

## Nitrate dynamics within the Pajaro River, a nutrient-rich, losing stream

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**Abstract.** The major ion chemistry of water from an 11.42-km reach of the Pajaro River, a losing stream in central coastal California, shows a consistent pattern of higher concentrations during the 2<sup>nd</sup> (dry) half of the water year. Most solutes are conserved during flow along the reach, but  $[\text{NO}_3^-]$  decreases by ~30% and is accompanied by net loss of channel discharge and extensive surface–subsurface exchange. The corresponding net  $\text{NO}_3^-$  uptake length is  $37 \pm 13$  km ( $42 \pm 12$  km when normalized to the conservative solute  $\text{Cl}^-$ ), and the areal  $\text{NO}_3^-$  uptake rate is  $0.5 \mu\text{mol m}^{-2} \text{s}^{-1}$ . The observed reduction in  $[\text{NO}_3^-]$  along the reach results from one or more internal sinks, not dilution by ground water, hill-slope water, or other water inputs. Observed reductions in  $[\text{NO}_3^-]$  and channel discharge along the experimental reach result in a net loss of 200–400 kg/d of  $\text{NO}_3^-$ -N, ~50% of the input load. High-resolution (temporal and spatial) sampling indicates that most of the  $\text{NO}_3^-$  loss occurs along the lower part of the reach, where there is the greatest seepage loss and surface–subsurface exchange of water. Stable isotopes of  $\text{NO}_3^-$ , total dissolved P concentrations, and streambed chemical profiles suggest that denitrification is the most significant  $\text{NO}_3^-$  sink along the reach. Denitrification efficiency, as expressed through downstream enrichment in  $^{15}\text{N}\text{-NO}_3^-$ , varies considerably during the water year. When discharge is greater (typically earlier in the water year), denitrification is least efficient and downstream enrichment in  $^{15}\text{N}\text{-NO}_3^-$  is greatest. When discharge is lower, denitrification in the streambed appears to occur with greater efficiency, resulting in lower downstream enrichment in  $^{15}\text{N}\text{-NO}_3^-$ .

**Key words:** rivers, solute transport, denitrification,  $^{15}\text{N}/^{14}\text{N}$ ,  $^{18}\text{O}/^{16}\text{O}$ .

The global rate of N fixation doubled during the 20<sup>th</sup> century because of numerous human activities, the most important of which is increased application of

fertilizer (Galloway et al. 1995, Vitousek et al. 1997).  $\text{NO}_3^-$  is more stable and mobile than other common fixed-N compounds. Therefore, increased loading of N is often expressed as elevated  $[\text{NO}_3^-]$  in streams (Duff and Triska 2000), i.e.,  $> \sim 70 \mu\text{M}$  (e.g., Holloway et al. 1998, Schiff et al. 2002, Böhlke et al. 2004). Adverse effects of elevated  $[\text{NO}_3^-]$  in streams are well documented and include eutrophication of coastal waters (Turner and Rabalais 1994, Neal and Jarvie 2005) and contamination of ground water (e.g., Böhlke and Denver 1995, Nolan 2001, Böhlke et al. 2002). Human health effects of  $\text{NO}_3^-$  in drinking water are

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widely known and have prompted the US Environmental Protection Agency to set a standard for maximum  $[\text{NO}_3^-]$  in drinking water of 714  $\mu\text{M}$  (10 mg N/L) (e.g., Nolan et al. 1997, Kendall 1998).

N export via streams is often lower than watershed inputs, implying that N sinks, along with accumulation in biomass and export to aquifers, are important in many watersheds (e.g., Sjodin et al. 1997, Alexander et al. 2000, Bernhardt et al. 2003). Relatively low  $[\text{NO}_3^-]$  in stream water, despite relatively high inputs, can be explained in some systems by  $\text{NO}_3^-$  removal in riparian buffer zones between discharging groundwater and stream channels (e.g., Peterjohn and Correll 1984, McMahon and Böhlke 1996, Cirimo and McDonnell 1997, Sebilo et al. 2003). However, the anthropogenic influence on global fixation of N is relatively recent, and it is not known how buffer zones might help to mitigate high  $\text{NO}_3^-$  in ground water on longer time scales (Galloway et al. 1995, Böhlke 2002); thus,  $\text{NO}_3^-$  contamination in both aquifers and streams may become a more significant problem in coming decades. Therefore, it is important to develop a better understanding of factors that control the spatial and temporal extent of  $\text{NO}_3^-$  sinks in watersheds, particularly instream sinks where  $[\text{NO}_3^-]$  is high, to quantify, control, and mitigate current and future impacts on the quality of both surface and ground water.

Many studies have documented uptake of nutrients during transport in streams. Uptake rates have been related to many environmental variables, including solar flux incident on the stream (Mulholland and Hill 1997, Hill et al. 2001), dissolved organic C concentrations (Bernhardt and Likens 2002), dissolved  $\text{O}_2$  concentrations (Christensen et al. 1990, Laursen and Seitzinger 2004), types of vegetation (Schade et al. 2001), and the effects of logging and other human activities (Sabater et al. 2000). The magnitude of surface–subsurface exchange is an important control over the potential nutrient uptake rate for a given reach (e.g., Duff and Triska 1990, 2000, Valett et al. 1996, Wondzell and Swanson 1996) because of the importance of processes occurring in and on stream sediments. Many streambed processes, including weathering reactions (Gooseff et al. 2002), sorption to streambed sediments (McKnight et al. 2002), and retention of colloids and sorbed materials (Ren and Packman 2004), can remove solutes from downstream transport. However, removal of nutrients, particularly  $\text{NO}_3^-$ , is commonly attributed to microbiological activity within the streambed (e.g., Triska et al. 1989, Cirimo and McDonnell 1997, Mulholland and Hill 1997, Butturini and Sabater 1999, Grimaldi and Chaplot 2000, Hinkle et al. 2001, Hall et al. 2002).

Unlike assimilative uptake, transformation of  $\text{NO}_3^-$  to  $\text{N}_2$  gas via denitrification removes fixed N from the stream system. Streambed seepage, i.e., the movement of water across the streambed, both entering and leaving the stream channel, and its influence on denitrification is of particular interest within losing streams that contribute water to underlying aquifers. Relatively few studies have been completed within losing streams with  $[\text{NO}_3^-]$  near or above drinking-water standards (e.g., Sjodin et al. 1997, Grimaldi and Chaplot 2000).

We present geochemical results and quantify relationships between streambed seepage and  $\text{NO}_3^-$  removal over a range of discharge and seepage rates within an experimental reach of a single stream. Results of differential discharge gauging and tracer experiments in the same reach are presented elsewhere and include independent estimates of surface–subsurface exchange rates (Ruehl et al. 2006). In our present study, we identify parts of the experimental reach where and when there are significant  $\text{NO}_3^-$  sinks, show that denitrification is the dominant mechanism of  $\text{NO}_3^-$  removal, place quantitative constraints on rates of  $\text{NO}_3^-$  cycling, and conclude that denitrification is strongly influenced by surface–subsurface exchange, even within this nutrient-rich, losing stream.

### Field Setting and Experimental Design

We instrumented and sampled an 11.42-km reach of the Pajaro River in the Pajaro Valley (Fig. 1A, B); see Ruehl et al. (2006) for more information concerning local geology, climate, and hydrology. The upper end of the experimental reach is located at a gauging station developed and maintained by the US Geological Survey (USGS; Station #11159000, Chittenden). Mean daily discharge at this station during the period of record varied from 0 to  $>600 \text{ m}^3/\text{s}$ , and peak discharge was  $>700 \text{ m}^3/\text{s}$  on several occasions. Annual precipitation in the basin is generally 20 to 60 cm/y. Most precipitation falls during winter and early spring, whereas late spring to autumn is generally dry. Temperatures rarely drop below freezing, so most precipitation in the basin falls as rain. Thus, 2 distinct hydrologic periods are apparent on stream-flow hydrographs and chemographs during each water year: 1) wet winter conditions, characterized by high and highly variable discharge and relatively low solute concentrations; and 2) dry summer conditions, characterized by lower flows (typically  $<1 \text{ m}^3/\text{s}$ ) and higher solute concentrations.

Land use in the Pajaro Valley (the western portion of the Pajaro River watershed) is dominated by agriculture (Los Huertos et al. 2001, PVWMA 2001), and 84%

of freshwater resources are used for irrigation (Hanson 2003). Local ground water currently is the source of virtually all irrigation water used in the Pajaro Valley and is extracted primarily from shallow alluvial and underlying Aromas aquifers (Muir 1977). About 65% of current groundwater extraction in the Pajaro Valley is overdraft, resulting in seawater intrusion near the coast and a loss of storage throughout the basin (PVWMA 2001). The impacts of overdraft on surface-water-groundwater interactions in the watershed are not well understood, but the experimental reach lost discharge via streambed seepage at a rate of 0.2 to 0.4 m<sup>3</sup>/s during the 2<sup>nd</sup> half of the 2002 to 2004 water years. Most of this loss occurred along the lower portion of the reach, where channel loss rates per unit stream length were typically 1 to 4 × 10<sup>-5</sup> m<sup>2</sup>/s (Ruehl et al. 2006). Given a typical stream width of 10 m, this range of channel loss rates suggests downward seepage velocities of 0.1 to 1 m/d. This value is consistent with observed head gradients directed into the streambed of 10 to 30%, given a hydraulic conductivity of 10<sup>-5</sup> m/s typical of sandy streambeds. Furthermore, elevated Br<sup>-</sup> was observed in piezometers at depths from 0.5 to 1.0 m below the streambed along the lower stretch 1 to 2 d after NaBr injections into the main channel, suggesting that channel water seeped into the streambed at rates ~0.1 to 1 m/d along this portion of the reach. It would be difficult to quantify similar rates of streambed seepage during (high) winter flows but, assuming that the documented loss extends throughout the water year, seepage along the experimental reach could make up ~20 to 40% of current sustainable watershed yield (Ruehl et al. 2006).

The historical influence of agricultural development in the Pajaro Valley hydrologic basin (Los Huertos et al. 2001) is readily apparent in [NO<sub>3</sub><sup>-</sup>] measured in river water collected at the Chittenden gauging station. Water quality is variable within and among years, but peak [NO<sub>3</sub><sup>-</sup>] has risen considerably over the last 50 y. [NO<sub>3</sub><sup>-</sup>] was generally <0.1 mM in the early to mid-1950s, but now commonly exceeds the drinking-water standard of 0.714 mM (Fig. 1C). Elevated NO<sub>3</sub><sup>-</sup> also is present in Pajaro Valley ground water: ~35% of 295 monitored wells have average concentrations above the drinking-water standard. Typically, the highest concentrations are found in the shallowest wells (PVWMA 2001).

The focus of our study was on changes in water chemistry that occurred downstream of the Chittenden gauging station, the reference point for all stream distances, along an 11.42-km reach (Fig. 1B). We established additional gauging stations at km 8.06 (2003 water year) and km 11.42 (2002–2004 water

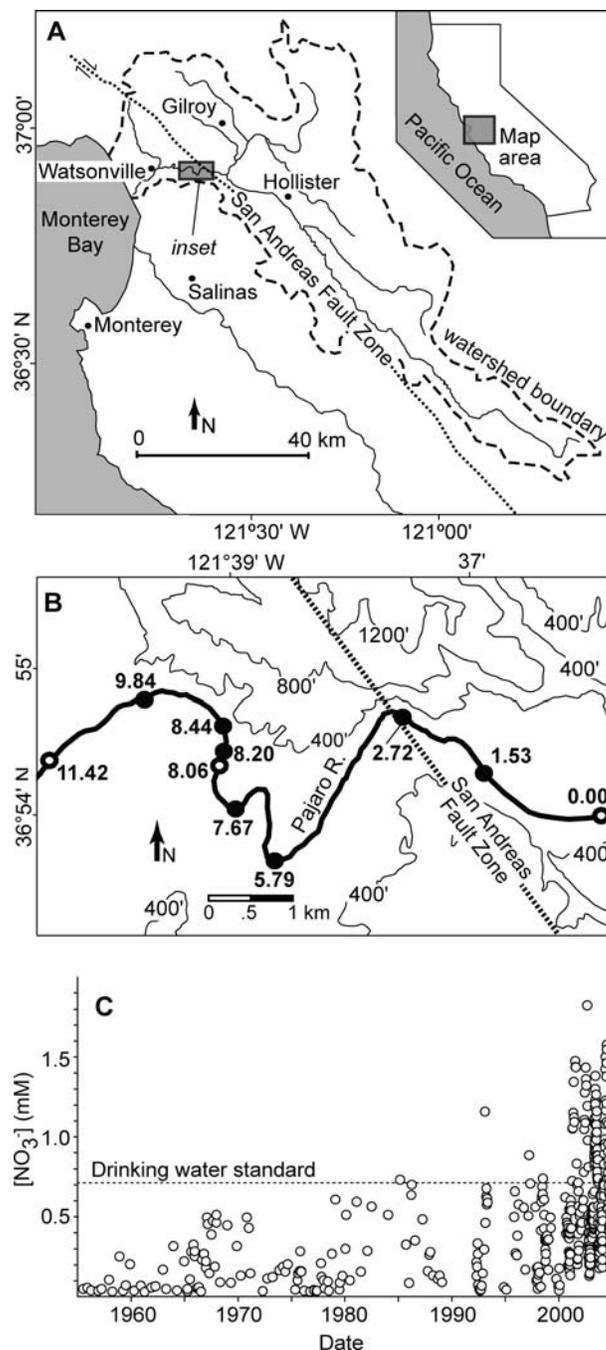


FIG. 1. Experimental locations and historical [NO<sub>3</sub><sup>-</sup>] from the Pajaro River, central coastal California. A.—Pajaro River watershed. B.—The 11.42-km experimental reach of the Pajaro River with all sampling and measurement locations identified on the basis of distance downstream from the top of the reach (boldface numbers, in km). C.—[NO<sub>3</sub><sup>-</sup>] at km 0.00 from 1952 to 2004.

years); additional stream-discharge measurements were made periodically at locations throughout the experimental reach to calibrate rating curves for the gauging stations and to quantify changes in discharge in the channel. During the summer and early autumn, discharge generally decreases downstream, with most of the loss occurring in the lower  $\sim 3$  km of the reach (Ruehl et al. 2006). We focused on the 2<sup>nd</sup> half of the water year. Mass balance of  $\text{NO}_3^-$  is simplified when there are no significant fluid inflows or outflows along the experimental reach other than channel discharge and streambed seepage, and quantifying changes in stream discharge (required for quantifying  $\text{NO}_3^-$  fluxes) is more difficult and less accurate in an absolute sense when discharge is  $>5$   $\text{m}^3/\text{s}$ . In addition, we knew that  $[\text{NO}_3^-]$  would be elevated during much of the measurement period, simplifying estimation of removal rates.

## Methods

### *Water sampling*

We conducted synoptic sampling of the experimental reach on 47 separate days throughout the 2002–2004 water years, with sampling at the top, bottom, and 1 to 9 intermediate sites. We collected samples in precleaned high-density polyethylene bottles after the bottles were rinsed  $3\times$  with stream water. We immediately placed samples on ice and filtered them in the lab through  $0.45\text{-}\mu\text{m}$  glass-fiber filters within 12 h of collection. We either analyzed samples within 48 h of collection or froze (anions and nutrients) or chilled (cations) them after filtration until immediately before analysis. In addition to synoptic sampling, we conducted diel sampling at a frequency of 2 h for 48-h periods at the top and bottom of stretches (subsections of the experimental reach) associated with tracer tests. We collected these samples with an automated sampler and recovered them from the field within 12 h of the last sample, returned them to the laboratory, and immediately filtered and stored them as described above. We filtered a subset of samples for isotopic analysis of  $\text{NO}_3^-$  through  $0.22\text{-}\mu\text{m}$  filters in the field upon collection, transported them to the laboratory on ice, and froze them until analysis.

We obtained samples from the streambed using passive dialysis samplers (peepers) and piezometers. A peeper is a rigid sheet of polycarbonate into which a series of 5-mL chambers are carved at 2-cm intervals. Chambers are filled with deionized water and a  $0.4\text{-}\mu\text{m}$  semipermeable polycarbonate membrane is attached, covering the openings to the chambers. Peepers are submerged in a container filled with deionized water and  $\text{N}_2$  is bubbled through the water around the

peepers for  $\geq 10$  d to deoxygenate the water in the chambers. Deoxygenated peepers are inserted into the streambed and left deployed for  $\geq 2$  wk, ensuring ample time for solutes to diffuse into the chambers and equilibrate with adjacent pore waters. Peepers are not intended to document transient processes, but the chemistry of fluids trapped in the chambers is most influenced by the last 12 to 24 h of diffusive exchange. We extracted peeper samples from the chambers, field-filtered them, and transported them on ice to the laboratory for analysis. We also obtained subsurface samples for chemical analyses from drive-point piezometers, installed at depths of 0.5 to 1.0 m into the streambed. Piezometer casings were purged several times before each sample was collected. Last, we took a small number of groundwater samples from agricultural-production wells in the vicinity of the experimental reach. We filtered, preserved, and analyzed piezometer and well samples using the same methods as surface-water samples.

### *Analytical methods*

We measured dissolved  $\text{O}_2$ , temperature, and pH of surface water in the field with a Hydrolab multiprobe system. We measured  $\text{NH}_4^+$ , soluble reactive P (SRP), and  $\text{NO}_3^- + \text{NO}_2^-$  by colorimetric flow-injection analysis (QuickChem 8000; Lachat Instruments, Loveland, Colorado). We measured  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  with ion chromatography (IC) (DX-100; Dionex, Sunnyvale, California). We measured major cations, Fe, Mn, and total dissolved P (TDP) by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 4300 ICP-OES; PerkinElmer, Wellesley, Massachusetts). TDP is an operational definition that includes P that passed through the  $0.45\text{-}\mu\text{m}$  glass-fiber filters used with the samples. We acidified samples for Fe and Mn to  $\text{pH} < 2$  with 6N HCl within 1 wk of collection, stored them for 3 to 5 d, and then analyzed them. External standards indicated that the accuracy was  $\sim 3\%$  for the IC, and  $\sim 2\%$  for colorimetric and ICP-OES measurements. We determined  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  (relative to Vienna Standard Mean Ocean Water) of  $\text{NO}_3^-$  at the USGS Stable Isotope Lab in Menlo Park, California, where samples were defrosted and analyzed using the denitrifier method similar to that described by Sigman et al. (2001) and Casciotti et al. (2002). Laboratory replicates were run for all but one sample, and standard deviations were consistently  $< 1\%$  for both  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ .

### *$\text{NO}_3^-$ loss and stable isotope calculations*

We quantified the rate at which the stream system acts as a net sink of  $\text{NO}_3^-$  using the net  $\text{NO}_3^-$  uptake

length, which can be conceptualized as the average downstream distance traveled by a NO<sub>3</sub><sup>-</sup> molecule before being removed from the main channel (Newbold et al. 1981, Stream Solute Workshop 1990). Net uptake lengths ( $S_w$ ) are based on downstream changes in [NO<sub>3</sub><sup>-</sup>] and, thus, reflect both sources and sinks within a given reach (e.g., Martí et al. 1997, Haggard et al. 2005). They are quantified as

$$S_{w,[NO_3]} = \left( \frac{[NO_3^-]_{top} - [NO_3^-]_{bottom}}{[NO_3^-]_{mean}} \right) L \quad [1]$$

where [NO<sub>3</sub><sup>-</sup>]<sub>top</sub> and [NO<sub>3</sub><sup>-</sup>]<sub>bottom</sub> are [NO<sub>3</sub><sup>-</sup>] at the top and bottom of the reach, [NO<sub>3</sub><sup>-</sup>]<sub>mean</sub> is the average of [NO<sub>3</sub><sup>-</sup>]<sub>top</sub> and [NO<sub>3</sub><sup>-</sup>]<sub>bottom</sub>, and  $L$  is the reach length. Use of equation 1 to calculate  $S_{w,[NO_3]}$  presumes that NO<sub>3</sub><sup>-</sup> uptake is 0<sup>th</sup>-order with respect to [NO<sub>3</sub><sup>-</sup>] (i.e., that the downstream decrease in [NO<sub>3</sub><sup>-</sup>] is linear).  $S_w$  values are commonly calculated assuming a 1<sup>st</sup>-order (i.e., exponential) decrease in [NO<sub>3</sub><sup>-</sup>] (e.g., Stream Solute Workshop 1990), but we used equation 1 because we compare  $S_{w,[NO_3]}$  to other surface–subsurface exchange rates that are independent of [NO<sub>3</sub><sup>-</sup>] and because results obtained using linear and exponential equations were virtually identical (see Discussion). When [NO<sub>3</sub><sup>-</sup>] from >2 locations along the reach were available,  $S_{w,[NO_3]}$  was calculated as the negative inverse of the slope obtained by regression of [NO<sub>3</sub><sup>-</sup>] on downstream distance (Stream Solute Workshop 1990). In these cases, correlation coefficients ( $r^2$ ) are presented to indicate how well the data fit the regression.

We also calculated  $S_{w,[NO_3]:[Cl]}$ , a dilution-corrected net NO<sub>3</sub><sup>-</sup>  $S_w$  based on the conservative solute Cl<sup>-</sup> (Haggard et al. 2005). The calculation is identical to that defined by equation 1, except that each [NO<sub>3</sub><sup>-</sup>] was divided by [Cl<sup>-</sup>] of the same sample. In addition, we calculated areal uptake rates ( $U$ ) corresponding to  $S_w$  values (Stream Solute Workshop 1990) as

$$U_{[NO_3]} = \frac{Q[NO_3^-]}{S_{w,[NO_3]}w} \quad [2]$$

where  $Q$  is stream discharge and  $w$  is stream width. We note that although other techniques such as <sup>15</sup>N-NO<sub>3</sub><sup>-</sup> additions may help to distinguish between net and gross NO<sub>3</sub><sup>-</sup> removal (e.g., Böhlke et al. 2004, Mulholland et al. 2004), this approach would be difficult in the Pajaro River because of its relatively high N-NO<sub>3</sub><sup>-</sup> flux of ~500 kg/d.

We compared  $S_{w,[NO_3]}$  values based on synoptic and diel sampling with length scales obtained through analysis of tracer-dilution breakthrough curves. Briefly, we injected solutions of Rhodamine-WT and NaBr at a constant rate into the main channel for 4 to 6 h on

12 separate days during 2003 and 2004. We fitted breakthrough curves using a 1-dimensional model of advection, dispersion, and storage exchange (Runkel 1998). We calculated characteristic length scales of transient storage exchange and inflow of tracer-free water, as well as a length scale corresponding to net channel loss of water measured by differential stream gauging. For more details, see Ruehl et al. (2006).

Stable isotopes of NO<sub>3</sub><sup>-</sup> are useful for assessing sources and for distinguishing between NO<sub>3</sub><sup>-</sup> sinks (e.g., Burns and Kendall 2002). Biologically mediated denitrification enriches residual NO<sub>3</sub><sup>-</sup> in both <sup>15</sup>N and <sup>18</sup>O, whereas other NO<sub>3</sub><sup>-</sup> sinks result in little or no enrichment. The magnitude of δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> enrichment associated with NO<sub>3</sub><sup>-</sup> removal is quantified through an enrichment factor,  $\epsilon_N$ , defined by a form of the Rayleigh equation (Sebilio et al. 2003),

$$\epsilon_N = \frac{\delta^{15}N - \delta^{15}N_0}{\ln[NO_3^-] - \ln[NO_3^-]_0}, \quad [3]$$

where δ<sup>15</sup>N = stable isotope ratio for N-NO<sub>3</sub><sup>-</sup>, and δ<sup>15</sup>N<sub>0</sub> and [NO<sub>3</sub><sup>-</sup>]<sub>0</sub> are the N stable-isotope ratio and concentration, respectively, of NO<sub>3</sub><sup>-</sup> prior to N removal. There is a similar enrichment factor,  $\epsilon_O$ , for O<sub>2</sub>. Processes that leave residual NO<sub>3</sub><sup>-</sup> enriched in <sup>15</sup>N or <sup>18</sup>O have negative enrichment factors because δ<sup>15</sup>N tends to increase as [NO<sub>3</sub><sup>-</sup>] decreases. Enrichment factors for δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> and δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> in surface waters were determined by regression of δ<sup>15</sup>N (or δ<sup>18</sup>O) on ln[NO<sub>3</sub><sup>-</sup>].

## Results

### Synoptic sampling

Concentrations of major cations and anions in Pajaro River water increased at individual sites along the reach during the 2<sup>nd</sup> half of the water year (Fig. 2A, B), as expected when stream discharge decreases. Concentrations of none of the major ions changed consistently from the upper to the lower end of the experimental reach during the 2<sup>nd</sup> half of the water year, with one notable exception: [NO<sub>3</sub><sup>-</sup>] decreased by ~30% late in the water year (Fig. 2C).  $S_w$  values were calculated for 14 late-year days on which synoptic sampling from ≥3 locations along the reach had occurred, and the average values of  $S_{w,[NO_3]}$  and  $S_{w,[NO_3]:[Cl]}$  were essentially identical (37 ± 13 and 42 ± 12 km, respectively; Table 1). Given typical late-year values of discharge, [NO<sub>3</sub><sup>-</sup>], and stream width, these  $S_w$ s correspond to  $U$ s of ~0.5 μmol m<sup>-2</sup> s<sup>-1</sup>. At times, [TDP] along the reach also decreased (Fig. 2D), although the magnitude of TDP reduction (~4 μM when observed) was much smaller than that for

$[\text{NO}_3^-]$  ( $\sim 400 \mu\text{M}$ ). These decreases in TDP were seen at the bottom of the experimental reach (km 11.42) late in the water year, when  $Q$  and velocities at that location were relatively low ( $<0.1 \text{ m}^3/\text{s}$  and  $<0.05 \text{ m/s}$ , respectively). Combined with an  $\sim 30\%$  decrease in Pajaro River discharge along the reach (Ruehl et al. 2006), the reduction in  $[\text{NO}_3^-]$  represents a large  $\text{NO}_3^-$  sink. Approximately 50% of the  $\text{NO}_3^-$  entering the reach at km 0.00 was not exported at km 11.42, a net loss of 200 to 400 kg/d N- $\text{NO}_3^-$  (Fig. 2E).

### Diel sampling

Diel sampling of surface water (Fig. 3A, B) was conducted at the top and the bottom of each stretch associated with tracer-injection experiments, yielding stretch-specific values of  $S_{w,[\text{NO}_3]}$  (Table 2). In general, variations in  $[\text{NO}_3^-]$  at individual sites (when present) show a diel pattern, with peaks and troughs separated by  $\sim 24 \text{ h}$ . In most cases,  $[\text{NO}_3^-]$  consistently decreased among sites along the lower part of the reach, downstream from km 7.67 (Fig. 3A), whereas  $[\text{NO}_3^-]$  often remained relatively constant along the upper 2.72 km of the reach (Fig. 3B).  $S_{w,[\text{NO}_3]}$  along the lower stretches was 11 to 25 km (Table 2). [SRP] along all stretches varied inconsistently during these intensive sampling periods, sometimes increasing and sometimes decreasing; overall changes in [SRP] were 2 orders of magnitude smaller than those for  $[\text{NO}_3^-]$  (Fig. 3A, B). During one intensive sampling period,  $[\text{NO}_3^-]$  increased from km 7.67 to 8.44, resulting in a negative  $S_{w,[\text{NO}_3]}$ , then decreased from km 8.44 to 9.84 (Fig. 3C).  $S_{w,[\text{NO}_3]}$  was usually greater (indicating slower  $\text{NO}_3^-$  removal) along the upper than the lower portion of the reach, or could not be calculated at all when there was no significant change in  $[\text{NO}_3^-]$  (Table 2).

### Porewater sampling

Porewater profiles obtained from peeper samples demonstrate that  $\text{NO}_3^-$  was removed, rapidly at times, in the streambed (Figs 4A, B, 5A–C). Most peepers were installed where it was determined that water moved into or out of the streambed, and conservative solutes such as  $\text{Cl}^-$  generally varied only slightly with depth. In contrast, solutes likely to be involved in mineralogical or biogeochemical reactions often varied considerably with depth below the stream bottom. N species concentrations were notably variable, with  $[\text{NO}_3^-]$  generally decreasing to a local minimum at 5 to 10 cm below the stream bottom. Multiple local maxima and minima in  $[\text{NO}_3^-]$  are apparent in some peeper profiles (e.g., Figs 4A, 5A–C), with low  $[\text{NO}_3^-]$  often accompanied by increases in [Mn] and [Fe] (for clarity,

only [Mn] is shown) and decreases in  $[\text{SO}_4^{2-}]$ . Small increases in  $[\text{NO}_2^-]$  and  $[\text{NH}_4^+]$  were sometimes collocated with decreases in  $[\text{NO}_3^-]$  (Figs 4A, 5A).

### Stable isotopes of $\text{NO}_3^-$

There was a broad trend of correlated enrichment in  $^{15}\text{N}$  and  $^{18}\text{O}$  of all  $\text{NO}_3^-$  samples, with a relative enrichment ( $\epsilon_N:\epsilon_O$ ) of  $\sim 2:1$  (Fig. 6A, B). This enrichment is consistent with biologically mediated denitrification (e.g., Cey et al. 1999, Lehmann et al. 2003). When  $[\text{NO}_3^-]$  in the subsurface water was lower than in the channel water, subsurface samples had higher  $\delta^{15}\text{N}\text{-NO}_3^-$  (Figs 4, 5) and the associated  $\epsilon_N$  was approximately  $-20\%$  (using eq. 3, calculations not shown), except when conservative solutes such as  $\text{Cl}^-$  also varied with depth (Fig. 4B). Both  $\delta^{18}\text{O}\text{-NO}_3^-$  and  $\delta^{15}\text{N}\text{-NO}_3^-$  in surface water increased with distance along the experimental reach, as  $[\text{NO}_3^-]$  decreased. Collectively, these data define enrichment factors for surface water of  $\epsilon_{N,\text{surf}} = -6.0$  to  $-19.9\%$  and  $\epsilon_{O,\text{surf}} = -1.6$  to  $-20\%$  (Fig. 7A, B, respectively). Two distinct regimes of  $\delta^{15}\text{N}\text{-NO}_3^-$  enrichment in surface water were observed. Samples collected on 26 August 2004 and 21 May 2004 had relatively high downstream enrichment in  $\delta^{15}\text{N}\text{-NO}_3^-$  ( $\epsilon_{N,\text{surf}} = -19.9\%$  and  $-17.3\%$ , respectively). In contrast, samples collected on 5 other days had  $\epsilon_{N,\text{surf}}$  between  $-6.0$  and  $-9.0\%$  (Fig. 7A). Greater enrichment was observed when discharge was relatively high ( $>\sim 0.3 \text{ m}^3/\text{s}$ ), and apparent  $\text{NO}_3^- S_w$  values were longer ( $S_{w,[\text{NO}_3]} > 100 \text{ km}$ ) (Fig. 8A). Downstream enrichment in  $\delta^{18}\text{O}\text{-NO}_3^-$  was much more variable (Fig. 7B), but the ratio of  $\epsilon_{N,\text{surf}}$  to  $\epsilon_{O,\text{surf}}$  decreased consistently toward the end of the water year, from  $\sim 2$  to  $\sim 0.5$  (Fig. 8B).

## Discussion

### Rates of $\text{NO}_3^-$ removal

$\text{NO}_3^-$  was quantitatively removed from the experimental reach during the 2<sup>nd</sup> half of the water year by one or more internal processes. This interpretation is based on quantitative reductions in  $[\text{NO}_3^-]$  relative to more conservative solutes, an observation that precludes dilution (either from lateral inflow of ground or surface water) as a possible explanation. The  $\text{NO}_3^-$  flux decreased along the reach by 200 to 400 kg N/d (Fig. 2E), and the  $\text{NO}_3^-$  lost from the channel either recharged underlying aquifers or was removed by temporary or permanent internal sinks (e.g., assimilation into biomass or denitrification, respectively). If metrics of  $\text{NO}_3^-$  uptake are based on this change in flux, the reach-averaged  $S_{w,[\text{NO}_3]}$  would be 9.5 km, equivalent to a  $U_{[\text{NO}_3]}$  of  $1.4 \mu\text{mol m}^{-2} \text{ s}^{-1}$ . However,

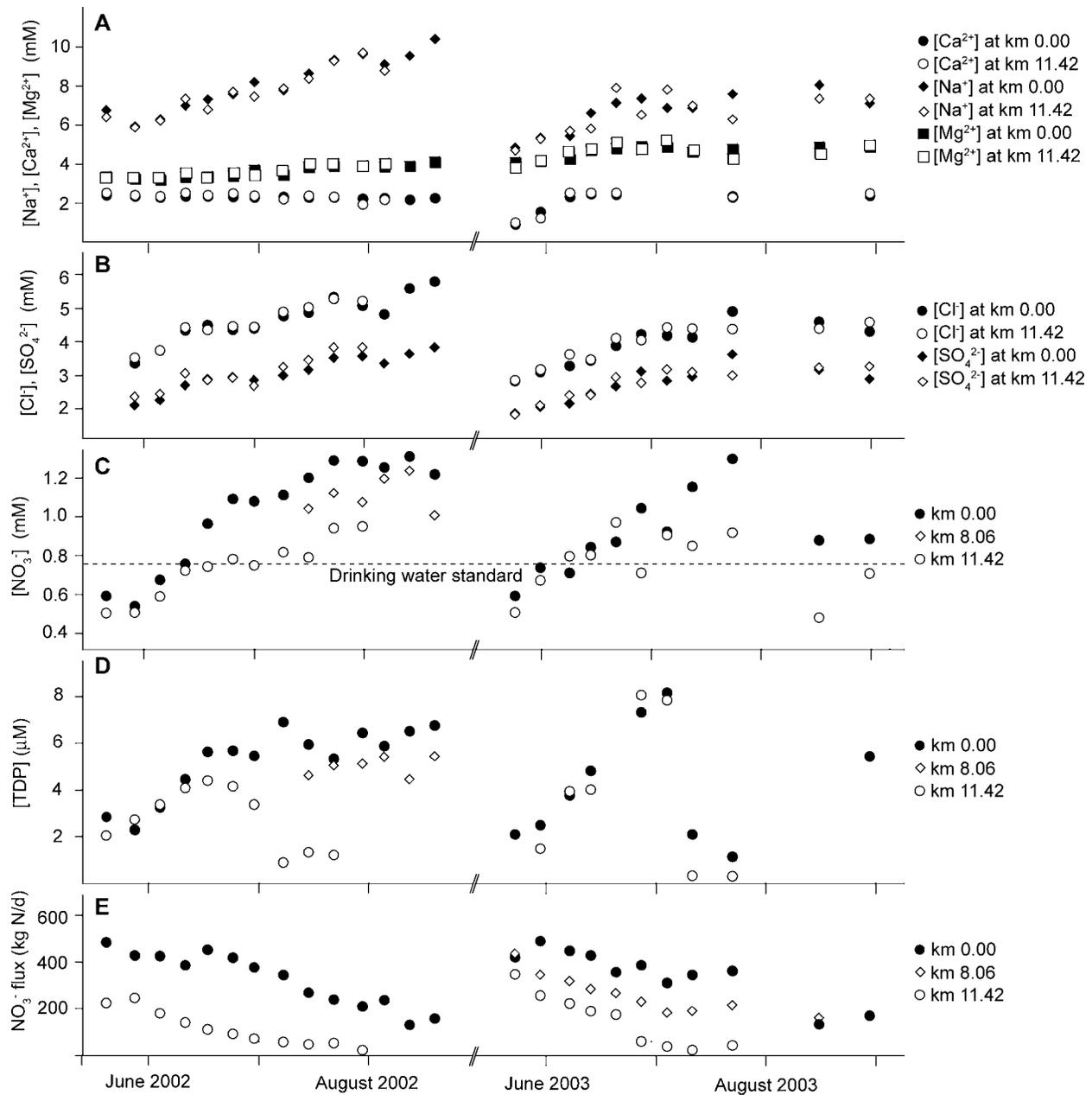


FIG. 2. Major cations ( $[\text{Na}^+]$ ,  $[\text{Mg}^{2+}]$ , and  $[\text{Ca}^{2+}]$ ) (A) and anions ( $[\text{Cl}^-]$ ,  $[\text{SO}_4^{2-}]$ ) (B),  $[\text{NO}_3^-]$  (C), [total dissolved P] ([TDP]) (D), and  $\text{NO}_3^-$ -N flux (E) in the Pajaro River during the 2<sup>nd</sup> half of the 2002 and 2003 water years.

these values include all  $\text{NO}_3^-$  in discharge lost from the channel and, therefore, could be considered a lower (upper) limit for  $S_{w, \text{NO}_3}$  ( $U_{\text{NO}_3}$ ) along the reach. If calculations are based on the change in  $[\text{NO}_3^-]$  instead of the  $\text{NO}_3^-$  flux,  $S_{w, \text{NO}_3}$  and  $U_{\text{NO}_3}$  are equal to  $37 \pm 13$  km and  $0.5 \mu\text{mol m}^{-2} \text{s}^{-1}$ , respectively.  $S_{w, \text{NO}_3}$  values calculated assuming an exponential downstream decrease in  $[\text{NO}_3^-]$  (e.g., Stream Solute Workshop 1990) were  $37 \pm 14$  km, or virtually identical to those assuming a linear decrease.

Dilution by inflow of hill-slope runoff or groundwater runoff did not contribute significantly to the downstream decrease in  $[\text{NO}_3^-]$ . There was no runoff during times when these measurements were made. Even in a strongly losing stream reach such as this one, it is possible that  $[\text{NO}_3^-]$  could be reduced via groundwater dilution, but 3 observations suggest that this process is negligible in this system. First, average  $S_w$  values based on late-year synoptic sampling were not significantly increased when corrected for the

TABLE 1. Comparison of  $\text{NO}_3^-$  uptake lengths ( $S_w$ ), with correlation coefficients, from late-year synoptic sampling.

Date	$n$	$S_{w,[NO_3]}$ (km)	$r^2_{[NO_3]}$	$S_{w,[NO_3]:[Cl]}$ (km)	$r^2_{[NO_3]:[Cl]}$
17 June 2002	3	44	0.99	50	0.99
24 June 2002	3	35	0.98	38	0.99
30 June 2002	3	31	0.97	32	0.97
8 July 2002	3	37	0.99	34	0.99
15 July 2002	4	31	0.75	27	0.89
22 July 2002	4	39	0.94	37	0.98
30 July 2002	4	38	0.99	36	0.97
5 August 2002	5	23	0.53	39	0.87
29 June 2003	6	34	0.83	38	0.86
6 July 2003	6	79	0.28	67	0.51
13 July 2003	8	30	0.87	26	0.89
27 July 2003	8	36	0.91	55	0.86
17 August 2003	11	34	0.45	53	0.25
23 July 2004	5	28	0.77	54	0.75

conservative solute  $\text{Cl}^-$  ( $S_{w,[NO_3]} = 37 \pm 13$  and  $S_{w,[NO_3]:[Cl]} = 42 \pm 12$  km). Second, other solute concentrations did not change significantly from the top to the bottom of the reach (Fig. 2A–D). Third, stable-isotope ratios of water ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) were constant along the reach, despite the fact that  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of groundwater samples near the river were distinctly different and would, therefore, probably have altered the isotopic signature of surface water if groundwater inflow were significant (Ruehl et al. 2006). We conclude that  $S_{w,[NO_3]}$  is an appropriate metric of  $\text{NO}_3^-$  removal in this system.

Comparison of  $S_{w,[NO_3]}$  values with hydrologic exchange lengths determined through differential gauging and tracer-dilution experiments (Ruehl et al. 2006) helps to place nutrient-cycling processes in context.  $S_{w,[NO_3]}$  along the lower part of the reach was of the same magnitude as inflow length ( $S_{w,I}$ , where  $S_{w,I}$  is the stream length required for inflow of tracer-free water to equal channel discharge), but 1 to 2 orders of magnitude larger than transient-storage exchange lengths ( $S_{w,[NO_3]} \gg S_{w,S}$ , where  $S_{w,S}$  is the average distance traveled by a water molecule before entering an adjacent storage zone; Fig. 9A, B, Table 2). At first, the consistency of  $S_{w,[NO_3]}$  and  $S_{w,I}$  may appear to conflict with the earlier assertion that dilution cannot explain the removal of  $\text{NO}_3^-$  during transport, but these interpretations are entirely consistent. If inflow of tracer-free water is primarily caused by stream water that enters the subsurface and follows a spatially or temporally long path before reentering the main channel, then the tracer-free water will have the same major ion chemistry as the stream except for nonconservative solutes like  $\text{NO}_3^-$ . Recent studies have shown that some river systems include hyporheic

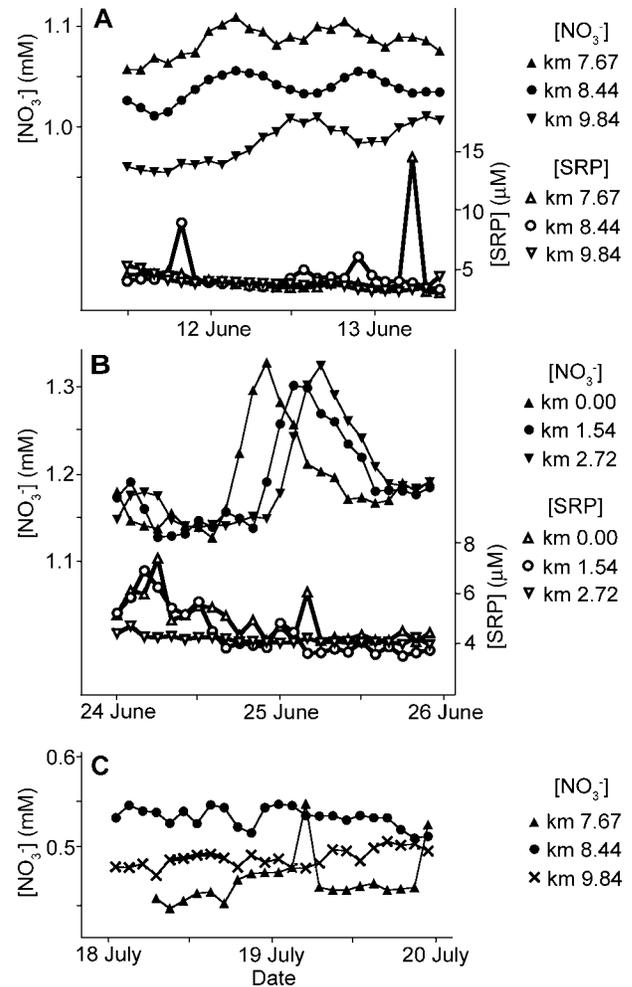


FIG. 3. High-resolution (spatial, temporal) records of  $[\text{NO}_3^-]$  and [soluble reactive P] ([SRP]) at the top and bottom of stretches immediately before the 15 June 2004 tracer experiment (A), soon after the 17 June 2004 tracer experiment (B), and immediately before the 20 July 2004 tracer experiment (C). No [SRP] data were available from 20 July 2004.

zones that exchange water with the main channel on time scales of weeks to months (Gooseff et al. 2003). Groundwater inflow would also lack injected tracer, but has a distinct chemistry and would be readily identified on this basis.

$\text{NO}_3^-$  loss in the upper part of the reach was observed during a single tracer experiment (19 May 2004); there was no significant net change in  $[\text{NO}_3^-]$  during other tracer experiments on this part of the experimental reach.  $S_{w,[NO_3]}$  and  $S_{w,I}$  values for the upper part of the reach calculated on the basis of the 19 May 2004 tracer experiment were both 2 to 5 $\times$  greater than equivalent lengths determined for the lower part of the reach, implying less vigorous exchange and nutrient-cycling processes in the upper part of the reach.

TABLE 2. Summary of stretch-specific NO<sub>3</sub><sup>-</sup> uptake lengths ( $S_w$ ), with hydrologic length scales (see text and Ruehl et al. 2006) when available. Lateral inflow length ( $S_{w,I}$ ) is the stream length required for inflow of tracer-free water to equal channel discharge. Storage exchange length ( $S_{w,S}$ ) is the average distance traveled by channel water before entering a storage zone. Channel loss length ( $S_{w,L}$ ) is the distance at which discharge ( $Q$ ) would reach 0 given observed seepage loss. N/C indicates that  $S_w$  was not calculated because downstream changes in [NO<sub>3</sub><sup>-</sup>] or  $Q$  were within the instrument precision (<20 μM for [NO<sub>3</sub><sup>-</sup>] and <5% for  $Q$ ). Dashes indicate where tracer analyses or discharge measurements were not done.

Date	Injection point (river km)	Length (m)	$Q_{in}$ (m <sup>3</sup> /s)	$Q_{out}$ (m <sup>3</sup> /s)	$S_{w,[NO_3]}$ (km)	$S_{w,I}$ (km)	$S_{w,S}$ (km)	$S_{w,L}$ (km)
26 August 2003	7.67	530	0.099	0.058	11	6.6	4.6	1.0
28 August 2003	5.79	930	0.22	0.19	34	8.5	0.11	8.4
		950	0.19	0.12	N/C	2.0	0.28	2.0
2 September 2003	2.72	3070	0.19	0.16	330	15	1.1	19
4 September 2003	0.00	1530	0.2	0.2	N/C	7.7	0.78	N/C
		1190	0.2	0.19	N/C	-	-	23
17 May 2004	5.79	1880	0.66	0.58	N/C	-	-	15
		3730	0.58	0.49	107	-	-	22
19 May 2004	0.00	2720	0.67	0.66	53	27	1.9	N/C
		3070	0.66	0.61	208	-	-	39
15 June 2004	7.67	770	0.26	0.26	19	9.6	1.4	N/C
		1400	0.26	-	25	-	-	-
17 June 2004	0.00	2720	0.32	0.29	N/C	10	-	28
20 July 2004	7.67	650	0.13	0.11	-10	7.2	1.3	3.9
		1520	0.11	-	22	-	-	-
22 July 2004	0.00	1530	0.21	0.21	N/C	8.1	0.65	N/C
		1190	0.21	0.21	N/C	-	-	N/C
31 August 2004	7.67	770	0.28	0.27	N/C	7.0	0.34	21
2 September 2004	0.00	1530	0.37	0.38	N/C	27	1.0	N/C
		1190	0.38	0.33	N/C	-	-	8.4

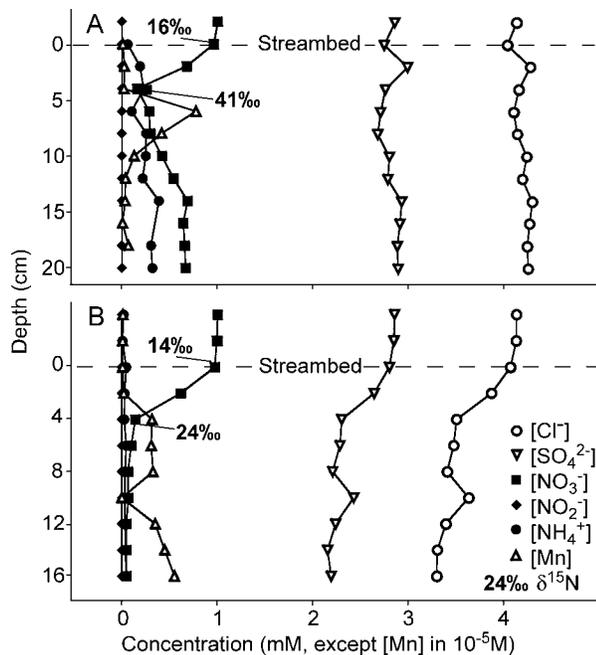


FIG. 4. Porewater profiles at km 2.72 on 16 July 2003, obtained from peeper (streambed) samplers on the left side of the channel (A) and the channel center (B). Stable isotope ratios for N-NO<sub>3</sub><sup>-</sup> are indicated when applicable. The apparent enrichment in δ<sup>15</sup>N ( $\epsilon_N$ ) is -22‰ in panel A and -5‰ in panel B.

$S_{w,[NO_3]}$  values in the experimental reach tend to be longer than those reported in smaller, more pristine systems, largely because of the higher discharge and [NO<sub>3</sub><sup>-</sup>] of the Pajaro River. For example,  $S_{w,[NO_3]}$  values of ~0.1 to 1.0 km were reported in 1<sup>st</sup>-order New Mexico streams (Valett et al. 1996), and  $S_{w,[NO_3]}$  values of 0.004 to 3.4 km were reported for a higher-order Arizona stream (Martí et al. 1997). Both of these systems have [NO<sub>3</sub><sup>-</sup>] <12 μM and much lower  $Q$  than the Pajaro River.  $S_{w,[NO_3]}$  values of 0.1 to 0.4 km were reported in a small ( $Q < 0.06$  m<sup>3</sup>/s) Kansas stream with [NO<sub>3</sub><sup>-</sup>] as great as ~100 μM (Dodds et al. 2002). These authors also reported  $U_{[NO_3]}$  values of 0.1 to 1.2 μmol m<sup>-2</sup> s<sup>-1</sup>, similar to values determined for the Pajaro River and other N-rich streams in Denmark (Christensen et al. 1990), Ontario (Hill 1979), and Colorado (Sjodin et al. 1997).

Peeper data also are useful for estimating  $S_{w,[NO_3]}$  values. Several profiles were collected from the lower part of the experimental reach, where strong downward seepage occurs (Fig. 5A–C). One explanation for vertical variations in streambed chemistry in this area is that stream water with high [NO<sub>3</sub><sup>-</sup>] was swept downward into the streambed, where facultative denitrifiers consumed NO<sub>3</sub><sup>-</sup> at different rates throughout the day. Assuming that these microbes became more active when dissolved O<sub>2</sub> levels decreased at

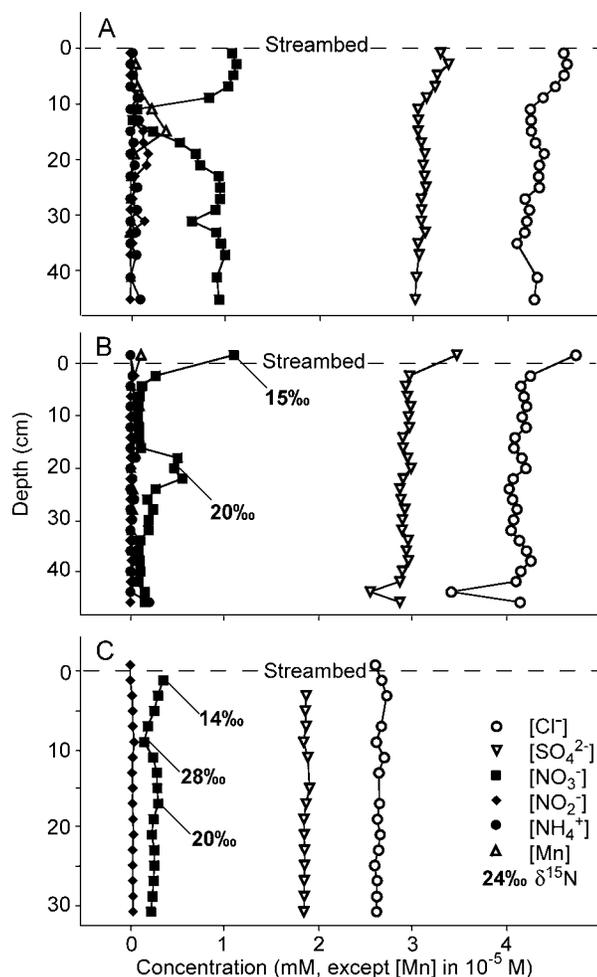


FIG. 5. Porewater profiles near km 8, obtained from peeper (streambed) samplers at km 8.06 on 9 July 2003, when channel discharge was  $\sim 0.2 \text{ m}^3/\text{s}$  (A), at km 8.08 on 9 July 2003 (B), and at km 8.06 on 1 September 2004 (C). The apparent enrichment in  $\delta^{15}\text{N}$  ( $\epsilon_N$ ) is  $-16\text{‰}$  in panel B and  $-16\text{‰}$  in panel C.

night, downward seepage rates of  $\sim 20 \text{ cm/d}$  ( $\sim 2 \times 10^{-6} \text{ m/s}$ ) are implied by the spatial distribution of  $\text{NO}_3^-$  variations in the stream bed. This seepage rate corresponds to length-averaged channel loss at  $\sim 3 \times 10^{-5} \text{ m}^2/\text{s}$ , consistent with differential discharge measurements and observed head gradients (Ruehl et al. 2006). This seepage rate and the magnitude of  $\text{NO}_3^-$  variations correspond to  $U_{[\text{NO}_3]} \approx 2 \mu\text{mol m}^{-2} \text{ s}^{-1}$  at the peeper sampling sites, consistent with the stretch-specific calculations of  $U_{[\text{NO}_3]}$  described above.

#### Mechanisms of $\text{NO}_3^-$ removal

$\text{NO}_3^-$  removal in the Pajaro River may occur via both assimilative and dissimilative pathways. Assimilative uptake (production of new biomass) causes a

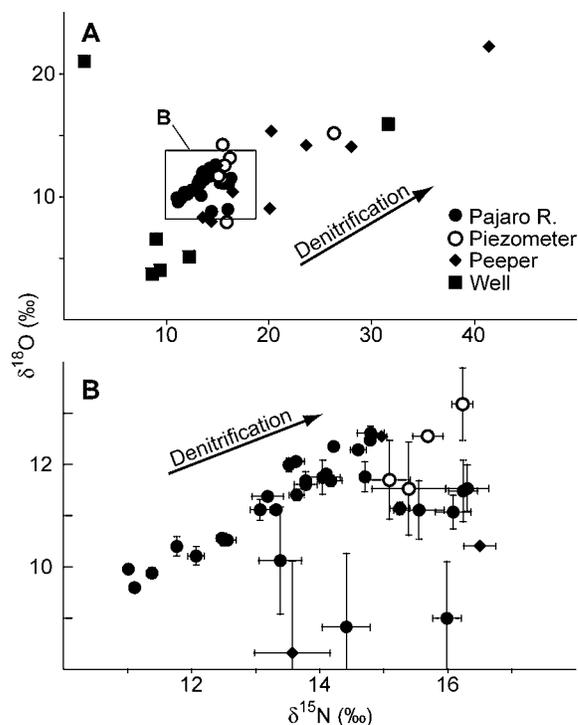


FIG. 6. Stable-isotope ratios of  $\text{NO}_3^-$ , with arrows indicating the relative enrichment expected for denitrification. A.— $\delta^{18}\text{O}$  vs  $\delta^{15}\text{N}$  for all samples analyzed. B.—Magnification of panel A, showing surface-water samples and isotopically similar piezometer and peeper samples.

temporary change in the nature of the aquatic N reservoir, in that N can return rapidly to the stream through degradation and mineralization. In contrast, dissimilative removal through denitrification results in gaseous products that are exported from the system. Assimilative uptake is the dominant  $\text{NO}_3^-$  sink in many pristine stream systems (Duff and Triska 2000), and is likely to be active within the experimental reach of the Pajaro River as well, but denitrification appears to be the dominant  $\text{NO}_3^-$  sink in this system and is primarily responsible for the net loss in  $\text{NO}_3^-$ .

Production of new biomass requires both N and P in an  $\sim 30:1$  atomic ratio for freshwater systems (Hecky et al. 1993). No significant decreases in [SRP] were seen accompanying large decreases in  $[\text{NO}_3^-]$  during diel sampling (Fig. 3A, B), and  $\text{NO}_3^-:\text{TDP}$  removal ratios in the experimental reach observed during synoptic sampling were consistently  $>200$ . These results suggest that biomass production in the Pajaro River stream ecosystem is more strongly P limited than it is N limited, although the extent to which organisms may use P that is not dissolved in the water column (e.g., sorbed onto sediments) is unknown. The mineralization of organic matter would release both dissolved N and P into the river and, thus, would not

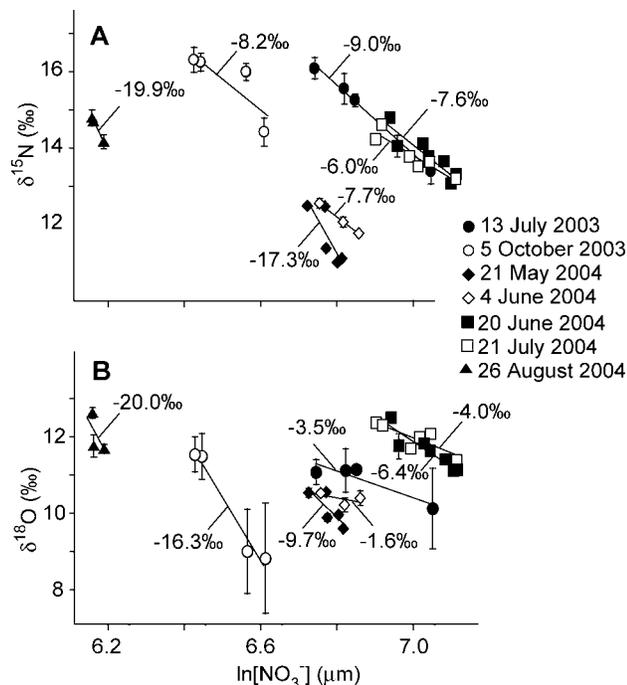


FIG. 7. Apparent fractionation of stable isotopes of NO<sub>3</sub><sup>-</sup> in surface-water samples for δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> vs ln[NO<sub>3</sub><sup>-</sup>] (A) and δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> vs ln[NO<sub>3</sub><sup>-</sup>] (B) for samples collected on 7 dates between 13 July 2003 and 26 August 2004. The slopes of the best-fit lines are the apparent enrichments in δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> ( $\epsilon_{N,surf}$ ) and δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> ( $\epsilon_{O,surf}$ ), respectively.

result in the observed net downstream decrease in NO<sub>3</sub><sup>-</sup> relative to P.

We recognize that SRP is an incomplete measure of changes in total P (Dodds 2003), and acknowledge that assimilative uptake may be responsible for some of the net NO<sub>3</sub><sup>-</sup> removal in this system. However, based on the composite set of physical and chemical observations, assimilative uptake is probably much less important than dissimilative processes (e.g., denitrification) or is balanced by mineralization of organic matter followed by nitrification and, therefore, not responsible for much of the observed downstream removal of NO<sub>3</sub><sup>-</sup>. Other recent riverine studies have concluded that assimilative uptake is more rapid than dissimilative processes (e.g., Mulholland et al. 2004), but generally involves smaller flows and lower solute concentrations than those of the Pajaro River. In addition, the earlier studies tended to focus on gross NO<sub>3</sub><sup>-</sup> removal rather than net NO<sub>3</sub><sup>-</sup> removal, as in the present study.

NO<sub>3</sub><sup>-</sup> isotopic data provide some of the strongest evidence that denitrification is the primary mechanism of NO<sub>3</sub><sup>-</sup> removal in the experimental reach, and variations in observed isotopic enrichment are probably linked to the dynamics of surface–subsurface

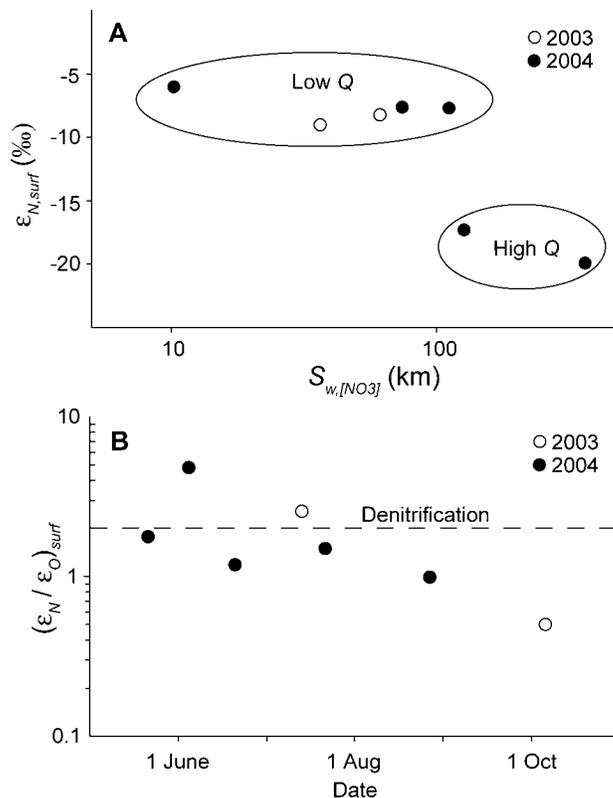


FIG. 8. Trends in apparent enrichment of NO<sub>3</sub><sup>-</sup> stable isotopes in surface water. A.—Enrichment in <sup>15</sup>N ( $\epsilon_{N,surf}$ ) vs NO<sub>3</sub><sup>-</sup> uptake length ( $S_{w,[NO_3]}$ ). B.—Ratio of  $\epsilon_{N,surf}$  to  $\epsilon_{O,surf}$  vs day of the year for 2003 and 2004 samples.

exchange. Numerous studies have explored relationships between NO<sub>3</sub><sup>-</sup> transformations and δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> and δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> in aquatic settings. Enrichments observed in laboratory cultures of denitrifiers and marine settings and aquifers often have been greater in magnitude ( $\epsilon_N$  as low as  $-40\text{‰}$ ) than enrichment observed in streams and coastal sedimentary settings (Lehmann et al. 2003).  $\epsilon_N$  values closer to 0 in many field settings may result from extremely rapid (and complete) denitrification, elevated temperatures, and diffusion limitation of denitrification (Mariotti et al. 1988). Benthic denitrification may be diffusion limited in the absence of significant advective exchange between sediments and surface water (Brandes and Devol 1997, Sebilo et al. 2003, Sigman et al. 2003, Lehmann et al. 2004). In one set of laboratory experiments, diffusion-limited denitrification indicated  $\epsilon_N = -3.7\text{‰}$ , whereas denitrification with more extensive water–sediment interaction resulted in  $\epsilon_N = -18\text{‰}$  (Sebilo et al. 2003). If diffusion limitation is sufficiently strong, enrichment can be driven close to 0 (Brandes and Devol 1997).

In surface-water samples from the Pajaro River,  $\epsilon_N$

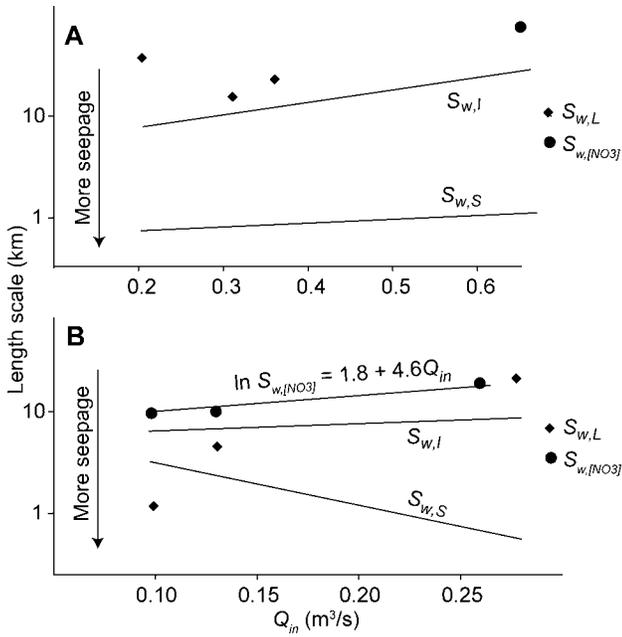


FIG. 9.  $NO_3^-$  uptake lengths ( $S_{w,[NO_3]}$ ) plotted as a function of channel discharge for injections at km 0.00 (A) and km 7.67 (B). Included are observed trends in inflow lengths ( $S_{w,I}$ ; the stream length required for inflow of tracer-free water to equal channel discharge), storage exchange lengths ( $S_{w,S}$ ; the average distance traveled by a water molecule before entering an adjacent storage zone), and channel loss lengths ( $S_{w,L}$ ; the distance at which discharge would equal 0 given observed seepage loss).

values were often  $\sim 2 \times \epsilon_O$  values (Fig. 6), consistent with results from many field studies (e.g., Cey et al. 1999, Lehmann et al. 2003). Downstream enrichment in  $\delta^{15}N-NO_3^-$  in the experimental reach occurred in 2 distinct regimes: a high- $Q$  regime in which reduction of  $[NO_3^-]$  was modest, and a low- $Q$  regime in which reduction of  $[NO_3^-]$  was more intense. During high- $Q$  periods,  $\epsilon_{N,surf}$  associated with the downstream reduction in  $[NO_3^-]$  was  $-17\%$  to  $-20\%$  (Fig. 8A), as observed in other river and shallow marine systems (e.g., Brandes and Devol 1997, Kellman and Hillaire-Marcel 1998, Dhondt et al. 2003, Sebilo et al. 2003). In contrast, during low- $Q$  periods,  $\epsilon_{N,surf}$  was  $-6\%$  to  $-9\%$  (Fig. 8A).

Although diffusion-limited denitrification may occur in this system, it is not a satisfactory explanation for the bimodal enrichment pattern of  $^{15}N$ . The local influence of diffusion limitation on isotopic fractionation during denitrification is apparent in results from one set of peeper samples recovered at km 2.72 (Fig. 4B). Most other streambed chemical profiles were consistent with rapid vertical fluid advection, but strong gradients in conservative solutes such as  $Cl^-$  from km 2.72 indicated more diffusive conditions, and

enrichment in  $NO_3^-$  isotopes was weak ( $\epsilon_N \approx -5\%$  and  $\epsilon_O \approx -3\%$ ). However, diffusion-limited denitrification is unlikely to contribute significantly to overall  $NO_3^-$  removal along the reach. Based on the diffusion coefficient for  $NO_3^-$  (Li and Gregory 1974) and the geometry of the stream, even if the  $[NO_3^-]$  decreased from 1 to 0 mM across the upper 2 cm of the entire stream-streambed interface of the reach, the daily  $NO_3^-$  removal rate would be  $< 3$  kg/d,  $\sim 1\%$  of that observed.

Instead, we propose that the bimodal pattern of enrichment in  $^{15}N$  is caused by variations in the efficiency of denitrification, i.e., the fraction of  $NO_3^-$  that is removed when denitrification occurs, in association with differences in surface-subsurface water exchange. This variation in efficiency can be quantified by considering an idealized 2-box model representing surface and subsurface regions (Fig. 10A). For steady-state flow conditions, we use observed changes in surface  $[NO_3^-]$  and  $\delta^{15}N-NO_3$  ( $\Delta NO_{3,surf}$  and  $\Delta \delta^{15}N_{surf}$ , respectively) and the subsurface isotopic enrichment factor for  $\delta^{15}N-NO_3$  ( $\epsilon_{N,sub} \approx -20\%$ ) to calculate the resulting apparent enrichment in surface water ( $\epsilon_{N,surf}$ ). If subsurface denitrification is extremely efficient, there will be little fractionation observed in surface water (Fig. 10B), even if there is a large reduction in  $[NO_3^-]$ , because little  $NO_3^-$  will return from the subsurface ( $\epsilon_{N,surf} \rightarrow 0$ ). At the other extreme, if only a small fraction of the  $NO_3^-$  that is exchanged with the subsurface is denitrified, the enrichment apparent in surface water will approach that in the subsurface ( $\epsilon_{N,surf} \rightarrow \epsilon_{N,sub}$ ).

During high- $Q$  conditions on the Pajaro River, subsurface microbes can be selective during denitrification, consistent with observed surface enrichment of  $-17$  to  $-20\%$ . During low- $Q$  conditions, subsurface denitrification efficiency would be relatively high, forcing microbes to be less selective, and resulting in lower enrichment of residual  $^{15}N-NO_3$  in surface water (Fig. 10B). Peeper profiles from the lower portion of the reach support this interpretation:  $NO_3^-$  removal in the subsurface was more complete when discharge was  $\sim 0.2$   $m^3/s$  and surface fractionation was relatively weak (Fig. 5A, B) than when  $Q$  was  $\sim 0.4$   $m^3/s$  and  $\epsilon_{N,surf} \approx -20\%$  (Fig. 5C).

Based on this model and geochemical observations shown earlier, we estimate that during high- $Q$  conditions, 25 to 45% of  $NO_3^-$  in the main channel exchanges with the subsurface, where it is inefficiently denitrified. This exchange lowers  $[NO_3^-]$  of surface water by just 5 to 10%, and shifts  $\delta^{15}N-NO_3$  values such that  $\epsilon_{N,surf} = -17\%$  to  $-20\%$  (Fig. 10B). In contrast, during low- $Q$  conditions, 35 to 45% of  $NO_3^-$  in the channel exchanges with the subsurface

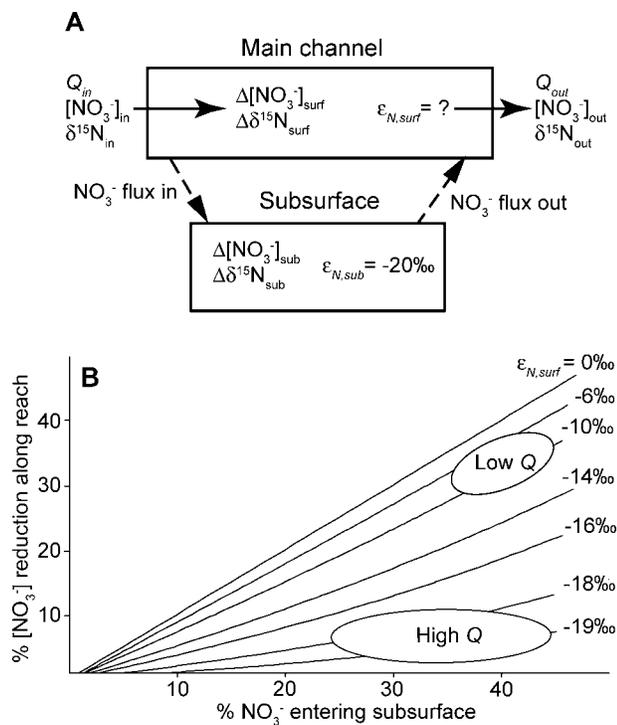


FIG. 10. Box model and calculations of surface–subsurface exchange and associated denitrification. A.—Conceptual configuration of the box model. Water passes along the main channel with constant discharge. Denitrification occurs in subsurface storage zones, with a resulting Rayleigh isotopic enrichment ( $\epsilon_{N,sub}$ ) of  $-20\text{‰}$ . This denitrification causes a decrease in surface  $[NO_3^-]$  ( $\Delta[NO_3^-]_{surf}$ ), with an apparent fractionation of  $^{15}N$ - $NO_3^-$  ( $\epsilon_{N,surf}$ ). B.—Downstream surface enrichment in  $^{15}N$ - $NO_3^-$  (curves of equal  $\epsilon_{N,surf}$ ), assuming a fraction of  $NO_3^-$  entering the reach is subject to denitrification in the subsurface. Regions corresponding to low discharge (low- $Q$ ) and high discharge (high- $Q$ ) conditions are shown. See text for discussion.

and is efficiently denitrified, lowering  $[NO_3^-]$  of surface water by  $\sim 30\%$ , and shifting surface  $\delta^{15}N$ - $NO_3^-$  values such that  $\epsilon_{N,surf} = -6\text{‰}$  to  $-9\text{‰}$  (Fig. 10B). This scenario contrasts with that interpreted for many more pristine stream systems, where the presence of C or nutrients appears to provide the primary limitation on denitrification. In the experimental reach of the Pajaro River, the extent of surface–subsurface exchange relative to  $Q$  appears to be the most important control on denitrification, particularly when apparent  $NO_3^-$  removal rates are highest. If stream water lost to underlying aquifers is subject to similar biogeochemical processes during these times, then up to  $\sim 75\%$  of the  $NO_3^-$  in recharging surface waters, or  $\sim 250$  kg N/d, would be removed before entering underlying aquifers. This quantity should be considered an upper limit because it is unlikely that recharging water is

completely denitrified. A lower limit for the percentage of  $NO_3^-$  removed from recharging waters would be  $\sim 30\%$ , or  $\sim 100$  kg N/d, because all recharging water passes through the streambed and only a fraction of surface water enters the streambed.

The downstream enrichment in  $^{18}O$ - $NO_3^-$  was not as consistent as that for  $^{15}N$ - $NO_3^-$ . It varied over a large range and did not fall into distinct regimes. However, the ratio of  $\epsilon_{N,surf}$  to  $\epsilon_{O,surf}$  decreased consistently with time, from  $\sim 2$  (consistent with denitrification) to  $\sim 0.5$  (Fig. 8B). One explanation for this trend is that nitrification becomes increasingly important as the water year progresses; a subset of diel observations suggest that there may be an internal source for  $NO_3^-$  late in the water year along parts of the experimental reach (Fig. 3C). The coupling of denitrification to nitrification could result in the incorporation into residual  $NO_3^-$  of isotopically heavy atmospheric  $O_2$ , which has  $\delta^{18}O = 23.5\text{‰}$  (Keeling 1995), or light N (if an  $NH_4^+$  source were depleted in  $^{15}N$ ). Either or both of these effects could result in a decrease in  $(\epsilon_N/\epsilon_O)_{surf}$ . If nitrification is important along the experimental reach, then gross denitrification rates in this system may be considerably greater than estimates based on the net decrease in  $[NO_3^-]$ . Additional work along the experimental reach will be required to assess the importance of nitrification relative to denitrification and to determine the cause for high variability in  $\epsilon_{O,surf}$ .

In conclusion, during the 2<sup>nd</sup> (dry) half of the water year,  $[NO_3^-]$  decreased consistently along an 11.42-km experimental reach of the Pajaro River by  $\sim 30\%$ , at a time when there was a significant loss of channel discharge and extensive surface–subsurface exchange. The observed decrease in  $[NO_3^-]$  and channel discharge along this reach represent an absolute  $NO_3^-$  sink of  $\sim 50\%$ , making up a net removal rate of 200 to 400 kg/d N- $NO_3^-$ . The associated  $S_{w,[NO_3]}$  and  $U_{[NO_3]}$  were  $37 \pm 13$  km and  $0.5 \mu\text{mol m}^{-2} \text{s}^{-1}$ , respectively.

High-resolution (temporal and spatial) sampling shows that most of the  $NO_3^-$  loss occurs along the lower part of the reach, which is also the stretch along which seepage loss and surface–subsurface exchange are most rapid. Stretch-specific values of  $S_{w,[NO_3]}$  from the lower part of the reach were as low as  $\sim 10$  km. Porewater chemical profiles from the lower part of the reach suggest that denitrification within the streambed can occur at rates consistent with rates derived from downstream changes in  $[NO_3^-]$  and channel geometry.

Downstream enrichments in  $^{15}N$ - and  $^{18}O$ - $NO_3^-$  suggest that denitrification is the primary  $NO_3^-$  sink in the reach during the times studied. A box model illustrates how stream  $\delta^{15}N$ - $NO_3^-$  may be controlled by changes in denitrification efficiency in the shallow

streambed. Differences in denitrification efficiency could explain variations in  $\varepsilon_{N,surf}$  during the water year. When discharge is greater, denitrification is least efficient and the isotopic fractionation apparent in surface water is greatest. When discharge is lower, denitrification is more efficient, resulting in a lower apparent isotopic fractionation. If  $\text{NO}_3^-$  lost via net channel loss of water is similarly denitrified, this loss could account for the removal of 30 to 75% of  $\text{NO}_3^-$  recharging shallow aquifers, or 100 to 250 kg N/d. Contemporaneous nitrification along the experimental reach, as inferred from enrichment of  $^{18}\text{O}-\text{NO}_3^-$  relative to  $^{15}\text{N}-\text{NO}_3^-$ , may lead to an underestimate of gross denitrification rates within this system.

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