}_3^-$ in the flood tide. This fraction of “new” or nitrified N was then multiplied by the mass of NO_3^- in the ebb tide.

Although most nitrification in the system occurs in the unvegetated creek sediments and creek banks (Dollhopf et al. 2005), we adjusted nitrification rates to whole study areas (i.e., 8.4 and 12.4 ha) for comparison to other N cycle processes. We assumed that over the period of an individual tidal cycle, nitrification is the only significant source of NO_3^- within the study areas other than ^{15}N -labeled NO_3^- in floodwater. This assumption is supported by salt balances that show minimal groundwater (and therefore groundwater NO_3^-) seepage.

Tracer N uptake into sediments of the creek bottom, mudflat, and tall *S. alterniflora* habitats was calculated from bulk sediment $\delta^{15}\text{N}$ and %N (see Eq. 1) of the upper 2 cm of sediment. The tracer was not detected in deeper sediments. Soils of the marsh platform were dominated by macrophyte roots, so tracer fate in this habitat was estimated from deposited sediments and roots.

RESULTS

Hydrology and tidal balance

During July and August 2005, tidal amplitude varied from 2.1 to 3.4 m at the PoAs, and mean tidal exchange volumes were 11 480 m³ (range = 1950–43 500 m³) in the reference creek and 27 500 m³ (range = 8000–98 360 m³) in the fertilized creek. The ^{15}N semidiurnal samplings (24 and 27 July 2005) were conducted during marsh platform-flooding tides; on 24 July the fertilized marsh was completely inundated, with 5 cm of water over the highest part of the marsh. The reference marsh platform was only just covered by inundating water (<1 cm standing water on the highest part of the marsh). The 27 July tide was a partial flood tide, covering 3.4 ha of the 12.4-ha fertilized marsh system and a similar portion of the reference marsh system. Water fluxes were ~13 000 m³ and 11 000 m³ in the reference creek and ~22 000 m³ and 20 000 m³ (corrected volume) in the fertilized creek. Both creeks emptied almost entirely of water during each low tide, but the presence of tracer dye in the first hour of flood tides subsequent to dye addition (>12 hours after dye addition) showed that some residual water, <10% of the total tidal exchange volume, remained in the creek system seaward of the PoA during low tides and reentered the study areas. Flood and ebb tide volumes were balanced within 2% on most tides

throughout the season. Salt balances suggest negligible freshwater inputs to the reference creek (balances were within 1%) and a slight dilution at the fertilized creek (~3%), most likely from groundwater seepage.

Dissolved inorganic N and ^{15}N tracer concentrations

Ambient NO_3^- concentrations varied from 0.76 to 3.24 $\mu\text{mol/L}$ during the 2003–2004 field seasons (Appendix B). Lower concentrations were usually observed near high tide. During the first ^{15}N semidiurnal sampling, background NO_3^- in the reference creek was ~24% lower (1.3 $\mu\text{mol/L}$) than the mean July concentrations observed in previous years (~1.7 $\mu\text{mol/L}$), resulting in a volume-weighted mean floodwater $\delta^{15}\text{NO}_3^-$ of 1572‰. Ambient NO_3^- entering the reference creek during the second ^{15}N semidiurnal sampling was similar to baseline concentrations, resulting in a volume-weighted mean floodwater $\delta^{15}\text{NO}_3^-$ of 922‰. Because NO_3^- turnover times were short relative to travel time between the PoA and the sample collection point, enrichments are calculated from hourly, ambient NO_3^- concentrations in flood tidewater and continuous records of the tracer addition pump rates. During the second week of the tracer addition in the reference creek, background NO_3^- rose considerably (14–22 $\mu\text{mol/L}$) over 2003–2004 baseline concentrations and remained high until the end of monitoring approximately six weeks later. The source of the increased NO_3^- concentrations in the reference system is unknown. Volume-weighted NO_3^- concentrations in the fertilized creek were ~96 $\mu\text{mol/L}$ and ~84 $\mu\text{mol/L}$ and $\delta^{15}\text{NO}_3^-$ was ~650‰ during the two ^{15}N semidiurnal samplings.

Tidal cycle mass balances and short-term N processing

Gross and net tidal NO_3^- mass balances.—We note an important distinction between tracer $^{15}\text{NO}_3^-$ mass balances and NO_3^- mass balances: tracer $^{15}\text{NO}_3^-$ balances describe the fate of a discrete body of NO_3^- molecules, in this case the NO_3^- molecules that we isotopically labeled as they entered our study sites during a particular flood tide. Tracer $^{15}\text{NO}_3^-$ mass balances are used here to quantify gross NO_3^- processing. This includes all conversion or loss of labeled NO_3^- between the time of addition during the flood tide and the time of sample collection on the ebb tide. The NO_3^- balances describe net processing and are used to compare the total mass of NO_3^- , irrespective of isotopic composition, moving into creek sheds during flood tides and leaving creek sheds during ebb tides.

Rates and quantities of NO_3^- processing.—Gross processing of NO_3^- (based on tracer $^{15}\text{NO}_3^-$ mass balances) in the reference marsh was 100% and 98% during the ^{15}N semidiurnal samplings (Table 1, Appendix C); i.e., essentially all of the labeled tracer $^{15}\text{NO}_3^-$ entering the marsh during the flood tide was processed, and the NO_3^- exported in ebb tides was “new,” unlabeled NO_3^- that had been produced within the

TABLE 1. Materials fluxes and retention rates in the study systems in the Plum Island Sound estuary (Massachusetts, USA) during the two paired ^{15}N semidiurnal samplings conducted on 24 and 27 July 2005 (the third and ninth tides of the $^{15}\text{NO}_3^-$ addition).

Date and material sampled	Reference marsh			Fertilized marsh		
	In	Out	Retention (%)	In	Out	Retention (%)
24 July 2005						
Tidal water (m^3)	13 227	13 226	0.0	22 145	21 736	1.8
NO_3^- (mol)	36.39	10.67	70.7	2142	1502	29.9
$^{15}\text{NO}_3^-$ (mol)	1.98	0.00075	100.0	5.10	2.63	48.4
NH_4^+ (mol)	47.25	2.13	95.5	10.42	25.29	-142.7
$^{15}\text{NH}_4^+$ (mmol)	2.21	1.20	45.7	4.05	17.00	-319.8
TSS (kg)	175	195	-11.4	790	541	31.5
PN (mol)	68	51	25.0	140	160	-14.3
P^{15}N (mol)	0.19	0.31	-63.2	0.79	0.46	41.8
Phyto N (mol)	52.4	50.7	3.2	131	168	-28.2
Total tracer (mol)	1.98	0.32	83.8	5.1	3.11	39.0
27 July 2005						
Tidal water (m^3)	11 117	1116	90.0	20003	19 551	2.3
NO_3^- (mol)	28	36	-26.2	1679	1017	39.4
$^{15}\text{NO}_3^-$ (mol)	0.91	0.0183	98.0	4.00	1.57	60.8
NH_4^+ (mol)	26.89	13.81	48.6	23.75	137.30	-478.1
$^{15}\text{NH}_4^+$ (mmol)	8.43	1.06	87.4	10.20	80.34	-687.6
TSS (kg)	162	92	43.2	986	708	28.2
PN (mol)	73	62	15.1	154	191	-24.0
P^{15}N (mol)	0.08	0.03	62.5	0.39	0.41	-5.1
Phyto N (mol)	71	52.4	26.2	145	123	15.2
Total tracer (mol)	0.91	0.05	94.5	4.00	2.07	48.3

Notes: Nutrient fluxes are total masses of nutrients in moles (mol) or millimoles (mmol) for the individual tidal cycles and total mass of particulates. Negative retention values indicate a net export. Abbreviations are: TSS, total suspended sediments; P, particulate; Phyto, phytoplankton.

marsh during the tidal cycle. Thus, dissolved NO_3^- entering the reference creek experienced at least 100% turnover during these individual tidal cycles. Conservative estimates of the mass of NO_3^- processed (gross) in the reference marsh during the ^{15}N diurnal samplings were 0.48–0.61 mol $\text{NO}_3^- \cdot \text{N} \cdot \text{ha}^{-1} \cdot \text{h}^{-1}$. In the fertilized marsh the mass of N processed (gross) was ~40 times higher, 19.34–24.67 mol $\text{NO}_3^- \cdot \text{N} \cdot \text{ha}^{-1} \cdot \text{h}^{-1}$, but this is a smaller fraction (50–60%) of incoming labeled NO_3^- . Export of labeled NO_3^- (as a fraction of labeled NO_3^- that entered the marsh system on the flood tide) in the reference marsh increased between the first and second ^{15}N semidiurnal samplings from <0.01% (virtually undetectable) to ~2%. In contrast, fractions of unprocessed labeled NO_3^- in ebb tides of the fertilized marsh were relatively similar during the two ^{15}N semidiurnal samplings, ~50% and ~40% (Table 1, Appendix C).

Net NO_3^- retention (calculated using masses only) in the reference creek was 70% during the 24 July ^{15}N semidiurnal sampling; i.e., 36.39 mol NO_3^- was imported during the flood tide and 10.67 mol was exported during the ebb tide. During the 27 July ^{15}N semidiurnal sampling, however, we observed a net export of 26.2%, with 28.48 mol NO_3^- imported and 35.95 mol exported. In the fertilized system, similar fractions of net NO_3^- retention were observed during both ^{15}N semidiurnal samplings: 29.9% on 24 July and 39.4% on 27 July (2142 mol imported and 1502 mol exported and 1679 mol imported and 1017 mol exported, respectively; Table 1).

Production of $^{15}\text{NH}_4^+$ in the fertilized creek.—Detection of $^{15}\text{NH}_4^+$ during the first hour of the flood tide of the 24 July ^{15}N semidiurnal samplings (residual water from the previous tides) suggests a low rate of dissimilatory nitrate reduction to ammonium (DNRA) or microbial recycling ($\ll 1\%$ of incoming NO_3^-) during the first 48 h of the $^{15}\text{NO}_3^-$ addition (although see Discussion for a critical examination of DNRA in this system). The $^{15}\text{NH}_4^+$ balances did not change appreciably over the five-day paired tracer addition in either system (Table 1).

Suspended solids and seston.—The TSS concentrations in the fertilized system were consistently and significantly higher than those in the reference system (2004 and 2005, nonparametric paired t test, $P < 0.01$; Appendix D). The TSS balances varied considerably with net loss over some tides and net retention over others, although the reference and fertilized systems often behaved similarly during a given tidal cycle, e.g., TSS retention was relatively high in both systems on 10 August 2004 and 23 July 2005 (Appendix D).

Phytoplankton accounted for a majority (mean 89%) of sestonic N (PN) during the ^{15}N semidiurnal samplings (Table 1), with the remaining 11% likely contained in suspended microbial organisms. Surface water collected at high tide for a related project contained consistently lower TSS (10–30 g/m^3 ; LeMay 2007) than our samples (15–70 g/m^3) that were collected from lower in the water column, ~50 cm from the sediment surface. This suggests that at least half of the

TABLE 2. Summary NO₃-N mass balances in the study systems.

Fate of ¹⁵ N tracer in NO ₃ -N	Reference marsh, 3021 mol†		Fertilized marsh, 23 571 mol†	
	NO ₃ -N fate (mol)	Percentage of influx	NO ₃ -N fate (mol)	Percentage of influx
Export as unprocessed NO ₃ -N	33.2	1.1	10 714.3	45.5
Export as particulates (including phytoplankton)	286.3	9.5	2271.1	9.6
Export as NH ₄ -N	≪0.1	≪1	0.1	≪1
Sediments (creek, mudflat, tall <i>S. alterniflora</i>)	44.1	1.5	69.2	0.3
Sedimentation on the marsh platform	69.5	2.3	86.9	0.4
Aboveground <i>Spartina</i> spp. total	506.4	16.8	620.0	2.6
Belowground <i>Spartina</i> spp. estimate	810.3	26.8	992.0	4.2
Denitrification‡ (excluding creek banks)	20.8	0.7	512.0	2.2
DNRA‡	21.0	0.7	491.0	2.1
Unaccounted for	1229.7	40.7	7814.8	33.2
Total processed (influx – unprocessed export)	2988.2	98.9	12 857.1	54.5

Note: Fates are summed for the five days of the paired ¹⁵NO₃⁻ addition from expanded means of the two ¹⁵N semidiurnal samplings and from plant and sediment samples collected at the end of the five-day paired ¹⁵NO₃⁻ addition.

† Values refer to the total NO₃⁻ that entered each marsh system during the five-day paired ¹⁵NO₃⁻ addition.

‡ Estimated from measurements made in 2006 and 2007 by Koop-Jakobsen (2008). “DNRA” stands for dissimilatory nitrate reduction to ammonium.

TSS within the bounds of the study systems was not imported from Plum Island Sound, but was resuspended material from within the creeks. This also suggests that the water column phytoplankton pool might include a component of suspended benthic microalgae. Between 3% and 15% of ¹⁵NO₃⁻ added to the creeks during each of the ¹⁵N semidiurnal samplings was exported in particulate form (ebb tide P¹⁵N), with no consistent difference between the fertilized and reference systems. Flood tide PN collected ~100 m landward to the PoAs contained similar fractions (8–15%) of ¹⁵NO₃⁻ tracer, suggesting a relatively consistent rate of phytoplankton uptake and sorption to suspended particulates within 20–60 min of tracer addition (the travel time between PoAs and sample collection points).

Mean flood tide chlorophyll *a* concentrations were 4.7 and 8.3 µg/L in the reference creek and 8.9 and 15.3 µg/L in the fertilized creek during the 24 and 27 July ¹⁵N semidiurnal samplings, respectively. No pattern was evident in phytoplankton N mass balances. Net phytoplankton N flux in the reference system was approximately balanced during the first ¹⁵N semidiurnal sampling and showed a net retention of ~26% during the second. In the fertilized system 28% export and 15% retention was measured during the ¹⁵N diurnal samplings (Table 1).

Nitrification.—During both of the ¹⁵N diurnals, virtually all of the ¹⁵NO₃⁻ tracer added to the reference system was processed and replaced with new, unlabeled NO₃⁻ via nitrification within a single tidal cycle. Dilution through replacement was so high that it was equivalent to ~100% replacement. In fact, because so little ¹⁵NO₃⁻ tracer was detected in ebb tidewater, it was impossible to determine how many times the NO₃⁻ pool turned over during individual tidal cycles, and nitrification rates of 0.12 and 0.40 mol·ha⁻¹·h⁻¹ on 24 and 27 July underestimate true rates in the reference system. We note that water column NO₃⁻ turnover is a function of

ambient NO₃⁻ concentration, which was ~24% lower than average pre-experimental concentrations during the 24 July semidiurnal sampling (see *Discussion*). Lower-than-average NO₃⁻ concentrations contributed to the very fast turnover observed. Nitrification rates in the fertilized system could be quantified more accurately because ¹⁵NO₃⁻ tracer was measurable in ebb tidewater (<100% turnover): nitrification rates were 6.05 and 4.46 mol·ha⁻¹·h⁻¹ for the 24 and 27 July semidiurnal samplings.

Longer-term N processing

Deposition of sediment on the marsh platform.—Median sediment deposition rates did not differ between the reference and fertilized systems, but did decrease with distance from the creeks. Deposition rates were 1.95 g·m⁻²·d⁻¹ within 4 m of the creek, roughly corresponding to the tall *S. alterniflora* habitat, and 1.21 g·m⁻²·d⁻¹ on the marsh platform 10–50 m from the creeks (LeMay 2007). Organic matter content of deposited sediments did not differ significantly between creeks or with distance from the channel (LeMay 2007). Excess δ¹⁵N of sediments deposited during the paired ¹⁵N additions was 9.5‰ ± 2.6‰ (mean ± SE) in the fertilized system and 8.4‰ ± 1.8‰ in the reference system. Of NO₃⁻-N entering the reference and fertilized systems, 2.3% and 0.4% were deposited with sediments on the marsh platforms, respectively (Table 2). Thus deposition of suspended sediments and seston was not a major pathway of N removal.

Nitrogen uptake by creek sediments.—At the end of the five-day additions, the top 2 cm of bulk sediment in the unvegetated areas (creek bottoms, mudflats) and tall *S. alterniflora* habitat (creekbank) was enriched over baseline by 0.7–0.8‰ in the reference creek and 1.4–1.9‰ in the fertilized creek. This pool includes benthic microalgae, infauna and detrital N. Storage in sediments accounted for ~1.5% of the ¹⁵N tracer fate in the

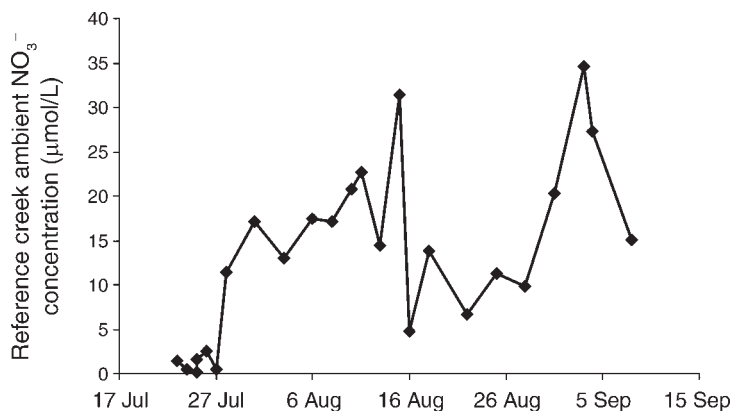


FIG. 2. Reference creek NO₃⁻ concentrations over the 2005 study season.

reference marsh and 0.3% in the fertilized marsh (Table 2). These estimates are conservative (low) because deeper sediments are not included. Labeled N that mixed deeply into the sediments cannot be quantified because the very large pool of N in sediments dilutes the tracer signal.

Flora.—Bulk uptake of NO₃⁻ by *Spartina* spp. was 1.75 mol·ha⁻¹·d⁻¹ in the reference system and ~10 mol·ha⁻¹·d⁻¹ in the fertilized system, or 16.8% of the total NO₃⁻ load in the reference system and only 2.6% in the fertilized system (aboveground pools only; Table 2).

Export of the tracer ¹⁵N

Ebb tide δ¹⁵NO₃⁻ in the reference creek began to increase relative to flood tide δ¹⁵NO₃⁻ approximately one week after the ¹⁵N addition was initiated (Fig. 2). Little ¹⁵N tracer was exported prior to this. Pore water collected from creekbanks where the highest rates of nitrification occur (Dollhopf et al. 2005) had NO₃⁻ concentrations of 1–10 µmol/L and δ¹⁵NO₃⁻ maxima that lagged two to three weeks behind the ebb tide δ¹⁵NO₃⁻ maxima. It is not possible to calculate pore water flux with existing data. A late-season increase in reference system pore water δ¹⁵NO₃⁻ (18 September, 21 d after the end of the ¹⁵NO₃⁻ addition) coincides with an increase in ebb tide δ¹⁵NO₃⁻.

DISCUSSION

Nitrate processing rates and pathways change as NO₃⁻ loading increases.—This study demonstrates large differences in NO₃⁻ processing and fate between salt marshes receiving natural (1.3 and 1.8 µmol/L) and elevated (~84 and 96 µmol/L) NO₃⁻ concentrations in floodwater. Our study also shows that the capacity of the natural salt marsh to process NO₃⁻ was exceeded in the fertilized marsh system. The relatively low ambient NO₃⁻ concentrations in the reference system allowed significant N turnover and a high efficiency of processing in the sestonic component in addition to marsh and creek surface processing, while the fate of labeled NO₃⁻ in the fertilized system was dominated by export in

unprocessed form. We note that the 100% processing rate observed in the reference system is likely driven primarily by sestonic turnover, and the rate is very sensitive to phytoplankton and NO₃⁻ concentrations. For comparison, unprocessed export was the dominant fate in the middle estuary, where NO₃⁻ concentrations were 18–25 µmol/L (Tobias et al. 2003), while planktonic diatoms settling into sediments were the largest sink in the upper estuary (0–3 µmol NO₃⁻/L; Holmes et al. 2000). We note, however, that the middle estuary study was conducted during a neap tide series when flooding of the large surface areas and plants of the marsh platform was limited.

The fact that organic N in sediments is generally the largest N pool in wetlands (e.g., Bowden 1987) and the demonstrated importance of rapidly sinking planktonic diatoms as an N sink in the upper reaches of the estuary (Holmes et al. 2000) lead us to suspect that sediments would be a major tracer sink in this study. But this was not the case. During the five-day paired tracer addition, only ~3.7% (13.5 mol·ha⁻¹·d⁻¹) and 0.7% (12.6 mol·ha⁻¹·d⁻¹) of the total NO₃⁻ load was sequestered in surface sediments of the reference and fertilized systems, respectively. The reduced role that benthic microalgae play in salt marsh creek N cycling compared to that in the upper estuary may be a result of shorter residence time, higher rates of flushing, or higher N content in sediments (signal swamping). In the salt marshes of the lower estuary examined here, a much larger surface area is flooded by tidal water than in the upper estuary. This study included large areas of marsh platform grasses with a much higher biomass than algae, while studies in the upper estuary primarily concerned water column N dynamics (Holmes et al. 2000, Tobias et al. 2003). In the reference creek, at least before NO₃⁻ concentrations increased, microalgae were likely using sediment-derived NH₄⁺ as their primary source of N. In the fertilized creek with high NO₃⁻ concentrations microalgae took up a larger mass of N, as expected. Microalgal biomass is limited by top-down control, and the N in this pool has a short residence time. This pool,



PLATE 1. The expansive salt marsh ecosystem of Plum Island, Massachusetts, USA. Tall *Spartina alterniflora* in the foreground creek bank habitat changes abruptly to *S. patens* habitat on the marsh platform. Photo credit: D. C. Drake.

therefore, cannot store large amounts of N except by producing detritus.

In the reference marsh, *Spartina* was the largest tracer N sink, while in the fertilized marsh known fates were dominated by export of unprocessed NO_3^- . Plants in the fertilized system sequestered a larger mass of N per unit area per day ($10 \text{ mol NO}_3^- \cdot \text{ha}^{-1} \cdot \text{d}^{-1}$) compared to those in the reference system ($1.75 \text{ mol NO}_3^- \cdot \text{ha}^{-1} \cdot \text{d}^{-1}$), but this was a much smaller fraction of the high N load entering the fertilized system. Like sediment sequestration, efficiency of plant uptake was higher at low NO_3^- loading rates. If plant uptake estimates are expanded to include belowground biomass using allometry (~ 1.6 times aboveground pools; Hopkinson and Schubauer 1984), 48% of incoming N is sequestered by plants in the reference system and 6.8% in the fertilized system.

Nitrogen turnover in salt marsh ecosystems.—Nitrate turnover in the water column calculated using ^{15}N dilution is a product of two processes: (1) uptake/removal of labeled NO_3^- , which affects NO_3^- concentration but not $\delta^{15}\text{NO}_3^-$ and (2) production of unlabeled NO_3^- via nitrification, which dilutes the $^{15}\text{NO}_3^-$ signal (decreases per mil) in the ebb tide. The 100% turnover in the reference creek results from both uptake of the small mass of NO_3^- moving into the system and a high rate of dilution with unlabeled N. We believe that the immediate uptake of NO_3^- in the reference system was mostly sestonic, but we were unable to measure this in ebb tide particulate ^{15}N . Potential reasons for this include that the movement of seston out of the system was uneven and our hourly sample collection may have missed pulses of export.

Ambient NO_3^- concentrations in the reference creek were either lower than or similar to pre-experimental concentrations during the paired ^{15}N semidiurnal samplings (Appendix A) but began to increase on day 7 of the ^{15}N addition (Fig. 2). Ebb tide $\delta^{15}\text{NO}_3^-$ began to increase on approximately day 3 of the addition and peaked on day 9 (Fig. 3). There are several potential explanations for increased export of labeled NO_3^- : (1) remineralization and export of labeled N, (2) re-release of labeled N into the water column through nitrification, and (3) after day 7, efficiency of removal of NO_3^- from the water column decreased as ambient NO_3^- concentrations rose.

The appearance of labeled inorganic N in ebb tides is indicative of several pathways depending on timing: $^{15}\text{NH}_4^+$ appearing within 24–48 h is likely from direct conversion of NO_3^- to NH_4^+ via DNRA or microbial recycling. We detected a small mass of $^{15}\text{NH}_4^+$ on the 24 July ebb tide (~ 36 h after the additions were initiated), suggesting activity in at least one of these pathways, although $^{15}\text{NH}_4^+$ accounted for only 0.0006% and 0.0033% in the reference and fertilized systems, respectively. Retention of $^{15}\text{NH}_4^+$ within the marsh is discussed below. Algal and microbial turnover will release $^{15}\text{NH}_4^+$ and $^{15}\text{NO}_3^-$ (via remineralization and nitrification) back into the system over periods of hours to weeks. Activity of this pathway is evident in fractions of tracer in ebb tides as NH_4^+ that increased by factors of 1.9 and 6.0 between days 2 and 5 of the additions.

We unintentionally introduced a spike in flood tide $\delta^{15}\text{NO}_3^-$ to the reference creek during the first few days of the experiment (an artifact of an unexpected increase

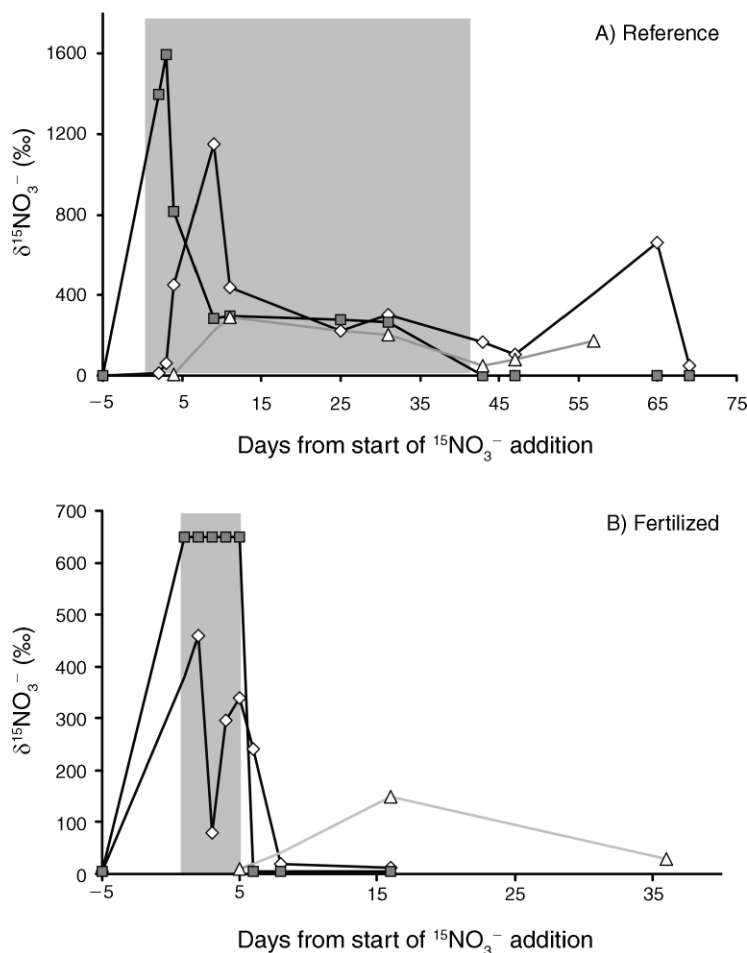


FIG. 3. Volume-weighted $\delta^{15}\text{NO}_3^-$ in flood tidewater (solid squares) and ebb tidewater (open diamonds) and unweighted pore water $\delta^{15}\text{NO}_3^-$ (open triangles) in the (A) reference and (B) fertilized marsh systems. Shaded areas mark the duration of $^{15}\text{NO}_3^-$ additions. The lag between patterns in the reference creek suggests an approximate one-week lag between tracer addition and when added nitrate is incorporated into the NH_4^+ pool through uptake and mineralization and then nitrified. A spike in $\delta^{15}\text{NO}_3^-$ on 26 September (25 days after the end of the ^{15}N addition) suggests late-season remineralization of the tracer that had been stored in marsh pools.

in background NO_3^- concentrations in weeks 2–6 of the addition; Fig. 3). A similar spike in ebb tide $\delta^{15}\text{NO}_3^-$ occurred five to seven days later. This likely reflects microbially mediated turnover operating on a small and very labile N pool relative to the mass of whole-marsh N, i.e., the time required for microorganisms such as bacteria and benthic algae to take up and remineralize labile water column NO_3^- . The lag between maximum $\delta^{15}\text{NO}_3^-$ in floodwater and pore water was at least two weeks in both systems, although infrequent sampling limits this inference. The delayed appearance of labeled N in pore water suggests that either surface water NO_3^- undergoes several transformations (e.g., uptake and remineralization by plants or microalgae) before it enters pore water or that labeled N is entering pore water via direct drainage, but only in relatively small quantities relative to the existing pool, i.e., is too dilute to detect initially.

A notable spike in ebb tide $\delta^{15}\text{NO}_3^-$ is seen in the late season (26 September), about one month after the end of the $^{15}\text{NO}_3^-$ addition. Although this is just one value and should be interpreted with caution, a post-addition spike is attributable to mineralization of senescing plant materials, algae, and other organisms.

Denitrification, DNRA, and unquantified fates.—A related study within the TIDE project determined that rates of denitrification and DNRA were more than an order of magnitude higher on the platform of the fertilized system than in the same habitats in the reference system (Koop-Jakobsen 2008). Denitrification rates were highest in the fertilized tidal creek sediment ($\sim 8 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$). On the marsh platform, denitrification was significantly lower ($< 0.6 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$), including denitrification activity in surface sediment as well as coupled nitrification–denitrification occurring at depth in the rhizosphere. The platform is only inundated

12% of the day on average, which significantly limits the access of the denitrifying agents to the added nitrate fertilizer. If $^{15}\text{NH}_4^+$ was produced through DNRA at rates measured by Koop-Jakobsen (2008) and then exported, we should have measured much higher concentrations of labeled NH_4 in ebb tidewater. This suggests that NH_4^+ produced by DNRA is recycled within the system rather than exported and that DNRA is playing a larger role in N processing in marsh and creek sediments than the tidal exchange fluxes suggest. Considering the rates measured by Koop-Jakobsen (2008), the fraction of NO_3^- fate accounted for by denitrification and DNRA was surprisingly small; denitrification and DNRA combined accounted for only $\sim 1.4\%$ of NO_3^- fate in the reference system and $\sim 4.3\%$ in the fertilized system over the five-day tracer addition.

Surprisingly large and similar fractions of tracer N were unaccounted for: 40.7% in the reference system and 33.2% in the fertilized system (Table 2). These fractions equate to a much larger mass of N in the fertilized system, $125.0 \text{ mol NO}_3^- \cdot \text{ha}^{-1} \cdot \text{d}^{-1}$, compared to $28.9 \text{ mol} \cdot \text{ha}^{-1} \cdot \text{d}^{-1}$ in the reference system. There are several potential explanations for this; the most likely is a high rate of denitrification in the creek banks, an important site of nitrification and where NO_3^- in surface water contacts the oxic-anoxic interface. This was not included in the Koop-Jakobsen study (2008), which instead targeted denitrification in the plant rhizosphere and creek bottom sediments. The “unaccounted for” fractions may also be partially explained by our consistently conservative estimations of $^{15}\text{NO}_3^-$ fate in the pools measured. Other potentially important unquantified fates include movement of tracer into pore water (in which ^{15}N enrichment but not total flux was measured), uptake by plants other than the dominant *Spartina* species, NH_4^+ volatilization, and uptake by epiphytic algae and microbes that were washed off of grasses prior to analyses.

Evidence of NO_3^- saturation.—The work presented here suggests that an ecosystem-scale NO_3^- processing capacity was exceeded in the fertilized salt marsh. When ambient NO_3^- concentrations were low, a high level of efficiency in N cycling was demonstrated (i.e., N was tightly cycled). Under the increased NO_3^- load in the fertilized system, export of unprocessed NO_3^- increased considerably, suggesting that the capacity of the marsh for N processing was exceeded. Our observations of decreased plant N uptake efficiency (Drake et al. 2008) and sediment N accumulation support this and may reflect N saturation or a switch to another type of limitation (e.g., by light or another nutrient). The potential saturation observed here is comparable to the nitrogen saturation hypothesis for forest ecosystems described by Aber et al. (1998). According to this hypothesis, increased N loading in N-limited forest ecosystems is reflected in a progressive N saturation “syndrome” that includes increased nitrification rates and increased NO_3^- mobility in soils and export in

surface waters. As in the salt marsh, these systemic changes reflect the sum of smaller changes in N cycling in all ecosystem components (vegetation, microbial communities, etc.).

Our study was conducted during the second year of fertilization and demonstrates some of the initial effects of increased nutrient load on salt marsh ecosystems. It is unknown how continued high rates of nutrient loading may manifest in the salt marsh, but possibilities include changes in species compositions, increased rates of sediment decay, or unknown cumulative effects. We also acknowledge that this N-cycling comparison is limited to two (large) salt marsh ecosystems and that the results are subject to pseudoreplication (although see Deegan et al. [2007] for a detailed discussion). Nevertheless, this study helps describe the limit of salt marshes as a mediator in the early years of surface water pollution.

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APPENDIX A

Methods relevant to paired ^{15}N tracer additions in the fertilized and reference salt marshes (*Ecological Archives* E090-179-A1).

APPENDIX B

Water fluxes and baseline volume-weighted nutrient concentrations of incoming tidewater in 2003–2004 (*Ecological Archives* E090-179-A2).

APPENDIX C

Figures illustrating short-term N cycling (*Ecological Archives* E090-179-A3).

APPENDIX D

Total suspended sediment (TSS) mass balances from 2004 to 2005, illustrating consistently higher TSS in the fertilized marsh (*Ecological Archives* E090-179-A4).