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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$_3$, 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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Nitrate is the dominant species of dissolved inorganic nitrogen (DIN) in most shallow, aerobic, aquifers (Kraynov 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$_4^+$ 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 $^{15}$N-NO$_3^-$ enrichment, to track in situ marsh processing of high NO$_3^-$ concentration groundwater loads. The technique of using an in situ $^{15}$N release within advection-dominated systems has been used in streams and small estuaries to elucidate DIN dynamics and trophic N transfer (Peterson et al. 1997; Holmes et al. 2000; Hughes et al. 2000; Tank et al. 2000). To our knowledge, this approach has not been combined with a natural gradient groundwater tracer study within a marsh discharge environment to provide a comprehensive accounting of nitrate fate and transport.

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 O₂) 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. NH₃ concentrations were determined by the phenol-hypochlorite method (Solorzano 1969). NO₃⁻ and NO₂⁻ concentrations were determined spectrophotometrically with and without cadmium reduction, respectively, by use of an Alpkem autoanalyzer (Alpkem 1992). Isolation of NH₄⁺ and NO₃⁻ for determination of ¹⁵N isotope enrichment followed the diffusion method outlined by Brooks et al. (1989). Recovery of DIN standards by diffusion was >90%. Isotopic analysis of ¹⁵N-NH₄⁺ 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. ¹⁵N-NO₃⁻ was analyzed at the University of California, Davis (UCD) Stable Isotope facility. Water samples for N₂O 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 porapak Q column and an electron capture detector. Total dissolved N₂O 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 ¹⁵N-N₂O at UCD.

Samples for dissolved N₂, Ar, and ¹⁵N-N₂ determination were pumped from wells into Hungate tubes containing ~150 mg of ZnCl₂ (preservative). Tubes were overfilled and sealed bubble free, stored underwater at 5°C, and analyzed for dissolved N₂ and Ar by use of membrane inlet mass spectrometry (Kana et al. 1994) within 2 months of collection. NO₂⁻ concentrations in samples after storage were within 10% of prestorage concentrations. ¹⁵N-N₂ 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 ¹⁵N-N₂ 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; CO₂ was cryogenically removed, and the remaining N₂ was analyzed for ¹⁵N 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 δ¹⁵N was observed among duplicate samples as a result of some atmospheric N₂ 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 ¹⁵N 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 δ¹⁵NH₄⁺ and δ¹⁵N₂O data by use of an isotope-based approach. The total DNF rate was calculated as the sum of the N₂O → N₂ and net NO₂⁻ → N₂O rates. The N₂O → N₂ rate was estimated by use of an isotope-based approach similar to that used for the DNRA rate calculation (with δ¹⁵N₂ and δ¹⁵N₂O data), whereas the net NO₂⁻ → N₂O rate was estimated from changes in N₂O concentration and plume travel time.

Estimation of DNRA and N₂O → N₂ rates: isotope-based calculations—In situ estimation of DNRA and N₂O → N₂ rates were based on the assumption that, within the plume, the peak isotopic enrichment of NH₄⁺ or N₂ was a function of the input rates of NH₄⁺ or N₂ 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

\[
\delta_p = \frac{K_U \delta_U + K_L \delta_L}{K_U + K_L} \quad (1a)
\]

where \(\delta_p\) was the enrichment of the product pool (NH₄⁺ or N₂), \(\delta_U\) was the enrichment of the unlabeled substrate outside the plume, \(\delta_L\) was the enrichment of the labeled substrate (¹⁵NO₃⁻ for DNRA, or ¹⁵N₂O for N₂O → N₂), \(K_U\) was the input rate of labeled substrate into NH₄⁺ or N₂, and \(K_L\) was the input rate of NH₄⁺ or N₂ from unlabeled sources outside the plume. Provided that the NH₄⁺ and N₂ 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 (NO₂⁻ or N₂O) into the respective reduced products (NH₄⁺ or N₂) 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 \(\delta_p\) equal to zero due to the high plume enrichments, and rearranging Eq. 1 to solve for \(K_L\) (Eq. 1b, Fig. 2).

\[
K_L = \frac{K_U \delta_U}{\delta_L - \delta_U} \quad (1b)
\]
Fig. 2. Processes effecting isotopic ratios in the $N_2$ and NH$_4^+$ pools and derivations of $N_2\rightarrow$N$_4$ and DNRA rates.

The $\delta_L$ and $\delta_P$ values used in the DNRA calculation were the $\delta^{15}NO$ and $\delta^{15}NH$ enrichments, respectively. The $\delta_L$ and $\delta_P$ values used in the $N_2\rightarrow N_2$ calculation were the $\delta^{15}N_2O$ and $\delta^{15}N_2$ enrichments, respectively. $K_U$ for $N_2$ was assumed to consist solely of the rate of in-mixing of unlabeled dissolved $N_2$ from ambient pore water (outside the plume) during plume dilution and calculated as the product of the pore-water $N_2$ 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 NH$_4^+$ consisted of an NH$_4^+$ 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 NH$_4^+$ 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 m$^3$ (0.75 m$^2$ 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 $NO_3^-\rightarrow N_2$ 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 $\delta_L$ and $\delta_P$ enrichments are equivalent. Therefore, an approach based on changes in $N_2O$ pool size with respect to time was used to estimate the in situ conversion rate of NO$_3^-$ to $N_2$. Because ambient $N_2O$ concentrations were negligible prior to the injection, the average net $NO_3^-\rightarrow N_2O$ rate (excluding $N_2O$ conversion to $N_2$) 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

$$NO_3^-\rightarrow N_2O = \left( C_{NO_3},t \right) + \left( \frac{MC_{NO_3}}{2} \right)$$

where $C_{NO_3}$ was the average $N_2O$ concentration in wells 2, 3, and 4 measured at peak Br$^{-}$ breakthrough, $t$ was the average time elapsed after the injection until peak Br$^{-}$ breakthrough at each well, and $C_{NO_3}/2$ was the mean $N_2O$ concentration in all wells between preinjection and peak Br$^{-}$ measurements. The net $NO_3^-\rightarrow N_2O$ rate was added to the $N_2O\rightarrow N_2$ rate to yield the total DNF rate (i.e., the gross $NO_3^-\rightarrow N_2O$ rate).

**$^{15}N$-nitrogen mass balance**—A total $^{15}N$ mass balance model for the period encompassing the entire Br$^{-}$ breakthrough curve (the first 67 d after the injection) was constructed to quantify the storage of N transferred from the NO$_3^-$ 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 contained within the top 10 cm of the subsurface. For the dissolved pools, each component of the model was determined for each well and then added to estimate the total mass bal-
ance. For sediment PON, data were averaged from duplicate cores and applied to the total sediment volume (75,000 cm$^3$), which was bounded by the injection points; wells 2, 3, and 4; and the base of the plume.

The $^{15}$N mass balance between $^{15}$N lost from the NO$_3^-$ pool and $^{15}$N incorporated into each of the product pools (NH$_4^+$, N$_2$O, N$_2$, and PON) for the entire experiment was defined by

$$\int C_{i,NO_3}^N A(u)n \, dt - \sum \int C_{i}^N A(u)n \, dt - \Delta C_{PON}^{15} V_{sed} = 0 \quad (4)$$

where $C_{i,NO_3}^N$ was the $^{15}$N concentration ($\mu$M $^{15}$N) of the NO$_3^-$ lost from the plume at time $t$, $C_i^N$ was the $^{15}$N concentration ($\mu$M $^{15}$N) incorporated into each of the dissolved product pools ($i = \text{NH}_4^+, \text{N}_2\text{O}, \text{N}_2$, and PON) at each sampling time, $\Delta C_{PON}^{15}$ was the $^{15}$N concentration ($\mu$moles $^{15}$N cm$^{-3}$ sediment) incorporated into the sediment PON pool at the end of the study, $A$ was the effective area of each well normal to discharge (500 cm$^2$ well$^{-1}$), $(u)$ was the average groundwater flow velocity between adjacent sampling times, $n$ was sediment porosity (0.56), and $V_{sed}$ 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$^-$ arrival at the target well. This initial flow velocity was scaled proportionally through the study according to changes in hydraulic gradient to yield a flow velocity for each sampling time. The concentration of $^{15}$N lost from the NO$_3^-$ pool at each sampling time for each well was calculated from concentration measurements of Br$^-$, NO$_3^-$, and $^{15}$NO$_3^-$, with use of Eqs. 5, 6, and 7.

$$C_{i,NO_3}^{15} = \dot{C}_{i,NO_3}^{15} - \dot{C}_{i,NO_3}^{15,obs} \quad (5)$$

$$\dot{C}_{NO_3}^{15} = C_{NO_3,0} \left( \frac{C_{Br^-}^{obs}}{C_{Br^-}^{0}} \right)(R_{NO_3} - 0.00365), \quad (6)$$

$$\dot{C}_{NO_3}^{15,obs} = C_{NO_3,ij}(R_{NO_3} - 0.00365), \quad (7)$$

where $C_{i,NO_3}^{15}$ and $\dot{C}_{i,NO_3}^{15,obs}$ were the observed and predicted $^{15}$N-NO$_3^-$ concentrations at time $t$, respectively, $C_{NO_3,0}$ and $C_{Br^-}^{0}$ were the nitrate and bromide concentrations in the injection wells immediately after injection of the first slug of injectate, respectively, $C_{NO_3,ij}$, and $C_{Br^-}^{obs}$ were the observed nitrate and bromide concentrations at the target well at time $t$, respectively, and $R$ was the ratio of $^{15}$N/$^{14}$N (natural abundance, 0.00365). $\dot{C}_{NO_3}^{15,obs}$ was the expected $^{15}$N-NO$_3^-$ concentration if NO$_3^-$ was a conservative solute.

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

$$C_i^N = (R_i - .00365)C_i \quad (8)$$

where $C_i$ and $R_i$ were the concentration and the $^{15}$N/$^{14}$N ratio of the NH$_4^+$, N$_2$O, or N$_2$ pools, respectively, and $i$ denotes either the NH$_4^+$, N$_2$O, or N$_2$ pools.

The concentration of $^{15}$N incorporated into sediment PON ($\Delta C_{PON}^{15}$) during the experiment was calculated from

$$\Delta C_{PON}^{15} = \Delta R_{PON} N_{PON} \rho \quad (9)$$

where $\Delta R_{PON}$ was the difference in the sediment $^{15}$N/$^{14}$N ratio between preinjection and day 100 of the experiment, and $N_{PON}$ and $\rho$ were the nitrogen content and bulk density (0.7 gdw cm$^{-3}$) 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 $-5 \text{ m}^2$ with a diffuse center of mass $-1.5 \text{ m}$ from the injection wells (Fig. 3). Transport time for the arrival of both peak Br$^-$ and NO$_3^-$ 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$^-$ breakthrough at wells 2, 3, and 4 on days 11, 17, and 24, respectively, were 4.5, 3, and 2.1 cm d$^{-1}$, respectively. The hydraulic...
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 to 3 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/C₀ for nitrate encountered at the target wells was 30%–50% of the C/C₀ for Br at peak values (Fig. 4), and the peak NO₃ concentrations ranged between 3000 and 7172 μM (Fig. 5). Nitrate loss rates calculated from peak Br⁻ and NO₃⁻ concentrations for the three wells averaged 420 μM d⁻¹ but ranged between 208 and 645 μM d⁻¹. Approximately 90% of the NO₃ mass was lost within 67 d, and peak losses in all wells were seen in the first 20–30 d. The isotopic enrichment (δ¹⁵N-NO₃⁻) for all wells averaged 75% 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 NO₃⁻ pool (equivalent to the δ¹⁵N-NO₃⁻ of the injectate) was indicative of the low ambient NO₃⁻ concentrations and negligible nitrification rates.

The NH₄⁺ 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). NH₄⁺ 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 δ¹⁵N-NH₄⁺ enrichments (between days 17 and 34) were observed in all wells within a range of 2000‰ and 2400‰. The lower peak enrichments (~25%–33% of the δ¹⁵N enrichment of the NO₃⁻ pool) reflect primarily isotopic dilution due to the release of NH₄⁺ 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.

N₂O 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 NO₃⁻ values (Fig. 7). N₂O concentrations returned to undetectable levels in all wells by day 82. δ¹⁵N-N₂O enrichments were constant within the estimate of error at values on a par with the enrichment of the NO₃⁻ source (7528‰ ± 200‰) for all measurements, which indicates negligible production of, or mixing of, unlabeled N₂O from outside the plume. Despite being produced from N₂O during denitrification, neither the dissolved N₂ concentration nor δ¹⁵N-N₂ showed patterns similar to the N₂O pool. Relative to predicted equilib-
Fig. 6. Ammonium concentrations and isotopic enrichments. Analytical precision for isotope analysis was within 1%H. Error bars for the ammonium concentrations represent the range of selected analytical duplicates.

Fig. 8. Observed and predicted equilibrium concentrations for dissolved \( \text{N}_2 \) and isotopic enrichments. "X" denotes predicted \( \text{N}_2 \) equilibrium concentration based on temperature and salinity (Weiss 1970). Open circles are the observed dissolved \( \text{N}_2 \) concentrations, with error bars representing an average error of 3% as determined from selected duplicates at all times. Isotopic enrichment of \( \text{N}_2 \) is reported as a range incorporating the uncertainty in estimating \( \delta^{15} \text{N} \) 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.

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 \( \text{N}_2 \text{O} \) concentrations were set at 20% of the mean. This value was derived from replicate standard headspace equilibrations.

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

The dissolved \( \text{N}_2 \) 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-
The 15N mass balance conservatively included only δ15N-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 NO3⁻ reducing potential in laboratory studies (Tobias et al. 2001b).

**In situ DNF and DNRA rate analysis**—The net in situ N2O production rate (NO3⁻ → N2O) of 201 μM N d⁻¹ was calculated from Eq. 3 by use of mean estimates of the peak N2O concentration (550 μM N), mixing rate (M) of 0.62 d⁻¹, and the average plume travel time (15.3 d). The in situ N2 production rate (N2O → N2) was calculated from Eq. 1b (Fig. 2) by use of the average peak enrichment of δ15N-N2O (7528‰) and δ15N-N2 (1590‰) and the mixing rate of ambient dissolved N2 into the plume. Under the assumption that ambient pore water was saturated with dissolved N2 (560 μM N2), mixing delivered 694 μmoles N as N2 to the plume each day (Kt). The N2O → N2 rate was therefore 186 μM N d⁻¹. The total DNF rate (defined as the sum of the net NO3⁻ → N2O and N2O → N2 rates) was 387 μM N d⁻¹.

The in situ DNRA rate was calculated from the average δ15NO3 enrichment of 7528‰, an average peak δ15NH4⁺ enrichment of 2216‰, the mixing rate of unlabeled NH4⁺ into the plume, and the input rate of unlabeled NH4⁺ from mineralization. Under the assumption that ambient pore water contained 80 μM NH4⁺, pore-water mixing supplied 50 μmoles of unlabeled NH4⁺ to the plume each day (Kp). 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 (K12,MIN) 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 NO3⁻ loss rates calculated independently from NO3⁻ 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 NO3⁻ 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 N2O evasion to the atmosphere. The total DNF rate was based in part on a net NO3⁻ → N2O rate estimate that neglected potential N2O evasion. Although the flux of N2O to the atmosphere was not directly measured, an upper limit constraint was applied by use of the maximum total NO3⁻ loss rate calcu-

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**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. δ15N-PON is reported in permil (%). Average range of duplicates is reported in parentheses.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>%N Preinjection</th>
<th>%N Postinjection</th>
<th>C:N Preinjection</th>
<th>C:N Postinjection</th>
<th>δ15N Preinjection</th>
<th>δ15N Postinjection</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–10</td>
<td>0.158 (.096)</td>
<td>0.204 (.003)</td>
<td>17.2 (1.5)</td>
<td>17.4 (2.0)</td>
<td>3.2 (0.4)</td>
<td>28.3 (1.1)</td>
</tr>
<tr>
<td>20–30</td>
<td>0.042 (.038)</td>
<td>0.277 (.263)</td>
<td>16.3 (5.6)</td>
<td>13.4 (1.4)</td>
<td>3.8 (0.7)</td>
<td>9.8 (2.6)</td>
</tr>
<tr>
<td>40–50</td>
<td>0.002 (.006)</td>
<td>0.124 (.021)</td>
<td>20.3 (1.6)</td>
<td>19.9 (1.1)</td>
<td>3.7 (1.5)</td>
<td>9.0 (1.3)</td>
</tr>
</tbody>
</table>
1985

Groundwater NO₃⁻ reduction in marshes

Fig. 10. Summary of ¹⁵N lost from NO₃⁻ 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 m 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 (NH₄⁺, N₂O, N₂, PON) divided by the NO₃⁻ (loss).

<table>
<thead>
<tr>
<th>Well</th>
<th>Br⁻</th>
<th>NO₃⁻ (loss)</th>
<th>NH₄⁺</th>
<th>N₂O</th>
<th>N₂</th>
<th>PON</th>
<th>Missing ¹⁵N</th>
<th>%¹⁵N recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1,282</td>
<td>2,329</td>
<td>9</td>
<td>507</td>
<td>128</td>
<td>283</td>
<td>1,402</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>1,161</td>
<td>2,687</td>
<td>20</td>
<td>305</td>
<td>115</td>
<td>283</td>
<td>1,964</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>2,841</td>
<td>5,453</td>
<td>28</td>
<td>198</td>
<td>191</td>
<td>283</td>
<td>4,753</td>
<td>13</td>
</tr>
<tr>
<td>Total</td>
<td>5,284</td>
<td>10,469</td>
<td>57</td>
<td>1010</td>
<td>434</td>
<td>849</td>
<td>8,119</td>
<td>22</td>
</tr>
</tbody>
</table>

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 NO₃⁻ 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 ¹⁵N₂O 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 ¹⁵N₂O storage but could underestimate ¹⁵N storage in NH₄⁺ and N₂ (Figs. 6–8). Although the ¹⁵NH₄⁺ and ¹⁵N₂ 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, NH₄⁺, N₂O, and N₂ during the experiment accounted for 22% of the ¹⁵N lost from the NO₃⁻ 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 N₂O (9.6%) or PON (8.1%), followed by N₂ (4.1%) and finally NH₄⁺ (0.5%).

Discussion

Low Br⁻ recovery in the mass balance (37%) relative to Br⁻ 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⁻ 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⁻ 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 NO₃⁻ loss from the plume.

The NO₃⁻ loss rates calculated from the peak of the breakthrough curves, when normalized to marsh area (0.49–1.5 mmoles N m⁻² hr⁻¹), were higher than denitrification rates reported for NO₃⁻-rich fresh and salt water marsh sediments (0.071–0.79 mmoles N m⁻² hr⁻¹; Kaplan et al. 1979; Hattori...
1983; Xue et al. 1999) but were consistent with the broad range (0.8–50 mmole-N m⁻² hr⁻¹) of observed DNRA rates in natural and nitrate amended estuarine sediments (Koike and Sorenson 1988). For the majority of the 67-d mass balance period, ambient nitrification rates were not sufficient to isotopically dilute the ^15NO³⁻ below the enrichment of the injectate. In contrast, the NH⁺₄ pool enrichment in this study was only 25%–33% of the ^15NO³⁻ signal, which indicates that 60%–75% of inputs to the NH⁺₄ pool originated from a non-labeled N source. MIN (the dominant N cycling process in most marshes) rates determined in sediment cores from the site were three times larger than potential DNRA rates determined from nitrate amended sediments (Tobias et al. 2001b). These laboratory results were consistent with the observed δ¹⁵N-NH₄⁺ in the plume originating from DNRA and being isotopically diluted by a factor of three by mineralization of relatively unlabeled PON.

The dominance of DNF as the favored NO⁻₃ reduction pathway was in agreement with previous studies (Cooke 1994; Xue et al. 1999) in freshwater wetlands, but the significant portion of total NO⁻₃ loss reduced via DNRA (30%) has also been demonstrated in anoxic groundwater microcosms (Bengtsson and An nadotter 1989) and in some estuarine sediments (Bonin et al. 1998). Pore-water H₂S concentrations were typically low at the site during high groundwater discharge (≥50 μM) and may have contributed to conditions favoring DNF (Sorenson 1987). However, the DNF:DNRA ratio of 2.2 was approximately the inverse of the DNF:DNRA ratio (0.42) measured in laboratory incubations of the same sediments (Tobias et al. 2001b) when H₂S concentrations were similarly low. Instead, we suggest that this discrepancy in DNF:DNRA ratios resulted from the order-of-magnitude higher (millimolar) NO⁻₃ concentrations observed in the in situ experiment. The resulting higher NO⁻₃: dissolved organic carbon ratio not only favored DNF over DNRA (King and Nedwell 1985; Tiedje 1988) but may also have combined with the small groundwater derived dissolved O₂ flux into the marsh sediments (Tobias et al. 2001b) to create conditions that lead to the accumulation of N₂O as the principle end product of denitrification (Firestone et al. 1980). Although a tracer experiment that uses millimolar NO⁻₃ concentrations may at first appear to be extreme, those concentrations are not out of the range of NO⁻₃ concentrations encountered in highly anthropogenically impacted waters both in the United States and globally. As such, the observed dominance of the NO⁻₃ → N₂O pathway suggests that increases in high NO⁻₃ delivery to wetlands may be accompanied by a concomitant rise in N₂O emissions from those wetlands to the atmosphere. Regardless of the favored end product of DNF at the high observed NO⁻₃ concentrations, DNRA reduced 30% of the incoming load and may be even more important in retaining groundwater N when NO⁻₃ loads are smaller.

Despite the fact that the peak in situ DNRA and DNF rate calculations approximated the peak total NO⁻₃ loss rates determined from NO⁻₃ and Br⁻ ratios, the mass balance of potential products accounted for only ~22% (48% if maximum N₂O evasion is assumed) of the ^15N lost from the NO⁻₃ pool. This inconsistency suggested that either N had a short turnover time in the products of DNRA (NH⁺₄) and DNF (N₂O or N₂) and was transferred to pools in the marsh not well characterized in this study or N was quickly exported from the ecosystem. Previous experiments in aquifers and marshes that have attempted to mass balance either labeled or unlabeled products after NO⁻₃ additions demonstrated higher total N mass recovery. However, these studies were conducted either deeper in the aquifer, where atmospheric exchange was limited and fewer potential biotic N sinks were available (Bates and Spalding 1998), or in marsh enclosures, which restricted potential routes of N export (Xue et al. 1999). Lower recovery in this study was not surprising considering the multiple pools within and unconfined nature of this experiment. We suggest that quick turnover followed by transfer into large, but poorly characterized, marsh N pools was the fate for ^15NH⁺₄ produced via DNRA, whereas rapid export to the atmosphere was the fate for the gaseous products of DNF.

Although we estimated that ~30% of the reduced NO⁻₃ was converted to NH⁺₄ via DNRA, the total ^15NH⁺₄ inventory during the study accounted for ~1% of the lost ^15NO⁻₃. The in situ NH⁺₄ production from DNRA in conjunction with the high mineralization rate was nearly balanced by rapid removal of NH⁺₄ (Anderson et al. 1997); otherwise, NH⁺₄ would have accumulated well in excess of concentrations observed. NH⁺₄ removal via nitrification was small, as was evidenced by the constancy of the δ¹⁵N-NH⁺₄ signal. Similarly, tidal inundation and flushing of the subsurface during the study period was small (Tobias et al. 2001a) and probably was not a negligible factor in maintaining the near steady-state NH⁺₄ concentrations. In the absence of high in situ nitrification rates or large physical losses of NH⁺₄, in-marsh uptake of NH⁺₄ must have been nearly equal to NH⁺₄ 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 ^15N in roots and rhizomes were not measured as part of the PON fraction, this pathway could account for a significant ^15N sink (White and Howes 1994) that was not measured during the experiment.

Immobilization of ^15NH⁺₄ is an alternate mechanism by which labeled NH⁺₄ generated from DNRA was removed from the dissolved pool. Under the assumption that ammonium concentrations were sufficiently high to inhibit assimilatory NO⁻₃ reduction (Bengtsson and An nadotter 1989), Smith et al. (1982) and Tiedje et al. (1981) demonstrated that peak N incorporation into sediment organic nitrogen (immobilization) from a labeled NO⁻₃ source flows initially either through NO⁻₃ or NH₂⁻. 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 NO⁻₃ loss, yet estimates of ^15N storage in PON accounted for only 8% of the ^15N loss from NO⁻₃. Although sediment PON has been shown to be the long-term repository for ^15N released into an estuary, this pool is difficult to accurately
Groundwater NO\textsuperscript{-} reduction in marshes

![Diagram](image)

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

quantify because of the high unlabeled N content and spatially variable \textsuperscript{15}N distribution (Holmes et al. 2000; Hughes et al. 2000). We suspect that the PO\textsuperscript{15}N inventory in this study may have been underestimated as a result of a conservative depth estimate of labeled sediments. If deeper sediment horizons (>10 cm) that showed potential isotopic enrichment (Table 1) were used in the mass balance calculation, the total \textsuperscript{15}N storage in PON would increase by a factor of 2.2. This increase would bring the PO\textsuperscript{15}N storage estimate to closer agreement with the estimated proportion of NO\textsuperscript{-} lost via DNRA. Despite uncertainties in PO\textsuperscript{15}N estimates, NH\textsubscript{4}\textsuperscript{+} itself appears unimportant in long-term storage of allochthonous N but instead serves as an important fast turnover link between DNRA and marsh N demands.

Likewise, DON has been shown to be an important intermediate in some \textsuperscript{15}N tracer experiments (Bronk et al. 1994) yet in this study would be a relatively minor long-term sink for \textsuperscript{15}N. DON concentrations determined on select samples were similar to pore-water NH\textsubscript{4}\textsuperscript{+} concentrations (~100 \mu M). Although the DO\textsuperscript{15}N was not measured, even if the pool was at maximal enrichment (i.e., equal to the enrichment of the NO\textsuperscript{-} pool), \textsuperscript{15}N storage in DON could account for no more than 5% of the \textsuperscript{15}N lost from nitrate in the mass balance.

In contrast to mechanisms of N retention linked to DNRA, much of the N reduced via DNF to N\textsubscript{2}O and N\textsubscript{2} was apparently exported from the marsh on relatively short timescales. The in situ DNF rate accounted for ~70% of the NO\textsuperscript{-} loss rate from the plume, yet the storage in the N\textsubscript{2}O and N\textsubscript{2} pools collectively accounted for only 14% of the \textsuperscript{15}N mass lost from the NO\textsuperscript{-} pool. The N\textsubscript{2}O concentrations and enrichment (Fig. 7) showed rapid production of labeled N\textsubscript{2}O whose source was the added \textsuperscript{15}NO\textsubscript{3}. However, of the total \textsuperscript{15}N measured in N\textsubscript{2}O, on average, <50% was subsequently observed in the N\textsubscript{2} pool of wells 2, 3, and 4. Despite the reported unimportance of N\textsubscript{2}O emission after NO\textsuperscript{-} additions to freshwater wetlands (Xue et al. 1999), deficits in the mass balance of N\textsubscript{2}O produced from NO\textsuperscript{-} during in situ aquifer C\textsubscript{2}H\textsubscript{2} block studies have suggested N\textsubscript{2}O loss from shallow aquifers (Bragan et al. 1997). The high N\textsubscript{2}O concentrations observed in this experiment were unique among wetland studies and were several orders of magnitude above saturation concentrations. High concentrations, combined with the close proximity of the plume to the atmosphere, suggested that N\textsubscript{2}O evasion contributed to the disparity between the high rates of N\textsubscript{2}O production and \textsuperscript{15}N\textsubscript{2}O storage. When the maximum potential N\textsubscript{2}O evasion rate (78 \mu M d\textsuperscript{-1}) was scaled to the entire 67-d mass balance period for the original volume of the plume, evasion could have accounted for a loss of 2155 \mu moles \textsuperscript{15}N from the N\textsubscript{2}O pool. When this value is added back to the \textsuperscript{15}N\textsubscript{2}O estimate in the mass balance (Table 2), \textsuperscript{15}N\textsubscript{2}O storage would increase by a factor of three and account for one quarter of all the missing \textsuperscript{15}N in the mass balance.

Similar to the N\textsubscript{2}O pool, because only a 15% increase in the dissolved N\textsubscript{2}O concentration was noted in the presence of large N\textsubscript{2}O isotope incorporation, N\textsubscript{2}O conversion to N\textsubscript{2} was probably rapidly followed by N\textsubscript{2} export to the atmosphere. Bates and Spalding (1998) demonstrated that 66% of N\textsubscript{2}O produced from denitrification in aquifer microcosms could be explained by increases in the N\textsubscript{2}/Ar ratio, whereas the remaining 34% of the N\textsubscript{2}O produced was believed to be lost to the atmosphere as a result of N\textsubscript{2}O supersaturation. Export of N\textsubscript{2} (and N\textsubscript{2}O) to the atmosphere may have been aided by gas stripping. The observed argon undersaturation in the pore water indicated a system subject to active gas stripping, potentially accelerated by bubble formation, which was periodically observed in some pore water samples warmed to ambient air temperature (Chanton et al. 1989). The pattern of Ar undersaturation mimicked that of N\textsubscript{2} supersaturation such that Ar stripping appeared to be closely tied to N\textsubscript{2} export (Figs. 8, 9). Given the Ar deficit, dissolved N\textsubscript{2}O concentrations and the solubility ratio of Ar to N (2.5), we estimated that the total amount of N\textsubscript{2}O stripped out of the system over the entire study was between 15 and 18 mmoles N. On the basis of this rough calculation, gas stripping of N\textsubscript{2}O could account for an additional 5% of the total \textsuperscript{15}N-NO\textsubscript{-} lost from all wells, effectively doubling the \textsuperscript{15}N\textsubscript{2}O storage estimate. Despite this potential increase, the N\textsubscript{2}O \textrightarrow N\textsubscript{2} rate accounted for ~30%–35% of the total rate of NO\textsuperscript{-} reduction, but the \textsuperscript{15}N\textsubscript{2}O storage would still account for <10% of the mass of \textsuperscript{15}N lost from the NO\textsuperscript{-} pool. Although some N\textsubscript{2}O may have been refixed, we suggest that the remaining missing N in the mass balance was lost as N\textsubscript{2} via evasion.

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}O 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}O was more than sufficient by nearly two orders of magnitude to account for the remaining lack of \textsuperscript{15}N in the N\textsubscript{2}O pool (Hartman and Hammond 1984; Wannikoff 1992). We
suggest that evasion and gas stripping were faster than the estimated \( \text{N}_2 \) production rate. Therefore, dissolved \( \text{N}_2 \) 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 \( \text{NO}_3^- \) was denitrification (70% of the total \( \text{NO}_3^- \) loss rate) with \( \text{N}_2\text{O} \) being the dominant end product (50%–60% of the total DNF rate). Of the 70% of the total groundwater \( \text{NO}_3^- \) load reduced via DNF (\( \text{N}_2 \) + \( \text{N}_2\text{O} \)), 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 \( \text{NO}_3^- \) 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 \( \text{NO}_3^- \) loads in the Ringfield marsh was a function of both \( \text{NO}_3^- \) load and the dominant mechanism of \( \text{NO}_3^- \) 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.

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