

In Situ Ground Water Denitrification in Stratified, Permeable Soils Underlying Riparian Wetlands

D. Q. Kellogg,* A. J. Gold, P. M. Groffman, K. Addy, M. H. Stolt, and G. Blazewski

ABSTRACT

The ground water denitrification capacity of riparian zones in deep soils, where substantial ground water can flow through low-gradient stratified sediments, may affect watershed nitrogen export. We hypothesized that the vertical pattern of ground water denitrification in riparian hydric soils varies with geomorphic setting and follows expected subsurface carbon distribution (i.e., abrupt decline with depth in glacial outwash vs. negligible decline with depth in alluvium). We measured in situ ground water denitrification rates at three depths (65, 150, and 300 cm) within hydric soils at four riparian sites (two per setting) using a ^{15}N -enriched nitrate "push-pull" method. No significant difference was found in the pattern and magnitude of denitrification when grouping sites by setting. At three sites there was no significant difference in denitrification among depths. Correlations of site characteristics with denitrification varied with depth. At 65 cm, ground water denitrification correlated with variables associated with the surface ecosystem (temperature, dissolved organic carbon). At deeper depths, rates were significantly higher closer to the stream where the subsoil often contains organically enriched deposits that indicate fluvial geomorphic processes. Mean rates ranged from 30 to 120 $\mu\text{g N kg}^{-1} \text{d}^{-1}$ within 10 m versus <1 to 40 $\mu\text{g N kg}^{-1} \text{d}^{-1}$ at >30 m from the stream. High denitrification rates observed in hydric soils, down to 3 m within 10 m of the stream in both alluvial and glacial outwash settings, argue for the importance of both settings in evaluating the significance of riparian wetlands in catchment-scale N dynamics.

INCREASED NITROGEN loading to coastal ecosystems has been associated with eutrophication through increased primary productivity (Ryther and Dunstan, 1971; Howarth, 1988; Valiela, 1995; National Academy of Sciences, 2000), and decreased dissolved oxygen (DO) levels resulting from subsequent algal die-offs and decomposition (Diaz, 2001; Goolsby et al., 2001; Rabalais et al., 2001). Increased N delivery to coastal waters has also been associated with the historic loss of eelgrass (Orth and Moore, 1983; Short and Burdick, 1996; Nixon et al., 2001). While sources of N are relatively well understood and quantified, management of N at the watershed scale is hampered by the uncertainty surrounding N sinks in the landscape (Howarth et al., 1996; Jordan et al., 1997). Riparian zones can function as important N sinks as ground water emerges into streams and coastal estuaries (Hill, 1996; Correll, 1997; Lowrance et al., 1997). However, among the large number of studies on ground water

N removal in riparian areas, there is much variability in reported N retention, sampling approaches, and site characteristics (Correll, 2000). There is also a high degree of spatial variability in riparian landscape characteristics across a watershed. This contributes to difficulties in applying the published research across a watershed.

Hydric soil, in riparian wetlands, serves as a useful indicator of ground water nitrate (NO_3^- -N) removal capacity in stratified deposits (Groffman et al., 1992, 1996; Simmons et al., 1992; Schnabel and Stout, 1994; Nelson et al., 1995; Norton and Fisher, 2000; Gold et al., 2001). These soils were found to have lower DO, shallower water tables, and higher ground water NO_3^- -N removal rates than nonhydric soils.

Biological and chemical transitions can occur over very short distances within hydric soils situated in riparian zones (Jones and Mulholland, 2000). For example, aerobic ground water became anaerobic over a horizontal distance of only 5 to 10 m (Nelson et al., 1995). Similarly, Robertson et al. (1991), Hedin et al. (1998), and Devito et al. (2000) all found significant ground water NO_3^- -N attenuation over a distance of <5 m, which they attributed to denitrification. Thus, narrow bands of hydric soils may have a significant effect on N delivery to coastal waters via ground water.

Ground water flow paths and retention times need to be combined with spatial variation of denitrification rates to achieve a more integrated understanding of riparian denitrification capacity (Hill, 1996; McClain et al., 2003). Willems et al. (1997) observed that the denitrification capacity of the riparian wetland soils in their field study was not fully utilized, based on stream NO_3^- -N concentrations, and surmised that local hydrology was the probable cause. The importance of ground water hydrology to the overall NO_3^- -N removal capacity of a riparian area is also the subject of discussion and research (Burt, 1997; Correll, 1997; Cirimo and McDonnell, 1997; Burt et al., 1999; Cey et al., 1999; Devito et al., 2000; Hill et al., 2000; Flite et al., 2001; Clément et al., 2002). However, these studies are limited in watershed-scale applicability because each intensively studied a single site.

Mappable geomorphic features show great potential for increasing our understanding of ground water denitrification capacity in riparian zones at the catchment scale (Pinay et al., 1995, 2000; Correll, 1997; Lowrance et al., 1997). Thus, Vidon and Hill (2004) proposed a conceptual model using hydrogeologic characteristics to describe probable ground water flow paths and residence times through riparian zones. Hill et al. (2004) studied ground water denitrification at five riparian sites in Canada, concluding that the occurrence of buried

D.Q. Kellogg, A.J. Gold, K. Addy, M.H. Stolt, and G. Blazewski, Department of Natural Resources Science, 105 Coastal Institute in Kingston, University of Rhode Island, Kingston, RI 02881. P.M. Groffman, Institute of Ecosystem Studies, Box AB, 65 Sharon Turnpike, Millbrook, NY 12545. Received 6 July 2004. *Corresponding author (qkellogg@uri.edu).

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677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: DO, dissolved oxygen; DOC, dissolved organic carbon.

organic-rich deposits were an important factor in the ground water denitrification potential of a riparian site, underlining the need to better understand riparian lithology and stratigraphy at the catchment scale. Because carbon (C) is the most important electron donor for sustaining denitrifying microbes (Myrold and Tiedje, 1985; Smith and Duff, 1988; Bradley et al., 1992; Starr and Gillham, 1993), the differences in soil C distribution due to geomorphology may influence ground water denitrification.

Glaciated regions such as the northeastern United States are often divided into three major geomorphic settings: glacial till deposits, glacial outwash and lacustrine sediments, and alluvial soils characterized by a recurring pattern of mineral layers and layers of higher organic C content. Thus, nitrate-enriched ground water flowing through alluvial soils possessing deeper carbon deposits than either outwash or till soils may undergo significant denitrification at depths greater than outwash or till soils if these buried alluvial organic deposits are bioavailable (Hill and Cardaci, 2004).

Rosenblatt et al. (2001) found that glacial till exhibited a lower occurrence of hydric riparian soils than outwash or alluvial settings, and an extremely high incidence of ground water seeps across those riparian zones that did have hydric soils. Ground water seeps reduce the potential for denitrification to occur as the ground water bypasses the biologically active zone of the soil and quickly traverses the riparian zone in surface rivulets to the stream (Warwick and Hill, 1988; Cirimo and McDonnell, 1997; Steinheimer et al., 1998; McHale et al., 2002). Hydraulic conductivity of glacial till is generally low, reducing the extent of ground water flux through these riparian settings. Therefore, glacial out-

wash and alluvial settings both show more promise for enhancing ground water denitrification capacity due to their greater hydraulic conductivities and ensuing ability to intercept a substantial portion of the ground water flux (Gold et al., 2001).

The objective of this study was to compare the vertical pattern and extent of microbial ground water denitrification in hydric soils located in glacial outwash vs. alluvial geomorphic settings. We hypothesized that the vertical distribution of denitrification would follow the expected vertical distributions of subsurface particulate C: denitrification rates in the saturated subsoil would drop precipitously with depth in outwash settings, but in alluvial settings, denitrification rates would remain at levels comparable with those in shallow ground water.

MATERIALS AND METHODS

Study Site Descriptions and Instrumentation

We studied four riparian wetland sites along lower order streams, all located within the Pawcatuck River watershed of Rhode Island, USA (Fig. 1). All sites were situated in low gradient (<3%) stratified deposits with water tables within 0.5 m of the soil surface. Two of these sites (hereafter referred to as Sites A and B) were located on glacial outwash deposits (Table 1). The setting classification for these sites was based on an initial field reconnaissance using soil augers within the upper portion of the soil, with the criteria for alluvial soils being the presence of multiple buried horizons that were high in organic matter. Subsequently, the soil profiles were classified from deep pits dug within 5 m of the sampling networks (see below) and temporarily purged of ground water using a high volume pump (Tables 1 and 2). Site A was located along an unnamed first-order tributary of Chickasheen Brook, South Kingstown, RI (41°28' N, 71°35' W), with sandy loam soil

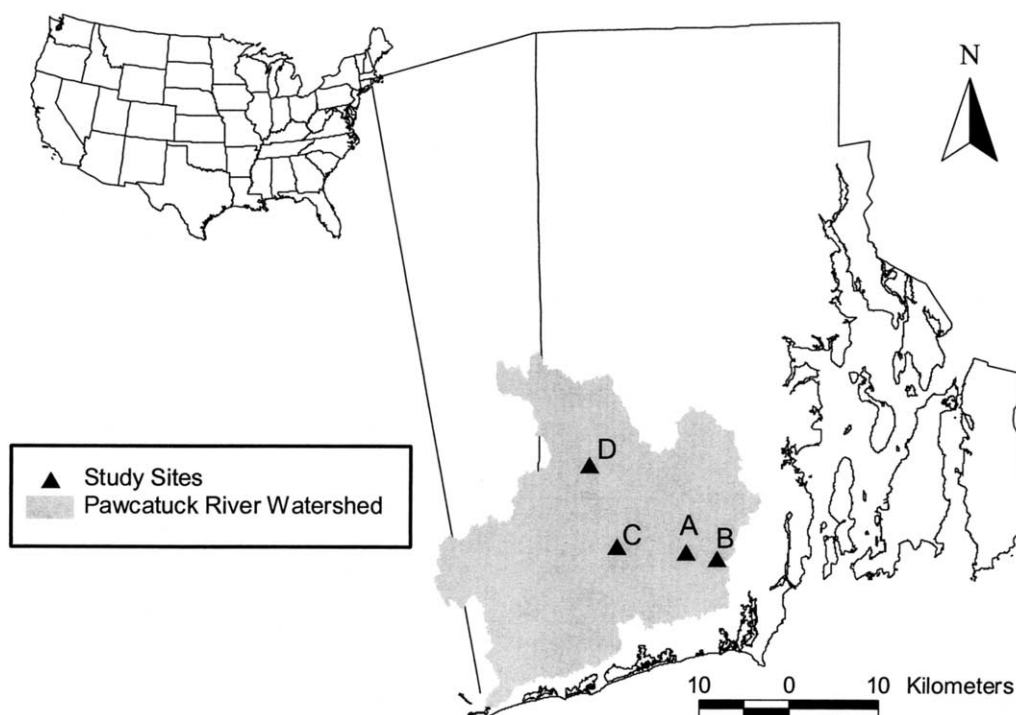


Fig. 1. Location of study Sites A, B, C, and D within the Pawcatuck River Watershed, Rhode Island, USA.

Table 1. Riparian site characteristics.

Setting†	Sampling distance from stream m	Soil in sampling area‡	Dominant vegetation	Thickness of organic surface horizon‡ cm	Carbon-rich horizons below the B horizon‡
Outwash§	9	sandy, mesic Terric Haplosaprist	Site A red maple (<i>Acer rubrum</i> L.), highbush blueberry (<i>Vaccinium corymbosum</i> L.)	45	yes
Outwash	80	sandy, mesic Aeric Endoaquept	Site B red maple, summersweet (<i>Clethra alnifolia</i> L.)	27	no
Alluvial	7	coarse-loamy, mesic Fluvaquentic Endoaquept	Site C red maple,ighbush blueberry, summersweet	9	yes
Alluvial	32	coarse-loamy, mesic Fluvaquentic Humaquept	Site D red maple,ighbush blueberry, summersweet	4	yes

† Based on field reconnaissance of the riparian zone.

‡ From pit descriptions of soil pits dug within 5 m of sampling array.

§ The pit description later argued for changing the classification to "alluvial," but this was rejected based on the thickness of the organic surface horizon and water table dynamics.

classified as a sandy, mesic Terric Haplosaprist. Site B was located along White Horn Brook, a second-order tributary of Worden Pond, South Kingstown, RI (41°28' N, 71°32' W), with sandy loam soil classified as a sandy, mesic Aeric Endoaquept. The other two sites (hereafter referred to as Sites C and D) are located on alluvial soils. Site C was located along Meadow Brook, a second-order tributary of the Pawcatuck River, Richmond, RI (41°29' N, 71°41' W) with sandy loam soil classified as a coarse-loamy mesic Fluvaquentic Endoaquept. Site D was located along Parris Brook, a third-order tributary to the Wood River, Exeter, RI (41°34' N, 71°43' W) with sandy loam soil classified as a coarse-loamy, mesic Fluv-aquentic Humaquept. The vegetation surrounding all the sites was forest or "old field" vegetation, where no known N applications had occurred for at least 20 yr. All four riparian sites were forested, dominated by red maple (*Acer rubrum* L.), thus minimizing vegetation effects (Table 1). Sites were remote, 200 to 500 m from any roads. The thickness of the organic surface horizon (Table 1) reflects the surface stability of these sites,

with the more fluviually active alluvial sites having a thinner organic surface horizon as compared with the two glacial outwash sites.

Within the hydric soils, at each site, we installed mini-piezometers (0.8-cm o.d.; 2-cm screen length [AMS, American Falls, ID]), attached to gas-impermeable Teflon tubing (0.7-cm o.d.) that extended above the soil surface. Ground water was pumped with a Masterflex L/S portable peristaltic pump (Cole Parmer, Vernon Hills, IL). At each site, three replicate mini-piezometers were placed at each of three depths below the soil surface: 65, 150, and 300 cm, with the exception of Site C where a confining layer forced us to install the deep wells at 260 cm. The study area where the mini-piezometers were installed was a zone of approximately 30 by 10 m. These areas were selected based on uniformity of vegetation and topography (i.e., the absence of berms, swales, or deep channels) rather than at a fixed distance from the stream. To minimize disturbance, we also avoided areas of extremely dense underbrush that would have required clearing to permit installation and

Table 2. Ambient ground water chemistry and selected soil characteristics. Values are the means ± standard errors, n = 6 except where noted.

Depth cm	DO†	NO ₃ -N‡ mg L ⁻¹	DOC§	pH	Pit samples¶	
					Carbon	Silt + clay (<0.05 mm) %
Site A, outwash setting						
65	5.7 ± 0.6	0.6 ± 0.1	1.5 ± 0.7	5.5 ± 0.2	4.9	30.1
150	7.4 ± 0.4	1.1 ± 0.1	0.8 ± 0.2	5.8 ± 0.0	0.2	6.8
300	6.7 ± 0.5	1.4 ± 0.4	0.5 ± 0.1	5.8 ± 0.0	no data	no data
Site B, outwash setting						
65	2.3 ± 0.4	<0.1 ± <0.1	13.4 ± 8.1	5.3 ± 0.1	0.2	1.6
150	4.8 ± 0.3	<0.1 ± <0.1	3.9 ± 1.7	5.6 ± 0.1	0.2	8.0
300	5.8 ± 0.8	<0.1 ± <0.1	1.8 ± 0.3	5.0 ± 0.1	no data	no data
Site C, alluvial setting						
65	2.0 ± 0.4	<0.1 ± <0.1	4.7 ± 0.9	5.5 ± 0.1	2.5	9.9
150	1.6 ± 0.5	<0.1 ± <0.1	4.0 ± 1.6	6.0 ± 0.1	0.6	44.8
260	1.0 ± 0.1	0.1 ± 0.1	2.2 ± 0.2	6.5 ± 0.0	no data	no data
Site D, alluvial setting						
65	2.4 ± 0.3	<0.1 ± <0.1	2.8 ± 1.3	5.3 ± 0.1	0.6	4.6
150	1.1 ± 0.2	<0.1 ± <0.1	0.7 ± 0.1	5.7 ± 0.0	0.3	3.4
300‡	0.8 ± 0.2	<0.1 ± <0.1	1.7 ± 0.4	6.5 ± 0.1	no data	no data

† Dissolved oxygen.

‡ n = 3.

§ Dissolved organic carbon.

¶ n = 1.

monitoring of the mini-piezometers. At any given depth mini-piezometers were at least 5 m apart laterally.

A network of mini-piezometer nests was also installed across the riparian zone from the upland to the stream and was used to establish flow paths in companion studies. We also installed water table wells at each site. Water table levels were recorded biweekly during spring and fall when water table depths were expected to change most rapidly, and bi-monthly during summer and winter.

Within the hydric soils of each site, a soil pit was dug to a depth of 1.5 to 2 m, and within 5 m of the mini-piezometers. To lower the water table during sampling and characterization, ground water was pumped from the pits with a Honda WP20X pump (American Honda Power Equipment Division, Alpharetta, GA) at 600 L min⁻¹. The pit soils were described and soil samples were taken from all horizons and analyzed for carbon content. Carbon contents were estimated for the 65- and 150-cm depths of the mini-piezometers by calculating the weighted average of % C in the horizons within ±10 cm of each depth. In addition to the soil pits, each site was characterized with a series of auger holes, located 2 m apart, along a transect orthogonal to the stream that extended from the stream edge to the upland. At each auger hole we documented the maximum depth of organically enriched media. Auger holes extended to a depth of 3 m where possible, except in situations where soil properties (stoniness, dense layers, loose consistency) prevented soil extraction with an auger.

Push-Pull Studies

We used the in situ push-pull method to examine ground water denitrification at each replicate mini-piezometer (Addy et al., 2002). The push-pull method uses a single mini-piezometer to introduce and extract a ground water plume containing ¹⁵N-enriched NO₃⁻-N and SF₆, a conservative gas tracer. Plume extraction occurs after a preset incubation period and the ground water samples are analyzed for ¹⁵N-enriched denitrification gases. Before beginning the denitrification studies, we performed conservative tracer tests on at least one mini-piezometer at each depth, allowing us to determine a suitable incubation time to achieve at least 70% tracer recovery. We “pushed” (i.e., injected) 10 L of previously collected ground water that had been amended with 80 mg L⁻¹ Cl⁻ as KCl, over a period of 1 h at an injection rate of 160 mL min⁻¹. The saturated hydraulic conductivity of the sandy media was relatively high, allowing the mini-piezometers to accommodate an even higher rate of injection and pumping with no observable effects on hydraulic head. After 24 h we “pulled” (i.e., extracted) ground water from the same mini-piezometer and adjusted incubation times based on tracer recovery. Incubation times were 22 to 24 h at Sites B, C, and D, but were limited to 4 to 5 h at Site A. This was due to the more rapid dilution of the introduced plume that was observed during our preliminary tracer recovery tests at this site and the logistical constraints of daylight hours.

A characteristic of this method is that water is likely to be pumped from and injected into sediments with the highest saturated hydraulic conductivity in the vicinity of the mini-piezometer. This allowed us to sample sediments that conducted the largest volumes of water at that depth, those sediments being the most critical portions of the media for ground water N transport.

Denitrification was studied at each site during at least one spring and one fall between November 1999 and May 2002. During each season, the sites being studied were subjected to a NO₃⁻-N push-pull test at least twice, with a 2-wk interval between trials. The first test was performed to allow the micro-

bial community to adjust to the change in NO₃⁻-N concentration (Aelion and Shaw, 2000). Denitrification is an inducible enzyme system, and many studies have shown that addition of NO₃⁻-N to anaerobic, carbon-rich sediments induces a denitrifying response (Payne, 1981). Moreover, denitrification enzymes have been found to persist in soils and sediments for weeks and months after induction (Smith and Parsons, 1985; Groffman, 1987; Martin et al., 1988; Parsons et al., 1991). These enzymes are then “ready to go” if denitrifying conditions return. Therefore, all analyses are based on the final push-pull test of one spring and one fall at each site. Shortly before the beginning of each sampling season, enough ground water was collected from each depth at each site to allow us to conduct all denitrification studies during that season using the same ground water. All ground water collected for the “pushed” solution was stored at 4°C. Throughout the study all ground water samples were stored on ice in the field and stored at 4°C in the laboratory.

Ground water to be analyzed for dissolved gases (N₂, N₂O, ¹⁵N₂, ¹⁵N₂O, SF₆) was collected using a 20-mL syringe attached to a gas-tight stainless steel apparatus and injected into a previously evacuated 150-mL glass bottle capped with a rubber septa. The headspace was then filled with high-purity helium gas to atmospheric pressure. To sample for dissolved gases, we used the phase equilibration headspace extraction technique (Lemon, 1981; Davidson and Firestone, 1988), storing samples at 4°C overnight, shaking, and sampling the bottle headspace with a syringe. Ground water to be analyzed for NO₃⁻-N and pH was collected in 150-mL Nalgene bottles (Nalge Nunc, Rochester, NY). Samples to be analyzed for dissolved organic carbon (DOC) were filtered through 25-mm ashed glass fiber filters, collected in 45-mL amber glass bottles, and fixed with 75 µL of 85% concentrated phosphoric acid.

Immediately before injection, we sampled each mini-piezometer for ambient ground water DO and temperature, and collected samples for analysis of ambient pH, DOC, NO₃⁻-N, N₂, N₂O, and SF₆ gases. We then “dosed” the mini-piezometers with 10 L of ground water, amended with 32 mg L⁻¹ NO₃⁻-N as KNO₃ enriched with 20 atom % ¹⁵N and SF₆. We bubbled the SF₆ gas mixture (100 µL L⁻¹ SF₆, 2 µL L⁻¹ O₂, balanced in He; unanalyzed mixture in portable cylinder; Matheson Trigas, Gloucester, MA) into the amended ground water using a sparge stone, adjusting the DO to previously measured ambient concentrations. We took samples of the dosing solution (one sample for dissolved gases N₂O, N₂, ¹⁵N₂O, ¹⁵N₂, and SF₆, and one sample for analysis of NO₃⁻-N) twice during the “push” phase. After the incubation period, samples were obtained from each mini-piezometer during extraction of the first 3 L where tracer recovery is highest, as follows: at 0.5-L intervals for dissolved gases (N₂, N₂O, ¹⁵N₂, ¹⁵N₂O, and SF₆), and at 1-L intervals for NO₃⁻-N, resulting in six gas samples and three liquid samples from each mini-piezometer during each “pull” phase from the core of the introduced plume. All samples used in denitrification rate calculations contained at least 2 mg L⁻¹ NO₃⁻-N to ensure that our denitrification rate estimates were not nitrate-limited (Schipper and Vojvodic-Vukovic, 1998). The pumping rate during sampling was between 0.1 and 0.2 L min⁻¹, for a total sampling time of about 1 h. We then sampled for ground water DO and temperature and pumped a total of 20 L from each mini-piezometer to ensure that the majority of the plume was extracted and removed from the site.

Denitrification Rate Calculations

We calculated the generation rate of the denitrification gases (N₂O and N₂) using the three gas samples that had the

highest tracer recovery (of six within-sample replicates), thus minimizing error from dilution and dispersion. To calculate masses of N_2O and N_2 gases (μmol) in our headspace extraction samples, we used equations and constants provided by Tiedje (1982) and Mosier and Klemedtsson (1994). The mass was then transformed to the mass of $^{15}\text{N}_2\text{O}-\text{N}$ or $^{15}\text{N}_2$ by multiplying it by the respective ^{15}N sample enrichment. The masses of $^{15}\text{N}_2\text{O}-\text{N}$ or $^{15}\text{N}_2$ generated during the incubation period were calculated as the mass present in the pulled sample minus the mass present in the pushed sample. The total masses of $\text{N}_2\text{O}-\text{N}$ and N_2 generated during the incubation period were then calculated by dividing the masses of $^{15}\text{N}_2\text{O}-\text{N}$ and $^{15}\text{N}_2$ by the dosed $\text{NO}_3^- - \text{N}$ atom %.

Gas production rates ($\text{N}_2\text{O}-\text{N} + \text{N}_2$) are expressed as $\mu\text{g N kg}^{-1} \text{d}^{-1}$ (total mass of $\text{N}_2\text{O}-\text{N}$ and N_2 per volume of water pulled/[dry mass of soil per volume of water pulled \times incubation period]). Each pulled sample represented 0.5 L of ground water that occupied approximately 0.0013 m^3 of soil (assuming a bulk density of 1650 kg m^{-3} , and a porosity of 0.38). The incubation period was defined as the length of time between the end of the push phase and the start of the pull phase because the core of the plume is expected to consist largely of the later injected ground water. Denitrification rates may be slightly underestimated since we did not measure NO_2^- and NO , other intermediates of the denitrification process, although these forms of N do not usually account for a substantial portion of denitrification products.

Analytical Methods

Ground water DO and temperature were measured with a Model 55 DO/temperature meter (YSI, Yellow Springs, OH). Ground water samples were analyzed for $\text{NO}_3^- - \text{N}$ using the SM 4500 $\text{NO}_3^- \text{F}$ automated cadmium reduction method (American Public Health Association, 1998) on an Alpkem RFA 300 Rapid Flow Autoanalyzer (O.I. Analytical, Wilsonville, OR), for DOC by infrared analysis using a Model 1010 carbon analyzer (O.I. Corporation, College Station, TX), and for pH on an Accumet Model 925 pH meter (Fisher Scientific, Pittsburgh, PA). 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 Ltd., Cheshire, UK) at the Stable Isotope Facility, UC Davis, Davis, CA. Concentrations of N_2O and SF_6 gases were analyzed by electron-capture gas chromatography on a Tracor Model 540 (ThermoFinnigan, Austin, TX). Samples taken from the soil pits were analyzed for C content using a CN Analyzer (Carlo Erba, Milan, Italy). Particle size distribution was determined for samples taken from the soil pits. Samples were treated with sodium hexametaphosphate solution and placed on a horizontal shaker overnight to disperse the primary particles (Kilmer and Alexander, 1949). Sand was separated from the silt and clay by wet sieving and sand fractions were separated using a nest of sieves. Silt and clay percentages were determined by the pipette method (Gee and Bauder, 1986).

Statistical Analyses

Kruskal–Wallis H tests (Ott, 1993) were performed to determine significant differences in ground water denitrification rates among depths within geomorphic setting and season ($P < 0.05$). With a significant Kruskal–Wallis H test, we used the Mann–Whitney U test (Ott, 1993) as the post hoc test to determine which depths were significantly different ($P < 0.05$). We used the Mann–Whitney U test to determine significant differences in ground water denitrification rates between

spring and fall. If the Kruskal–Wallis H test showed no significant difference among depths within a site and season, those rates were pooled to compare seasons within a site. If the Kruskal–Wallis H test showed significant differences among depths, seasons were compared within depth and site. Spearman Rank Order correlations were performed to determine significant correlations ($P < 0.05$ and $P < 0.01$) between ground water denitrification rates and (i) distance from the stream, (ii) DO, (iii) temperature, (iv) pH, (v) DOC, (vi) ambient $\text{NO}_3^- - \text{N}$, (vii) % C, and (viii) % silt + % clay. Comparison of ground water denitrification rates from the same piezometer and season between different years was made using the Pearson r statistic. All statistical analyses were performed on Statistica (StatSoft, 2002).

RESULTS

Preliminary results from the piezometric networks indicated that the upper 2.5 m of ground water flows in a generally horizontal path through all riparian zones. This showed that ground water flux interacts with all soil horizons to some degree. Ground water flow paths at these sites, essential to estimating the overall potential for a riparian area to act as a nitrogen sink, will be presented in a subsequent paper. During the sampling periods the mean values, across all sites, for ground water DO, DOC, and pH ranged from 0.8 to 7.4 mg L^{-1} , 0.7 to 13.4 mg L^{-1} , and 5.3 to 6.5, respectively (Table 2). The ambient ground water $\text{NO}_3^- - \text{N}$ concentrations were $< 0.1 \text{ mg L}^{-1}$ except at Site A where they reached 1.4 mg L^{-1} (Table 2). Pit samples from horizons within $\pm 10 \text{ cm}$ of the 65- and 150-cm mini-piezometer depths had weighted average carbon contents ranging from 0.2 to 4.9% (Table 2). Ground water temperature ranged from 7.6 to 13.6°C during the spring sampling season and from 9.2 to 15.5°C during the fall sampling season (Table 3). The temperature range during sampling did not differ with depth at any site.

Along the soil auger transects at Sites A, B, and C, the maximum depth of organically enriched media decreased with increasing distance from the stream (Table 4). At Site D, we lacked data below 1.5 m near the stream. However the maximum depth declined with distance from 20 to 60 m from the stream.

Ground water denitrification rates from the same mini-piezometer that had been sampled during the same season in two different years were significantly correlated ($r = 0.91$, $P < 0.05$; Fig. 2). This comparison served as a check on the reproducibility of the ground water denitrification rate data. Only one of the nine mini-piezometers that had ground water denitrification rates of $< 50 \mu\text{g N kg}^{-1} \text{d}^{-1}$ in the first year had a rate exceeding 50 $\mu\text{g N kg}^{-1} \text{d}^{-1}$ in the second year. Six of the mini-piezometers had ground water denitrification rates of $> 50 \mu\text{g N kg}^{-1} \text{d}^{-1}$ in the first year, but only one of these had a ground water denitrification rate of $< 50 \mu\text{g N kg}^{-1} \text{d}^{-1}$ in the second year.

Riparian ground water denitrification rates ranged from < 1 to 330 $\mu\text{g N kg}^{-1} \text{d}^{-1}$. In contrast to our hypothesis, we found no significant differences with depth at Site A, a glacial outwash site, either during the spring or fall, with means ($\pm \text{SE}$) ranging from 7 ± 6 to $132 \pm$

Table 3. Ground water temperature at mini-piezometers, water table depth at time of sampling, and summer minimum and dormant season maximum water table depths. Values are the means ± standard errors.

Depth cm	Ground water temperature		Depth to water table			
	Spring	Fall	Spring†	Fall†	Summer minimum	Dormant season maximum
	°C		cm below soil surface			
Site A, outwash setting						
65	10.2 ± 0.2	11.1 ± 0.2				
150	9.4 ± 0.2	11.2 ± 0.1	28.2 ± 0.2	28.0 ± 0.0	46	12
300	9.2 ± 0.2	11.0 ± 0.0	<i>n</i> = 3	<i>n</i> = 3		
Site B, outwash setting						
65	8.1 ± 0.0	11.5 ± 0.2				
150	7.6 ± 0.2	12.3 ± 0.1	14.7 ± 0.4	41.8 ± 0.4	54	7
300	9.7 ± 0.3	12.5 ± 0.1	<i>n</i> = 3	<i>n</i> = 3		
Site C, alluvial setting						
65	13.6 ± 0.5	11.8 ± 0.1				
150	11.7 ± 0.4	12.3 ± 0.0	14.0 ± 0.5	16.4 ± 3.7	98	-13‡
260	12.2 ± 0.3	15.5 ± 0.2	<i>n</i> = 2	<i>n</i> = 5		
Site D, alluvial setting						
65	9.0 ± 0.3	11.6 ± 0.1				
150	7.5 ± 0.1	9.2 ± 0.7	7.0 ± 0.0	28.5 ± 0.5	73	-5‡
300	no data	11.3 ± 0.1	<i>n</i> = 2	<i>n</i> = 2		

† Sample size reflects the number of days over which sampling occurred.
‡ Negative numbers indicate water table is above soil surface.

55 µg N kg⁻¹ d⁻¹ (Table 5). Only Site B demonstrated a significant drop in denitrification rates with depth, as hypothesized for sites located in glacial outwash settings, and then only during the spring. Mean ground water denitrification rates at Site B were comparatively low, ranging from <1 ± <1 to 40 ± 18 µg N kg⁻¹ d⁻¹.

Sites C and D, both located in alluvial settings, demonstrated no significant decline of ground water denitrification rates with depth, as hypothesized. However, the alluvial sites demonstrated large differences in the magnitude of mean ground water denitrification rates, with Site C ranging from 22 ± 7 to 140 ± 98 µg N kg⁻¹ d⁻¹ and Site D ranging from 1 ± 0.7 to 29 ± 25 µg N kg⁻¹ d⁻¹.

Locations of the mini-piezometers at each site were constrained by site characteristics, allowing for data collection on ground water denitrification rates over a range of distances from the stream across the four sites (Table 1). Sites that were located farther from the stream (>30 m) had lower mean denitrification rates (<40 µg N kg⁻¹ d⁻¹) at all depths in all seasons than sites that were located closer (<10 m) to the stream (>40 µg N kg⁻¹ d⁻¹). Ground water denitrification rates were significantly correlated (*P* < 0.01) with distance from the stream at both 150- and 260- to 300-cm depths (*r* = -0.54; *P* < 0.01 and *r* = -0.78; *P* < 0.01, respectively; Fig. 3).

At the 65-cm depth, there was no significant relation-

Table 4. Maximum depth of organically enriched media with distance from the stream. Data collected along transects using a soil auger.

Distance from the stream	Maximum depth of organically enriched media			
	Site A	Site B	Site C	Site D
	m			
0-20	1.1	1.75	3.0	≥1.5†
20-40	0.7	1.10	2.0	3.0
40-60	no data	0.75	1.5	2.3

† Limit of sampling depth.

ship between denitrification rate and distance from the stream. However, the denitrification rates were significantly correlated with ground water temperature (*r* = 0.44; *P* < 0.05) and DOC (*r* = 0.44; *P* < 0.05), though the latter two factors were not significantly correlated with each other. At the 65-cm depth, both % C and % silt + clay were also significantly correlated with distance from the stream (*r* = -0.8 and -0.8, respectively, *P* < 0.01).

At the 150-cm depth, in addition to distance from the stream, ground water denitrification rates were also significantly correlated with ground water temperature (*r* = 0.52; *P* < 0.01) and pH (*r* = 0.57; *P* < 0.01). Carbon

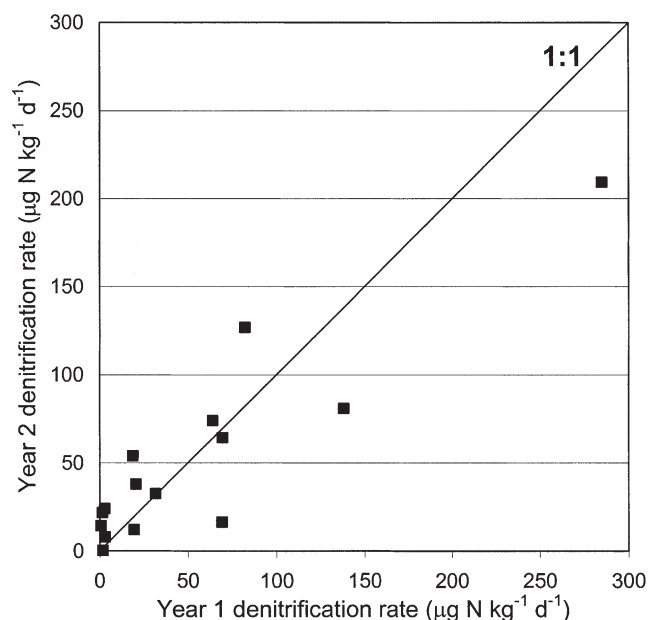


Fig. 2. Comparison of ground water denitrification rates from mini-piezometers that were sampled over two years, but during the same season. Rates from Year 1 were significantly correlated with rates from Year 2 with *r* = 0.91 at *P* < 0.05.

Table 5. In situ riparian ground water denitrification rates. Values are means \pm standard errors, $n = 3$.

Depth cm	Ground water denitrification rates			
	Spring	Fall	Pooled spring	Pooled fall
	$\mu\text{g N kg}^{-1} \text{d}^{-1}$			
	Site A, outwash setting			
65	7 \pm 6a†	132 \pm 55b		
150	11 \pm 4a	108 \pm 28b	29 \pm 11a	118 \pm 20b
300	70 \pm 19a	113 \pm 23b		
	Site B, outwash setting			
65	22 \pm 7a	40 \pm 18a		
150	3 \pm 2b	20 \pm 3a	0–22‡	0–40‡
300	0 \pm 0b	0 \pm 0ab		
	Site C, alluvial setting			
65	61 \pm 13a	140 \pm 98a		
150	117 \pm 56a	35 \pm 5a	96 \pm 24a	66 \pm 34a
260	109 \pm 51a	22 \pm 7a		
	Site D, alluvial setting			
65	2 \pm 0.3a	7 \pm 5a		
150	29 \pm 25a	21 \pm 17a	16 \pm 13a	10 \pm 6a
300	no data	1.4 \pm 0.7a		

† Values followed by different letters within sites are significantly different at $P < 0.05$ in a Kruskal–Wallis test with Mann–Whitney U test as post-hoc test. The Mann–Whitney U test ($P < 0.05$) was used to compare seasonal differences. Depths were pooled if they were found to have an insignificant Kruskal–Wallis test. The only significant Kruskal–Wallis test was found at Site B, so seasonal differences were compared by depth at Site B.

‡ Range of mean values at three depths.

content (% C) was again significantly correlated with distance from the stream ($r = -0.63$; $P < 0.01$).

At the 260- to 300-cm depth, in addition to distance from the stream, denitrification rates were also significantly correlated with pH ($r = 0.48$; $P < 0.05$).

Surprisingly, we observed no significant correlation between ground water denitrification rates and DO at any depth. No significant correlation was found between carbon content (% C) and denitrification rates at the 65- and 150-cm depths (Fig. 4), the only mini-piezometer depths for which carbon content data were available.

Seasonal variation of rates was most pronounced at outwash Site A, where fall denitrification rates were significantly higher than spring rates. At outwash Site B only the 150-cm depth demonstrated a significant difference in ground water denitrification rates between spring and fall, with fall rates also being significantly higher than spring rates ($P < 0.05$) (Table 5). Neither alluvial site demonstrated significant differences between spring and fall ground water denitrification rates.

DISCUSSION

The in situ ground water denitrification rates measured are within the range reported by previous studies. For example, Addy et al. (2002) used the same push–pull methods as we used in this study and observed a mean ground water denitrification rate of 97 $\mu\text{g N kg}^{-1} \text{d}^{-1}$ at a depth of 65 cm in a glacial outwash setting located within 10 m of the stream, and means of 123 and 2 $\mu\text{g N kg}^{-1} \text{d}^{-1}$ at a depth of 125 cm in a coastal marsh and fringe setting, respectively. In situ ground water denitrification rates measured at Site B are slightly lower than in situ NO_3^- -N removal rates previously measured at this site by Nelson et al. (1995), where land

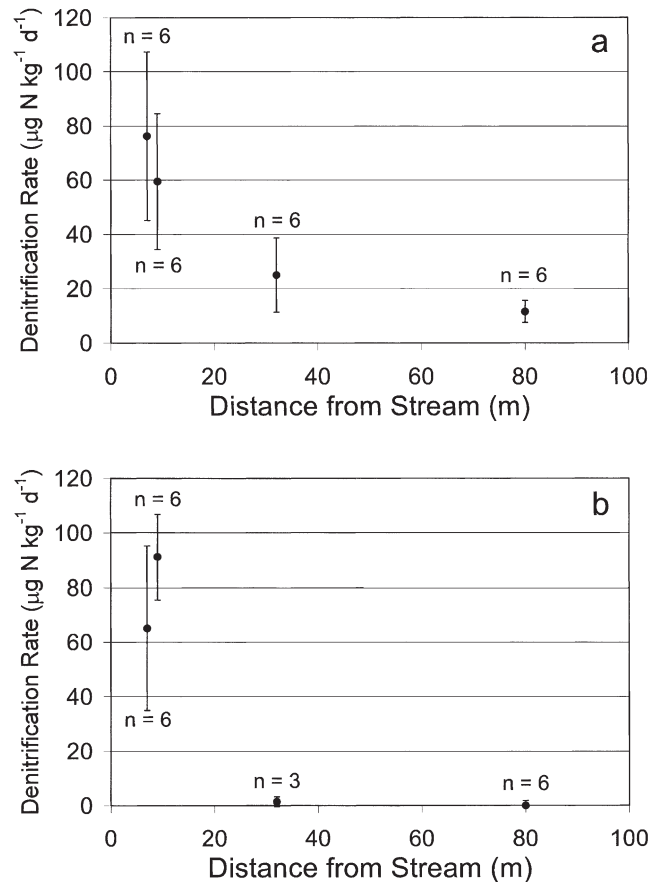


Fig. 3. Mean annual riparian ground water denitrification rates versus distance from the stream at (a) 150 cm and (b) 260 to 300 cm below the soil surface. Spearman rank correlations between denitrification rates and distance from the stream were significant at $P < 0.01$. Error bars signify ± 1 SE.

use and ground water NO_3^- -N concentrations have remained stable. Because NO_3^- -N removal rates include other removal mechanisms in addition to denitrification, such as plant uptake and microbial immobilization, the differences between the rates we observed and those observed by Nelson et al. (1995) may be explained by these other removal processes.

Based on these observations we accept the portion of our hypothesis that proposes that the pattern of ground water denitrification rates with depth will follow carbon distribution. However, we must reject that part of our hypothesis that proposes that carbon distribution in riparian settings mapped as glacial outwash is expected to decline with depth. In addition, while we did not formulate a hypothesis with regard to the magnitude of denitrification rates, we did observe differences among sites.

With respect to the pattern of ground water denitrification rates with depth, three of the four sites show no significant differences in rates with depth (Sites A, C, and D). These same three sites also possessed buried organically enriched lenses and/or layers in the vicinity of the sampling mini-piezometers, as compared with Site B.

The assumption that soils mapped as hydric outwash would uniformly exhibit declining carbon content with

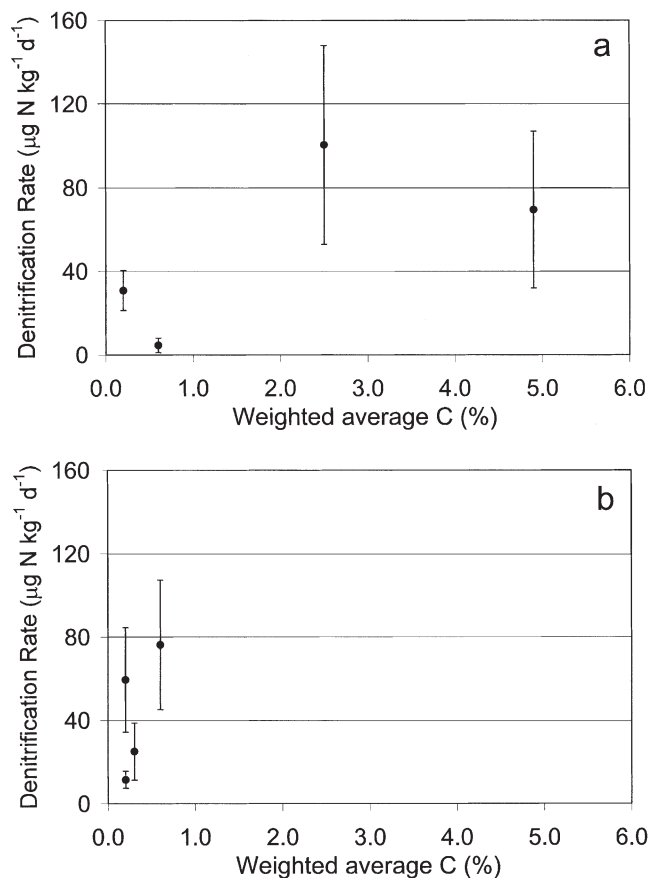


Fig. 4. Mean annual riparian ground water denitrification rates versus weighted average soil carbon content at (a) 65 cm and (b) 150 cm below the soil surface. Spearman rank correlations between denitrification rates and the weighted average of % C in samples from horizons at (a) 55 to 75 cm and (b) 140 to 160 cm below the soil surface were not significant. Error bars signify ± 1 SE ($n = 6$).

depth was challenged by Blazejewski (2003). A field reconnaissance study of lower order streams within our study area found soils mapped as hydric outwash (Rector, 1981) routinely had buried organically enriched horizons, and, as we observed with our soil auger transects, their presence was more likely with proximity to the stream. At 10 m from the stream 12 out of 18 sites on first-, second-, and third-order streams had buried organically enriched horizons to depths of 0.75 to 3.5 m. At 30 m from the stream the proportion dropped to 5 out of 18 sites. Thus, those soils mapped as hydric outwash in the soil survey are likely to exhibit alluvial characteristics within 10 m of the stream. These near-stream hydric settings have been subject to a long period of reshaping through fluvial action, such as stream meandering, as well as more episodic events, such as hurricanes (Leopold et al., 1992). Buried organic deposits have demonstrated the potential for high ground water denitrification rates (Fustec et al., 1991; Haycock and Burt, 1993; Devito et al., 2000; Hill et al., 2000, 2004).

With respect to the magnitude of rates across sites, we observed a correlation between denitrification rates and distance from the stream at both the 150- and 260- to 300-cm depths, with higher rates closer to the stream. Lowrance (1992) also observed that ground water deni-

trification potential at a depth of 60 cm was "substantial" only at the sampling location closest to the stream (10 m). In contrast, Schnabel et al. (1996) observed that in situ ground water denitrification rates increased with distance from the stream. However, this study measured NO_3^- -N removal rates within a plume flowing from a cultivated upland to a stream. Because much of the removal occurred near the field edge, it was postulated that microbial denitrification might have been nitrate-limited closer to the stream.

Although mean denitrification rates were low at alluvial Site D, located 32 m from the stream, one well at the 150-cm depth consistently yielded elevated rates, suggesting that subsurface denitrification "hot spots" may be present at this site. In contrast, at outwash Site B, located 80 m from the stream, no wells deeper than 65 cm showed elevated denitrification rates. These observations are consistent with observations yielded from the auger transects that found buried organically enriched media to be less likely with increased distance from the stream.

While we can only speculate on the causal nature of these relationships, these data suggest that the near-stream environment may be influencing not only carbon presence, but carbon availability and ground water denitrification rates, especially below 1 m. Thus, riparian soils mapped as hydric outwash, as well as those mapped as alluvial on county-scale soil surveys (e.g., 1:15 840), have the potential for substantial ground water denitrification to depths as great as 3 m within 10 m of the stream.

CONCLUSIONS

The contribution of riparian areas to the catchment-scale N budget is of great interest to both researchers and land use managers. Sites in this study were located in deep stratified sediments within glacial outwash and alluvial riparian settings. Correlations of site characteristics with in situ ground water denitrification rates varied with depth below the soil surface. At 65 cm, ground water denitrification rates varied with factors associated with the surface ecosystem (temperature, dissolved organic carbon). At deeper depths, ground water denitrification rates were significantly higher closer to the stream where the subsoil often contains organically enriched deposits that indicate fluvial geomorphic processes, such as intermittent flooding events and stream meandering. High ground water denitrification rates observed in hydric soils down to 3 m within 10 m of the stream in both alluvial and glacial outwash settings argue for the importance of both settings in evaluating the significance of riparian wetlands in catchment-scale N dynamics.

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