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VARIATIONS IN BASE-FLOW NITRATE FLUX IN A FIRST-ORDER STREAM AND RIPARIAN ZONE[1]

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ABSTRACT: Nonpoint source pollution, which contributes to contamination of surface waters, is difficult to control. Some pollutants, particularly nitrate (NO_3^-), are predominantly transmitted through ground water. Riparian buffer zones have the potential to remove contaminants from ground water and reduce the amount of NO_3^- that enters surface water. This is a justification for setting aside vegetated buffer strips along waterways. Many riparian zone hydrologic models assume uniform ground-water flow through organic-rich soil under reducing conditions, leading to effective removal of ground-water NO_3^- prior to discharge into a stream. However, in a small first-order stream in the mid-Atlantic coastal plain, base-flow generation was highly variable (spatially and temporally). Average base-flow NO_3^- loads were greater in winter than summer, and higher during a wetter year than in dryer years. Specific sections of the stream consistently received greater amounts of high NO_3^- ground water than others. Areas within the riparian zone responsible for most of the NO_3^- exported from the watershed are termed "critical areas." Over this 5-year study, most of the NO_3^- exported during base flow originated from a critical area comprising less than 10% of the total riparian zone land area. Allocation of resources to address and improve mitigation function in critical areas should be a priority for continued riparian zone research.

(KEY TERMS: surface water/ground-water interactions; nonpoint source pollution; nutrients; transport and fate; ground-water hydrology; wetlands.)

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INTRODUCTION

Nitrate (NO_3^-) is one of the most common agricultural contaminants found in ground water and surface water around the world (Craig and Weil, 1993; Lawrence, 1996; Tesoriero *et al.*, 2000), partly because it is readily soluble and transportable by ground water (Lowrance *et al.*, 1983; Crum *et al.*, 1990; Simmons *et al.*, 1992). Ground and surface-water NO_3^- loading is of concern because excess N creates conditions of environmental impairment such as eutrophication of surface waters, growth of microorganisms that cause water-borne diseases (e.g., *Pfisteria piscida*), and potential toxic effects on humans (Craig and Weil, 1993; Martin *et al.*, 1999). Riparian

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corridors are often considered to be effective sites for remediation of agricultural NO_3^- (Simmons *et al.*, 1992; Mitsch and Gosselink, 1993; Emmett *et al.*, 1994; Willems *et al.*, 1997; Ettema *et al.*, 1999).

Management requirements have focused mostly on riparian zone width (e.g., Bren, 1993; Cylinder *et al.*, 1995) with limited consideration for other influences on NO_3^- removal; yet there are several factors that affect the ability of riparian corridors to remove NO_3^- from the ecosystem. Topography—specifically the geomorphology of the hillslopes, valley, and stream—-strongly influences the hydrology of a system (Dunne, 1980). Because water is the medium of transport for NO_3^-, hydrological characteristics are likely to have an impact on NO_3^- movement. The transmissivity of sediments should influence NO_3^- dynamics in the system, as ground-water residence time within the subsurface affects NO_3^- behavior (Cooper, 1990; Jacinthe *et al.*, 1998). The geochemistry of the sediments also greatly influences rates of NO_3^- removal (Groffman *et al.*, 1992; Bohlke and Denver, 1995; Ashby *et al.*, 1998; Ettema *et al.*, 1999). Subsurface preferential flow paths such as macropores (pores that are significantly larger than average matrix porosity of that soil) can also affect ground water (Calver, 1990) and contaminant delivery patterns (Harvey and Nuttle, 1995; McCarty and Angier, 2000; Angier *et al.*, 2001).

Previous research on riparian buffers has indicated that some hydrological and geomorphologic settings can permit delivery of ground-water NO_3^- to the surface with limited NO_3^- removal. Such conditions can occur with incised streams (O'Connell, 1998; Groffman *et al.*, 2002), when there are high ground-water flow rates (Willems *et al.*, 1997), or if the ground water remains oxic throughout its flow path (Bohlke and Denver, 1995; Angier *et al.*, 2002; Mookherji *et al.*, 2003). In contrast, settings where streams are shallowly incised, vegetated corridors are wide, surface-saturated conditions frequently exist, and soils are high in organic C, should be ideal for enhanced NO_3^- removal (Korom, 1992; Ashby *et al.*, 1998).

Discharge of ground water through anaerobic high-C soil is typically associated with subsurface denitrification. Many riparian buffers have sediment layers with high denitrification potential (e.g., high denitrification enzyme activity), often in organic-rich near-surface layers (Groffman *et al.*, 1992; Lowrance, 1992a,b; Pavel *et al.*, 1996). If the water table is high, or if the surface is frequently flooded, this shallow soil layer will likely exhibit anaerobic conditions necessary for denitrification. However, the presence of anoxic conditions alone may not be sufficient to remove NO_3^- from exfiltrating ground water. Rapid discharge of ground water to the surface can circumvent NO_3^- removal processes by substantially reducing the residence time of ground water within shallow surface layers, as has been recorded in many studies (e.g., Hanson *et al.*, 1994; Ashby *et al.*, 1998; Devito *et al.*, 2000; Angier *et al.*, 2001). Visible zones of ground-water discharge to the surface may be associated with strong vertical hydraulic gradients (McCarty and Angier, 2000; Angier *et al.*, 2005). In a study by Devito *et al.* (2000), ground-water discharge (upwelling) areas showed consistently elevated NO_3^- concentrations (up to 20 mg-N/l) relative to neighboring inactive areas with low (<1 mg-N/l) porewater NO_3^- contents. Subsequent channelization of emergent ground water across the land surface, to a stream, can be an important NO_3^- delivery mechanism (Ashby *et al.*, 1998; Devito *et al.*, 2000; Angier *et al.*, 2002).

First-order stream heads, which typically occur at valley convergences (Dunne, 1980), are commonly associated with ground-water-sustained wetlands in humid low-relief areas such as the mid-Atlantic coastal plain (Haas, 1999). In high-relief areas, springs of emergent ground water typically occur at the hillslope base, and often serve as the source for the stream head (Dunne, 1980). In low-relief areas, ground water will likely emerge closer to the valley axis, but not necessarily directly into the stream channel (Angier *et al.*, 2004, 2005). Rapid emergence of ground water in these areas may allow significant amounts of NO_3^- to reach the surface despite the redox conditions associated with continuous surface saturation. The assumption that first-order riparian wetlands are highly effective at ground-water NO_3^- removal may be questionable if these areas are sustained by rapidly exfiltrating ground water. It is important to assess spatial and temporal NO_3^- variations to determine where likely zones of NO_3^- delivery might be, predict what conditions (climatological, geomorphological) might increase or decrease stream N loading, and perhaps adjust agricultural techniques accordingly.

The purpose of this study was to evaluate the relationship between ground-water exfiltration characteristics and stream NO_3^- patterns under base-flow conditions; the study was designed to assess spatial and temporal variations in NO_3^- delivery to a first-order stream channel, and to determine where the majority of stream NO_3^- originated and the conditions under which NO_3^- delivery to the surface was most prevalent. Are perennially saturated areas (e.g., permanent wetlands) and headwater riparian zones really the most effective areas for NO_3^- removal? Or will NO_3^- most readily reach the surface as a result of rapid discharge of ground water? A central objective was to compare the relative effectiveness of different areas within a riparian zone and identify specific (measurable and observable) hydrological characteristics associated with heterogenous NO_3^- delivery and transport patterns under base-flow conditions. Much of the supporting information cited here, particularly elucidation of ground-water flow paths and the effect of preferential flow on stream nitrate concentrations, has been presented previously (e.g., Angier *et al.*, 2001, 2005). The principal novel information presented here regards discerning specific differences in stream nitrate flux at various points along a stream and relating those observed differences to spatial and temporal variations in nitrate movement and fate within the adjacent riparian zone and determining quantitative flux contributions from specific areas as a proportion of total stream (base flow) NO_3^- flux.

MATERIALS AND METHODS

Site Description

The site chosen for this study was a first-order stream with an associated riparian zone, contained within a first-order agricultural watershed in the mid-Atlantic coastal plain (Figure 1). The study site was part of a larger watershed experiment (Daughtry *et al.*, 2001) conducted at the USDA Beltsville Agricultural Research Center in Beltsville, Maryland. The riparian zone study site (Figure 1) was bordered to the west by an agricultural production field consisting of a 20-ha field that drained into a small north-to-south flowing first-order stream within the riparian zone. This field was cropped with corn for the duration of the study, and received applications of mostly synthetic sidedress N-fertilizers (and some manure) that served as the primary source of NO_3^- in this watershed. To the east of the upstream part of the riparian zone was a smaller (4 ha) upland field that was also cropped with corn. This small eastern field (Figure 1) drained mostly into a low-lying wetland area to the south of the small field and east of the main riparian study area (Angier *et al.*, 2005). The full length of the first-order stream was 1,100 meters, which then emptied into a larger, higher-order stream (Beaver Creek) at the termination of the study area. The entire watershed area was 69 ha, of which approximately 40% was reserved for agriculture. The riparian corridor (study area) consisted of a vegetated area bounding the length of the stream, and varied in width from 60 meters at its narrowest point, to more than 250 meters. The riparian corridor (delineated by forested boundary) comprised 10% (7 ha) of the total catchment area. The remaining 50% consisted mostly of undeveloped nonriparian forested areas.

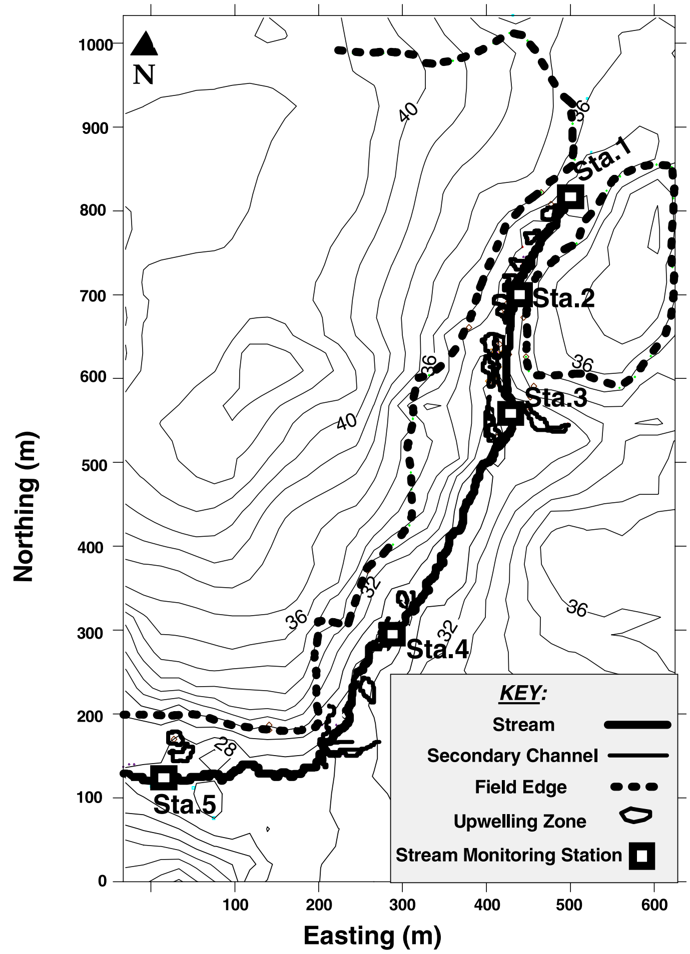

FIGURE 1. Plan-View Topographic Map of Study Site Showing Orientation of Stream and Secondary Channels, Locations of Monitoring Stations, Forest Boundary, and Upwelling Zones. Topographic lines in meters above sea level (1-meter intervals). Riparian zone bounds stream, between eastern and western field edges.

The riparian zone soil was Typic Haplosaprist (Keys to Soil Taxonomy, 2003), Johnston silt-loam, very poorly drained (Maryland Soil Series). The riparian histosol was approximately 2-meter deep, beneath which was an oxic sand aquifer (McCarty and Angier, 2000). There is an oxic inversion in the wetland, with oxic ground water penetrating up through the soil profile and dissolved oxygen concentrations decreasing upward, varying according to rate of groundwater movement (Angier *et al.*, 2002).

Visible distinctions among various sections within the riparian zone appeared to reflect differences in hydrological characteristics (Angier *et al.*, 2005). The (upstream) portion of the riparian zone between Stations 2 and 3, representing less than 10% of the total riparian zone land area, contained many sections that were continually water saturated. Surface-saturated areas in this part of the riparian zone were sustained by continuously discharging ground water, which could be seen in places emerging onto the surface through macropores. Some of this discharged ground water, where exfiltration rates were particularly high, was channelized across the floodplain surface and into the stream. Macropores within the stream channel also contributed water from the subsurface directly into the stream. Ground-water-maintained saturated conditions in this area persisted even after 6 weeks with no rain (summer 1999), when conditions in the rest of the watershed were very dry. Previous studies have indicated that one possible explanation for the constant and seemingly disproportionate discharge of ground water into the section between Stations 2 and 3 may at least in part result from stratigraphic conditions in the adjacent agricultural field west of the riparian zone (Angier *et al.*, 2001; Daughtry *et al.*, 2001). A semi-restricting subsurface clay layer in the upland appears to dip and tilt toward this part of the riparian zone, directing ground water from a fairly large (9 ha) portion of the upland field into a relatively small (0.6 ha) area within the riparian zone (Daughtry *et al.*, 2001; Walthall *et al.*, 2001). The lower (downstream) portion of the riparian zone, between Stations 3 and 5, had few or no zones of surface saturation, depending on antecedent rainfall conditions. Stream discharge ceased in the lower part of the channel during prolonged droughts, whereas the stream continuously flowed and surface-saturated areas always persisted within the upstream section (between Stations 2 and 3) regardless of drought conditions.

Stream Water

Monitoring discharge in this small, low gradient (0.7% slope) stream required construction of permanent channel flumes affixed with v-notch weirs, each of which were hand-calibrated for rating purposes. Discharge from weirs was measured with a calibrated bucket and stopwatch; stream water level was measured directly with a meter stick. Calibrations were performed for the full range of base-flow conditions, encompassing the v-notch from <1 cm height to 15 cm (notch-full). A total of 185 measurements was taken, and a rating curve for each weir notch was developed.

Five locations for weir placement were selected based upon channel morphology and adjacent riparian zone and upland (agricultural) field characteristics (see Figure 1). This configuration was chosen so that different reaches along the stream channel (between stations) could be compared. Station 1 drained the uppermost, zero-order, nonagriculturally impacted portion of the system; flow in this station only occurred during winter and wet periods. Data from Station 1 was not included in this study, because discharge only occurred in this station about half the time, and measured stream NO_3^- concentrations were always consistent with background, nonagriculturally influenced, water sources (<1 mg/l) (Lawrence, 1996). Station 2, 105 meters downstream from Station 1, marked the first monitoring point for agricultural influences. This part of the channel functioned essentially as the stream head during dry periods; water flowed continuously here, even in drought conditions. Station 3 was 154 meters below Station 2 and drained the part of the riparian zone that constituted a perpetual wetland (based on hydrological characteristics and obligate vegetation). Station 4, 346 meters downstream of Station 3, was surrounded by a part of the riparian zone where wetland conditions were more intermittent. Station 5, 449 meters below Station 4, marked the terminus of the study area, where the first-order stream drained into a higher-order stream channel.

Each of these stations was instrumented with autosamplers (900MAX Portable Samplers; American Sigma, Loveland, CO), fitted with ultrasonic detectors that continuously measured and logged water heights (60 cm back from the weir) in 10-min intervals. Stream water samples from each of the stations were collected by hand (weekly), and by autosampler (for hourly sampling over 24-hour cycles, and for storm flow sampling).

Data presented here (collected between December 1998 and August 2003) represented only base-flow conditions, when all of the stream discharge originated as ground water. Criteria for base flow included elevated stream discharge resulting from higher-than-average annual rainfall but excluded elevated stream discharge reflecting poststorm event ground-water pulses (exemplified by the tailing limbs of storm hydrographs), so that only nearly steady-state conditions were evaluated. We discarded all data for at least a 60-hour period following storm events. By these criteria, base-flow discharge, and NO_3^- flux, rates at Station 5 (the outflow point of this stream) ranged from 0-10 l/s and 0-33 mg-N/s, respectively.

Base-flow-only conditions were selected for this study for several reasons. Base-flow conditions dominated in this stream, as is typical for low-order streams with shallow water tables (Harvey *et al.*, 1996). Over the course of this 5-year study, base-flow conditions prevailed 87% of the time and accounted for 65% of total stream discharge. Evidence collected from storm events indicated that stream NO_3^- flux was typically lower during runoff conditions and increased as ground-water contributions represented a greater proportion of poststorm stream discharge, as has been observed in other studies (e.g., Lucey and Goolsby, 1993). Additionally, ground-water contributions from specific areas could be identified, isolated and measured under base-flow conditions; during runoff it was not possible to determine the extent of contributions to total stream discharge from individual localized sources within the riparian zone.

Samples for chemical analysis were stored at 4°C if not immediately analyzed. Samples were analyzed for NO_3^- (detection limit 0.25 mg/l) with an Ion Chromatograph (Dionex DX-120 IC; Dionex, Sunnyvale, California) fitted with an anion exchange column (Dionex IonPac AS9-SC; Dionex). Flux was determined by multiplying NO_3^- concentration with streamflow.

Ground Water

There were two distinct areas within the riparian zone (between Stations 2 and 3) where ground water discharged to the surface was channelized, allowing direct measurement of ground-water discharge rates from these points. This was accomplished by temporarily placing "mini-weirs" into these subchannels near their origin points, which were zones of intense, focused ground-water exfiltration (upwelling). Mini-weirs were also placed at the ends of these sub-channels, where they drained into the main stream channel, to measure flow and N-flux at both points along the "head" and "mouth" of each subchannel. The mini-weirs consisted of stainless steel sheets 70 cm wide and 25 cm high, with a 90° notch cut. They were placed at each selected point and sealed along the sides with packed soil and clay, and discharge was allowed to re-equilibrate for a minimum of 18 hours before measurements and samples were taken. Measurement was performed with a calibrated cup and stopwatch, with six repetitions averaged. Only one of the subchannels yielded consistently useable (and reportable) results; there were occasional problems verifying the integrity of the flow path for the other subchannel. Where possible, macropores that discharged ground water directly from the subsurface into the side of the stream channel (above the waterline) were also measured with calibrated cup and stopwatch.

Rainfall Data

Rainfall data were obtained from a nearby weather station (1.4 km from the study site), managed by Farm Operations Branch, USDA/BARC. Rainfall amounts were determined from a tipping bucket rain collector, measured at 5-min intervals. Snowfall amounts in winter were measured and logged as rainfall equivalents; all precipitation data are referred to as rainfall.

Average monthly rainfall was calculated for the 30-year period from 1972 to 2002. For the four complete years encompassed by this study (1999-2002), 1999 had 27% less total annual rainfall than the 30-year average of 1113 mm, 2000 had 22% more rain, 2001 was 3% above average, and 2002 had a 38% deficit. Thus, 1999 and 2002 were drier than "normal," 2001 was essentially average, and 2000 was wetter than normal, based on 30-year average total annual rainfall. Conditions during much of 1999 were actually even drier; however, hurricane Floyd in September 1999 somewhat mitigated the annual rain deficit.

Statistical Analyses

Linear and nonlinear regression analyses were performed on streamflow, stream NO_3^- concentrations, and NO_3^- flux datasets (SigmaPlot 10.0; Systat Software, Inc., Richmond, California). Linear regression utilized the following formula:

$$f = y^0 + ax \tag{1}$$

Nonlinear (sigmoidal) regression was also performed on some datasets, to better capture the combined influences of higher NO_3^- concentrations and higher streamflow rates on stream NO_3^- flux. The formula for the three-parameter sigmoidal regression applied was

$$f = a/(1 + \exp(-(x - x^0)/b)) \tag{2}$$

This type of curve was applied to NO_3^- flux *vs.* stream discharge analysis because it best represented observed stream NO_3^- patterns (and was a better fit for the data). A simple linear relationship would suggest that stream NO_3^- flux was determined solely by stream discharge; however, stream NO_3^- concentrations were also observed to increase as stream base flow increased. The sigmoidal curve contains two inflection points: where sufficient streamflow was generated to allow nitrate concentrations to increase along with increased discharge, and where (under wetter conditions) additional, low-NO_3^- water sources started to contribute to streamflow. Thus, the steep, central part of a sigmoidal curve expresses the combined impacts of higher flows and higher concentrations on stream NO_3^- flux. The "s-shaped" sigmoidal relationship between streamflow and NO_3^- flux was more apparent when data from higher (nonbase flow) discharge conditions was included, where the effect of

TABLE 1. Average Seasonal and Annual N-Flux at Stations 2, 3, 4, and 5 (standard deviation in parentheses), and Percentage of Average Annual Flux Averages From Station 5 Contributed by Each Station.

	Station 5	Station 4	Station 3	Station 2
Average winter flux, 1999-2002 (mg-N/s)	16.4 (±7.4)	15.8 (±7.6)	11.5 (±4.7)	4.7 (±2.3)
Average spring flux 1999-2002 (mg-N/s)	7.1 (±4.6)	7.2 (±4.7)	6.4 (±3.2)	2.6 (±1.5)
Average summer flux 1999-2002 (mg-N/s)	3.2 (±2.7)	3.6 (±3.5)	3.8 (±3.2)	1.3 (±1.2)
Average autumn flux 1999-2002 (mg-N/s)	4.9 (±1.5)	5.6 (±2.7)	4.3 (±0.9)	1.8 (±0.5)
1999 Average base-flow flux (mg-N/s)	3.2 (±2.6)	3.8 (±3.0)	3.5 (±1.6)	1.1 (±1.0)
2000 Average base-flow flux (mg-N/s)	10.0 (±6.0)	10.5 (±4.7)	8.1 (±1.8)	3.4 (±1.6)
2001 Average base-flow flux (mg-N/s)	10.8 (±5.8)	11.2 (±6.0)	8.8 (±3.5)	4.1 (±1.4)
2002 Average base-flow flux (mg-N/s)	4.3 (±2.9)	4.8 (±2.9)	3.6 (±1.8)	1.3 (±0.7)
Average of annual flux averages (mg-N/s)	7.1 (±3.4)	7.6 (±3.2)	6.0 (±2.5)	2.5 (±1.2)
% of annual flux averages (compared to flux out of Station 5)	100	107	85	35

dilution from runoff and nitrate-poor water sources was observed; however, as all the data presented here reflect base-flow conditions, the top, flattened portions of the sigmoidal regression curves were truncated.

Stream NO_3^- flux was averaged by year (1999-2002) and by season. A "season" is here defined as a 3-month period, including the following: winter (January-March), spring (April-June), summer (July-September), and autumn (October-December). Each year's data was subdivided and averaged according to season as well. Table 1 allows comparison of average flux for each station according to year, season, and annual averages. NO_3^- flux was averaged by year (1999-2002) and by season. Each seasonal 3-month interval was individually averaged (for all base-flow data) for Stations 2, 3, 4, and 5. In addition, averages for each season encompassing 1999-2002 were determined for each station, as were annual averages of all yearly averages (1999-2002). The apparently high standard deviations recorded reflect the highly variable characteristics of stream NO_3^- in this ecosystem.

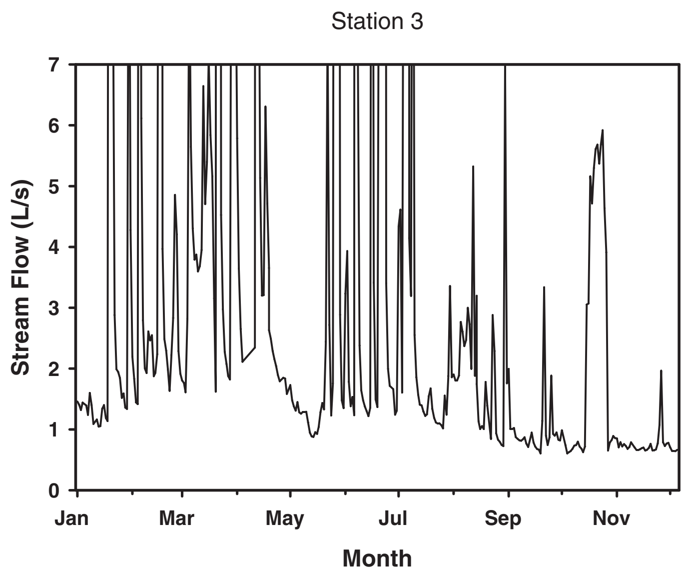

FIGURE 2. Annual Stream Hydrograph, 2001: Station 3. All flow conditions (base flow and nonbase flow), up to 7 l/s, are depicted.

RESULTS

Temporal Variations in Stream NO_3^- *Concentrations*

All data presented here were obtained during base flow, from December 1998 to August 2003. Figure 2 is a full hydrograph for 2001 (all flows included) from Station 3. Flow rates greater than 7 l/s are excluded, as no base flows higher than this were recorded at this station. However, this does not mean that all flows depicted in Figure 2 are base-flow conditions—this scaling was done simply to show detail for the lower-flow setting of the hydrograph. Observe how high-flow conditions quickly revert back to low-flow conditions. Figure 3 shows base-flow-only streamflow for Station 3 (Figure 3a) and Station 5 (Figure 3b) from December 1998 to August 2003. Note that stream base flow is generally higher in winter/spring than in summer/autumn, especially at Station 5. There are apparent annual and seasonal variations in base flow NO_3^- concentrations (Angier *et al.*, 2001) and NO_3^- flux (Table 1) in this stream system. NO_3^- concentrations in exported water (Station 5) were generally lower in drier years (1999 and 2002) than wetter years.

Base-flow stream discharge, NO_3^- concentrations, and NO_3^- flux were higher on average for a given year during winter and early spring, consistent with other studies in the eastern U.S. (e.g., Lowrance *et al.*, 1984a,b; Pionke *et al.*, 1996; Correll *et al.*, 1999; Martin *et al.*, 1999). Higher stream discharge in general yielded higher NO_3^- concentrations (Figure 4), so the combination of higher discharge

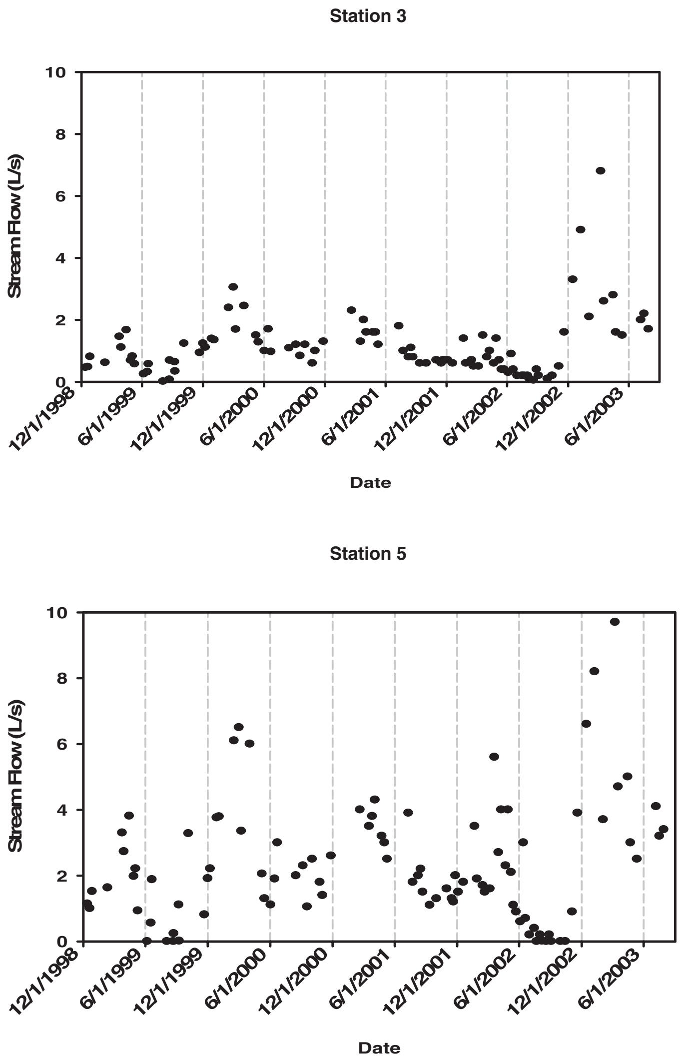

FIGURE 3. Streamflow at Station 3 (a) and Station 5 (b), December 1998 to August 2003. Base-flow conditions only.

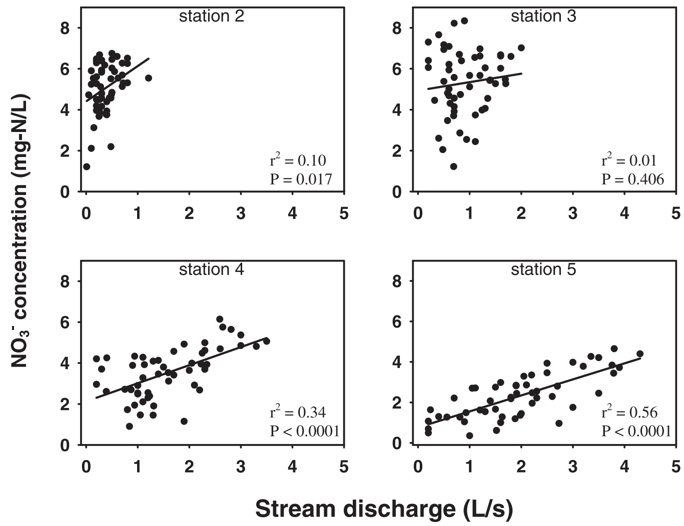

FIGURE 4. Stream Nitrate-N Concentrations Plotted Against Stream Discharge at Stations 2, 3, 4, and 5, Showing N Increase With Higher Flows. Base-flow conditions only.

and higher NO_3^- concentrations usually resulted in greater stream NO_3^- fluxes in winter than summer, especially in wetter years.

Spatial Patterns in NO_3^- *Concentrations*

Ground-water NO_3^- concentrations in the aquifer beneath the riparian histosol were fairly uniform (15-20 mg-N/l) at the same depth (2.5 meter below surface) throughout the riparian zone (Angier *et al.*, 2002). This relative spatial uniformity was observed throughout the study period, with comprehensive ground-water samples obtained at 3-month intervals. Thus, the subsurface pool of NO_3^- at 2.5 meter depth was assumed to be spatially and temporally similar. However, stream NO_3^- concentrations varied greatly along the stream channel, with discernable, consistent patterns. In most cases the highest concentrations were found at Stations 2 and 3 (see Figure 4). This portion of the riparian zone was bounded by agricultural fields on both sides (east and west of the riparian zone), whereas the downstream section was bounded only on the west (see Figure 1). Hydrologic head and gradient data from piezometers across the upper part of the riparian zone (from the western field edge to the small eastern field edge) indicated that while the dominant horizontal direction of ground-water flow from the large western field was perpendicular to the stream channel, the horizontal component of ground-water movement from the eastern field was at an oblique angle to the stream, with much of the ground water likely emerging into the lowland south of the small field (Figure 1) rather than directly into the riparian corridor (Angier *et al.*, 2005). NO_3^- concentrations in ground water obtained from piezometer transects trending west from this small field toward the stream channel exhibited lower values (0-6 mg-N/l) than samples obtained from transects trending east from the large western agricultural field into the riparian zone (0-28 mg-N/l), indicating that little NO_3^- was delivered to the riparian zone from this small eastern agricultural field.

The relationship between stream NO_3^- concentrations and discharge varied locally. As stream discharge increased, NO_3^- concentrations clearly increased at Stations 4 and 5 (r^2 = 0.34-0.56, respectively; p < 0.0001), but not as evidently at Stations 2 and 3 (r^2 = 0.1-0.01; p = 0.017-0.406, respectively) (Figure 4). Stream discharge at Stations 2 and 3 was generated within the portion of the riparian zone that consistently displayed the highest NO_3^- concentrations in surface water and shallow ground water. In contrast, NO_3^- concentrations at Stations 4 and 5 were generally lowest during low-flow conditions, and increased as stream discharge increased (Figure 4).

Ground water added to the stream between Stations 3 and 5 was relatively low in NO_3^-, as evidenced by low NO_3^- concentrations in ground water from wells sampled directly in the stream channel. Less ground water overall was added to the stream along these downstream sections (Angier *et al.*, 2005), and shallow ground water sampled from piezometers within the top meter of riparian soil was consistently lower in NO_3^- (0-2 mg-N/l) than ground water sampled from the same depths upstream (0-16 mg-N/l). Downstream of Station 3, dormant macropores along the stream channel side were observed to become active only during high base-flow (and higher flow) conditions. Generally, NO_3^- concentrations in macropore water from intermittent downstream sources were higher (~4 mg-N/l) than in shallow (<1 meter depth) ground water taken from nearby piezometers, but not as high as water from continuously discharging macropores in the upstream region (3-9 mg-N/l), where as much as 10% of NO_3^- flux (at Station 3) was contributed by a single large macropore (Angier *et al.*, 2005).

NO_3^- *Flux—Temporal and Spatial Variability*

We documented seasonal and interannual effects in stream NO_3^- flux. Figure 5 shows all recorded base-flow NO_3^- flux values at each station from December 1998 to August 2003. Seasonal and annual variations can be seen more clearly in Figure 6, which shows seasonal flux averages for Station 5, from spring 1999 to spring 2003. The percentage of annual flux averages discharged through Station 5 that was represented by each station is given in Table 1. The station displaying the highest NO_3^- flux varied according to stream discharge (Table 1). In general, for high (e.g., winter) base-flow conditions, Station 5 exhibited the greatest NO_3^- flux; Station 3 showed the highest flux when streamflow was lowest (e.g., summer). While Station 4 most often displayed the highest NO_3^- flux, Station 3 provided proportionately the highest percentage of flux that ultimately discharged from the stream (at Station 5) (see Table 1). The NO_3^- flux from Station 5 was greatest during the winter months (Figure 6) in a relatively wet year (2000 and 2003).

Figure 7 shows the relationship between streamflow and NO_3^- flux. Patterns observed in measured stream NO_3^- flux (Figure 7) reflected both increased stream discharge and higher NO_3^- concentrations; the steep central portion of the curve represents the combined impact of increased discharge (inherent in the flux calculations) and higher NO_3^- concentration (particularly at Stations 4 and 5—see Figure 4), with the curve flattening at the top from the influence of dilution accompanying higher discharge and onset of overland flow contributions.

We analyzed the change in NO_3^- flux along each stream reach (between stations) as a function of change in stream discharge along that same reach (Figure 8). Between Stations 2 and 3, there was a steady and consistent increase in flux as flow increased (upper right quadrate in Figure 8). The pattern was similar between Stations 3 and 4, but in this case there was usually a net loss of NO_3^- flux

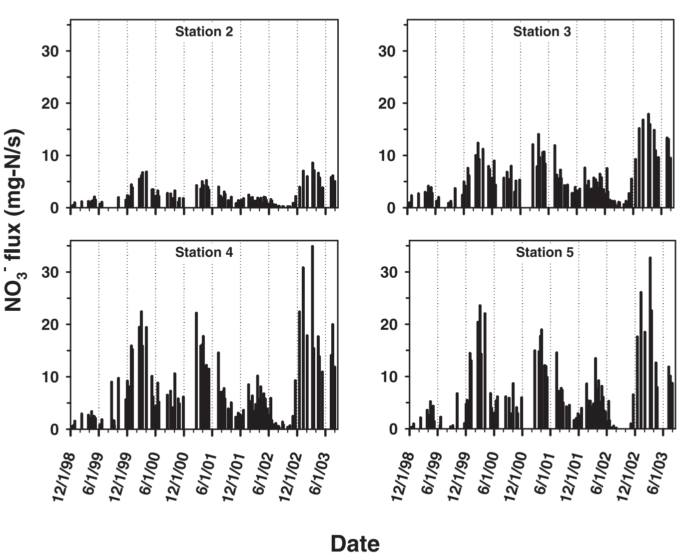

FIGURE 5. Stream Nitrate-N Flux at Stations 2, 3, 4, and 5, December 1998 to August 2003. Each bar represents a single data point (sample); vertical dashed lines represent 6-month units. Base-flow conditions only.

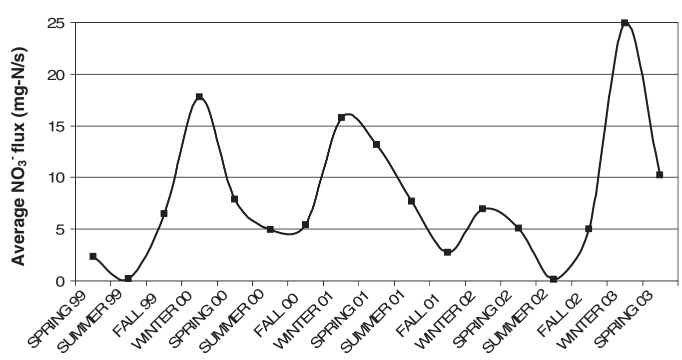

FIGURE 6. Average Seasonal Stream Nitrate-N Flux at Station 5, Spring 1999 to Spring 2003, Displaying Seasonal and Annual Variations. Base-flow conditions only.

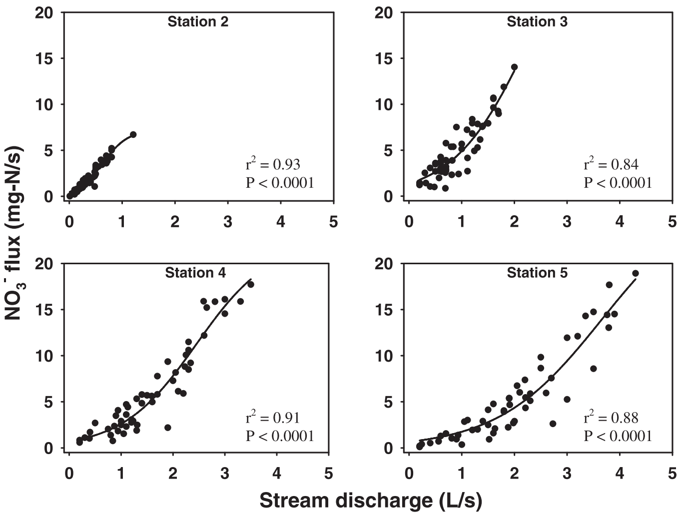

FIGURE 7. Stream Discharge Plotted Against Stream Nitrate-N Flux at Stations 2, 3, 4, and 5, December 1998 to August 2003; Exhibiting N-Flux Increase as a Function of Higher Streamflow Accompanied by Higher N Concentrations. Base-flow conditions only.

under low base-flow conditions (Figure 8); when streamflow increase was less than ~0.6 l/s, NO_3^- flux typically decreased. Station 5 exhibited different tendencies—in most cases there was a net loss of NO_3^- flux between Stations 4 and 5, even when discharge increased substantially (lower right quadrate). Only when streamflow increased by more than ~1.2 l/s was there always an increase in NO_3^- flux along this reach. Trend lines show that there is a more rapid increase in NO_3^- flux with increasing discharge upstream (Stations 2-3) than downstream; however, perhaps the most important point here is that there is progressively greater loss of NO_3^- downstream (as evidenced by data points in the lower quadrates, indicating loss of flux). Under most conditions, NO_3^- concentrations decreased downstream, and flux often decreased even when discharge between Stations 3 and 5 increased. For high base-flows, NO_3^- flux increased at every point along the stream.

NO_3^- flux in one of the subchannels, where it drained into the main stream channel upstream of Station 3, increased as discharge within the subchannel increased. High discharge in the subchannel corresponded with higher discharge in the main stream channel. Unlike the main stream channel, the discharge *vs.* flux relationship in the subchannel appeared to be linear; this was because NO_3^- concentrations in the ground-water upwelling source of this subchannel were always high and fairly constant, so flux was simply a function of discharge. Thus, this subchannel was a consistent source of stream NO_3^-, regardless of other conditions.

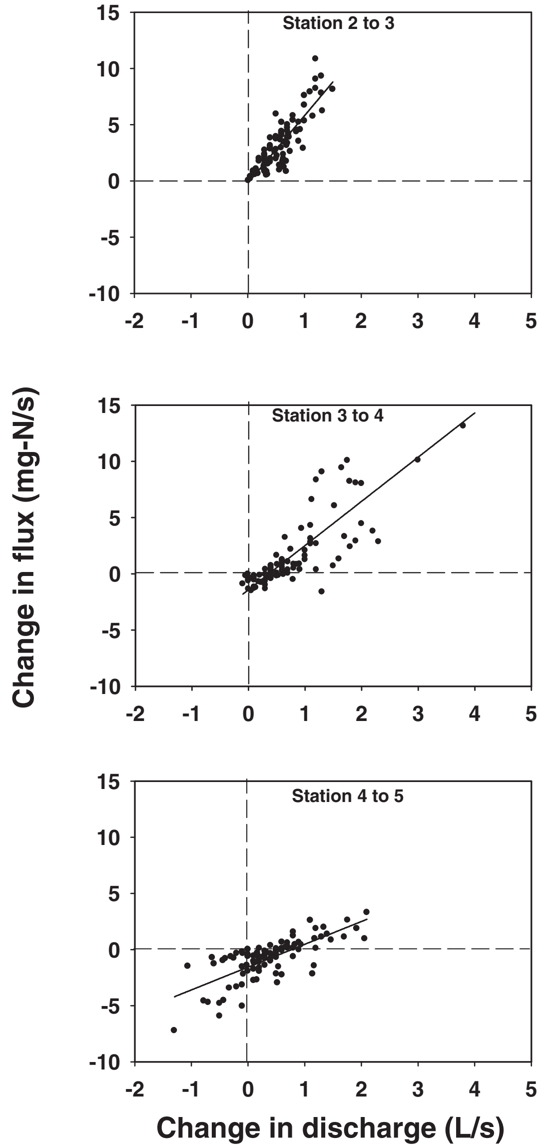

FIGURE 8. Changes in Stream Discharge Compared to Changes in Stream Nitrate-N Flux; Between Stations 2 and 3 (top), Stations 3 and 4 (center), and Stations 4 and 5 (bottom). Upper right quadrates indicate increase in streamflow accompanied by increase in N-flux, lower right quadrates indicate streamflow increase accompanied by loss of N-flux, lower left quadrates show loss of both flow and flux. Base-flow conditions only.

DISCUSSION

There were large seasonal variations in stream NO_3^- patterns at this site. This was at least partly due to lack of uptake of water (and nutrients) by vegetation in the dormant (winter) season, accompanied by higher stream discharge. Regardless of season or rainfall patterns, certain portions of the riparian zone—specifically ground-water upwelling zones between Stations 2 and 3—consistently contributed disproportionately to base-flow stream NO_3^- flux (reflected in average nitrate flux along that stream reach—see Table 1).

According to Angier *et al.* (2005), the upstream section of the riparian zone was characterized by high piezometric heads and positive vertical hydraulic gradients in the floodplain. Conversely, high piezometric heads and high vertical hydraulic gradients directly beneath the stream channel, and lower heads and gradients under the adjacent riparian floodplain (plus the absence of visible ground-water upwelling onto the land surface) indicated that most of the ground water contributing to stream discharge at Stations 4 and 5 was likely delivered directly into the stream channel rather than onto the land surface. However, during high base-flow conditions, upwelling zones appeared on the downstream portion of the floodplain, and dormant macropores along the stream channel side were observed to become active.

Other studies have demonstrated how preferential flow paths (such as macropore networks) can become more active, and represent increasing proportions of overall ground-water flow, as moisture conditions increase (e.g., Tsuboyama *et al.*, 1994; Sidle *et al.*, 1995). In this study, such activated preferential flow paths likely provided additional NO_3^- sources to the lower stream reaches during elevated base flows. In addition, the presence of a vadose zone in this part of the riparian zone (as opposed to upstream where there was little or no vadose zone) probably allowed some NO_3^- storage, which was subsequently conveyed to the stream as water table levels rose. This phenomenon has been documented in other studies (e.g., Lucey and Goolsby, 1993; Groffman *et al.*, 2002, 2004) as well. The stream section between Stations 3 and 5 became a net contributor to total stream NO_3^- load only under elevated base-flow conditions. It is unlikely that flux increases in the stream resulted from instream nitrification processes (such as conversion of NH_4^+), because stream water samples typically contained little or no other forms of N besides NO_3^- and mineralization rates for microbially available organic N in the stream would have been much lower than NO_3^- flux rates.

Disparities in NO_3^- delivery to the stream appeared to reflect the individual dynamics of the adjoining riparian areas. Hydrological and/or geochemical conditions downstream were presumably more amenable to NO_3^- removal—or, alternately, less prone to delivering NO_3^- to the stream. This was especially true for low-flow regimes, when ground-water delivery to the stream was slowest. For higher base flows, though, more ground water was forced through the system, and at a faster rate. The few small areas of ground-water upwelling in the downstream portion of the riparian zone, inactive under low base-flow conditions, became visible sources of surface water during periods of higher base flow, with a concomitant increase in stream NO_3^- flux.

Many studies evaluating the effects of wet *vs*. dry years on NO_3^- delivery have concluded that denitrification increases during wet years (Lowrance, 1992a,b; Simmons *et al.*, 1992; Ashby *et al.*, 1998), so stream NO_3^- concentrations hypothetically should be lower. Presumably in wet years, the water table in the floodplain is higher and thus closer to the top layers of riparian soil (which typically have the greatest denitrification potential), so more of the ground water would then be forced to move through the most biologically active shallow soils (Ashby *et al.*, 1998). In addition, there may be more dilution resulting from more rainfall. Water table levels (determined from wells) at this site, however, usually remained within the upper (0-50 cm deep) layer of riparian soil, which should have encouraged nitrate removal (Groffman *et al.*, 1992; Lowrance, 1992a,b; Pavel *et al.*, 1996). During dry, low rainfall and low stream discharge conditions (typically in summer), ground water discharged to the surface at a slower rate, presumably allowing more contact time with the potentially denitrifying sediments and more efficient N removal. Similar phenomena applied to water within the stream channel itself: in drier conditions there was longer residence time, greater contact with carbon-rich channel bed material, and fewer active macropores along the channel sides delivering high-NO_3^- ground water directly into the stream. There was also more loss of water (mostly through transpiration) along the stream in 1999 and 2002 (drier years); consequently, NO_3^- flux was diminished (Figure 6, Table 1).

Instream NO_3^- *Processing*

For denitrification reactions to occur, there generally need to be anoxic or low suboxic conditions (Lawrence, 1996; Martin *et al.*, 1999). As with the riparian zone subsurface, there were anoxic and suboxic conditions within the stream channel as well. Stagnant pools formed around natural stream dams that consisted of large woody debris. There were often large areas of biofilm observed on the stream surface. These biofilms likely formed in response to added C in the stream from decaying leaves and organic matter that accumulated in the channel, especially in autumn. These circumstances can provide favorable zones for nutrient removal within the stream channel. Thus, there was potential for instream NO_3^- removal within this ecosystem.

Evidence of instream NO_3^- processing was most apparent when there was loss in total stream NO_3^- flux under gaining stream conditions. Figure 9 shows

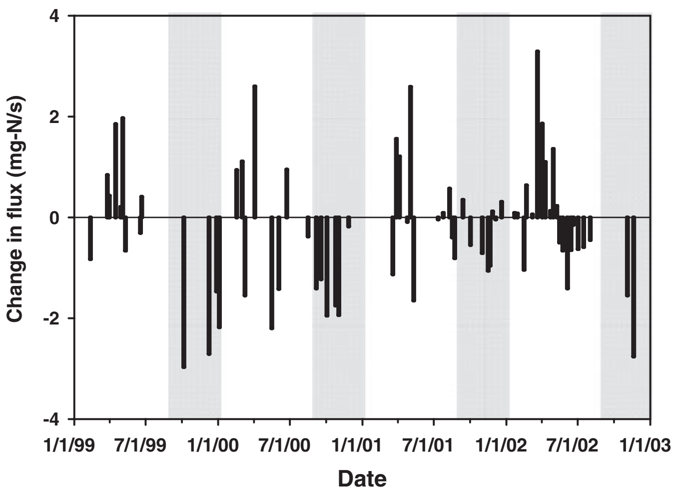

FIGURE 9. Changes in Stream Nitrate-N Flux (positive and negative) Between Stations 4 and 5, January 1999 to January 2003, Showing Loss of Flux Predominately in Autumn (gray sections). Gaining stream and base-flow conditions only.

change in NO_3^- flux (positive and negative) between Stations 4 and 5 only for those times when there was an increase in streamflow between these stations. This stream interval is depicted because evidence for instream N loss was most apparent here, and the impact on N export (from Station 5) can be seen. Loss of stream NO_3^- flux occurred most often, and most acutely, in the autumn months (gray-shaded areas in Figure 9), when there appeared to be increased carbon available within the stream channel in the form of decaying leaves. Under these conditions, where increase in stream discharge was accompanied by a decrease in NO_3^- flux, instream NO_3^- processing was the likely removal mechanism. Simultaneous loss of NO_3^- rich stream water to the ground water and replacement with low NO_3^- ground water was unlikely, as piezometric data at those times indicated only positive gradients from ground water to stream channel. Because plant uptake of NO_3^- is largely a passive process, streamside vegetation could not explain all the NO_3^- loss in the stream, particularly when there was overall gain rather than loss in stream discharge. Thus, microbial utilization of NO_3^-, in the presence of organic C was the most likely mechanism for instream NO_3^- removal under these circumstances: gaining stream but not high base-flow conditions, decaying plant residues within the stream channel, zones of stagnant and/or slow-moving water in those stream reaches where NO_3^- loss was observed.

Streamflow Rates and Riparian Buffer Function

Stream NO_3^- concentrations were highly variable at this site. The greater the flow increase per unit stream channel length (Angier *et al.*, 2001), the higher the NO_3^- concentrations found. Base-flow stream NO_3^- concentrations tended to be highest under high-moisture (high-flow) conditions; maximum base-flow NO_3^- flux conveyed by this stream occurred under elevated base-flow conditions (Figure 4). Higher base-flow conditions resulted in a greater ability for NO_3^- to bypass the remediative properties of the riparian ecosystem. Preferential flow mechanisms appeared to become more prominent during higher base-flow conditions, with higher ground-water discharge rates in upwelling zones, greater flow through subchannels, and formerly inactive subchannels and streamside macropores becoming active (Angier *et al.*, 2005); thus, a greater proportion of total stream discharge was accounted for by measured preferential flow pathways (e.g., upwelling zones, secondary channel discharge, macropore discharge). The impact of this on stream base-flow N-flux can be seen in Table 1 and Figure 6, with relatively "wetter" years (e.g., 2000) and seasons (winter) showing higher average exported N-loads.

NO_3^- loss within the stream channel also appeared to be affected by stream discharge rates. Instream NO_3^- processing was observed under low-to-moderate base-flow conditions. Higher streamflow rates were likely associated with shorter instream residence times (greater water velocity), reduced contact between the water column and stream bed (lower surface-to-volume ratio for water within the channel), and flushing out of sites (such as natural dams and woody obstructions) conducive to instream NO_3^- processing. The steep portion of stream NO_3^- flux patterns evident in Figure 7 resulted partly from less efficient removal of NO_3^- from ground water, inhibition of instream nutrient processing, and less overall residence time, combining to diminish the remediation capacity of the entire ecosystem.

"Critical Areas" Within Riparian Zones

Certain critical areas within the riparian zone contributed disproportionately to stream NO_3^- flux, and were responsible for most of the NO_3^- that was exported from the watershed during base flow. The greatest increase in NO_3^- flux per unit stream length occurred between Stations 2 and 3 under most base-flow conditions (Figure 10). Much of the observed difference in NO_3^- delivery along different stream sections was associated with the total amounts of water added to the stream in those reaches; generally, those areas that contributed most to stream discharge were also those areas where the highest surface-water NO_3^- concentrations were found. Thus, there were areas within the riparian

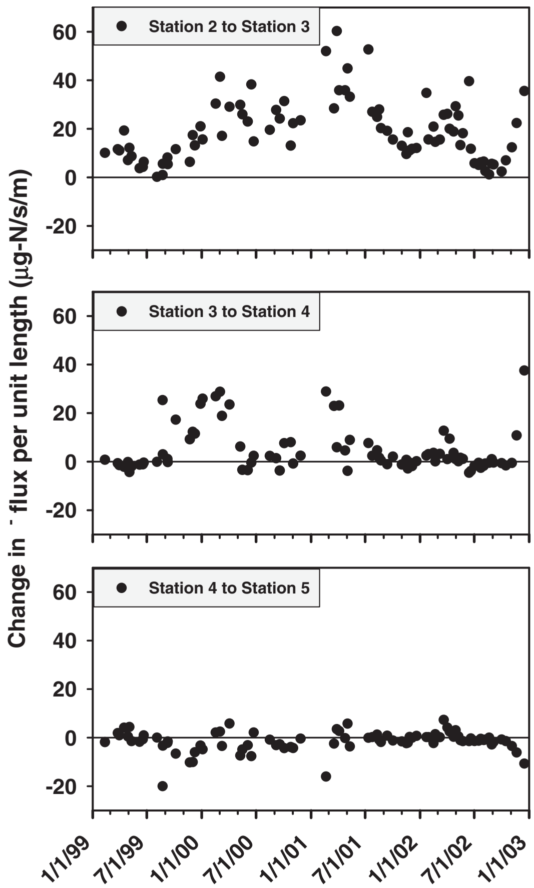

FIGURE 10. Changes in Stream Nitrate-N Flux per Unit Stream Length (Normalized for Distance Between Stations), January 1999 to January 2003. Flux changes, denoted in micrograms per second per meter of stream length, are plotted along the *y*-axis for Stations 2 to 3 (top), 3 to 4 (center), 4 to 5 (bottom).

zone that contributed disproportionately to base-flow stream NO_3^- flux (Table 1, Figures 5, 6, and 10), by contributing greater volumes of agriculturally influenced ground water, and by allowing more bypass of NO_3^- removal mechanisms within the ecosystem. Areas that were always saturated were the same areas, where the greatest proportion of NO_3^--bearing ground water emerged (and ultimately entered the stream channel). This in turn affected the overall NO_3^- removal capability of the entire ecosystem.

Consistent streamflow increases between Stations 2 and 3, coupled with consistently high NO_3^- concentrations, meant that (under most base-flow conditions) the majority of the stream NO_3^- flux came from this upper part of the riparian zone. Thus, this area was responsible for most of the NO_3^- that was exported from the watershed during base flow; 50% of the average annual base-flow NO_3^- flux (the percent flux added between Stations 2 and 3—see Table 1) was contributed by a portion of the riparian floodplain that represented less than 10% of the total riparian land area. The rest of the riparian system appeared to be relatively more effective at NO_3^- removal, except under high base-flow conditions. The area around Station 3 was in effect a critical area in terms of NO_3^- export potential for the entire ecosystem. So, while riparian zones as a whole perform a function disproportionate to their size relative to the entire watershed (Ettema *et al.*, 1999; Martin *et al.*, 1999), within riparian zones there can be critical areas whose impact is disproportionate compared with the riparian zone as a whole. Noncritical areas within a riparian zone may require less attention (e.g., narrower forested corridors), while critical areas may require additional mitigation techniques [conservative tillage/fertilizer application methods for nearby agricultural fields, wider buffer strips, additional buffers (such as grass buffer strips), etc.]. Addressing the conditions that predominate in critical areas and allocating resources to identify and manage these types of areas will improve the overall contaminant mitigation function of riparian ecosystems.

CONCLUSIONS

According to much of the literature, wide (at least 50 feet) riparian wetlands associated with unincised first-order streams in low-relief areas should be highly effective areas for NO_3^- removal (Brinson, 1988; Cylinder *et al.*, 1995; Schnabel *et al.*, 1996; Ashby *et al.*, 1998; Ettema *et al.*, 1999; Peterson *et al.*, 2001). This was not observed at this study site, however. It was in the wetland near the stream head, where the stream channel was least incised (and the riparian buffer still more than 100-feet wide), that the highest NO_3^- concentrations in the stream water were usually detected. Portions of the watershed (downstream) where the channel was more incised usually exhibited lower stream water NO_3^- content. The continuously saturated (critical) areas near the stream head had a significantly greater potential for delivering NO_3^- to the stream, both in terms of concentration and flux. The downstream areas in contrast often showed a marked decrease in stream water NO_3^- concentrations and fluxes within the channel, indicating likely instream NO_3^- removal. This phenomenon often occurred when total streamflow decreased, so dilution was not a feasible cause. In addition, NO_3^- fluxes sometimes decreased even when flows increased, indicating instream NO_3^- processing in the absence of other possible removal mechanisms (e.g., loss to ground water or plant uptake).

NO_3^- movement and behavior, and delivery to the stream, were nonuniform in this ecosystem. Most of this variability was attributable to substantial spatial differences in hydrological conditions within the riparian zone. However, conceptual models for riparian ground-water contaminant removal typically presume uniformity in ground-water movement and delivery to stream. Proposals and regulations for riparian zone construction, management, and protection are then based upon these simple models. Attempts to characterize riparian buffer contaminant mitigation potential by applying a simplified hydrologic regime to the system will likely result in overestimation of remediation capacity. The presence of a generous buffer and conditions presumably favorable to N removal do not assure that this function will be uniformly effective. It appears that hydrology, particularly as it pertains to the robustness of streamflow generation in a given area, can dictate the likelihood for an area to convey ground-water NO_3^-; greater amounts of ground-water discharge to the surface can correlate with greater stream NO_3^- loads in critical areas. Identifying and addressing these critical areas should help improve the performance of riparian buffer zones and optimize the allocation of land and resources for the purpose of *in situ* natural ecosystem contaminant mitigation.

Thus, from this study (combined with previous research on this subject), it appears that: (1) headwater wetlands are typically sustained by copious ground-water discharge; (2) rapid, focused ground-water discharge is associated with high NO_3^- concentrations; (3) relatively small saturated areas characterized by active ground-water discharge can be a major source of stream NO_3^-; (4) ground-water-fed continuously saturated riparian wetlands may be less, rather than more, effective at removal of NO_3^- from ground water than intermittently surface-saturated areas with deeper water tables; (5) first-order agricultural catchments that drain into ground-water-sustained (perennially saturated) riparian zones may require additional mitigation strategies, such as minimizing use of fertilizers and/or increasing buffer widths. Rather than being locales where NO_3^- removal is most effective, saturated headwater wetlands may be riparian areas where this function is less effective than currently assumed. Although it appeared that substantial amounts of NO_3^- were removed from all areas of the riparian zone—surface-water concentrations were typically lower than contributing ground-water concentrations (Angier *et al.*, 2005)—certain sections were consistently more prone to allow NO_3^- to enter the stream. Understanding conditions that determine spatial and temporal variability in NO_3^- delivery can help in developing strategies to reduce excess nutrients exported from agricultural watersheds.

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