

Spatial and Temporal Variation in Groundwater Nitrate Removal in a Riparian Forest

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ABSTRACT

We quantified nitrate (NO_3^-) removal rates from groundwater in a red maple (*Acer rubrum* L.) riparian forest subjected to NO_3^- dosing. The site was in Southern New England on soils classified as sandy mixed mesic Haplaquept soils and contained somewhat poorly (SPD) and poorly drained (PD) soils. The specific objectives were to examine groundwater NO_3^- removal rates within a riparian forest with respect to: (i) soil drainage class; (ii) depth below the water table; and (iii) time of year. We created 16 experimental dosing/monitoring stations at two depths along three soil drainage class transects (SPD, SPD/PD, PD). We added solution containing NO_3^- and Br^- continuously for 11 mo to a dosing well at each station. Groundwater was monitored at sampling wells 0.6 m downgradient of the dosing well. Nitrate removal rates were determined by coupling changes in the $\text{NO}_3^-/\text{Br}^-$ ratio with groundwater flux estimates from each experimental station. Although located just 20 m downgradient, the PD transects had substantially higher NO_3^- removal rates and lower dissolved oxygen than the SPD transects. Both the SPD/PD and PD transects had considerable NO_3^- -N removal capacity throughout the upper 1.5 m of the groundwater ($16\text{--}46 \mu\text{g kg}^{-1} \text{d}^{-1}$). Rates were not significantly influenced by temperature. The scale of variation in removal rates suggests that high resolution soil and groundwater maps may be needed when riparian forests are to be used for water quality management.

RIPARIAN FORESTS have been shown to have a high capacity to prevent the movement of nitrate (NO_3^-) in surface runoff and groundwater flow from upland agricultural and residential land uses into streams (Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1984). Nitrate, a federally regulated drinking water pollutant and a prime agent of eutrophication in marine and freshwater ecosystems, is the most commonly detected groundwater pollutant in the USA (Ryther and Dunstan, 1971; Keeney, 1987; USEPA, 1990). Maintenance and restoration of riparian zones to control NO_3^- pollution is a key component of several state and federal nonpoint-source pollution control efforts (Vellidis et al., 1993; NRC, 1993).

Despite widespread claims about the role of riparian forests in nonpoint-source pollution control, several aspects of their function related to spatial and temporal variability are unclear. Although several studies have demonstrated that riparian forests located on wet organic soils have a high ability to attenuate groundwater NO_3^- (Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985; Pinay and Decamps, 1988; Simmons et al., 1992; Jordan et al., 1993; Haycock and Pinay, 1993), riparian forests on more well-drained mineral soils appear to be much less effective (Lowrance, 1992; Simmons et al., 1992). In riparian forests dominated by wetlands, a greater proportion of groundwater-borne NO_3^- moves within the biologically active zone of

the soil and is thus susceptible to uptake by plants and microbes. However, the site-specific characteristics that influence attenuation processes in riparian forests dominated by wetland/upland transition zones are much less clear (Simmons et al., 1992; Haycock and Pinay, 1993).

There is much uncertainty about the mechanisms of groundwater NO_3^- removal (Lowrance, 1992; Groffman et al., 1992). Several studies have observed NO_3^- disappearance from groundwater during winter months (Lowrance et al., 1984; Simmons et al., 1992; Haycock and Pinay, 1993; Haycock and Burt, 1993; Jordan et al., 1993). In these situations, denitrification and/or microbial immobilization in the subsurface must be responsible for observed NO_3^- removal. While subsurface denitrification has been observed in several studies (Trudell et al., 1986; Slater and Capone, 1987; Smith and Duff, 1988; Francis et al., 1989; Obenhuber and Lowrance, 1991), other studies have found the potential for denitrification in the subsurface to be low or nonexistent, usually due to a lack of available carbon (C) (Parkin and Meisinger, 1989; Groffman et al., 1992; Bradley et al., 1992; McCarty and Bremner, 1992; Johnson and Wood, 1992; Yeomans et al., 1992; Starr and Gillham, 1993).

In a previous study in glacial outwash soils in Rhode Island, we measured low rates of in vitro subsurface denitrification in sites that demonstrated a high capacity for in situ groundwater NO_3^- removal in winter (Simmons et al., 1992; Groffman et al., 1992). Lowrance (1992) reported a similar conundrum in the Southeastern Coastal Plain in Georgia. Our previous work also found high spatial variation in NO_3^- removal within riparian forests, with removal ranging from <20% in some relatively dry upland/wetland transition zone soils to >90% in very poorly drained or hydric soils.

In this study, we quantified in situ groundwater NO_3^- removal rates in a natural, undisturbed, riparian forest receiving nutrient enrichment. The specific objectives were to examine groundwater NO_3^- removal rates within a riparian forest with respect to: (i) soil drainage class; (ii) depth below groundwater table; and (iii) time of year. In a companion study completed at the same location, laboratory microcosms were used to characterize and quantify microbial processes potentially involved in NO_3^- removal at the site (G. Howard, unpublished data). Our experimental system was designed to allow us to calculate actual NO_3^- removal rates rather than simply the percentage of NO_3^- removal. Calculation of removal rates facilitates applications to watershed scale analysis, as well as the comparison of in situ hydrologic studies with laboratory-based microcosm microbial studies.

METHODS

Site Description

The study area was in Southern New England at the Peckham Farm of the University of Rhode Island. The site was adjacent

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Abbreviations: PD, poorly drained; SPD, somewhat poorly drained; DO, dissolved oxygen.

to White Horn Brook, a second order stream and tributary of the Pawcatuck River. The latitude and longitude coordinates of the site are at 41°29'N and 71°32'W, respectively. Elevation at the site is 30 m (msl). The surficial geology consists of glaciofluvial deposits of structureless, granitic, sands, and loamy sands with an average surface slope of 3%. The study area is within a riparian forest, dominated by red maple (*Acer rubrum* L.) with understory shrub vegetation predominated by sweet pepperbush (*Clethra alnifolia* L.), blueberry (*Vaccinium corymbosum* L.), swamp azalea [*Rhododendron viscosum* (L.) Torr.] and inkberry [*Ilex glabra* (L.) Gray]. The site was directly downgradient of an old field that had not been intensively cultivated for at least 20 yr. Soils at the site were mapped to delineate morphological characteristics with particular attention to redoximorphic features (Wright and Sautter, 1988). Based on the soil mapping, we located our experiment on somewhat poorly drained and poorly drained soils within the site, respectively defined as having redoximorphic features at approximately 45 and 20 cm from the ground surface. The poorly drained portions of the site meet the hydric soil classification criteria in Rhode Island.

The hydraulic conductivity and texture of all the soils were similar, but the soil characteristics varied in response to depth to the water table. Drainage classes within a toposequence that primarily developed in response to variation in depth to water table have been described by Pickering and Veneman (1984) and Veneman and Bodine (1982). The soils were classified as sandy mixed mesic Haplaquepts. While the color and structure of the B horizon varied spatially throughout the two drainage classes, the C horizon, which consisted of medium to fine sand (effective diam., 0.15 mm; uniformity index, 5.0), was extremely similar with regard to texture, color, and structure throughout the two drainage classes. Throughout each of the four sampling periods within this study, the water table at all experimental sites remained within the C horizon.

A grid of 42, 9-cm diam. hand-augered soil borings were installed into the water table and water table elevations were surveyed. Groundwater equipotential lines were determined and the groundwater flow direction was assumed to be perpendicular to the equipotential lines.

Field Instrumentation

Experimental stations (Fig. 1) consisted of a 15-cm diam. dosing well surrounded by a partial ring of six monitoring wells (1.8-cm diam.). The monitoring wells were 0.6 m away from the dosing well and spanned a 120° arc in the downgra-

dient direction. The monitoring wells were spaced 25 cm apart on the ground surface. All wells were constructed of PVC pipe with a screened slot size of 0.25 mm. We installed dosing wells that were screened at a depth of either 0 to 80 cm (shallow dosers) or 100 to 150 cm (deep dosers) below the seasonal high water table depth, as identified by redoximorphic features of the soil. Monitoring wells had 35 cm of screen at depths coinciding with either the middle or lower portions of the dosing well screen. A bentonite seal was placed above the screened interval and below the ground surface of each well to prevent vertical movement of water along the well casing.

As indicated in Fig. 1A, the experimental stations were grouped along three soil drainage boundaries (transects). These boundary transects were identified as poorly drained (PD), somewhat poorly/poorly drained (SPD/PD), and somewhat poorly drained (SPD). To avoid contamination from upgradient dosing stations, each drainage class boundary transect was located approximately perpendicular to groundwater flow direction and offset laterally from adjacent transects by approximately 14 m. In addition, the experimental stations were at least 7 m apart along a line of equipotential.

Three shallow and three deep experimental dosing stations were installed along each transect, except at the SPD transect. Due to the spatial constraints of the site, only one deep dosing station was installed in the SPD transect. The experimental stations were grouped into six treatments, consisting of combinations of dosing depths (shallow or deep) and drainage class boundary transects (PD, SPD/PD, SPD). Along the SPD/PD and the PD transects, we alternated deep and shallow experimental stations, thus spacing the replicate stations of these treatments by approximately 14 m. The SPD shallow experimental stations were approximately 7 m apart (Fig. 1A). Each treatment contained three dosing stations, except the deep SPD treatment, which had one dosing station. A total of 16 monitoring stations, consisting of nine shallow and seven deep stations, were installed.

Groundwater Dosing

A solution of primary standard grade KNO_3 and KBr was added to each dosing station at a 1:1 (mass) ratio of $\text{NO}_3^-/\text{Br}^-$ from 30 Jan. to 20 Dec. 1992. Bromide was used as a conservative, noninteractive tracer to characterize water flow and hydrodynamic processes (Lee et al., 1980; Sudicky et al., 1983; LeBlanc et al., 1991) and to determine the extent to which physical processes contributed to reduction in NO_3^-

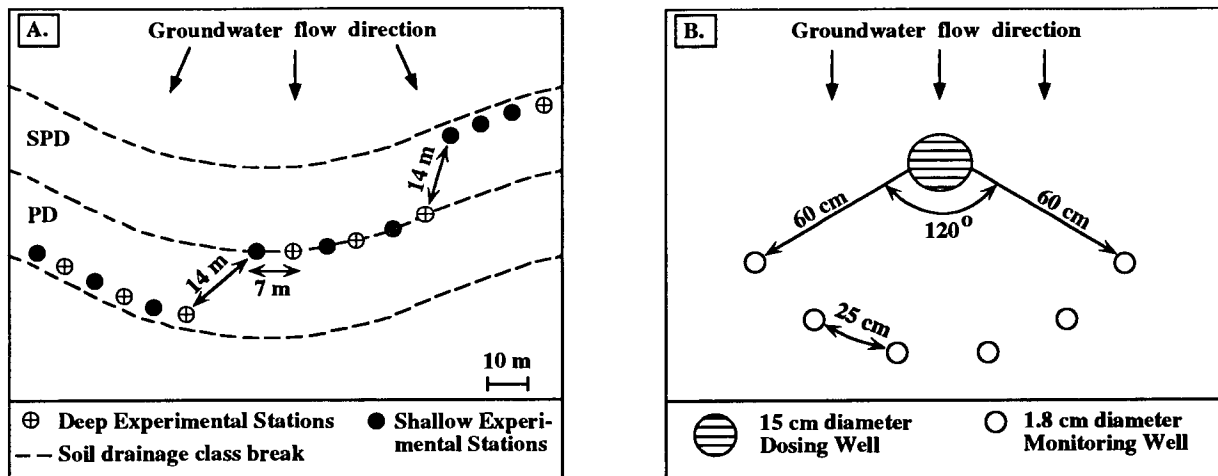


Fig. 1. (A) Schematic plan view diagram of experimental site showing locations of soil drainage classes and experimental stations. SPD, somewhat poorly drained soil; PD, poorly drained soil; (B) schematic plan view diagram of an individual experimental dosing/monitoring station.

concentrations. Decreases in Br^- concentration at the monitoring well were attributed to mixing, diffusion, and dispersion; we assume that these physical processes acted to reduce NO_3^- concentrations by the same extent. When NO_3^- concentrations in the monitoring wells decreased below Br^- concentrations, the decrease was attributed to biological removal processes. The $\text{NO}_3^-/\text{Br}^-$ or $\text{NO}_3^-/\text{Cl}^-$ ratios have been used in numerous studies to document NO_3^- removal in situations with dispersion and dilution (Jacobs and Gilliam, 1985; Trudell et al., 1986; Warwick and Hill, 1988; Lowrance, 1992). Based on sampling before dosing, ambient NO_3^- concentrations ranged from nondetectable ($<1.30 \text{ mg NO}_3^- \text{ L}^{-1}$) to a maximum of 4.8 mg L^{-1} . Approximately 88% of the samples showed the nondetectable levels of NO_3^- . Ambient concentrations of Br^- were consistently $<0.2 \text{ mg L}^{-1}$. Once the application of compounds commenced, wells without elevated Br^- concentrations ($<0.2 \text{ mg L}^{-1}$) were considered to represent ambient groundwater.

To approximate ambient groundwater chemistry in the dosing solution, we mixed the chemicals with groundwater collected from an on-site recovery well immediately upgradient of the transects. Water collection was performed using a hand-operated vacuum purging system and all mixing and decanting steps were conducted to ensure minimal aeration of the solution.

A set volume of 3500 mL wk^{-1} of dosing solution was added to each doser for the entire study. This rate equalled 2.7 cm d^{-1} . The dosing solution was added manually twice daily at $250 \text{ mL application}^{-1}$ from January through the first week of April to match the dosing regime expected from an automated dosing device that was under construction. However, the automated system never functioned properly, and we altered our dosing to either daily or twice weekly intervals for the remainder of the study. Within each of the four intensive sampling periods (described below), the dosing method was held constant for all dosing stations.

Throughout the study, our goal was to maintain Br^- concentrations in the monitoring wells above 30 mg L^{-1} to facilitate comparison with other field scale studies of groundwater NO_3^- , since the Br^- concentrations were intended to represent the potential concentrations of groundwater NO_3^- introduced from an upland source to the riparian soils. Because of temporal changes in the hydraulic gradient of the groundwater and the water table (i.e., in the volume of water in the dosing wells available to dilute the introduced dosing solution), the Br^- concentrations changed slowly in response to a fixed dose of Br^- and NO_3^- . Based on routine sampling throughout the study, we made an adjustment to the weekly mass of Br^- and NO_3^- introduced to the dosing stations several weeks before each of the four intensive sampling periods (described below). Following the adjustment, the weekly mass of NO_3^- and Br^- introduced to each doser was always held constant throughout a sampling period.

Over the entire study, we detected the introduced plume ($\text{Br}^- > 0.2 \text{ mg L}^{-1}$) in 571 groundwater samples. At each of the experimental stations, one or two of the monitoring wells consistently had Br^- concentrations well above 5 mg L^{-1} , suggesting that the plume produced by the dosing wells was relatively narrow and stable. While shifts in the plume direction were noted, the lateral and vertical extent of the plume within each experimental station remained quite constant throughout the study.

Experimental Stations: Sampling and Site Characterization

Although dosing occurred continuously throughout the study, groundwater monitoring focused on four intensive sampling periods, each 4 to 6 wk in duration, centered on the months of March, June, September, and November of 1992.

The monitoring wells were first purged of three well volumes using a hand vacuum pump (Soil Moisture Corp., Santa Barbara, CA) before the sample was obtained. The samples were collected in acid-washed (10% sulfuric) 125-mL polyethylene sample containers and stored at 4°C until analyzed.

During each sampling period, we measured groundwater elevation weekly and dissolved oxygen (DO) and temperature biweekly from wells within each of the transects. Dissolved oxygen and temperature data were obtained in the field using a YSI Model 57 DO Meter.

During the first study period, the average pore water velocity of each experimental station was directly measured using a groundwater tracer. The groundwater tracer study began in February 1992, when each doser received 0.5 L d^{-1} of a Br^- solution. Monitoring wells were sampled until the tracer concentration became relatively constant. To account for the effects of dispersion, the average pore water velocity was estimated from the time coinciding with a concentration of Br^- that was one-half the eventual maximum (Jury et al., 1991). We assumed this simple breakthrough model to be adequate for our situation, since the saturated media had minimal clay particles and was very homogeneous. During Period 1, the average pore water velocities of the experimental stations, as determined by the tracer studies, ranged from 2.5 to 5.8 cm d^{-1} with an overall average of 3.7 cm d^{-1} . Based on these values the travel time through the experimental unit (i.e., from the dosers to the monitoring wells) during Period 1 averaged about 16 d. To reflect temporal differences in travel time between the four different sampling periods, we adjusted the tracer derived velocities by an adjustment factor based on the [mean hydraulic gradient per period of interest/mean hydraulic gradient observed during the tracer study] ratio.

A total of eight hand excavated observation test pits (three each at the PD and SPD/PD transects and two at the SPD transect) were installed to the water table during July 1992 when the water table was at its lowest level of the study. The low water table permitted soil characterization and sampling of media that was below the water table most of the year. We analyzed soil samples for particle-size distribution by the methods described by Day (1965) and percent C using a Carlo Erba 1500 C-N-S analyzer. Undisturbed cores for bulk density determinations (Blake, 1965) were also obtained from the C horizon.

Depth below ground surface of the C horizon and the water table increased from the PD to SPD transects (Tables 1 and 2). The water table remained below both the B horizon and the visible root zone in all treatments during each of the four periods of study.

Table 1. Selected soil characteristics beneath three soil transects in a riparian forest. Values are mean, (standard error), and number of samples.

Soil transect	C horizon characteristics	
	Depth below ground cm	Organic C content %
PD†	29 (6)a‡ 3	0.13 (0.03) 3
SPD/PD†	44 (3)b 3	0.12 (0.02) 3
SPD†	61 (1)c 2	0.12 (0.03) 2

† PD = transect located along the wetland portion of the poorly drained soil; SPD/PD = transect located along the somewhat poorly and poorly drained soil break; SPD = transect located along the upland portion of somewhat poorly drained soil.

‡ Values followed by different scripts within each column are significantly different in a one-way analysis of variance with a Fisher's least significant difference test. An absence of letters in a column indicates no significant difference between treatments.

Table 2. Mean water table depths below ground beneath three soil transects in a riparian forest. Values are mean, (standard error), and number of samples.

Soil drainage transect	Sampling period				Studywide
	March	June	September	November	
	cm				
PD†	42.6 (0.9)a‡ 48	62.0 (1.3)a 48	50.6(1.4)a 36	36.8 (2.1)a 24	49.6(1.0)a 156
SPD/PD†	68.5 (1.1)b 48	87.6 (1.5)b 48	76.8(1.6)b 36	60.7 (2.6)b 24	75.1 (1.1)b 156
SPD†	84.8 (1.4)c 32	103.6 (2.1)c 32	94.3 (2.0)c 24	77.5 (3.4)c 16	92.0 (1.4)c 104

† PD = transect located along the wetland portion of the poorly drained soil; SPD/PD = transect located along the somewhat poorly and poorly drained soil break; SPD = transect located along the upland portion of somewhat poorly drained soil.

‡ Values followed by different scripts within each column are significantly different in a one-way analysis of variance with a Fisher's least significant difference test.

Laboratory Analysis

Each water sample was analyzed for Br^- with an ion specific electrode and an Orion Research EA 940 Ionanalyzer using the known addition technique (Orion Res., 1982). Results were accurate to within 5%. All samples with elevated Br^- concentrations were selected for NO_3^- analysis, whereas samples that exhibited background concentrations of Br^- were randomly submitted for NO_3^- analysis to check on background concentrations. Nitrate analysis of water samples was performed using a colorimetric, automated cadmium reduction method on an Alpkem RFA 300 Rapid Flow Analyzer (Alpkem Corp., 1986). Results were reported with a detection limit for NO_3^- of 1.30 mg L^{-1} .

Nitrate Removal Determination

Nitrate removal rates ($\mu\text{g N kg}^{-1} \text{ d}^{-1}$) were determined by coupling results of the $\text{NO}_3^-/\text{Br}^-$ analyses from the monitoring wells with period-adjusted groundwater flux estimates from the experimental stations. The concentrations of Br^- and NO_3^- measured in the dosing and monitoring wells are average concentrations over the cross-sectional area defined by the dimensions of the well-screens. Thus, we defined a control volume (Hemond and Fechner, 1994) from which NO_3^- removal was considered. The control volume was represented by the length of flow (L in m) between each doser and monitoring well, and a cross-sectional area (A in m^2) perpendicular to flow direction that was equal to the width of the doser (0.15 m) times the height of the well screen. Although the plume dispersed beyond the defined control volume, in most cases the introduced plume remained very narrow over the 60 cm of travel from the dosing well. Typically, one or two of the six monitoring wells downgradient from the dosing wells received concentrations of Br^- dramatically higher than the surrounding wells.

We calculated the mass of the soil within the control volume (M_s) from:

$$M_s = A \times L \times P_b \quad [1]$$

where

- M_s = dry mass of soil in the control volume (kg)
- A = cross sectional area of control volume (m^2)
- L = length of flow between dosing and monitoring wells (m)
- P_b = bulk density of C horizon media (1650 kg m^{-3})

In some wells during June and September, the water table was lower than the top of the well screen and the height was computed as the depth of the screen within the groundwater.

The volume of groundwater leaving the control volume per day (Freeze and Cherry, 1979) or the daily flow rate (Q) was determined from:

$$Q = V \times n \times A \quad [2]$$

where

- Q = daily flow rate ($\text{m}^3 \text{ d}^{-1}$)
- V = period-adjusted average pore water velocity (m d^{-1})
- n = effective porosity ($0.37 \text{ cm}^3 \text{ cm}^{-3}$; estimated from bulk density measurements)

The daily mass of Br^- (M_{Br}) leaving the control volume per day was assumed to reflect the interaction of loading with physical processes such as mixing, dispersion, and diffusion. In our calculation we assume that plant uptake of Br^- is negligible since the groundwater remained within the C horizon and below the visible root zone during all the sampling periods. If plant uptake of Br^- did occur, our approach will underestimate the biological removal rates of groundwater NO_3^- . The daily mass of Br^- leaving the control volume was determined by:

$$M_{\text{Br}} = [\text{Br}^-] \times Q \quad [3]$$

where

- M_{Br} = mass of Br^- leaving the control volume (g d^{-1})
- $[\text{Br}^-]$ = concentration of Br^- in monitoring well (g m^{-3})

Similarly, the actual mass of NO_3^- leaving the control volume per day (M_{NO_3}) was determined by:

$$M_{\text{NO}_3} = [\text{NO}_3^-] \times Q \quad [4]$$

where

- M_{NO_3} = mass of NO_3^- leaving the control volume (g d^{-1})
- $[\text{NO}_3^-]$ = concentration of NO_3^- in the monitoring well (g m^{-3})

The difference between the potential and actual mass of NO_3^- leaving the control volume per day equals the mass of NO_3^- retained or removed per day (MR_{NO_3}).

$$MR_{\text{NO}_3} = (M_{\text{Br}} - M_{\text{NO}_3}) \times 10^6 \mu\text{g g}^{-1} \quad [5]$$

where

- (MR_{NO_3}) = mass of NO_3^- retained or removed ($\mu\text{g d}^{-1}$)

The groundwater NO_3^- -N removal rate was then obtained by dividing the mass of NO_3^- removed per day (MR_{NO_3}) by the mass of soil within the control volume (M_s) and expressed in μg of NO_3^- -N removed kg^{-1} soil d^{-1} .

Statistical Analysis

Differences among treatments were determined by analysis of variance for the entire study period, within each of the four sampling periods and between periods using the General Linear Models procedure of the Statistical Analysis System (SAS Inst., 1985a,b). The study period data used in mean comparisons is the summation of all observations from each of the four sampling periods. Means that were significantly different based on the ANOVA ($P < 0.10$) were separated using a Fisher's protected least significant difference test. Depth to water table data for each period were pooled by transect, since differences between the deep and shallow dosing stations were within the accuracy limits of our measurements. Within each sampling period, differences in groundwater temperature between treatments varied by $<1.5^\circ\text{C}$ and the data from all treatments were pooled for comparisons between periods. Site characteristic data were correlated to NO_3^- removal rates using the Spearman's rank correlation test.

We restricted our NO_3^- removal rate computations to a subset of the total samples. A lower cutoff of $1.30 \text{ mg } \text{NO}_3^- \text{ L}^{-1}$ was set to minimize the situations where rates were NO_3^- limited. A lower cutoff of $5 \text{ mg } \text{L}^{-1} \text{ Br}^-$ was selected to minimize inaccuracies in removal rate estimates that could result from occasional increases in background NO_3^- concentrations. A total of 445 samples had NO_3^- and Br^- concentrations above the cutoff criteria.

In the case of NO_3^- -N removal rates, analysis of variance was performed using log transformed data to reduce the asymmetric distribution of the data. Weekly measurements from each monitoring well were pooled by sampling period, since each of the sampling periods consisted of relatively homogeneous conditions of groundwater depth, temperature, and dissolved oxygen. To assist in the selection of the appropriate sampling unit for use as replicates in the ANOVA (i.e., dosing stations separated by 7–28 m vs. individual monitoring wells within each station separated by distances <1.0 m) we used GEO-EAS (Englund and Sparks, 1991) to examine the variance in NO_3^- removal rate vs. lag distance within a treatment. The resulting variogram displayed a very high nugget effect, with $>60\%$ of the total variance occurring at mean lag values <0.5 m. This finding is corroborated by a number of other studies that have found very high spatial variability in soil N dynamics (Parkin, 1987; Christensen et al., 1990; Parsons et al., 1991). Accordingly, we defined each monitoring well as an individual replication for comparisons of treatments. The median values that resulted from the transformed data, defined by Warrick and Nielsen (1980) as the antilog of the log transformed mean, are reported to aid in the interpretation of N removal rate data. Coefficients of variation were calculated from the untransformed data and are reported to indicate relative measures of variability.

RESULTS

Site Characteristics

The shallowest water tables occurred in November and the deepest water tables occurred in June (Table 2). The mean water table depths for each sampling period and over the entire study were significantly different between transects. The difference between the PD and SPD transects remained very consistent throughout each

sampling period. Within each sampling period, the depth to the water table was relatively constant, with <10 cm of variation.

For the entire study, mean DO concentrations in the groundwater ranged from $2.4 \text{ mg } \text{L}^{-1}$ in the PD shallow wells to $8.4 \text{ mg } \text{L}^{-1}$ in the SPD wells (Table 3), increasing from the wettest to the driest transects. The DO of the groundwater in the PD treatments was significantly lower than the SPD/PD and SPD treatments within each sampling period and over the entire study. As expected, differences in groundwater temperatures between sampling periods were significantly different (Table 3).

Nitrate/Bromide Concentration Ratios

For each treatment scatter plots of the period-pooled Br^- and NO_3^- concentrations from each monitoring well are displayed in Fig. 2, along with the mean ratio of $[\text{NO}_3^-]/[\text{Br}^-]$. Data pairs located below the 1:1 line indicate removal of NO_3^- in excess of dilution and dispersion. The mean ratios per treatment provide a qualitative comparison of NO_3^- removal between treatments. The shallow PD treatment had the lowest ratio at 0.71, while the mean ratio of 1.03 for the deep, SPD treatment suggests that little removal occurred within that treatment. Based on the pattern of the data pairs, there is no compelling trend in NO_3^- concentrations related to Br^- concentrations, suggesting that zero-order kinetics can be used to model the removal process. Zero-order kinetics are often applied to describe N reactions in soils (Sparks, 1989).

Nitrate Removal Rates

During the study period significant differences between treatments were observed in groundwater NO_3^- removal rates (Table 4). The treatments located in the drainage class with the shallowest water table (PD) generally displayed the greatest N removal. Significant differences in NO_3^- removal rates were also observed between periods when data were pooled by period (Table 5). November, with the highest water tables, had the highest removal rate, while the lowest removal was noted in June, when the deepest water tables occurred.

There was a significant, but weak, inverse correlation between NO_3^- -N removal rate and depth to water table within most periods and over the entire study ($r = -0.41$, $P < 0.05$). During the entire study, a weak but significant inverse relationship was found between NO_3^- -N removal rate and DO ($r = -0.37$, $P < 0.05$), but no significant relationship was found with groundwater temperature.

Only the driest transect (SPD) displayed a significant difference in NO_3^- removal with depth on a study-wide basis. The deep treatment of the SPD transect, which was dosed at an average depth of 1.75 m belowground, had significantly lower N removal rates than the shallow treatment of the SPD transect.

Table 3. Mean groundwater dissolved oxygen concentrations from two depths beneath three soil transects in a riparian forest. Values are mean (standard error) and number of samples.

Soil drainage transect	Dosing depth	Sampling period				Studywide
		March	June	September	November	
		mg L ⁻¹				
PD†	Shallow	3.2 (0.7)a‡ 8	2.3 (0.1)a 12	1.7 (0.3)a 11	2.6 (0.2)a 17	2.4 (0.2)a 48
	Deep	3.0 (0.3)a 9	4.2 (0.5)b 12	3.8 (0.6)b 13	3.0 (0.4)a 16	3.5 (0.2)b 50
SPD/PD†	Shallow	9.0 (0.7)b 8	6.7 (0.5)c 12	6.1 (0.6)cd 9	5.8 (0.5)b 14	6.7 (0.3)c 43
	Deep	10.1 (0.3)b 8	8.3 (0.2)d 12	6.3 (0.3)cd 14	5.9 (0.3)b 18	7.2 (0.3)c 52
SPD†	Shallow	10.6 (0.4)b 5	7.6 (0.2)cd 9	5.4 (0.4)c 10	6.6 (0.4)bc 20	7.0 (0.3)c 44
	Deep	10.5 (0.2)b 4	8.3 (0.3)d 4	7.4 (0.3)d 3	7.7 (0.4)c 8	8.4 (0.3)d 19
Mean groundwater temperatures in a riparian forest						
		°C				
Period means¶		4.9 (0.1)a 42	13.4 (0.1)b 61	15.3 (0.1)c 60	10.1 (0.1)d 93	

† PD = transect located along the wetland portion of the poorly drained soil; SPD/PD = transect located along the somewhat poorly and poorly drained soil break; SPD = transect located along the upland portion of somewhat poorly drained soil; Shallow = screened interval is approximately 0 to 80 cm below maximum high water table; Deep = screened interval is approximately 100 to 150 cm below maximum high water table.

‡ Values followed by different scripts within each column are significantly different in a one-way analysis of variance with a Fisher's least significant difference test.

¶ Values followed by different scripts within the row are significantly different in a one-way analysis of variance with a Fisher's least significant difference test.

DISCUSSION

Spatial Variation

We observed significant spatial and temporal variation in site physicochemical parameters and NO₃⁻ removal rates. Water table, DO levels, and NO₃⁻ removal rates varied significantly over the approximately 20 m of down-

gradient distance between the SPD and PD transects. While groundwater was strongly aerobic (6–10 mg L⁻¹ DO) and well below the biologically active A and B soil horizons in the SPD transect, DO levels were much lower (approximately 3.0 mg L⁻¹) and water table levels were generally within 50 cm of the soil surface in the PD transect. During the entire study, the median NO₃⁻-N removal rate

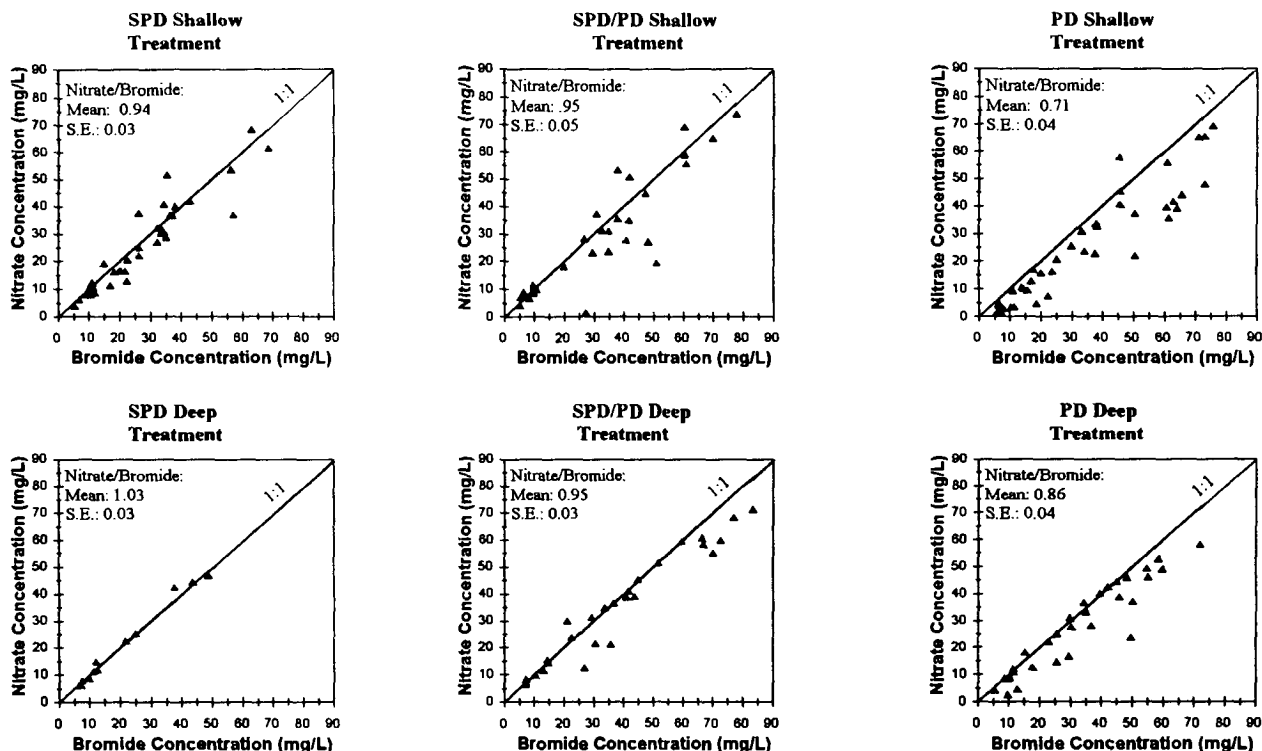


Fig. 2. Period-pooled groundwater NO₃⁻ and bromide concentrations from each monitoring well of six dosing locations (i.e., treatments) within a riparian forest. Data pairs located below the 1:1 line indicate removal of NO₃⁻ in excess of dilution and dispersion. SE = standard error.

Table 4. Groundwater NO₃⁻-N removal rates in a riparian forest. Values are median (coefficient of variation of untransformed values) and number of samples.

Soil drainage transect	Dosing depth	Sampling period				Studywide
		March	June	September	November	
		$\mu\text{g kg}^{-1} \text{d}^{-1}$				
PD†	Shallow	29.0 (0.66)ab‡	23.4 (0.51)	49.1 (0.64)a	89.9 (0.83)	46.4 (1.05)a
	Deep	57.8 (0.77)a	6.0 (0.88)	41.7 (0.72)a	59.2 (1.16)	30.0 (1.41)ab
		8	8	11	13	40
		6	9	6	11	32
SPD/PD†	Shallow	9.4 (1.36)b	20.7 (1.38)	4.3 (1.17)b	35.6 (1.48)	16.1 (1.67)bc
	Deep	26.5 (1.06)ab	10.0 (1.53)	44.5 (0.82)a	19.7 (1.58)	20.3 (1.21)b
		8	10	4	9	31
		4	9	7	6	26
SPD†	Shallow	8.6 (1.02)b	14.6 (0.88)	19.2 (0.51)a	85.3 (0.87)	21.8 (1.48)ab
	Deep	20.3 (0.26)ab	4.6 (0.52)	1.9 (1.42)b	22.7 (0.31)	7.9 (0.85)c
		7	12	8	9	36
		2	4	2	3	11

† PD = transect located along the wetland portion of the poorly drained soil; SPD/PD = transect located along the somewhat poorly and poorly drained soil break; SPD = transect located along the upland portion of somewhat poorly drained soil; Shallow = screened interval is approximately 0 to 80 cm below maximum high water table; Deep = screened interval is approximately 100 to 150 cm below maximum high water table.

‡ Values followed by different scripts within each column are significantly different in a one-way analysis of variance with a Fisher's least significant difference test. Analysis was performed on log-transformed values. An absence of letters in a column indicates no significant difference between treatments.

from the PD shallow groundwater treatment was more than twice the median rates in the shallow treatments of the SPD or SPD/PD transects. Our results suggest that both the SPD/PD and PD transects had considerable NO₃⁻ removal capacity throughout the upper 1.5 m of the groundwater. Since much of the groundwater NO₃⁻ exported from uplands may not move in the uppermost portion of the water table, it is important to document the effective depth of removal process in riparian areas.

The spatial variation in NO₃⁻ removal rates that we observed has implications for the use of riparian forests for groundwater NO₃⁻ attenuation. The data reinforce the conclusions of our previous study (Simmons et al., 1992), which suggested that while hydric soils have a uniformly high capacity for NO₃⁻ removal, the NO₃⁻ removal capacity of upland/wetland transition zone soils is more variable. Riparian zones dominated by upland or transitional soils may be less effective at preventing groundwater NO₃⁻ movement into streams or wetlands than sites dominated by hydric soils.

The scale of the spatial variation that we observed presents challenges for widespread incorporation of soil drainage classes into practical management guidelines for riparian forests. Our site, which is typical of many riparian areas in southern New England, had very finely divided soil drainage classes (separated by approximately 10 m), which had distinct groundwater NO₃⁻ removal capacities. Establishing relationships between readily

mappable site characteristics such as soil drainage class, depth to groundwater, and groundwater NO₃⁻ removal rates may be a promising approach for developing riparian management guidelines. However, the resolution of standard soil maps (13 m at a scale of 1:15 840) and groundwater maps used as input to many geographic information systems developed for land management is too coarse to incorporate the differences we observed in this study (Thompson, 1988). It may be necessary to develop high-resolution, large-scale soil and groundwater maps to guide the preservation, management, and establishment of riparian forests.

Temporal Variation

Temporal patterns of NO₃⁻ removal in this study were complex. Temperature was not the major controller of rates. Removal rates did not increase significantly from March into June, despite a >8°C increase in temperature (Table 3). Median removal rates in November were more than double those observed in June, although temperatures were lower in November.

The fact that the highest removal rates were observed in the dormant season (e.g., November) suggests that microbial processes such as immobilization and denitrification were responsible for much of the observed groundwater NO₃⁻ removal rather than plants. If plants were the dominant *sink* for NO₃⁻, we would expect removal rates to be highest during the growing season. However, as a confounding factor, the water table was markedly higher (about 30 cm) in all transects in November than in June, likely as a result of increased evapotranspiration in June. We expect plant-dominated removal to be strongly controlled by variation in the depth of the water table since plant root biomass has been shown to decline sharply with depth (Ehrenfeld et al., 1992).

The increase in NO₃⁻ removal rates that we observed over the course of this study may be due to induction of microbial NO₃⁻ removal processes by our experimental NO₃⁻ loading. We have observed increases in denitrification rate in the surface horizon of riparian forest soils

Table 5. Groundwater NO₃⁻-N removal rates in different periods of the year in a riparian forest. Values are median (coefficient of variation of untransformed values) and number of samples.

Sampling period			
March	June	September	November
$\mu\text{g kg}^{-1} \text{d}^{-1}$			
19.0 (1.07)bc†	12.3 (1.53)c	25.0 (0.97)b	53.2 (1.10)a
51	52	38	51

† Values followed by the same letter within a row are not significantly different in a one-way analysis of variance with a Fisher's least significant difference test. Analysis was performed on log-transformed values.

subjected to NO_3^- loading at other sites in our area (Hanson et al., 1994a,b). Such increases are unlikely in the subsurface due to strong C limitation of subsurface microbes, but the possibility needs to be tested.

Nitrate Removal Rates

Observed NO_3^- removal rates were high enough to suggest that this riparian zone could remove significant amounts of upland-derived NO_3^- , thus reducing its export to streams. For example, using a NO_3^- -N removal rate of $20 \mu\text{g N kg}^{-1} \text{d}^{-1}$ (the approximate median of all six treatments) and the bulk density at our study site (1.65 g cm^{-3}), the groundwater NO_3^- -N removal capacity of the uppermost 1.0 m of the groundwater in a riparian zone would be about $120 \text{ kg ha}^{-1} \text{ yr}^{-1}$. The groundwater NO_3^- -N removal rates we observed are higher than those predicted from other field investigations of riparian areas (Lowrance et al., 1983; Cooper et al., 1986; Correll and Weller, 1989); however, the rates observed in these previous studies may have been limited by NO_3^- loading. In addition, because our study was based on a comparatively brief loading period (about 1 yr), the removal rates that we observed may not represent long-term performance. Further investigations are required on the mechanisms responsible for NO_3^- removal before we can fully evaluate the long-term removal capacity of riparian areas.

ACKNOWLEDGMENTS

The authors thank G.W. Loomis and W.R. Wright for their assistance with soil mapping and characterization; H. Pionke and A.P. Gamedinger for their helpful advice on this manuscript; and R. Simmons, M. Khan, R. Puffer, and M. Salerno for technical assistance. Funding for this project was provided by the USDA-CSRS Special Water Grants Program under Grant no. 91-34214-6031. Contribution no. 3095 from the Rhode Island Agricultural Experiment Station.

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