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EFFECTS OF STREAM RESTORATION ON DENITRIFICATION IN AN URBANIZING WATERSHED

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Abstract. Increased delivery of nitrogen due to urbanization and stream ecosystem degradation is contributing to eutrophication in coastal regions of the eastern United States. We tested whether geomorphic restoration involving hydrologic "reconnection" of a stream to its floodplain could increase rates of denitrification at the riparian-zone–stream interface of an urban stream in Baltimore, Maryland. Rates of denitrification measured using in situ ^{15}N tracer additions were spatially variable across sites and years and ranged from undetectable to >200 μg N·(kg sediment)$^{-1}$·d^{-1}. Mean rates of denitrification were significantly greater in the restored reach of the stream at 77.4 ± 12.6 μg N·kg^{-1}·d^{-1} (mean ± SE) as compared to the unrestored reach at 34.8 ± 8.0 μg N·kg^{-1}·d^{-1}. Concentrations of nitrate-N in groundwater and stream water in the restored reach were also significantly lower than in the unrestored reach, but this may have also been associated with differences in sources and hydrologic flow paths. Riparian areas with low, hydrologically "connected" streambanks designed to promote flooding and dissipation of erosive force for storm water management had substantially higher rates of denitrification than restored high "nonconnected" banks and both unrestored low and high banks. Coupled measurements of hyporheic groundwater flow and in situ denitrification rates indicated that up to 1.16 mg NO_3^--N could be removed per liter of groundwater flow through one cubic meter of sediment at the riparian-zone–stream interface over a mean residence time of 4.97 d in the unrestored reach, and estimates of mass removal of nitrate-N in the restored reach were also considerable. Mass removal of nitrate-N appeared to be strongly influenced by hydrologic residence time in unrestored and restored reaches. Our results suggest that stream restoration designed to "reconnect" stream channels with floodplains can increase denitrification rates, that there can be substantial variability in the efficacy of stream restoration designs, and that more work is necessary to elucidate which designs can be effective in conjunction with watershed strategies to reduce nitrate-N sources to streams.

Key words: Chesapeake Bay, USA; eutrophication; nitrogen; stream restoration; urbanization.

Introduction

Many coastal water bodies in the United States now receive large loads of nitrogen as a result of land use change (e.g., Howarth et al. 1996, Vitousek et al. 1997, Paul and Meyer 2001). In the Chesapeake Bay watershed, rapid expansion of urban, suburban, and exurban land (Brown et al. 2005, Jantz et al. 2005) has coincided with increases in eutrophication, hypoxia, and harmful algal blooms in coastal waters (e.g., Boesch et al. 2001, Howarth et al. 2002, Kemp et al. 2005). Land use change has complicated efforts to identify sources and "sinks" of nitrogen in this watershed (Boesch et al. 2001), and many river miles of suburban and urban streams are now being restored in the Chesapeake Bay watershed and other areas of the United States with ancillary objectives of improving water quality (Bernhardt et al. 2005, Hassett et al. 2005). Despite the billions of dollars currently invested in the >37 000 stream restoration projects in the United States, there are few actual measurements of the effects of stream restoration on denitrification (Bernhardt et al. 2005, Hassett et al. 2005). We quantified rates of denitrification at the riparian-zone–stream interface of an urbanizing watershed using an in situ stable isotope approach and investigated the potential for stream restoration associated with storm water management to increase rates of denitrification in riparian sediments.

Although fluxes of total nitrogen from river basins have doubled globally since pre-industrial times (Green et al. 2004), it is estimated that only between 20% and 30% of the nitrogen that is added to large watersheds of the eastern United States is delivered to coastal waters

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(Howarth et al. 1996, Boyer et al. 2002). A considerable amount of nitrogen appears to be removed via denitrification, the microbial conversion of nitrate to N_2 and N_2O gases (e.g., Alexander et al. 2000, Seitzinger et al. 2002). From a landscape perspective, the interface of riparian zones and streams may be a "hot spot" of denitrification due to low oxygen and subsidies of bioavailable organic carbon from streams and upland sources in these zones (e.g., Peterjohn and Correll 1984, Hedin et al. 1998, McClain et al. 2003). Small streams can constitute up to 85% of total stream length within drainage networks (Peterson et al. 2001), and rates of denitrification have been shown to increase in riparian groundwater with increasing proximity to streams (Hedin et al. 1998, Kellogg et al. 2005). Recent in situ measurements have shown that denitrification removes ~15% of nitrate in forest streams with very low concentrations of nitrate (Mulholland et al. 2004) and can remove 34–50% of nitrate in agricultural streams with higher concentrations of nitrogen (Böhlke et al. 2004, Pribyl et al. 2005).

In many urbanizing areas, the capacity of streams and rivers to process and remove nitrogen has been impaired due to the effects of surrounding land use change (Groffman et al. 2002, Grimm et al. 2005, Kaushal et al. 2006). Increased inputs of nitrogen to headwater streams from anthropogenic sources and domestic wastewater can saturate biological demand, leading to increased downstream transport of nitrogen (Bernot and Dodds 2005, Gücker and Pusch 2006). Channel incision as a result of erosive runoff from impervious surfaces (Wolman 1967, Henshaw and Booth 2000) can reduce contact between water in the channel and the streambed and subsurface zones of nitrogen uptake and removal in sediments (Paul and Meyer 2001, Groffman et al. 2002, Sweeney et al. 2004). Reduced infiltration capacity in watersheds due to impervious surfaces such as roadways and parking lots, in combination with stream incision, can also lead to marked reductions in riparian water tables and soil moisture levels. Reductions in riparian water tables decrease hydrologic "connectivity" between riparian groundwater and the stream (Groffman et al. 2002, Walsh et al. 2004) and contribute to transmission of nitrate to streams via deeper hydrologic flow paths in riparian zones (Groffman et al. 2002, 2003, Böhlke et al. 2007). These hydrologic changes can reduce denitrification rates in riparian zones and also cause incoming nitrate from groundwater to bypass active sites of riparian denitrification (Groffman et al. 2003, Böhlke et al. 2007).

In response to widespread urban stream degradation, many suburban and urban streams and rivers are being restored in the Chesapeake Bay region and the United States (Bernhardt et al. 2005, Hassett et al. 2005, Wohl et al. 2005). The primary goals of most of these restorations are promoting geomorphic stability and/or improved storm water management practices, but water quality improvement is often listed as an ancillary goal of these efforts (Bernhardt et al. 2005, Hassett et al. 2005). Previous work has suggested that stream restoration has the potential to improve water quality (e.g., Stanley and Doyle 2002, Mayer et al. 2003, Groffman et al. 2005), and recent work suggests that stream restoration techniques may influence N retention via alteration of hydrologic residence time (e.g., Kasahara and Hill 2006, Boulton 2007, Bukaveckas 2007, Roberts et al. 2007). Little is currently known, however, about the specific types of restoration that are most effective and the relative role of denitrification in N uptake and transformation, and more empirical data is needed to evaluate efficacy and variability across restoration sites, given that the number of restoration projects is rapidly growing (Wohl et al. 2005, Palmer and Bernhardt 2006).

In this study, we quantified the effects of geomorphic stream restoration on rates of in situ N removal via denitrification using ^{15}N-based "push-pull" methods (e.g., Istok et al. 1997, Addy et al. 2002, Whitmire and Hamilton 2005) along the riparian-zone–stream interface of a coastal stream in Baltimore, Maryland, USA. This stream had been partially restored based on geomorphic reconstruction of the stream channel following design models of Rosgen (1996) using high armored banks and also an experimental floodplain subreach that did not use rigid structures to fix the stream channel in place. We hypothesized that stream restoration has the potential to increase denitrification rates at the riparian-zone–stream interface in an urbanizing watershed, but that restoration designs promoting low banks with increased hydrologic connectivity at the riparian-zone–stream interface would show the highest rates of denitrification. A secondary objective was to investigate the potential importance of the riparian-zone–stream interface as a site for mass removal of nitrate-N by coupling measured in situ denitrification rates with estimates of groundwater flow. Results of the present study provide estimates of in situ denitrification along the riparian-zone–stream interface of a restored stream and make a further contribution toward the investigation of the importance of denitrification rates associated with degraded urban ecosystems and certain forms of stream restoration.

Methods

Site description

Minebank Run is a low-order stream with a watershed area of ~8.47 km^2 located in Baltimore County, Maryland (latitude 39°24′43″ N, longitude 76°33′12.5″ W; Fig. 1). It lies in the Piedmont physiographic province of the eastern United States with its headwaters originating from a storm drain in a densely urbanized section of Towson, Maryland, and drains into the Gun Powder River, a tributary of the Chesapeake Bay. The segment of the Minebank Run watershed related to the present study was developed in the 1950s and 1960s, prior to implementation of storm

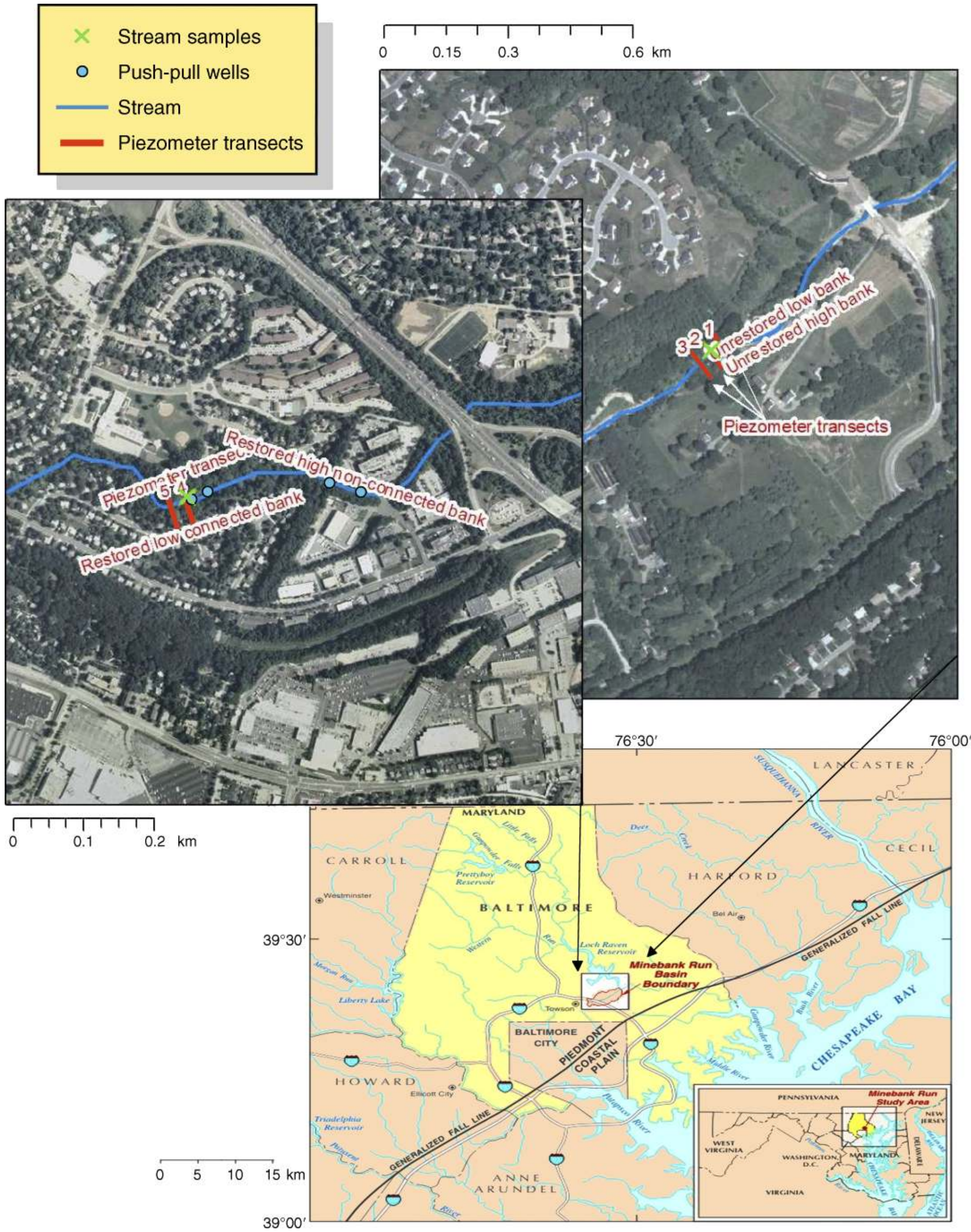

FIG. 1. Location of the Minebank Run study area, Baltimore County, Maryland, USA. Detailed locations are indicated in the unrestored and restored reaches of Minebank Run for groundwater wells used in the in situ denitrification measurements, sampling sites for stream water chemistry, and piezometer transects used for groundwater chemistry and hydrologic flow measurements. The figure is reprinted from Doheny et al. (2006).

water management regulations. Approximately 30–35% of the drainage area is covered by impervious surfaces, with 81% of the land area classified as urban/suburban, 17% as forest/open space, and 2% as agriculture/farmland (Doheny et al. 2006). The watershed ranges in elevation from ~122–152 m above sea level at the drainage boundaries to ~46–122 m above sea level in the stream valley. Stream slopes are ~1% in most locations, but tend to be somewhat larger in the headwater areas. The combination of fairly large stream slopes, significant relief, and impervious surfaces in the headwater areas cause the stream stage to increase and decrease very rapidly during storms (Doheny et al. 2006; Biohabitats, Inc., et al., *unpublished manuscript*).

The long-term annual mean precipitation for Baltimore is 106.7 cm, and annual precipitation at Minebank Run was 83.7 cm, 163.0 cm, and 131.3 cm, respectively, during water years 2002, 2003, and 2004 (Doheny et al. 2006). During water years 1997 to 2004, annual runoff averaged ~41.9 cm and annual mean discharge averaged ~0.099 m^3/s (Doheny et al. 2006). Instantaneous flood discharges exceeded 42.475 m^3/s in response to storm events occasionally during years from 1997 to 1998 with substantial erosive force in the stream channel leading to severe degradation of banks, exposed sewer lines, and fractures in concrete structures (Doheny et al. 2006).

Stream restoration

The headwater reach of Minebank Run, draining 2.07 km^2 of the watershed, was restored in 1998 and 1999, and a lower reach of the stream draining 6.40 km^2 of the watershed was left unrestored and slated for restoration. The Baltimore County Department of Environmental Protection and Resource Management (DEPRM) used geomorphic reconstruction techniques to remediate severe stream incision from erosion and increase geomorphic stability in the headwater reach (Fig. 2A). Restoration efforts included filling the channel with sediment, cobbles, and boulders and constructing point bars, riffles, and meander features along the reach and creating step-pool sequences. In the riparian zone, dominant planted trees included *Acer saccarum*, *Fagus grandifolia*, *Liriodendron tulipifera*, *Quercus alba*, and *Q. rubra*, and planted shrubs and herbs included dominant varieties such as *Kalmia latifolia*, *Andropogon gerardii*, and *Panicum virgatum*. Banks were stabilized in some reaches by employing one or more of the following techniques: reshaping slopes to reconnect the channel to the floodplain, embedding root wads, planting cover vegetation, and covering with erosion mats. In some areas, incised, high banks prone to erosion were armored with rocks and channelized to keep water in the stream and rapidly transport water away from commercial properties, with less potential for overbank flooding (Fig. 2B). A "nonconnected" armored and channelized subreach was selected for the present study, ~50 m in length. In other areas away from commercial properties, low banks were engineered to promote flooding over the banks and dissipation of erosive force, creating low, hydrologically "connected" riparian areas (Fig. 2C). This hydrologically connected subreach in the present study was ~150 m in length. Mean bank height in the entire restored reach was significantly lower at 77.0 ± 11.0 cm (mean ± SE; $N = 12$ replicates) than mean bank height in the entire unrestored reach at 114.7 ± 7.4 cm ($N = 21$ replicates; two-sample t test, $t = 2.928$, $P = 0.006$).

In the unrestored reach, steeply eroded banks and general geomorphic instability were common, with incision of up to 2–3 m revealing the bedrock in some places. Riparian zones along the unrestored section of Minebank Run consist of mixed hardwood, second growth forest interspersed among mowed grass areas in a county park.

Stream and groundwater sampling

Surface water samples from Minebank Run were collected approximately every two weeks from April 2003 to December 2005 in both the unrestored and the restored reaches of Minebank Run. Time series samples for nitrate concentrations were collected at U.S. Geological Survey (USGS) gauged station 0158397925, Minebank Run at Intervale Court near Towson, Maryland, since June of 2004 and USGS station 0158397967, Minebank Run near Glen Arm, Maryland, since July of 2002 (information on site locations, descriptions, and data from the USGS stations is *available online*).[6,7] Groundwater was sampled in the unrestored and restored reaches during April, July, and October 2003 and May 2004. Groundwater was collected with a peristaltic pump through a flow cell and Hydrolab (Hach, Loveland, Colorado, USA) from piezometer nests installed in the stream channel and stream banks. The network of piezometers was designed to quantify spatial and temporal variability of hydrology and biogeochemistry among stream features that were altered significantly by the restoration. Piezometers for groundwater chemistry were installed along three perpendicular transects in a severely incised and eroding section of the unrestored reach and along two perpendicular transects in the restored reach where restored channel features included low, hydrologically connected banks for spreading of water over the floodplain and dissipation of erosive force.

Piezometers consisted either of 2.5 cm diameter stainless steel pipes or 0.95-cm polypropylene tubing screened at the lower 15 cm with 0.25-mm stainless steel mesh. Piezometers were arranged in nests of three wells placed ~1 m apart with screens positioned 61, 122, and 183 cm below the surface of the streambed. Stream bank piezometers were installed 7.7 ± 1.9 m from the stream channel thalweg at depths that matched the mean elevation of the channel piezometers. One additional piezometer nest was installed along the middle transect of the unrestored reach to account for a large meander in the stream at that position. Piezometers in the restored reach were located between two automated stream gauges operated by the U.S. Geological Survey that recorded stream flow at five-minute intervals. Distances between transects were 38 m in the restored reach and 72 m and 45 m in the unrestored reach. A total of 33 piezometers and four surface water stations (located between the piezometer transects) were sampled at the unrestored reach. Eighteen piezometers and three surface water stations (located between the piezometer transects) were sampled at the restored reach. Samples

[6] ⟨http://nwis.waterdata.usgs.gov/nwis/nwisman/?site_no=0158397925⟩

[7] ⟨http://waterdata.usgs.gov/nwis/uv?0158397967⟩

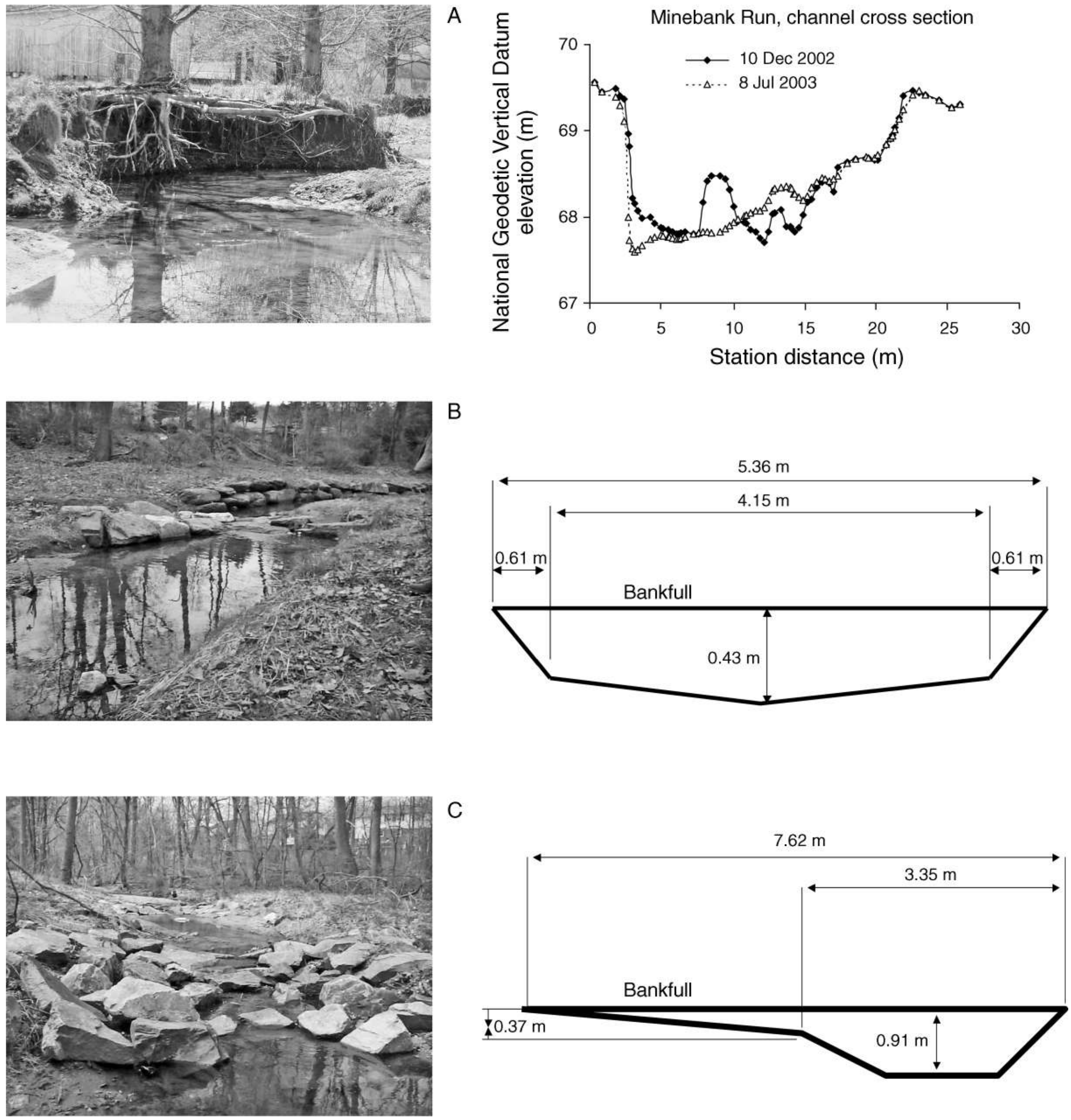

FIG. 2. (A) Unrestored reach of Minebank Run showing extreme incision of banks and the stream channel. The cross section shifted on 10 December 2002 (dark line) and became more incised on 8 July 2003 (lighter line). (B) Restored "nonconnected" reach showing armoring of banks with rocks and channelized stream cross sections that promote rapid drainage of surface water away from commercial property and decrease connections between the stream and the riparian zone. (C) Restored "connected" reach showing step pool sequences, meanders, and engineered stream cross sections that promote overland flooding to dissipate erosive force.

were stored on ice and acidified to pH 2 and/or filtered with 0.45-μm filters before subsequent chemical analyses for water chemistry.

Measurement of in situ denitrification rates

We measured rates of in situ denitrification rates in both low and high banks of the restored and unrestored reaches of Minebank Run using a push-pull method (similar to Trudell et al. 1986, Istok et al. 1997, Addy et al. 2002) in June 2003, November 2003, and June 2004. Measurements of denitrification were taken during these months to quantify N removal during spring before summer base-flow conditions and during autumn before snow cover. Detailed descriptions of the method can be found in Addy et al. (2002) and Kellogg et al. (2005). Briefly, we "pushed" (i.e., injected) 10 L of previously collected groundwater amended with ^{15}N-enriched NO_3^- and SF_6 into a single mini-piezometer and then "pulled" (i.e., extracted) groundwater from the same mini-piezometer after an incubation period of 4 h. Prior to injection, the groundwater was adjusted to ambient dissolved oxygen concentrations to mimic aquifer conditions. Groundwater samples were analyzed for ^{15}N-enriched denitrification gases (N_2O and N_2) and a conservative tracer (SF_6) to provide information on the recovery of the introduced plume. Denitrification rates were estimated from only the "core" of the plume (the first 2 L of the plume pulled from the mini-piezometer) after the incubation period to minimize the confounding effects of dispersion and advection.

Mini-piezometers (similar to those described by Winter et al. [1988]) consisting of small steel well points (1.8-cm outer diameter, 2-cm screen length; AMS, American Falls, Idaho, USA) attached to gas-impermeable Teflon tubing extending into the sediment were installed in four locations to a depth of 0.5 m below the adjacent streambed. In the unrestored reach, two mini-piezometers were installed on a high bank affected by deep channel incision and three were installed on a low opposite bank. In the restored reach, two mini-piezomenters were established in an area where low banks were engineered to promote flooding over the banks (i.e., a low, hydrologically "connected" riparian area), and two were established in a high bank that was armored and stabilized by stones (i.e., a hydrologically "nonconnected" area). In both unrestored and restored reaches, the two to three wells on a given bank were placed >5 m apart. Locations of wells were assumed to be independent because previous work has shown that denitrification rates can be "patchy" over smaller spatial scales such as these (Gold et al. 1998). In all four locations, mini-piezometers were established ~0.5 m from the stream bank.

To prepare for in situ NO_3^- removal push-pull tests, we collected 10 L of groundwater from each mini-piezometer ~24–48 h before performing isotopic push-pull tests on each mini-piezometer (10 L of water was drawn from each well before being pushed back into the same piezometer for denitrification measurements). Groundwater from each piezometer was stored at 4°C (maximum of two-day storage in a carboy) until the push-pull test. Each individual dosing solution specific to a piezometer consisted of 10 L of ambient groundwater enriched with 32 mg Br^-/L (as KBr) and 32 mg NO_3^--N/L (as KNO_3; isotopically enriched [20 atom percent ^{15}N]). Because nitrate concentrations were enriched relative to background, this may have contributed to elevated denitrification rates representing potential rates instead of actual rates. Previous work has suggested, however, that denitrification may be less limited by nitrate concentrations when background nitrate concentrations are high and may be limited instead by microbial diffusional constraints (Myrold and Tiedje 1985). SF_6 (100 μL/L) balanced in helium (Matheson Trigas, Gloucester, Massachusetts, USA) was bubbled into the dosing solution to saturate the solution with SF_6 and lower the dissolved oxygen (DO) to ambient levels (~20 min per solution).

Samples of the dosing solution were taken for dissolved solute and gas analysis (NO_3^-, N_2, N_2O, $^{15}N_2$, $^{15}N_2O$) during each push phase. The 10-L dosing solution was pushed into mini-piezometers with a peristaltic pump at a slow rate (~10 L/h) to minimize changes in the hydraulic potential surrounding the mini-piezometer. After a 4-h incubation period, we obtained samples (the pull phase) of groundwater from each mini-piezometer. Groundwater from the mini-piezometers was pumped slowly (9–13 L/h) to avoid generating air bubbles within the tubing. Groundwater and gas samples were collected at periodic intervals throughout the pull phase. All groundwater samples for water chemistry were stored at 4°C until analysis.

Groundwater samples to be analyzed for dissolved gases (N_2, N_2O, $^{15}N_2$, $^{15}N_2O$, SF_6) were collected with a syringe attached to an airtight sampling apparatus made of stainless steel tubing connected to the peristaltic pump. These groundwater samples were injected into an evacuated serum bottle, and the headspace was filled with high purity He gas. After incubating overnight at 4°C and shaking, we sampled the bottle headspace to extract SF_6 and the gases produced by denitrification (N_2 and N_2O) (Lemon 1981, Davidson and Firestone 1988).

Analytical methods

Dissolved oxygen and temperature of groundwater were measured with a Model 55 DO/temperature meter (YSI, Yellow Springs, Ohio, USA). Groundwater and stream samples were analyzed for NO_3^--N using an automated cadmium reduction method on an Alpkem Rapid Flow Autoanalyzer or Lachat Flow Injection Analyzer (Hach, Loveland, Colorado, USA). Dissolved organic carbon (DOC) was analyzed by high-temperature oxidation in the presence of a catalyst by a Shimadzu TOC 5000 autoanalyzer (Shimadzu, Columbia, Maryland, USA). Concentrations and isotopic composition of N_2 and N_2O gases were determined on a PDZ Europa 20-20 continuous flow isotope ratio mass spectrometer coupled to a PDZ Europa TGII trace gas analyzer (Sercon, Cheshire, UK) at the Stable Isotope Facility, University of California, Davis, California, USA. Concentrations of N_2O and SF_6 gases were analyzed by electron-capture gas chromatography on a Tracor Model 540 (ThermoFinnigan, Austin, Texas) at the Institute of Ecosystem Studies in Millbrook, New York, USA.

Denitrification rate calculations

We calculated the generation rate of the denitrification gases (N_2 and N_2O) using the three field replicate gas samples with the highest tracer recovery (of six within-sample replicates) similar to Addy et al. (2005) and Kellogg et al. (2005), thus minimizing error from dilution and dispersion. In order to calculate the masses of N_2O-N and N_2 gases (in micrograms) in our headspace extraction samples, we used equations and constants provided by Tiedje (1982) and Mosier and Klemedtsson (1994). The masses of N_2O-N and N_2 were transformed to the mass of $^{15}N_2O$-N and $^{15}N_2$ by multiplying by their respective ^{15}N sample enrichment proportion (the ratio of pulled atom percent to pushed atom percent, both corrected for ambient atom percent). Sample $^{15}N_2O$-N and $^{15}N_2$ gas production rates were expressed as micrograms of N per kilogram per day (total mass of $^{15}N_2O$-N or $^{15}N_2$ per volume of water pulled/[dry mass of sediment per volume of water pulled × incubation period]). Each pulled sample represented 1 L of groundwater that occupied 4.37 kg of sediment (bulk density, ~1.65 g/cm^3 from field measurements; porosity, 0.38). Denitrification rates were calculated as the sum of $^{15}N_2O$-N and $^{15}N_2$ generation rates.

Groundwater flow through the riparian-zone–stream interface

Temporal and spatial variability in hydrologic flow and residence time of groundwater at the riparian-zone–stream interface were characterized across three piezometer transects of the unrestored stream reach (transects 1–3), and they were characterized across one transect closest to denitrification measurements in the restored reach nearest the restored, low, connected bank where groundwater flow data was available (transect 4) (Fig. 3). In both unrestored and restored reaches, piezometer networks used for characterization of hydrologic flow and residence time were located near push-pull measurements. Groundwater elevation values in piezometers were measured on dates coinciding with push-pull denitrification measurements or following the push-pull denitrification measurements, and simple assumptions using continuous water level data were made to provide an estimate of range in flow and hydrologic residence time along the reach. Groundwater flow was split into left and right bank compartments of dimensions 1.5 × 1.5 × 1.5 m on both sides of the stream thalweg. Flow in each compartment was estimated by calculating vertical and horizontal gradients based on measurements of water levels in piezometers and applying Darcy's law:

$$q = -k\left(\frac{\partial h}{\partial x}\vec{i} + \frac{\partial h}{\partial z}\vec{k}\right) = k\frac{\partial h}{\partial s}$$

where k was the hydraulic conductivity measured by slug tests at each site. The horizontal gradient, $\partial h/\partial x$, was calculated as the difference between the piezometer water levels in the stream bank and streambeds. Concurrently, the vertical gradient, $\partial h/\partial z$, was determined using the water levels in streambed piezometers. The flow vector on either side of the center line of the stream thalweg was then defined by determining its gradient, $\partial h/\partial s$, and direction counterclockwise from horizontal, θ, using the following two equations (Freeze and Cherry 1979):

$$\left|\frac{\partial h}{\partial s}\right| = \sqrt{\left[\left(\frac{\partial h}{\partial x}\right)^2 + \left(\frac{\partial h}{\partial z}\right)^2\right]}$$

$$\tan\theta = \left[\frac{\partial h}{\partial z} \Big/ \frac{\partial h}{\partial x}\right].$$

Once the magnitude of the flow vector and its direction were known, it was possible to calculate the length of the flow path line, s, through the vertical depth of the compartment and the associated travel time, t, along that path line using $s = \text{depth}/\cos(90 - \theta)$ and $t = s/(q/n)$, where n was a field-measured value of porosity. Finally, a volumetric flow for the compartment was also determined:

$$Q = qA$$

where q is the velocity of flow through the compartment expressed as distance per time and A is the cross sectional area of the compartment perpendicular to the flow vector.

Nitrate removal at the riparian-zone–stream interface

Estimates of groundwater flow on 10 June 2003, 21 November 2003, and 28 May 2004 (as close to dates for push-pull tracer tests as possible) were coupled with coinciding measurements of in situ denitrification rates to investigate the importance of mass nitrate removal at the riparian-zone–stream interface in the unrestored reach. We could only estimate groundwater flow on dates directly coinciding with the push-pull measurements in the unrestored reach. Instead, groundwater flow was only measured in the restored reach following push-pull measurements, and mean denitrification rates were coupled with the range of observed flow conditions from August to November 2004 to estimate a potential range of N removal. We avoided direct comparisons between mass removal rates between reaches (unlike comparisons of in situ dentrification rates) because measurements of groundwater flow were not directly concurrent in the unrestored and restored reaches, although hydrologic flow in the restored reach has showed very little variation across multiple years of monitoring (E. Striz, *unpublished data*). Therefore, differences in denitrification rates across sites were compared by actual measurements using the isotopic ^{15}N push-pull methods, and estimates of mass removal were only used in elucidating the potential role of the riparian-zone–stream interface in mass nitrate-N removal in both unrestored and restored reaches.

Estimates of mass removal were calculated using the following assumptions: (1) the relatively small 1.5 × 1.5 × 1.5 m streambed compartment acted as a steady state complete mix reactor with constant groundwater flow, (2) the denitrification process followed zero order kinetics such that the rates measured from push-pull tests were constant in space and time for the compartment, (3) the denitrification rate was constant with

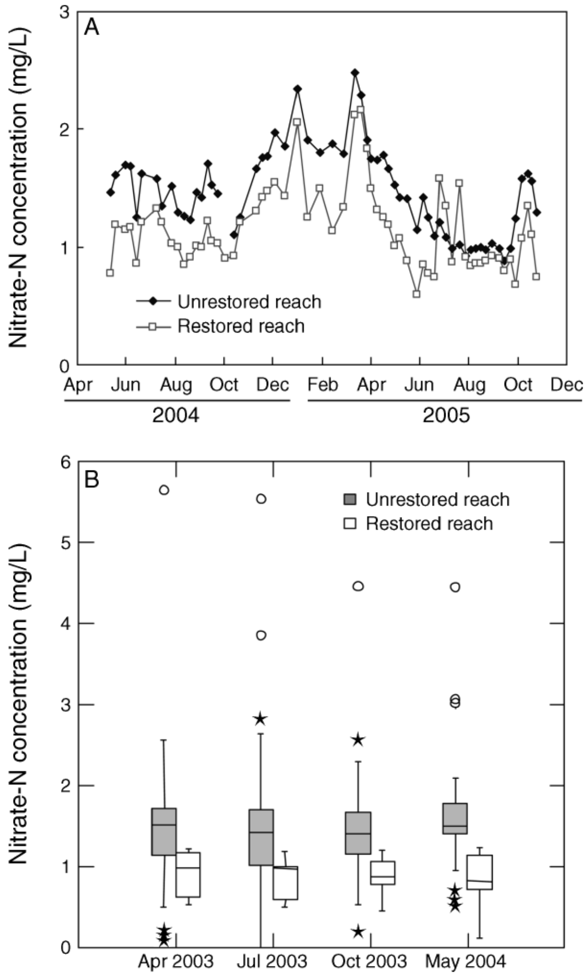

FIG. 3. (A) Concentrations of NO_3^- in stream water in the restored reach and unrestored reach sampled monthly from May 2004 to October 2005. The restored reach had significantly lower concentrations of NO_3^- in stream water than the unrestored reach (paired t test, $P < 0.05$, $t = 5.06$). (B) Mean NO_3^- concentrations in groundwater in the restored reach (closest to the hydrologically connected subreach) and unrestored reach of Minebank Run across four dates between April 2003 and May 2004. The center vertical line of the box-and-whisker plot marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall. Box edges indicate the first and third quartiles. Stars (★) and circles (○) represent outside values: stars denote values 1.5× the interquartile range, and the circles denote values that are 3× the interquartile range. The restored reach had significantly lower concentrations of NO_3^- in groundwater than the unrestored reach averaged over all sampling dates (t test, $P < 0.001$).

concentration and temperature, and (4) there was sufficient input of nitrate into the compartment to support the mass removal rates measured with the push-pull method. Although it is difficult to determine a rate constant from single well measurements (Schroth and Istok 2006), zero order kinetics and a mixed reactor model were chosen in this case, similar to Haggerty et al. (1998) and Whitmire and Hamilton (2005). These assumptions were supported given the short distances (meters) and time frames (hours) considered in this study.

In order to calculate the nitrate mass removal in the compartment, the measured denitrification rate from the push-pull samples was first converted to a compartment fluid volume basis using field-measured values of bulk density, ρ_b, and porosity, n:

$$\text{nitrate mass removal} = \text{rate}(\rho_b/n)$$

where the nitrate mass removal is measured in micrograms of NO_3^- per cubic meter of fluid per day, the rate is measured in micrograms of NO_3^- per kilogram of soil per day, and porosity is measured in kilograms per cubic meter. The total mass of nitrate removed per cubic meter of groundwater was determined by multiplying the converted denitrification rate by the residence time, t, and total volume of the stream compartment, V, where $t = nV/Q$ and $V = wlh$. Using the groundwater flow rates, Q, from the field measured conductivity and hydraulic gradients and the seasonal measurements of in situ denitrification rates, the mass removal of nitrate for each of the transect compartments was calculated on dates with coinciding push-pull denitrification measurements and information on groundwater flow.

Statistical analysis

Statistical analyses were performed using Systat, Version 11 (Systat, Richmond, California, USA). Differences in nitrate concentrations in stream water across the study reaches were evaluated using a paired t test. Differences in nitrate concentrations in groundwater were evaluated using a two-sample t test with pooled variance. Differences in DOC concentrations in groundwater were evaluated using a two-sample t test with pooled variance. We evaluated differences in denitrification rates across restoration status, bank type, and seasonality at the riparian-zone–stream interface using repeated-measures ANOVA. A fully factorial model (all interactions included) was used with the following three factors: (1) restoration status (restored vs. unrestored), (2) bank type (low bank vs. high bank), and (3) season. In order to accurately represent variability in the push-pull method, field replicates (i.e., repeated measures) were taken that consisted of three individual measurements of denitrification at each well during a sampling date. To compare the effect of restoration, five push-pull wells were sampled in the unrestored reach and four push-pull wells were sampled in the restored reach. The effects of bank type (low vs. high) were compared by sampling the two to three wells on each of two to three high and low banks in restored and unrestored reaches. The effect of seasonality was compared among three dates of push-pull measurements (May 2003, November 2003, and June 2004). Given the labor intensiveness of the ^{15}N push-pull method, sample sizes were limited to a total of 26 ^{15}N tracer additions and push-pull measurements conducted during our study. The relationship

TABLE 1. In situ groundwater denitrification rates (means ± SE, $N = 3$ replicates per well).

Well number	Site description	Groundwater denitrification rate (μg N·kg soil^{-1}·d^{-1}) June 2003	November 2003	June 2004	Pooled seasons
1	unrestored, low bank	0.2 ± 0.1	0.1 ± 0.0	181.9 ± 30.3	60.7 ± 31.5
2	unrestored, low bank	13.8 ± 5.2	5.2 ± 2.9	130.9 ± 31.1	48.8 ± 22.7
3	unrestored, low bank	8.2 ± 7.9	0.1 ± 0	no datum	4.2 ± 0.2
4	unrestored, high bank	58.2 ± 47.8	0.2 ± 0	0.1 ± 0.0	19.5 ± 16.9
5	unrestored, high bank	10.5 ± 8.3	7.8 ± 4.9	102.4 ± 4.8	40.2 ± 15.9
6	restored, high, nonconnected bank	4.3 ± 4.2	20.0 ± 5.3	99.0 ± 37.9	41.1 ± 18.4
7	restored, high, nonconnected bank	7.8 ± 3.5	22.9 ± 3.4	47.7 ± 4.4	26.1 ± 6.1
8	restored, low, connected bank	32.0 ± 2.9	31.4 ± 7.0	262.3 ± 36.5	108.6 ± 40.0
9	restored, low, connected bank	112.6 ± 21.1	121.2 ± 18.5	234.8 ± 1.7	156.2 ± 21.3

Note: The study was conducted in Minebank Run, a low-order stream with a watershed area of ~8.47 km^2, located in Baltimore County, Maryland, USA.

between mass removal of nitrate-N in the unrestored reach and the scenario in the restored reach and hydrologic residence time was evaluated by linear regression analysis.

RESULTS

The nitrate-N concentration of stream water in the unrestored reach, 1.47 ± 0.05 mg/L, was significantly higher than the nitrate-N concentration of stream water of the restored reach, 1.15 ± 0.04 mg/L ($t = 5.06$, $N = 62$, $P < 0.01$; Fig. 3A). The nitrate-N concentration in groundwater in the unrestored reach, 1.55 ± 0.08 mg/L, also was significantly higher than the nitrate-N concentration in the restored reach, 0.84 ± 0.06 mg/L averaged over all sampling dates ($t = 3.98$, $N = 147$, $P < 0.001$; Fig. 3B). Mean concentrations of DOC across all dates were also significantly lower in the restored reach than the unrestored reach ($t = 2.63$, $N = 147$, $P < 0.01$), and DOC concentrations were typically low and <1 mg/L in both reaches.

During the sampling periods, riparian groundwater denitrification rates ranged from <1 to 262 μg N·kg^{-1}·d^{-1} for all unrestored and restored sites (Table 1). The mean values for groundwater dissolved oxygen (DO) and temperature for all push-pull wells ranged from 3.1 mg/L to 5.3 mg/L and 14.5°C to 17.6°C, respectively (Table 2), and showed no pattern with denitrification rates. Denitrification rates varied widely and were highest during spring 2004. Results from the repeated-measures ANOVA using three factors (restoration, bank height, and season) showed significant differences in mean denitrification rates between restored and unrestored sites ($F_{1,14} = 8.8$, $P = 0.01$; Fig. 4A), denitrification rates varied across seasons ($F_{2,14} = 25.1$, $P < 0.001$; Fig. 4B), and denitrification rates were higher at the low-bank, hydrologically connected sites than at the high-bank sites ($F_{1,14} = 20.3$, $P < 0.001$; Fig. 4B). Over all seasons, denitrification rates were 77.4 ± 12.6 μg N·kg^{-1}·d^{-1} at restored sites and 34.8 ± 8.0 μg N·kg^{-1}·d^{-1} at unrestored sites (Fig. 4A). The hydrologically connected, low-bank, restored site consistently had significantly higher mean in situ rates of denitrification than the other sites (Fig. 4B), a result that also produced a significant interaction between restoration and bank height ($F_{1,14} = 7.2$, $P = 0.02$). A significant interaction between bank height and season was a function of very high denitrification rates in low banks during the June 2004 sampling date ($F_{2,14} = 7.9$, $P = 0.005$). There were no significant differences in replicates within subjects, indicating that the replicate measures in wells did not trend upward or downward. Likewise, no replicate by factor interactions were significant, and no trends occurred among the replicates within the factors (all P values > 0.14).

Results from piezometer studies indicated that there was active hydrologic exchange at the riparian-zone–stream interface in the unrestored reach. Regional shallow groundwater showed a general flow toward

TABLE 2. Dissolved oxygen and temperature of ambient groundwater in push-pull wells on June 2003, November 2004, and June 2004 (means ± SE, $N = 3$ sampling dates).

Well number	Site description	Dissolved oxygen (mg/L)	Temperature (°C)
1	unrestored, low bank	5.3 ± 1.2	15.6 ± 1.7
2	unrestored, low bank	4.5 ± 0.5	15.9 ± 1.1
3	unrestored, low bank	4.9 ± 0.8	16.2 ± 1.5
4	unrestored, high bank	4.1 ± 0.9	15.2 ± 0.6
5	unrestored, high bank	3.7 ± 0.7	15.5 ± 0.5
6	restored, high, nonconnected bank	4.5 ± 1.3	17.6 ± 3.4
7	restored, high, nonconnected bank	3.6 ± 1.3	15.9 ± 1.9
8	restored, low, connected bank	3.6 ± 0.8	14.5 ± 2.1
9	restored, low, connected bank	3.1 ± 1.7	15.8 ± 1.7

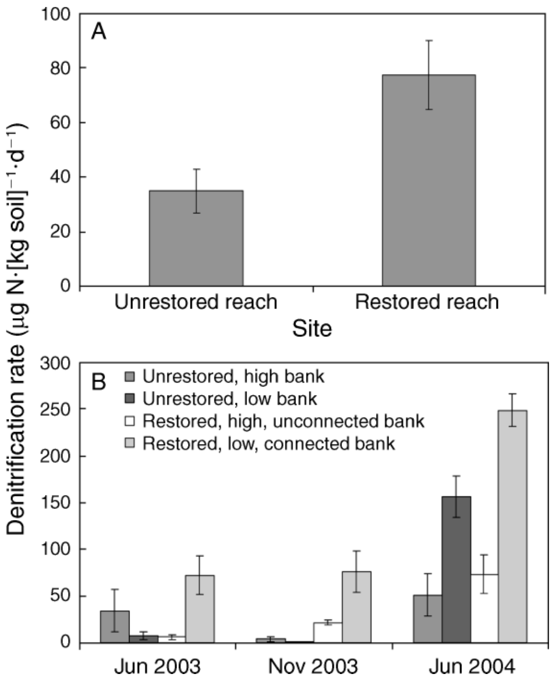

FIG. 4. (A) Mean in situ denitrification rates over all sites in both the restored and unrestored reaches of Minebank Run. Values are means ± SE of four or five wells in each reach, sampled three times between May 2003 and June 2004. Restored sites showed a higher overall mean denitrification rate than unrestored sites (ANOVA, $P = 0.01$). (B) In situ denitrification rates across four different riparian-zone–stream interfaces in the unrestored and restored reaches. Values are means ± SE of two or three wells in each site, sampled three times between May 2003 and June 2004. Denitrification rates varied widely and were highest during spring 2004 with hydrologically connected sites showing the highest denitrification rates across all seasons. Results from the repeated-measures ANOVA using three factors (restoration, bank height, and season) showed significant differences in mean denitrification rates between restored and unrestored sites ($F_{1,14} = 8.8$, $P = 0.01$), across seasons ($F_{2,14} = 25.1$, $P < 0.001$), and between high and low banks ($F_{1,14} = 20.3$, $P < 0.001$).

the west (Fig. 5A), but vertical cross-sections of groundwater equipotentials near the stream indicated that flow could vary in direction and amount over the scale of a few meters. Groundwater flow moved from the bank into the stream or parallel to the stream in piezometer transect 1 (Fig. 5B); flow moved from both banks and strongly upward into the stream in piezometer transect 2 (Fig. 5C); and stream flow moved down from the center of the bed and outward roughly equally into both banks in piezometer transect 3 (Fig. 5D). Across sampling periods and transects, it was estimated that hydrologic flow through a 1.5 × 1.5 × 1.5 m compartment at the riparian-zone–stream interface ranged from 0.14 m^3/d to 2.64 m^3/d and hydrologic residence time of this groundwater ranged from 0.5 to 9.31 d. Piezometer transect 3, where water flowed from the stream into the banks, showed the longest hydrologic residence time at the riparian-zone–stream interface of 2.4–9.31 d, and rates of flow were very slow at only 0.14–0.43 m^3/d. Other transects (where water flowed from the banks into the stream) had shorter residence times of <5 d and faster flow rates of 0.22–2.64 m^3/d. In contrast, hydrologic flows in the restored reach in piezometer transect 4 showed a relatively uniform discharge across seasons in the same direction from the bank to the stream.

Mass removal of nitrate-N in groundwater at the riparian-zone–stream interface of the unrestored reach was considerable, but it varied based on hydrologic flow paths and residence time (Table 3). For all sampling periods and piezometer transects, estimated mass removal in flow through the 1.5 × 1.5 × 1.5 m compartment of sediment in the hyporheic–stream interface ranged from 0.007 mg NO_3^--N/L over 0.95 d to 7 mg NO_3^--N/L over 9.31 d. Piezometer transect 3, which had the slowest hydrologic flow rates, showed the highest rates of nitrate-N removal in the compartment with a mean of 1.74 mg NO_3^--N removed per liter of groundwater flow over a mean residence time of 4.97 d. Piezometer transects 1 and 2, which had higher flow rates, had lower mean rates of nitrate-N removal of 0.20–0.57 mg NO_3^--N/L over mean residence periods of 1.19–2.54 d, respectively.

In the restored reach, we estimated removal of nitrate-N in a scenario by applying the mean in situ denitrification rate measured in the restored, low, connected bank during 2003–2004 to a range in hydrologic conditions measured in the same subreach shortly following the period of study (August 2004 to November 2004). Under this scenario, the potential for mass removal of NO_3^- would range from 1.46 mg nitrate-N/L over a span of 1.91 d to 2.81 mg nitrate-N/L over a span of 3.67 d (Table 4). Mass removal of nitrate-N at the riparian-zone–stream interface in both the unrestored reach and the scenario in the restored reach suggested a linear relationship with hydrologic residence time (unrestored reach, $R^2 = 0.87$, $N = 18$, $P < 0.05$; restored scenario, $R^2 = 0.70$, $N = 8$, $P < 0.05$; Fig. 6).

DISCUSSION

The in situ groundwater denitrification rates measured in the present study, from 4.1 to 156.2 μg N·kg^{-1}·d^{-1}, are similar to those reported for other riparian wetlands in the northeastern United States using push-pull methodology. Most comparably, Addy et al. (2002) and Kellogg et al. (2005) observed denitrification rates ranging from <1 to 330 μg N·kg^{-1}·d^{-1} in riparian sites in Rhode Island, USA. Push-pull measurements of denitrification are increasing in the literature (e.g., Istok et al. 1997, Addy et al. 2002, 2005, Kellogg et al. 2005, Whitmire and Hamilton 2005) because this technique allows determination of in situ rates of nitrogen removal and denitrification. In sites with low NO_3^- concentrations, the method may artificially increase denitrification rates by exposing microbial communities to increased levels of nitrate (Kellogg et al. 2005) and by promoting

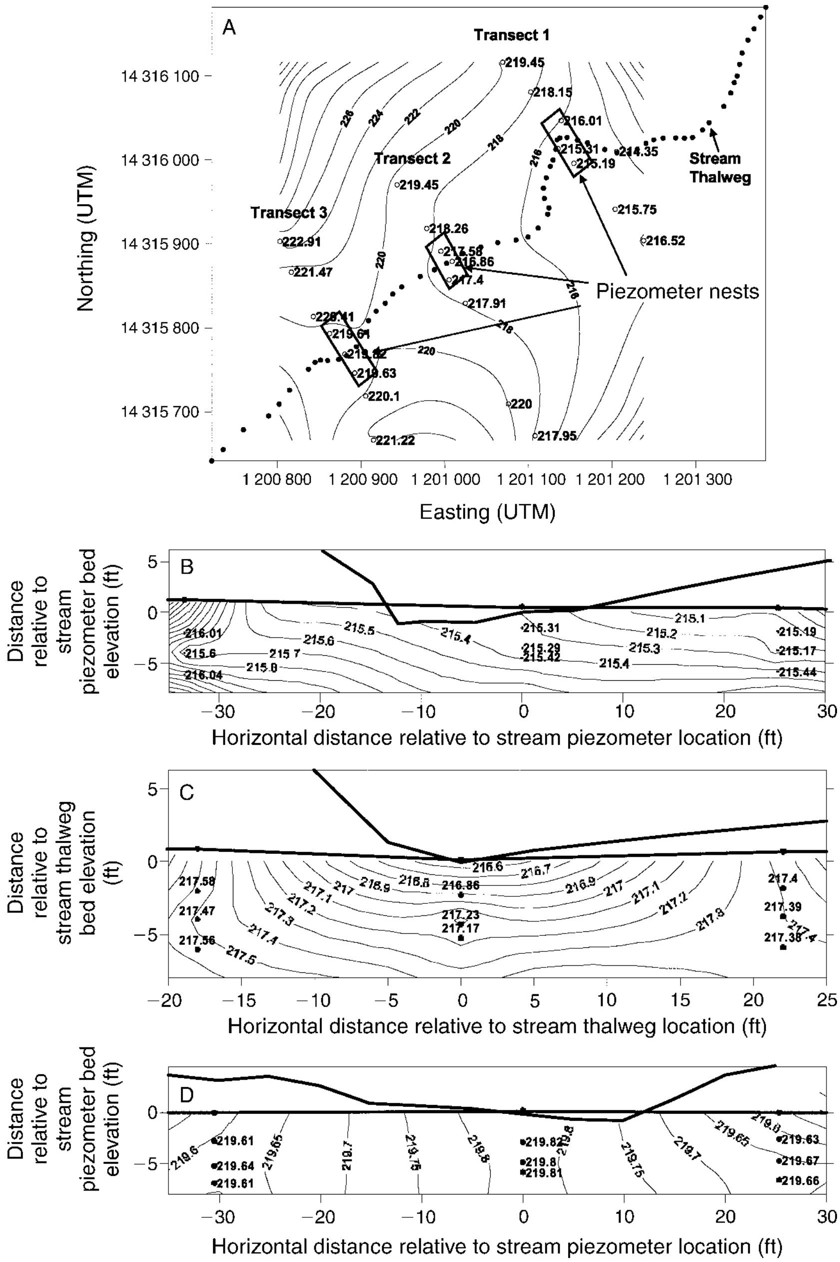

FIG. 5. (A) Horizontal flow field of groundwater in the unrestored reach of Minebank Run at the scale of hundreds of feet (1 foot = 0.304 m) on 10 June 2003. (B) Vertical flow field of groundwater at piezometer transect 1 on 10 June 2003. (C) Vertical flow field of groundwater at piezometer transect 2 on 10 June 2003. (D) Vertical flow field of groundwater at piezometer transect 3 on 10 June 2003.

small-scale mixing within transport-limited reaction zones (Smith et al. 2005). An additional problem with the push-pull method is that it can be difficult to identify a rate constant from single-well measurements, which complicates calculations of mass removal rates (Whitmire and Hamilton 2005, Schroth and Istok 2006). Furthermore, the labor and expense associated with isotopic tracer additions such as the push-pull method allow relatively fewer measurements of denitrification than with other laboratory-based techniques (Groffman et al. 2006). Despite these challenges, the relatively large volume of groundwater and soil encompassed by the method in the field allows scaling up of in situ field observations to a level that may be potentially useful for managers and helpful in identifying practices that improve water quality.

Our results suggest that stream restoration associated with storm water management that increases hydrologic connectivity can increase denitrification rates, and it supports the idea that the riparian-zone–stream interface

TABLE 3. Groundwater flow through a 1.5 × 1.5 × 1.5 m box adjacent to the unrestored reach of Minebank Run representing the riparian-zone–stream interface.

Site and date	Q (m^3/d)	Direction	Denitrification rate (μg N·kg^{-1}·d^{-1})	Residence time (d)	Nitrate removal (μg N/m^3)
Transect 1, south bank					
10 June 2003	1.80	stream to bank	34.4	0.79	107.4
21 November 2003	2.50	stream to bank	4.0	0.57	9.0
28 May 2004	2.64	stream to bank	51.3	0.54	109.5
Transect 1, north bank					
10 June 2003	1.33	bank to stream	7.4	2.17	61.9
21 November 2003	1.82	bank to stream	1.8	1.59	11.0
28 May 2004	1.93	stream to bank	156.0	1.50	901.0
Transect 2, south bank					
10 June 2003	0.31	bank to stream	34.4	3.58	728.8
21 November 2003	0.36	bank to stream	4.0	3.01	71.3
28 May 2004	0.22	bank to stream	51.3	4.97	1510.0
Transect 2, north bank					
10 June 2003	1.24	bank to stream	7.4	1.11	34.3
21 November 2003	1.45	bank to stream	1.8	0.95	7.1
28 May 2004	0.86	bank to stream	156.0	1.60	1044.1
Transect 3, south bank					
10 June 2003	0.30	stream to bank	34.4	3.50	764.9
28 May 2004	0.14	stream to bank	51.3	7.41	2417.1
Transect 3, north bank					
10 June 2003	0.30	stream to bank	7.4	4.20	149.8
21 November 2003	0.42	stream to bank	1.8	2.97	25.8
28 May 2004	0.14	stream to bank	156.0	9.31	7004.7

Note: Estimates of mass removal of nitrate (micrograms of N removed per cubic meter of groundwater flow) were obtained by coupling measurements of in situ denitrification rates (micrograms of N removed per kilogram of soil per day) on different sides of the banks coinciding with measurements of groundwater flow.

can be an active site for denitrification rates (Groffman et al. 1996, Hill 1996, Hedin et al. 1998, Kellogg et al. 2005). We observed substantial denitrification rates in both the unrestored and restored reaches of Minebank Run. In particular, the restored, low, connected bank had consistently and significantly higher in situ denitrification rates measured by the push-pull tracer technique across seasons. Wider channel width and decreased channel incision with well-developed riparian vegetation may have increased hydrologic connectivity between groundwater and upper soil horizons and, thereby, affected denitrification rates (Groffman et al. 2002, 2003). Increased hydrologic interaction with organic-rich soils underlying well-developed vegetation in the riparian zone can stimulate higher denitrification rates at the riparian-zone–stream interface in the restored, low, connected bank of Minebank Run by providing organic carbon as a substrate for increased denitrification activity (e.g., Groffman and Crawford 2003). Step-pool sequences and meanders similar to those in the low, connected subreach have also been shown to increase hydrologic residence times and nitrogen retention in transient storage zones at the riparian-zone–stream interface (Malard et al. 2002, Kasahara and Hill 2006)

TABLE 4. Groundwater flow through a 1.5 × 1.5 × 1.5 m box adjacent to the restored reach of Minebank Run representing the riparian-zone–stream interface.

Date	Q (m^3/d)	Denitrification rate (μg N·kg^{-1}·d^{-1})	Residence time (d)	Nitrate removal (μg N/m^3)
6 August	0.29	132.4	3.67	2806.5
2 September	0.55	132.4	1.91	1460.6
14 September	0.42	132.4	2.49	1904.1
21 September	0.42	132.4	2.49	1580.0
29 September	0.45	132.4	2.39	1516.6
5 October	0.41	132.4	2.60	1649.8
20 October	0.39	132.4	2.81	2202.7
17 November	0.37	132.4	2.98	2329.8

Note: The potential importance of estimates of mass removal of nitrate (in micrograms of N removed per cubic meter of groundwater flow) was investigated by coupling an average measurement of in situ denitrification rate during the study (in micrograms of N removed per kilogram of soil per day) on the south bank of transect 4 with a range of measurements of bank-to-stream groundwater flow during a three-month period in 2004 following denitrification measurements.

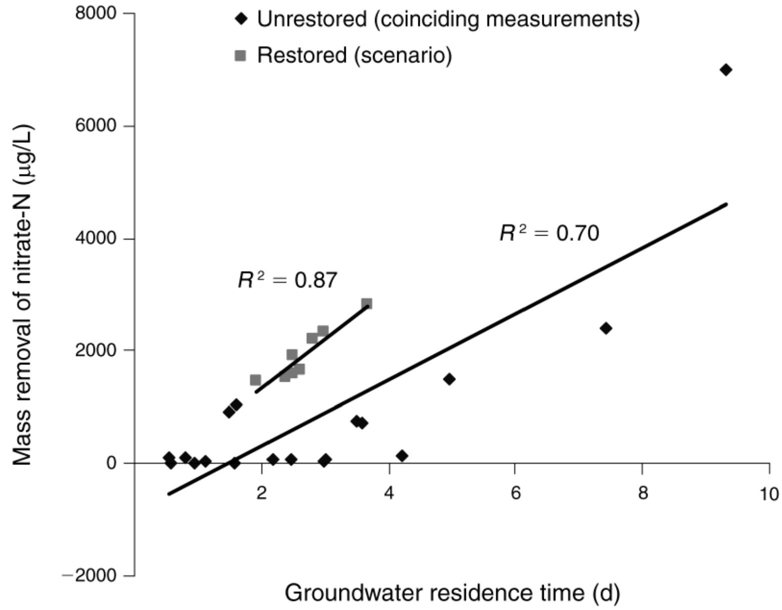

FIG. 6. Relationship between hydrologic residence time and mass removal of nitrate-N in the unrestored reach (obtained using coinciding measurements of denitrification rates and groundwater flow) and the potential relationship between hydrologic residence time and mass removal of nitrate-N in the restored reach (obtained from a scenario using mean denitrification rates in a restored, low, connected bank during 2003–2004 and groundwater flow rates following denitrification measurements in 2004).

relative to straighter runs (e.g., Hill et al. 1998, Gücker and Boechat 2004). Therefore, hydrologic flow paths also may have been important in fostering higher denitrification rates in the low, connected bank, and recent work at the same site with conservative tracer injections has shown that lateral groundwater inputs along the riparian-zone–stream interface can be substantial (C. Klocker, *unpublished data*). Restoration activities focused on increasing hydrologic "connectivity" in riparian zones may be important in enhancing denitrification rates via multiple mechanisms such as soil organic carbon availability and hydrologic flow paths, which deserve further research attention (e.g., Fennessy and Cronk 1997, Groffman et al. 2003, Mayer et al. 2005, Boulton 2007).

The higher in situ denitrification rates in the restored reach appeared to coincide with the lower nitrate-N concentrations in groundwater wells in this reach. It is possible, however, that the lower concentrations of nitrate in groundwater were not entirely attributable to the significantly higher dentrification rates, but also to differences in sources of nitrate delivery in this reach. For example, there may have been downstream sources of pollution that elevated the concentration of nitrate-N in the groundwater of the unrestored reach relative to the restored reach. The very high rates of in situ denitrification and potential for mass removal at the riparian interface, however, were suggestive that N removal by microbes may have been important at Minebank Run.

Coupling of the high denitrification rates with groundwater flow rates suggested that mass removal of nitrate-N at the riparian-zone–stream interface could be substantial in both unrestored and restored reaches. In the unrestored reach, the groundwater flow and the hydrologic residence times that we measured may have been potentially high enough to reduce NO_3^- concentrations by up to 0.20–1.74 mg NO_3^--N/L, depending on groundwater flow rates/residence time. These estimates suggested that even in the unrestored reach, denitrification rates may have the potential to substantially influence groundwater NO_3^- concentrations, which typically range from 1 to 2 mg nitrate-N/L. Our estimates of nitrate-N removal for the hydrologically connected, low-bank, restored site based on a scenario using in situ denitrification measurements and groundwater residence data following denitrification measurements also showed a high potential for mass removal of nitrate-N (ranging from 1.46 mg nitrate-N/L over 1.91 d to 2.81 mg nitrate-N/L over 3.67 d). Although the estimates of mass removal between unrestored and restored reaches were not directly comparable due to differences in time periods of hydrologic measurements (unlike measurements of in situ denitrification), they both suggest that considerable amounts of nitrate-N could be removed at the riparian-zone–stream interface due to high denitrification rates coupled with hydrologic flow and that hydrologic residence time in the riparian-zone–stream interface may be an important factor. Nitrate-N removal appeared to be higher across a similar range of hydrologic residence times than the unrestored reach, suggesting that the effects of restoration on factors such as soil organic carbon and hydrologic paths in riparian zones in Minebank Run may have also been important (Groffman and Crawford 2003, Mayer et al. 2003). The estimates of mass removal are consistent with other studies in riparian zones showing that some forms of riparian buffer restoration and management can potentially contribute to reducing nitrate-N concentrations in riparian groundwater (e.g., Pinay et al. 1993, Fennessy and Cronk 1997, Tockner et al. 1999).

A growing body of work now suggests that stream restoration may have the potential to influence stream hydrology and hydrologic residence time (e.g., Kasahara and Hill 2006, Bukaveckas 2007, Loheide and Gorelick 2007, Roberts et al. 2007). In particular, hydrologic exchange and increased residence time may foster environmental conditions (i.e., reduced redox conditions and metabolic activity) that promote higher in situ denitrification rates at the riparian-zone–stream interface of channels and riparian zones (e.g., Hedin et al. 1998, Sobczak et al. 2003, Boulton 2007). Because riparian organic matter, geomorphology, hydrologic flow paths, and underlying geology may all play roles in explaining variations in denitrification rates (e.g., Alexander et al. 2000, Stanley and Doyle 2002, Groffman and Crawford 2003, Gücker and Boechat 2004, Wollheim et al. 2006), all of these factors should be considered and further evaluated in the efficacy of restoration designs aimed at increasing both denitrification rates and mass removal of nitrate-N in riparian zones. In particular, further research on coupled restoration practices with storm water management may be useful because it may be desirable to create conditions with high denitrification rates in urban areas where water from the landscape is concentrated (Pouyat et al. 2007).

Our results suggest that restoration practices for storm water management that foster "connectivity" between the stream and the riparian zone can increase rates of in situ denitrification in stream banks and that mass nitrate-N removal may be substantial at the riparian-zone–stream interface. Our results also suggest that there can be substantial variability in denitrification rates among restoration designs based on hydrological connectivity and bank height and that continuing work is necessary to identify which types of stream restoration practices will be most effective at removing nitrogen (e.g., Stanley and Doyle 2002, Kasahara and Hill 2006, Palmer and Bernhardt 2006, Bukaveckas 2007, Roberts et al. 2007). Because of uncertainties concerning the magnitude and range of nitrate-N removal possible, until more is known, stream restoration by itself is not appropriate for compensatory mitigation but may complement watershed-based management strategies for reducing nitrate-N sources to streams. Key questions relate to how the potential for denitrification and mass nitrogen removal at the riparian-zone–stream interface changes with growth of new riparian vegetation and changes in soil organic matter, responses to increased or decreased storm water flows, and the relative contribution of denitrification at the riparian-zone–stream interface to whole-stream denitrification. It is important to recognize that restored streams in urban watersheds may have a different capability of transforming nitrogen at the riparian-zone–stream interface than streams in undeveloped watersheds that have been much more thoroughly studied (e.g., Peterson et al. 2001, Hall and Tank 2003, Mulholland et al. 2004, Kaushal and Lewis 2005). Expansion of in situ measurements of denitrification and hydrologic fluxes to other restoration sites and comparisons with forest reference and suburban ecosystems will be critical in determining and/or establishing any effective standards for potential water quality improvements associated with riparian and stream restoration in urban areas.

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