THE INFLUENCE OF GEOMORPHIC SETTING ON GROUND WATER DENITRIFICATION IN FORESTED RIPARIAN WETLANDS

BY

DOROTHY Q. N. KELLOGG

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

ENVIRONMENTAL SCIENCE

UNIVERSITY OF RHODE ISLAND

2005

DOCTOR OF PHILOSOPHY DISSERTATION

OF

DOROTHY Q. N. KELLOGG

APPROVED:

Dissertation Committee:

Major Professor ______________________________

____

____

____

DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND

2005

ABSTRACT

Riparian wetlands are potentially significant landscape features for controlling the export of ground water nitrate (NO_3^-–N), to surface waters. Variability at both the reach and watershed scales has thwarted efforts to predict watershed-scale potential for riparian ground water nitrogen removal, and to effectively manage riparian zones based on functional assessments. Removal of ground water NO_3^-–N through microbial denitrification is influenced by the presence of subsurface organic C, and by ground water flow paths that determine retention time within the riparian subsurface ecosystem. Because geomorphic setting can describe depositional features that influence ground water flow path and the occurrence of subsurface C, it has the potential to serve as an indicator for riparian ground water denitrification potential. Moreover, if riparian geomorphology relates to N removal, then watershed-scale assessments of N export could be assisted with the availability of easily mapped geomorphic settings. Glaciated regions such as the northeastern United States are often divided into three major geomorphic settings: glacial till deposits, glacial outwash, and alluvial soils. Previous research has questioned the potential for ground water denitrification within riparian wetlands situated in glacial till, based on the high frequency of surface seeps that dramatically reduce retention times. In contrast, riparian wetlands situated in glacial outwash and alluvium are frequently characterized by low gradient, deep, stratified sediments that can transmit high ground water fluxes and where retention times can be considerable. The objective of this research was to (1) compare the vertical pattern and extent of microbial ground water denitrification in riparian wetland (hydric) soils located in

glacial outwash vs. alluvial geomorphic settings, and (2) assess the potential for ground water to interact with biologically active areas of deep, stratified soils underlying riparian zones situated in glacial outwash and alluvial settings. To quantify ground water denitrification in discrete locations of riparian aquifers, we modified and evaluated an in situ method based on conservative tracers and ^{15}N-enriched nitrate (Manuscript I). 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 (Manuscript II). 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, regardless of setting. We measured piezometric heads along a transect perpendicular to the stream, from the stream to the upland, at four riparian sites (two per setting) during a period of sustained high water table. We used a two-dimensional ground water flow model to estimate the associated piezometric surfaces, flow paths, and fluxes through the subsurface riparian ecosystem, defined as the stream to upland, to a depth of 3 m (Manuscript III). Modeling results showed that at the time when piezometric heads were measured ground water flux was substantial through the riparian subsurface ecosystem at all sites, with more complex flow paths than hypothesized, and with no apparent relationship between the geomorphic setting of these sites and the observed flow patterns. At all sites evapotranspiration (ET) dominated the hydrologic budget, ranging from 44% to 92% of the total outflux. Outflux to the stream was <10% of the total outflux at all sites. Within 10 m of the stream, where observed ground water denitrification rates were highest [Manuscript II], retention times along flow paths to the stream combined with denitrification rates resulted in the potential removal by denitrification of >10 mg L^{-1} NO_3^-–N at three of the four sites. Average annual watershed estimates that accounted for periods of low ET showed that these riparian wetlands could be transmitting about 8% of the upland recharge through ET. A nitrogen budget of the riparian wetland sites using a hypothetical development scenario in the uplands showed that three of the four sites could potentially remove or store about 25% of the upland ground water N load, with about 75% carried further downgradient to emerge lower in the watershed as either ET or baseflow. The fourth site could potentially remove or store about 90% of the upland ground water N load. Minimal N (0% to 9%) would have reached the stream. The low flux to the stream during periods of elevated evaporative demand suggests that non-hydric and till riparian areas provide much of the baseflow at this time, and argues for protection of infiltration and natural flow patterns throughout the watershed. Still unexplored is the role riparian wetlands may play when vegetation is dormant, as well as the role that root depth may have in maintaining ET during the growing season.

ACKNOWLEDGEMENTS

My deepest gratitude goes to Dr. Arthur Gold, whose steady guidance, insight, humor, and patience have made this a truly rewarding and fun experience. His sense of humor and unwavering trust as I navigated research challenges combined with parenthood made this work possible. Special thanks to my committee members, Dr. Peter Groffman for his cheerful support and thoughtful participation, and for always asking the challenging questions, and Dr. Charles Roman who has given me excellent advice throughout.

I thank Drs. Mark Stolt and Dr. Robert Thompson for being part of my comprehensive exam committee. I'm especially indebted to Dr. Stolt for his constant and helpful participation and for his lab's cooperative efforts throughout this project.

I would also like to thank Dr. Barbara Nowicki for being a part of my defense committee and for her cheerful collaboration with our lab, and Dr. Candace Oviatt for chairing my defense.

Kelly Addy has my lasting affection and gratitude for sharing her friendship, her office, her extensive knowledge and experience, and her calm wisdom throughout the years, all of which were sorely missed during her maternity leaves.

Thanks to my other cohorts in grime, fellow graduate students Adam Rosenblatt, Gary Blazejewski, and Tara Watson, who worked alongside me and generously shared the load, both literally and figuratively. Thanks to all our coastal fellows, Gina Ferendo, Drew Grande, Tom Liddy, and Mike St. Pierre, who showed great stamina and ingenuity in the field and in the lab, and to the URI Watershed Hydrology laboratory assistants Stephen Austin, Kate Banick, Chelsea Coker, Kate Crowell, Jenny Davis, Missy Lefebvre, Steve McCandless, Anthony Morales, Filipe Reis, Edwin Requintina, Emily Troiano, and Hans van Lingen for lab and field assistance.

I am grateful to Jon Cole for SF_6 insights; Gary Speiran at the U.S. Geological Survey for his insights on riparian ground water flow; David Harris for mass spectrometry analysis at the UC Davis Stable Isotope Facility; Linda Green for nitrate analysis; Jim McKenna for DOC analyses; IES laboratory assistants Jessica Kriebel, Sabrina LaFave, Abraham Parker, Abraham Parker, and Emilie Stander for analytical support.

I am deeply grateful to Mr. and Mrs. Maurice Gordon, and to the State of Rhode Island, for generously allowing us to maintain study sites on their land.

I thank the Rhode Island Agricultural Experiment Station, the United States Department of Agriculture National Research Initiative, and the National Science Foundation for funding this research.

Thanks to the Department of Natural Resources and to Barb Brown, and her able successor, Patty Harrington, for keeping me out of administrative trouble.

To the many extended family, friends, and neighbors who have provided sustenance, both emotional and physical, you will always be dear to me.

Finally, I am blessed with a family that has tolerated with love, grace, and humor the many hours spent in the field, in the lab, at my desk, and not least, commuting to and from these places. To my children, Sam and Louisa, go my

profound thanks for dealing with sub-standard laundry, meals, and general motherly upkeep, to my mom, for her frequent visits to help minimize the effects of all these, and most of all, to my husband, Dave, who willingly filled in with way-above-standard laundry, meals, and fatherly upkeep, and who gave me steadfast support all through this great adventure.

PREFACE

This dissertation is written in the MANUSCRIPT FORMAT as specified in the guide to theses and dissertations, University of Rhode Island.

Hypotheses stated in my dissertation proposal were:

a) Outwash settings will exhibit a sharp and regular decline in carbon content with increasing depth, accompanied by an abrupt decline in groundwater denitrification rates. Alluvial settings will be characterized by buried deposits of carbon and will not exhibit a sharp decrease in groundwater denitrification rates with increasing depth.

b) Flow paths through outwash riparian zones will direct most of the groundwater flux below the upper portion of the hydric soil and thus much of the flow will bypass the hypothesized zone of denitrification. In contrast, a greater proportion of the groundwater flux in alluvial settings will have the opportunity to interact with carbon-rich deposits located deeper in the soil, allowing for a higher overall groundwater denitrification potential in alluvial settings.

Objectives laid out in my dissertation proposal for this research were:

1) Develop a rapid in situ method for evaluating groundwater denitrification potential in a spatially explicit manner (i.e., isolating specific depths below the surface) within a riparian zone;

2) Compare the vertical extent of denitrification in riparian hydric soils located in glacial outwash vs. alluvial settings;

3) Characterize the pattern of groundwater flow from uplands through hydric riparian soils in glacial outwash vs. alluvial settings;
4) Link groundwater flow paths with denitrification rates to characterize the overall groundwater denitrification potential in hydric riparian soils in glacial outwash vs. alluvial settings;
5) Explore opportunities for applying, at the watershed scale, insights gained in this study on the potential for riparian zones to function as sinks for groundwater nitrogen. Identify continued gaps in our knowledge that limit our ability to scale up, and suggest approaches to refine our understanding of riparian groundwater denitrification potential at the watershed scale.

Manuscript I addresses Objective (1), and was published in 2002:

Addy, K.L., D.Q. Kellogg, A.J. Gold, P.M. Groffman, G. Ferendo, and C. Sawyer. 2002. In situ push-pull method to determine ground water denitrification in riparian zones. *Journal of Environmental Quality* 31:1017–1024.

Manuscript II addresses Hypothesis (a) and Objective (2), and was published in 2005:

Kellogg, D.Q., A.J. Gold, P.M. Groffman, K.Addy, M.H. Stolt, and G. Blazejewski. 2005. In situ ground water denitrification in stratified, permeable soils underlying riparian wetlands. *Journal of Environmental Quality* 34:524-533.

Manuscipt III addresses Hypothesis (b) and Objectives (3), (4), and (5), and has been prepared in general manuscript format, to be submitted to *Hydrological Processes*.

The site identification letters (A through D) used in Manuscripts II and III refer to the same sites. The site identification letters (A and B) used in Manuscript I refer to sites distinct from those referenced in Manuscripts II and III.

TABLE OF CONTENTS

LIST OF TABLES

Manuscript I:

Manuscript II:

Manuscript III:

LIST OF FIGURES

Manuscript II:

Manuscript III:

MANUSCRIPT I:

In situ push-pull method to determine ground water denitrification in riparian zones

(Coauthors: Kelly Addy, Arthur J. Gold, Peter M. Groffman, Gina Ferendo, and Carl Sawyer)

(Published in 2002 in *Journal of Environmental Quality* 31:1017-1027)

ABSTRACT

To quantify ground water denitrification in discrete locations of riparian aquifers, we modified and evaluated an in situ method based on conservative tracers and ^{15}N-enriched nitrate. Ground water was "pushed" (i.e., injected) into a mini-piezometer and then "pulled" (i.e., extracted) from the same mini-piezometer after an incubation period. This push-pull method was applied in replicate mini-piezometers at two Rhode Island riparian sites, one fresh water and one brackish water. Conservative tracer pretests were conducted to determine incubation periods, ranging from 5 to 120 h, to optimize recovery of introduced plumes. For nitrate push-pull tests, we used two conservative tracers, sulfur hexafluoride and bromide, to provide insight into plume recovery. The two conservative tracers behaved similarly. The dosing solutions were amended with ^{15}N-enriched nitrate that enabled us to quantify the mass of denitrification gases generated during the incubation period. The in situ push-pull method detected substantial denitrification rates at a site where we had

previously observed high denitrification rates. At our brackish site, we found high rates of ground water denitrification in marsh locations and minimal denitrification in soils fringing the marsh. The push-pull method can provide useful insights into spatial and temporal patterns of denitrification in riparian zones. The method is robust and results are not seriously affected by dilution or degassing from ground water to soil air. In conjunction with measurements of ground water flowpaths, this method holds promise for evaluating the influence of site and management factors on the ground water nitrate removal capacity of riparian zones.

INTRODUCTION

Although riparian zones can markedly decrease the flux of nitrogen from watersheds, major questions surround the influence of site and management factors on the ground water nitrogen (N) removal capacity of riparian zones (Hill, 1996). In particular, we are still developing our understanding of the response of riparian ground water nitrate removal to water table dynamics (Correll, 1997), soil drainage class (Simmons et al., 1992; Nelson et al., 1995), surficial geology (Lowrance et al., 1997), and vegetation (Haycock and Pinay, 1993; Osborne and Kovacic, 1993; Addy et al., 1999). Within a riparian zone, we need to resolve the factors that influence the depth of the biologically active zone (i.e., the portion of the saturated zone that is altered by the riparian ecosystem and generates substantial nitrogen transformations). In addition, there is a great need to evaluate the effectiveness of various riparian zone restoration and management approaches on riparian zone function (Lowrance et al., 1995; Schultz et al., 1995; Clausen et al., 2000). The extent of questions surrounding riparian ground water nitrate removal argues for timely and affordable in situ methods of assessment.

Hill (1996) summarized the types of field and laboratory studies that have contributed to our understanding of ground water nitrate-N (NO_3^-–N) dynamics in riparian zones. Field studies often rely on intensive well networks that track changes in nitrate concentrations as ground water moves through a riparian zone. Many of these studies (Peterjohn and Correll, 1984, Jacobs and Gilliam, 1985; Lowrance, 1992; Haycock and Pinay, 1993; DeVito et al., 2000; Hill et al., 2000) are situated on riparian sites downgradient from a source of nitrate-enriched ground water (e.g., cropland). Other field studies introduce an enriched plume of nitrate into the ground water and observe transformations following an incubation period or travel path (Trudell et al., 1986; Simmons et al., 1992; Nelson et al., 1995, Starr et al., 1996; Verchot et al., 1997). These in situ studies are well suited to evaluate the ground water nitrate removal capacity of riparian zones, but they require extensive time and effort and often cannot directly explore the removal mechanisms (i.e., plant uptake vs. microbial immobilization vs. microbial denitrification).

A major challenge in field studies is that reductions in nitrate concentrations can occur as a result of both biological removal processes as well as physical processes (i.e., dispersion or dilution with other ground water of low nitrate concentration). Many field studies compare changes in nitrate concentrations along a flowpath to changes in "conservative" tracer concentrations along the flowpath to account for physical processes. Changes in ambient chloride to nitrate ratios are often used in studies downgradient of agricultural lands (Jacobs and Gilliam, 1985;

Lowrance, 1992; Verchot et al., 1997; Devito et al. 2000; Hill et al., 2000). Bromide to nitrate ratios are commonly used where enriched plumes are introduced within the ground water, either through natural gradient tests where transformations are observed in downgradient wells (Simmons et al., 1992; Nelson et al., 1995; Smith et al., 1996) or within the injection well over a series of different time periods (Trudell et al., 1986). Recent studies suggest that these anion tracers are susceptible to plant uptake, potentially confounding the reliability of tracers in certain situations (Kung, 1990; Schnabel et al., 1996; Whitmer et al., 2000). In addition, these anion tracers are of limited value in coastal riparian zones where brackish ground water has high ambient concentrations of chloride (Cl^-) and bromide (Br^-).

Another approach to examining ground water nitrate removal is to conduct laboratory microcosm studies with aquifer sediments; however such studies do not always corroborate observations from the field (Groffman et al., 1996). Samples of media from different depths below the water table are difficult to obtain, microcosm rates are often lower than in situ derived rates and, most importantly, the small sample size used in microcosm assays can generate extremely high variability. Several studies suggest that ground water nitrate removal might occur in small patches or "hotspots" that might be missed using microcosm techniques (Parkin, 1987; Christensen et al., 1990b; Jacinthe et. al., 1998). Mesocosm studies (Gold et al., 1998; Jacinthe et al., 1998; Addy et al., 1999) with >10 kg undisturbed aquifer sediments can provide insights into riparian ground water denitrification; however, obtaining mesocosms from below the water table is highly labor intensive.

Here, we present a rapid, in situ method based on conservative tracers and ^{15}N-enriched nitrate to quantify ground water denitrification in discrete locations of riparian aquifers. Our method was adapted from the *push-pull* method (Trudell et al., 1986; Istok et al., 1997) where a single piezometer was used for both dosing and sampling of ground water. Application of this method at fresh water and brackish water sites with different hydrologic properties is also considered.

METHODS

Approach

We adapted the push-pull method (Trudell et al., 1986; Istok et al., 1997) to estimate in situ rates of denitrification in the shallow aquifer of riparian zones rapidly and at scales relevant to riparian research. We "pushed" (i.e., injected) 10 L of previously collected ground water, into a mini-piezometer and then "pulled" (i.e., extracted) ground water from the same mini-piezometer after an incubation period (Figure 1.1). Prior to injection, the ground water was amended with ^{15}N-enriched nitrate and Br^-. Then, this amended solution was adjusted to ambient dissolved oxygen (DO) concentrations to mimic aquifer conditions by bubbling a sulfur hexafluoride (SF_6) gas mixture through the dosing solution. We used relatively brief incubation periods (i.e., 5 to 72 h) to optimize recovery of the introduced plume. Two conservative tracers, gaseous tracer SF_6 and soluble anion Br^-, provided insight into the recovery of the introduced plume. To minimize the effects of confounding factors such as dilution and dispersion, denitrification rates were estimated from only the "core" of the plume (i.e., the first 2 L of the plume pulled from the mini-piezometer after the

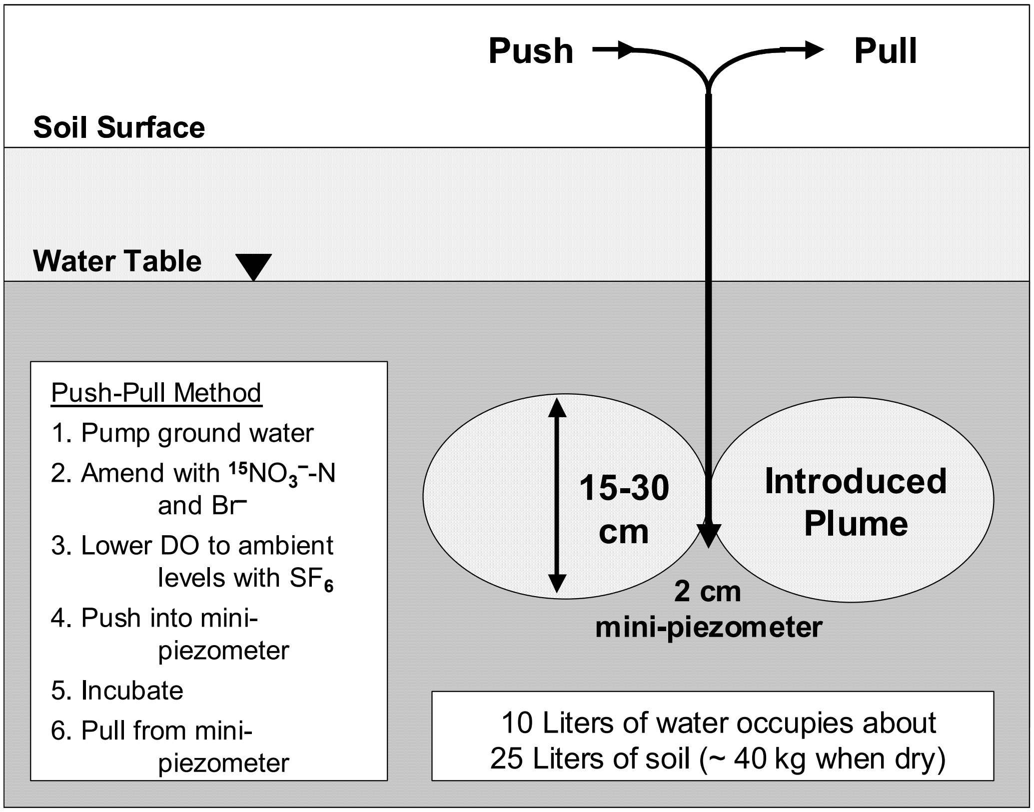

Figure 1.1. Schematic of the in situ push-pull mini-piezometer method.

incubation period). This portion of the plume consistently exhibited the highest conservative tracer recovery rate. In sandy media (bulk density = 1.65 g cm^{-3}, porosity = 0.38) the 2-L plume core interacts with 8.7 kg (dry wt.) of soil.

Site Descriptions

We field-tested the in situ mini-piezometer method at two riparian sites in Rhode Island. Site A was a streamside riparian area where Addy et al. (1999) previously found high rates of ground water nitrate removal. By using Site A, we could compare denitrification rates generated by the in situ push-pull mini-piezometer method to rates obtained using the mesocosm method (Addy et al., 1999). Site B was a coastal riparian area with brackish ground water where we explored the ability of this method to discern differences in denitrification rates at two discrete locations located in different ground water environments separated by less than 15 m.

Site A was located along Tanyard Brook, a first-order tributary of Watchaug Pond, Charlestown, RI (41°22'N, 71°42'W). Soils at the site were poorly drained sands and loamy sands derived from glaciofluvial deposits (average slope of 3%) and classified as sandy, mixed, mesic Typic Humaquepts. Vegetation included a mix of emergent vegetation, sedges, bluegrass (*Poa* spp.) and brome grass (*Bromus inermis* Leyss.) with an overstory dominated by speckled alder [*Alnus incana* (L.) Moench subsp. *rugosa* (Du Roi) R.T. Clausen]. Further site characterization can be found in Table 1.1.

Site B was located along Brushneck Cove, a tidally influenced cove of Narragansett Bay, Warwick, RI (41°41'N, 71°24'W). We explored two discrete

Table 1.1. Site characteristics.

	Site A	**Site B** marsh	**Site B** fringe
Number of replicate mini-piezometers	3	4	3
Depth of mini-piezometers,† cm	65	125	125
Water table depth at dosing time,† cm	44	19	92
Ground water temperature, ‡ °C	14.1	15.7	13.3
Dissolved oxygen,‡ mg L^{-1}	2.9	0.9	2.3
pH‡	6.5	4.2	4.9
Dissolved organic C,‡ mg L^{-1}	39.6	7.2	5.5
NO_3^-–N,‡ mg L^{-1}	0.4	0.0	0.0
Br^-,‡ mg L^{-1}	0.0	NA§	NA§
Salinity,‡ g L^{-1}	0.0	13.4	0.1
Soil texture class¶	Loamy sand	Fine sand	Fine sand

† Depth below soil surface.
‡ Mean value of replicate mini-piezometers.
§ Not applicable.
¶ Based on analysis of sample collected from soil pits dug in the vicinity of mini-piezometers.

locations below the water table at Site B within (i) the salt "marsh" and (ii) the transition area between the salt marsh and the upland, the area referred hereafter as the "fringe." At both locations, we assessed ground water denitrification in fine sands derived from glaciofluvial deposits. Mineral soils in the marsh were below a 30- to 90-cm-thick organic horizon, whereas no organic horizon was present in the fringe location. Marsh soils were very poorly drained, classified as sandy, mixed, eudic, mesic Terric Sulfihemists and tidally inundated twice daily (average slope of 3%). Fringe soils were somewhat poorly drained, classified as mixed, mesic Typic Psammaquents and rarely tidally inundated (average slope of 10%). Vegetation was dominated by smooth cordgrass (*Spartina alterniflora* Loisel.) in the marsh location and by marsh elder [*Iva frutescen*s Pursh var. *oraria* (Bartlett) Fernald & Griscom], sea lavender [*Limonium carolinianum* (Walter) Britton] and seaside goldenrod (*Solidago sempervirens* L.) in the fringe location. Further site characterization can be found in Table 1.1.

<u>Mini-Piezometer Instrumentation</u>

The mini-piezometers, similar to the sampling system described by Winter et al. (1988), are small steel well points (1.8-cm o.d., 2-cm screen length; AMS, American Falls, ID) attached to gas-impermeable Teflon tubing (0.7-cm o.d.) that extend into the soil. We used the AMS gas vapor probe system to install the mini-piezometers. After installation, the narrow hole surrounding the mini-piezometer and tubing was backfilled with sand and bentonite to prevent water flow along the side of the tubing.

In sandy media, we were able to install and develop at least three mini-piezometers in one day.

At Site A, we installed three replicate mini-piezometers in the mineral soil at 65 cm below the soil surface. At Site B, four marsh and three fringe replicate mini-piezometers were installed in mineral soil at 125 cm below the soil surface (total of seven mini-piezometers at Site B). Replicate mini-piezometers were at least 2.5 m apart. To develop the mini-piezometers we pumped at least one liter of water from each. Water was sampled with a Masterflex L/S portable peristaltic pump (Cole Parmer, Vernon Hills, IL). From each mini-piezometer, we measured ground water temperature and ambient concentrations of DO, NO_3^-–N, Br^-, dissolved organic carbon (DOC) and salinity prior to the tracer push-pull pretests and nitrate push-pull tests. At all mini-piezometer locations, soil samples were collected from nearby soil pits for analysis of soil textural class. During the study at Site A, the water table was 44 cm below the soil surface. During the study at Site B, the water table at low tide was 19 and 92 cm below the soil surface in the marsh and fringe, respectively.

Hydrologic Characterization: Push-Pull Pretest

Prior to the in situ nitrate study, we conducted an in situ conservative tracer push-pull pretest at both sites. This tracer pretest provided insight into the relationship between the length of incubation period and plume recovery. The recovery rate of the tracer reflected the extent of ground water advection, dispersion, and diffusion that occurred during the push phase and incubation period. We then adjusted the length of the incubation period for the in situ nitrate push-pull test to obtain high rates of tracer recovery in the plume core (i.e., the first 2 L extracted in the pull phase).

We used SF_6 as the pretest conservative tracer at both sites. Prior to the pretest, we collected 10 L of ground water from one mini-piezometer at Site A, the Site B marsh, and the Site B fringe. The three ground water solutions were each bubbled with a mixture of SF_6-O_2-N_2 (100 mg L^{-1} SF_6, 2 mg L^{-1} O_2, balanced in N_2; unanalyzed mixture in portable cylinder; Matheson Trigas, Gloucester, MA) to saturate the solutions with SF_6 (approximately 20 min per solution). These amended ground water solutions were pushed into the same mini-piezometer via a peristaltic pump. The amended dosing solution was sampled during the push phase to obtain the undiluted concentration of SF_6 (C_o). The plume was left in the ground for at least the same incubation period we expected to use in our in situ nitrate push-pull test. After the incubation period, we pulled two to three times the dosing volume, taking samples at 1- to 6-L intervals. We analyzed gas extracted from ground water (method described below) for SF_6 and determined the recovery of this tracer at each sampled interval.

We selected 10 L as our injected ground water volume for experimental and logistical reasons. Experimentally, 10 L of ground water interacts with a large volume of aquifer material, around 44 kg of soil (bulk density = 1.65 g cm^{-3}, porosity = 0.38). This injection volume also helps to minimize dilution in the plume core. Logistically, 10 L of ground water solution is relatively easy to transport into and out of remote sites and can be pushed into the wells in a reasonable time period even with low pumping rates.

After at least 2 wk, we resampled the pretested mini-piezometers and analyzed for SF_6 to ensure that tracer concentrations were at ambient levels before conducting another pretest with a shorter incubation period if the original pretest recovery was poor or before conducting the in situ nitrate push-pull test. If SF_6 concentrations were still above ambient levels, we extracted additional volumes of water or waited additional time until ambient concentrations were found. At Site A, we conducted 120-h and 72-h incubated SF_6 pretests in May and November of 1999, respectively. At Site B, we conducted a 24-h and 5-h incubated SF_6 pretest in June and July of 2000, respectively.

In Situ Nitrate Push-Pull Test

We conducted in situ nitrate push-pull tests at Site A in November 1999 and at Site B in October 2000. To prepare for the in situ nitrate push-pull tests, we collected bulk quantities of ground water from one mini-piezometer at Site A, the Site B marsh and the Site B fringe. Ground water was stored at 4°C (maximum of 2-wk storage) until the push-pull test. Each dosing solution (10 L per mini-piezometer) at Site A consisted of ambient ground water enriched with 32 mg L^{-1} Br^- (as KBr) and 32 mg L^{-1} isotopically enriched (20 atom % ^{15}N) NO_3^-–N (as KNO_3^-–N). Site B dosing solutions were similar, except they did not contain Br^- because high ambient Br^- concentrations in the brackish ground water limited its usefulness as a tracer here.

Prior to injection, we bubbled the SF_6 mixture into the dosing solution to saturate the solution with SF_6 and lower the DO to ambient levels (approximately 20 min per solution). We then capped the carboy, filled its headspace with the SF_6 gas mixture and sealed its vents for transport to the study site. Alternatively, a gas-impermeable bag could have been used to collect ground water, receive the enriched solution, and reinject the ground water solution without exposing it to the atmosphere (Smith et al., 1991, 1996). We found that the carboy setup facilitated the use of the SF_6 gas tracer.

The 10 L dosing solutions were pushed into mini-piezometers over the course of an hour with the peristaltic pump at very low rates (10 to 12 L h^{-1}) to minimize changes in the hydraulic potential surrounding the mini-piezometer. The dosing solution carboy was maintained under constant pressure through connection to the SF_6 cylinder. A small quantity of the dosing solution (targeted 500 ml and measured later in the lab) was left at the bottom of the carboy to measure DO and ensure that the DO content remained stable. Based on the pretest results, the incubation period was set at 72 h at Site A and 5 h at Site B. At Site B, the incubation period occurred in the period approximately 2 h before low tide to 3 h after low tide, when Site B was not inundated with tidal water. After the incubation period, we pulled 18 L of ground water from each mini-piezometer. We pumped ground water from the mini-piezometers slowly (9 to 13 L h^{-1}) to avoid generating gas bubbles within the tubing. We collected ground water samples at periodic intervals throughout the pull and push phases. Dissolved gases were extracted from ground water samples as described below. All ground water samples were stored at 4 ºC until analysis.

Conservative Tracer Recovery Estimates

For each mini-piezometer, we calculated the recovery or C/C_o of the conservative tracers where C was the pulled ground water concentration following incubation and C_o was the original pushed ground water concentration (Freeze and Cherry, 1979). Relative concentration profiles were created by plotting the C/C_o versus the normalized plume volume (cumulative pulled volume when the sample was collected/total pushed volume).

Gas Extraction from Ground Water

To sample for N_2, N_2O and SF_6 gases in ambient, pushed, and pulled samples, we used the phase equilibration headspace extraction technique (Lemon, 1981; Davidson and Firestone, 1988). We collected ground water samples with a syringe attached to an air-tight sampling apparatus made of stainless steel tubing connected to the peristaltic pump. These ground water samples were injected into an evacuated serum bottle and the headspace was filled with high-purity argon gas. After incubating overnight at 4 ºC and shaking, we sampled the bottle headspace to extract SF_6 and gases produced by denitrifying microbes (N_2 and N_2O).

Denitrification Rate Calculations

Only samples taken from the plume core (i.e., first 2 L extracted in the pull phase with tracer recovery > 80%) were used in denitrification rate calculations. To calculate the masses of N_2O-N and N_2 gases (µg) in our headspace extraction samples, we used equations and constants provided by Tiedje (1982) and Mosier and

Klemedtsson (1994). The mass of N_2O-N or N_2 was transformed to the mass of $^{15}N_2O$-N or $^{15}N_2$ by multiplying it by the respective ^{15}N sample enrichment proportion (ratio of pulled atom % of the dissolved N_2 and N_2O-N to pushed NO_3^-–N atom %, both corrected for ambient atom %). Sample $^{15}N_2O$-N and $^{15}N_2$ gas production rates were expressed as μg N kg^{-1} d^{-1} (total mass of $^{15}N_2O$-N or $^{15}N_2$ per volume of water pulled/[dry mass of soil per volume of water pulled x incubation period]).

Each pulled sample represented 1 L of ground water that occupied 4.37 kg of soil (bulk density = 1.65 g cm^{-3}, porosity = 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 since the plume core would consist mostly of the later injected ground water. Denitrification rates were the sum of $^{15}N_2O$-N and $^{15}N_2$ generation rates. Denitrification rates may be underestimated since we did not measure NO_2^- and NO, other intermediates of the denitrification process.

All samples used in denitrification calculations contained at least 2 mg L^{-1} NO_3^-–N to ensure that our denitrification rate estimates were not limited by the amount of nitrate available (Schipper and Vojvodic-Vukovic, 1998).

Another option to quantify ground water nitrate transformations was to generate ground water nitrate removal estimates based on differences between Br^- and NO_3^-–N concentrations. However, at the relatively short incubation periods used in the push-pull design, notable rates of nitrate removal (i.e., 5–15 μg N kg^{-1} d^{-1}) require Br^- and NO_3^-–N concentrations at resolutions at the 0.1 mg L^{-1} level. Therefore, we chose to estimate only denitrification rates from our samples.

Denitrification rates are derived from the total concentration of $^{15}N_2O$-N and $^{15}N_2$ gases obtained through mass spectrometer analysis and were of finer resolution (at the μg L^{-1} level) than Br^- and NO_3^-–N data (at the 0.5 mg L^{-1} level) obtained from ion chromatography.

Analytical Methods

Ground water DO and temperature were measured with a YSI Model 55 DO/temperature meter (YSI, Yellow Springs, OH). Ground water samples were analyzed for NO_3^-–N and Br^- (detection limit: 0.2 mg L^{-1}) on a DX-120 ion chromatograph (Dionex, Sunnyville, CA), for dissolved organic carbon by infrared analysis using an O.I. Corporation (College Station, TX) Model 1010 carbon analyzer, for pH on an Accumet Model 925 pH meter (Fisher Scientific, Pittsburgh, PA) and for salinity on a YSI Model 30 salinity/conductivity/temperature meter. Concentrations and isotopic composition of N_2 and N_2O gases were determined on a dual inlet isotope ratio mass spectrometer (Stable Isotope Facility, UC Davis, Davis, CA) as described by Mosier and Schimel (1993). Concentrations of N_2O and SF_6 gases were analyzed by electron-capture gas chromotography (Tracor [Houston, TX] 540). Soil texture was determined by dry sieve analysis (Troeh and Thompson, 1993).

Statistical Analyses

Paired *t* tests (Ott, 1993) were performed to determine significant differences in (i) recovery (C/C_o) of SF_6 within the plume core between different incubation periods in each mini-piezometer and (ii) recovery (C/C_o) between Br^- and SF_6 in Site A mini-piezometers. Mann-Whitney *U* tests (Ott, 1993) were performed to determine significant differences in (i) denitrification rates observed at Site A and those determined in the Addy et al. (1999) mesocosm study and (ii) denitrification rates at the marsh and fringe locations at Site B. All statistical analyses were performed on Statistica for Windows (StatSoft,1999).

RESULTS AND DISCUSSION

Recovery of Conservative Tracer: Pretest

Selecting an appropriate incubation period based on hydrologic properties of specific sites was a critical component of the push-pull mini-piezometer method. At both sites, we found significantly higher recovery ($p < 0.01$) of the pretest tracer SF_6 in the plume core using the shorter incubation period. With the 120-h incubated pretest at Site A, the highest recovery of SF_6 was only 28% (Figure 1.2). With the 72-h incubated pretest at Site A, recovery of SF_6 improved to >80% in the plume core (Figure 1.2). At Site B, we recovered no SF_6 after the 24-h incubation, but SF_6 recovery in the 5-h incubation (data not shown) was comparable to the 72-h incubated pretest results at Site A. Clearly, the 72-h incubation at Site A and the 5-h incubation at Site B were well suited to determine denitrification rates with minimal dilution influences on the introduced plume.

A variety of site factors, including hydraulic conductivity and hydraulic gradient, can affect the extent of plume displacement and dilution via advection and dispersion. These site factors can require rigorous field effort to elucidate and

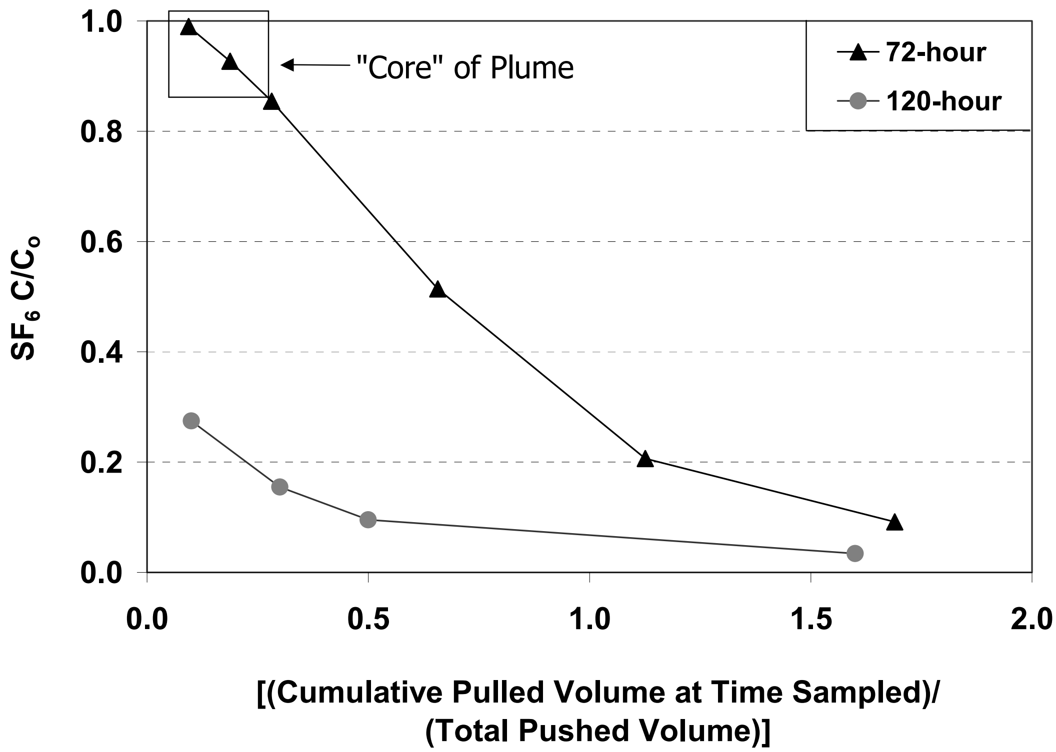

Figure 1.2. Relative concentration profiles of SF_6 from the 72- and 120-h conservative tracer push-pull pretests at Site A. The term C represents the concentration of the sample pulled from the mini-piezometer. The term C_o represents the concentration of the dosing solution originally pushed into the mini-piezometer.

incorporate into sampling designs. Conducting a push-pull tracer pretest was an efficient approach to estimate the effects of advection and dispersion on an introduced plume. By modifying incubation period length in a series of SF_6 pretests, we obtained high recovery of the tracer in the plume core at both sites. The range in incubation periods required to generate similar plume recoveries suggests substantial variation in hydrologic factors between sites; however, the push-pull mini-piezometer method should be equally effective in determining denitrification rates at both sites as long as we have high plume recovery. Since Site B was tidally influenced, there was unusually high hydraulic gradient around low tide, indicating the need for shorter incubation periods.

With the appropriate incubation period, the in situ push-pull mini-piezometer method should be effective at characterizing ground water nitrate dynamics at a range of sites. Further exploration of this method is needed at heterogeneous sites. When we pretested Sites A and B, we only used one mini-piezometer per location for characterization since the soil was fairly uniform within sites. However, at sites with less homogeneous soils, multiple mini-piezometers may need to be pretested with conservative tracers to determine the appropriate incubation period for each specific location.

Recovery of Conservative Tracers: Nitrate Push-Pull Tests

In the nitrate push-pull tests, tracer recovery in the plume core of all mini-piezometers at both Sites A and B exceeded 80%, indicating minimal loss due to physical processes. Tracer concentration in the pulled samples dropped steadily after the first 2 L extracted. Concentrations approached ambient levels after we extracted close to two dosing volumes from mini-piezometers. Within each mini-piezometer at Site A, the relative concentration profiles of Br^- and SF_6 were very similar (Figure 1.3). In each mini-piezometer at Site A, Br^- recovery was not significantly different from SF_6 recovery. The difference in Br^- and SF_6 recovery at each point of measurement within the plume never exceeded 10% in any mini-piezometer.

Bromide has been used as the conservative tracer in many riparian ground water nitrate studies (Simmons et al., 1992; Nelson et al., 1995; Starr et al., 1996), but its value as a tracer may be compromised if it is subjected to plant uptake. SF_6 is a gaseous tracer that has been found to behave conservatively in sandy aquifers (Wilson and Mackay, 1993, 1996). Sulfur hexaflouride is not suspected of plant uptake and can be used in situations where high ambient ion concentrations confound the use of Cl^- and Br^-, as in tidal riparian areas; however, its value as a conservative ground water tracer could potentially be compromised by degassing. The similarities in the high recoveries of both Br^- and SF_6 in the plume core demonstrated that this portion of the plume was not substantially altered by physical or biological processes, enhancing our confidence in denitrification estimates based on ^{15}N-enriched gas in samples from this portion of the plume.

Denitrification Rates: Nitrate Push-Pull Tests

The in situ nitrate push-pull test detected substantial denitrification rates at Site A, where we had previously observed high denitrification rates (Addy et al., 1999). However, denitrification rates obtained from the in situ nitrate push-pull test (mean =

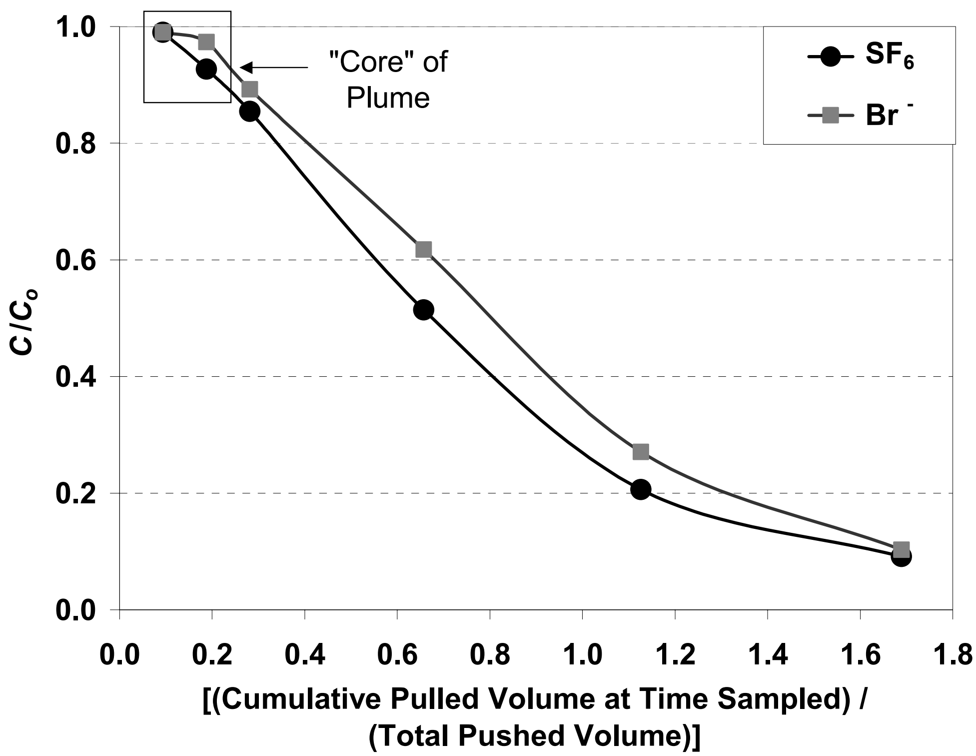

Figure 1.3. Relative concentration profiles of conservative tracers (Br^- and SF_6) from the 72-h in situ nitrate push-pull test in one Site A mini-piezometer. The term C represents the concentration of the sample pulled from the mini-piezometer. The term C_o represents the concentration of the dosing solution originally pushed into the mini-piezometer.

96.7 μg N kg^{-1} d^{-1}, SE = 19.7) were significantly greater ($p < 0.05$ level) than those found by Addy et al. (1999) using mesocosms from the same depth (Figure 1.4). The variation in denitrification rates between replicates was comparable with results obtained from other mesocosm and in situ dosing-well studies (Nelson et al., 1995; Gold et al., 1998; Addy et al., 1999).

The higher denitrification rates detected with this in situ method compared with mesocosms taken from the same location (Addy et al., 1999) may have resulted from seasonality and labile carbon limitations within the Addy et al. (1999) study. In a long-term in situ study at a similar riparian site in Rhode Island, Nelson et al. (1995) found significantly higher rates of ground water nitrate removal in November, the time of our in situ nitrate push-pull test, than in June, when Addy et al. (1999) collected mesocosms. Nelson et al. (1995) speculated that root turnover in the autumn might enhance denitrification rates at that time period. In addition, the mesocosms may have underestimated daily denitrification rates since the results were generated from a closed system over a 50-d period and the labile carbon supply may have dwindled over the course of the study. Hotspots of microbial activity may persist for only days to weeks (Christensen et al., 1990b) but are constantly replenished in natural systems (Christensen et al., 1990a). In our in situ nitrate push-pull test, incubation periods were relatively brief and capable of exploiting recurring pools of labile carbon that result from an intact plant-soil-hydrologic system.
In situations with low ground water nitrate removal rates and relatively brief incubation periods (i.e., less than 24 h), the resolution of ion chromatograph methods may obscure direct comparison of nitrate removal estimates based on changes in Br^-

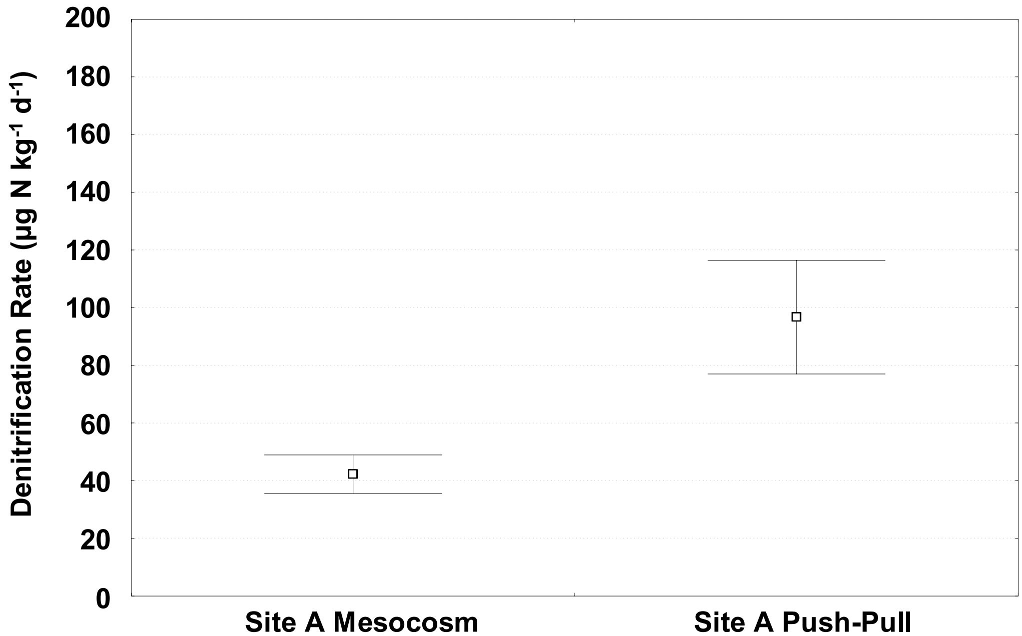

Figure 1.4. Ground water denitrification rates from the in situ nitrate push-pull test conducted at Site A. Values for mesocosm data are the mean (SE) of three replicate mesocosms (Addy et al., 1999) and values for push-pull data are the mean (SE) of three replicate mini-piezometers.

to NO_3^-–N ratios with denitrification rates derived from ^{15}N-enriched N_2 and N_2O, as mentioned earlier in the Methods. However based on our 72-h incubations at Site A, we found that in situ push-pull estimates of denitrification rates agreed closely with mass balance estimates of nitrate removal corrected for dilution. The mean denitrification rate at Site A was 96.7 μg N kg^{-1} d^{-1}, equivalent to a change in concentration of 1.3 mg NO_3^-–N L^{-1} over the 72-h incubation. This value is near the observed changes in mean NO_3^-–N concentration within the plume core of those Site A mini-piezometers, ranging from 1.4 to1.9 mg N L^{-1}. The discrepancy could result from losses due to other removal processes, such as immobilization, dissimilatory nitrate reduction to ammonium, or plant uptake, and from differences in the precision of the different analytical procedures.

At Site B, we found significantly higher denitrification rates (Figure 1.5; $p < 0.05$) in marsh mini-piezometers (mean = 123.2 μg N kg^{-1} d^{-1}, SE = 63.8) than in fringe mini-piezometers (mean = 2.1 μg N kg^{-1} d^{-1}, SE = 1.4). These results are in accordance with the difference in ground water denitrification rates expected for these types of ecosystems.

Potential Confounding Factors

Several factors could confound the denitrification rate estimates from ^{15}N gas generation in the push-pull mini-piezometer method: (i) dilution of denitrification gases, (ii) degassing from ground water to soil air, and (iii) a lag time between dosing and microbial response. However, the specific set of conditions associated

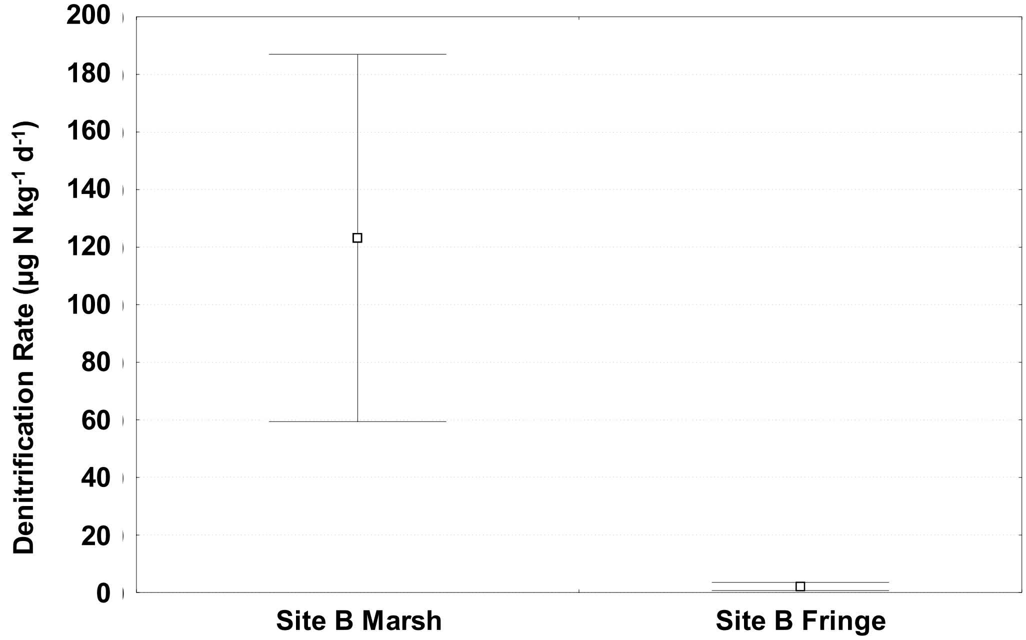

Figure 1.5. Ground water denitrification rates from the in situ nitrate push-pull test conducted at Site B. Values are the mean (SE) of four marsh and three fringe mini-piezometers.

with the push-pull mini-piezometer method suggests that the method is quite robust and likely to yield useful results over a range of conditions.

During incubation, ground water velocity contributes to displacement and dilution through advection and dispersion, while concentration gradients contribute through molecular diffusion (Freeze and Cherry, 1979). Because it is extremely difficult to directly measure these processes and the physical factors governing them, we rely on conservative tracers to characterize their effects. At the beginning of the incubation period, we assume no concentration gradient of the denitrification gases, N_2 and N_2O, within the injected plume. As incubation and denitrification progress, these gases increase within the plume and are subject to the same processes governing tracer dilution.

The second factor that could contribute to the loss of denitrification gases before sampling is the movement of dissolved gases from the ground water to the air (i.e., degassing). While minor amounts of degassing may have occurred, the excellent agreement between SF_6 and Br^- recoveries suggests that degassing is not a major process affecting our results (Figure 1.3). For degassing to occur, gases must first move vertically upward from the introduced plume to the air-water interface. Assuming no vertical ground water velocity component at the mini-piezometer tip, degassing would require that transverse dispersion and molecular diffusion account for the flux of gases to the air-water interface – a highly unlikely occurrence given the combination of brief incubation periods, low transverse dispersivities and low rate of molecular diffusion in most soils. In addition, the movement of denitrification gases into the soil air is impeded by the partial saturation of the capillary fringe and the slow air exchange through the porous media, thus reducing the concentration difference at the interface that drives degassing. Although the likelihood of degassing is minor, we now use He rather than N_2 to make up the balance of the SF_6 mixture, minimizing N_2 concentration gradients between the plume and the soil air at the start of the incubation.

The third factor that should be considered when interpreting denitrification rates is the possibility of a time lag between dosing a mini-piezometer and the response of the microbial community (Aelion and Shaw, 2000), particularly over short incubation periods and at pristine sites where there is very low ambient nitrate. In these cases, it may be important to conduct multiple in situ nitrate push-pull tests over several weeks at a site to allow the microbial community the opportunity to respond.

<u>Advantages of the Push-Pull Mini-Piezometer Method</u>

The push-pull mini-piezometer method has many advantages for use in determining rates of in situ ground water nitrate removal in riparian zones:

(i) Site instrumentation with multiple replicates was relatively easy. We were able to characterize hydrologic properties and quantify ground water denitrification rates at a site within several weeks.

(ii) This in situ design provided only minimal soil and hydrological disturbance.

(iii) Our push-pull tests encompassed 8.7 kg (dry weight) of soil which aggregates microsites of denitrification providing great advantages over microcosm-based estimates of denitrification.

(iv) We were able to isolate both $^{15}N_2O$ and $^{15}N_2$ to measure directly in situ denitrification, thus avoiding the use of acetylene. Acetylene is used to quantify denitrification by causing the reaction to terminate at N_2O (Balderston et al., 1976; Yoshinari and Knowles, 1976; Groffman et al., 1999). However, there can be a number of complications in the use of acetylene, including the inhibition of nitrification, incomplete diffusion of acetylene into active denitrification sites in soil, provision of energy to denitrifiers, and the failure to terminate denitrification at N_2O under low nitrate conditions (Groffman et al., 1999). All of these potential problems were avoided with the use of ^{15}N-enriched nitrate.

(v) We found little evidence of SF_6 degassing even when our introduced plume was within 16 cm of the water table, indicating the usefulness of SF_6 as a ground water conservative tracer in estuarine and fresh water settings.

(vi) In addition, our gas analysis provided N_2 to N_2O ratios generated by denitrification, a potentially important finding for researchers interested in greenhouse gases (Groffman et al., 2000).

The push-pull mini-piezometer method can provide useful insights into spatial and temporal patterns of denitrification in riparian zones. In conjunction with measurements of ground water flowpaths (Devito et al., 2000; Hill et al., 2000), this method holds promise for establishing the role of riparian zones in the flux of nitrate within watersheds.

AKNOWLEDGEMENTS

The authors would like to thank Mark Stolt and Adam Rosenblatt for site identification and soil classification; Jon Cole for SF_6 insights; David Harris for mass spectrometry analysis; Filipe Reis, Tom Liddy, Kate Banick, Chelsea Coker and Kate Crowell for field and lab assistance; and Barbara Nowicki, Edwin Requintina, Jim McKenna, Jenny Davis, Alan Lorefice, Emilie Stander and Abraham Parker for analytical support. We thank the landowners for use of their property. USDA NRICGP Grant no. 99-35102-8266 and NSF Award no. OCE9975349. This paper is a contribution of the Rhode Island Agricultural Experiment Station (no. 3897) and the Institute of Ecosystem Studies.

REFERENCES

Addy, K.L., A.J. Gold, P.M. Groffman, and P.A. Jacinthe. 1999. Ground water nitrate removal in subsoil of forested and mowed riparian buffer zones. *Journal of Environmental Quality* 28:962-970.

Aelion, C.M., and J.N. Shaw. 2000. Denitrification in South Carolina (USA) coastal plain aquatic sediments. *Journal of Environmental Quality* 29:1696-1703.

Balderston, W.L., B. Sherr, and W.J. Payne. 1976. Blockage of acetylene of nitrous oxide reduction in *Pseudomonas perfectomarinus*. *Applied and Environmental Microbiology* 31:504-508.

Christensen, S., P. Groffman, A. Mosier, and D.R. Zak. 1990. Rhizosphere denitrification: a minor process but indicator of decomposition activity. Pages 199-211 *in* N.P. Revsbech and J. Sorensen, eds. *Denitrification in soil and sediment*. Plenum Press, New York.

Christensen, S., S. Simkins, and J.M. Tiedje. 1990. Temporal patterns of soil denitrification: their stability and causes. *Soil Science Society of America Journal* 54:1614-1618.

Clausen, J.C., K. Guillard, C.M. Sigmund, and K. Martin Dors. 2000. Water quality changes from riparian buffer restoration in Connecticut. *Journal of Environmental Quality* 29:1751-1761.

Correll, D.L. 1997. Buffer zones and water quality protection: General principles. Pages 7-20 *in* N.E. Haycock, T. Burt, K. Goulding, and G. Pinay, eds. *Buffer zones: their processes and potential in water protection*. Quest Environmental, Harpenden, UK.

Davidson, E.A., and M.K. Firestone. 1988. Measurement of nitrous oxide dissolved in soil solution. *Soil Science Society of America Journal* 52:1201-1203.

Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. *Journal of Environmental Quality* 39:1075-1084.

Freeze, R.A., and J.A. Cherry. 1979. *Groundwater.* Prentice Hall, Englewood Cliffs, NJ.

Gold, A.J., P.A. Jacinthe, P.M. Groffman, W.R. Wright, and R.H. Puffer. 1998. Patchiness in groundwater nitrate removal in a riparian forest. *Journal of Environmental Quality* 27:146-155.

Groffman, P.M., A.J. Gold, and K. Addy. 2000. Nitrous oxide production in riparian zones and its importance to national emission inventories. *Chemosphere-Global Change Science* 2:291-299.

Groffman, P.M., E. Holland, D.D. Myrold, G.P. Robertson, and X. Zou. 1999. Denitrification. Pages 272-288 *in* G.P. Robertson, C.S. Bledsoe, D.C. Coleman, and P. Sollins, eds. *Standard soil methods for long term ecological research*. Oxford University Press, New York.

Groffman, P.M., G. Howard, A.J. Gold, and W.M. Nelson. 1996. Microbial nitrate processing in shallow groundwater in a riparian forest. *Journal of Environmental Quality* 25:1309-1316.

Haycock, N.E., and G. Pinay. 1993. Groundwater nitrate dynamics in grass and poplar vegetated riparian buffer strips during the winter. *Journal of Environmental Quality* 22:273-278.

Hill, A. 1996. Nitrate removal in stream riparian zones. *Journal of Environmental Quality* 25:743-755.

Hill, A.R., K.J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and organic carbon. *Biogeochemistry* 51:193-223.

Istok, J.D., M.D. Humphrey, M.H. Schroth, M.R. Hyman, and K.T. O'Reilly. 1997. Single-well, "push-pull" test for in situ determination of microbial activities. *Ground Water* 35:619-631.

Jacinthe, P.A., P.M. Groffman, A.J. Gold, and A. Mosier. 1998. Patchiness in microbial nitrogen transformations in groundwater in a riparian forest. *Journal of Environmental Quality* 27:156-164.

Jacobs, T.C., and J.W. Gilliam. 1985. Riparian losses of nitrate from agricultural drainage waters. *Journal of Environmental Quality* 14:472-478.

Kung, K.-J.S. 1990. Influence of plant uptake on the performance of bromide tracer. *Soil Science Society of America Journal* 54:975-979.

Lemon, E. 1981. Nitrous oxide in freshwaters of the Great Lakes Basin. *Limnology and Oceanography* 26:867-879.

Lowrance, R. 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. *Journal of Environmental Quality* 21:401-405.

Lowrance, R., L. Altier, J.D. Newbold, R.R. Schnabel, P.M. Groffman, J.M. Denver, D.L. Correll, J.W. Gilliam, J.L. Robinson, R.B. Brinsfield, K.W. Staver, W. Lucas, and A.H. Todd. 1997. Water quality functions of riparian forest buffers in Chesapeake Bay watersheds. *Environmental Management* 21:687-712.

Lowrance, R., G. Vellidis, and R.K. Hubbard. 1995. Denitrification in a restored riparian forest wetland. *Journal of Environmental Quality* 24:808-815.

Mosier, A.R., and L. Klemedtsson. 1994. Measuring denitrification in the field. Pages 1047-1065 *in* R.W. Weaver, S. Angle, P. Bottomley, D. Bezdicek, S. Smith, A. Tabatabai, et al., eds. *Methods of soil analysis, Part 2: Microbiological and biochemical properties, 2nd ed.* Soil Science Society of America, Madison, WI.

Mosier, A.R., and D.S. Schimel. 1993. Nitrification and denitrification. Pages 181-208 *in* R. Knowles and T.H. Blackburn, eds. *Nitrogen isotope techniques*. Academic Press, Orlando, FL.

Nelson, W.M., A.J. Gold, and P.M. Groffman. 1995. Spatial and temporal variation in groundwater nitrate removal in a riparian forest. *Journal of Environmental Quality* 24:691-699.

Osborne, L.L., and D.A. Kovacic. 1993. Riparian vegetated buffer strips in water quality restoration and stream management. *Freshwater Biology* 29:243-258.

Ott, R.L. 1993. *An introduction to statistical methods and data analysis, 4th ed.* Duxbury Press, Belmont, CA.

Parkin, T.B. 1987. Soil microsites as a source of denitrification variability. *Soil Science Society of America Journal* 51:1194-1199.

Peterjohn, W.T., and D.L. Correll. 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. *Ecology* 65:1466-1475.

Schipper, L., and M. Vojvodic-Vukovic. 1998. Nitrate removal from groundwater using a denitrification wall amended with sawdust: field trial. *Journal of Environmental Quality* 27:664-668.

Schnabel, R.R., L.F. Cornish, W.L. Stout, and J.A. Schaffer. 1996. Denitrification in a grassed and a wooded, valley and ridge, riparian ecotone. *Journal of Environmental Quality* 25:1230-1235.

Schultz, R.C., J.P. Colletti, T.M. Isenhart, W.W. Simpkins, C.W. Mize, and M.L. Thompson. 1995. Design and placement of a multi-species riparian buffer strip system. *Agroforestry Systems* 29:201-226.

Simmons, R.C., A.J. Gold, and P.M. Groffman. 1992. Nitrate dynamics in riparian forests: groundwater studies. *Journal of Environmental Quality* 21:656-665.

Smith, R.L., S.P. Garabedian, and M.H. Brooks. 1996. Comparison of denitrification activity measurements in groundwater using cores and natural-gradient tracer tests. *Environmental Science and Technology* 30:3448-3456.

Smith, R.L., B.L. Howes, and S.P. Garabedian. 1991. In situ measurement of methane oxidation in groundwater by using natural-gradient tracer tests. *Applied Environmental Microbiology* 57:1997-2004.

Starr, J.L., A.M. Sadeghi, T.B. Parkin, and J.J. Meisinger. 1996. A tracer test to determine the fate of nitrate in shallow groundwater. *Journal of Environmental Quality* 25:917-923.

StatSoft. 1999. *Statistica for Windows*. StatSoft, Tulsa, OK.

Tiedje, J.M. 1982. Denitrification. Pages 1011-1025 *in* A.L. Page, R.H. Miller, and D.R. Keeney, eds. *Methods of soil analysis, Part 2: Chemical and microbiological properties, 2nd ed.* Agronomy Monograph 9. American Society of Agronomy & Soil Science Society of America, Madison, WI.

Troeh, F.R., and L.M. Thompson. 1993. *Soils and soil fertility, 5th ed*. Oxford University Press, New York.

Trudell, M.R., R.W. Gillham, and J.A. Cherry. 1986. An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. *Journal of Hydrology* 83:251-268.

Verchot, L.V., E.C. Franklin, and J.S. Gilliam. 1997. Nitrogen cycling in Piedmont vegetated filter zones: II. Subsurface nitrate removal. *Journal of Environmental Quality* 26:337-347.

Whitmer, S., L. Baker, and R. Wass. 2000. Loss of bromide in a wetland tracer experiment. *Journal of Environmental Quality* 29:2043-2045.

Wilson, R.D., and D.M. Mackay. 1993. The use of sulfur hexafluoride as a conservative tracer in saturated sandy media. *Ground Water* 31:719-724.

Wilson, R.D., and D.M. Mackay. 1996. SF_6 as a conservative tracer in a saturated media with high intragranular porosity or high organic carbon content. *Ground Water* 34:241-249.

Winter, T.C., J.W. LaBaugh, and D.O. Rosenberry. 1988. The design and use of a hydraulic potentiomanometer for direct measurement of differences in hydraulic head between groundwater and surface water. *Limnology and Oceanography* 33:1209-1214.

Yoshinari, T. and R. Knowles. 1976. Acetylene inhibition of nitrous oxide reduction by denitrifying bacteria. *Biochemical and Biophysical Research Communications* 69:705-710.

MANUSCRIPT II:

In situ ground water denitrification in stratified, permeable soils underlying riparian wetlands

(Coauthors: Arthur J. Gold, Peter M. Groffman, Kelly Addy, Mark H. Stolt, and Gary Blazejewski)

(Published in 2005 in *Journal of Environmental Quality* 34:524-533)

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 μg N kg^{-1} d^{-1} within 10 m versus <1 to 40 μg N kg^{-1} 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.

INTRODUCTION

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; Cirmo 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 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; Cirmo 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 outwash 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 (Figure 2.1). 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; distinct from Sites A and B in Manuscript I) were located on glacial outwash deposits (Table 2.1). 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 2.1 and 2.2). 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 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,

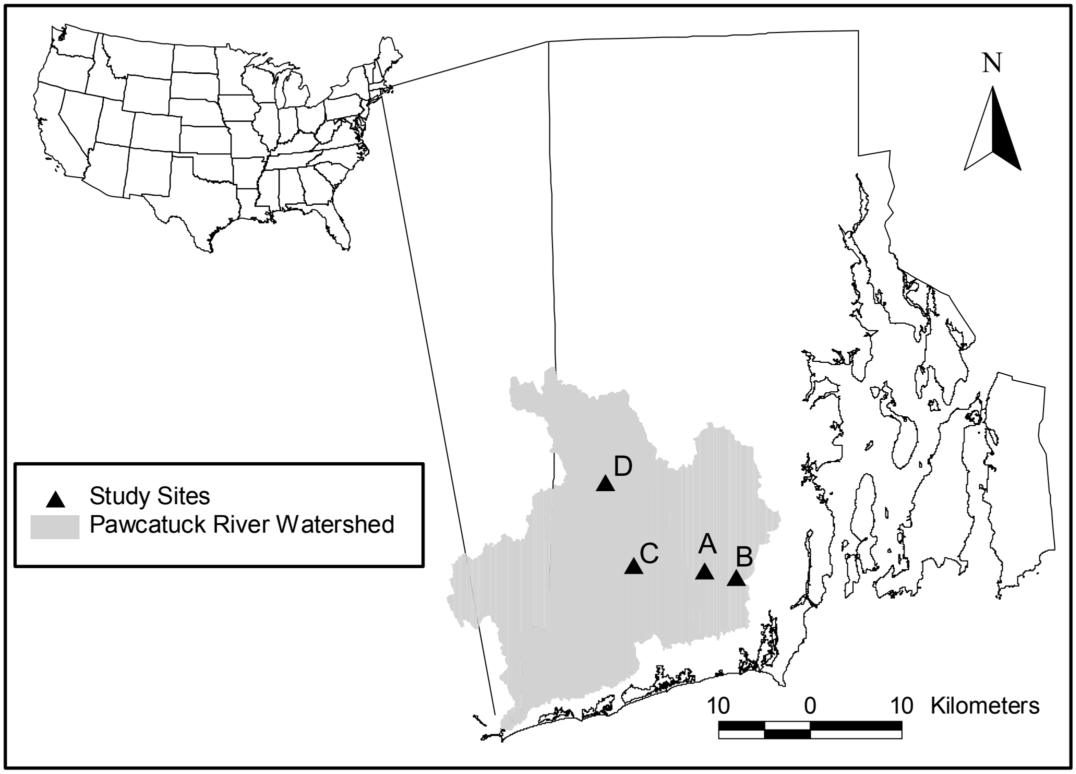

Figure 2.1. Location of study Sites A, B, C, and D within the Pawcatuck River Watershed, Rhode Island, USA.

Table 2.1. Riparian site characteristics.

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

mesic Fluvaquentic 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 2.1). Sites were remote, 200 to 500 m from any roads. The thickness of the organic surface horizon (Table 2.1) reflects the surface stability of these sites, with the more fluvially 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 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 bimonthly 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 ^{15}N-enriched NO_3^-–N and SF_6, a conservative gas tracer. Plume extraction occurs after a preset incubation period and the ground water samples are analyzed for ^{15}N-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 NO_3^{-}–N push–pull test at least twice, with a 2-wk interval between trials. The first test was performed to allow the microbial community to adjust to the change in NO_3^-–N concentration (Aelion and Shaw, 2000). Denitrification is an inducible enzyme system, and many studies have shown that addition of NO_3^-–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 (N_2, N_2O, $^{15}N_2$, $^{15}N_2O$, SF_6) 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 NO_3^-–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, NO_3^-–N, N_2, N_2O, and SF_6 gases. We then "dosed" the mini-piezometers with 10 L of ground water, amended with 32 mg L^{-1} NO_3^-–N as KNO_3 enriched with 20 atom % ^{15}N, and SF_6. We bubbled the SF_6 gas mixture (100 µL L^{-1} SF_6, 2 µL L^{-1} O_2, 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 N_2O, N_2, $^{15}N_2O$, $^{15}N_2$, and SF_6, and one sample for analysis of NO_3^-–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 (N_2, N_2O, $^{15}N_2$, $^{15}N_2O$, and SF_6), and at 1-L intervals for NO_3^-–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} NO_3^-–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 (N_2O and N_2) 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 $^{15}N_2O$-N or $^{15}N_2$ by multiplying it by the respective ^{15}N sample enrichment. The masses of $^{15}N_2O$-N or $^{15}N_2$ 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 N_2O-N and N_2 generated during the incubation period were then calculated by dividing the masses of $^{15}N_2O$-N and $^{15}N_2$ by the dosed NO_3^-–N atom %.

Gas production rates (N_2O-N + N_2) are expressed as µg N kg^{-1} d^{-1} (total mass of N_2O-N and N_2 per volume of water pulled/[dry mass of soil per volume of water pulled x 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 NO_3^-–N using the SM 4500 NO_3 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 NO_3^-–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

Table 2.2. Ambient ground water chemistry and selected soil characteristics. Values are the means ± standard errors, n = 6 except where noted.

Depth	DO†	NO_3^-–N‡	DOC§	pH	Pit samples¶ Carbon	Pit samples¶ Silt + clay (<0.05 mm)
cm	----mg L^{-1}----				----%----	
			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.

for a riparian area to act as a nitrogen sink, will be presented in a subsequent paper (Manuscript III). 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 2.2). The ambient ground water NO_3^-–N concentrations were <0.1 mg L^{-1} except at Site A where they reached 1.4 mg L^{-1} (Table 2.2). Pit samples from horizons within ±10 cm of the 65- and 150-cm mini-piezometer depths had weighted average carbon contents ranging from 0.2 to 4.9% (Table 2.2). 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 2.3). 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 2.4). 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 ($r = 0.91$, $P < 0.05$; Figure 2.2). 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 μg N kg^{-1} d^{-1} in the first year had a rate exceeding 50 μg N kg^{-1} d^{-1} in the second year. Six of the mini-piezometers had ground water denitrification rates of >50 μg N kg^{-1} d^{-1} in the first year, but only one of these had a ground water denitrification rate of <50 μg N kg^{-1} d^{-1} in the second year.

Table 2.3. 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.

	Ground water temperature		Depth to water table			
Depth	Spring	Fall	Spring†	Fall†	Summer minimum	Dormant season maximum
cm	-----------°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	*n* = 3	*n* = 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	*n* = 3	*n* = 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	*n* = 2	*n* = 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	*n* = 2	*n* = 2		

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

Table 2.4. 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.

Table 2.5. In situ riparian ground water denitrification rates. Values are means ± standard errors, $n = 3$.

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

Riparian ground water denitrification rates ranged from <1 to 330 μg N kg^{-1} 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 (±SE) ranging from 7 ± 6 to 132 ± 55 μg N kg^{-1} d^{-1} (Table 2.5). 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 2.1). 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; Figure 2.3).

At the 65-cm depth, there was no significant relationship between denitrification rate and distance from the stream. However, the denitrification rates

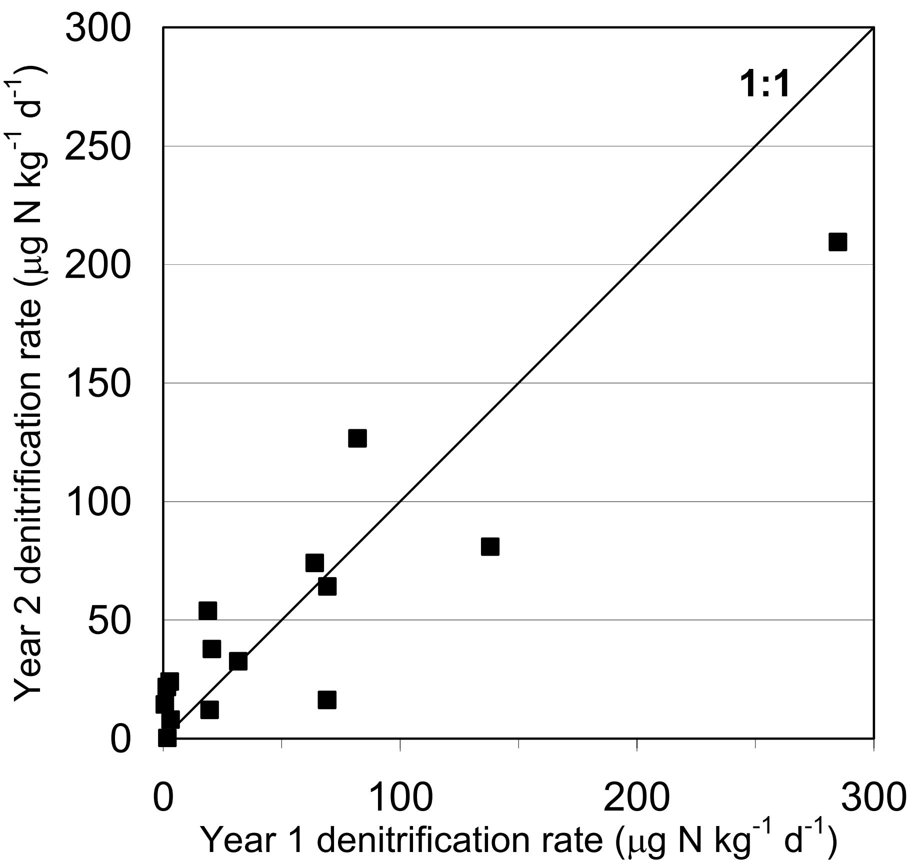

Figure 2.2. Comparison of ground water denitrification rates from mini-piezometers that were sampled over two years, but during the same season. Rates from Year 1 were significantly correlated with rates from Year 2 with $r = 0.91$ at $P < 0.05$.

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 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 (Figure 2.4), 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 2.5). Neither alluvial site demonstrated significant differences between spring and fall ground water denitrification rates.

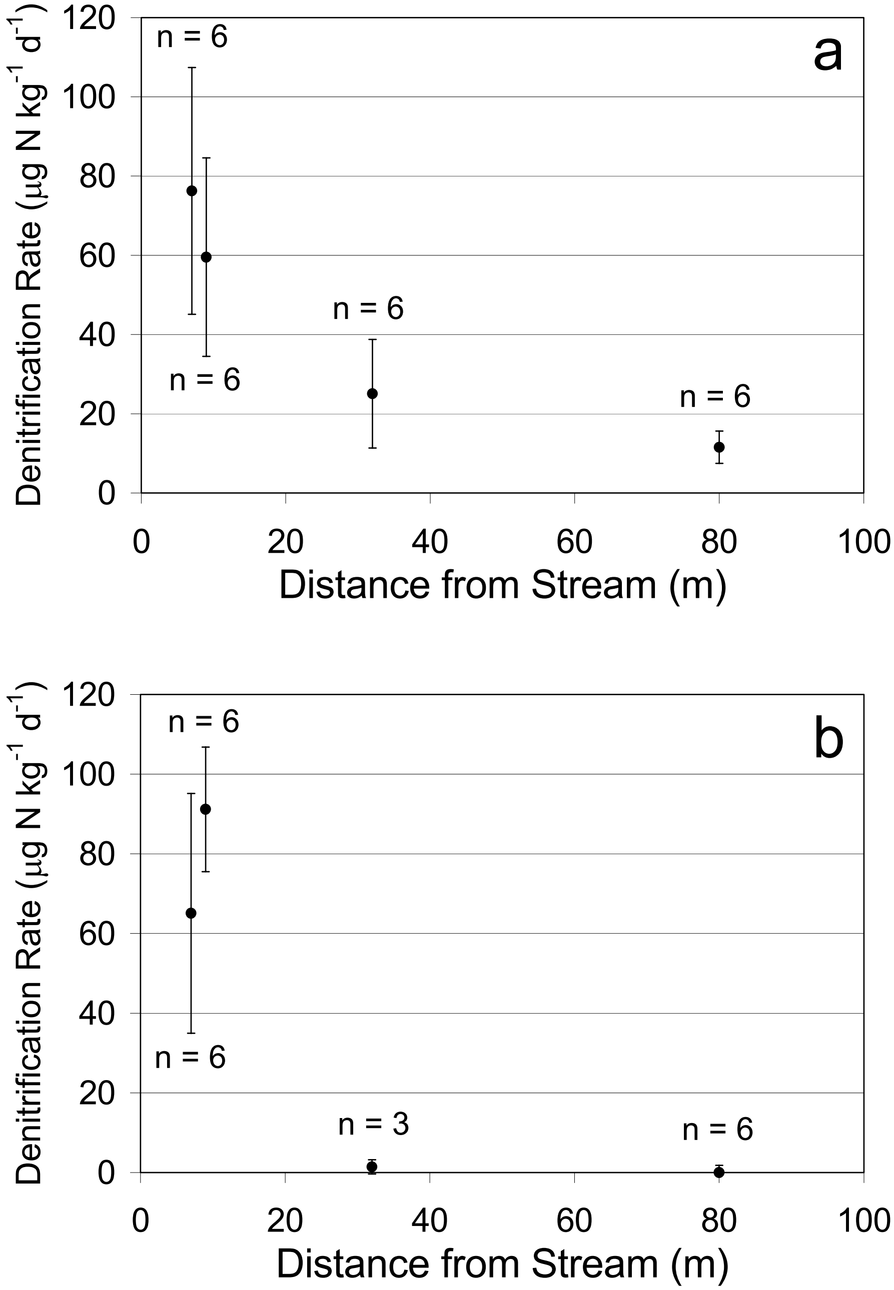

Figure 2.3. Mean annual riparian ground water denitrification rates versus distance from the stream at (a) 150 cm and (b) 260 to 300 cm below the soil surface. Spearman rank correlations between denitrification rates and distance from the stream were significant at $P < 0.01$. Error bars signify ±1 SE.

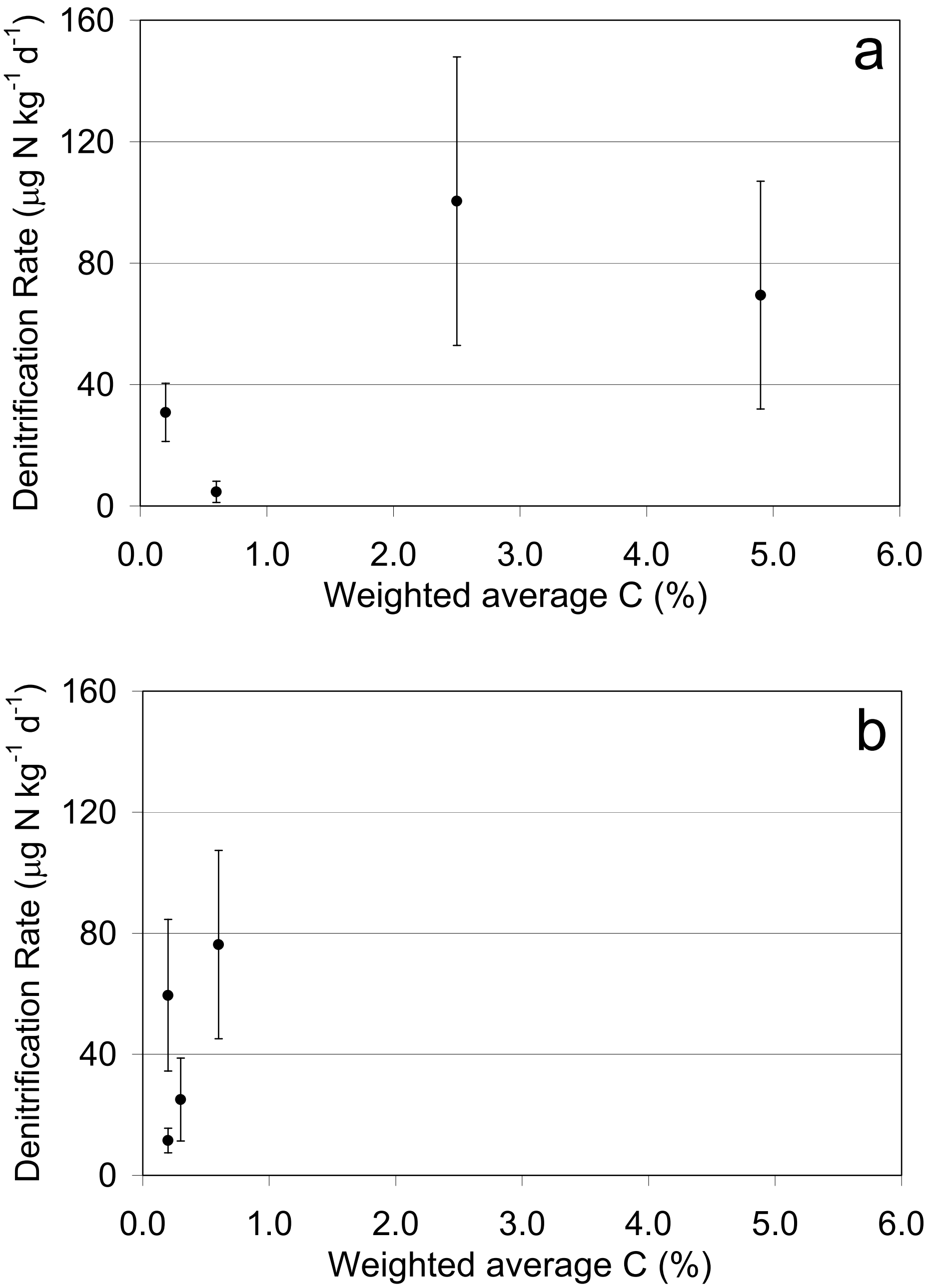

Figure 2.4. Mean annual riparian ground water denitrification rates versus weighted average soil carbon content at (a) 65 cm and (b) 150 cm below the soil surface. Spearman rank correlations between denitrification rates and the weighted average of % C in samples from horizons at (a) 55 to 75 cm and (b) 140 to 160 cm below the soil surface were not significant. Error bars signify ±1 SE (n = 6).

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 μg N kg^{-1} 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 μg N kg^{-1} 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 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 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 denitrification 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.

ACKNOWLEDGMENTS

The authors thank Dave Harris at the UC Davis Stable Isotope Facility; Jim McKenna for DOC analyses; Linda Green for nitrate analysis; Adam Rosenblatt for field assistance; URI Coastal Fellows Gina Ferendo, Drew Grande, Tom Liddy, and Tara Watson for laboratory and field assistance; URI Watershed Hydrology laboratory assistants Stephen Austin, Kate Banick, Chelsea Coker, Kate Crowell, Missy Lefebvre, Steve McCandless, Anthony Morales, Filipe Reis, Edwin Requintina, Emily Troiano, and Hans van Lingen for lab and field assistance; IES laboratory assistants Jessica Kriebel, Sabrina LaFave, Abraham Parker, and Emilie Stander; and all landowners for generously allowing us to maintain study sites on their land. This research was supported by USDA NRICGP Grant no. 99-35102-

8266. This paper is a contribution of the Rhode Island Agricultural Experiment Station (no. 4065) and the Institute of Ecosystem Studies.

REFERENCES

Addy, K.L., D.Q. Kellogg, A.J. Gold, P.M. Groffman, G. Ferendo, and C. Sawyer. 2002. In situ push-pull method to determine ground water denitrification in riparian zones. *Journal of Environmental Quality* 31:1017–1024.

Aelion, C.M., and J.N. Shaw. 2000. Denitrification south Carolina (USA) coastal plain aquatic sediments. *Journal of Environmental Quality* 29:1696–1703.

American Public Health Association. 1998. *Standard methods for the examination of water and wastewater*. American Public Health Association, Washington, DC.

Blazejewski, G. 2003. *Carbon in riparian zone subsoils: morphology and spatial distribution.* M.S. thesis. University of Rhode Island, Kingston.

Bradley, P.M., M. Fernandez, Jr., and F.H. Chapelle. 1992. Carbon limitation of denitrification rates in an anaerobic ground water system. *Environmental Science & Technology* 6:2377–2381.

Burt, T.P. 1997. The hydrological role of floodplains within the drainage basin system. Pages 21–32 *in* N.E. Haycock, T. Burt, K. Goulding, and G. Pinay, eds. *Buffer zones: their processes and potential in water protection*. Quest Environmental, Harpenden, UK.

Burt, T.P., L.S. Matchett, K.W.T. Goulding, C.P. Webster, and N.E. Haycock. 1999. Denitrification in riparian buffer zones: the role of floodplain hydrology. *Hydrological Processes* 13:1451–1463.

Cey, E.E., D.L. Rudolph, R. Aravena, and G. Parkin. 1999. Role of the riparian zone in controlling the distribution and fate of agricultural nitrogen near a small stream in southern Ontario. *Journal of Contaminant Hydrology* 37:45–67.

Cirmo, C.P., and J.J. McDonnell. 1997. Linking the hydrologic and biochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review. *Journal of Hydrology (Amsterdam)* 199:88–120.

Clément, J.C., G. Pinay, and P. Marmonier. 2002. Seasonal dynamics of denitrification along topohydrosequences in three different riparian wetlands. *Journal of Environmental Quality* 31:1025–1037.

Correll, D.L. 1997. Buffer zones and water quality protection: general principles. Pages 7–20 *in* N.E. Haycock, T. Burt, K. Goulding, and G. Pinay, eds. *Buffer zones: their processes and potential in water protection*. Quest Environmental, Harpenden, UK.

Correll, D.L. 2000. The current status of our knowledge of riparian buffer water quality functions. Pages 5–10 *in* P.J. Wigington, Jr., and R.L. Beschta, eds. *Proceedings of the International Conference on Riparian Ecology and Management in Multi-Land Use Watersheds*, Portland, OR. August 27–31, 2000. American Water Resources Association, Middleburg, VA.

Davidson, E.A., and M.K. Firestone. 1988. Measurement of nitrous oxide dissolved in soil solution. *Soil Science Society of America Journal* 52:1201–1203.

Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. *Journal of Environmental Quality* 29:1075–1084.

Diaz, R.J. 2001. Overview of hypoxia around the world. *Journal of Environmental Quality* 30:275–281.

Flite, O.P., III, R.D. Shannon, R.R. Schnabel, and R.R. Parizek. 2001. Nitrate removal in a riparian wetland of the Appalachian valley and ridge physiographic province. *Journal of Environmental Quality* 30:254–261.

Fustec, E., A. Mariotti, X. Grillo, and J. Sajus. 1991. Nitrate removal by denitrification in alluvial ground water: role of a former channel. *Journal of Hydrology (Amsterdam)* 123:337–354.

Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. Pages 383–411 *in* A. Klute, ed. *Methods of soil analysis. Part 1. Physical and mineralogical methods, 2nd ed.* Agronomy Monograph 9. American Society of Agronomy and Soil Science Society of America, Madison, WI.

Gold, A.J., P.M. Groffman, K. Addy, D.Q. Kellogg, M. Stolt, and A.E. Rosenblatt. 2001. Landscape attributes as controls on ground water nitrate removal capacity of riparian zones. *Journal of the American Water Resources Association* 37:1457–1464.

Goolsby, D.A., W.A. Battaglin, B.T. Aulenbach, and R.P. Hopper. 2001. Nitrogen input to the Gulf of Mexico. *Journal of Environmental Quality* 30:329–336.

Groffman, P.M. 1987. Nitrification and denitrification in soil: a comparison of incubation, enzyme assay and enumeration techniques. *Plant and Soil* 97:445–450.

Groffman, P.M., A.J. Gold, and R.C. Simmons. 1992. Nitrate dynamics in riparian forests: microbial studies. *Journal of Environmental Quality* 21:666–671.

Groffman, P.M., G. Howard, A.J. Gold, and W.M. Nelson. 1996. Microbial nitrate processing in shallow groundwater in a riparian forest. *Journal of Environmental Quality* 25:1309–1316.

Haycock, N.E., and T.P. Burt. 1993. Role of floodplain sediments in reducing the nitrate concentration of subsurface runoff: a case study in the Cotswolds, UK. *Hydrological Processes* 7:287–295.

Hedin, L.O., J.C. von Fischer, N.E. Ostrom, B.P. Kennedy, M.G. Brown, and G.P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. *Ecology* 79:684–703.

Hill, A.R. 1996. Nitrate removal in stream riparian zones. *Journal of Environmental Quality* 25:743–755.

Hill, A.R., and M. Cardaci. 2004. Denitrification and organic carbon availability in riparian wetland soils and subsurface sediments. *Soil Science Society of America Journal* 68:320–325.

Hill, A.R., K.J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparian zone: Interactions between hydrology and supplies of nitrate and organic carbon. *Biogeochemistry* 51:193–223.

Hill, A.R., P.G.F. Vidon, and J. Langat. 2004. Denitrification potential in relation to lithology in five headwater riparian zones. *Journal of Environmental Quality* 33:911–919.

Howarth, R. 1988. Nutrient limitation of net primary production in marine ecosystems. *Annual Review of Ecology and Systematics* 19:89–110.

Howarth, R.W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch, and Z. Zhao-Liang. 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. *Biogeochemistry* 35:75–139.

Jones, J.B., and P.J. Mulholland. 2000. *Streams and ground waters*. Academic Press, San Diego, CA.

Jordan, T.E., D.L. Correll, and D.E. Weller. 1997. Effects of agriculture on discharges of nutrients from coastal plain watersheds of Chesapeake Bay. *Journal of Environmental Quality* 26:836–848.

Kilmer, V.J., and L.T. Alexander. 1949. Methods of making analyses of soils. *Soil Science* 68:15–24.

Lemon, E. 1981. Nitrous oxide in freshwaters of the Great Lakes Basin. *Limnology and Oceanography* 26:867–879.

Leopold, L.B., M.G. Wolman, and J.P. Miller. 1992. *Fluvial processes in geomorphology*. Dover Publications, New York.

Lowrance, R. 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. *Journal of Environmental Quality* 21:401–405.

Lowrance, R., L.S. Altier, J.D. Newbold, R.R. Schnabel, P.M. Groffman, J.M. Denver, D.L. Correll, J.W. Gilliam, J.L. Robinson, R.B. Brinsfield, K.W. Staver, W. Lucas, and A.H. Todd. 1997. Water quality functions of riparian forest buffers in Chesapeake Bay watersheds. *Environmental Management* 21:687–712.

Martin, K., L.L. Parsons, R.E. Murray, and M.S. Smith. 1988. Dynamics of soil denitrifier populations: relationships between enzyme activity, most probable number counts, and actual N gas loss. *Applied and Environmental Microbiology* 54:2711–2716.

McClain, M.E., E.W. Boyer, C.L. Dent, S.E. Gergel, N.B. Grimm, P.M. Groffman, S.C. Hart, J.W. Harvey, C.A. Johnston, E. Mayorga, W.H. McDowell, and G. Pinay. 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems* 6:301–312.

McHale, M.R., J.J. McDonnell, M.J. Mitchell, and C.P. Cirmo. 2002. A field-based study of soil water and groundwater nitrate release in an Adirondack forested watershed. *Water Resources Research* 38:2-1 to 2-17.

Mosier, A.R., and L. Klemedtsson. 1994. Measuring denitrification in the field. Pages 1047–1065 *in* R.W. Weaver, J.S. Angle, and P.S. Bottomley, eds. *Methods of soil analysis. Part 2. Microbiological and biochemical properties.* Soil Science Society of America Book Series 5. Soil Science Society of America, Madison, WI.

Myrold, D.D., and J.M. Tiedje. 1985. Establishment of denitrification capacity in soil: Effects of carbon, nitrate and moisture. *Soil Biology and Biochemistry* 17:819–822.

National Academy of Sciences. 2000. *Clean coastal waters: understanding and reducing the effects of nutrient pollution*. National Academy Press, Washington, DC.

Nelson, W.M., A.J. Gold, and P.M. Groffman. 1995. Spatial and temporal variation in groundwater nitrate removal in a riparian forest. *Journal of Environmental Quality* 24:691–699.

Nixon, S.W., B. Buckley, S. Granger, and J. Bintz. 2001. Responses of a very shallow marine ecosystem to nutrient enrichment. *Human and Ecological Risk Assessment* 7:1457–1481.

Norton, M.M., and T.R. Fisher. 2000. The effects of forest on stream water quality in two coastal plain watersheds of the Chesapeake Bay. *Ecological Engineering* 14:337–362.

Orth, R.J., and K.A. Moore. 1983. Chesapeake Bay: An unprecedented decline in submerged aquatic vegetation. *Science (Washington, DC)* 222:51–53.

Ott, R.L. 1993. *An introduction to statistical methods and data analysis, 4th ed.* Duxbury Press, Belmont, CA.

Parsons, L.L., R.E. Murray, and M.S. Smith. 1991. Soil denitrification dynamics: spatial and temporal variations of enzyme activity, populations, and nitrogen gas loss. *Soil Science Society of America Journal* 55:90–95.

Payne, W.J. 1981. *Denitrification*. John Wiley & Sons, New York.

Pinay, G., V.J. Black, A.M. Planty-Tabacchi, B. Gumiero, and H. Decamps. 2000. Geomorphic control of denitrification in large river floodplain soils. *Biogeochemistry* 50:163–182.

Pinay, G., C. Ruffinoni, and A. Fabre. 1995. Nitrogen cycling in two riparian forest soils under different geomorphic conditions. *Biogeochemistry* 30:9–29.

Rabalais, N.N., R.E. Turner, and W.J. Wiseman, Jr. 2001. Hypoxia in the Gulf of Mexico. *Journal of Environmental Quality* 30:320–329.

Rector, D.D. 1981. *Soil survey of Rhode Island*. United States Department of Agriculture - Soil Conservation Service, in cooperation with the Rhode Island Agricultural Experiment Station, Washington, DC.

Robertson, W.D., J.A. Cherry, and E.A. Sudicky. 1991. Ground-water contamination from two small septic systems on sand aquifers. *Ground Water* 29:82–92.

Rosenblatt, A.E., A.J. Gold, M.H. Stolt, P.M. Groffman, and D.Q. Kellogg. 2001. Identifying riparian sinks for watershed nitrate using soil surveys. *Journal of Environmental Quality* 30:1596–1604.

Ryther, J.H., and W.M. Dunstan. 1971. Nitrogen, phosphorus, and eutrophication in the coastal marine environment. *Science (Washington, DC)* 171:1008–1013.

Schipper, L., and M. Vojvodic-Vukovic. 1998. Nitrate removal from groundwater using a denitrification wall amended with sawdust: field trial. *Journal of Environmental Quality* 27:664–668.

Schnabel, R.R., L.F. Cornish, W.L. Stout, and J.A. Shaffer. 1996. Denitrification in a grassed and a wooded, valley and ridge, riparian ecotone. *Journal of Environmental Quality* 25:1230–1235.

Schnabel, R.R., and W.L. Stout. 1994. Denitrification losses from two Pennsylvania floodplain soils. *Journal of Environmental Quality* 23:344–348.

Short, F.T., and D.M. Burdick. 1996. Quantifying eelgrass habitat loss in relation to housing development and nitrogen loading in Waquoit Bay, Massachusetts. *Estuaries* 19:730–739.

Simmons, R.C., A.J. Gold, and P.M. Groffman. 1992. Nitrate dynamics in riparian forests: groundwater studies. *Journal of Environmental Quality* 21:659–665.

Smith, M.S., and L.L. Parsons. 1985. Persistence of denitrifying enzyme activity in dried soils. *Applied and Environmental Microbiology* 49:316–320.

Smith, R.L., and J.H. Duff. 1988. Denitrification in a sand and gravel aquifer. *Applied and Environmental Microbiology* 54:1071–1078.

Starr, R.C., and R.W. Gillham. 1993. Denitrification and organic carbon availability in two aquifers. *Ground Water* 31:934–947.

StatSoft. 2002. *Statistica 6.0*. StatSoft, Tulsa, OK.

Steinheimer, T.R., K.D. Scoggin, and L.A. Kramer. 1998. Agricultural chemical movement through a field-size watershed in Iowa: surface hydrology and nitrate losses in discharge. *Environmental Science & Technology* 32:1048–1052.

Tiedje, J.M. 1982. Denitrification. Pages 1011–1025 *in* A.L. Page, R.H. Miller, and D.R. Keeney, eds. *Methods of soil analysis. Part 2. Chemical and microbiological properties, 2nd ed*. Agronomy Monograph 9. American Society of Agronomy and Soil Science Society of America, Madison, WI.

Valiela, I. 1995. *Marine ecological processes, 2nd ed.* Springer-Verlag, New York.

Vidon, P.G.F., and A.R. Hill. 2004. Landscape controls on nitrate removal in stream riparian zones. *Water Resources Research* 40, W03201, doi:10.1029/2003WR002473.

Warwick, J., and A.R. Hill. 1988. Nitrate depletion in the riparian zone of a small woodland stream. *Hydrobiologia* 157:231–240.

Willems, H.P.L., M.D. Rotelli, D.F. Berry, E.P. Smith, R.B. Reneau, Jr., and S. Mostaghimi. 1997. Nitrate removal in riparian wetland soils: effects of flow rate, temperature, nitrate concentration and soil depth. *Water Research* 31:841–849.

MANUSCRIPT III:

Ground water hydrology and denitrification in stratified, permeable soils underlying riparian wetlands

(Coauthors: Arthur J. Gold, Peter M. Groffman, Kelly Addy, Mark H. Stolt, and Gary Blazejewski)

ABSTRACT

The ground water denitrification potential of riparian zones in deep soils, such as glacial outwash and alluvium, may affect watershed nitrogen export. In these settings, substantial ground water can flow through low-gradient permeable, stratified sediments. We hypothesized that ground water flow paths underlying riparian wetlands situated in glacial outwash and alluvium would largely bypass the observed zone of denitrification, emerging to a stream along a short vertical flow path with low retention time within the biologically active riparian subsurface ecosystem. We measured piezometric heads and in situ hydraulic conductivity along a transect perpendicular to the stream, from the stream to the upland, at four riparian sites (two per setting) during a period of sustained high water table. We used a two-dimensional finite-element ground water flow model to estimate the associated piezometric surfaces, flow paths, and fluxes through the subsurface riparian ecosystem (upland to stream, to a depth of 3 m). Modeling results showed that at the time when piezometric heads were measured ground water flux was substantial through the riparian subsurface ecosystem at all sites, with more complex flow paths

than hypothesized, and with no apparent relationship between geomorphic setting and observed flow patterns. At all sites evapotranspiration (ET) dominated the hydrologic budget, ranging from 44% to 92% of the total outflux. Ground water upwelling in response to ET increases opportunities for nitrogen transformations as ground water moves through the organically rich surface soils. Outflux to the stream was <10% of the total outflux at all sites. Within 10 m of the stream, where observed ground water denitrification rates were highest [Manuscript II], retention times along flow paths to the stream combined with denitrification rates resulted in the potential removal by denitrification of >10 mg L^{-1} NO_3^-–N at three of the four sites. Average annual watershed estimates that accounted for periods of low ET showed that these riparian wetlands could be transmitting about 8% of the upland recharge through ET. High water tables that facilitate upwelling in response to ET are a key component to the functioning of these riparian wetlands, underlining the need to maintain their hydrologic integrity. A nitrogen budget of the riparian wetland sites using a hypothetical development scenario in the uplands showed that three of the four sites could potentially remove or store about 25% of the upland ground water N load, with about 75% carried further downgradient to emerge lower in the watershed as either ET or baseflow. The fourth site could potentially remove or store about 90% of the upland ground water N load. Minimal N (0% to 9% of the upland ground water N load) would have reached the stream. The low flux to the stream during periods of elevated evaporative demand suggests that non-hydric and till riparian areas provide much of the baseflow at this time, and argues for protection of infiltration and natural flow patterns throughout the watershed.

INTRODUCTION

In recent years concerns regarding nitrogen (N) contamination of ground water, and its subsequent export to streams and coastal areas have become increasingly urgent. Nitrogen poses a health risk to humans when it is present in drinking water (Vitousek et al., 1997; U.S. Geological Survey, 1999), and plays a role in promoting the eutrophication of coastal waters, leading to the degradation of valuable estuarine habitats (Howarth et al., 1996; Vitousek et al., 1997; National Academy of Sciences, 2000).

Nitrate (NO_3^-–N) is the most common and mobile form of inorganic nitrogen found in ground water. Plant uptake, microbial assimilation, and denitrification are all important sinks for ground water NO_3^-–N. Plant uptake and microbial assimilation transform and store NO_3^-–N, and may generate NO_3^-–N losses during decomposition. Microbial denitrification, the reduction of NO_3^-–N to N_2 and/or N_2O gases, represents a permanent sink for catchment N. Redox status plays an important role in determining the potential for microbial denitrification, as does the presence of organic carbon as an energy source. As decomposition of organic matter proceeds and oxygen is depleted, NO_3^-–N is then utilized as an electron acceptor.

In temperate climates, ground water sustains stream base flow, carrying dissolved contaminants, including NO_3^-–N, into streams and ultimately to coastal waters. Estimates of the extent to which baseflow contributes to the annual export of N from catchments are upwards of 80% in some areas (Hill, 1991; Schilling and Zhang, 2004). Jordan et al. (1997) noted that as the proportion of baseflow increased, the concentration of NO_3^-–N increased in streams draining catchments with varying proportions of cropland. Burns et al. (1998) also observed high NO_3^-–N concentrations in deep ground water emerging from seeps.

Riparian areas, especially those with high water table (i.e., hydric soils) or buried organic horizons, have demonstrated the capacity for significant removal of ground water NO_3^-–N by denitrification (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). They often possess both low redox potentials and high soil organic matter, and their position on the landscape may provide for the interception of significant portions of ground water flow emerging into streams. However, enormous variability in riparian characteristics across regions and within catchments has made attempts to predict the effectiveness of riparian areas as N sinks extremely difficult. Early studies of riparian areas focused on intensive characterization of a single site. The accumulation of knowledge gained from these studies highlighted riparian variability without allowing us to draw generalized conclusions (Correll, 2000).

For riparian denitrification of ground water to be effective, nitrate-laden ground water flow must intercept areas that favor denitrification (Figure 3.1.a). For this reason ground water flow path has been identified as an important factor in explaining the observed variability in riparian function. Soil hydrologic characteristics, as well as topography, are responsible for determining ground water flow paths through riparian areas, and consequently the potential for ground water denitrification (Haycock and Burt, 1993; Burt, 1997; Willems et al., 1997; Burt et al., 1999; Cey et al., 1999; Devito et al., 2000; Hill et al., 2000; Norton and Fisher, 2000; Flite et al., 2001; Gold et al., 2001; Burt et al., 2002; Puckett et al., 2002; Schiff et al., 2002; Wigington et al., 2003; Clément et al., 2003; Maître et al., 2003; Sabater et al., 2003; Angier et al., 2004). Geomorphology has been identified as a possible means with which to generalize estimates of riparian function to the catchment scale (Pinay et al., 1995; Correll, 1997; Lowrance et al., 1997; Quinn et al., 2001). More recently, hydrogeomorphology has been proposed to identify areas of high, medium, or low likelihood for NO_3^-–N removal (Hill et al., 2004; Vidon and Hill, 2004a; Vidon and Hill, 2004b; Vidon and Hill, 2004c). Other attempts at "scaling up" that have tried to account for riparian ground water flow path variability have included estimating the ratio of contributing hillslope area to a riparian area (McGlynn and Seibert, 2003), using GIS tools to evaluate soil properties, aquifer thickness, and water table elevation within a riparian area (Maître et al., 2005), or linking landscape features with water quality data to develop a predictive model (Baker et al., 2001).

Of particular concern is the potential for nitrate-laden ground water to bypass areas with high denitrification potential as seeps, underflow (Figure 3.1.b), or diversion through highly permeable sediments (Gold et al., 2001). Seeps that emerge to rapidly flow as rivulets across a riparian area have significantly less opportunity for denitrification to occur (Warwick and Hill, 1988; Burt, 1997; Burns et al., 1998; Schiff et al., 2002; Wigington et al., 2003). Underflow may occur in deep permeable sediments or in situations where shallow layers of low hydraulic conductivity result in flow below the riparian ecosystem into deeper, more permeable media (Burt, 1997). Diversion of flow through deposits of highly permeable sediments may

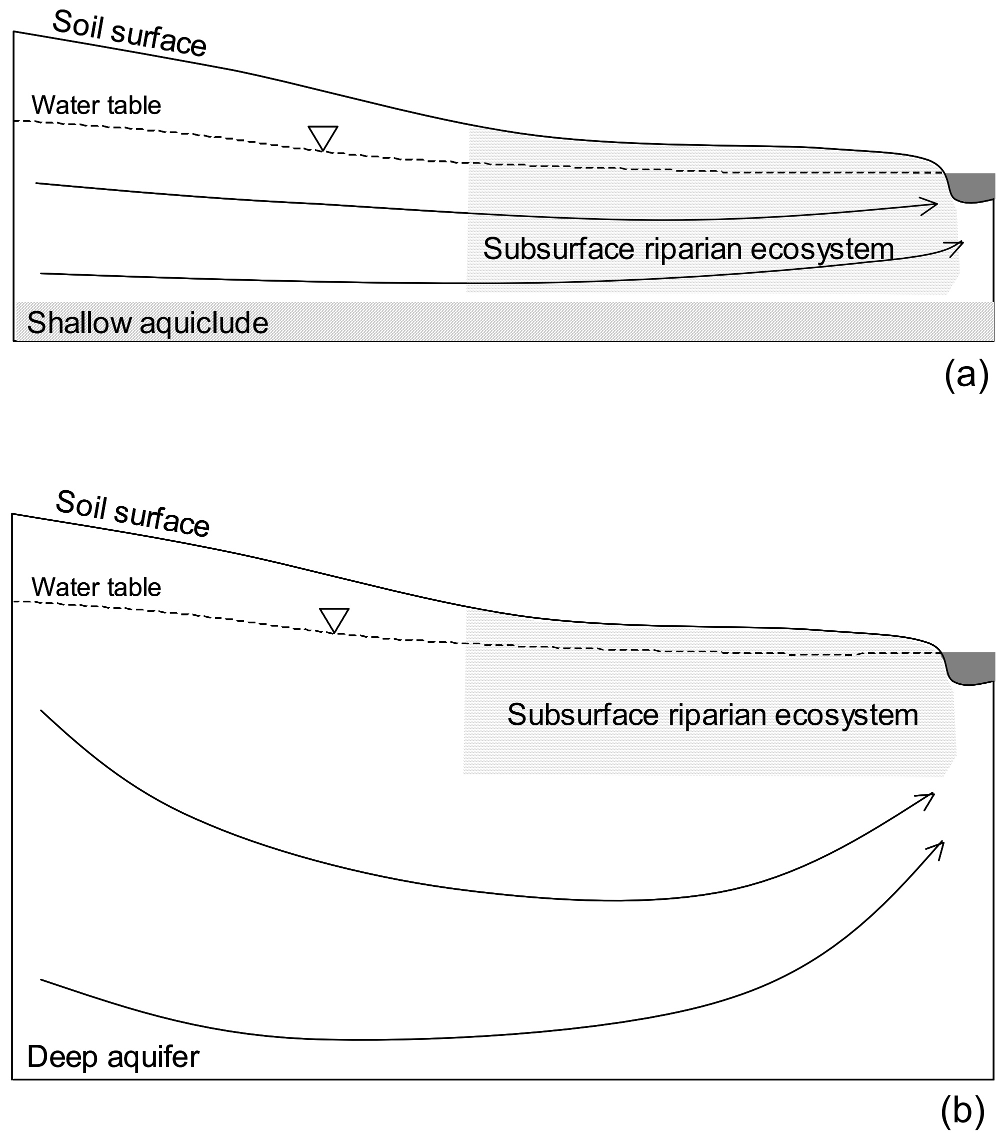

Figure 3.1. Conceptual cross-sections of riparian ground water flow paths to a stream in a shallow aquifer (a) compared with a deep aquifer (b). It is hypothesized that ground water flow in deep aquifers will bypass the subsurface riparian ecosystem, reducing the opportunity for ground water NO_3^- removal through riparian biogeochemical transformations.

transport ground water through sediments that are low in organic matter, and at a rapid transmission rate, requiring long distances for significant transformation (Puckett et al., 2002; Smith et al., 2004).

Glaciated regions such as the northeastern United States are often divided into three major geomorphic settings: glacial till deposits, glacial outwash, and alluvial soils. Because the push-pull method [Manuscript I] was found to be unsuitable for till settings, this study focused on riparian areas situated in glacial outwash and alluvial settings. There may be mechanisms for ground water denitrification in till settings, but several factors argue against till settings having a high potential for nitrate removal. Frequently saturated hydraulic conductivities are extremely low and variable, and ground water flow paths tend to follow unpredictable preferential pathways. Rosenblatt et al. (2001) found that glacial till demonstrated a lower occurrence of hydric soils within riparian zones than did glacial outwash or alluvial settings. Moreover, they observed a high incidence of ground water seeps across those riparian zones that did possess hydric soils implying a reduced potential for groundwater nitrate removal in till settings. Till sites still warrant additional study, however.

Many glacial outwash and alluvial riparian zones occur above deep aquifers that transmit substantial flow from a catchment. In these settings upwelling from deep aquifers into the stream may bypass the biologically active zone of a riparian area, dramatically reducing its ground water NO_3^-–N removal effectiveness (Gold et al., 2001; Puckett et al., 2002; Figure 3.1).

The purpose of this study was to assess the potential for ground water to interact with biologically active areas of deep, stratified soils underlying riparian zones situated in glacial outwash and alluvial settings. Of particular interest are the potential relationships between pathways and retention times of ground water through the riparian subsurface ecosystem, and the likelihood for ground water NO_3^-–N flux to the stream.

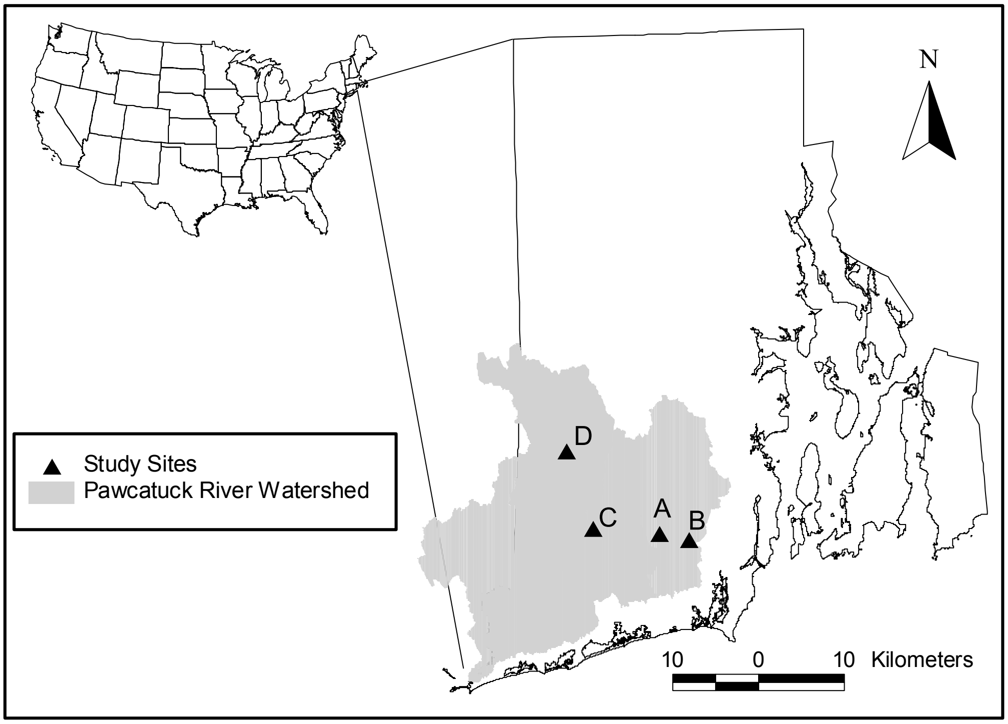

Figure 3.2 . Location of study Sites A, B, C, and D within the Pawcatuck River Watershed, Rhode Island, USA. Sites A and B are in glacial outwash settings, sites C and D are in alluvial settings.

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 (Figure 3.2). 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; the same sites referenced in Manuscript II [Kellogg et al., 2005], but distinct from Sites A and B in Manuscript I) were located on glacial outwash deposits. The setting classification for these sites was based upon 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. Site A was located along an unnamed first-order tributary of Chickasheen Brook, South Kingstown, RI (41º28'N, 71º35'W), with sandy loam soil 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 (41º28'N, 71º32'W), with sandy loam soil classified as a sandy, mesic Aeric Endoaquept. The other two sites (hereafter referred to as Sites C and D; the same sites referenced in Manuscript II [Kellogg et al., 2005]) were located on alluvial soils. Site C was located along Meadow Brook, a second-order tributary of the Pawcatuck River, Richmond, RI (41º29'N, 71º41'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 (41º34'N, 71º43'W) with sandy loam soil classified as a coarse-loamy, mesic Fluvaquentic Humaquept. The vegetation

Table 3.1. Site characteristics

Setting	Stream order	Soil in sampling area	Dominant vegetation	Thickness of organic surface horizon
				cm
			Site A	
Outwash	1	sandy, mesic Terric Haplosaprist	red maple (*Acer rubrum* L.), highbush blueberry (*Vaccinium corymbosum* L.)	45
			Site B	
Outwash	2	sandy, mesic Aeric Endoaquept	red maple, summersweet (*Clethra alnifolia* L.)	27
			Site C	
Alluvial	2	coarse-loamy, mesic Fluvaquentic Endoaquept	red maple, highbush blueberry, summersweet	9
			Site D	
Alluvial	3	coarse-loamy, mesic Fluvaquentic Humaquept	red maple, highbush blueberry, summersweet	4

surrounding all the sites was forest or "old field" vegetation, where no known N applications had occurred for at least 20 years. All four riparian sites were forested, dominated by red maple (*Acer rubrum* L.), thus minimizing vegetation effects (Table 3.1). Sites were remote, 200 to 500 m from any roads. The thickness of the organic surface horizon (Table 3.1) reflected the surface stability of these sites, with the more fluvially active alluvial sites having a thinner organic surface horizon as compared to the two glacial outwash sites. The average annual precipitation in the Pawcatuck watershed is approximately 1.3 m, with roughly 0.7 m recharging the ground water, 0.55 m returning to the atmosphere through ET, and 0.05 m entering streams through overland runoff (Dickerman et al., 1997).

Ground water denitrification potential, within the hydric soils at each site, was previously assessed in a companion study by the push-pull method (Kellogg et al., 2005). At each site, three replicate mini-piezometers (0.7-cm o.d.) were placed at each of three depths below the soil surface: 0.65 m, 1.5 m, and 3 m, with the exception of Site C where a confining layer forced us to install the deep wells at 2.6 m. Ground water was extracted from each mini-piezometer, spiked with ^{15}N-enriched NO_3^-–N and a conservative tracer, then pumped (“pushed”) back into each mini-piezometer. After an incubation period the introduced plume was extracted (“pulled”), and the ground water denitrification rate obtained by examining the production of ^{15}N-enriched denitrification gases. Elevated NO_3^-–N concentrations were used in the dosing solution, providing insight into conditions where NO_3^-–N concentrations would not limit denitrification rates.

The study area where the push-pull 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 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 at each site along a transect extending from the upland to the stream. Hydraulic heads in the mini-piezometers were recorded during periods of sustained high flows, excluding storm events, using a water level meter (Solinst Canada Ltd., Georgetown, Ontario Canada) modified to permit use in the narrow mini-piezometers. Based on a review of data collected monthly in the Pawcatuck watershed over 26 years (U.S. Geological Survey, 2005), stream NO_3^-–N loads increased markedly with increasing river discharge, exhibiting a strong linear relationship, and emphasizing the importance of understanding the role of riparian zones in NO_3^-–N flux to streams at times of sustained high flow. On two sites we also collected data during sustained periods of low flow to gain some insights into flow path variability at our sites.

The soil morphology of 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 depth of horizons based on soil texture and color, and the occurrence and 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. Along the transect, soil pits were dug to a depth of 1.5 to 2 m, near the upland edge and near the denitrification test 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 excavated, described, and samples taken from all horizons.

We also installed water table wells (4-cm i.d.; slotted the full length) at each site. The topography and relative elevation of all mini-piezometer and water table wells were surveyed along each transect using a transit level. Water table levels were recorded at the same time as mini-piezometer hydraulic heads, and additionally biweekly during spring and fall when water table depths were expected to change most rapidly, and bimonthly during summer and winter.

Saturated hydraulic conductivity, Ks, was estimated at each mini-piezometer along the transect using the Hvorslev field slug test method (Freeze and Cherry, 1979) with an analytical solution modified to reflect the small-diameter mini-piezometers.

Riparian Ground Water Modeling

To gain insight into the hydrologic balance and ground water dynamics of the riparian area, we modeled ground water fluxes at each site for a selected date during a period of high water table, in April and May of 2002 and 2003, using FLONET/TRANS v3.1(Waterloo Hydrologic Inc., 1997). FLONET is a two-dimensional steady-state finite-element ground water flow model that uses standard numerical methods for flow net construction (Freeze and Cherry, 1979). Although the water table was elevated at the time of field sampling, "leaf out" had commenced, with full canopy achieved by early May.

We modeled the riparian ground water down to a depth of 3 m within a cross-sectional plane along a transect from the upland to the stream. This area was considered to be the "subsurface riparian ecosystem". We also modeled fluxes at two sites for a selected date during a period of low water table. Ground water flow patterns were considerably more complex at low water table, so detailed results are not included here. One limitation of using a two-dimensional model is the inability to model down-valley flow, perpendicular to the cross-section. Although this third dimension is not considered here, a planar analysis can still provide some insights into the extent of upwelling of deep ground water and a conservative (i.e., minimum) estimate of retention times. Estimated flow paths would be lengthened if we were to consider the down-valley component, and therefore retention times and potential for ground water NO_3^-–N transformation within the riparian zone would be greater than estimated from our analyses.

We identified generalized flow path components (Figure 3.3) and quantified these for each site based on the flow nets generated by the model. Influx pathways included (i) lateral flow from the shallow (within the top 3 m) aquifer, originating from the upland or beneath the stream from a location outside the modeled riparian system, and (ii) upwelling from the deeper (below 3 m) aquifer. Outflux pathways

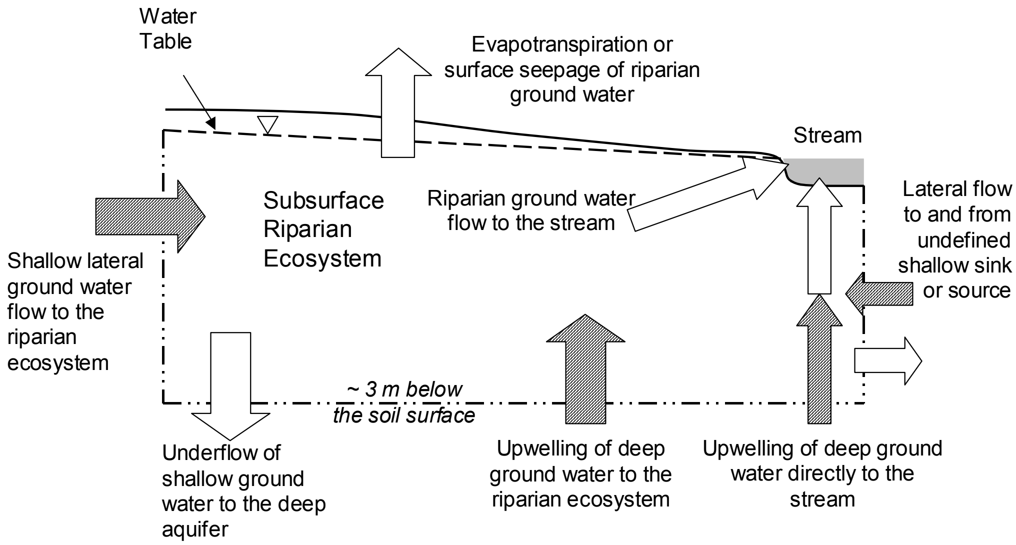

Figure 3.3. Generalized flow paths representing influx (striped arrows) and outflux (open arrows) components of the subsurface riparian ecosystem.

included (i) ET or surface seepage out through the water table, (ii) underflow to the deeper aquifer, (iii) lateral flow below the stream to a location outside the modeled riparian system, and (iv) flow into the stream. We considered surface seepage to have occurred when the modeled flow net generated a water table at or above the soil surface. Lateral flow beneath the stream was characterized as having an undefined source or sink, lacking definitive data. This type of flow could occur as the result of a buried channel of higher hydraulic conductivity.

We defined soil properties (Ks and porosity) in the model using field data as a guide (Figure 3.4). Ks was modeled as anisotropic (Kx for lateral flow, Kz for vertical flow), with Kz generally being on the order of 10 to 100 times less than Kx (Freeze and Cherry, 1979), and Kx more closely approximating the field-measured values. We assigned porosity a value of 0.38, except when soils were gravelly, where a value of 0.4 was assigned. These values are typical for the media found at our sites (Nelson et al., 1995; Freeze and Cherry, 1979).

The modeling process was an iterative one, where we specified boundary conditions, i.e., fluxes or a fixed head, where the fixed head was the stream level measured in the field. We then compared the resultant water table and modeled piezometric heads to the field-measured water table levels and piezometric heads. We continued to adjust the fluxes until modeled piezometric heads approximated the piezometric heads measured in the field. Piezometric surfaces were mapped with respect to the streambed for convenience. At all sites, vertical flux from the water table was an important component, with regional daily ET rates guiding initial flux estimates used in the modeling.

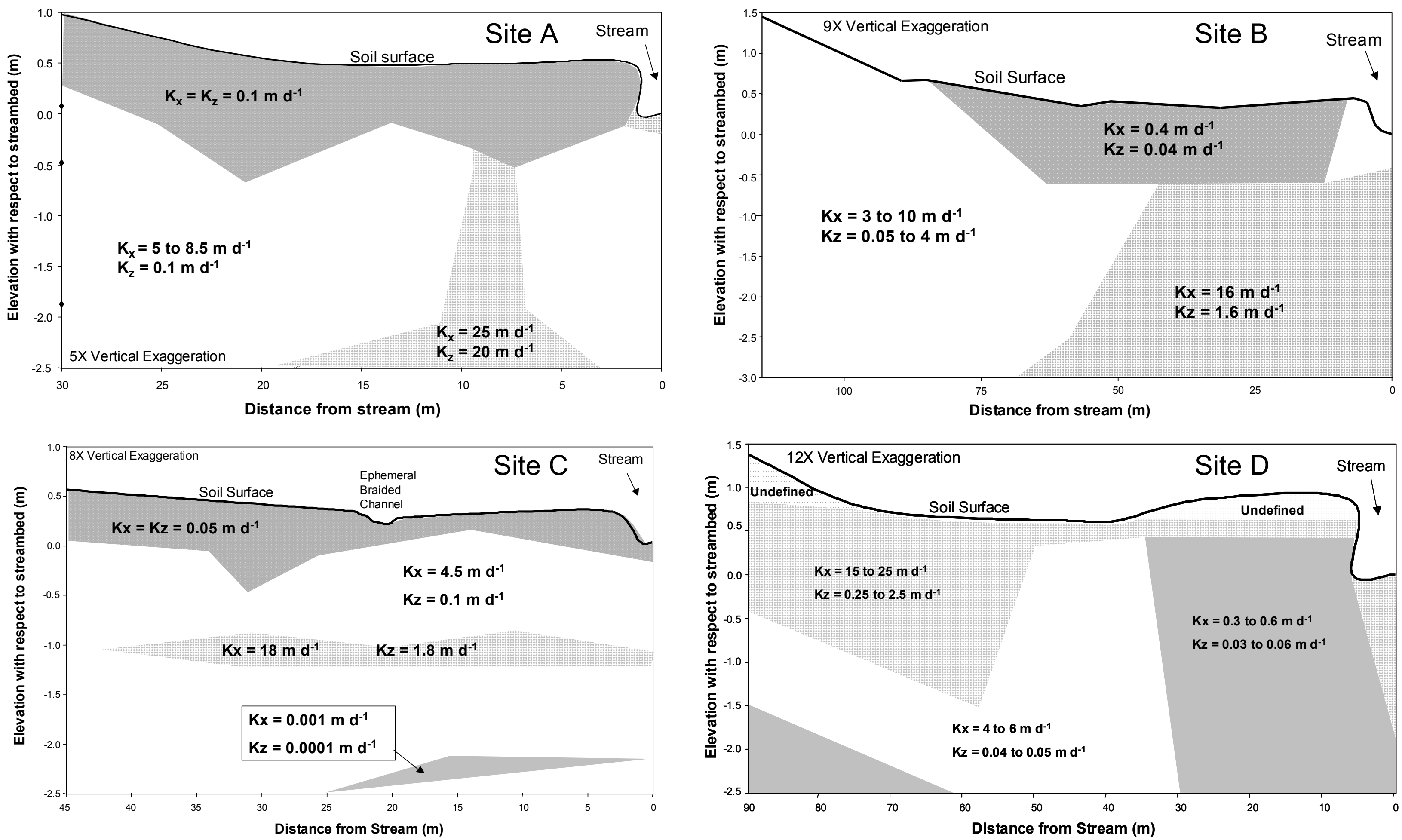

Figure 3.4. Soil property definitions used in the FLONET model. Kx was based on saturated hydraulic conductivities measured in the field at each mini-piezometer. Kz was assigned a value 10 to 100 times less than Kz. Soil depositional patterns were determined from an intensive array of auger holes along the transect.

We used flowtubes generated by the model to estimate the total flux along each of the generalized pathways (Figure 3.3). Flowtubes are characterized by a constant flux ($m^2\ d^{-1}$) along their length, with specific discharge ($m\ d^{-1}$) being the flux divided by the flow tube width. Because specific discharge is the product of pore water velocity and porosity, narrower flowtubes reflect higher pore water velocities. Total flux along a pathway was estimated by counting the number of flowtubes along a pathway and multiplying by the constant flux represented by each flowtube.

The field data were gathered over a period of one or two hours in the middle of the day, suggesting that the ET rates that we arrived at through the modeling process, and that had been based upon the gathered field data, most likely reflected a rate at or near the hourly maximum. ET rates, expressed in the model as (Area/Time) and assuming a riparian area of 1 m X riparian width, were normalized among sites by dividing by the riparian width.

Acknowledging that ET rates are sensitive to factors that vary with time and space such as air temperature, wind speed, and humidity, we obtained a rough estimate of daily and annual ET rates at our sites for the purpose of comparing those rates to field studies that measured ET directly. We therefore calculated a rough estimate of the average daily ET rate by assuming that maximum hourly ET was active over a 5-h period, from 10 00 to 15 00. Estimates of average annual ET assumed that ET was active from April through October, representing 65.2% of the annual daylight hours on a cumulative monthly basis at 41º Latitude (Jensen et al., 1990), thus multiplying the average daily rate by 0.652 and 365 d y^{-1}.

We also used the flownets to provide insight into ground water denitrification within 10 m of the stream because the near-stream area was more likely to be subjected to fluvial processes that provide subsurface carbon to fuel microbial activity (Devito et al., 2000; Blazejewski, 2003; Hill et al., 2004), and has been the subject of intense interest by researchers. We observed that in situ potential denitrification rates were highest closest to the stream (Kellogg et al., 2005), suggesting that this near-stream area may play a critical role in controlling ground water NO_3^-–N delivery to streams. Estimating ground water NO_3^-–N removal by denitrification within 10 m of the stream required coupling estimates of retention time with potential denitrification rates. We therefore estimated a range of flow path lengths for each pathway within 10 m of the stream at each site. By coupling flow path lengths with representative pore water velocities, we estimated a range of retention times.

We then multiplied in situ potential denitrification rates (Kellogg et al., 2005) by the range of retention times to obtain a range for NO_3^-–N removal by denitrification along each pathway found to be active within 10 m of the stream. We assumed similar potential denitrification rates 1 to 3 m below the stream to those observed in the ground water at the same sites and at the same depth, but at a distance of 5 to 20 m from the stream. Because our in situ denitrification rates were observed in conditions that were not N-limited, the NO_3^-–N removal rates by denitrification are potential, rather than actual. Actual NO_3^-–N removal rates by denitrification would likely be limited by existing ground water NO_3^-–N concentrations.

Watershed Perspective

A major question in riparian ground water denitrification work is the extent to which riparian areas are connected hydrologically to contributing uplands. In an effort to estimate hydrologic connectivity between our riparian areas and the uplands, we estimated the average watershed area that would contribute ground water to a 100 m stream reach at each site. Based on our modeling results, we estimated the average annual flux through our riparian areas, using six months of flux data from the high flow data, and six months of estimated flux from the low flow data. Based on an assumed average annual ground water recharge, we estimated the watershed area contributing ground water flux to a 100 m reach at each site. Because our results showed that riparian wetland ET was a major outflux pathway at the time of measurement, we explored the extent to which upland recharge might contribute to meeting riparian wetland ET demand on an average annual basis.

The watersheds of our riparian sites were largely forested with very low ground water NO_3^-–N concentrations. We explored the extent to which these riparian areas might potentially remove ground water NO_3^-–N on an annual basis by postulating a development scenario in the upland of the watershed and working out a nitrogen budget of the riparian areas. We scaled up to a 100 m stream reach and estimated the annual nitrogen load to the watershed if the upland were developed as medium-high density residential (approximately 12 dwelling units per hectare) with onsite septic systems. These types of unsewered development densities are not uncommon in the villages of New England.

To estimate N loading to the upland ground water we used the MANAGE model (Joubert et al., 1996; Kellogg et al., 1997), a mass balance N loading model that estimates annual loading to ground water derived from published work focused on the soils, practices, and climate of southern New England. We estimated the upland ground water N load to be 68 kg ha^{-1} as the result of fertilizer, septic system inputs, and atmospheric deposition. We then estimated a concentration of 9.4 mg L^{-1} NO_3^-–N carried in upland recharging ground water and moving into the riparian subsurface ecosystem. Based on flow paths, retention times, and field-measured potential ground water denitrification rates, we estimated the extent to which the postulated upland ground water N load could be transformed or removed within the riparian area. We also estimated the annual NO_3^-–N load to the stream. We assumed that a) the water supply originated within the watershed, and that the septic systems therefore did not import water to the watershed, b) no dilution occurred during upland ground water flow through the riparian area, and c) no denitrification occurred outside of the 10 m nearest the stream. The first two assumptions created a bias towards more NO_3^-–N removal/transformation because of higher ground water NO_3^-–N concentrations, while the third assumption created a bias towards less removal/transformation.

RESULTS

The saturated hydraulic conductivities measured in the field varied widely within each site, ranging from $<10^{-4}$ m d^{-1} in silty lenses to as high as 22 m d^{-1} in layers of gravelly sand. Moreover, the pattern of hydraulic conductivities varied considerably between the sites. However, all sites had zones of elevated Ks (> 10 m d^{-1}) in the subsurface, able to support substantial ground water fluxes. In the model our assigned values for Kx ranged from 0.001 m d^{-1} for a silty lens at Site C to as high as 25 m d^{-1} for gravelly sand at Sites A and D (Figure 3.4).

Ground water flow patterns at all sites were complex and demonstrated a range of influx and outflux pathways (Figures 3.5 to 3.8), reflecting the variability in soil properties and hydraulic gradients throughout the sites. Unique depositional patterns at each site were reflected in the unique patterns of hydraulic conductivities and flow paths, showing no apparent relationship between the geomorphic setting of these sites and the observed flow patterns.

The hydrologic water balance as determined from the modeling results showed that the total ground water flux through the riparian ecosystem ranged from 0.28 m^2 d^{-1} at Site B to 0.88 m^2 d^{-1} at Site A (Table 3.2). For a 100 m stream reach, the range of influxes would translate to 28 m^3 d^{-1} at Site B to 88 m^3 d^{-1} at Site A. At all sites the influx was fairly evenly divided between lateral flow from the shallow aquifer and upwelling from the deep aquifer, except at site B, where lateral flow of shallow ground water dominated (Figure 3.9). Three of the four sites (A, B, and D) displayed a distinct area of upwelling within 25 m of the stream. At Site C there was a confining layer about 3 m below the soil surface and within 10 m of the stream,

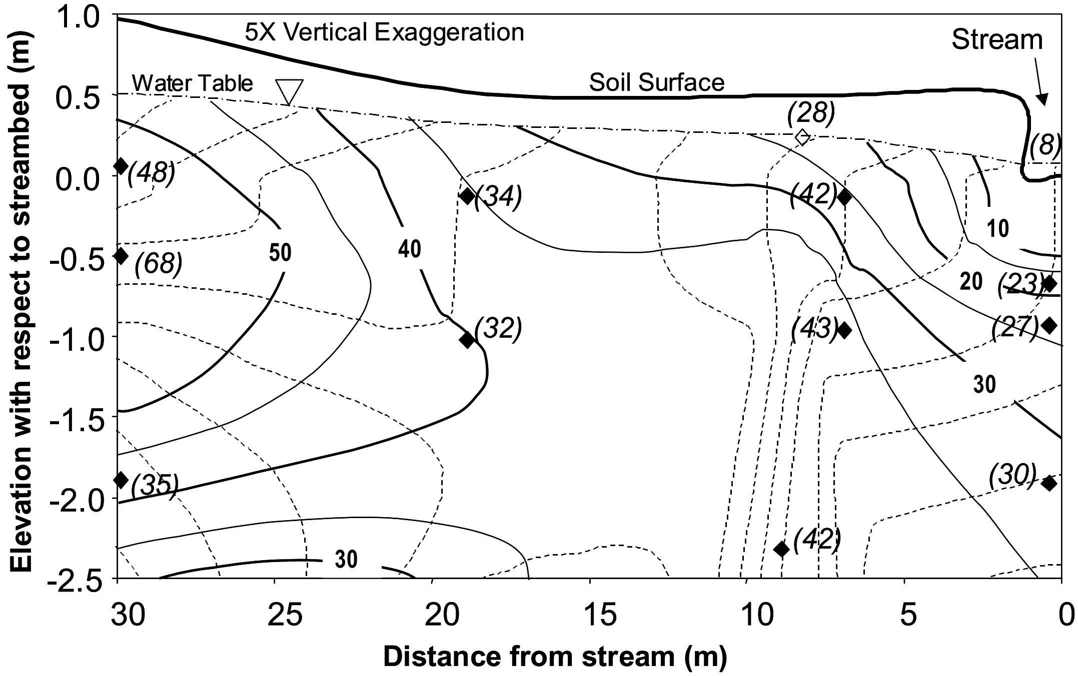

Figure 3.5. Cross-section of transect at Site A during a period of high water table. Data were collected on May 29, 2003. Piezometer locations are designated with solid diamonds, water table well location with open diamond. Italic numbers in parentheses are measured piezometric heads (cm) with respect to the streambed. Water table, flowtubes, and piezometric surfaces were derived from the FLONET groundwater flow model, using measured piezometric heads, water table, and stream height. Solid lines indicate piezometric surfaces, dashed lines indicate flowtubes. Flux within each flowtube is 0.05 m^2d^{-1}. Narrower flowtubes reflect greater pore water velocity. Horizontal flow components are greater than depicted due to vertical exaggeration. Flow at this site is dominated by upwelling of deep ground water, lateral flow of shallow ground water from the upland, and evapotranspiration.

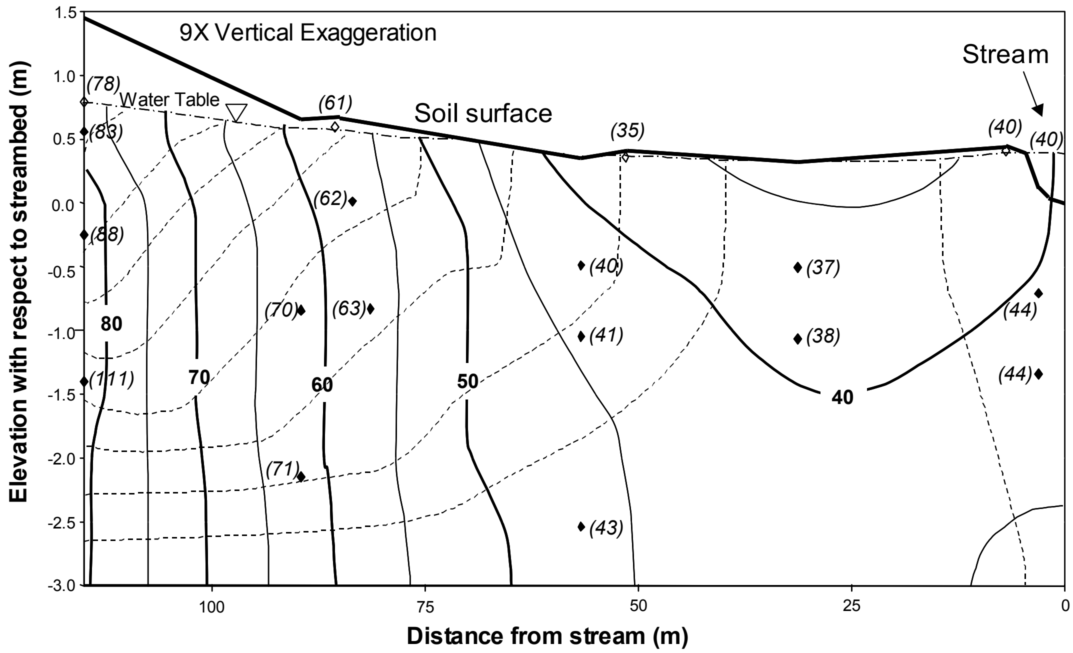

Figure 3.6. Cross-section of transect at Site B during a period of high water table. Data were collected on April 29, 2003. Piezometer locations are designated with solid diamonds, water table well location with open diamond. Italic numbers in parentheses are measured piezometric heads (cm) with respect to the streambed. Water table, flowtubes, and piezometric surfaces were derived from the FLONET groundwater flow model, using measured piezometric heads, water table, and stream height. Solid lines indicate piezometric surfaces, dashed lines indicate flowtubes. Flux within each flowtube is 0.025 m^2d^{-1}. Narrower flowtubes reflect greater pore water velocity. Horizontal flow components are greater than depicted due to vertical exaggeration. This site is dominated by lateral flow of shallow ground water from the upland, and evapotranspiration.

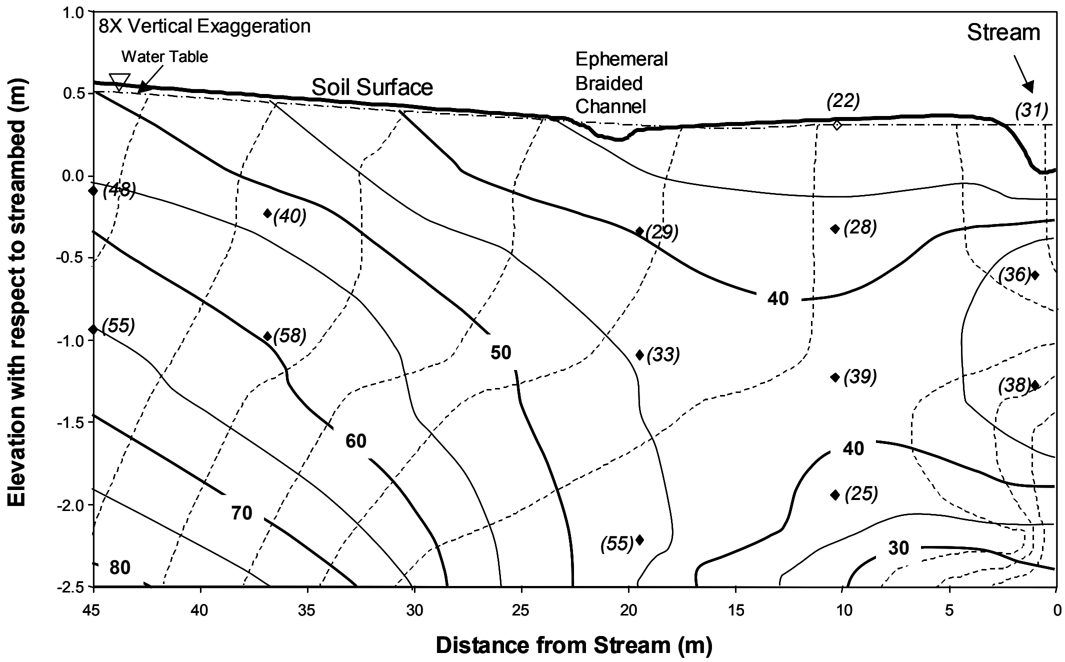

Figure 3.7. Cross-section of transect at Site C during a period of high water table. Data were collected on April 15, 2002. Piezometer locations are designated with solid diamonds, water table well location with open diamond. Italic numbers in parentheses are measured piezometric heads (cm) with respect to the streambed. Water table, flowtubes, and piezometric surfaces were derived from the FLONET groundwater flow model, using measured piezometric heads, water table, and stream height. Solid lines indicate piezometric surfaces, dashed lines indicate flowtubes. Flux within each flowtube is 0.05 $m^2 d^{-1}$. Narrower flowtubes reflect greater pore water velocity. Horizontal flow components are greater than depicted due to vertical exaggeration. Flow at this site is dominated by upwelling of deep groundwater, lateral flow of shallow ground water from below the stream, and evapotranspiration.

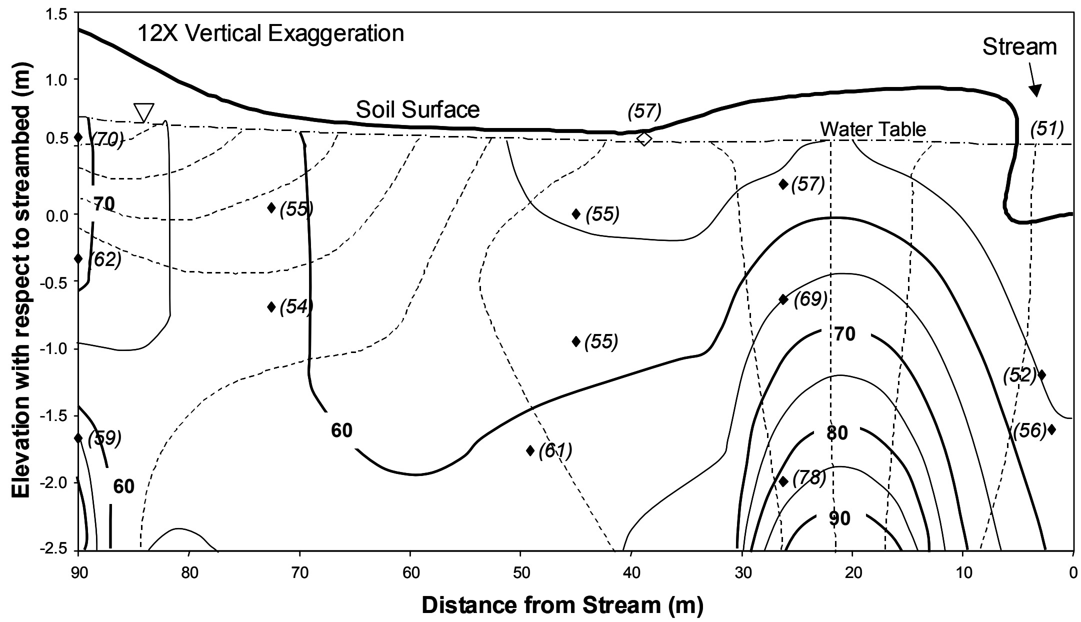

Figure 3.8. Cross-section of transect at Site D during a period of high water table. Data were collected on May 9, 2003. Piezometer locations are designated with solid diamonds, water table well location with open diamond. Italic numbers in parentheses are measured piezometric heads (cm) with respect to the streambed. Water table, flowtubes, and piezometric surfaces were derived from the FLONET groundwater flow model, using measured piezometric heads, water table, and stream height. Solid lines indicate piezometric surfaces, dashed lines indicate flowtubes. Flux within each flowtube is 0.05 m^2d^{-1}. Narrower flowtubes reflect greater pore water velocity. Horizontal flow components are greater than depicted due to vertical exaggeration. Flow at this site is dominated by upwelling of deep groundwater, lateral flow of shallow ground water from the upland, and evapotranspiration.

Table 3.2. Hydrologic water balance of a cross-section of the riparian ecosystem (0 to 3 m depth) from the upland edge to the stream, for a period of high water table, as modeled with FLONET.

Site	A	B	C	D
Date	5/29/03	4/29/03	4/15/02	5/9/03
	------------------------------ $m^2 d^{-1}$	------------------------------		
Influx				
Shallow lateral flow	0.42 (48%)	0.24 (86%)	0.32 (55%)	0.24 (47%)
Deep upwelling	0.46 (52%)	0.04 (14%)	0.26 (45%)	0.27 (53%)
Total Influx	0.88	0.28	0.58	0.51
Outflux				
To the stream	0.07 (8%)	< 0.01	0.05 (8.5%)	0.03 (6%)
To the water table (ET† or seepage)	0.39 (44%)	0.28 (100%)	0.37 (64%)	0.47 (92%)
Underflow	0.21 (24%)	< 0.01	0.15 (26%)	0.01 (2%)
Undefined	0.21 (24%)	< 0.01	0.01 (1.5%)	< 0.01
Total Outflux	0.88	0.28	0.58	0.51

† Evapotranspiration

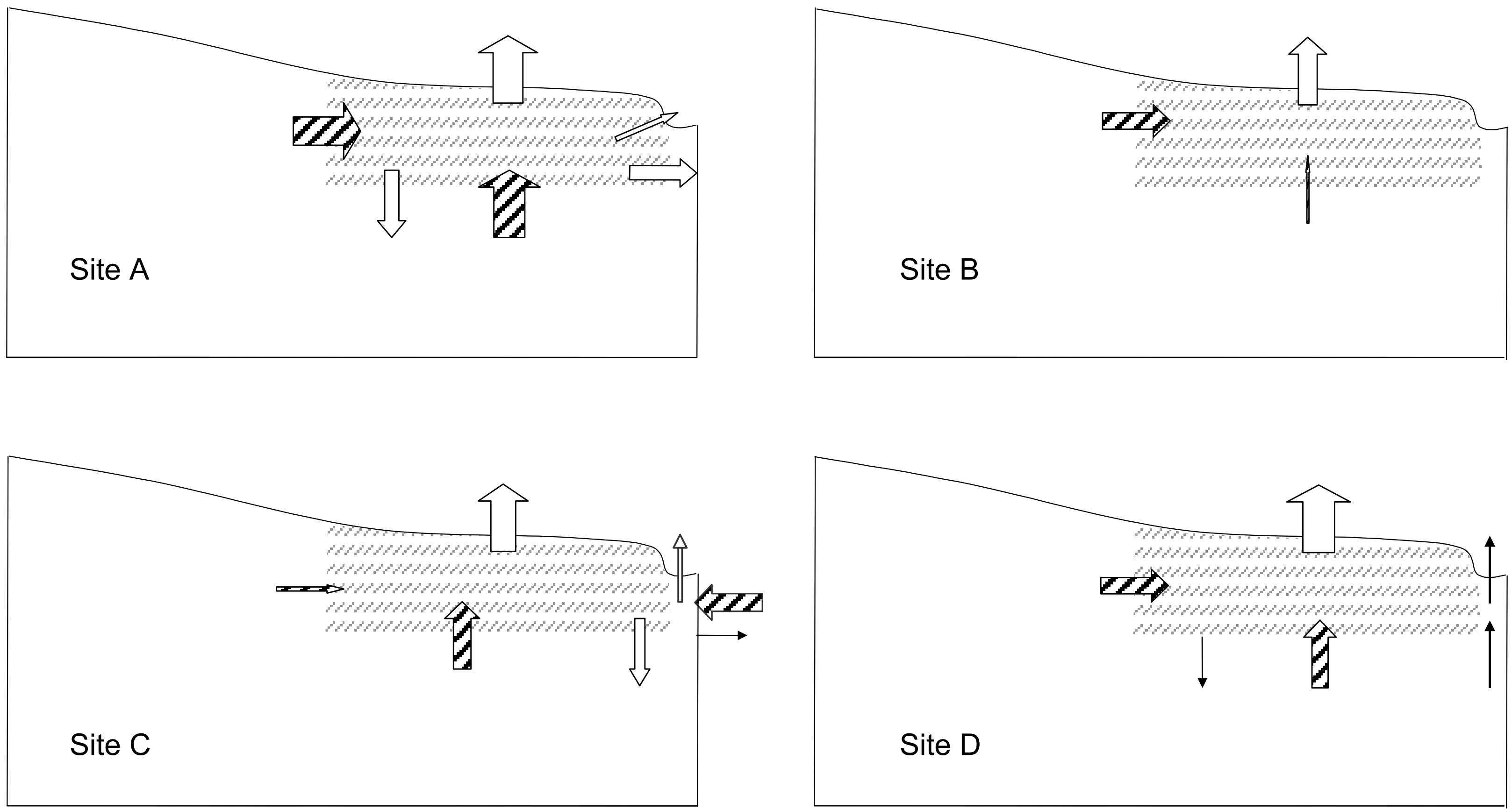

Figure 3.9. Generalized flow paths representing influx (striped arrows) and outflux (open arrows) components of the subsurface riparian ecosystems at Sites A through D. Arrow widths represent flux magnitude along each pathway.

likely inhibiting upwelling influx near the stream. At Site C there was evidence, however, of significant upwelling at > 25 m from the stream, consistent with transect augering data that showed coarser material at depth starting at 25 m from the stream and continuing to the upland.

The outflux was dominated at all sites by outflux to the water table (ET or surface seepage), ranging from 0.28 m^2 d^{-1} at Site B to 0.47 m^2 d^{-1} at Site D, with the proportion of total outflux to the water table ranging from 44% at Site A to 100% at Site B. Underflow to the deep aquifer was notable at Sites A and C, comprising approximately one fourth of the total outflux at these sites. Lateral outflow to an undefined sink was only important at Site A, with a flux of 0.21 m^2 d^{-1} (24% of the total outflux). Flux to the stream was < 10% of the total outflux at all sites, ranging from <0.01 m^2 d^{-1} at Site B to 0.07 m^2 d^{-1} at Site A.

The underflow at Site A was the diversion of lateral shallow flow from the upland, perhaps the result of a silty loam lens found at about 20 m from the stream and at a depth of 0.6 to 0.95 m below the soil surface. The underflow at Site C appeared to be a diversion of lateral flow from beneath the stream as the result of a confining layer at a depth of about 2.5 m.

Site A was the only site with any appreciable outflux below the stream to an undefined sink (Figure 3.9). We observed lenses of low permeability below the stream at depths of 1 m to 1.5 m, suggesting preferential flow through coarser media below these lenses.

Outflux to the water table was potentially composed of both ET and seepage to the soil surface. Only Sites B and C exhibited surface seepage (Table 3.3), where

Table 3.3. Evapotranspiration and surface seepage as ground water outflux from the water table during a period of high water table, as modeled with FLONET.

Site	B	C
Date	4/29/03	4/15/02
	------------ m^2 d^{-1} ------------	
Surface seepage	0.10 (36%)	0.05 (14%)
ET†	0.18 (64%)	0.32 (86%)
Total ET and seepage	0.28	0.37

† Evapotranspiration

Table 3.4. Estimated normalized maximum hourly, average daily, and average annual evapotranspiration rates based on FLONET modeling results.

Site	A	B	C	D
Normalized maximum hourly ET rate (mm h^{-1})	0.54	0.08	0.27	0.24
Normalized average daily ET rate (mm d^{-1})†	2.7	0.4	1.35	1.2
Normalized average annual ET rate (mm y^{-1})‡	643	95	321	238

† Assuming 5 hours of peak daylight from 10 00 to 15 00.
‡ Assuming 65.2% cumulative monthly percentage of daytime hours from April to October (Jensen et al., 1990).

we observed ephemeral and poorly defined channels with a deep organic layer. Even accounting for the surface seepage, ET was the dominant outflux at all sites, ranging from 0.18 $m^2 d^{-1}$ at Site B to 0.47 $m^2 d^{-1}$ at Site D, with the portion of total outflux ranging from 44% at Site A to 92% at Site C. Normalized estimates of maximum hourly ET rates ranged from 0.08 mm h^{-1} to 0.54 mm h^{-1}, and normalized estimates of average daily ET rates ranged from 0.4 mm d^{-1} to 2.7 mm d^{-1} (Table 3.4).

During the period of time selected for monitoring and modeling, ground water outfluxes to the stream at all sites was surprisingly low (<10% of the total outflux), almost all originating from the upwelling of deep ground water (Table 3.5). On one site (Site B) the stream was bank full, with a low berm separating it from the seepage area, likely resulting in reverse flow from the stream into the streambank (Freeze and Cherry, 1979; Winter et al., 1999). The flow was directed toward the low area about 25 m from the stream, with ground water emerging as seepage. This area has an organic layer of at least 0.5 m and no defined channel.

In order to investigate ground water denitrification within the riparian area as ground water approached the stream, we focused on the ground water fluxes and retention times within 10 m of the stream, a zone expected to possess a higher probability for increased microbial denitrification than areas farther from the stream (Devito et al., 2000; Blazejewski, 2003; Hill et al., 2004; Kellogg et al., 2005). Retention time, the time that ground water NO_3^-–N has for interaction with denitrifying microbes in the riparian subsurface ecosystem, influences the effectiveness of a riparian area to remove ground water NO_3^-–N through denitrification. To estimate a range of retention times for each pathway, we first

Table 3.5. Ground water flux to the stream, originating as either lateral flow from the shallow aquifer or upwelling from the deeper aquifer, and flowing either directly to the stream or through the riparian ecosystem and then to the stream, as modeled with FLONET. No lateral flow from the shallow aquifer on the upland end of the riparian zone reached the stream at any site.

Site	A	B	C	D
Date	5/29/03	4/29/03	4/15/02	5/9/03
	---------------------- $m^2\ d^{-1}$	----------------------		
Flow from the shallow aquifer directly to the stream	< 0.01	< 0.01	**0.05**	< 0.01
Upwelling directly to the stream	< 0.01	< 0.01	< 0.01	**0.03**
Upwelling to the riparian ecosystem and then to the stream	**0.07**	< 0.01	< 0.01	< 0.01
Total flux to the stream	0.07	< 0.01	0.05	0.03
Portion of the total outflux	8%	<1%	8.5%	6%

estimated a range of ground water flow path lengths and pore water velocities. By dividing the flow path length (m) by the pore water velocity (m d^{-1}), we estimated the retention time (d). We estimated potential NO_3^-–N removal along each pathway by multiplying in situ potential denitrification rates by retention times.

While overall retention time and resulting potential NO_3^-–N removal is important along all pathways within 10 m of the stream, it is the outflux pathways tothe stream that are the most critical for evaluating the role of riparian zones in watershed N export. All other pathways would provide opportunities for further riparian N transformations. Ground water outflux through the water table allows for plant uptake and interaction with the carbon-rich surface horizons, exposing ground water NO_3^-–N to a wide range of biological cycling processes, and resulting in gaseous losses or long term storage. The other possible outflux pathways (lateral flux to an undefined sink and underflow) imply a longer retention time as they flow towards the stream.

Site A had one pathway that traveled laterally through the riparian zone before emerging at the stream (Table 3.6). This pathway had an estimated potential removal by denitrification of 10 mg L^{-1} NO_3^-–N, over an almost 80 day retention time. Site B did not demonstrate any outflux to the stream; all outflux went to the water table (Table 3.7). In contrast, Sites C and D (Tables 3.8 and 3.9, respectively) showed ground water influx upwelling and flowing as outflux directly into the streambed, effectively bypassing the riparian ecosystem. The flux to the stream at Site D was slightly less than at Site C. However, Sites C and D showed markedly different NO_3^-–N removals by denitrification (1.7 mg L^{-1} at Site C compared to 21 -

Table 3.6. Site A potential riparian NO_3^--N removal by denitrification, down to 3 m and within 10 m of the stream, and along a 100 m stream reach. Flow path lengths and pore water velocities were modeled with FLONET. Removal was converted to mg L^{-1} assuming that 4.37 kg of soil held 1 L of ground water, based on a porosity value of 0.38, typical for soils found at our sites.

Site A mean in situ denitrification rate for spring†: 29 μg (kg of soil)$^{-1}$ d^{-1}

Pathway‡	Flow Path Length	Pore Water Velocity	Retention Time	Potential NO_3^--N removal	Flux through 100 m reach of near-stream area
	m	m d^{-1}	d	mg L^{-1}	m^3 d^{-1}
From the deep aquifer to:					
Water table (ET§ or seepage)	3 to 8	0.11	27 to 73	3.4 to 9.3	15
Indirectly to the stream through the subsurface riparian ecosystem	11	0.14	79	10	7
Undefined sink	6 to 10	0.22	27 to 45	3.4 to 5.7	21

† In situ denitrification rates are from Kellogg et al. (2005).
‡ Influx from the shallow aquifer did not generate flux to the final 10 m of the stream-riparian system.
§ Evapotranspiration.

Table 3.7. Site B potential riparian NO_3^--N removal by denitrification, down to 3 m and within 10 m of the stream, and along a 100 m stream reach. Flow path lengths and pore water velocities were modeled with FLONET. Removal was converted to mg L^{-1} assuming that 4.37 kg of soil held 1 L of ground water, based on a porosity value of 0.38, typical for soils found at our sites.

Site B mean in situ denitrification rate for spring†: 22 μg (kg of soil)$^{-1}$ d^{-1}

Pathway‡	Flow Path Length	Pore Water Velocity	Retention Time	Potential NO_3^--N removal	Flux through 100 m reach of near-stream area
	m	m d^{-1}	d	mg L^{-1}	m^3 d^{-1}
From the deep aquifer to:					
Water table (ET§ or seepage)	5 to 12	0.009	556 to 1333	> 50	3

† In situ denitrification rates are from Kellogg et al. (2005). Site B was the only site that exhibited significantly different rates with depth: 22 μg kg^{-1} d^{-1} at 0.65 m, 3 μg kg^{-1} d^{-1} at 1.5 m, and <0.1 μg kg^{-1} d^{-1} at 3 m. Using the rate of 3 μg kg^{-1} d^{-1}, the estimated removal would be 7.3 to 17.5 mg L^{-1}.

‡ Influx from the shallow aquifer did not generate flux to the final 10 m of the stream-riparian system.

§ Evapotranspiration.

Table 3.8. Site C potential riparian NO_3^--N removal by denitrification, down to 3 m and within 10 m of the stream, and along a 100 m stream reach. Flow path lengths and pore water velocities were modeled with FLONET. Removal was converted to mg L^{-1} assuming that 4.37 kg of soil held 1 L of ground water, based on a porosity value of 0.38, typical for soils found at our sites.

Site C mean in situ denitrification rate for spring†: 96 μg (kg of soil)$^{-1}$ d^{-1}

Pathway‡	Flow Path Length	Pore Water Velocity	Retention Time	Potential NO_3^--N removal	Flux through 100 m reach of near-stream area
	m	m d^{-1}	d	mg L^{-1}	m^3 d^{-1}
From the shallow aquifer to:					
Water table (ET§ or seepage)	2 to 12	0.04	50 to 300	21 to >50	6
Underflow	2 to 12	2.66	1 to 6	0.4 to 2.5	14
Directly to the stream	1	0.28	4	1.7	5

† In situ denitrification rates are from Kellogg et al. (2005).
‡ Influx from the deep aquifer did not generate flux to the final 10 m of the stream-riparian system.
§ Evapotranspiration.

Table 3.9. Site D potential riparian NO_3^--N removal by denitrification, down to 3 m and within 10 m of the stream, and along a 100 m stream reach. Flow path lengths and pore water velocities were modeled with FLONET. Removal was converted to mg L^{-1} assuming that 4.37 kg of soil held 1 L of ground water, based on a porosity value of 0.38, typical for soils found at our sites.

Site D mean in situ denitrification rate for spring†: 16 μg (kg of soil)$^{-1}$ d^{-1}

Pathway‡	Flow Path Length	Pore Water Velocity	Retention Time	Potential NO_3^--N removal	Flux through 100 m reach of near-stream area
	m	m d^{-1}	d	mg L^{-1}	m^3 d^{-1}
From the deep aquifer to:					
Water table (ET§ or seepage)	3 to 12	0.02	150 to 600	10.5 to 42	2
Directly to the stream	3 to 6	0.01	300 to 600	21 to 42	3

† In situ denitrification rates are from Kellogg et al. (2005).
‡ Influx from the shallow aquifer did not generate flux to the final 10 m of the stream-riparian system.
§ Evapotranspiration.

42 mg L^{-1} at Site D) along the pathway to the stream. This was because of an enormous difference in estimated Ks below the stream, reflected in the estimated retention times (4 d at Site C compared to 300 to 600 d at Site D). The retention time overwhelmed the fact that the in situ potential denitrification rate observed at Site C was six times that observed at Site D. While Site D exhibited the kind of direct upwelling to the stream from the deeper aquifer that was hypothesized, estimated NO_3^-–N removal by denitrification along the flow path was substantial.

The upward flux to the stream at Site C appeared to originate from the shallow aquifer on the opposite side of the stream (Figures 3.7 and 3.9). Although the NO_3^-–N removal was extremely low along a very short flow path, this did not take into account the possibility for NO_3^-–N removal within the riparian subsurface ecosystem on the opposite side of the stream.

Watershed Perspective Results

The Pawcatuck watershed is about 850 km^2 with a total stream length of 1640 km, and a total riparian length of 3280 km. It follows that the average area draining through 100 m of riparian-stream reach would be 2.6 Ha. Because our riparian flux estimates were based on data collected during a period of high water table, we estimated the average annual flux through the riparian area using six months of high flow, and six months of low flow. The data collected during a period of low water table showed the flux to be about 75% of the flux at high water table.

On an average annual basis, the estimated watershed area contributing to the total ground water flux through each riparian zone was substantially more than the riparian area alone, with the possible exception of Site B, indicating a considerable linkage with upland areas (Table 3.10). Site A had the largest estimated contributing area, while the estimated contributing area for Site B was the smallest of the four sites. Sites C and D had estimated contributing areas that were very close to the Pawcatuck watershed average for a 100 m riparian-stream reach.

DISCUSSION

The variety of flow paths at the four riparian sites suggests a more dynamic and complex system than is often conceived in schematics describing ground water movement through riparian wetland soils (e.g., Correll, 1997; Gold et al., 2001). While alluvial settings, with layers of often significantly varying soil properties have previously been found to possess preferential flow and complex patterns of seepage and upwelling (Haycock and Burt, 1993; Burt, 1997; Burt et al., 1999; Devito et al., 2000; Flite et al., 2001), very small variations in topography, hydraulic conductivity, and hydraulic gradient can also result in complex preferential hydrologic pathways, even in relatively uniform aquifers (Freeze and Cherry, 1979; Anderson and Kneale, 1982). Site B, an outwash site, exhibits the simplest flow paths, though still does not conform to our simple conception of riparian ground water flow (Figure 3.1).

Similar to our observation of ground water contributions coming from both a shallow and a deeper aquifer, Hill (1990) found indications of two distinct sources, shallow and deep, for ground water entering the near-stream zone. Clément et al. (2003) identified three reservoirs contributing to stream flow: hillslope, a deep confined aquifer, and an unconfined aquifer.

The lateral outflux of ground water below the stream, as at Site A, is suggestive of a buried channel of coarser texture and higher hydraulic conductivity than the soils directly below the stream. Haycock and Burt (1993) described preferential flow from the near-stream zone to a buried channel in a floodplain riparian zone, resulting in preferential drainage of ground water down-valley. Clément et al. (2003) observed that a buried channel dominated ground water flow at three riparian sites along a fourth-order stream.

Although Hill et al. (2000) suggested that denitrification may not effectively remove NO_3^-–N from ground water transported at depth through permeable sediments unless interaction occurs with localized supplies of organic carbon, Puckett and Cowdery (2002) found deep, long flow paths with a 70-year travel time below a riparian area situated on outwash, allowing sufficient time to effectively reduce ground water NO_3^-–N even with limited organic carbon. Puckett et al. (2002) observed upwelling of deep ground water to a river, concluding that the riparian zone only had a minor role in preventing NO_3^-–N from reaching the river. However, long flow paths, even those in deep sediments with extremely low denitrification rates, may produce a marked reduction in ground water NO_3^-–N.

The domination of ET on outflux at our sites was similar to that found by Bosch et al. (1994) who noted that the riparian forest water demand in the Georgia (USA) Coastal Plain was met by ground water flowing along the stream bottom as well as ground water entering from the upslope during the summer months. Bosch et al. (1996) estimated that aquifer discharge to the stream from a Georgia Coastal Plain forested riparian area bordering a second order stream accounted for only 3%

of the annual precipitation, and that ET accounted for 67% of the annual precipitation (or 807 mm y^{-1}). Lowrance et al. (1983) estimated annual ET from a riparian forest ecosystem also in Georgia to be 4.56×10^6 m^3 over an area of 4.70×10^6 m^2, or an average depth of 969 mm y^{-1}. It is not unexpected that our estimated average annual ET rates are about half of those observed in Georgia, given our more northern latitude. The estimated maximum hourly ET rates obtained from the modeling exercise ranged from 0.08 mm h^{-1} to 0.54 mm h^{-1} and fall within the range observed from field studies of temperate forested areas. Kelliher et al. (1993) observed a median maximum hourly ET rate of 0.46 mm h^{-1} from coniferous forests and grasslands. The estimated average daily ET rates obtained from the modeling exercise ranged from 0.4 to 2.7 mm d^{-1}, slightly lower than observations of Hayashi et al. (1998), who measured a daily ET rate of 3.1 mm d^{-1} from a prairie wetland located in Saskatchewan, Canada.

ET flux at our sites had the consequence of reducing shallow upland ground water contributions to the stream. The piezometric field measurements occurred during the day, in late April and into May, when evaporative demand is elevated, influencing the ground water flow patterns. As expected, the two sites where data were gathered in May (Sites A and D), when “leaf out” was full, showed no indications of surface seepage when modeled, as compared to the two sites where data were gathered in April (Sites B and C), before full canopy cover. The field data and resulting flownets do not reflect low ET rates expected at night, and during the winter months. It is not clear how the modeled flow patterns would change when ET

Table 3.10. Average annual ground water flux estimates for a hypothetical 100 m stream reach-riparian system at each site, and the estimated Pawcatuck watershed area contributing ground water flux to each riparian area.

Average annual precipitation = 1.3 m
Average annual ground water recharge = 0.7 m

Site	A	B	C	D
Ave. annual flux through a 100 m reach of subsurface riparian ecosystem (m^3)†	28,105	8,943	18,524	16,288
Width of riparian zone (m)	30	90	50	80
Area of riparian zone along 100 m stream reach (Ha)	0.3	0.9	0.5	0.8
Estimated watershed area contributing average annual ground water flux to the subsurface riparian ecosystem (Ha)‡	4.0	1.3	2.6	2.3

† Assuming 6 months of high flow and 6 months low flow. Low flow is estimated as 75% of high flow, based on low flow measurements taken at the sites.
‡ Within the Pawcatuck watershed, the average area contributing ground water flux to a 100 m riparian-stream reach is estimated as (watershed area)/(riparian length) = 2.6 Ha per100 m of riparian-stream reach..

is reduced, but surface seepage and increased flux to the stream are the most likely alternatives during periods of high water table in the winter months.

Another consequence of ET as a major ground water outflux pathway at these riparian sites was that, compared to outflux directly to the stream, the opportunity for ground water NO_3^-–N transformations would be vastly increased due to the likely plant and microbial cycling of N near the soil surface, resulting in either gaseous losses or long-term storage.

Watershed Perspective

With the exception of Site B, our estimates of watershed areas contributing ground water influx to a 100 m riparian-stream reach at each of our sites was considerably greater than the riparian area itself, indicating that these riparian areas transmit substantial fluxes of upland ground water. Upwelling influx from the deep aquifer also suggests a larger contributing area (Winter et al., 1999). Site A with the highest upwelling influx, also had the largest estimated contributing watershed area, while Site B with no observed upwelling had the smallest estimated contributing watershed area. These observations support the notion that these high water table riparian areas situated in low gradient, permeable settings can play an important role in mediating upland ground water flux to the stream.

The surprisingly small proportion of the total flux that contributed to stream flow at our riparian sites is likely a function of the extremely low-gradient settings in which they are situated, as well as the relatively high rate of ET during the period of observation. The high proportion of flux that is transmitted through the riparian ecosystem as ET and surface seepage suggests that these low gradient, lower order riparian and stream settings should be considered as continuous integrated riparian-stream systems.

The potential of these low gradient, permeable, hydric riparian areas for reducing ground water NO_3^-–N inputs to streams rests partially on their ability to meet evaporative demand. In the Pawcatuck watershed, this type of riparian area (i.e., situated in either outwash or alluvial settings, and having hydric soils >10 m wide) bordered 39.2% of the drainage network (Rosenblatt et al., 2001). In contrast, in non-hydric and/or till riparian areas ET will not be a major sink for ground water upwelling to the root zone and is less likely to mediate ground water NO_3^-–N outflux from the watershed to the stream network.

However, because of the seasonal nature of ET, the effect of riparian wetland ET on upland ground water flux on an average annual basis would be more limited than our modeling results suggest. As an example, consider a 100 m reach with a watershed area of 2.6 Ha (the average Pawcatuck watershed area contributing flow to a 100 m stream reach), a hypothetical riparian width of 50 m, and an upland area of about 2.1 Ha. Assuming that riparian wetlands never experience drought stress, we estimated the average annual ET based on the so-called "pan" ET (representing ET from an open water body) multiplied by an ET coefficient that is dependent upon vegetation, humidity, and wind (0.85 in this case; Jensen et al., 1990). The average annual Class A pan ET for a station within the Pawcatuck is roughly 0.76 m (National Weather Service Cooperative Observer Station No. 374266, Kingston, RI), giving an estimated average annual riparian ET of 0.65 m. Because of rainfall variability, ET without drought stress cannot be met by rainfall alone. In the absence of irrigation, the difference would most likely be drawn from ground water originating as upland recharge. In Rhode Island, based on long-term daily soil moisture models, well-watered vegetation grown in sandy loam soils requires about 0.29 m of supplemental watering to avoid drought stress (Gold et al., 1988).

The average annual ET in the upland could be estimated as the average annual ET without irrigation, i.e., the difference between ET demand (0.65 m) less the additional "irrigation" (0.29 m), or about 0.36 m. This would generate roughly 0.89 m of average annual upland recharge (assuming average annual precipitation of 1.3 m and overland flow of 0.05 m). Applied over an upland area of 2.1 Ha, average annual upland ground water recharge would be about 18690 m^3. In the riparian area, assuming sandy loam soils, the additional ET drawn from upland recharge (i.e., "irrigation") would be 0.29 m over an area of 0.5 Ha, or 1450 m^3. The riparian ET obtained from upwelling from the water table represents just over 8% of the average annual upland recharge. Going through this exercise for silty loam soils yields a similar result (just under 8%).

Estimated total average annual transformation of N within the riparian ecosystem ranged from 16% (Site C) to 90% (Site B) of the N load to the upland. Even so, estimated average annual flux of N to the stream was negligible for all the sites except Site C, where a very short retention time below the stream yielded delivery of 9% of the upland N load to the stream.

The minimal delivery of N to the stream suggested complete N removal as ground water traveled from the upland source to the stream. Sites A, C, and D could

Table 3.11a. Average annual N flux through riparian sites for a hypothetical scenario where upland was developed as medium-high density residential (approximately 12 dwelling units ha^{-1}) with individual septic systems.
(%) signifies percent of average annual upland ground water N load.

Site	A	B	C	D
Average annual upland ground water N load (kg N y^{-1})	252	27	143	102
Average annual flux of upland ground water through the riparian area via ET† (m^3 y^{-1})	870	2610	1450	2320
Average annual N flux to shallow root zone via ET of upland ground water‡ (kg N y^{-1})	6.3 (3%)	20.6 (80%)	11.5 (8%)	18.3 (19%)
Average annual N loss via ground water denitrification within 10 m of the stream§ (kg N y^{-1})	53.5 (21%)	2.7 (10%)	12.0 (8%)	11.7 (11%)
Total average annual N load from the upland transformed within the riparian ecosystem¶ (kg N y^{-1})	59.8 (24%)	20.6 (90%)	20.8 (16%)	25.9 (30%)
Average annual flux of N to the stream (kg N y^{-1})	0.9 (0.4%)	0 (0%)	12.3 (9%)	0 (0%)
Average annual flux of N out of the riparian area as bypass flow (kg N y^{-1})	196.8 (76%)	6.4 (10%)	112.3 (75%)	76.1 (69%)

† Estimated upland ground water flux through the riparian area to meet ET demand (see text) 0.29 m, multiplied by the riparian area (m^2).
‡ Estimated as 9.4 mg N L^{-1} x flux, except within last 10 m where transformation via ET was N limited.
§ Removal via each pathway estimated as the denitrification rate multiplied by the rentention time (Tables 3.6 to 3.9) for potential removal in mg N L^{-1}, with an upper limit of 9.4 mg L^{-1} (i.e., N limited). Then multiplied by the average annual ground water flux leaving the riparian area via each pathway. N limitation was encountered at all sites along one or more pathways within 10 m of the stream.
¶ Mass that was either transported to the shallow root zone or denitrified within the riparian area. Remainder either reached the stream or left the riparian area as bypass flow.

Table 3.11b Assumptions used in hypothetical upland development scenario

Medium-high density development with onsite septic systems in upland
Drinking water is from within the watershed (no imported water)
N load is in the form of NO_3^-–N when it reaches the water table
Average annual precipitation = 1.3 m
Average annual ET from forested Pawcatuck subwatershed = 0.55 m
Percent pervious area of medium-high density development = 65%
Adjusted average annual ET from developed upland = 0.65 x 0.55 m = 0.35 m
Average annual surface runoff from upland development (assuming soil hydrologic group A) = 0.23 m
Average annual upland ground water recharge from precipitation = 0.72 m
Average annual upland ground water N load from septic systems, fertilizers, and atmospheric deposition = 68 kg ha^{-1}
Average concentration of NO_3^-–N in upland recharge = 9.4 mg L^{-1}

potentially transmit around 70% to 75% of the upland load downgradient within either the shallow or deep aquifers, to emerge lower in the watershed as either ET or streamflow. This implies longer retention times and other opportunities for N transformations as ground water flows “downstream”.

The hypothetical upland development scenario posed for the purpose of examining the potential for these riparian areas to transform N originating in upland ground water recharge was simple but yielded some valuable insights (Table 3.11). The estimated average annual flux of N to the shallow root zone (where a host of N transformation pathways exist) of the riparian ecosystem as a result of ET demand ranged from 3% (Site A) to 80% (Site B) of the average annual load to the upland. This pathway was greater than or equal to the estimated loss of NO_3^-–N through ground water denitrification within 10 m of the stream that ranged from 8% (Site C) to 21% (Site A). At all sites, within 10 m of the stream, denitrification was N-limited along one or more pathways, as was ET of ground water that had lost NO_3^-–N through denitrification.

The riparian N budget suggests the importance of including the third dimension, i.e., longitudinal flow, in studies of riparian ground water denitrification. In addition, this study demonstrated the potential importance of riparian ET in riparian-stream NO_3^-–N dynamics. In addition, the low contribution of these sites to stream flow during periods of active ET suggest that non-hydric and glacial till settings provide a large portion of the base flow, and it is therefore critical to maximize infiltration in developed upland areas throughout the watershed through mechanisms such as low impact development.

In light of riparian zones as ET focal points, it is particularly important to maintain their hydrologic integrity. All of the riparian areas in this study had hydric (i.e., wetland) soils, associated with a frequently high water table, where ET is rarely limited. At non-hydric riparian sites the water table is, by definition, lower. In New England a deeper water table, regardless of soil texture, leads to reduced annual ET due to irregular rainfall, causing drought stress (Acreman et al., 2003). In sandy non-hydric soils, the unsaturated zone above the water table can develop unsaturated hydraulic conductivities that are markedly lower than saturated hydraulic conductivities. The coarser the media, the more dramatic the difference between saturated and unsaturated hydraulic conductivity, and the sharper the drop with decreasing moisture (Hillel, 1998). In non-hydric riparian sites the low unsaturated hydraulic conductivity limits upwelling from the underlying water table. As a result, non-hydric riparian areas with permeable, sandy soils are expected to have periods of limited ET due to unsaturated soils between the root zone and water table.

Any alterations that reduce ET at these hydric riparian sites would increase the risk of ground water NO_3^-–N flux towards the stream by eliminating a valuable and potentially sizeable ground water NO_3^-–N sink. As pointed out by Gold and Kellogg (1997) depth to the water table can have a dramatic effect on the upwelling of ground water in response to ET. Riparian areas where the water table has been lowered by increased urbanization in the watershed (Groffman et al., 2002) cannot meet evaporative demand, reducing ET, and increasing the risk of ground water movement directly to streams.

Further investigations are clearly warranted to better define and characterize the riparian hydrologic balance. In particular, piezometric data needs to be collected and modeled during periods of high water table, but in the absence of ET, i.e., late November, to gain a clearer understanding of the magnitude in the shift of riparian flow paths. In addition, studies should be conducted to explore the potential for deep-rooted vegetation, such as trees and shrubs, to maintain ET longer than shallow-rooted grassy vegetation, in the presence of a lowered water table, with implications for riparian buffer management.

ACKNOWLEDGEMENTS

The authors thank Adam Rosenblatt for field assistance; URI Coastal Fellows Gina Ferendo, Drew Grande, Tom Liddy, Mike St. Pierre, and Tara Watson for laboratory and field assistance; URI Watershed Hydrology laboratory assistants Kate Banick, Chelsea Coker, Edwin Requintina, and Emily Troiano, for lab and field assistance; Carl Sawyer for technical assistance; Gary Speiran at the U.S. Geological Survey for his insights on riparian ground water flow; and all landowners for generously allowing us to maintain study sites on their land. This research was supported by USDA NRICGP Grant no. 99-35102-8266. This paper is a contribution of the Rhode Island Agricultural Experiment Station and the Institute of Ecosystem Studies.

REFERENCES

Acreman, M.C., R.J. Harding, C.R. Lloyd, and D.D. McNeil. 2003. Evaporation characteristics of wetlands: experience from a wet grassland and a reedbed using eddy correlation measurements. *Hydrology and Earth System Sciences* 7:11-21.

Anderson, M.G., and P.E. Kneale. 1982. The influence of low-angled topography on hillslope soil-water convergence and stream discharge. *Journal of Hydrology* 57:65-80.

Angier, J., G. McCarty, C. Rice, and K. Bialek. 2004. Riparian ecosystems and buffers: multi-scale structure, function, and management. *Proceedings of the American Water Resources Association Summer Specialty Conference*. June 28-30, 2004. Olympic Valley, CA.. American Water Resources Association, Middleburg, VA.

Baker, M.E., M.J. Wiley, and P.W. Seelbach. 2001. GIS-based hydrologic modeling of riparian areas: implications for stream water quality. *Journal of the American Water Resources Association* 37:1615-1628.

Blazejewski, G. 2003. *Carbon in riparian zone subsoil: morphology and spatial distribution.* M.S. thesis. University of Rhode Island, Kingston.

Bosch, D.D., R.K. Hubbard, L.T. West, and R.R. Lowrance. 1994. Subsurface flow patterns in a riparian buffer system. *Transactions of the American Society of Agricultural Engineers* 37:1783-1790.

Bosch, D.D., J.M. Sheridan, and R.R. Lowrance. 1996. Hydraulic gradients and flow rates of a shallow coastal plain aquifer in a forested riparian buffer. *Transactions of the American Society of Agricultural Engineers* 39:865-871.

Burns, D.A., P.S. Murdoch, and G.B. Lawrence. 1998. Effect of groundwater springs on NO_3^- concentrations during summer in Catskill Mountain streams. *Water Resources Research* 34:1987-1996.

Burt, T.P. 1997. The hydrological role of floodplains within the drainage basin system. Pages 21–32 *in* N.E. Haycock, T. Burt, K. Goulding, and G. Pinay, eds. *Buffer zones: their processes and potential in water protection*. Quest Environmental, Harpenden, UK.

Burt, T.P., L.S. Matchett, K.W.T. Goulding, C.P. Webster, and N.E. Haycock. 1999. Denitrification in riparian buffer zones: the role of floodplain hydrology. *Hydrological Processes* 13:1451-1463.

Burt, T.P., G. Pinay, F.E. Matheson, N.E. Haycock, A. Butturini, J.C. Clément, S. Danielescu, D.J. Dowrick, M.M. Hefting, A. Hillbricht-Ilkowska, and V. Maître. 2002. Water table fluctuations in the riparian zone: comparative results from a pan-European experiment. *Journal of Hydrology* 265:129-148.

Cey, E.E., D.L. Rudolph, R. Aravena, and G. Parkin. 1999. Role of the riparian zone in controlling the distribution and fate of agricultural nitrogen near a small stream in southern Ontario. *Journal of Contaminant Hydrology* 37:45-67.

Clément, J-C., L. Aquilina, O. Bour, K. Plaine, T.P. Burt, and G. Pinay. 2003. Hydrological flowpaths and nitrate removal rates within a riparian floodplain along a fourth-order stream in Brittany (France). *Hydrological Processes* 17:1177-1195.

Correll, D.L. 1997. Buffer zones and water quality protection: general principles. Pages 7–20 *in* N.E. Haycock, T. Burt, K. Goulding, and G. Pinay, eds. *Buffer zones: their processes and potential in water protection*. Quest Environmental, Harpenden, UK.

Correll, D.L. 2000. The current status of our knowledge of riparian buffer water quality functions. Pages 5–10 *in* P.J. Wigington, Jr., and R.L. Beschta, eds. *Proceedings of the International Conference on Riparian Ecology and Management in Multi-Land Use Watersheds*, Portland, OR. August 27–31, 2000. American Water Resources Association, Middleburg, VA.

Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. *Journal of Environmental Quality* 29:1075-1084.

Dickerman, D.C., J.D. Kliever, and J.R. Stone. 1997. *Hydrogeology, water quality, and simulation of ground-water-development alternatives in the Usqueaug-Queen ground-water reservoir, southern Rhode Island*. U.S. Geological Survey Water-Resources Investigations Report 97-4126. United States Geological Survey, Providence, RI.

Flite, O.P., III, R.D. Shannon, R.R. Schnabel, and R.R. Parizek. 2001. Nitrate removal in a riparian wetland of the Appalachian Valley and Ridge physiographic province. *Journal of Environmental Quality* 30:254-261.

Freeze, R. A., and J. A. Cherry. 1979. *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, NJ.

Gold, A.J., P.M. Groffman, K. Addy, D.Q. Kellogg, M. Stolt, and A.E. Rosenblatt. 2001. Landscape attributes as controls on ground water nitrate removal capacity of riparian zones. *Journal of the American Water Resources Association* 37:1457-1464.

Gold, A.J., and D.Q. Kellogg. 1997. Modelling internal processes of riparian buffer zones. Pages 192—207 *in* N.E. Haycock, T. Burt, K. Goulding, and G. Pinay, eds. *Buffer zones: their processes and potential in water protection*. Quest Environmental, Harpenden, UK.

Gold, A., T. Weaver, E. Porter, and J. Opaluch. 1988. Potential water use conflicts generated by irrigated agriculture in Rhode Island. *Northeastern Journal of Agriculture and Resource Economics* 17:8-14.

Groffman, P.M., N.J. Boulware, W.C. Zipperer, R.V. Pouyat, L.E. Band, and M.F. Colosimo. 2002. Soil nitrogen cycle processes in urban riparian zones. *Environmental Science & Technology* 36:4547-4552.

Groffman, P.M., A.J. Gold, and R.C. Simmons. 1992. Nitrate dynamics in riparian forests: microbial studies. *Journal of Environmental Quality* 21:666–671.

Groffman, P.M., G. Howard, A.J. Gold, and W.M. Nelson. 1996. Microbial nitrate processing in shallow groundwater in a riparian forest. *Journal of Environmental Quality* 25:1309–1316.

Hayashi, M., G. van der Kamp, and D.L. Rudolph. 1998. Water and solute transfer between a prairie wetland and adjacent uplands, 1. Water balance. *Journal of Hydrology* 207:42-55.

Haycock, N.E., and T.P. Burt. 1993. Role of floodplain sediments in reducing the nitrate concentration of subsurface run-off: a case study in the Cotswolds, UK. *Hydrological Processes* 7:287-295.

Hill, A.R. 1990. Ground water flow paths in relation to nitrogen chemistry in the near-stream zone. *Hydrobiologia* 206:39-52.

Hill, A.R. 1991. A ground water nitrogen budget for a headwater swamp in an area of permanent ground water discharge. *Biogeochemistry* 14:209-224.

Hill, A.R., K.J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and organic carbon. *Biogeochemistry* 51:193-223.

Hill, A.R., P.G.F. Vidon, and J. Langat. 2004. Denitrification potential in relation to lithology in five headwater riparian zones. *Journal of Environmental Quality* 33:911-919.

Hillel, D. 1998. *Environmental soil physics*. Academic Press, San Diego, CA.

Howarth, R.W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch, and Z. Zhao-Liang. 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Biogeochemistry* 35:75-139.

Jensen, M.E., R.D. Burman, and R.G. Allen (eds.). 1990. *Evapotranspiration and irrigation water requirements*. ASCE Manuals and Reports on Engineering Practice No. 70. American Society of Civil Engineers, New York, NY.

Jordan, T.E., D.L. Correll, and D.E. Weller. 1997. Relating nutrient discharges from watersheds to land use and streamflow variability. *Water Resources Research* 33:2579-2590.

Joubert, L., D.Q. Kellogg, and A.J. Gold. 1996. Watershed nonpoint assessment and nutrient loading using the Geographic Information System-based MANAGE method. Pages 144-149 *in Proceedings of Watershed '96*, Baltimore, MD. June 8 – 12, 1996. U.S. Environmental Protection Agency.

Kelliher, F.M., R. Leuning, and E.-D. Schulze. 1993. Evaporation and canopy characteristics of coniferous forests and grasslands. *Oecologia* 95:153-163.

Kellogg, D.Q., A.J. Gold, P.M. Groffman, K.Addy, M.H. Stolt, and G. Blazejewski. 2005. In situ ground water denitrification in stratified, permeable soils underlying riparian wetlands. *Journal of Environmental Quality* 34:524-533.

Kellogg, D.Q., L. Joubert, and A.J. Gold. 1997. MANAGE: A Method for Assessment, Nutrient-loading, And Geographic Evaluation of Nonpoint Pollution. University of Rhode Island Cooperative Extension, Department of Natural Resources Science. Kingston, RI. Retrieved12/12/05 from http://www.uri.edu/ce/wq/mtp/html/man_fs.html.

Lowrance, R., L.S. Altier, J.D. Newbold, R.R. Schnabel, P.M. Groffman, J.M. Denver, D.L. Correll, J.W. Gilliam, J.L. Robinson, R.B. Brinsfield, K.W. Staver, W. Lucas, A.H. Todd. 1997. Water quality functions of riparian forest buffers in Chesapeake Bay watersheds. *Environmental Management* 21:687-712.

Lowrance, R.R., R.L. Todd, and L.E. Asmussen. 1983. Waterborne nutrient budgets for the riparian zone of an agricultural watershed. *Agriculture, Ecosystems and Environment* 10:371-384.

Maître, V., A.C. Cosandey, E. Desagher, and A. Parriaux. 2003. Effectiveness of groundwater nitrate removal in a river riparian area: the importance of hydrogeological conditions. *Journal of Hydrology* 278:76-93.

Maître, V., A.C. Cosandey, A. Parriaux, and C. Guenat. 2005. A methodology to estimate the denitrifying capacity of a riparian wetland. *Journal of Environmental Quality* 34:707-716.

McGlynn, B.L., and J. Seibert. 2003. Distributed assessment of contributing area and riparian buffering along stream networks. *Water Resources Research* 39, 1082, doi:10.1029/2002WR001521.

National Academy of Sciences. 2000. *Clean coastal waters: understanding and reducing the effects of nutrient pollution*. National Academy Press, Washington, DC.

Nelson, W.M., A.J. Gold, and P.M. Groffman. 1995. Spatial and temporal variation in groundwater nitrate removal in a riparian forest. *Journal of Environmental Quality* 24:691-699.

Norton, M.M., and T.R. Fisher. 2000. The effects of forest on stream water quality in two coastal plain watersheds of the Chesapeake Bay. *Ecological Engineering* 14:337-362.

Pinay, G., C. Ruffinoni, and A. Fabre. 1995. Nitrogen cycling in two riparian forest soils under different geomorphic conditions. *Biogeochemistry* 30:9-29.

Puckett, L.J. and T.K. Cowdery. 2002. Transport and fate of nitrate in a glacial outwash aquifer in relation to ground water age, land use practices and redox processes. *Journal of Environmental Quality* 31:782-796.

Puckett, L.J., T.K. Cowdery, P.B. McMahon, L.H. Tornes, and J.D. Stoner. 2002. Using chemical, hydrologic, and age dating analysis to delineate redox processes and flow paths in the riparian zone of a glacial outwash aquifer-stream system. *Water Resources Research* 38, 10.1029/2001WR000396.

Quinn, J.M., P.M. Brown, W. Boyce, S. Mackay, A. Taylor, and T. Fenton. 2001. Riparian zone classification for management of stream water quality and ecosystem health. *Journal of the American Water Resources Association* 37:1509-1515.

Rosenblatt, A.E., A.J. Gold, M.H. Stolt, P.M. Groffman, and D.Q. Kellogg. 2001. Identifying riparian sinks for watershed nitrate using soil surveys. *Journal of Environmental Quality* 30:1596–1604.

Sabater, S., A. Butturini, J-C. Clément, T. Burt, D. Dowrick, M. Hefting, V. Maître, G. Pinay, C. Postolache, M. Rzepecki, and F. Sabater. 2003. Nitrogen removal by riparian buffers along a European climatic gradient: patterns and factors of variation. *Ecosystems* 6:20-30.

Schiff, S.L., K.J. Devito, R.J. Elgood, P.M. McCrindle, J. Spoelstra, and P. Dillon. 2002. Two adjacent forested catchments: dramatically different NO_3^- export. *Water Resources Research* 38, No. 12, 1292, doi:10.1029/2000WR000170.

Schilling, K., and Y-K Zhang. 2004. Baseflow contribution to nitrate-nitrogen export from a large, agricultural watershed, USA. *Journal of Hydrology* 295:305-316.

Schnabel, R.R., and W.L. Stout. 1994. Denitrification losses from two Pennsylvania floodplain soils. *Journal of Environmental Quality* 23:344–348.

Simmons, R.C., A.J. Gold, and P.M. Groffman. 1992. Nitrate dynamics in riparian forests: Groundwater studies. *Journal of Environmental Quality* 21:659-665.

Smith, R.L., J.K. Böhlke, S.P. Garabedian, K.M. Revesz, and T. Yoshinari. 2004. Assessing denitrification in groundwater using natural gradient tracer tests with ^{15}N: in situ measurement of a sequential multistep reaction. *Water Resources Research* 40, W07101, doi:10.1029/2003WR002919.

U.S. Geological Survey. 1999. *The quality of our nation's waters: nutrients and pesticides*. U.S. Geological Survey Circular 1225. United States Geological Survey, Reston, VA.

U.S. Geological Survey. 2005. *Water quality samples for Rhode Island, USGS 01118500 Pawcatuck River at Westerly, RI*. Retrieved 7/15/05 from http://nwis.waterdata.usgs.gov/ri/nwis/qwdata?site_no=01118500&agency_cd=USGS&format=inventory_retrieval.

Vidon, P.G.F., and A.R. Hill. 2004a. Landscape controls on nitrate removal in stream riparian zones. *Water Resources Research* 40, W03201, doi:10.1029/2003WR02473.

Vidon, P.G.F., and A.R. Hill. 2004b. Landscape controls on the hydrology of stream riparian zones. *Journal of Hydrology* 292:210-228.

Vidon, P., and A.R. Hill. 2004c. Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology. *Biogeochemistry* 71:259-283.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G. Likens, P. Matson, D.W. Schindler, W.H. Schlesinger, and D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications* 7:737-750.

Warwick, J. and A.R. Hill. 1988. Nitrate depletion in the riparian zone of a small woodland stream. *Hydrobiologia* 157:231-240.

Waterloo Hydrologic Inc. 1997. *FLONET/TRANS v3.1 User Guide*. Waterloo Centre for Groundwater Research, Waterloo, Ont.

Wigington, P.J., Jr., S.M. Griffith, J.A. Field, J.E. Baham, W.R. Horwath, J. Owen, J.H. Davis, S.C. Rain, and J.J. Steiner. 2003. Nitrate removal effectiveness of a riparian buffer along a small agricultural stream in western Oregon. *Journal of Environmental Quality*. 32:162-170.

Willems, H.P.L., M.D. Rotelli, D.F. Berry, E.P. Smith, R.B. Reneau, Jr., and S. Mostaghimi. 1997. Nitrate removal in riparian wetland soils: effects of flow rate, temperature, nitrate concentration and soil depth. *Water Research* 31:841-849.

Winter, T.C., J.W. Harvey, O.L. Franke, and W.M. Alley. 1999. *Ground water and surface water: a single resource*. U. S. Geological Survey Circular 1139. United States Geological Survey, Denver, CO.

BIBLIOGRAPHY

Acreman, M.C., R.J. Harding, C.R. Lloyd, and D.D. McNeil. 2003. Evaporation characteristics of wetlands: experience from a wet grassland and a reedbed using eddy correlation measurements. *Hydrology and Earth System Sciences* 7:11-21.

Addy, K.L., A.J. Gold, P.M. Groffman, and P.A. Jacinthe. 1999. Ground water nitrate removal in subsoil of forested and mowed riparian buffer zones. *Journal of Environmental Quality* 28:962-970.

Addy, K.L., D.Q. Kellogg, A.J. Gold, P.M. Groffman, G. Ferendo, and C. Sawyer. 2002. In situ push-pull method to determine ground water denitrification in riparian zones. *Journal of Environmental Quality* 31:1017–1024.

Aelion, C.M., and J.N. Shaw. 2000. Denitrification in South Carolina (USA) coastal plain aquatic sediments. *Journal of Environmental Quality* 29:1696-1703.

American Public Health Association. 1998. *Standard methods for the examination of water and wastewater*. American Public Health Association, Washington, DC.

Anderson, M.G., and P.E. Kneale. 1982. The influence of low-angled topography on hillslope soil-water convergence and stream discharge. *Journal of Hydrology* 57:65-80.

Angier, J., G. McCarty, C. Rice, and K. Bialek. 2004. Riparian ecosystems and buffers: multi-scale structure, function, and management. *Proceedings of the American Water Resources Association Summer Specialty Conference*. June

28-30, 2004. Olympic Valley, CA.. American Water Resources Association, Middleburg, VA.

Baker, M.E., M.J. Wiley, and P.W. Seelbach. 2001. GIS-based hydrologic modeling of riparian areas: implications for stream water quality. *Journal of the American Water Resources Association* 37:1615-1628.

Balderston, W.L., B. Sherr, and W.J. Payne. 1976. Blockage of acetylene of nitrous oxide reduction in *Pseudomonas perfectomarinus*. *Applied and Environmental Microbiology* 31:504-508.

Blazejewski, G. 2003. *Carbon in riparian zone subsoils: morphology and spatial distribution.* M.S. thesis. University of Rhode Island, Kingston.

Bosch, D.D., R.K. Hubbard, L.T. West, and R.R. Lowrance. 1994. Subsurface flow patterns in a riparian buffer system. *Transactions of the American Society of Agricultural Engineers* 37:1783-1790.

Bosch, D.D., J.M. Sheridan, and R.R. Lowrance. 1996. Hydraulic gradients and flow rates of a shallow coastal plain aquifer in a forested riparian buffer. *Transactions of the American Society of Agricultural Engineers* 39:865-871.

Bradley, P.M., M. Fernandez, Jr., and F.H. Chapelle. 1992. Carbon limitation of denitrification rates in an anaerobic ground water system. *Environmental Science & Technology* 6:2377–2381.

Burns, D.A., P.S. Murdoch, and G.B. Lawrence. 1998. Effect of groundwater springs on NO_3^- concentrations during summer in Catskill Mountain streams. *Water Resources Research* 34:1987-1996.

Burt, T.P. 1997. The hydrological role of floodplains within the drainage basin system. Pages 21–32 *in* N.E. Haycock, T. Burt, K. Goulding, and G. Pinay, eds. *Buffer zones: their processes and potential in water protection*. Quest Environmental, Harpenden, UK.

Burt, T.P., L.S. Matchett, K.W.T. Goulding, C.P. Webster, and N.E. Haycock. 1999. Denitrification in riparian buffer zones: the role of floodplain hydrology. *Hydrological Processes* 13:1451–1463.

Burt, T.P., G. Pinay, F.E. Matheson, N.E. Haycock, A. Butturini, J.C. Clément, S. Danielescu, D.J. Dowrick, M.M. Hefting, A. Hillbricht-Ilkowska, and V. Maître. 2002. Water table fluctuations in the riparian zone: comparative results from a pan-European experiment. *Journal of Hydrology* 265:129-148.

Cey, E.E., D.L. Rudolph, R. Aravena, and G. Parkin. 1999. Role of the riparian zone in controlling the distribution and fate of agricultural nitrogen near a small stream in southern Ontario. *Journal of Contaminant Hydrology* 37:45–67.

Christensen, S., P. Groffman, A. Mosier, and D.R. Zak. 1990. Rhizosphere denitrification: a minor process but indicator of decomposition activity. Pages 199-211 *in* N.P. Revsbech and J. Sorensen, eds. *Denitrification in soil and sediment*. Plenum Press, New York.

Christensen, S., S. Simkins, and J.M. Tiedje. 1990. Temporal patterns of soil denitrification: their stability and causes. *Soil Science Society of America Journal* 54:1614-1618.

Cirmo, C.P., and J.J. McDonnell. 1997. Linking the hydrologic and biochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review. *Journal of Hydrology (Amsterdam)* 199:88–120.

Clausen, J.C., K. Guillard, C.M. Sigmund, and K. Martin Dors. 2000. Water quality changes from riparian buffer restoration in Connecticut. *Journal of Environmental Quality* 29:1751-1761.

Clément, J-C., L. Aquilina, O. Bour, K. Plaine, T.P. Burt, and G. Pinay. 2003. Hydrological flowpaths and nitrate removal rates within a riparian floodplain along a fourth-order stream in Brittany (France). *Hydrological Processes* 17:1177-1195.

Clément, J.C., G. Pinay, and P. Marmonier. 2002. Seasonal dynamics of denitrification along topohydrosequences in three different riparian wetlands. *Journal of Environmental Quality* 31:1025–1037.

Correll, D.L. 1997. Buffer zones and water quality protection: General principles. Pages 7-20 *in* N.E. Haycock, T. Burt, K. Goulding, and G. Pinay, eds. *Buffer zones: their processes and potential in water protection*. Quest Environmental, Harpenden, UK.

Correll, D.L. 2000. The current status of our knowledge of riparian buffer water quality functions. Pages 5–10 *in* P.J. Wigington, Jr., and R.L. Beschta, eds. *Proceedings of the International Conference on Riparian Ecology and Management in Multi-Land Use Watersheds*, Portland, OR. August 27–31, 2000. American Water Resources Association, Middleburg, VA.

Davidson, E.A., and M.K. Firestone. 1988. Measurement of nitrous oxide dissolved in soil solution. *Soil Science Society of America Journal* 52:1201-1203.

Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. *Journal of Environmental Quality* 39:1075-1084.

Diaz, R.J. 2001. Overview of hypoxia around the world. *Journal of Environmental Quality* 30:275–281.

Dickerman, D.C., J.D. Kliever, and J.R. Stone. 1997. *Hydrogeology, water quality, and simulation of ground-water-development alternatives in the Usqueaug-Queen ground-water reservoir, southern Rhode Island*. U.S. Geological Survey Water-Resources Investigations Report 97-4126. United States Geological Survey, Providence, RI.

Flite, O.P., III, R.D. Shannon, R.R. Schnabel, and R.R. Parizek. 2001. Nitrate removal in a riparian wetland of the Appalachian valley and ridge physiographic province. *Journal of Environmental Quality* 30:254–261.

Freeze, R.A., and J.A. Cherry. 1979. *Groundwater.* Prentice Hall, Englewood Cliffs, NJ.

Fustec, E., A. Mariotti, X. Grillo, and J. Sajus. 1991. Nitrate removal by denitrification in alluvial ground water: role of a former channel. *Journal of Hydrology (Amsterdam)* 123:337–354.

Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. Pages 383–411 *in* A. Klute, ed. *Methods of soil analysis. Part 1. Physical and mineralogical* *methods, 2nd ed.* Agronomy Monograph 9. American Society of Agronomy and Soil Science Society of America, Madison, WI.

Gold, A.J., P.M. Groffman, K. Addy, D.Q. Kellogg, M. Stolt, and A.E. Rosenblatt. 2001. Landscape attributes as controls on ground water nitrate removal capacity of riparian zones. *Journal of the American Water Resources Association* 37:1457–1464.

Gold, A.J., P.A. Jacinthe, P.M. Groffman, W.R. Wright, and R.H. Puffer. 1998. Patchiness in groundwater nitrate removal in a riparian forest. *Journal of Environmental Quality* 27:146-155.

Gold, A.J., and D.Q. Kellogg. 1997. Modelling internal processes of riparian buffer zones. Pages 192—207 *in* N.E. Haycock, T. Burt, K. Goulding, and G. Pinay, eds. *Buffer zones: their processes and potential in water protection*. Quest Environmental, Harpenden, UK.

Gold, A., T. Weaver, E. Porter, and J. Opaluch. 1988. Potential water use conflicts generated by irrigated agriculture in Rhode Island. *Northeastern Journal of Agriculture and Resource Economics* 17:8-14.

Goolsby, D.A., W.A. Battaglin, B.T. Aulenbach, and R.P. Hopper. 2001. Nitrogen input to the Gulf of Mexico. *Journal of Environmental Quality* 30:329–336.

Groffman, P.M. 1987. Nitrification and denitrification in soil: a comparison of incubation, enzyme assay and enumeration techniques. *Plant and Soil* 97:445–450.

Groffman, P.M., N.J. Boulware, W.C. Zipperer, R.V. Pouyat, L.E. Band, and M.F. Colosimo. 2002. Soil nitrogen cycle processes in urban riparian zones. *Environmental Science & Technology* 36:4547-4552.

Groffman, P.M., A.J. Gold, and K. Addy. 2000. Nitrous oxide production in riparian zones and its importance to national emission inventories. *Chemosphere-Global Change Science* 2:291-299.

Groffman, P.M., A.J. Gold, and R.C. Simmons. 1992. Nitrate dynamics in riparian forests: microbial studies. *Journal of Environmental Quality* 21:666–671.

Groffman, P.M., E. Holland, D.D. Myrold, G.P. Robertson, and X. Zou. 1999. Denitrification. Pages 272-288 *in* G.P. Robertson, C.S. Bledsoe, D.C. Coleman, and P. Sollins, eds. *Standard soil methods for long term ecological research*. Oxford University Press, New York.

Groffman, P.M., G. Howard, A.J. Gold, and W.M. Nelson. 1996. Microbial nitrate processing in shallow groundwater in a riparian forest. *Journal of Environmental Quality* 25:1309-1316.

Hayashi, M., G. van der Kamp, and D.L. Rudolph. 1998. Water and solute transfer between a prairie wetland and adjacent uplands, 1. Water balance. *Journal of Hydrology* 207:42-55.

Haycock, N.E., and T.P. Burt. 1993. Role of floodplain sediments in reducing the nitrate concentration of subsurface runoff: a case study in the Cotswolds, UK. *Hydrological Processes* 7:287–295.

Haycock, N.E., and G. Pinay. 1993. Groundwater nitrate dynamics in grass and poplar vegetated riparian buffer strips during the winter. *Journal of Environmental Quality* 22:273-278.

Hedin, L.O., J.C. von Fischer, N.E. Ostrom, B.P. Kennedy, M.G. Brown, and G.P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. *Ecology* 79:684–703.

Hill, A.R. 1990. Ground water flow paths in relation to nitrogen chemistry in the near-stream zone. *Hydrobiologia* 206:39-52.

Hill, A.R. 1991. A ground water nitrogen budget for a headwater swamp in an area of permanent ground water discharge. *Biogeochemistry* 14:209-224.

Hill, A. 1996. Nitrate removal in stream riparian zones. *Journal of Environmental Quality* 25:743-755.

Hill, A.R., and M. Cardaci. 2004. Denitrification and organic carbon availability in riparian wetland soils and subsurface sediments. *Soil Science Society of America Journal* 68:320–325.

Hill, A.R., K.J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and organic carbon. *Biogeochemistry* 51:193-223.

Hill, A.R., P.G.F. Vidon, and J. Langat. 2004. Denitrification potential in relation to lithology in five headwater riparian zones. *Journal of Environmental Quality* 33:911–919.

Hillel, D. 1998. *Environmental soil physics*. Academic Press, San Diego, CA.

Howarth, R. 1988. Nutrient limitation of net primary production in marine ecosystems. *Annual Review of Ecology and Systematics* 19:89–110.

Howarth, R.W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch, and Z. Zhao-Liang. 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. *Biogeochemistry* 35:75–139.

Istok, J.D., M.D. Humphrey, M.H. Schroth, M.R. Hyman, and K.T. O'Reilly. 1997. Single-well, "push-pull" test for in situ determination of microbial activities. *Ground Water* 35:619-631.

Jacinthe, P.A., P.M. Groffman, A.J. Gold, and A. Mosier. 1998. Patchiness in microbial nitrogen transformations in groundwater in a riparian forest. *Journal of Environmental Quality* 27:156-164.

Jacobs, T.C., and J.W. Gilliam. 1985. Riparian losses of nitrate from agricultural drainage waters. *Journal of Environmental Quality* 14:472-478.

Jensen, M.E., R.D. Burman, and R.G. Allen (eds.). 1990. *Evapotranspiration and irrigation water requirements*. ASCE Manuals and Reports on Engineering Practice No. 70. American Society of Civil Engineers, New York, NY.

Jones, J.B., and P.J. Mulholland. 2000. *Streams and ground waters*. Academic Press, San Diego, CA.

Jordan, T.E., D.L. Correll, and D.E. Weller. 1997. Effects of agriculture on discharges of nutrients from coastal plain watersheds of Chesapeake Bay. *Journal of Environmental Quality* 26:836–848.

Jordan, T.E., D.L. Correll, and D.E. Weller. 1997. Relating nutrient discharges from watersheds to land use and streamflow variability. *Water Resources Research* 33:2579-2590.

Joubert, L., D.Q. Kellogg, and A.J. Gold. 1996. Watershed nonpoint assessment and nutrient loading using the Geographic Information System-based MANAGE method. Pages 144-149 *in Proceedings of Watershed '96*, Baltimore, MD. June 8 – 12, 1996. U.S. Environmental Protection Agency.

Kelliher, F.M., R. Leuning, and E.-D. Schulze. 1993. Evaporation and canopy characteristics of coniferous forests and grasslands. *Oecologia* 95:153-163.

Kellogg, D.Q., A.J. Gold, P.M. Groffman, K.Addy, M.H. Stolt, and G. Blazejewski. 2005. In situ ground water denitrification in stratified, permeable soils underlying riparian wetlands. *Journal of Environmental Quality* 34:524-533.

Kellogg, D.Q., L. Joubert, and A.J. Gold. 1997. MANAGE: A Method for Assessment, Nutrient-loading, And Geographic Evaluation of Nonpoint Pollution. University of Rhode Island Cooperative Extension, Department of Natural Resources Science. Kingston, RI. Retrieved 12/12/05 from http://www.uri.edu/ce/wq/mtp/html/man_fs.html.

Kilmer, V.J., and L.T. Alexander. 1949. Methods of making analyses of soils. *Soil Science* 68:15–24.

Kung, K.-J.S. 1990. Influence of plant uptake on the performance of bromide tracer. *Soil Science Society of America Journal* 54:975-979.

Lemon, E. 1981. Nitrous oxide in freshwaters of the Great Lakes Basin. *Limnology and Oceanography* 26:867-879.

Leopold, L.B., M.G. Wolman, and J.P. Miller. 1992. *Fluvial processes in geomorphology*. Dover Publications, New York.

Lowrance, R. 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. *Journal of Environmental Quality* 21:401-405.

Lowrance, R., L.S. Altier, J.D. Newbold, R.R. Schnabel, P.M. Groffman, J.M. Denver, D.L. Correll, J.W. Gilliam, J.L. Robinson, R.B. Brinsfield, K.W. Staver, W. Lucas, and A.H. Todd. 1997. Water quality functions of riparian forest buffers in Chesapeake Bay watersheds. *Environmental Management* 21:687–712.

Lowrance, R.R., R.L. Todd, and L.E. Asmussen. 1983. Waterborne nutrient budgets for the riparian zone of an agricultural watershed. *Agriculture, Ecosystems and Environment* 10:371-384.

Lowrance, R., G. Vellidis, and R.K. Hubbard. 1995. Denitrification in a restored riparian forest wetland. *Journal of Environmental Quality* 24:808-815.

Maître, V., A.C. Cosandey, E. Desagher, and A. Parriaux. 2003. Effectiveness of groundwater nitrate removal in a river riparian area: the importance of hydrogeological conditions. *Journal of Hydrology* 278:76-93.

Maître, V., A.C. Cosandey, A. Parriaux, and C. Guenat. 2005. A methodology to estimate the denitrifying capacity of a riparian wetland. *Journal of Environmental Quality* 34:707-716.

Martin, K., L.L. Parsons, R.E. Murray, and M.S. Smith. 1988. Dynamics of soil denitrifier populations: relationships between enzyme activity, most probable number counts, and actual N gas loss. *Applied and Environmental Microbiology* 54:2711–2716.

McClain, M.E., E.W. Boyer, C.L. Dent, S.E. Gergel, N.B. Grimm, P.M. Groffman, S.C. Hart, J.W. Harvey, C.A. Johnston, E. Mayorga, W.H. McDowell, and G. Pinay. 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems* 6:301–312.

McGlynn, B.L., and J. Seibert. 2003. Distributed assessment of contributing area and riparian buffering along stream networks. *Water Resources Research* 39, 1082, doi:10.1029/2002WR001521.

McHale, M.R., J.J. McDonnell, M.J. Mitchell, and C.P. Cirmo. 2002. A field-based study of soil water and groundwater nitrate release in an Adirondack forested watershed. *Water Resources Research* 38:2-1 to 2-17.

Mosier, A.R., and L. Klemedtsson. 1994. Measuring denitrification in the field. Pages 1047-1065 *in* R.W. Weaver, S. Angle, P. Bottomley, D. Bezdicek, S. Smith, A. Tabatabai, et al., eds. *Methods of soil analysis, Part 2: Microbiological and biochemical properties, 2nd ed.* Soil Science Society of America Book Series 5. Soil Science Society of America, Madison, WI.

Mosier, A.R., and D.S. Schimel. 1993. Nitrification and denitrification. Pages 181-208 *in* R. Knowles and T.H. Blackburn, eds. *Nitrogen isotope techniques*. Academic Press, Orlando, FL.

Myrold, D.D., and J.M. Tiedje. 1985. Establishment of denitrification capacity in soil: Effects of carbon, nitrate and moisture. *Soil Biology and Biochemistry* 17:819–822.

National Academy of Sciences. 2000. *Clean coastal waters: understanding and reducing the effects of nutrient pollution*. National Academy Press, Washington, DC.

Nelson, W.M., A.J. Gold, and P.M. Groffman. 1995. Spatial and temporal variation in groundwater nitrate removal in a riparian forest. *Journal of Environmental Quality* 24:691-699.

Nixon, S.W., B. Buckley, S. Granger, and J. Bintz. 2001. Responses of a very shallow marine ecosystem to nutrient enrichment. *Human and Ecological Risk Assessment* 7:1457–1481.

Norton, M.M., and T.R. Fisher. 2000. The effects of forest on stream water quality in two coastal plain watersheds of the Chesapeake Bay. *Ecological Engineering* 14:337–362.

Orth, R.J., and K.A. Moore. 1983. Chesapeake Bay: An unprecedented decline in submerged aquatic vegetation. *Science (Washington, DC)* 222:51–53.

Osborne, L.L., and D.A. Kovacic. 1993. Riparian vegetated buffer strips in water quality restoration and stream management. *Freshwater Biology* 29:243-258.

Ott, R.L. 1993. *An introduction to statistical methods and data analysis, 4th ed.* Duxbury Press, Belmont, CA.

Parkin, T.B. 1987. Soil microsites as a source of denitrification variability. *Soil Science Society of America Journal* 51:1194-1199.

Parsons, L.L., R.E. Murray, and M.S. Smith. 1991. Soil denitrification dynamics: spatial and temporal variations of enzyme activity, populations, and nitrogen gas loss. *Soil Science Society of America Journal* 55:90–95.

Payne, W.J. 1981. *Denitrification*. John Wiley & Sons, New York.

Peterjohn, W.T., and D.L. Correll. 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. *Ecology* 65:1466-1475.

Pinay, G., V.J. Black, A.M. Planty-Tabacchi, B. Gumiero, and H. Decamps. 2000. Geomorphic control of denitrification in large river floodplain soils. *Biogeochemistry* 50:163–182.

Pinay, G., C. Ruffinoni, and A. Fabre. 1995. Nitrogen cycling in two riparian forest soils under different geomorphic conditions. *Biogeochemistry* 30:9–29.

Puckett, L.J. and T.K. Cowdery. 2002. Transport and fate of nitrate in a glacial outwash aquifer in relation to ground water age, land use practices and redox processes. *Journal of Environmental Quality* 31:782-796.

Puckett, L.J., T.K. Cowdery, P.B. McMahon, L.H. Tornes, and J.D. Stoner. 2002. Using chemical, hydrologic, and age dating analysis to delineate redox processes and flow paths in the riparian zone of a glacial outwash aquifer-stream system. *Water Resources Research* 38, 10.1029/2001WR000396.

Quinn, J.M., P.M. Brown, W. Boyce, S. Mackay, A. Taylor, and T. Fenton. 2001. Riparian zone classification for management of stream water quality and ecosystem health. *Journal of the American Water Resources Association* 37:1509-1515.

Rabalais, N.N., R.E. Turner, and W.J. Wiseman, Jr. 2001. Hypoxia in the Gulf of Mexico. *Journal of Environmental Quality* 30:320–329.

Rector, D.D. 1981. *Soil survey of Rhode Island*. United States Department of Agriculture - Soil Conservation Service, in cooperation with the Rhode Island Agricultural Experiment Station, Washington, DC.

Robertson, W.D., J.A. Cherry, and E.A. Sudicky. 1991. Ground-water contamination from two small septic systems on sand aquifers. *Ground Water* 29:82–92.

Rosenblatt, A.E., A.J. Gold, M.H. Stolt, P.M. Groffman, and D.Q. Kellogg. 2001. Identifying riparian sinks for watershed nitrate using soil surveys. *Journal of Environmental Quality* 30:1596–1604.

Ryther, J.H., and W.M. Dunstan. 1971. Nitrogen, phosphorus, and eutrophication in the coastal marine environment. *Science (Washington, DC)* 171:1008–1013.

Sabater, S., A. Butturini, J-C. Clément, T. Burt, D. Dowrick, M. Hefting, V. Maître, G. Pinay, C. Postolache, M. Rzepecki, and F. Sabater. 2003. Nitrogen removal by riparian buffers along a European climatic gradient: patterns and factors of variation. *Ecosystems* 6:20-30.

Schiff, S.L., K.J. Devito, R.J. Elgood, P.M. McCrindle, J. Spoelstra, and P. Dillon. 2002. Two adjacent forested catchments: dramatically different NO_3^- export. *Water Resources Research* 38, No. 12, 1292, doi:10.1029/2000WR000170.

Schilling, K., and Y-K Zhang. 2004. Baseflow contribution to nitrate-nitrogen export from a large, agricultural watershed, USA. *Journal of Hydrology* 295:305-316.

Schipper, L., and M. Vojvodic-Vukovic. 1998. Nitrate removal from groundwater using a denitrification wall amended with sawdust: field trial. *Journal of Environmental Quality* 27:664-668.

Schnabel, R.R., L.F. Cornish, W.L. Stout, and J.A. Schaffer. 1996. Denitrification in a grassed and a wooded, valley and ridge, riparian ecotone. *Journal of Environmental Quality* 25:1230-1235.

Schnabel, R.R., and W.L. Stout. 1994. Denitrification losses from two Pennsylvania floodplain soils. *Journal of Environmental Quality* 23:344–348.

Schultz, R.C., J.P. Colletti, T.M. Isenhart, W.W. Simpkins, C.W. Mize, and M.L. Thompson. 1995. Design and placement of a multi-species riparian buffer strip system. *Agroforestry Systems* 29:201-226.

Short, F.T., and D.M. Burdick. 1996. Quantifying eelgrass habitat loss in relation to housing development and nitrogen loading in Waquoit Bay, Massachusetts. *Estuaries* 19:730–739.

Simmons, R.C., A.J. Gold, and P.M. Groffman. 1992. Nitrate dynamics in riparian forests: groundwater studies. *Journal of Environmental Quality* 21:656-665.

Smith, M.S., and L.L. Parsons. 1985. Persistence of denitrifying enzyme activity in dried soils. *Applied and Environmental Microbiology* 49:316–320.

Smith, R.L., J.K. Böhlke, S.P. Garabedian, K.M. Revesz, and T. Yoshinari. 2004. Assessing denitrification in groundwater using natural gradient tracer tests with ^{15}N: in situ measurement of a sequential multistep reaction. *Water Resources Research* 40, W07101, doi:10.1029/2003WR002919.

Smith, R.L., and J.H. Duff. 1988. Denitrification in a sand and gravel aquifer. *Applied and Environmental Microbiology* 54:1071–1078.

Smith, R.L., S.P. Garabedian, and M.H. Brooks. 1996. Comparison of denitrification activity measurements in groundwater using cores and natural-gradient tracer tests. *Environmental Science and Technology* 30:3448-3456.

Smith, R.L., B.L. Howes, and S.P. Garabedian. 1991. In situ measurement of methane oxidation in groundwater by using natural-gradient tracer tests. *Applied Environmental Microbiology* 57:1997-2004.

Starr, J.L., A.M. Sadeghi, T.B. Parkin, and J.J. Meisinger. 1996. A tracer test to determine the fate of nitrate in shallow groundwater. *Journal of Environmental Quality* 25:917-923.

Starr, R.C., and R.W. Gillham. 1993. Denitrification and organic carbon availability in two aquifers. *Ground Water* 31:934–947.

StatSoft. 1999. *Statistica for Windows*. StatSoft, Tulsa, OK.

StatSoft. 2002. *Statistica 6.0*. StatSoft, Tulsa, OK.

Steinheimer, T.R., K.D. Scoggin, and L.A. Kramer. 1998. Agricultural chemical movement through a field-size watershed in Iowa: surface hydrology and nitrate losses in discharge. *Environmental Science & Technology* 32:1048–1052.

Tiedje, J.M. 1982. Denitrification. Pages 1011-1025 *in* A.L. Page, R.H. Miller, and D.R. Keeney, eds. *Methods of soil analysis, Part 2: Chemical and microbiological properties, 2nd ed.* Agronomy Monograph 9. American Society of Agronomy & Soil Science Society of America, Madison, WI.

Troeh, F.R., and L.M. Thompson. 1993. *Soils and soil fertility, 5th ed*. Oxford University Press, New York.

Trudell, M.R., R.W. Gillham, and J.A. Cherry. 1986. An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. *Journal of Hydrology* 83:251-268.

U.S. Geological Survey. 1999. *The quality of our nation's waters: nutrients and pesticides*. U.S. Geological Survey Circular 1225. United States Geological Survey, Reston, VA.

U.S. Geological Survey. 2005. *Water quality samples for Rhode Island, USGS 01118500 Pawcatuck River at Westerly, RI*. Retrieved 7/15/05 from http://nwis.waterdata.usgs.gov/ri/nwis/qwdata?site_no=01118500&agency_cd=USGS&format=inventory_retrieval.

Valiela, I. 1995. *Marine ecological processes, 2nd ed.* Springer-Verlag, New York.

Verchot, L.V., E.C. Franklin, and J.S. Gilliam. 1997. Nitrogen cycling in Piedmont vegetated filter zones: II. Subsurface nitrate removal. *Journal of Environmental Quality* 26:337-347.

Vidon, P.G.F., and A.R. Hill. 2004a. Landscape controls on nitrate removal in stream riparian zones. *Water Resources Research* 40, W03201, doi:10.1029/2003WR002473.

Vidon, P.G.F., and A.R. Hill. 2004b. Landscape controls on the hydrology of stream riparian zones. *Journal of Hydrology* 292:210-228.

Vidon, P., and A.R. Hill. 2004c. Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology. *Biogeochemistry* 71:259-283.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G. Likens, P. Matson, D.W. Schindler, W.H. Schlesinger, and D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications* 7:737-750.

Warwick, J., and A.R. Hill. 1988. Nitrate depletion in the riparian zone of a small woodland stream. *Hydrobiologia* 157:231–240.

Waterloo Hydrologic Inc. 1997. *FLONET/TRANS v3.1 User Guide*. Waterloo Centre for Groundwater Research, Waterloo, Ont.

Whitmer, S., L. Baker, and R. Wass. 2000. Loss of bromide in a wetland tracer experiment. *Journal of Environmental Quality* 29:2043-2045.

Wigington, P.J., Jr., S.M. Griffith, J.A. Field, J.E. Baham, W.R. Horwath, J. Owen, J.H. Davis, S.C. Rain, and J.J. Steiner. 2003. Nitrate removal effectiveness of a riparian buffer along a small agricultural stream in western Oregon. *Journal of Environmental Quality*. 32:162-170.

Willems, H.P.L., M.D. Rotelli, D.F. Berry, E.P. Smith, R.B. Reneau, Jr., and S. Mostaghimi. 1997. Nitrate removal in riparian wetland soils: effects of flow rate, temperature, nitrate concentration and soil depth. *Water Research* 31:841–849.

Wilson, R.D., and D.M. Mackay. 1993. The use of sulfur hexafluoride as a conservative tracer in saturated sandy media. *Ground Water* 31:719-724.

Wilson, R.D., and D.M. Mackay. 1996. SF_6 as a conservative tracer in a saturated media with high intragranular porosity or high organic carbon content. *Ground Water* 34:241-249.

Winter, T.C., J.W. Harvey, O.L. Franke, and W.M. Alley. 1999. *Ground water and surface water: a single resource*. U. S. Geological Survey Circular 1139. United States Geological Survey, Denver, CO.

Winter, T.C., J.W. LaBaugh, and D.O. Rosenberry. 1988. The design and use of a hydraulic potentiomanometer for direct measurement of differences in hydraulic head between groundwater and surface water. *Limnology and Oceanography* 33:1209-1214.

Yoshinari, T. and R. Knowles. 1976. Acetylene inhibition of nitrous oxide reduction by denitrifying bacteria. *Biochemical and Biophysical Research Communications* 69:705-710.