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Retention of NO_3^- in an upland stream environment: A mass balance approach

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Abstract. Models of the effects of atmospheric N deposition in forested watersheds have not adequately accounted for the effects of aquatic and near-stream processes on the concentrations and loads of NO_3^- in surface waters. This study compared the relative effects of aquatic and near-stream processes with those from the terrestrial ecosystem on the retention and transport of NO_3^- in two contrasting stream reaches of the Neversink River, a forested watershed in the Catskill Mountains of New York that receives among the highest load of atmospheric N deposition in the northeastern United States. Stream water samples were collected every two hours and ground-water and tributary samples were collected daily at base flow conditions during four 48-hour periods from April to October 1992, and NO_3^- mass balances were calculated for each site. Results indicated diurnal variations in stream NO_3^- concentrations in both reaches during all four sampling periods; this is consistent with uptake of NO_3^- by photoautotrophs during daylight hours. Mass-balance results revealed significant stream reach losses of NO_3^- at both sites during all sampling periods. The diurnal variations in NO_3^- concentrations and the retention of NO_3^- relative to terrestrial contributions to the stream reaches were greater downstream than upstream because physical factors such as the head gradients of inflowing ground water and the organic matter content of sediment are more favorable to uptake and denitrification downstream. The mass retention of NO_3^- increased as the mean 48-hr stream discharge increased at each site, indicating that the responsible processes are dependent on NO_3^- supply. Low stream temperatures during the April sampling period, however, probably reduced the rate of retention processes, resulting in smaller losses of NO_3^- than predicted from stream discharge alone. Water samples collected from the stream, the hyporheic zone, and the alluvial ground water at sites in both reaches indicated that the net effect of hyporheic processes on downstream NO_3^- transport ranged from conservative mixing to complete removal by denitrification. The relative effects of biological uptake and denitrification as retention mechanisms could not be quantified, but the results indicate that both processes are significant. These results generally confirm that aquatic and near-stream processes cause significant losses of NO_3^- in the Neversink River, and that the losses by these processes at downstream locations can exceed the NO_3^- contributions to the stream from the terrestrial environment during summer and fall base-flow conditions. Failure to consider these aquatic and near-stream processes in models of watershed response to atmospheric N deposition could result in underestimates of the amount of NO_3^- leaching from forested ecosystems and to an inability to unequivocally relate geographic differences in NO_3^- concentrations of stream waters to corresponding differences in terrestrial processes.

Introduction

The Catskill Mountain region of New York State receives nitrogen (N) from atmospheric sources at an annual rate of 10 to 15 kg/ha; this is among the highest rates of atmospheric N deposition in the northeastern United States (Ollinger et al. 1993). Increasing NO_3^- concentrations in upland streams in the Catskills during the past two decades suggest that upland watersheds may be approaching N saturation, wherein inputs of N exceed the biological demand (Murdoch & Stoddard 1993). Increases in NO_3^- concentrations in forested, headwater streams that receive large atmospheric N loads are of concern because the accompanying acidity and attendant high aluminum concentrations can adversely affect aquatic organisms (Stoddard 1994). Nitrate concentrations in surface waters generally increase with increasing atmospheric N deposition loads in watersheds that are not impacted by urban or agricultural land uses (Stoddard 1994). Differences in stream NO_3^- concentrations in watersheds receiving equal atmospheric N loads have been attributed to differences in: (1) the N demand of forest vegetation (Ohrui & Mitchell 1997), (2) hydrologic factors such as storage (Creed et al. 1996; Burns et al. 1997), and (3) land-use history (Aber et al. 1997).

Most research on the effects of atmospheric N deposition on upland watersheds has failed to consider the role of aquatic and near-stream processes (Aber et al. 1991; Stoddard 1994), as have the most widely applied watershed-acidification models (Christopherson et al. 1982; Cosby et al. 1985). This paper addresses this potential oversight by separating the NO_3^- contributions to surface waters from the terrestrial environment with those derived from aquatic and near-stream processes through a mass balance analysis of NO_3^- in a Catskill Mountain river.

Nitrogen is a macronutrient in aquatic ecosystems that is necessary for structural synthesis in bacteria, fungi, algae, and macrophytes (Allan 1995). Although phosphorus is generally considered the growth limiting nutrient in freshwater (Allan 1995), nitrogen (Triska et al. 1984; Holmes et al. 1996), or nitrogen and phosphorus (Rosemond et al. 1993) can be growth limiting in some aquatic ecosystems. Nitrogen demand is generally high relative to its supply in a typical stream or river (Vallentyne 1974); thus, N concentrations in running waters are strongly affected by aquatic uptake and other biogeochemical cycling processes. Nitrogen is retained in a wide variety of stream and river environments (Hill 1981; Cooper 1990; Christensen et al. 1990: Triska et al. 1990a; Mulholland 1992), and one estimate is that about 40% of riverborne N is lost through denitrification before it reaches the oceans (Seitzinger 1988).

The transport of nutrients in running waters is strongly affected by the mixing of stream water with ground water in the near-stream environment. The boundary between the terrestrial and aquatic ecosystem is frequently referred to as the hyporheic zone (Hynes 1983), where depletion of oxygen can result in a complex series of aerobic and anaerobic biogeochemical processes as waters mix. The hyporheic zone can vary in width from a few mm (Christensen et al. 1990) to tens of meters (Triska et al. 1990b). The extent of N transformations in a stream and its hyporheic zone depends on several physical and chemical factors, including: the duration and intensity of light (Triska et al. 1983; Nielsen et al. 1990), substrate grain size (Hill 1983), hydraulic gradient (Valett et al. 1994; Findlay 1995), availability of labile carbon (Faafeng & Roseth 1993), concentrations of N species (Hill 1981; Holmes et al. 1996), and stream velocity (Horner & Welch 1981). The hyporheic zone has been shown to affect the downstream movement of N through (1) the physical storage and release of water (Triska et al. 1989; Triska et al. 1990a), (2) denitrification (Christensen et al. 1990), and (3) nitrification (Triska et al. 1990b; Holmes et al. 1996). Denitrification and nitrification can occur in close proximity within stream sediments and can shift at a given location in time; thus, the hyporheic zone can serve as either a net source or sink for stream N, depending on which process is dominant at a given time or location. Many studies have reported that denitrification, which results in a net loss of NO_3^- from the stream, is the predominant hyporheic process that affects downstream transport (Kaushik et al. 1975; Van Kessel 1977; Hill 1981; Christensen et al. 1990), but others have shown that nitrification, which results in a net addition of NO_3^- to the stream, can be the predominant hyporheic process (Triska et al. 1990a; Valett 1994). Nitrogen transport in streams can also be affected by uptake in aquatic macrophytes (Casey 1977; Cooper 1990), or uptake by autotrophic and heterotrophic epilithic communities (Kaushik et al. 1975; Triska et al. 1989; Mulholland 1992). The relative importance of these N cycling processes in stream ecosystems can be difficult to determine because many transformations can occur simultaneously. The net effects of these aquatic and hyporheic processes on stream N transport, however, can be assessed from mass balances developed for individual stream reaches.

Most studies of stream-N movement have not compared the N contribution from the terrestrial ecosystem to the effects of aquatic and hyporheic processes on mass balances of N in the stream itself (Christensen et al. 1990; Triska et al. 1990a, b). The availability of N for processing in streams depends ultimately on the amount of N that is transported from terrestrial and atmospheric environments to the stream, but the N-processing capacity of aquatic ecosystems (including the hyporheic zone) relative to the rate of N supply from the terrestrial and atmospheric sources is not well known. Failure to consider the effects of the aquatic ecosystem on the temporal and spatial patterns of NO_3^- concentrations could result in inaccurate models of watershed N cycling and incorrect classifications of the N-saturation status of watersheds. The objective of this study was to: (1) compare the relative effects of aquatic and hyporheic processes with the contribution from the terrestrial ecosystem through calculating mass balances of NO_3^- in two contrasting stream reaches of the Neversink River at base flow during four different periods in the growing season, and (2) identify the principal processes that affect downstream NO_3^- movement in these reaches.

Study site

The upper Neversink River is a clear, high-gradient mountain river that flows about 30 km along two branches from its source on Slide Mountain (1274 m elevation) to its mouth at the Neversink reservoir (445 m elevation), a supply of water for New York City (Figure 1). Two stream reaches were chosen for study on the West Branch – one is a 586 m-long upper reach beneath a closed canopy of deciduous trees; the other is a 1022 m-long lower reach with mainly meadow and open canopy. The reaches were chosen to represent the range of light and stream-gradient conditions typical of the Neversink River above the reservoir. Additional characteristics of the two stream reaches are listed in Table 1. The Neversink River generally has total phosphorus concentrations of less than 0.01 mg/L, a level below which lakes are classified as oligotrophic (Wetzel 1983; although defining trophic status for streams and rivers may be invalid (Hynes 1969). The low productivity of this river is reflected by the high water clarity and the relatively thin epilithic community. A thin layer of epilithon coats the rocks on the bottom of the upper reach, whereas the lower reach has a thicker coating of epilithon containing observable periphyton. Additionally, the upper reach has submerged or partially submerged colonies of liverwort growing on bedrock.

The Neversink River watershed is underlain by nearly flat-lying Devonian sandstone and conglomerate with interbedded shale and siltstone, overlain by till deposits and alluvium (Rich 1934; Buttner 1977). The till derived largely from the most recent glaciation, is thicker in stream valleys than on the steep upper slopes. Soils in the Neversink watershed are classified as inceptisols, and generally range from 0.1 to 1.5 m in thickness. Stream-channel material consists of sand and gravel that has been reworked extensively by alluvial processes. The alluvium is generally only a few meters wide in headwater streams, but widens to several hundred meters downstream. The stream flows directly on exposed and submerged bedrock in parts of the upper reach, but little bedrock is evident in the lower reach.

Vegetation below an elevation of 1000 m is primarily northern hardwood forest in which three tree species are predominant – american beech

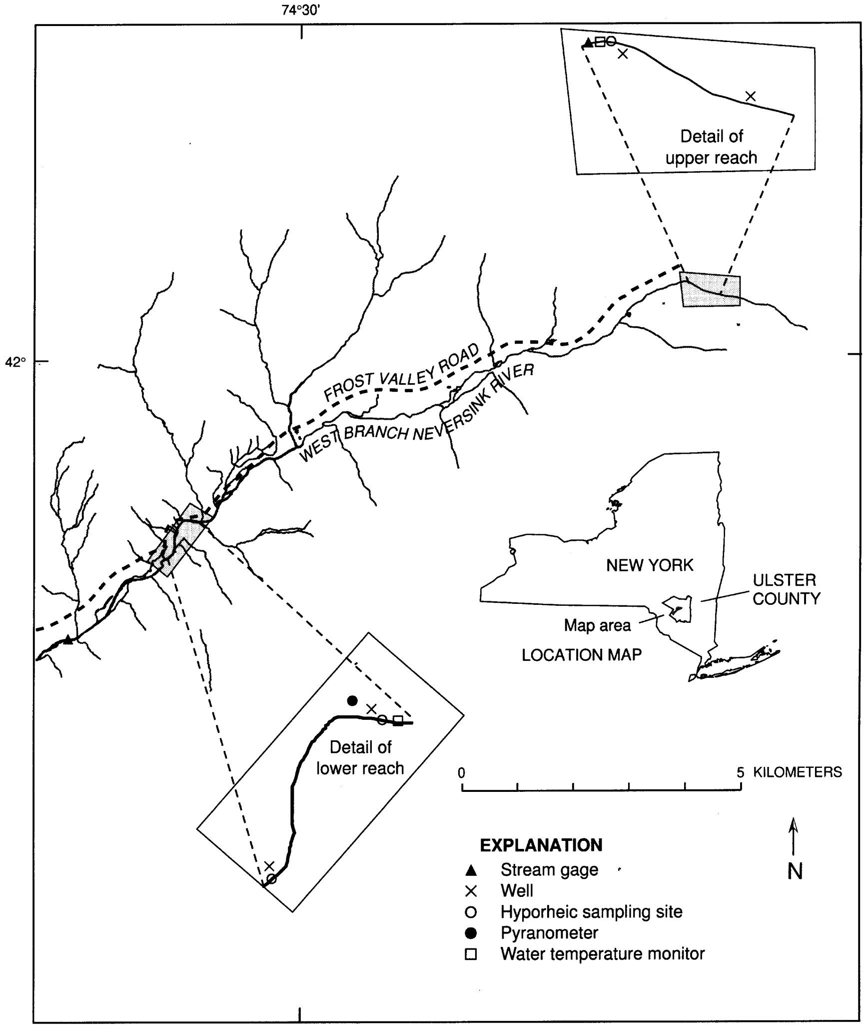


Figure 1. Locations of the sampling sites in the two stream reaches studied on the West Branch Neversink River.

(*Fagus grandifolia*), sugar maple (*Acer saccharum*), and yellow birch (*Betula alleghaniensis*). The predominant species at higher elevations are red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*). The forests of the Neversink watershed, like others in the Catskill region, were cut extensively during the 1800's, but those above 850 m elevation generally remain free from significant human disturbance.

Table 1. Physical characteristics of the two stream reaches on the West Branch Neversink River. Values listed as ranges represent those measured during the four mass balance experiments in 1992.

Characteristics	Upper stream reach	Lower stream reach
Length (m)	586	1021
Depth range at upstream end (m)	0.1–0.3	0.3–0.7
Width range at upstream end (m)	0.8–2.5	13.4–17.8
Velocity range at upstream end (m/s)	0.1–0.3	0.1–0.3
Drainage area at upstream end (km^2)	1.67	54.6
Stream gradient	0.1	0.0095
Tree canopy	Closed	Open
Streambed sediment	Sand and gravel (some bedrock)	Sand and gravel

Methods

Field

Samples of stream water were collected by automated samplers for chemical analysis at 2-hour intervals at the upstream and downstream ends of each reach, and daily at tributaries, springs, and in wells during four 48-hour periods in early spring (April 14–16, 1992), late spring (June 2–4, 1992), midsummer (July 28–30, 1992), and fall (Sept. 29–Oct. 1, 1992). Samples were removed from the automated sampler daily and stored at 4 °C until they were returned to the laboratory. The sampling periods generally coincided with base-flow conditions, except for July 29, when 1.1 cm of rain fell during a thunderstorm.

Water temperature was recorded by an automated system at 15-min intervals during the four sampling periods. The instrument and thermocouple probes were calibrated according to procedures described by Gordon & Katzenbach (1983). Incident light energy flux was measured with a silicon pyranometer placed in an open field near the upstream end of the lower reach.

Two wells were installed near the stream in each reach (Figure 1). The wells were cased with 32-mm i.d. stainless steel, and had 430 mm long screens at the bottom. The wells were placed far enough from the stream to be outside the hyporheic zone, but close enough to obtain representative samples of ground water before it entered the hyporheic zone. The wells in the upper reach were placed so the bottoms were in sandy alluvium at depths of about 600 mm, and a minimum of 1 m from the stream edge (although this distance varied with flow conditions). The steep rocky slopes that rise abruptly from either stream bank in the upper reach prevented the placement of wells farther than about 1 m from the stream. The wells in the lower reach were placed so the bottoms were in sandy alluvium at depths of about 1 m, and 2 meters from the stream edge. Ground-water head was higher than the stream level near the wells in both reaches, indicating that the stream was gaining flow from the shallow ground-water system.

Samples of ground water and of stream water mixed with ground water in the hyporheic zone were collected with a minipiezometer (Winter et al. 1988) at depths of 10 to 400 mm below the streamwater/sediment interface. Each set of 3 to 6 samples were collected at two locations in the lower stream reach (one location was sampled twice), and at one location in the upper stream reach on September 29 and October 13, 1994. Streambed sediment samples were collected at the same three sites on October 13, 1994 for analysis of denitrification potential.

Laboratory

Samples were filtered through 0.4-μm membrane filters upon arrival at the laboratory and stored at 4 °C until analysis. Nitrate, Cl^-, and SO_4^{2-} were analyzed by ion chromatography, and NH_4^+ was analyzed by the phenolate method in an automated spectrophotometric procedure according to methods described in Lawrence et al. (1995). Data quality objectives for precision and accuracy of these analyses are 10% (coefficient of variation), and these objectives were met more than 95% of the time during the study period (Lincoln et al. 1996).

The denitrification potential of stream sediment was measured in the laboratory by the acetylene-block technique as described in Duff & Triska (1990), except that a larger percentage of the headspace was removed from the flasks during gas sampling, necessitating a head-space-volume correction to calculate N_2O concentration. Analyses reported herein are in nmol N_2O/mL sediment slurry/hr. Seven replicate samples from each site were analyzed, and the mean values are reported here.

Mass-balance calculations

Mass balances of NO_3^-, Cl^- (upper reach), and SO_4^{2-} (lower reach) were calculated according to the following:

$$m_d = m_u + m_t + m_g + \Delta m \tag{1}$$

where

m_d = mass of constituent at downstream end of reach
m_u = mass of constituent at upstream end of reach

m_t = mass of constituent from tributaries
m_g = mass of constituent from ground water
Δm = gain or loss of mass along reach

For conservatively transported constituents such as Cl^-, the following is expected:

$$m_d - (m_u + m_t + m_g) = 0, \text{ and } \Delta m = 0 \tag{2}$$

whereas, for nonconservatively transported constituents the following would be expected:

$$m_d - (m_u + m_t + m_g) = \Delta m \tag{3}$$

The Δm value was assumed to represent changes resulting from aquatic and hyporheic processes, and this value was compared to the NO_3^- contribution to the reach from the terrestrial ecosystem as follows:

$$[\Delta m/(m_t + m_g)] \times 100 = M_a \tag{4}$$

where

$m_t + m_g$ = terrestrial contribution to stream reach
M_a = change in mass of constituent along stream reach, expressed as a percentage of the terrestrial contribution.

The Δm value was also compared to the mass of NO_3^- transported by the stream at the upstream end of each reach as follows:

$$\Delta m/m_u \times 100 = M_b \tag{5}$$

where

M_b = change in mass of constituent along stream reach expressed as a percentage of the upstream contribution.

A stream may gain or lose NO_3^- through the wide variety of biogeochemical processes discussed previously. If these processes result in a net removal of NO_3^- from the stream, then Δm will be negative, whereas if these processes result in a net addition of NO_3^- to the stream, then Δm will be positive. Mass balances of Cl^- were compared with those of NO_3^- to assess the accuracy of the water balance. Chloride is generally not in high demand as a nutrient and is not affected significantly by biogeochemical processes; therefore, its Δm value should be zero. This assumption was valid for the upper reach, but not the lower reach because salt is applied to the road that follows the stream throughout the length of the reach (Figure 1). Inputs of Cl^- to this reach could not be calculated because no wells were installed in the area where the road is closest to the river; therefore, SO_4^{2-} was used to check the accuracy of the water balance in this reach. Biological uptake is not likely to significantly lower SO_4^{2-} concentrations because the supply of sulfur from atmospheric deposition exceeds its biological demand in the Northeast (Mitchell et al. 1992). Adsorption of SO_4^{2-} in the alluvial sand and gravel that underlies the stream channel also is unlikely to affect SO_4^{2-} concentrations because of the low surface area and lack of oxide minerals and organic matter in this material. Sulfate may be lost by reduction to S^{2-} in the hyporheic zone, but chemical profiles of stream-sediment pore water collected during this study indicate that SO_4^{2-} reduction only minimally affects stream-reach mass balances.

The stream load at the upstream (m_u) and downstream (m_d) end of each reach was calculated at 15-min intervals throughout each 48-hr mass balance period as the product of stream concentration and stream volume. The concentration of each sample collected was assumed to be equivalent to the concentration of that constituent in the stream from 1 hr before sample collection to 1 hr after sample collection. Stream stage from gages at the downstream end of the upper reach and about 1500 m downstream of the lower reach (Figure 1) was used to estimate discharge every 15 minutes. These estimated discharges were assumed to represent the 15 min between the succeeding and preceding 7.5 minutes and were multiplied by time to obtain a 15 min volume (v_u = volume at upstream end of reach, and v_d = volume at downstream end of reach). A relation was developed between stream discharge measured by a current meter (Rantz and others 1982) at the upstream end of the upper reach and discharge from the gage at the downstream end of that reach based on 15 measurements taken during the study:

$$\text{gaged discharge (m}^3\text{/s)} = 1.437 \times \text{measured upstream discharge} - 0.000302;\ r^2 = 0.96,$$

and discharge was then estimated at the upstream end of the upper reach for every 15 min interval. A corresponding relation for the lower reach was developed between gaged discharge downstream of the reach and measured discharge at both the upstream and downstream ends of the reach based on 12 measurements taken during the study at each site:

$$\text{gaged discharge (m}^3\text{/s)} = 1.18 \times \text{measured upstream discharge} + 0.121;\ r^2 = 0.99,$$

$$\text{gaged discharge (m}^3\text{/s)} = 1.08 \times \text{measured downstream discharge} + 0.0918;\ r^2 = 0.99$$

Discharges were then estimated for both ends of the reach for every 15 min interval.

The mass contribution (m_t) to each reach from tributaries on 3 dates during each sampling period (each 48-hr sampling period occurred over 3 dates) was calculated as the concentration in the daily tributary sample multiplied by the tributary volume from 1 daily flow measurement (as close to where the tributary entered the stream as the measurement could be made), by assuming that flow and concentration were constant for each date. Most of the tributaries entering either reach are ground-water seeps that reach the land surface close to the stream channel (especially in the upper reach, because stream banks are steep). No perennial streams enter the upper reach, and two enter the lower reach.

The ground-water mass contribution (m_g) was calculated by multiplying the volume of ground-water inflow by the mean daily concentration from the two wells along each reach. The volume of ground-water inflow was calculated as follows:

$$v_g = v_d - (v_u + v_t) \tag{6}$$

where

v_g = volume of ground water inflow
v_d = volume of stream water at downstream end of reach
v_u = volume at of stream water at upstream end of reach
v_t = volume of tributary inflow

Results and discussion

The two most likely causes of stream NO_3^- retention at base flow in the two reaches were: (1) denitrification and subsequent degassing of N_2 in the hyporheic zone, and (2) uptake by the epilithic communities (and by liverwort in the upper reach). The most likely source of stream NO_3^- increases at base flow in the two reaches (in addition to the terrestrial contribution defined previously) was mineralization and nitrification in the hyporheic zone. The relative effects of these processes were inferred from diurnal patterns in stream NO_3^- concentrations, mass balances for NO_3^-, depth profiles of NO_3^- and NH_4^+ concentrations through the hyporheic zone, and incubations of streambed sediment to measure denitrification rates.

Table 2. Diurnal changes in stream NO_3^- concentrations in the two reaches from 4:00 PM to 4:00 AM for the eight 24-hour periods in which samples were collected. The change is expressed as both an absolute difference in concentration (μmol/L) and as a percentage of the 4:00 PM concentration.

		Change in concentration			
		First 24-hours		Second 24-hours	
Reach	Month	μmol/L	Percent	μmol/L	Percent
Upper	April	0.2	1.0	1.3	5.9
	June	1.7	18.3	0.3	2.8
	July	1.0	10.5	0.6	5.7
	Sept.	0.7	10.1	1.0	13.3
Lower	April	4.0	21.8	2.8	16.7
	June	2.9	32.2	2.5	24.5
	July	2.0	13.8	0.5	3.0
	Sept.	1.3	13.7	2.1	21.4

Temporal changes in stream NO_3^- concentrations

Stream NO_3^- concentrations in both reaches generally showed diurnal fluctuations, indicating that uptake by aquatic photoautotrophs has a significant effect on NO_3^- concentrations in the Neversink River (Figure 2). Nitrate concentrations were generally lowest in the late afternoon and highest in the early morning before sunrise during the majority of the eight diurnal cycles that were monitored in both stream reaches (increases in NO_3^- concentrations late in the afternoon of July 29 were associated with a rain storm). The diurnal change, determined by subtracting the stream NO_3^- concentration at 4 a.m. (generally closest to the time when the maximum NO_3^- concentration occurred) from the concentration at 4 p.m. (generally closest to the time when the minimum NO_3^- concentration occurred) on the previous day, was generally greater in the lower reach than in the upper reach. Diurnal fluctuations in NO_3^- concentrations in the upper reach were similar during all four sampling periods, but those in the lower reach were greatest during April. Diurnal variability in the upper reach ranged from 1.0 to 18.3% (of the 4 p.m. concentration), with a mean of 8.4% for the eight 24-hour sampling periods (Table 2). The lower reach had greater variability, ranging from 3.0 to 32.2% with a mean of 18.4%. The greatest diurnal variability in the lower reach was in June, and in the upper reach was in September.

Diurnal fluctuations in stream NO_3^- concentrations frequently differed significantly on consecutive days. For example, stream NO_3^- concentrations in the upper reach varied by 18.3% during the first 24 hours of the June sampling period, but only 2.8% during the second 24 hours. Similarly, stream NO_3^-

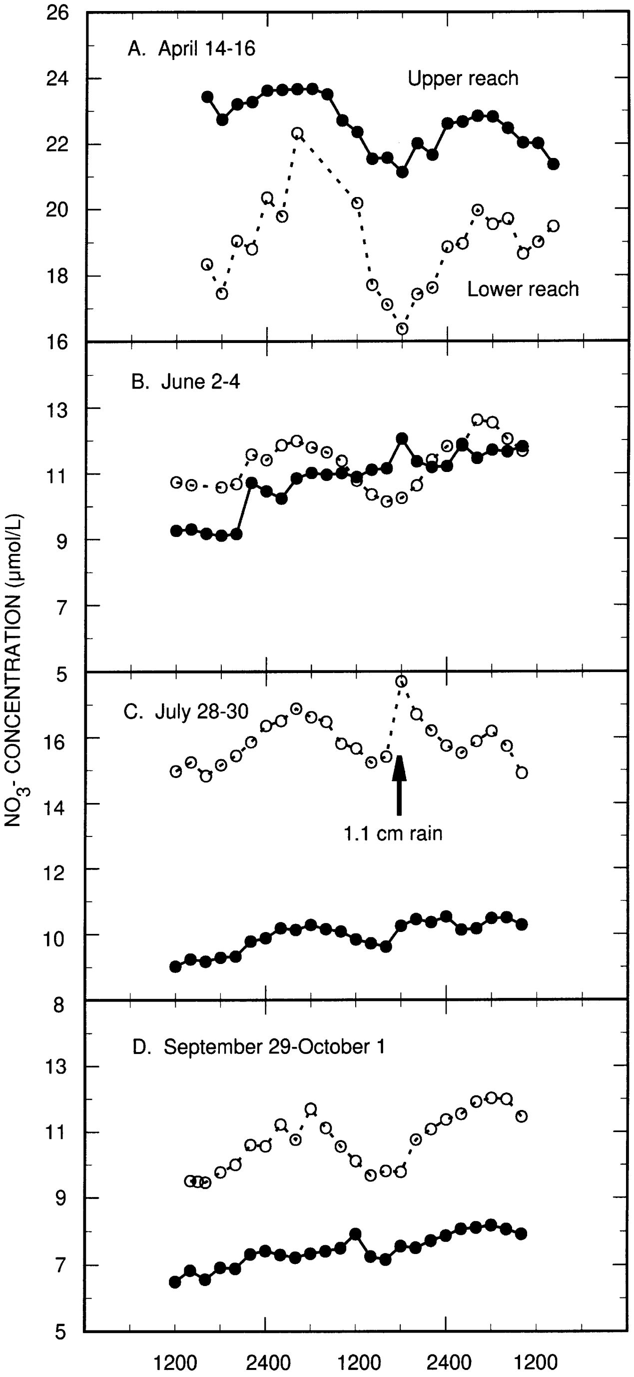


Figure 2. Nitrate concentrations at downstream end of the upper stream reach and at upstream end of the lower stream reach during the four 48-hr sampling periods in 1992: (A) April 14–16, (B) June 2–4, (C) July 28–30, and (D) Sept. 29–Oct. 1.

concentrations in the lower reach varied by 13.8% during the first 24 hours of the July sampling period, but only 3.0% during the second 24 hours. The July fluctuations in the lower reach were affected by a thunderstorm on July 29 that caused stream discharge to nearly double and stream NO_3^- concentrations to increase from about 15 to almost 18 μmol/L from 4:00 p.m. to 6:00 p.m. (Figure 2c). Nitrate concentrations increased in the early morning hours of July 30 but did not reach as high a value as they had in the previous morning. These data suggest that NO_3^- movement from the soil to the stream observed during rainstorms in this region (Murdoch & Stoddard 1992; Wigington et al. 1996) disrupts the diurnal cycle of stream NO_3^- concentrations characteristic of base-flow conditions. Biological uptake of NO_3^- in the stream may have contributed to the decreased NO_3^- concentrations immediately after the storm, since rainstorms can promote new growth in the periphyton community by scouring tissue from surfaces, resulting in rapid uptake soon after a storm (Grimm 1987; Triska et al. 1989). A more likely explanation, however, is flow cessation in shallow flowpaths that transmit NO_3^- rich water to the stream (Brown et al. 1997).

Mass balances

The mass balances generally indicate that a significant amount of NO_3^- was lost during transport from the top to the bottom of each reach (Table 3; Figure 3). The loss of NO_3^- from each reach (expressed as the mass in kg, Δm) was greatest in the June sampling period and least in the April sampling period (Table 3). In all sampling periods, NO_3^- losses in both reaches generally increased as mean streamflow increased, but the NO_3^- losses during the April sampling period were less than would be predicted by a simple linear relation between Δm and streamflow based on all data (Figure 4). Alternatively, the mass losses in June can be interpreted as atypically high at both sites. These results suggest that NO_3^- losses in the early spring, are limited by the rate at which NO_3^- can be removed from stream water through biogeochemical processes, whereas NO_3^- losses later in the spring and through the fall are limited by the NO_3^- supply in the stream. The downstream losses of NO_3^- may have been limited in April by low stream temperatures (mean = 2.8 °C in the upper reach and 3.7 °C in the lower reach). Seasonal differences in available light probably did not cause smaller stream NO_3^- losses in April than during the other sampling periods. The total incident-light energy flux measured by the pyranometer was 516 kW/m^2 during the April sampling period – less than the 644 kW/m^2 measured during the June sampling period, but greater than the 476 kW/m^2 measured during the July sampling period (loss of power prevented data collection during the September sampling period). Additionally, the canopy on deciduous trees had not developed by mid-April;

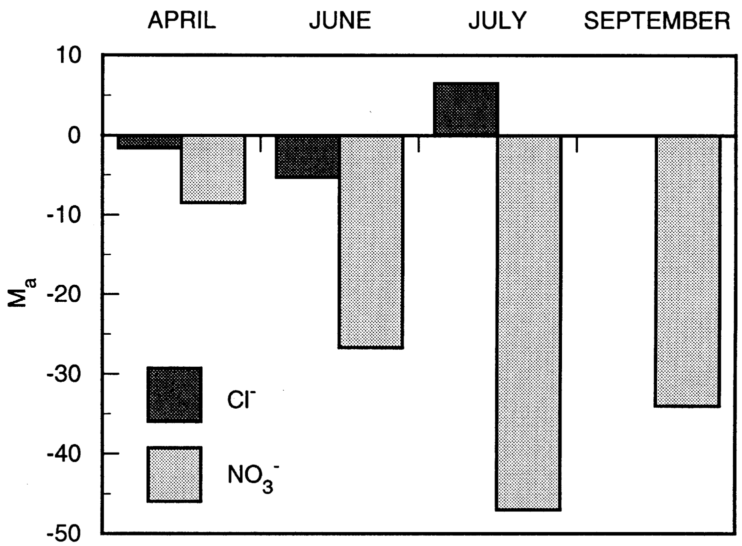
Table 3. Mass balances for NO_3^- in the two reaches during the four 48-hr sampling periods. The values are expressed by three methods: (1) as the residual of the mass balance (Δm), (2) as the residual divided by the sum of the mass that entered each reach from ground-water and tributary flow expressed as a percentage (M_a), and (3) as the residual divided by the mass transported by the stream at the upstream end of the reach expressed as a percentage (M_b). The negative values indicate a mass loss of NO_3^- through the reach.

	Upper reach			Lower reach		
Month	Δm (kg)	M_a (%)	M_b (%)	Δm (kg)	M_a (%)	M_b (%)
April	−0.31	−8.5	−3.6	−10.5	−22.5	−3.1
June	−1.47	−26.7	−16.4	−34.6	−68.4	−11.7
July	−0.54	−47.0	−29.0	−19.6	−113.3	−18.6
Sept.	−0.53	−34.0	−26.1	−16.8	−115.9	−24.3

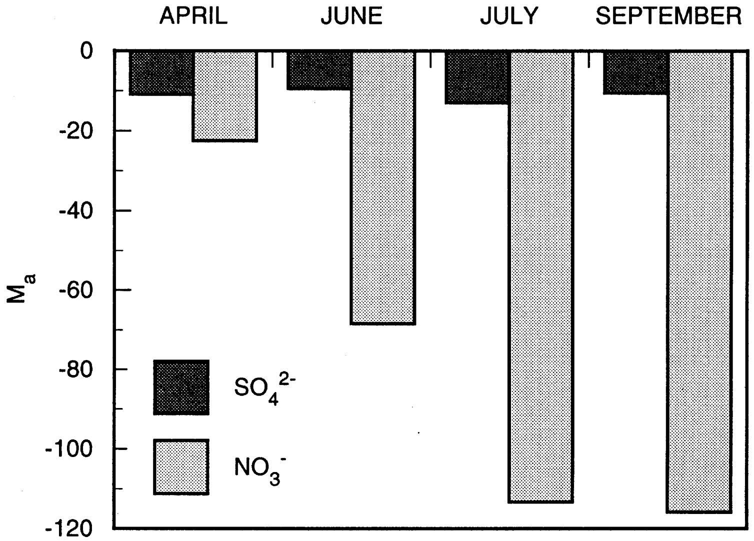
thus, available light would have reached the stream (particularly in the upper reach) more readily in April than during the other sampling periods.

The stream losses of NO_3^- (M_a and M_b) were greatest during the July sampling period at the upper reach and during the September sampling period at the lower reach (Table 3). The values of Δm generally decreased from the June to September sampling periods in both reaches, whereas the values of M_a and M_b generally increased during the same periods, indicating that both the terrestrial and upstream supply of NO_3^- to the stream reaches decreased more than the stream losses of NO_3^- did for these sampling periods. The mass losses of NO_3^- (Δm) and losses relative to terrestrial supply (M_a) from stream water were greater in the lower reach than in the upper reach, but were greater relative to stream supply (M_b) in the upper reach. The loss of NO_3^- from stream water in the lower reach in the July and September sampling periods was large enough to result in a decline in the total mass of NO_3^- transported from the upstream end to the downstream end of the reach, despite a significant influx of NO_3^- from tributaries and ground water. The differences in the mass balances (as expressed by M_a) for the conservative constituents are small, indicating that the uncertainty in the water balance was insignificant in relation to the values of M_a for NO_3^- (Figure 3). The M_a values for SO_4^{2-} in the lower reach were greater than those for Cl^- in the upper reach, possibly because SO_4^{2-} is nonconservative in the hyporheic zone (data that support this hypothesis are presented in the next section).

The mass-balance results, together with the diurnal patterns in stream NO_3^- concentrations, indicate that assessing the relative effects of aquatic and hyporheic processes in the two stream reaches is dependent on how the mass balance is expressed. Stream NO_3^- contributions, mass loss of NO_3^-, and mass loss of NO_3^- relative to terrestrial NO_3^- contributions to the stream were



A. Upper reach



B. Lower reach

Figure 3. Mass balances for (A) NO_3^- and Cl^- in the upper reach, and (B) NO_3^- and SO_4^{2-} in the lower reach during the four sampling periods expressed as the residual of the mass balance divided by the sum of the mass that entered each reach from ground-water and tributary flow and expressed as a percentage (M_a). Negative values indicate a mass loss of the constituent through the reach; positive values indicate a mass gain of the constituent through the reach.

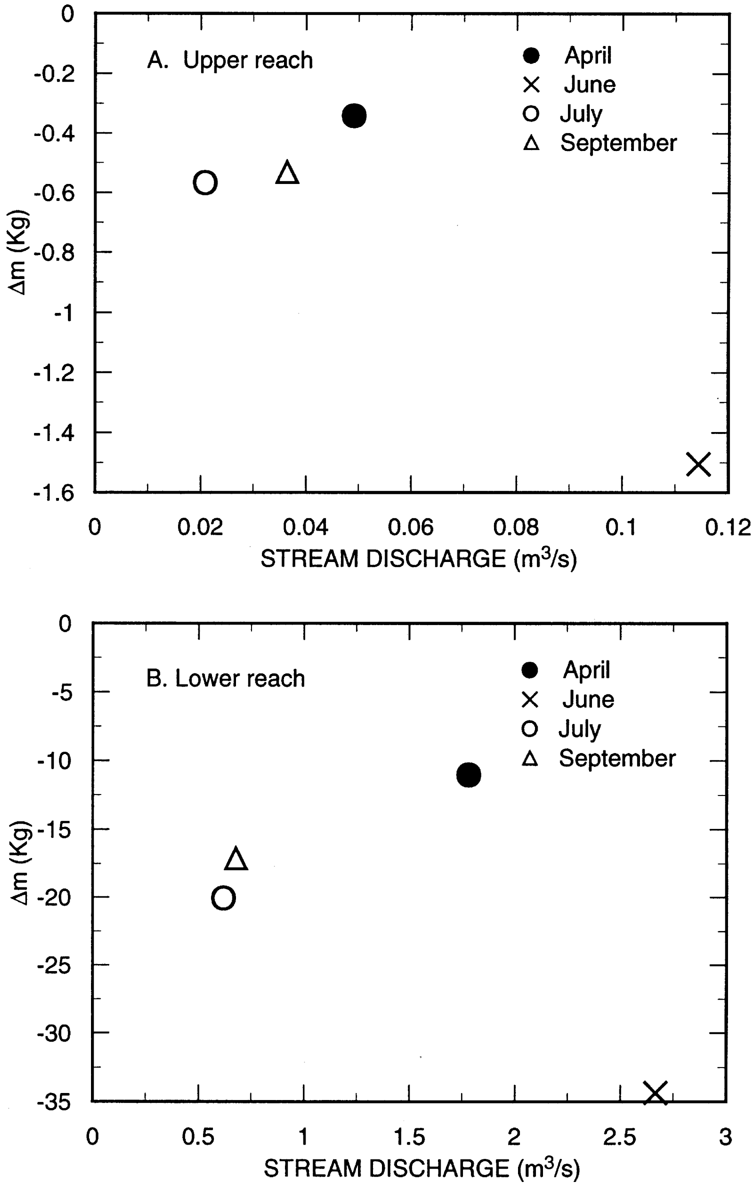


Figure 4. Residual of the mass balance for NO_3^- (Δm) for each sampling period as a function of mean stream discharge in (A) Upper reach, and (B) Lower reach.

greater in the lower reach than the upper reach. When the NO_3^- mass balance is expressed relative to the mass of NO_3^- transported in the stream, however, the effects of aquatic and hyporheic processes are greater in the upper reach

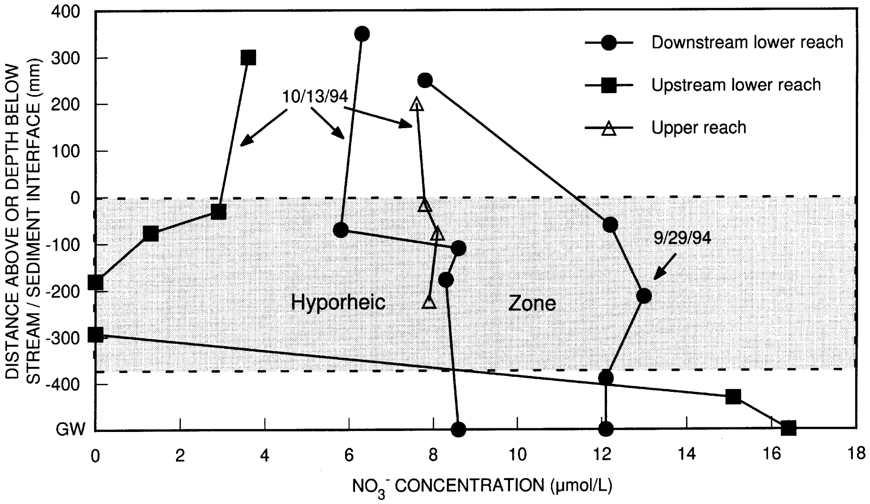


Figure 5. Profiles of NO_3^- concentrations in the stream, through the hyporheic zone, and into the alluvial ground water at three locations on the West Branch Neversink River on Sept. 29, 1994 and Oct. 13, 1994. The symbol GW indicates a sample collected from a well about 2 m from the stream and 3-4 m from where the other samples were collected.

than the lower reach. This apparent discrepancy between the two reaches may result from the competing effects of downstream changes in stream volume/streambed surface and changes in stream gradient and streambank steepness. In the upper reach, the stream is shallow and narrow (Table 1), and therefore, the channel surface area is greater relative to stream volume than in the lower reach. The greater relative area of rock and stream sediment surface in the upper reach could result in a greater loss of NO_3^- relative to the transported mass than in the lower reach. Nitrate losses relative to the terrestrial NO_3^- contribution to the stream were likely greater in the lower reach because streambanks are less steep than in the upper reach, resulting in greater residence times in the hyporheic zone. Additionally, the stream gradient was less in the lower reach, allowing a greater accumulation of organic matter in streambed sediments, and therefore, a greater likelihood of anoxic conditions conducive to denitrification in the lower reach (Figure 5).

Role of other N species

Nitrate was the only form of dissolved N for which mass balances were calculated. Ammonium, measured in all samples collected during the study, was typically below the laboratory reporting limit of 2 μmol/L (Lawrence et al. 1995), indicating low NH_4^+ concentrations relative to NO_3^- concentrations in the Neversink River. Dissolved organic N (DON) concentrations were not measured during this study, but are assumed to be low relative to NO_3^- concentrations because dissolved organic carbon (DOC) concentrations are generally low in the Neversink River (100 to 200 μmol/L at base flow). More recent analyses of dissolved N species in the West Branch Neversink River indicated a mean of 84% NO_3^-, 7% NH_4^+, and 9% DON in biweekly samples collected from June 1993 through April 1995 at the downstream end of the upper reach (G.M. Lovett pers. commun.). These data indicate that NO_3^- is the dominant dissolved N species in surface waters of the Neversink watershed, and that NH_4^+ and DON are only minor components of N mass balances. The role of particulate forms of N were not assessed in this study.

Relative effects of denitrification and N uptake

Evidence of denitrification was assessed through analysis of a series of water samples collected from the stream through the hyporheic zone and into the shallow ground water at two sites in the lower reach and one site in the upper reach. Results indicate that as ground water mixed with stream water in the hyporheic zone, the dominant processes varied from conservative mixing to complete removal of NO_3^- by denitrification (Figure 5).

Results from the downstream site on the lower reach differed on the two sampling dates; no significant decrease in NO_3^- concentrations was evident in a transect from the stream through the hyporheic zone to the ground water on September 29, 1994, whereas the NO_3^- concentration of a sample collected at a depth of about 70 mm below the stream-sediment interface in the hyporheic zone on October 13, 1994 was less than that of the stream water and ground water, suggesting potential NO_3^- removal from solution in the hyporheic zone (Figure 5). Results from the upstream site in the lower reach indicated large losses of NO_3^- through denitrification during exchange in the hyporheic zone at this location. Two of the samples – collected at depths of 180 and 290 mm, respectively – had no measurable NO_3^- concentrations, but had measurable NH_4^+ concentrations of 3.8 and 3.1 μmol/L which are generally indicative of reducing conditions. These two samples also showed evidence of sulfate reduction by the “rotten egg” smell of H_2S, and had SO_4^{2-} concentrations that were 10 to 30 μmol/L less than in stream water and ground water. Together, these data are consistent with the characteristic transformations that occur when oxygen, then NO_3^-, become depleted, and alternative terminal electron acceptors such as SO_4^{2-} are utilized by microorganisms (Lovley et al. 1994). This sampling location at the lower reach was chosen because it was in a quiescent section of the reach, where the stream sediment was rich in organic matter and, therefore, a likely site for reduction processes. Most of the stream sediment in the Neversink consists of sand and gravel, with a steep stream gradient that provides little opportunity for settling of organic matter, which is generally necessary for oxygen depletion in hyporheic flowpaths. Results from another study indicate that no losses of dissolved oxygen, DOC, or NO_3^- were evident in two hyporheic flowpaths that extend for 18 m in the West Branch of the Neversink River (W.V. Sobczak pers. commun.). Therefore, the site that provided strong evidence of denitrification probably represents only a small percentage of the upper Neversink River.

Laboratory incubations of stream sediment collected on October 13, 1994 had moderate denitrification potentials of 0.09 and 0.10 nmol N_2O/ml/hr for the sampling sites at the upper reach and the downstream site at the lower reach, respectively, and a greater rate of 0.84 nmol N_2O/ml/hr for the upstream site on the lower reach. The results are generally consistent with those from the water samples collected in the hyporheic zone at each of these sites. The site at which the incubated sediment had the greatest rate of denitrification coincided with NO_3^- absence in the hyporheic zone. The low but measurable rates of denitrification from the sediment at the other two sites indicates some potential for denitrification when conditions are suitable.

Stream-reach mass balances calculated for daytime periods were compared with those calculated for nightime periods to assess the relative effects of denitrification and N uptake on the downstream movement of NO_3^-. If uptake by photoautotrophs is the dominant cause of NO_3^- losses in a stream reach, less NO_3^- would be expected to move downstream during the day than at night, but if denitrification is the dominant cause of stream NO_3^- losses, then day and night downstream movement of NO_3^- should be similar.

Mass balances (M_a) of NO_3^- in the day were similar to those at night in the upper reach during each sampling period (Table 4). Mass balances of NO_3^- in the lower reach showed greater differences between day and night than those in the upper reach, but no consistent pattern was evident. The downstream movement of NO_3^- was more conservative in the day than at night during the April and June sampling periods, and was the opposite in the July and September sampling periods. The lack of a consistent day-to-night difference in the mass balances for NO_3^- may reflect that uncertainty in the method of calculation was greater than any real day-to-night differences.

The lack of strong differences between day and night mass balances of NO_3^- do not necessarily indicate that biological uptake is an insignificant source of NO_3^- losses from the stream. Algal uptake of nutrients in the dark has been demonstrated in both the laboratory and marine environment (Collos & Salwyk 1980), and significant uptake of NO_3^- at night has been demonstrated in the riverine environment and may be related to decomposition of detritus by heterotrophs (Triska et al. 1989). Also, light has been shown to inhibit denitrification because it enables photoautotrophic activity that causes oxygen penetration into the hyporheic zone (Nielsen et al. 1990). Although evidence

Table 4. Day and night mass balances of NO_3^- in the two reaches. The values are expressed as the residual of the mass balance (Δm), and as the residual divided by the sum of the mass that entered each reach from ground water and tributary flow expressed as a percentage (M_a). Day represents the period from sunrise to sunset.

		Day		Night	
Reach	Month	Δm (kg)	M_a (%)	Δm (kg)	M_a (%)
Upper	April	−0.17	−8.5	−0.14	−8.5
	June	−0.98	−28.2	−0.49	−24.1
	July	−0.32	−47.1	−0.22	−46.8
	Sept.	−0.26	−34.2	−0.27	−33.8
Lower	April	−4.2	−16.6	−6.3	−29.6
	June	−20.9	−65.3	−13.6	−73.1
	July	−12.0	−120.0	−7.6	−104.1
	Sept.	−7.9	−125.2	−8.9	−118.7

from other studies suggests that the separation of NO_3^- mass balances into day and night periods is not a reliable method for quantifying the effects of uptake on stream NO_3^- concentrations, the diurnal changes observed provide strong evidence that the uptake of NO_3^- is greater during the day than at night in the reaches studied.

Conclusions and significance

The results of this study have shown that NO_3^- is generally not transported conservatively at base flow within this upland stream environment in which NO_3^- is the dominant dissolved N species. Mass balances of NO_3^- for two contrasting stream reaches revealed greater losses relative to stream NO_3^- transport in the upper reach, and greater losses relative to tributary and groundwater contributions in the lower reach. During summer and fall base flow, aquatic and hyporheic processes removed more NO_3^- from the lower reach than was added by tributaries and ground water; and thus, the downstream load decreased. The mass-balance results indicate that the downstream losses of NO_3^- in both reaches were generally related to streamflow and thus, to the NO_3^- supply, except during the April sampling period, when low water temperatures may have slowed the rate of aquatic and hyporheic processes. A diurnal pattern of changes in stream NO_3^- concentrations at base flow in the two study reaches suggests that uptake by photoautotrophs was an important cause of downstream losses of NO_3^-, but the mass balance data do not provide quantitative evidence of the relative roles of denitrification and N uptake in the losses of NO_3^- from the stream. Complete removal of NO_3^- was observed in the hyporheic zone of a quiescent section of the lower reach of the stream where organic matter had accumulated in the streambed sediment, indicating that denitrification does occur in the Neversink River. Resolving the relative importance of these two processes in the downstream movement of NO_3^- warrants further study because of the long-term implications for the N cycle in forested watersheds such as the Neversink that receive large loads of atmospheric N. Denitrification represents a permanent loss of N through diffusion and degassing, but N taken up by stream biota can become available again through mineralization and nitrification.

The results of this study indicate that the failure to include aquatic and hyporheic processes in models of the effects of atmospheric N deposition on stream NO_3^- concentrations could result in erroneous predictions, even in steep, headwater watersheds. Data presented here suggest that some of the stream-to-stream differences in NO_3^- concentrations in watersheds that receive similar rates of atmospheric N deposition could result from differences in physical characteristics of the stream environment that affect the aquatic and hyporheic processing of N.

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