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Tracking the fate of a high concentration groundwater nitrate plume through a fringing marsh: A combined groundwater tracer and in situ isotope enrichment study

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Abstract

A groundwater plume enriched in $^{15}$NO$_3$ was created upgradient of a mesohaline salt marsh. By measuring the changes in concentration and isotopic enrichment of NO$_2$, NO$_3$, N$_2$O, N$_2$, NH$_4$, and particulate organic nitrogen (PON) during plume transport through the marsh, in situ rates of dissimilatory nitrate reduction to ammonium (DNRA) and denitrification (DNF) were estimated, as well as N storage in the reduced N pools. For groundwater discharge within the top 10 cm of marsh, NO$_3$ removal was 90% complete within the 50 cm of marsh nearest the upland border. The peak NO$_3$ loss rate from the plume ranged from 208 to 645 $\mu$M·d$^{-1}$. Rates of DNRA (180 $\mu$M·d$^{-1}$) and DNF (387–465 $\mu$M·d$^{-1}$) processed 30% and 70% of the NO$_3$ load, respectively. Terminal N$_2$O production was approximately equal to N$_2$ production rates during DNF. Comparison of $^{15}$N lost from the $^{15}$NO$_3$ pool and $^{15}$N gained in each of the reduced products accounted for only 22% of the reduced $^{15}$N, thus indicating N export from the system. Despite high rates of DNRA, the NH$_4$ produced was not a long-term repository for the groundwater-derived N but was instead rapidly immobilized into marsh PON and retained on longer timescales. The small inventory of $^{15}$N in the N$_2$O and N$_2$ pools relative to DNF rates, coincident with an undersaturation of dissolved argon, indicated that denitrified N was exported to the atmosphere on short timescales. The relative magnitudes of DNF and DNRA in conjunction with the immobilization of NH$_4$ and evasion of N gases dictated the extent of export versus retention of the groundwater NO$_3$ load.

Groundwater enriched in nitrogen has been recognized as an important nonpoint nutrient source to nearshore ecosystems, yet little is understood about the behavior of nitrogen (N) at biogeochemically reactive discharge interfaces (Capone and Bautista 1985; Giblin and Gaines 1990; Valiela et al. 1992). One such interface exists at the ecotone between the shallow aquifer and marsh-fringed estuaries. Because discharge often concentrates at or near the shore-

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line (Reilly and Goodman 1985; Bokuniewicz 1992), the importance of fringing marshes in attenuating groundwater N loads to adjacent aquatic or marine systems has been argued (Harvey and Odum 1990; Howes et al. 1996). Fringing marshes can function as groundwater nitrogen “buffers” only if a significant proportion of the total groundwater discharge contacts the marsh. Although salt balances calculated for tidal creeks draining some New England pocket marshes indicate substantial marsh/groundwater interaction (Valiela and Teal 1979; Howes et al. 1996), discharge through fringing coastal and riparian marshes may constitute only a small percentage of the total groundwater derived nitrate flux to adjacent water masses (Bøhlke and Denver 1995; Portnoy et al. 1997; Nowicki et al. 1999). Yet these relatively small fluxes of groundwater and nitrogen (on an estuarine scale) can be large enough to periodically influence the water and nitrogen balance of the fringing marsh ecosystem itself (Tobias et al. 2001a,b). Therefore, quantification of the mechanisms of nitrogen processing, specifically pathways that result in the retention of or accelerate losses of N, assumes a more critical role in defining the influence of groundwater nitrogen sources on the marsh ecosystem.
Nitrate is the dominant species of dissolved inorganic nitrogen (DIN) in most shallow, aerobic, aquifers (Kranyov et al. 1992; Fetter 1993) and is the most frequently encountered form of anthropogenically enriched DIN discharging from shallow aquifers in the coastal zone (Valiela and Teal 1979; Reay et al. 1993; Portnoy et al. 1997). Marsh sediments with high organic carbon and low redox potential typically demonstrate high rates of potential nitrate reduction. In many wetland studies, denitrification has been considered to be solely responsible for observed nitrate disappearance in sediments in the absence of direct denitrification (DNF) measurements (Xue et al. 1999). Although DNF has figured prominently in the N budget of some New England marshes subject to large groundwater nitrate fluxes, most efforts to study nitrate reduction in marsh or subtidal sediments have not considered alternate nitrate reduction pathways (Valiela and Teal 1979; Koike and Sorenson 1988; Howes et al. 1996).

Dissimilatory nitrate reduction to ammonium (DNRA) may constitute a greater proportion of total NO$_3^-$ reduction in sediments that contain high electron donor:electron acceptor ratios (i.e., DOC: NO$_3^-$; Tiedje 1988). Laboratory and microcosm incubations have demonstrated that the DNRA contribution to total nitrate reduction appears to be small in freshwater systems but comparable to DNF rates in some salt marsh and anoxic marine sediments (Koike and Hattori 1978; King and Nedwell 1985; Bowden 1986). The rapid biotic and abiotic immobilization of NH$_3$ found in wetland sediments may serve as a link between DNRA and N storage in the sediment particulate organic nitrogen (PON) pool (Smith et al. 1982; Bowden 1986; White and Howes 1994; Anderson et al. 1997). Unlike the gaseous products of denitrification (N$_2$O and N$_2$), which may be subject to evasion on relatively short timescales, nitrogen in the PON detrital fraction is prone to more extensive cycling within the sediments and tends to be sequestered on the timescale of years (White and Howes 1994). Therefore, we suggest that the specific pathway of nitrate reduction may dictate the extent of export versus retention of this allochthonous nitrogen source within the ecosystem.

Herein we describe the relative importance of denitrification and nitrate reduction to ammonium with respect to the total consumption of groundwater nitrate during discharge into a mesohaline fringing marsh. In this advection-dominated discharge zone, traditional techniques used to measure N cycling processes, which require the isolation of sediments into cores or slurries, were avoided (Koike and Sorenson 1988; Knowles 1990). Instead, we chose a relatively novel approach that combined a conservative ground-water tracer (bromide) with an in situ novel approach that combined a conservative ground-water tracer (bromide) with an in situ

Site description and methods

The Ringfield marsh study site is located in the Colonial National Historical Park (37°16'42"N, 76°35'16"W) on the Ringfield Peninsula near the confluence of King Creek and the York River in southeastern Virginia (Fig. 1). The steep (1:1) forested upland slope transitions into a 25-m wide wetland composed of a mixed community of Spartina cynosuroides and Spartina alterniflora (short form). Marsh stratigraphy consists of the upper 30–80 cm of anoxic marsh sediment underlain by a semicontinuous layer (10–20 cm thick) of lower permeability glauconitic silty sand. Below 150–200 cm, the glauconitic deposits grade into cleaner oxidized iron-rich sands and shell hash of pre-Holocene origin. The site receives maximal groundwater discharge from January through July and little to no discharge from August through November (Tobias et al. 2001a).

**Tracer release**—To simulate high groundwater NO$_3^-$ loads, a concentrated NO$_3^-$ groundwater plume enriched in $^{15}$N-NO$_3^-$ and a conservative tracer (Br$^-$) was created in the shallow aquifer at the border between the upland and the marsh. As the plume discharged into the shallow subsurface of the marsh, the dissolved concentrations and the $^{15}$N isotopic enrichments of NO$_3^-$, NH$_4^+$, N$_2$O, and N$_2$ were measured from wells located in the marsh. Nitrogen incorporated into the sediments (PON) was measured in cores taken before the injection and at the end of the study.

The injectate of K$^{15}$NO$_3^-$ and KBr was prepared on site by use of groundwater pumped from the injection wells. The final target injectate concentrations for N-NO$_3^-$ and Br$^-$ was 0.12 and 1.0 molar, respectively. The target $^{15}$N enrichment was 7600‰–7800‰, and a total of 5 liters of injectate was released into each of the three injection wells. To release the injectate, injection wells were first pumped dry after insertion of a PVC liner, the well volume (now dry) was filled with injectate, and the liner removed. This single slug was
followed by a constant drip at a rate of ~150 ml hr\(^{-1}\) for 33 h. The injectate was kept on ice during the drip, and an ultra-high-purity He headspace in the injection reservoir was maintained to prevent atmospheric oxidation of the suboxic (2–3 mg L\(^{-1}\) O\(_2\)) injectate during the release. The injection and target wells were screened from 5 to 45 cm below the marsh surface, although previous observations during well installations indicated that primary source of water in the marsh wells was from the more hydraulically conductive upper 10 cm of the marsh rhizosphere. Wells were sealed to the atmosphere and sampled for 100 d postinjection. Wells were purged of three well volumes, or to dryness, under a He headspace and allowed to recharge while venting the headspace through a water trap prior to sampling.

**Characterization of bromide and nitrogen pools**—The Br\(^-\) concentrations in water collected from the target wells were measured in the laboratory by use of an Orion 94–35 Br\(^-\)-specific electrode after temperature equilibration. All DIN samples were filtered (0.2 μm) in the field. NH\(_2\) concentrations were determined by the phenol-hypochlorite method (Solorzano 1969). NO\(_3\) and NO\(_2\) concentrations were determined spectrophotometrically with and without cadmium reduction, respectively, by use of an Alpkem autoanalyzer (Alpkem 1992). Isolation of NH\(_4\) and NO\(_3\) for determination of \(^{15}\)N isotopic enrichment followed the diffusion method outlined by Brooks et al. (1989). Recovery of DIN standards by diffusion was >90%. Isotopic analysis of \(^{15}\)N-NH\(_4\) was performed at the University of Virginia (UVA) Stable Isotope Facility on a VG Optima isotope ratio mass spectrometer (IRMS) coupled to a C: H: N elemental analyzer. \(^{15}\)N-NO\(_3\) was analyzed at the University of California, Davis (UCD) Stable Isotope facility. Water samples for N\(_2\)O analysis were collected and equilibrated in the field with an equal volume He headspace in a sealed syringe by shaking vigorously for 1 min. After equilibration, headspace was transferred to a gas-tight syringe and analyzed by use of a Shimadzu GC-8 gas chromatograph equipped with a poropak Q column and an electron capture detector. Total dissolved N\(_2\)O was determined after correction of headspace concentrations by use of the Ostwald coefficient (Weiss and Price 1980). The remaining headspace sample was transferred into pre-evacuated “Exetainers” (Europa Scientific Inc.) and analyzed for \(^{15}\)N-N\(_2\)O at UCD. Samples for dissolved N\(_2\), Ar, and \(^{15}\)N-N\(_2\) determination were pumped from wells into Hungate tubes containing ~150 mg of ZnCl\(_2\) (preservative). Tubes were overfilled and sealed bubble free, stored underwater at 5°C, and analyzed for dissolved N\(_2\) and Ar by use of membrane inlet mass spectrometry (Kana et al. 1994) within 2 months of collection. NO\(_3\) concentrations in samples after storage were within 10% of prestorage concentrations. \(^{15}\)N-N\(_2\) was determined on split samples within 2 weeks of collection, following a modification of the methods of Nielsen (1992). A 4-ml ultra-high-purity He headspace was introduced into the Hungate tubes containing the water samples for \(^{15}\)N-N\(_2\) analysis. Tubes were vortexed for 5 min and allowed to equilibrate submerged in water under refrigeration for 48 h. After equilibration, 1.5 ml of headspace gas was removed; CO\(_2\) was cryogenically removed, and the remaining N\(_2\) was analyzed for \(^{15}\)N by use of a dual inlet Prism IRMS at UVA. Although analytical precision was ~0.3%, a 10%–80% error (isotopic depletion) in the measured \(^{15}\)N\(_2\) was observed among duplicate samples as a result of some atmospheric N\(_2\) contamination of the samples during processing.

Isotope incorporation into the sediment organic nitrogen pool (PON) from 0 to 50 cm was determined from cores collected between the injection points and the nearest row of target wells prior to the injection and on day 100 after the injection. No cores were collected during the experiment, to minimize impact on plume transport. Exchangeable DIN was removed from 10-cm core subsections via KCl (2N) extraction, followed by resuspension of sediment in distilled water and centrifugation. The %N, C: N, and \(^{15}\)N of the PON were determined on the acidified and dried sediments simultaneously by use of the Elemental Analyzer–IRMS at UVA.

**In situ DNRA and DNF rate analyses**—Average peak in situ DNRA and DNF rates for wells 2, 3, and 4 were calculated by use of two methods. The DNRA rate was calculated from the \(^{15}\)NH\(_3\) and \(^{15}\)N\(_2\)O data by use of an isotope-based approach. The total DNF rate was calculated as the sum of the N\(_2\)O → N\(_2\) and net NO\(_3\) → N\(_2\)O rates. The N\(_2\)O → N\(_2\) rate was estimated by use of an isotope-based approach similar to that used for the DNRA rate calculation (with \(^{15}\)N\(_2\) and \(^{15}\)N\(_2\)O data), whereas the net NO\(_3\) → N\(_2\)O rate was estimated from changes in N\(_2\)O concentration and plume travel time.

**Estimation of DNRA and N\(_2\)O → N\(_2\) rates: isotope-based calculations**—In situ estimation of DNRA and N\(_2\)O → N\(_2\) rates were based on the assumption that, within the plume, the peak isotopic enrichment of NH\(_4\) or N\(_2\) was a function of the input rates of NH\(_4\) or N\(_2\) from labeled and unlabeled sources. The generalized isotope-mixing equation, which related the isotopic enrichment of a product pool to the inputs of labeled and unlabeled sources, was

\[
\delta_p = \frac{K_U \delta_U + K_L \delta_L}{K_U + K_L} \tag{1a}
\]

where \(\delta_p\) was the enrichment of the product pool (NH\(_4\) or N\(_2\)), \(\delta_U\) was the enrichment of the unlabeled substrate from outside the plume, \(\delta_L\) was the enrichment of the labeled substrate (\(^{15}\)NO\(_3\) for DNRA, or \(^{15}\)NO\(_2\) for N\(_2\)O → N\(_2\)), \(K_U\) was the input rate of labeled substrate into NH\(_4\) or N\(_2\), and \(K_U\) was the input rate of NH\(_4\) or N\(_2\) from unlabeled sources outside the plume. Provided that the NH\(_4\) and N\(_2\) pools turn over relatively quickly (faster than the travel time from the injection to the well) and are in near steady state, the gross in situ rate of incorporation of labeled substrate (NO\(_3\) or N\(_2\)O) into the respective reduced products (NH\(_4\) or N\(_2\)) can be calculated solely from measurements of the isotopic enrichment of the substrates and products and estimates of the production rate of the unlabeled product by setting \(\delta_U\) equal to zero due to the high plume enrichments, and rearranging Eq. 1 to solve for \(K_L\) (Eq. 1b, Fig. 2).

\[
K_L = \frac{K_U \delta_p}{\delta_L - \delta_p} \tag{1b}
\]
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**Fig. 2. Processes effecting isotopic ratios in the N₂ and NH₄ pools and derivations of N₂O → N₂ and DNRA rates.**

The δ_i and δ_p values used in the DNRA calculation were the δ¹⁵NO and δ¹⁵NH₄ enrichments, respectively. The δ_i and δ_p values used in the N₂O → N₂ calculation were the δ¹⁵N₂O and δ¹⁵N₂ enrichments, respectively. K_u for N₂ was assumed to consist solely of the rate of in-mixing of unla-
beled dissolved N₂ from ambient pore water (outside the plume) during plume dilution and calculated as the product of the pore-water N₂ concentration and the pore-water in-
mixing rate. This pore-water in-mixing rate was determined from Br⁻ concentrations according to

\[ M = \frac{1}{t} \left( \frac{C_{Br^{-},0}}{C_{Br^{-},t}} - 1 \right) \]

where \( M \) was the average rate of ambient pore water mixing into each liter of injectate (liters pore water per liter plume water per day). \( C_{Br^{-},0} \) and \( C_{Br^{-},t} \) were the Br⁻ concentrations of the injectate and of the plume at the target well at the peak of the breakthrough curve, respectively, and \( t \) was the time elapsed between injectate release and the appearance of the Br⁻ peak at the target well. K_u for NH₄⁺ consisted of an NH₄⁺ in-mixing term (\( K_{u,1} \)) and a mineralization (MIN) term (\( K_{u,2} \); Fig. 2). \( K_{u,1} \) was calculated as the product of the in-mixing rate and the pore water NH₄⁺ concentration. \( K_{u,2} \) was the MIN rate determined in laboratory core incubations of shallow marsh sediments from the site (Tobias et al. 2001b). The mineralization rate reported by Tobias et al. (2001b) was normalized to a liter of pore water under the assumption of a sediment control volume of 0.075 m³ (0.75 m² of plume area by 10 cm of plume thickness), sediment water content of 56%, and a sediment bulk density of 0.7 gDW cm⁻³ prior to use in the DNRA rate calculation.

*Estimation of the net NO₂⁻ → N₂O rate: concentration-based calculations—*Equation 1 cannot be used to estimate rates when the mass of the product pool is not near steady state or when the δ_i and δ_p enrichments are equivalent. Therefore, an approach based on changes in N₂O pool size with respect to time was used to estimate the in situ conversion rate of NO₂⁻ → N₂O. Because ambient N₂O concentrations were negligible prior to the injection, the average net NO₂⁻ → N₂O rate (excluding N₂O conversion to N₂) for the period between the start of the injection and the appearance of peak Br⁻ at wells 2, 3, and 4 was calculated according to

\[ \text{NO}_2^- \rightarrow \text{N}_2 \text{O} = \left( \frac{C_{\text{N}_2\text{O},t}}{t} \right) + \left( \frac{MC_{\text{N}_2\text{O},t}/2}{t} \right) \]

where \( C_{\text{N}_2\text{O},t} \) was the average N₂O concentration in wells 2, 3, and 4 measured at peak Br⁻ breakthrough, \( t \) was the av-
erage time elapsed after the injection until peak Br⁻ break-
through at each well, and \( C_{\text{N}_2\text{O},t}/2 \) was the mean N₂O concentration in all wells between preinjection and peak Br⁻ measurements. The net NO₂⁻ → N₂O rate was added to the N₂O → N₂ rate to yield the total DNF rate (i.e., the gross NO₂⁻ → N₂O rate).

\(^{15}\text{N}-\text{nitrogen mass balance—A total }^{15}\text{N mass balance model for the period encompassing the entire Br⁻ breakthrough curve (the first 67 d after the injection) was con-
structed to quantify the storage of N transferred from the NO}_3^- \text{ pool to each of the identified product pools. The data used in the model originated from three target wells nearest the injection points (wells 2, 3, and 4) and the cores collected for PON characterization (Fig. 1). Each well was assumed to be representative of pore water passing within 25 cm (i.e., one half of the distance to the adjacent well) to a depth of 10 cm (estimated plume thickness). The depth of 10 cm was chosen for the mass balance calculations because hydraulic head data indicated strong vertical (upward) flow, and pumped boreholes were observed to recharge with water primarily from more conductive root-bearing sediments con-
tained within the top 10 cm of the subsurface. For the dis-
olved pools, each component of the model was determined for each well and then added to estimate the total mass bal-
The 15N mass balance between 15N lost from the NO\textsubscript{3} pool and 15N incorporated into each of the product pools (NH\textsubscript{4}, N\textsubscript{2}O, N\textsubscript{2}, and PON) for the entire experiment was defined by

\[
\int C_{\text{NO}_3}^{15} A(u)n \, dt - \sum \int C_{\text{PON}}^{15} A(u)n \, dt - \Delta C_{\text{PON}}^{15} V_{\text{sed}} = 0 \tag{4}
\]

where \( C_{\text{NO}_3}^{15} \) was the 15N concentration (\( \mu \text{M} \) 15N) of the NO\textsubscript{3} pool at each sampling time, \( A(u)n \) was the average groundwater flow velocity between adjacent sampling times, \( n \) was sediment porosity (0.56), and \( V_{\text{sed}} \) was the sediment volume bounded by the target wells and the injection wells. Groundwater flow velocity at the start of the experiment was calculated by dividing the distance between the injection wells and target wells (50 cm) by the travel time required for the peak Br\textsuperscript{−} arrival at the target well. This initial flow velocity was scaled proportionally to changes in hydraulic gradient to yield a flow velocity for each sampling time. The concentration of 15N lost from the NO\textsubscript{3} pool at each sampling time for each well was calculated from concentration measurements of Br\textsuperscript{−}, NO\textsubscript{3}, and 15NO\textsubscript{3}, with use of Eqs. 5, 6, and 7.

\[
C_{\text{NO}_3,j}^{15} = C_{\text{NO}_3,j}^{15} - C_{\text{NO}_3,j}^{15} \tag{5}
\]

\[
\dot{C}_{\text{NO}_3,j}^{15} = C_{\text{NO}_3,0} \left( \frac{C_{\text{Br}^-}}{C_{\text{Br}^-}} \right) (R_{\text{NO}_3} - 0.00365), \tag{6}
\]

\[
\overline{C}_{\text{NO}_3,j}^{15} \tag{7}
\]

where \( \overline{C}_{\text{NO}_3,j}^{15} \) and \( \dot{C}_{\text{NO}_3,j}^{15} \) were the observed and predicted 15N-NO\textsubscript{3} concentrations at time \( t \), respectively, \( C_{\text{NO}_3,0} \) and \( C_{\text{Br}^-} \) were the nitrate and bromide concentrations in the injection wells immediately after injection of the first slug of injectate, respectively, and \( R \) was the ratio of 15N/14N (natural abundance, 0.00365). \( \dot{C}_{\text{NO}_3,j}^{15} \) was the expected 15N-NO\textsubscript{3} concentration if NO\textsubscript{3} was a conservative solute.

The concentration of 15N incorporated into each of the reduced dissolved pools (\( C_{i}^{15} \)) was determined for each well at each time from

\[
C_{i}^{15} = (R_{i} - .00365)C_{j} \tag{8}
\]

where \( C_{i} \) and \( R_{i} \) were the concentration and the 15N/14N ratio of the NH\textsubscript{4}, N\textsubscript{2}O, or N\textsubscript{2} pools.

The concentration of 15N incorporated into sediment PON (\( \Delta C_{\text{PON}}^{15} \)) during the experiment was calculated from \( \Delta C_{\text{PON}}^{15} = \Delta R_{\text{PON}}N_{\text{PON}}\rho \) (9), where \( \Delta R_{\text{PON}} \) was the difference in the sediment 15N/14N ratio between preinjection and day 100 of the experiment, and \( N_{\text{PON}} \) and \( \rho \) were the nitrogen content and bulk density (0.7 gdw cm\textsuperscript{−3}) of the sediment, respectively.

**Results**

**Plume transport**—Initially, the plume did not migrate as a uniform solute front from the injection wells but instead followed preferential flow paths centered about wells 2 and 4 (Fig. 3). By day 6, the majority of the mass in the plume was located within the sediment volume between the injection points and the first target well fence. By day 24, the two plume centers had merged into one center of mass located near well 3, and by day 60 the plume had migrated to an area of ~5 m\textsuperscript{2} with a diffuse center of mass ~1.5 m from the injection wells (Fig. 3). Transport time for the arrival of both peak Br\textsuperscript{−} and NO\textsubscript{3} concentrations at the wells used in the mass balance were comparable, which suggests similar physical transport behavior of the two anions. The groundwater flow velocity calculated from peak Br\textsuperscript{−} breakthrough at wells 2, 3, and 4 on days 11, 17, and 24, respectively, were 4.5, 3, and 2.1 cm d\textsuperscript{−1}, respectively.
head–adjusted linear velocities showed a linear decrease in the discharge velocity to rates at day 90 that were an average of 50% of the initial velocities for the three wells. Coincident with the decrease in discharge, pore water salinity increased from 0% at the start of the experiment to 3–5% by day 100. The highest Br$^-\$ concentration was encountered in well 4 and indicated that much of plume flowed through the vicinity of well 4. The total Br$^-\$ passing through wells 2, 3, and 4 accounted for ~37% of the Br$^-\$ released.

**Characterization of the N pools**—Maximal $C/C_0$ for nitrate encountered at the target wells was 30%–50% of the $C/C_0$ for Br$^-\$ at peak values (Fig. 4), and the peak NO$_3^-$ concentrations ranged between 3000 and 7172 μM (Fig. 5). Nitrate loss rates calculated from peak Br$^-\$ and NO$_3^-$ concentrations for the three wells averaged 420 μM d$^{-1}$ but ranged between 208 and 645 μM d$^{-1}$. Approximately 90% of the NO$_3^-$ mass was lost within 67 days. The total Br$^-\$ concentration at peak values for the three wells was 30%–50% of the $C/C_0$ for Br$^-\$ at peak values (Fig. 4), and the peak NO$_3^-$ concentrations ranged between 3000 and 7172 μM (Fig. 5). Nitrate loss rates calculated from peak Br$^-\$ and NO$_3^-$ concentrations for the three wells averaged 420 μM d$^{-1}$ but ranged between 208 and 645 μM d$^{-1}$. Approximately 90% of the NO$_3^-$ mass was lost within 67 days, and peak losses in all wells were seen in the first 20–30 days. The isotopic enrichment ($\delta^{15}N$-NO$_3^-$) for all wells averaged 7528% and varied within 10% of the mean for all periods, except the last sampling dates for wells 2 and 3 (Fig. 5). This relatively constant level of enrichment in the NO$_3^-$ pool (equivalent to the $\delta^{15}N$-NO$_3^-$ of the injectate) was indicative of the low ambient NO$_3^-$ concentrations and negligible nitrification rates.

The NH$_4^+$ concentrations and isotopic enrichments followed a similar temporal pattern in well 3, and to a lesser extent in wells 2 and 4, through the duration of the study (Fig. 6). NH$_4^+$ concentration ranged between 10.6 and 80.0 μM at the start of the injection and climbed to 56–145 μM during the study. Similar maximal $^{15}$N-NH$_4^+$ enrichments (between days 17 and 34) were observed in all wells and ranged between 2000% and 2400%o. The lower peak enrichments (~25%–33% of the $^{15}$N enrichment of the NO$_3^-$ pool) reflect primarily isotopic dilution due to the release of NH$_4^+$ created during the mineralization of unlabeled PON in sediments within the plume. By day 100, both the concentration and the enrichment decreased from peak values to an average of 60% and 20% of their maximum values, respectively.

N$_2$O concentrations in all wells were undetectable at the start of the experiment and rose to maximal values (200–400 μM) on days coincident with peak Br$^-\$ and NO$_3^-$ values (Fig. 7). N$_2$O concentrations returned to undetectable levels in all wells by day 82. $\delta^{15}$N-N$_2$O enrichments were constant within the estimate of error at values on a par with the enrichment of the NO$_3^-$ source (7528% ± 200%o) for all measurements, which indicates negligible production of, or mixing of, unlabeled N$_2$O from outside the plume.

Despite being produced from N$_2$O during denitrification, neither the dissolved N$_2$ concentration nor $\delta^{15}$N$_2$ showed patterns similar to the N$_2$O pool. Relative to predicted equilib-
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Fig. 6. Ammonium concentrations and isotopic enrichments. Analytical precision for isotope analysis was within 1%. Error bars for the ammonium concentrations represent the range of selected analytical duplicates.

Fig. 7. Dissolved nitrous oxide concentrations and isotopic enrichments. Analytical precision for isotope analyses ranged between 28% and 200%, and the error bars represent the poorest analytical precision observed (200%). Estimates of error for N$_2$O concentrations were set at 20% of the mean. This value was derived from replicate standard headspace equilibrations.

Fig. 8. Observed and predicted equilibrium concentrations for dissolved N$_2$ and isotopic enrichments. "X" denotes predicted N$_2$ equilibrium concentration based on temperature and salinity (Weiss 1970). Open circles are the observed dissolved N$_2$ concentrations, with error bars representing an average error of 3% as determined from selected duplicates at all times. Isotopic enrichment of N$_2$ is reported as a range incorporating the uncertainty in estimating $\delta^{15}$N due to atmospheric contamination during sample processing. Isotopic values on selected duplicates varied between 10% and 80%. The midpoint of the reported range was used in the rate and mass balance calculations.

rrium concentrations, there was a maximum dissolved N$_2$ supersaturation of $\sim 100$ $\mu$M (Fig. 8). This was equivalent to an increase in dissolved N$_2$ of 15% above saturation concentrations predicted by temperature and salinity. The dissolved N$_2$ subsidy disappeared by day 100, when the observed N$_2$ concentrations were at parity with equilibrium concentrations. The ranges of $\delta^{15}$N-N$_2$ enrichment increased more slowly than the N$_2$O and NH$_4^+$ pools and initially plateaued in all wells at day 34 (Fig. 8). Because of the constant in-mixing of ambient unlabeled N$_2$, peak $\delta^{15}$N-N$_2$ enrichments were $\sim 20\%$ of the $\delta^{15}$N-N$_2$O values. Enrichments declined slightly after day 60 but did not rebound to near pre-injection levels within the 100 d.

The dissolved N$_2$ subsidy was coincident with a deficit in dissolved Ar concentrations relative to predicted equilibrium values (Fig. 9). The observed Ar concentrations fell below the predicted Ar equilibrium (saturation) concentrations predicted by salinity and temperature by day 24 in all wells. The maximum Ar deficit was 77% of the predicted equilib-
ment PON had increased by 25%, 6%, and 5%, respectively. The $^{15}$N mass balance conservatively included only $\delta^{15}$N-PON data from 0–10 cm because it was the only horizon that showed unequivocal isotope incorporation. This horizon was the zone within which we believe the plume was confined and which demonstrated the maximal NO$_3^−$ reducing potential in laboratory studies (Tobias et al. 2001b).

In situ DNF and DNRA rate analysis—The net in situ N$_2$O production rate (NO$_3^−$ → N$_2$O) of 201 µM N d$^{-1}$ was calculated from Eq. 3 by use of mean estimates of the peak N$_2$O concentration (550 µM N), mixing rate (M) of 0.62 d$^{-1}$, and the average plume travel time (15.3 d). The in situ N$_2$O production rate (N$_2$O → N$_2$) was calculated from Eq. 1b (Fig. 2) by use of the average peak enrichment of $\delta^{15}$N$_2$O (7528‰) and $\delta^{15}$N$_2$ (1590‰) and the mixing rate of ambient dissolved N$_2$ into the plume. Under the assumption that ambient pore water was saturated with dissolved N$_2$ (560 µM N$_2$), mixing delivered 694 µmoles N as N$_2$ to the plume each day ($K_m$). The N$_2$O → N$_2$ rate was therefore 186 µM N d$^{-1}$. The total DNF rate (defined as the sum of the net NO$_3^−$ → N$_2$O and N$_2$O → N$_2$ rates) was 387 µM N d$^{-1}$.

The in situ DNRA rate was calculated from the average $\delta^{15}$NO$_3^−$ enrichment of 7528‰, an average peak $\delta^{15}$NH$_4^+$ enrichment of 2216‰, the mixing rate of unlabeled NH$_4^+$ into the plume, and the input rate of unlabeled NH$_4^+$ from mineralization. Under the assumption that ambient pore water contained 80 µM NH$_4^+$, pore-water mixing supplied 50 µmoles of unlabeled NH$_4^+$ to the plume each day ($K_m$). The resulting in situ DNRA rate of 180 µM N d$^{-1}$ was calculated from Eq. 1b (Fig. 2) after the incorporation of an estimated mineralization rate ($K_{NH_4}$) of 216 ng N gdw$^{-1}$ hr$^{-1}$ (Tobias et al. 2001b). The estimated mineralization rate used in the calculation was a conservative annual average for the site reported by Tobias et al. (2001b) for the previous year.

The sum of the in situ DNRA and DNF rates was 567 µM N d$^{-1}$. This total rate was within the range of total NO$_3^−$ loss rates calculated independently from NO$_3^−$ and Br$^−$ ratios (208–645 µM N d$^{-1}$) and ~135% of the average loss rate. DNF and DNRA represent 68% and 32% of the total NO$_3^−$ reduction, respectively, yielding a DNF:DNRA ratio of 2.1. The relative proportions of DNF and DNRA, however, may have been altered by the magnitude of N$_2$O evasion to the atmosphere. The total DNF rate was based in part on a net NO$_3^−$ → N$_2$O rate estimate that neglected potential N$_2$O evasion. Although the flux of N$_2$O to the atmosphere was not directly measured, an upper limit constraint was applied by use of the maximum total NO$_3^−$ loss rate calu-

![Fig. 9. Predicted and observed dissolved argon concentrations. Errors ranged from 0.01–0.19 µM on the basis of selected duplicates.](image)

Table 1. Characterization of the sediment PON pool prior to the injection and on day 100 (postinjection). Reported values are the average of measurements from duplicate cores at both sampling periods located within 1 m and 50 cm of the upland border for the preinjection and postinjection cores respectively. $\delta^{15}$N-PON is reported in per mil (‰). Average range of duplicates is reported in parentheses.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>%N</th>
<th>C:N</th>
<th>$\delta^{15}$N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Preinjection</td>
<td>Postinjection</td>
<td>Preinjection</td>
</tr>
<tr>
<td>0–10</td>
<td>.158 (.096)</td>
<td>.204 (.003)</td>
<td>17.2 (1.5)</td>
</tr>
<tr>
<td>20–30</td>
<td>.042 (.038)</td>
<td>.277 (.263)</td>
<td>16.3 (5.6)</td>
</tr>
<tr>
<td>40–50</td>
<td>.002 (.006)</td>
<td>.124 (.021)</td>
<td>20.3 (1.6)</td>
</tr>
</tbody>
</table>
Groundwater NO<sub>3</sub> reduction in marshes

Fig. 10. Summary of 15N lost from NO<sub>3</sub> and 15N gained in each of the reduced dissolved N pools during the experiment.

Table 2. Balance sheet of 15N loss and gains by well. Bromide and 15N are shown in mmoles and mM moles, respectively. Total 15N masses shown were derived from integrating the curves in Fig. 10 with respect to discharge after cumulative discharge estimation at each sample time using equation 4. The %15N recovered was calculated as the sum of all product pools (NH<sub>4</sub>, NO, N<sub>2</sub>, PON) divided by the NO<sub>3</sub> (loss).

<table>
<thead>
<tr>
<th>Well</th>
<th>Br&lt;sup&gt;-&lt;/sup&gt;</th>
<th>NO&lt;sub&gt;3&lt;/sub&gt; (loss)</th>
<th>NH&lt;sub&gt;4&lt;/sub&gt;</th>
<th>N&lt;sub&gt;2&lt;/sub&gt;</th>
<th>PON</th>
<th>Missing 15N</th>
<th>%15N recovered</th>
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<td>2,329</td>
<td>9</td>
<td>507</td>
<td>128</td>
<td>283</td>
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<td>305</td>
<td>115</td>
<td>283</td>
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<tr>
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<td>5,453</td>
<td>28</td>
<td>198</td>
<td>191</td>
<td>283</td>
<td>4,753</td>
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<tr>
<td>Total</td>
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<td>10,469</td>
<td>57</td>
<td>1010</td>
<td>434</td>
<td>849</td>
<td>8,119</td>
</tr>
</tbody>
</table>

Discussion

Low Br<sup>-</sup> recovery in the mass balance (37%) relative to Br<sup>-</sup> released in the injection wells indicated that two thirds of the plume escaped characterization. Although discrete flow paths between target wells may have transported some of the plume undetected, much of the missing Br<sup>-</sup> probably flowed past the wells on the marsh surface. Large vertical hydraulic gradients (Tobias et al. 2001a) toward the surface were evidenced by discharging seeps, and Br<sup>-</sup> was detected in ponded surface water within the sampling grid. As a result of these vertical gradients and higher conductivity of shallow marsh sediments (Tobias et al. 2000a), most of the plume was likely confined to the upper 10 cm of the sediment during discharge. These shallow sediments possessed the highest nitrate reducing potential of any sediment strata underlying the marsh (Tobias et al. 2001b) and help account for the high rate of NO<sub>3</sub> loss from the plume.

The NO<sub>3</sub> loss rates calculated from the peak of the breakthrough curves, when normalized to marsh area (0.49–1.5 mmoles N m<sup>–2</sup> hr<sup>–1</sup>), were higher than denitrification rates reported for NO<sub>3</sub>-rich fresh and salt water marsh sediments (0.071–0.79 mmoles N m<sup>–2</sup> hr<sup>–1</sup>; Kaplan et al. 1979; Hattori

15N mass balance—The 15N stored in each of the dissolved reduced N pools was small relative to the amount of 15N lost from the NO<sub>3</sub> pool for all sample periods (Fig. 10). Storage in these dissolved pools was smallest in the well with the fastest discharge velocity (well 4) and dominated by 15N<sub>2</sub>O in all wells. The mass balance technique of integrating 15N mass curves is most accurate when the curves for all constituents return to preinjection levels within the mass balance period. As such, this approach may provide the most reasonable estimate of 15N<sub>N</sub>O storage but could underestimate 15N storage in NH<sub>4</sub> and N<sub>2</sub> (Figs. 6–8). Although the 15NH<sub>4</sub> and 15N<sub>2</sub> mass curves remain elevated above background by the end of the mass balance period, the resulting underestimate in storage was likely to be insignificant because of the small total magnitude of the 15N mass in each of the pools. Total 15N incorporated into PON, NH<sub>4</sub>, NO, and N<sub>2</sub> during the experiment accounted for 22% of the 15N lost from the NO<sub>3</sub> pool during the mass balance period (Table 2). Despite a more than twofold difference among total 15N recovery among the wells and the low total 15N recovery, the dominant measured sink for 15N in all wells measured was either N<sub>2</sub>O (9.6%) or PON (8.1%), followed by N<sub>2</sub> (4.1%) and finally NH<sub>4</sub> (0.5%).
H\textsubscript{2}S concentrations were similarly low. Instead, we suggest calculations of the same sediments (Tobias et al. 2001) DNF:DNRA ratio of 2.2 was approximately the inverse of to conditions favoring DNF (Sorenson 1987). However, the those wetlands to the atmosphere. Regardless of the favored Smith et al. (1982) and Tiedje et al. (1981) demonstrated ilatory NO reduction (Bengtsson and Annadotter 1989), specifically sampled. Because the 15 N in roots and rhizomes were present but not specifically sampled. Because the 15 N in roots and rhizomes were not measured as part of the PON fraction, this pathway could account for a significant 15 N sink (White and Howes 1994) that was not measured during the experiment. Immobilization of 15NH\textsubscript{4} is an alternate mechanism by which labeled NH\textsubscript{4} generated from DNRA was removed from the dissolved pool. Under the assumption that ammonium concentrations were sufficiently high to inhibit assimilatory NO\textsubscript{3} reduction (Bengtsson and Annadotter 1989), Smith et al. (1982) and Tiedje et al. (1981) demonstrated that peak N incorporation into sediment organic nitrogen (immobilization) from a labeled NO\textsubscript{3} source flows initially either through NO\textsubscript{3} or NH\textsubscript{3}. Specifically, high immobilization rates (in pace with ammonification) in marshes have been proposed to explain the co-occurrence of high rates of gross ammonification with steady-state ammonium concentrations (Anderson et al. 1997). However in the present study, DNRA calculations accounted for ~30% of the reduced NO\textsubscript{3} was converted to NH\textsubscript{4} via DNRA, the total 15NH\textsubscript{4} inventory during the study accounted for ~1% of the lost 15NO\textsubscript{3}. The in situ NH\textsubscript{4} production from DNRA in conjunction with the high mineralization rate was nearly balanced by rapid removal of NH\textsubscript{4} (Anderson et al. 1997); otherwise, NH\textsubscript{4} would have accumulated well in excess of concentrations observed. NH\textsubscript{4} removal via nitrification was small, as was evidenced by the constancy of the δ15N-NO\textsubscript{3} signal. Similarly, tidal inundation and flushing of the subsurface during the study period was small (Tobias et al. 2001a) and probably was a negligible factor in maintaining the near steady-state NH\textsubscript{4} concentrations. In the absence of high in situ nitrification rates or large physical losses of NH\textsubscript{4}, in-marsh uptake of NH\textsubscript{4} must have been nearly equal to NH\textsubscript{3} production. Although marsh macrophytes can be considerable sinks for new N (White and Howes 1994; Dai and Weigert 1997), no above-ground macrophyte biomass was actively growing within the area bounded by the injection and target wells used to construct the mass balance and was thus not sampled. However, roots and rhizomes were present but not specifically sampled. Because the 15 N in roots and rhizomes were not measured as part of the PON fraction, this pathway could account for a significant 15 N sink (White and Howes 1994) that was not measured during the experiment.

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Groundwater NO\textsubscript{3}\textsuperscript{-} \rightarrow \text{DNF} \rightarrow N\textsubscript{2}O \rightarrow N\textsubscript{2} \rightarrow \text{Atmosphere} \text{NH}_{4}^{+} \rightarrow \text{Immobilization} \rightarrow \text{Marsh} \text{(All rates in } \mu\text{M-N d}^{-1})

Fig. 11. Rate summary of N loss pathways from groundwater NO\textsubscript{3}-. N\textsubscript{2}O evasion (78 \muM N d\textsuperscript{-1}) was estimated by the difference under the assumption of the maximum total NO\textsubscript{3} loss rate (645 \muM N d\textsuperscript{-1}) calculated from NO\textsubscript{3} to Br\textsuperscript{-} ratios. N\textsubscript{2} evasion was calculated from N\textsubscript{2} mass balance under the assumption of a net rate of N\textsubscript{2} accumulation of 12 \muM N d\textsuperscript{-1} calculated from the 15% N\textsubscript{2} supersaturation normalized to travel time. The lower limit of immobilization assumed 18% storage of 15\textsuperscript{N} in PON (i.e., 60% of the DNRA rate). The upper limit of immobilization assumed that the immobilization rate of NH\textsubscript{4}+ kept pace with mineralization (Anderson et al. 1997) and thus exceeded the DNRA rate.

Groundwater NO\textsubscript{3}-. N\textsubscript{2}O evasion (78 \muM N d\textsuperscript{-1}) was estimated by the difference under the assumption of the maximum total NO\textsubscript{3} loss rate (645 \muM N d\textsuperscript{-1}) calculated from NO\textsubscript{3} to Br\textsuperscript{-} ratios. N\textsubscript{2} evasion was calculated from N\textsubscript{2} mass balance under the assumption of a net rate of N\textsubscript{2} accumulation of 12 \muM N d\textsuperscript{-1} calculated from the 15% N\textsubscript{2} supersaturation normalized to travel time. The lower limit of immobilization assumed 18% storage of 15\textsuperscript{N} in PON (i.e., 60% of the DNRA rate). The upper limit of immobilization assumed that the immobilization rate of NH\textsubscript{4}+ kept pace with mineralization (Anderson et al. 1997) and thus exceeded the DNRA rate.

Evasion rates of gases from aqueous environments are difficult to quantify accurately, and it is beyond the scope of this article to derive a confident estimate of evasion of N\textsubscript{2} from this sedimentary environment. Nevertheless, a first approximation of evasion at the water table–atmosphere interface based on the concentration and gas piston velocity of N\textsubscript{2} was more than sufficient by nearly two orders of magnitude to account for the remaining lack of 15\textsuperscript{N} in the mass balance.

Evasion of N\textsubscript{2} from groundwater NO\textsubscript{3}-. N\textsubscript{2}O evasion (78 \muM N d\textsuperscript{-1}) was estimated by the difference under the assumption of the maximum total NO\textsubscript{3} loss rate (645 \muM N d\textsuperscript{-1}) calculated from NO\textsubscript{3} to Br\textsuperscript{-} ratios. N\textsubscript{2} evasion was calculated from N\textsubscript{2} mass balance under the assumption of a net rate of N\textsubscript{2} accumulation of 12 \muM N d\textsuperscript{-1} calculated from the 15% N\textsubscript{2} supersaturation normalized to travel time. The lower limit of immobilization assumed 18% storage of 15\textsuperscript{N} in PON (i.e., 60% of the DNRA rate). The upper limit of immobilization assumed that the immobilization rate of NH\textsubscript{4}+ kept pace with mineralization (Anderson et al. 1997) and thus exceeded the DNRA rate.
suggest that evasion and gas stripping were faster than the estimated N$_2$ production rate. Therefore, dissolved N$_2$ concentrations in excess of the observed 15% oversaturation were never detected.

In summary (Fig. 11), up to 90% of the groundwater nitrate load discharging into the Ringfield marsh was reduced rapidly in the upper 10 cm of sediment within the first 50 cm marshward of the upland border. The primary fate of the NO$_3^-$ was denitrification (70% of the total NO$_3^-$ loss rate) with N$_2$O being the dominant end product (50%–60% of the total DNF rate). Of the 70% of the total groundwater NO$_3^-$ load reduced via DNF (N$_2$ + N$_2$O), an estimated 53%–80% was exported to the atmosphere rapidly as a result of evasion and gas stripping. DNRA accounted for 30% of the total NO$_3^-$ loss rate, and the ammonium pool appeared to be a highly active intermediate between DNRA and the ultimate immobilization of new N into PON. The amount of N retained from groundwater NO$_3^-$ loads in the Ringfield marsh was a function of both NO$_3^-$ load and the dominant mechanism of NO$_3^-$ reduction. This study illustrated both the merit of using whole-system isotope releases to determine in situ process rates independent of mass-balance estimates and the need for more extensive multipool sampling in future tracer studies, to achieve better agreement between mass-balance estimates and rate calculations.

References

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