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GROUNDWATER NITRATE REMOVAL IN
FORESTED AND SUBURBAN VEGETATED RIPARIAN WETLAND SOILS:
A MESOCOSM MASS BALANCE APPROACH

BY
KELLY L. ADDY

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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1997

MASTER OF SCIENCE THESIS

OF

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APPROVED:

Thesis Committee

Major Professor

DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND

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ABSTRACT

Although riparian zones can remove nitrate (NO_3^-) from groundwater, the interaction between vegetation type, subsurface patches of elevated organic matter, and NO_3^- removal rates is still uncertain. The goal of my study was to examine the effects of vegetation type on groundwater NO_3^- removal rates in poorly drained riparian subsoils with four treatments, two “forested” and two “suburban” treatments. I also examined the variability in NO_3^- removal rates between riparian sites and the relationship between patches of elevated organic matter in the subsoil and groundwater NO_3^- removal rates. My study was based on a mesocosm approach to simulate NO_3^- dynamics in the shallow groundwater. These mesocosms were obtained from paired forested and suburban (mowed vegetation dominated by non-woody species) vegetated areas at two different sites. Intact horizontal mesocosms (15 cm diam., 40 cm long PVC cores) were extracted from fine to medium textured sands. The soils were derived from stratified glacial drift and were classified as Typic humaquepts or Umbric endoaquods. At each site, I obtained mesocosms from at least 35 cm below the dormant season water table depth. These mesocosms were placed in a controlled environmental chamber and continuously dosed with bromide and NO_3^- amended groundwater for 71 days. Mass balance calculations were completed to determine the rate of groundwater NO_3^- -N removal from each saturated mesocosm.

There was no significant difference in groundwater NO_3^- removal rates between forested and suburban vegetated areas within sites. However, there were significant

differences in groundwater NO_3^- removal rates between sites. Groundwater NO_3^- removal rates were correlated with the total mass of carbon contained within small, amorphous or root-like, dark-stained patches of elevated organic matter. By determining the mean mass of patch per mesocosm per treatment, these patches were found to constitute 0.5 to 16.8 % of the mesocosm mass. There was a significant correlation between dry mass of roots and mass of patch material C contained within mesocosms.

The inflow groundwater contained negligible concentrations of ammonium-N (NH_4^+ -N). However, NH_4^+ -N was observed in the outflow of eleven of twelve mesocosms. NH_4^+ -N was found in the outflow groundwater even before NO_3^- amendments were commenced. This suggests that the NH_4^+ was generated within the mesocosms and was produced by mineralization of pools of organic N within the mesocosms rather than by dissimilatory reduction of NO_3^- . Temporal and treatment related trends in NH_4^+ generation were not the same as NO_3^- -N removal trends indicating that different processes are responsible for the fate of each form of N.

The existing type of vegetation cover did not influence groundwater NO_3^- removal; rather the quantity and/or quality of subsoil patches of elevated organic matter appear to be a critical factor in NO_3^- removal from groundwater in vegetated riparian zones. These results suggest that the NO_3^- abatement function of vegetated riparian zones is not limited to native forest ecosystems. Further investigations on the linkage between vegetation type, subsurface patches of elevated organic matter, and groundwater N removal are warranted. However, suburban vegetated riparian zones may prove useful for limiting the export of NO_3^- from watersheds.

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PREFACE

This thesis is organized into the manuscript format as described in the guidelines on thesis preparation of the URI Graduate School. The body of the text is divided into four sections, corresponding to the format of journal articles. The appendices contain a literature review of related topics, an addendum to methods, all pertinent field and laboratory data, and a complete bibliography.

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INTRODUCTION

Nitrate (NO_3^-) is the most commonly detected groundwater pollutant in wells in the United States (US EPA, 1990). NO_3^- is a federally registered drinking water contaminant and at high concentrations can cause methemoglobinemia (blue-baby syndrome) in infants. NO_3^- also has been linked to eutrophication of coastal waters, and watershed management of nitrogen (N) is a major coastal issue (Ryther and Dunstan, 1971; Howarth et al., 1996; Jordan et al., 1997).

As a form of non-point source pollution, NO_3^- originates at diffuse sources, including septic systems and agricultural fields (Keeney, 1986; Gold et al., 1990; Weiskel and Howes, 1992). Researchers studying coastal watersheds ranging from local scales (1000 ha) to regional scales (Mississippi Basin) have found that less than one-third of the estimated net anthropogenic N input to watersheds is discharged to coastal waters (Jordan et al., 1997; Howarth et al., 1996). These studies suggest that we need additional research to identify and improve our understanding of watershed sinks of N.

Many studies have shown that riparian zones have the ability to remove NO_3^- from groundwater (Hill, 1996; Gilliam et al., 1997). Riparian zones are functionally defined as areas where energy and matter are exchanged between uplands and surface waters (Gregory, 1991). However, there is considerable uncertainty as to the relative importance of plant uptake and microbially mediated processes of groundwater NO_3^- removal and if the type of vegetation cover influences this removal (Korom, 1992; Gilliam, 1994; Hill, 1996; Gilliam et al., 1997).

Within riparian zones, there is considerable spatial variability in groundwater NO_3^- removal. Generally, denitrification activity is unevenly distributed throughout the soil, with the greatest activity occurring in uppermost soil horizons (Lind and Eiland, 1989; Ambus and Lowrance, 1991; Lowrance, 1992; McCarty and Bremner, 1992; Starr and Gillham, 1993; Lowrance et al., 1995). Numerous studies (Davidson and Swank, 1986; Groffman and Tiedje, 1989; Groffman et al., 1992; Simmons et al., 1992; Hanson et al., 1994; Nelson et al., 1995) have found that NO_3^- removal and denitrification activity are greater in poorly drained (PD) soils (wetland edge) than in moderately well drained soils (upland edge). PD soils are water-saturated for longer periods of time, promoting anaerobic conditions and the accumulation of organic matter, thus enhancing the potential for denitrification (Korom, 1992).

An interesting aspect of riparian zone research is the discrepancy between groundwater NO_3^- removal in companion field and laboratory microcosm studies. Microcosm laboratory studies using media from shallow aquifers have consistently found low denitrification rates (Pennock et al., 1992; Groffman et al., 1996). In contrast, high NO_3^- removal rates in shallow riparian groundwater have been observed in a large number of field studies based on groundwater well networks (Hill, 1996). The disparity between these studies may be due to plant NO_3^- uptake, which would not be included in the laboratory microcosm studies. In addition, differences in sample volume between field and laboratory studies may be responsible for such discrepancies. Laboratory measured microbial activity may not adequately represent field-measured activity because field studies encompass a greater extent of the heterogeneity of natural soils (Smith et al.,

1996). Parkin (1987) and Christensen et al. (1990a) postulate that the majority of denitrification in surface soils may occur in microsites or “hotspots” of organic matter that are often unevenly distributed through the soil. As sample volume increases, there is a greater chance of incorporating these hotspots of activity, and denitrification variability may decrease (Starr et al., 1995).

Recently, a laboratory mesocosm study (Gold et al., in review; Jacinthe et al., in review) with 12 kg of soil per mesocosm produced groundwater NO_3^- removal rates comparable to a riparian field study at the same site (Nelson et al., 1995). Mesocosms (“medium-sized worlds”) are intermediate between field and microcosm studies. Mesocosms are samples large enough to incorporate the natural physical and biological heterogeneity of soil but still small enough to manipulate under controlled experimental conditions (Odum, 1983). In contrast to this mesocosm study, microcosms with less than 50 g of subsoil showed negligible removal rates at these sites (Groffman et al., 1996). In the mesocosm study, PD sites exhibited high groundwater NO_3^- removal and contained dark-stained patches of elevated organic matter. Moderately well drained mesocosms displayed no groundwater NO_3^- removal and did not contain any such patches.

Most recent riparian zone research has focused on forested areas (Lowrance et al., 1984; Peterjohn and Correll, 1984; Ambus and Lowrance, 1991; Lowrance, 1992; Simmons et al., 1992; Hanson et al., 1994; Nelson et al., 1995; Groffman et al., 1996; Starr et al., 1996; Gold et al., in review; Jacinthe et al., in review). As a result of these studies, it is generally accepted that forested riparian zones have the ability to serve as N sinks. Fewer studies have examined the difference in N removal between forested and

non-forested riparian zones (Haycock and Pinay, 1993; Osbourne and Kovacic, 1993; Lowrance et al, 1995; Schnabel et al., 1996). Grassed riparian sites have often been found to have lower N removal rates than forested riparian sites, but in a few instances, substantial removal has been observed in grassed riparian sites. More studies are needed to determine whether there are substantial differences in groundwater N removal between forested and non-forested riparian subsoils.

There is great interest by policy makers in using riparian zones to protect water quality. Restoration of vegetated riparian zones may play a critical role in the mitigation of N loading from both agricultural and unsewered suburban development. I suggest that riparian zone restoration and maintenance programs may meet with greater success if the landowner has flexibility in the use and design of the riparian area (Desbonnet et al., 1994). In developed suburban areas, riparian zones may obtain greater support if the public can use the riparian area for a variety of purposes, including nature walking, picnicking, and obtaining a scenic view of an adjacent waterbody (Desbonnet et al., 1994). Therefore, an obvious question arises: within a riparian zone, can a mix (“suburban” vegetation) of lawn, shrubs, and trees maintain the same extent of groundwater N removal as forested areas? The answer to this question will have great implications in the development of many riparian zone management plans.

The goal of my study was to examine the effects of vegetation type on groundwater NO_3^- removal in the subsoil of PD riparian zones. The carbon available for microbial activity from different vegetation types may differ both quantitatively and qualitatively (McKenney et al., 1995). I hypothesize that greater amounts of groundwater

NO_3^- will be removed from forested riparian areas than suburban vegetated riparian areas because forests may generate deeper roots that may create more patches of elevated organic matter in subsoils to facilitate denitrification in groundwater.

My study was based on a saturated mesocosm approach. These mesocosms were obtained from paired forested vegetated and suburban vegetated areas at two different riparian sites. Since the groundwater NO_3^- in these saturated mesocosms was not subjected to plant uptake, only microbially mediated removal processes were examined.

Objectives

The specific objectives of this study were:

- 1) to compare groundwater NO_3^- removal rates between forested and suburban vegetated riparian areas;
- 2) to explore variability in groundwater NO_3^- removal rates between sites of similar soils, drainage, and vegetation;
- 3) to investigate the relationship between subsoil patches of elevated organic matter and groundwater NO_3^- removal rates within the shallow groundwater of vegetated riparian zones.

METHODS

Overview of Methods

I created saturated mesocosms to simulate shallow aquifer dynamics in forested and suburban riparian zones. The mesocosms consisted of large, undisturbed soil cores (15 cm diam., 40 cm long Schedule 35 PVC pipe) obtained from the upper portion of the saturated zone. The mesocosms received a constant inflow of groundwater amended with Bromide (Br^-) and NO_3^- -N at a 1:1 ratio for 71 days. N loss within the saturated mesocosms was determined by a mass balance approach, based on the difference between the inflow and outflow mass of NO_3^- -N over the entire study. At the conclusion of the study, I related the extent of patches of elevated organic matter within the mesocosms to observed N losses.

Site Characterization

Two study sites, “North Kingstown” and “Charlestown,” were selected for this project. At each site, I selected two different vegetated areas, “suburban” and “forested.” The four treatments in my study were:

1. North Kingstown site, suburban vegetated area
2. North Kingstown site, forested vegetated area
3. Charlestown site, suburban vegetated area
4. Charlestown site, forested vegetated area

Suburban areas abutted forested areas. Suburban areas were defined as areas that were at

least 5 m away from the adjacent forest and were dominated by mowed non-woody emergent vegetation, such as grasses and sedges. Within each site the paired suburban and forested vegetated riparian areas were similar in soil type and hydrology.

One criterion in site selection was that all sites be located in PD soils, since PD riparian soils have been shown to have a substantial capacity for NO_3^- removal (Nelson et al., 1995). At each site, intensive field soil surveys were performed to delineate the extent of PD soils. I also sought sites with glacial outwash parent material of fine to medium sands at depths below the seasonal high water table. Finer textured soil media tend to have low hydraulic conductivities and often generate surface seeps that negate the importance of groundwater removal process investigations in these areas. Coarser soil media also would not have been suitable for this study because it would have made the core extraction procedure more difficult.

We dug three pits in the suburban area and three pits in the forested area at both the North Kingstown and Charlestown sites. One core was extracted from each pit. I conducted detailed soil morphological investigations at each pit (Appendix C). I recorded thickness and depth of O, A, B, and C horizons in each pit. Within each of these horizons, I described the soil texture, soil color, and boundary divisions. Samples of matrix material in O, B, and C horizons and patches of elevated organic matter found below 50 cm from the surface were collected and stored at 4 °C to be used later for analyses of texture, percent moisture, percent carbon (C), and additional tests for a companion study on microbial processes.

North Kingstown Site

Setting

The first study site is located in North Kingstown, Rhode Island in the Pettaquamscutt watershed (41°32'N, 71°28') (Fig. 1). The site drains to a first order tributary of Silver Spring Lake. The site is approximately 75 m from the tributary. The site consists of two abutting vegetated areas: a suburban backyard and a hardwood forest (Fig. 2). The soil at both areas consists of PD outwash material. Surface water from both the suburban and forested areas drains to a vernal pool located within the forested area.

Geology and Soils

The surficial geology of the North Kingstown site is composed of glaciofluvial deposits with 0-3% slopes. Soils are classified as Typic humaquepts. The pH of the C horizon was 4.6 and 6.0 at the forested area and the suburban area, respectively.

Vegetation

The mowed suburban area is dominated by sedges (*Carex sp.*), a variety of mosses, violets (*Viola sp.*), dandelions (*Taraxacum officinale*), and clover (*Trifolium sp.*). This area was deforested approximately 80 years ago. Mowing occurs at least every 2 weeks during the summer. Fringing the backyard on two sides are several red maple trees (*Acer rubrum*) (18-23 cm diam.) and a few common sassafras trees (*Sassafras varifolium*) (25-42 cm diam.). Pits dug in this suburban area were at least 5 m away from trees (Fig. 2). However, when digging the pits, we observed tree roots and smelled a sassafras aroma as sassafras roots were cut. Portions of each pit lay below the canopy of the neighboring trees

Figure 1. Location of North Kingstown, RI riparian zone study site (source: USGS topographic map, 7.5 minute Wickford quadrangle, scale: 1:24000). General location is within the box. At the owners' request, the exact location is not identified.

Figure 2. Plan view schematic of the North Kingstown study site showing location of vegetated areas and position of soil pits. One undisturbed horizontal mesocosm was obtained 67.5 cm below the surface in each soil pit.

North Kingstown Study Site

North Kingstown Suburban Area

North Kingstown Red Maple Forested Area

(all forested pits are within 1 m of woody vegetation)

Note: Figure not drawn to scale

The dominant overstory species of the North Kingstown forested area is red maple (8-27 cm diam.). Trees are approximately 0.5 to 3 m apart. The average age of the overstory trees was between 40 and 45 years. Forest understory species include royal fern (*Osmunda regalis*), spice bush (*Lindera benzoin*), viburnum (*Viburnum sp.*), poison ivy (*Rhus radicans*), sweet pepperbush (*Clethra alnifolia*), red maple saplings, and a few young oak saplings (*Quercus sp.*). The pits in this forested area were positioned within 1 m of woody vegetation (Fig. 2).

Charlestown Site

Setting

The second study site is located in Charlestown, Rhode Island in the Pawcatuck watershed (41°22'N, 71°42') (Fig. 3). The site drains into Tanyard Brook, a first order tributary of Watchaug Pond. The site is approximately 75 m from the brook. The site is separated from a personal residence by a road that was built upon deposited fill materials. The suburban area is closest to the road (Fig. 4). From about 1960 to 1980, this site was used as a large garden. Horse manure was applied as the principal form of fertilizer. The garden was then abandoned in the early 1980's. A portion of the site reverted back to forest and another portion was managed by mowing.

Geology and Soils

The surficial geology of this site is composed of glaciofluvial deposits with 0-3% slopes. The soils in the suburban area are classified as Typic humaquepts, but the soils in the forested area are classified as Umbric endoaquods. The only difference between these two soils is that the latter has a 5 cm thick Bh layer, an illuviation of organic matter.

Figure 3. Location of Charlestown, RI riparian zone study site (source: USGS topographic map, 7.5 minute Carolina and Quonochontaug quadrangles, scale: 1:24000). General location is within the box. At the owners' request, the exact location is not identified.

Figure 4. Plan view schematic of the Charlestown study site showing location of vegetated areas and position of soil pits. One undisturbed horizontal mesocosm was obtained 57.5 cm below the surface in each soil pit.

Charlestown Study Site

immediately above the C horizon. The pH of the C horizon was 6.5 and 7.0 at the forested area and the suburban area, respectively.

Vegetation

The mowed suburban area is dominated by emergent vegetation, including bluegrass (*Poa sp.*), Brome grass (*Bromus inermis*), tussock sedge (*Carex stricta*), beaked sedge (*Carex rostrata*), cinnamon fern (*Osmunda cinnamomea*), sensitive fern (*Onoclea sensibilis*), bedstraw (*Galium sp.*), horsetail (*Equisetum sp.*), white clover (*Trifolium repens*), and very young red maple and speckled alder saplings (*Alnus rugosa*). Mowing occurs twice a year. Pits within the suburban area were dug at least 6 m from the forest edge (Fig. 4). The pits were not located below the canopy of the adjacent forest.

Speckled alder (8-16 cm diam.) dominates the overstory of the Charlestown forested area. The overstory speckled alder trees were approximately 18 to 23 years old. The understory includes red maple saplings, spice bush, skunk cabbage (*Symplocarpus foetidus*), sensitive fern, viburnum, royal fern, cinnamon fern, sweet pepperbush, and blueberry (*Vaccinium corymbosum*). Pits in this area were dug only 1 to 1.5 m within the forest because the PD section of the forest was a fairly narrow strip. Pits were dug within 1 m of woody vegetation in this forested area (Fig. 4).

Groundwater Monitoring and Sampling

Water table wells, consisting of slotted 3.8 cm diam. PVC pipe, were installed at the North Kingstown forested area, at the North Kingstown suburban area, and midway between the suburban and forested pits at the Charlestown location. I measured the depth

to the water table using a stick and measuring tape. The water table depth was measured approximately every 1-2 weeks in spring and summer months and every 3-4 weeks in fall and winter months (Appendix D). I took groundwater samples from each well once in the summer of 1996. Wells were purged, samples extracted with a vacuum pump, and then the samples were stored at 4 °C in acid-washed bottles for later analysis of background NO_3^- -N concentration at each site. Groundwater dissolved oxygen concentrations were measured periodically within the water table wells with a YSI dissolved oxygen/temperature model 55 meter. The groundwater dissolved oxygen content was 2.0 mg L⁻¹ and 2.1 mg L⁻¹ at the North Kingstown and Charlestown sites, respectively.

Core Extraction

Three replicate, horizontal soil cores (15 cm diam., 40 cm long Schedule 35 PVC pipe) were taken from each forested and suburban area (6 cores per site). One pit was dug for each core extracted. We dug pits to the approximate dimensions of 90 cm by 120 cm by 90 cm deep. We randomly located three pits within each forested and suburban area. Each pit was at least 2 m away from the adjacent pit. Cores were extracted in July and August of 1996 at the low annual water table to obtain media at least 30 cm below the dormant season water table level of the area. When possible, cores were extracted on the same day as the pits were dug, but the pit was not exposed longer than 5 days before the core was extracted.

We extracted cores horizontally from a randomly selected side of the pit by pressing the core into the soil with an 8 ton hydraulic jack (Appendix B). At the North

Kingstown site, we extracted cores from a depth of 67.5 cm (midpoint of the core) from the surface. We extracted Charlestown cores from a depth of 57.5 cm (midpoint of the core) because an elevated water table prevented deeper extraction. Extracted cores were stored at 4 °C.

A slight bias may have been introduced into the forested cores when we selected which side of the pit to extract cores. Cores were not directed into the side of a pit immediately below a main tree trunk. However, pit selection was not biased by tree distribution; we used hacksaws to cut through large tree roots close to the surface. Therefore, it was possible to extract cores relatively close to trees within forested areas. We did not find impenetrable, thick tree roots at core extraction depths, 50-75 cm below the ground's surface.

Experimental Design

Once all 12 cores were extracted, I transported them to the Institute of Ecosystem Studies (IES) in Millbrook, NY in August of 1996 where the experiment was completed. At IES, I capped both ends of the cores with flat PVC end-caps. Above a 1 cm PVC spacer in the interior of the cap, the soil within the core rested on a 1/8 in. circular plexiglass plate with a series of 1/8 in. holes drilled into it. Before placement in the cap, I wrapped this permeable plexiglass plate in nylon to act as a coarse filter and stabilize the soil within the core. I screwed one 1/16 in. polypropylene adapter into each cap within the spacer section. I then attached the caps to the cores with silicone. To allow the silicone to dry, the cores were stored at room temperature overnight.

Throughout dosing, the mesocosms sat vertically in a controlled climate chamber maintained at a constant temperature of 13 °C (Fig. 5). This temperature represents the groundwater temperature observed in a riparian forest in November when the water table is expected to inundate the sampling location (Nelson, 1995). An Ismatec multi-channel peristaltic pump (Cole Palmer, IL) continuously pumped dosed groundwater from four 10 L carboys (wrapped in aluminum foil to prevent light penetration) into the bottom of each mesocosm through the adapter. Each carboy fed three mesocosms. Water exited the mesocosms through the adapter in the top cap. The water flowing out of the cap passed through a PVC enclosure with a silicone cell (Jacinthe & Dick, 1996) inside to collect gases (for a companion study on microbial processes) and then into an acid-washed container. The pumping rate was set to 234 ml day⁻¹. The mesocosms had an estimated pore volume of 2665 cm³ (bulk density=1.65 g cm⁻³; porosity=0.38) and an expected retention time of 11.4 days. Every 2 to 3 days, outflow volumes were recorded and representative samples were stored in 20 ml polyethylene scintillation vials. The samples were stored at 4 °C until analysis.

Dissolved oxygen (DO) concentrations were controlled in the storage carboys at 2 mg L⁻¹. This DO concentration was established by bubbling high-purity mixtures of O₂/Ar gas through the inflow solution. DO within the carboys was measured every 2-3 days and adjusted back to 2 mg L⁻¹ if needed. The majority of tubing in the set-up was stainless steel to prevent diffusion of atmospheric O₂ from entering the solution. A study using the same design determined that the DO concentration in the mesocosm outflow groundwater

Figure 5. Schematic of mesocosm dosing set-up with oxygen regulated inflow groundwater solution stored in a carboy and samplers for water and gas outflows. The mesocosm, identified as “soil” in the figure, is a column 15 cm diam. and 40 cm long. (Schematic by Pierre Jacinthe)

closely matched the set DO concentration of the inflow groundwater (Jacinthe et al., in review).

Groundwater Dosing

All mesocosms received the groundwater from the same source of amended groundwater. Groundwater was collected from a shallow well located in the PD soil drainage class at Peckham Farm, University of Rhode Island, Kingston, Rhode Island (Gold et al., in review). I pumped groundwater out of the well with a submersible drainage pump into 20 gal storage containers. These containers were stored at 4 °C until transport to IES where they were stored in the controlled climate chamber. The average ambient concentrations of Br^- and NO_3^- -N in this groundwater were 0.2 mg L^{-1} (the detection level) and 0.4 mg L^{-1} , respectively.

Deionized water was pumped through the mesocosms for seven days (days – 6 to 0) until the mesocosms were saturated and the outflow rate equaled the inflow rate. For the next 9 day period (days 1-9), groundwater amended with $5.2 \text{ mg L}^{-1} \text{ Br}^-$ (as KBr) was pumped through the mesocosms. This Br^- only dosing period was included to observe the extent of mineralized nitrogen within the mesocosms. The use of Br^- also served to document if preferential flow was occurring in the mesocosms. We carefully monitored Br^- concentrations to assure that high Br^- concentrations did not appear in the first several days following the inception of Br^- dosing.

For the following 71 days (days 10-80), the mesocosms received groundwater amended with $5.2 \text{ mg L}^{-1} \text{ Br}^-$ and $5.2 \text{ mg L}^{-1} \text{ NO}_3^-$ -N (as KNO_3). Addition of Br^- was

continued to ensure that the dosing concentration remained stable throughout this period. Due to a pump malfunction, flow through the mesocosms was suspended for 6 days (days 54-60).

After the 71 days of Br^- and NO_3^- -N dosing, unamended groundwater was pumped through all mesocosms for 36 days (days 81-116). This stage was completed to flush the amendments from the mesocosms. Flushing was deemed complete when Br^- concentrations dropped to negligible levels. In total, the mesocosms were dosed with groundwater for a total of 116 days.

The inflow and outflow groundwater was sampled every 2-3 days and representative samples were stored in 20 ml polyethylene scintillation vials at 4 °C. A total of 22 inflow groundwater samples from each carboy were analyzed for Br^- and NO_3^- -N. Five inflow groundwater samples from each carboy were also analyzed for NH_4^+ -N. A total of 40 outflow groundwater samples from each mesocosm were analyzed for Br^- and NO_3^- -N. 18 outflow groundwater samples from each mesocosm were also analyzed for NH_4^+ -N.

I also included a single “blank” in the experimental design to determine if NO_3^- removal occurred within the groundwater dosing system exclusive of the soil. This blank consisted of a 3 L acid-washed glass bottle connected to the peristaltic pump. This blank was added to the experimental design partway into the mesocosm Br^- and NO_3^- -N dosing period on day 17. The blank received the same groundwater doses as the aquifer mesocosms. Groundwater was pumped through the blank at the same flow rate as the mesocosm flow rate. The bottle was hooked into the system containing 3 L of

groundwater amended with $3 \text{ mg L}^{-1} \text{ Br}^-$ and $\text{NO}_3^- \text{-N}$. The 3 L bottle had an average retention time of 12.8 days. The outflow water from this bottle was sampled every 2-3 days and representative samples were stored in 20 ml polyethylene scintillation vials at 4°C .

Characterization of Mesocosms

Once the groundwater dosing of the mesocosms was complete (day 116), I disassembled the mesocosms. After draining for a few hours, the mesocosms were laid horizontally, and I cut a slit down one length of each mesocosm with a hand saw and pried off the caps. I pushed the soil out of the mesocosms in 5 cm intervals (8 intervals per 40 cm long mesocosm) for characterization. Within each interval, I separated visible roots and dark-stained patches of elevated organic matter from the matrix material. Roots, patches, and matrix material were weighed out separately and representative samples were stored at 4°C . In the Charlestown forested mesocosms, two of the three mesocosms contained portions of the Bh horizon. This Bh horizon was sampled along with the patch material. I traced the cross-sectional face of each interval of the mesocosms on clear transparencies, distinguishing between roots and stained organic matter patches, to help qualitatively describe the extent and shape of patch material. The characterization process extended over two days. I stored unsampled portions of the mesocosms at 4°C .

Analytical Methods

DO was measured with a Cole Palmer 1.2 cm diam. probe (Cole Palmer, Niles, IL).

Inflow and outflow water samples were stored at 4 °C until analysis. Samples were analyzed for NO_3^- -N and Br^- on a Dionex 2000 ion chromatograph (Dionex, Sunnyville, CA) and for NH_4^+ -N on an Alpkem 300 Rapid Flow Analyzer (RFA) (Alpkem Corp., 1986). Inflow groundwater samples were also prepared by potassium persulfate digestion and analyzed for total N on the Alpkem 300 RFA. Soil pit samples were analyzed for % C on a Carlo-Erba CNS analyzer, for percent moisture (Liu and Evett, 1997), and for texture (Troeh and Thompson, 1993). Matrix soil samples and plant roots taken directly from the mesocosms during final destructive sampling were also analyzed for percent moisture. We obtained the dry mass of soil and roots by drying the samples at 104 °C and 60 °C, respectively, for 24 hours. A companion study is underway to examine gas outflow from the soil mesocosms as well as to determine immobilization and microbial transformation rates in patch and matrix material from the mesocosms.

Mass Balance Calculations

NO_3^- removal within the mesocosms was determined using a mass balance approach. I obtained the daily inflow and outflow concentrations of NO_3^- -N on sampling dates and then used linear interpolation to estimate the daily concentrations on unsampled dates. Mass of NO_3^- -N entering the mesocosms per day was determined by:

$$\text{DailyINFLOW}_{\text{NO}_3\text{-N}} = [\text{NO}_3^-\text{-N}]_{\text{inflow}} \times Q \quad (1)$$

where

$\text{DailyINFLOW}_{\text{NO}_3\text{-N}}$ = mass of NO_3^- -N entering the mesocosm per day (mg d^{-1})

$[\text{NO}_3^-\text{-N}]_{\text{inflow}}$ = daily concentration of NO_3^- -N in the inflow solution (mg L^{-1})

Q = daily outflow volume per mesocosm (0.234 L d^{-1})

The total mass of NO_3^- -N ($\text{MassINFLOW}_{\text{NO}_3\text{-N}}$) that entered each mesocosm over 116 days of groundwater dosing was then determined as the sum of the daily inflow masses.

The mass of NO_3^- -N leaving each mesocosm per day was determined by:

$$\text{DailyOUT}_{\text{NO}_3\text{-N}} = [\text{NO}_3^-]_{\text{outflow}} \times Q \quad (2)$$

where

$\text{DailyOUT}_{\text{NO}_3\text{-N}}$ = mass of NO_3^- -N leaving the mesocosm (mg d^{-1})

$[\text{NO}_3^-]_{\text{outflow}}$ = daily concentration of NO_3^- -N in the outflow solution (mg L^{-1})

The total outflow mass of NO_3^- -N ($\text{MassOUT}_{\text{NO}_3\text{-N}}$) that left each mesocosm over the whole course of the experiment was then determined as the sum of the daily outflow masses.

The mass of groundwater NO_3^- -N removed or retained in the mesocosms was:

$$\text{MR}_{\text{NO}_3\text{-N}} = \text{MassINFLOW}_{\text{NO}_3\text{-N}} - \text{MassOUT}_{\text{NO}_3\text{-N}} \quad (3)$$

where

$\text{MR}_{\text{NO}_3\text{-N}}$ = the total mass of groundwater NO_3^- -N removed or retained in the mesocosms over 116 days of groundwater dosing (mg)

Outflow Br^- and NO_3^- -N concentrations versus time were also plotted for each mesocosm to examine the trends in NO_3^- removal (Appendix E).

In order to compare the mesocosm groundwater NO_3^- removal to other studies in the literature, I expressed groundwater NO_3^- removal as a rate:

$$\text{RR}_{\text{NO}_3\text{-N}} = [(\text{MR}_{\text{NO}_3\text{-N}})/(\text{Mass of Core} \times \text{Days})] \times (1,000,000) \quad (4)$$

where

RR_{NO_3-N} = estimated NO_3^- -N removal rate per mesocosm ($\mu g\ kg^{-1}\ d^{-1}$)

Mass of core = dry mass of core calculated from: core volume x dry bulk density =
11,663 g

Days = 116 days of groundwater dosing

Mass balance calculations for the blank were completed as for the mesocosms
except that:

$$MassOUT_{NO_3-N} = MassINFLOW_{NO_3-N} + \Delta MassBlank_{NO_3-N} \quad (5)$$

where:

$\Delta MassBlank_{NO_3-N}$ = mass of NO_3^- -N in this control at the beginning of blank dosing
minus the mass of NO_3^- -N in the blank at the end of the experiment.

The final outflow NO_3^- -N concentration from this control was $0.8\ mg\ L^{-1}$.

NO_3^- removal rate was compared to the total C estimates within the matrix and
patch material of each mesocosm. Total C in mesocosm matrix material was determined
by:

$$TC_{matrix} = \text{Dry Mass of Matrix within a mesocosm} \times (\%C_{matrix}/100) \quad (6)$$

where

TC_{matrix} = total C in matrix of each mesocosm (g)

$\%C_{matrix}$ = %C of matrix material

Mass of C in patch material (TC_{patch}) was determined in a similar fashion.

Mass balance calculations for NH_4^+ -N and NH_4^+ -N generation rates were
determined in a similar fashion to those for NO_3^- -N removal rates. I did not use linear
interpolation to estimate daily NH_4^+ -N concentrations since I analyzed fewer samples for

NH_4^+ -N. Rather, I divided the experimental days into 10 day intervals. I took the average NH_4^+ -N concentration from analyzed samples in each interval and used this value as the daily concentration value within that specific interval. I also plotted outflow NH_4^+ -N concentrations over time to determine if there were any patterns in NH_4^+ -N generation (Appendix F). To determine the net dissolved inorganic N (DIN) removal rate, the generation rate of NH_4^+ -N was subtracted from the removal rate of NO_3^- -N.

Data Analysis

Statistical analyses were performed on the NO_3^- -N removal rate data to determine significant differences between treatments. The Mann-Whitney U Test (Ott, 1993) for nonparametric data was conducted to determine significant differences in NO_3^- -N removal rates between forested and suburban areas at each site. The Mann-Whitney U Test was used because the sample sizes were small (only 3 replicates per treatment). No significant differences were found between forested and suburban areas; therefore, forested and suburban data were pooled at each site. Another Mann-Whitney U Test was then performed to determine significant differences in NO_3^- -N removal rates between North Kingstown and Charlestown sites. Similar Mann-Whitney U Tests were performed on NH_4^+ -N generation rates and net DIN removal rates.

I used Spearman's Rank Correlation test (Ott, 1993) to explore the relationship between:

1) NO_3^- -N removal rates and the mass of patch material C, 2) NO_3^- -N removal rates and the mass of matrix material C, 3) NO_3^- -N removal rates and the mass of total C in the mesocosms, 4) NO_3^- -N removal rates and the dry mass of roots in the mesocosms, and 5)

the mass of match material C and the dry mass of roots in the mesocosms. Spearman's Rank Correlation test was used because the data were not related linearly. All statistical analyses were performed on Statistica for Windows (StatSoft, Inc., Tulsa, OK). Differences and correlations were considered statistically significant at the $P < 0.05$ level.

RESULTS

Site Characteristics

Soil morphology differed between sites but was generally similar within sites (Table 1 and Appendix C). Mean depth to the C horizon differed significantly between sites, but not between vegetated areas at the same site. There was one distinct soil characteristic at the Charlestown forested area. This was the only site that contained a 5 cm thick Bh horizon, which is an illuvial accumulation of organic matter, just above the C horizon (Appendix C). Two out of three Charlestown forested mesocosms contained portions of this Bh horizon. Grain size distribution between sites and vegetated areas was very similar (Table 1). The effective diameter (d_{10}) of grain size had a small range, from 0.065 to 0.15 mm. Likewise the uniformity index varied very little, from 2.33 to 4.31. Background NO_3^- -N concentrations in groundwater at both sites were low, ranging from 0.065 to 0.585 mg L^{-1} (Table 1).

Water table dynamics differed between sites (Table 2 and Appendix D). During the 1996 growing season (May-October), the water table was consistently closer to the surface at the Charlestown site than at the North Kingstown site. However, there is evidence that the water table at the Charlestown site may typically drop further below the surface than the maximum 45 cm depth observed in the summer of 1996. This evidence is the presence of the Bh horizon, ranging in depths from 40.5 to 50 cm below the surface, at the Charlestown forested area. For this Bh horizon to form, I suggest that the water table typically falls to this depth for an extended period during the time of illuviation and that this water table is the barrier causing organic matter accumulation in this zone. As further

Table 1. Site characteristics of shallow riparian aquifers used as treatments in the mesocosm study. Values are mean (standard error).

Characteristic	Treatment			
	N.Kingstown Forested	N.Kingstown Suburban	Charlestown Forested	Charlestown Suburban
Sampling depth† (cm)‡	67.5	67.5	57.5	57.5
Average depth to C horizon (cm) ‡	61 (5.9)	60 (7.4)	53 (3.5)	45 (2.5)
Effective Diameter (d_{10} in mm)	0.065	0.085	0.090	0.150
Uniformity Index ($d_{60}:d_{10}$)	4.31	2.94	3.00	2.33
Background groundwater NO_3^- -N (mg L^{-1})	0.14	0.07	0.59	§

† Sampling depth reported as the center depth of 15 cm diam. horizontal cores during core extraction

‡ Depths reported as depths below the surface

§ Only one water table well was installed at the Charlestown site

Table 2. Water table characteristics of shallow riparian aquifers used as treatments in the mesocosm study. Values are mean (standard error).

	Treatment		
	N. Kingstown Forested	N. Kingstown Suburban	Charlestown site †
Mean 1996 growing season (May-Oct) water table depth (cm) ‡	66 (6.7)	71 (6.1)	31 (.4)
Maximum 1996 growing season water table depth (cm) ‡	104	107	45
Mean dormant season (Nov-April) water table depth (cm) ‡	5.3 (5.9)	23 (6.6)	22 (1.6)
Minimum dormant season water table depth (cm) ‡	Surface ponding	2.5	19
Mean 1997 growing season (May-July) water table depth (cm) ‡	59 (30.5)	21 §	42 (8.7)
Maximum 1997 growing season water table depth (cm) ‡	115	21 §	57

† Only one water table well was installed at the Charlestown site

‡ Depths reported at depths below the surface

§ The water table well at the North Kingstown suburban area was removed in May of 1997 after only one reading was made for the growing season on 1997

evidence, the average water table depth (42 cm) for May-July in 1997 and the maximum July 1997 water table depth (57 cm) were substantially deeper than these same characteristics in 1996.

Because the Charlestown site contained only one water table well, I was only able to compare water table depths between vegetated areas at the North Kingstown site. At the North Kingstown site, water table depths were similar between forested and suburban areas during the 1996 growing season. However, during the dormant season (November-April), the water table was generally closer to the surface at the North Kingstown forested area than at the North Kingstown suburban area. In addition, the forested area had water pooled on the surface during part of the dormant season. In the dormant season, water table dynamics at the Charlestown site were similar to those at the North Kingstown suburban area.

Flow Characteristics

The pattern and rate of flow through the saturated mesocosms can be characterized by the breakthrough of the conservative tracer, Br^- . Bypass flow or macropore flow did not occur in any of the mesocosms. No high Br^- concentration was observed in the outflow of any mesocosm during the first several days of dosing. Instead, there was a gradual increase in Br^- concentration over time (Fig. 6 and Appendix E). After one pore volume of outflow, the concentration of a conservative tracer in a homogeneous media is expected to be half the inflow concentration (Hillel, 1980). The 0.5 relative concentration (outflow concentration/inflow concentration, i.e. C/C_0) of Br^-

Figure 6. Outflow groundwater NO_3^- -N and Br^- concentrations of shallow riparian aquifer mesocosms. Dosing schedule: days 1-9: inflow amended with Br^- only; days 10-80: inflow amended with NO_3^- -N and Br^- ; days 81-116: inflow unamended. (A) Outflow NO_3^- -N concentrations were close to Br^- concentrations throughout dosing (after the initial lag due to NO_3^- -N additions beginning 9 days later). This indicates low rates of NO_3^- removal; (B) Outflow NO_3^- -N concentrations are substantially lower than Br^- concentrations. This indicates high rates of NO_3^- removal. The dip in NO_3^- -N concentration around day 61 corresponds with the pump shutdown (days 54-60).

North Kingstown Suburban Mesocosm #4

Charlestown Suburban Mesocosm #7

occurred after days 9 to 16 (0.74 to 1.40 pore volumes) of Br^- addition to the mesocosms, indicating very little retardance of flow or preferential flow through the mesocosms (Li and Ghodrati, 1994). There were no observable differences in between sites. This suggests that any differences in NO_3^- removal rates observed between mesocosms was the result of internal N processing as opposed to retention time.

Nitrate in Blank Treatment

No groundwater NO_3^- removal was observed in the blank treatment. Br^- and NO_3^- -N concentrations were not exactly at a 1:1 ratio since the groundwater itself contained a small amount of background NO_3^- -N, ranging from 0.3 to 0.4 mg L^{-1} (Fig. 7). Once the groundwater amendments were discontinued, the outflow NO_3^- -N and Br^- concentrations gradually declined to negligible levels. NO_3^- -N and Br^- concentrations did not completely flush from the blank. This lack of flushing may have occurred because the blank had a larger volume (3 L) and a corresponding longer retention time than the pore volume of the mesocosms (2.7 L). The absence of NO_3^- removal in the blank treatment indicates that any NO_3^- removal observed in mesocosm was due to processes within the mesocosm soil.

Groundwater Nitrate Removal Rates

There were no significant differences in groundwater NO_3^- -N removal rates between forested and suburban areas at either site (Fig. 8). Therefore, the removal rates from forested and suburban areas were pooled together at each site. The Charlestown site (mean: 40.6 $\mu\text{g kg}^{-1} \text{d}^{-1}$; S.E.: 4.4) had significantly higher groundwater NO_3^- -N removal

Figure 7. Outflow groundwater NO_3^- -N and Br^- concentrations from the blank treatment. Dosing schedule: days 17-80: inflow amended with NO_3^- -N and Br^- (initial concentration within the 3 L blank bottle was 3.0 mg L⁻¹ NO_3^- -N and Br^-); days 81-116: inflow unamended. There was no evidence of NO_3^- removal in the blank.

Blank Treated with Amendments

Figure 8. Groundwater NO_3^- -N removal rates from aquifer mesocosms taken from beneath poorly drained soils in forested and suburban vegetated riparian zones. Values are mean (standard error) of three replicate mesocosms per treatment over a 116 day experiment.

Mean Groundwater Nitrate-N Removal Rates Forested and Suburban Mesocosms

rates than the North Kingstown site (mean: $6.8 \mu\text{g kg}^{-1} \text{d}^{-1}$; S.E.: 3.9).

Patterns in Outflow Bromide and Nitrate Concentration

After Br^- amendments of groundwater were initiated (day 1), outflow Br^- concentrations gradually increased and stabilized at the inflow concentration (5.2 mg L^{-1}) (Fig. 6 and Appendix E). After groundwater amendments of Br^- stopped (day 80), the Br^- concentrations gradually declined. This rise and fall in concentration was fairly symmetrical. Br^- behaved conservatively in my study because the mass of Br^- pumped into the mesocosms was equal to the mass of Br^- in the outflow groundwater samples. In eight mesocosms, the final outflow Br^- concentrations (day 116) were below the detection level (0.2 mg L^{-1}); therefore, all Br^- was flushed out of these mesocosms. In the remaining four mesocosms, the final outflow Br^- concentrations (day 116) ranged from 0.4 to 0.6 mg L^{-1} indicating that most of the amendments were flushed from the mesocosms. Pumping of groundwater through the mesocosms should have continued for an additional day or two to completely flush the Br^- from the mesocosms.

As expected, the rise in outflow NO_3^- -N concentration lagged behind the rise in outflow Br^- concentration because NO_3^- -N amendments did not commence until 9 days after Br^- amendments. Like the outflow Br^- concentrations, outflow NO_3^- -N concentrations gradually rose after NO_3^- -N amendments began; however, the outflow NO_3^- -N concentrations rose to varying levels in different mesocosms (Fig. 6 and Appendix E). In the absence of NO_3^- removal, the NO_3^- -N concentration should mimic the Br^- concentration because they were added at a 1:1 ratio.

The difference between outflow groundwater Br^- and NO_3^- -N concentrations indicates the extent of groundwater NO_3^- removal (Fig. 6). For example, because outflow NO_3^- -N concentrations in Fig. 6a are relatively close to the outflow Br^- concentrations from days 30-95, comparatively little NO_3^- was removed from mesocosm #4. In contrast, outflow NO_3^- -N concentrations in mesocosm #7 (Fig. 6b) remained at less than half the outflow Br^- concentration for most of the experiment, indicating greater groundwater NO_3^- removal. In general, outflow NO_3^- -N concentrations were closer to outflow Br^- concentrations in the North Kingstown mesocosms than the in Charlestown mesocosms indicating less groundwater NO_3^- removal in the North Kingstown mesocosms.

Over time, the outflow NO_3^- -N concentrations gradually rose. This suggests that removal rates decreased over the course of the study. As expected, once Br^- and NO_3^- -N amendments were discontinued (day 80), the outflow NO_3^- -N concentrations gradually declined, approaching the detection level (0.2 mg L^{-1}). The final outflow NO_3^- -N concentration in five of the mesocosms was below this detection level. In the remaining seven mesocosms, the final NO_3^- -N concentrations ranged from 0.3 to 0.6 mg L^{-1} .

Following the six days of pump stoppage (days 54-60), I observed a rapid decline and then rebound in outflow NO_3^- -N concentration in several of the mesocosms. The Charlestown mesocosms experienced a greater decline in outflow NO_3^- -N concentrations at this point than the North Kingstown mesocosms. In general, the higher the outflow NO_3^- -N concentration before the pump stoppage, the less the concentration dipped in response to this increase in groundwater retention time.

Ammonium Generation in Mesocosms

No NH_4^+ -N was added to the groundwater inflow of the mesocosms. The inflow NH_4^+ -N concentration was consistently less than the detection level (0.1 mg L^{-1}). All the inflow total N was in the form of NO_3^- -N. NH_4^+ -N was observed in the outflow groundwater even before NO_3^- -N amendments commenced. This suggests that the NH_4^+ -N detected in the outflow groundwater had been generated internally within the mesocosms. However, the observed NH_4^+ -N concentrations in all mesocosms were generally low, never rising above 1.9 mg L^{-1} .

The outflow NH_4^+ -N concentration varied substantially in magnitude and pattern between vegetated areas (Fig. 9 and Appendix F). Among the suburban vegetated mesocosms, the outflow NH_4^+ -N concentrations were generally either negligible throughout groundwater dosing or were initially negligible and then experienced a slight increase before the completion of groundwater dosing (Fig. 9a). All the forested mesocosms had initial outflow NH_4^+ -N concentrations greater than 0.9 mg L^{-1} . In general, the outflow NH_4^+ -N concentrations in these forested mesocosms gradually declined throughout groundwater dosing (Fig. 9b). The pattern of outflow NH_4^+ -N concentrations did not correspond with the outflow NO_3^- -N concentration patterns.

By day 60, outflow NH_4^+ -N concentrations in all mesocosms were less than 0.9 mg L^{-1} . By the end of groundwater dosing (day 116), NH_4^+ -N concentrations in all mesocosms declined to or near the detection level. There was no apparent rise or fall in NH_4^+ -N concentrations that can be attributed to the pump stoppage (days 54-60).

The NH_4^+ -N generation rates were significantly higher in North Kingstown

Figure 9. Outflow groundwater NH_4^+ -N concentrations of shallow riparian aquifer mesocosms. Dosing schedule: days 1-9: inflow amended with Br^- only; days 10-80: inflow amended with NO_3^- -N and Br^- ; days 81-116: inflow unamended. Inflow groundwater contained negligible NH_4^+ -N concentrations ($<0.1 \text{ mg L}^{-1}$) throughout the study. (A) Outflow concentrations from mesocosm #6 represent the general pattern of NH_4^+ -N concentrations in suburban vegetated mesocosms of shallow riparian aquifer soil; (B) Outflow concentrations from mesocosm #12 represent the general pattern of NH_4^+ -N concentrations in forested mesocosms of shallow riparian aquifer soil.

North Kingstown Suburban Mesocosm #6

Charlestown Forested Mesocosm #12

forested vegetated mesocosms (mean: $12.8 \mu\text{g kg}^{-1} \text{d}^{-1}$; S.E.: 1.5) than in North Kingstown suburban vegetated mesocosms (mean: $5.6 \mu\text{g kg}^{-1} \text{d}^{-1}$; S.E.: 1.6).

Charlestown forested vegetated mesocosms generated more $\text{NH}_4^+\text{-N}$ (mean: $10.4 \mu\text{g kg}^{-1} \text{d}^{-1}$; S.E.: 1.4) than the Charlestown suburban vegetated mesocosms (mean: $6.1 \mu\text{g kg}^{-1} \text{d}^{-1}$; S.E.: 2.9) although this difference was not significant. These trends in $\text{NH}_4^+\text{-N}$ generation rates contrast with the trends in $\text{NO}_3^-\text{-N}$ removal rates which only exhibited significant differences between sites and not between vegetated areas.

Net Dissolved Inorganic Nitrogen Removal Rates

Because $\text{NH}_4^+\text{-N}$ was generated within the mesocosms, I determined the net dissolved inorganic nitrogen (DIN) removal rates. I did not observe any differences in overall trends between $\text{NO}_3^-\text{-N}$ removal rates and DIN removal rates. No significant differences in net DIN removal rates were found between the forested areas and the suburban areas at either site. After pooling forested and suburban vegetated removal rates at each site, I found that Charlestown net DIN removal rates (mean: $32.3 \mu\text{g kg}^{-1} \text{d}^{-1}$; S.E.: 3.8) were significantly higher than North Kingstown net DIN removal rates (mean: $-0.7 \mu\text{g kg}^{-1} \text{d}^{-1}$; S.E.: 3.4). When taking into account $\text{NH}_4^+\text{-N}$ generation, N removal rates at the Charlestown site remain substantial.

Root and Patch Characteristics

Dark-stained patches of elevated organic matter were found in all mesocosms (Table 3). There was no significant difference in mass of patch material between areas

Table 3: Characteristics of patches of elevated organic matter found within shallow riparian aquifer mesocosms. Values are mean (standard error).

Treatment	Mass of Patch		C in Patch	
	% (by mass) of Patch in Mesocosm	Total Mass of Patch per Mesocosm (g)	% C of Patch†	Mass of Patch Material C per Mesocosm (g)
North Kingstown Forested	5.0 (4.51)	489.1 (437.68)	1.4 (0.20)	5.4 (4.72)
North Kingstown Suburban	0.5 (0.20)	56.7 (22.21)	1.2 (0.26)	0.7 (0.35)
Charlestown Forested†	16.8 (1.41)	1535.6 (95.85)	2.8 (0.49)	42.0 (7.78)
Charlestown Suburban	15.29 (10.07)	1455.6 (718.36)	1.3 (0.12)	20.6 (14.49)

† Patches of organic matter in two of the Charlestown forested mesocosms included portions of the Bh horizon

‡ % C of matrix material ranged from 0.16 to 0.59% and was not significantly different between treatments

within a site. However, the mass of patch material in Charlestown mesocosms (mean: 1495.6 g; S.E.: 433.8) was significantly greater than the mass of patch material in North Kingstown mesocosms (mean: 272.9 g; S.E.: 218.5). The appearance of individual patches of elevated organic matter did not vary between treatments. Some of the dark-stained patches of elevated organic matter resembled root channels where the root had completely decomposed. Fine roots or fine root masses were sometimes found within these patches. However, most frequently these patches were amorphous features in the soil, ranging in size from 2 mm by 2 mm to almost covering the entire cross-section of a mesocosm's 15 cm diameter face.

Occasionally in the Charlestown mesocosms, I observed streaking of organic matter that was difficult to separate from the matrix material as "patch." Also unique to the Charlestown forested area was the 5 cm thick Bh horizon that two of the three mesocosms intercepted. Aside from these observations, I did not observe any marked differences in patch material between sites or vegetated areas.

Patch material contained between 0.63 and 3.51% C while matrix material contained only between 0.16 and 0.59% C. There was no significant difference in the mass of patch material C in mesocosms between forested and suburban areas at either site (Table 3). After pooling the forested and suburban vegetated data, I determined there was significantly more mass of patch material C in Charlestown mesocosms (mean: 31.3 g; S.E.: 8.8) than in North Kingstown mesocosms (mean: 3.0 g; S.E.: 2.4). The mass of patch material C per mesocosm was significantly correlated ($r_s = 0.81$) with NO_3^- -N removal rates (Fig. 10a). However, NO_3^- -N removal rates were not significantly

Figure 10. Relationship between groundwater NO_3^- -N removal rates and C per mesocosms. (A) NO_3^- -N removal rates were significantly correlated with the mass of patch material C per mesocosm; (B) NO_3^- -N removal rates were not significantly correlated with the mass of matrix material C per mesocosm; (C) NO_3^- -N removal rates were significantly correlated with the total mass of C contained within mesocosms.

A)

Relationship Between Nitrate Removal Rates and Mass of Patch Material Carbon

CF: Charlestown Forested
NKF: North Kingstown Forested

CS: Charlestown Suburban
NKS: North Kingstown Suburban

$R_s = 0.81$

B)

Relationship Between Nitrate Removal Rates and Matrix Material Carbon

CF Charlestown Forested

CS: Charlestown Suburban

NKF North Kingstown Forested

NKS: North Kingstown Suburban

 $R_s = 0.44$

C)

Relationship Between Nitrate Removal Rates and Total Mass of Carbon in Mesocosms

CF: Charlestown Forested

CS: Charlestown Suburban

NKF: North Kingstown Forested

NKS: North Kingstown Suburban

 $R_s = 0.75$

correlated with the mass of matrix material C per mesocosm (Fig. 10b). The total mass of C within the mesocosms was also found to be significantly correlated ($r_s = 0.75$) with NO_3^- -N removal rates (Fig. 10c); however, this correlation was not independent of the mass of patch material C and matrix material C.

Roots were found in all mesocosms. I was unable to quantify the extent of root decomposition or mineralization in the mesocosms. The mass of dry roots contained within mesocosms was significantly correlated ($r_s = 0.62$) with the mass of patch material C per mesocosm (Fig. 11). However, unlike the patch material C, the dry mass of roots per mesocosm was not significantly correlated with NO_3^- -N removal rates (Fig. 12).

Figure 11. Relationship between mass of patch material C and dry mass of plant roots per mesocosm.

Relationship Between Patch Material Carbon and Dry Mass of Mesocosm Roots

CF: Charlestown Forested CS: Charlestown Suburban
NKF: North Kingstown Forested NKS: North Kingstown Suburban

$R_s = 0.62$

Figure 12. Relationship between groundwater NO_3^- -N removal rates and dry mass of plant roots per mesocosm.

Relationship Between Nitrate Removal Rates and Dry Mass of Mesocosm Roots

CF: Charlestown Forested CS: Charlestown Suburban
 NKF: North Kingstown Forested NKS: North Kingstown Suburban

$R_s = 0.54$

DISCUSSION

By using intact saturated mesocosms of subsurface riparian soil, I was able to compare microbially mediated groundwater NO_3^- removal between forested and mowed suburban vegetated riparian areas. I found no significant difference in groundwater NO_3^- -N removal rates between forested and mowed suburban vegetated riparian areas. My results corroborate the findings of Lowrance et al. (1995).

These results may have profound impacts on the role of riparian zone management for the control of N losses in coastal watersheds. However, it is important to recognize that forested riparian zones serve many other functions, including wildlife habitat, surface water sediment and pollutant removal, and stream habitat (Golet et al., 1993). Up to now, riparian zone management plans have considered forested vegetation to be a critical component of riparian zones in order for groundwater NO_3^- removal to occur (Desbonnet, 1994; Altier, 1996). My study results cannot be extended to encompass large grassed areas. In suburban areas, vegetated areas are often comprised of a mix of mowed vegetation and woody vegetation. At both sites in my study, suburban soil pits were located only 5-6 m from trees (Figs. 2 and 4). In addition, at the North Kingstown site, I noted tree roots in the soil while digging the suburban vegetated pits. At the Charlestown suburban area, I noticed alder saplings that would grow to be 45 cm tall in the interval since the last mowing of the previous summer (September) and the first mowing of the following year (June). Thus, the lack of intrasite differences in my study may be the result of similar below ground rooting patterns within the two vegetated areas.

NH_4^+ was observed in outflow groundwater even before NO_3^- was added to the inflow groundwater. This suggests that NH_4^+ was internally generated within the mesocosms through mineralization of existing pools of organic N rather than produced by dissimilatory reduction of NO_3^- . The change in NH_4^+ -N concentration over time noted in the mesocosms indicates that conditions responsible for NH_4^+ flux within the mesocosms were not static. The NH_4^+ generation rates and patterns of outflow concentrations were substantially different between forested and suburban areas within sites. The brief elevated NH_4^+ concentrations in the early part of groundwater dosing suggest that the core extraction disturbance effects were short-lived in the mesocosms. NH_4^+ generation was not significantly different between similarly vegetated sites. The NH_4^+ generation trends are in striking contrast to the NO_3^- removal rates that did not reflect vegetation differences but rather exhibited site differences. Because of these different trends, NH_4^+ generation may be linked to a different set of processes than groundwater NO_3^- removal. However, because of the negligible net DIN removal rate at the North Kingstown site, the results from the mesocosm study do not support the concept that all PD soils are large sinks for N. I will focus my discussion on groundwater NO_3^- removal rather than DIN dynamics.

Groundwater NO_3^- -N removal rates observed at both sites (Charlestown site mean: $40.6 \mu\text{g kg}^{-1} \text{d}^{-1}$; North Kingstown mean: $6.8 \mu\text{g kg}^{-1} \text{d}^{-1}$) are similar to rates found at a similar site in a field study based on groundwater well networks ($46.4 \mu\text{g kg}^{-1} \text{d}^{-1}$) (Nelson et al., 1995). A saturated mesocosm study at that site obtained a mean NO_3^- removal rate of $5.4 \mu\text{g N kg}^{-1} \text{d}^{-1}$ (Gold et al., in review). I can also express groundwater NO_3^- removal on a kg ha^{-1} of riparian zone basis. Assuming an active depth of 1 m and using mean site

removal rates for the 116 days of the groundwater dosing experiment, groundwater NO_3^- -N removal equals $41 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and $245 \text{ kg ha}^{-1} \text{ yr}^{-1}$ at the North Kingstown and Charlestown sites, respectively.

Even though groundwater NO_3^- removal was greater at the Charlestown site, the North Kingstown NO_3^- removal rates were still substantial for riparian zone subsurface soils. The higher the groundwater NO_3^- removal rates at the Charlestown site versus the North Kingstown site may have been influenced by the slight difference in the depth of core extraction between sites. Due to an elevated water table at the Charlestown site, I was unable to extract cores from the same depth as the North Kingstown site. Cores were extracted at 67.5 cm and 57.5 cm (midpoint of 15 cm diam. core) below the surface at the North Kingstown and Charlestown sites, respectively. In general, denitrifying activity has been shown in microcosm studies to decrease with depth into the soil profile (Lind and Eiland, 1989; Ambus and Lowrance, 1991; Lowrance, 1992; McCarty and Bremner, 1992; Starr and Gillham, 1993; Lowrance et al., 1995). However, the majority of denitrification activity has been found to be isolated within the A horizon, generally within the top 10 cm of the soil profile. Since most of the Charlestown cores were taken entirely from the C horizon, the NO_3^- removal rates at 10 cm deeper in the profile may not have differed substantially from those observed in my study.

There has been much discussion in the literature over the relative role of plant uptake and microbial processes in riparian zone groundwater NO_3^- removal (Hill, 1996). An advantage of this mesocosm approach is that by excluding plant uptake I could examine groundwater NO_3^- removal rates generated by microbially mediated processes.

However, plants may play a role in subsurface processes aside from plant uptake.

Anaerobic microsites can develop in the root vicinity, creating conditions favorable for denitrification (Woldendorp, 1963; Brar, 1972; Klemetsson et al., 1987). Plant roots are the primary source of organic matter in deeper soils (Head, 1973). Living roots excrete organic substances into the soil which may become substrates for denitrification (Grineva, 1961; Head, 1973; Bailey, 1976; Christensen et al., 1990). This contribution of C by plant roots has been found to correspond with higher rates of denitrification in rhizosphere soil (Smith and Tiedje, 1979). However, the age and type of plant may determine the effects of root excretions on denitrification (Woldendorp, 1962; Shamoot et al., 1968; Haider et al., 1985, Qian and Doran, 1996). In general, metabolically active roots contribute more organic matter and stimulate denitrification more than senesced roots (Woldendorp, 1963; Volz et al., 1976). Artificially killed roots may contain more reserve carbohydrates available for decomposition than naturally senesced roots which may have transferred these carbohydrates to other plant parts (McClaugherty et al., 1984).

All mesocosms in my study contained plant roots, some of which were probably killed artificially during the course of the experiment. Dead roots do not actively excrete organic substances, thus the only C contribution from these roots would have been via decomposition. I was not able to quantify the extent of decomposition and mineralization of the roots found in the mesocosms. Thus, some of the N dynamics observed in this study may be the result of roots artificially killed rather than from patch dynamics.

Consequently, the groundwater NO_3^- removal rates presented by my mesocosm study do not represent in-situ microbially mediated groundwater NO_3^- removal rates.

The dry mass of plant roots was not significantly correlated with NO_3^- removal rates. This suggests that plant roots may not be the sole indicator of NO_3^- removal potential. Since these roots were found to be significantly correlated with patches of elevated organic matter within mesocosms, plant roots may play a role in the formation of such patches. Groundwater NO_3^- removal rates were significantly correlated with the total mass of patch material C suggesting that these patches of elevated organic matter may be “hotspots” of microbial activity. The percentage of patch material and the mass of patch material C in the subsoil may be useful indicators of NO_3^- removal potential in the subsurface.

Although no significant differences in NO_3^- removal between forested and suburban areas were observed at the Charlestown site, two of the three Charlestown forested vegetated mesocosms contained portions of the Bh horizon, an illuvial zone enriched in organic matter. These mesocosms had the highest mass of C, but did not consistently have markedly higher N removal rates than other mesocosms at the same site. This suggests that the Bh horizon did not markedly influence groundwater NO_3^- removal to a great extent.

Land use legacy may have also played a role in the difference in NO_3^- removal rates between sites. The Charlestown site was cultivated and received horse manure applications for approximately 20 years until the early 1980's. Manure applications have been shown to increase the amount of organic matter in surface soils (Rice et al., 1988; Nat. Res. Council, 1993; Darwish et al., 1995). In addition, cultivation processes have been found to translocate C substrates deeper into the soil profile (Sotomayor and Rice,

1996). This previous cultivation and manuring may have contributed a greater mass of patch material C in the subsurface of the Charlestown site. Also, vegetation differences between sites may have influenced the intersite differences in NO_3^- removal. Unlike the North Kingstown site, the Charlestown site contained speckled alder trees. Alders have the capability of fixing atmospheric N. In addition, alders have been shown to produce higher amounts of nutrient-rich litter biomass annually and increase soil organic matter more than other tree species (Bormann et al., 1994).

The differences in growing season hydrology between the two sites may be responsible for some of the differences in mass of patch material C and/or observed groundwater NO_3^- removal rates. The mean 1996 growing season water table depth observed at the Charlestown site was approximately 30 cm higher than at the North Kingstown site. In 1997, the maximum depth of the water table varied over 50 cm between sites. The greater mass of patch material C in the subsurface at the Charlestown site may be due to lower rates of decomposition that occur under saturated conditions (Donahue et al., 1983). In addition, if the upper portion of the C horizon at the Charlestown site remains saturated, as in the growing season of 1996, it is more likely to remain anaerobic. These conditions are favorable for denitrification (Korom, 1992). However, data from the 1997 growing season indicates that the difference in hydrology between sites may not be significant in all years. Also, the mesocosms remained saturated throughout the groundwater dosing experiment so water levels did not directly influence nitrate removal rates in my study.

Christensen et al. (1990b) found that hotspots of microbial activity had a limited

longevity, persisting from a few days to a few weeks. Outflow groundwater NO_3^- removal gradually declined over the course of my study; this suggests that any hotspots of microbial activity within my mesocosms also had a limited longevity or a gradual decline in their strength. My results may reflect artificially induced microbial activity. The existing roots within the mesocosms may have died and generated a pulse of C available for microbial processes. Bijay-Singh et al. (1988) suggested that denitrification rates are likely to be controlled by the mineralization of organic C within the soil.

The variability in NO_3^- removal rates between replicates within the four treatments suggests that the mesocosms in this study were not large enough or more replicate cores should have been taken to encompass the natural soil heterogeneity. The coefficients of variation ranged from 4% to 191% for the four treatments. In all treatments, there was at least one mesocosm with relatively high groundwater NO_3^- -N removal rates, i.e. greater than $16 \mu\text{g kg}^{-1} \text{d}^{-1}$.

Further Studies

In order to gain a complete understanding of the processes responsible for NO_3^- dynamics in my mesocosms, one cannot simply rely on a mass balance approach of water-born NO_3^- . Complementary studies to my thesis will be undertaken to examine the mechanisms controlling NO_3^- removal within the mesocosms. In order to examine the role of denitrification and immobilization, the N added to these mesocosms was labeled with ^{15}N (5 atom % ^{15}N). To compute a complete N mass balance, gas and soil samples need to be analyzed for ^{15}N . Also, fresh samples of patches of elevated organic matter and

matrix material from each site in this study will be examined for denitrification potential to determine the extent of variation in the microbial activity of patch and matrix material between and within sites.

There is also the need for research beyond the extent of my project. Additional studies need to be completed to explore further the role of mowed vegetated riparian areas in removing groundwater NO_3^- . In particular, work is needed in riparian areas that are isolated from woody vegetation. In addition to vegetation management, it would be interesting to study the effect of other alterations, such as changes in soil structure and soil drainage, in riparian zones on water quality functions.

My work bolsters the need for further research that examines the role of roots and patches of elevated organic matter on subsurface NO_3^- removal processes in riparian zones. Most importantly from a management perspective, my work suggests that a range of riparian vegetation can promote groundwater NO_3^- removal. Flexibility in regulations centered on the design and maintenance of vegetated suburban riparian landscapes may be able to generate wide public acceptance and compliance without compromising water quality protection.

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APPENDIX A: Literature Review

LITERATURE REVIEW

Pollution is recognized to be deleterious to human health and the environment. Point source pollution originates at a discrete, identifiable location, such as a smokestack or pipe. This characteristic makes point source pollution easier to contain and regulate than non-point source pollution (NPSP). Consequently, research interest has shifted to studying the mechanisms affecting the fate and transport of NPSP. Nitrate (NO_3^-) is an example of NPSP that is discharged over large areas from diffuse sources. NO_3^- is the most commonly detected pollutant in groundwater wells in the US (US EPA, 1990) and is a federally registered drinking water contaminant. At high concentrations, NO_3^- can cause methemoglobinemia (blue-baby syndrome) in infants. NO_3^- also has been linked to eutrophication of coastal waters and watershed management of nitrogen (N) is a major coastal issue (Ryther and Dunstan, 1971; Howarth et al., 1996; Jordan et al., 1997).

NO_3^- enters groundwater from a variety of sources. Undisturbed and unmanaged forests are expected to contribute very little NO_3^- to groundwater. However, forests may contribute high levels of NO_3^- to groundwater when a large disturbance, such as fire or clear cutting, occurs (Keeney, 1986). Agricultural fertilizer and manure applications have the potential to leach high levels of NO_3^- into groundwater (Keeney, 1986). Groundwater NO_3^- can also originate at septic tanks (Keeney, 1986; Weiskel and Howes, 1992). A study conducted in southern New England found that silage corn fields and septic systems contributed substantially more NO_3^- to groundwater than home lawns treated with fertilizer or forests (Gold et al, 1990). Other potential sources of NO_3^- include atmospheric

deposition, industrial discharges, and animal feedlots.

Our understanding of watershed N is beset by uncertainties surrounding the role of N “sinks” – areas within a watershed capable of removing N from the groundwater.

Researchers studying coastal watersheds ranging from local scales (1000 ha) to regional scales (Mississippi Basin) have found that less than one-third of the estimated net anthropogenic N input is discharged to coastal waters (Jordan et al., 1997; Howarth et al., 1996). These studies suggest that we need additional research to improve our understanding of watershed sinks of N.

Riparian Zones

Riparian zones are functionally defined as areas where energy and matter are exchanged between terrestrial and aquatic ecosystems (Gregory, 1991). Since riparian zones lie between uplands and wetlands, there is significant variability in soils, water table elevations, dissolved oxygen (DO) levels, organic matter content, and vegetation. A convenient way to categorize this variability is by using soil drainage classes.

Soil Drainage Class

Soil drainage classes are separated according to the depth to redoximorphic features, indicative of seasonal high water table elevations (Wright and Sautter, 1988). Redoximorphic features are spots in the soil where iron has been reduced and reoxidized causing a color change in the soil (Singer and Munns, 1991). Redoximorphic features typically occur where the water table fluctuates between the growing and dormant seasons (Wright and Sautter, 1988).

Catenas are sequences of soils derived from similar parent material but categorized into different soil drainage classes (Wright and Sautter, 1988). There are seven possible soil drainage classes in complete soil catenas that range from upland locations toward waterbodies: excessively drained, somewhat excessively drained, well drained (WD), moderately well drained (MWD), somewhat poorly drained (SWPD), poorly drained (PD) and very poorly drained (VPD) (Wright and Sautter, 1988). Soil drainage classes roughly estimate the frequency and duration of soil saturation (Wright and Sautter, 1988). The excessively well drained class is dry for most of the year, and the VPD class has the water table at or near the surface for a substantial portion of the year. Redoximorphic features form closer to the ground's surface in PD and VPD soils. A riparian zone is generally composed of soils ranging from MWD to VPD soils.

Water-Saturation and Oxygen

As previously mentioned, the water table is near or at the ground's surface for a significant portion of the year in PD and VPD areas. In the summer when evapotranspiration is active, the water table in these areas may drop further below the surface. In PD red maple swamps in Rhode Island, the water table fluctuates on average 71.2 cm throughout the year (Golet et al., 1993).

Diffusion of oxygen into soils cannot occur when interconnected soil pores are absent or blocked with water (Singer and Munns, 1991). In saturated soils, the oxygen cannot be replaced, and anoxic conditions develop once the oxygen is consumed by soil organisms and plant roots. Therefore, PD soils are frequently anoxic since they experience long-term saturation.

Organic Matter

Organic matter consists of living or dead plant and animal residues (Donahue et al., 1983). In general, cultivated soils only contain 1-5% organic matter, most of which is isolated in surface soils (Donahue et al., 1983). Decomposition is influenced by a number of factors, including soil moisture. Under anoxic soil conditions, both microbial decomposition and plant growth slow down (Donahue et al., 1983). As mentioned previously, the period of water saturation increases and DO concentrations decrease toward the PD and VPD areas of a soil catena. As a result, decomposition proceeds at reduced rates in these areas, and organic matter accumulates in these soils.

Vegetation

Vegetation type in an area is influenced by the site's hydrology (Mitsch and Gosselink, 1993). From MWD to VPD soils in a riparian zone the hydrology changes dramatically which may account for the great diversity in vegetation cover contained within a single riparian zone. Vegetation in the PD and VPD sections of riparian zones needs to be tolerant of or have adaptations to withstand frequently flooded and anoxic conditions (Mitsch and Gosselink, 1993).

Riparian Zones as Sinks for Nitrate

Riparian buffer zones have long been accepted as a Best Management Practice (BMP) for soil and water conservation in agricultural areas by removing sediment from surface water runoff (Gilliam et al., 1997). Riparian zone functions are not limited to surface water remediation. There is a general consensus in the literature that riparian zones are a significant sink for groundwater NO_3^- in the subsurface, but many of the details

surrounding the processes and mechanics of this NO_3^- removal remain elusive (Hill, 1996; Gilliam et al., 1997).

Mechanisms of Groundwater Nitrate Removal

Recent studies in riparian zones have tried to elucidate the mechanisms responsible for NO_3^- attenuation (Hill, 1996). NO_3^- is often considered conservative in groundwater (Keeney, 1986; Starr and Gillham, 1993), but several studies suggest that NO_3^- may be removed from groundwater by selected mechanisms in some aquifers. Some possible removal mechanisms include: 1) immobilization in microbial biomass, 2) dissimilatory NO_3^- reduction to ammonium (DNRA), 3) plant uptake, and 4) denitrification (Korom, 1992). Plant uptake and denitrification are generally considered to be the dominant processes responsible for NO_3^- removal in riparian zones (Hill, 1996).

Immobilization and Dissimilatory Nitrate Reduction to Ammonium

During immobilization, microbes consume NO_3^- for cell growth and metabolism. Microorganisms do not uptake NO_3^- if ammonium (NH_4^+) is readily available (Paul and Juma, 1981). Microbes only assimilate as much NO_3^- as required for their growth (Tiedje et al., 1981). In DNRA, microbes reduce NO_3^- to NH_4^+ under anaerobic conditions without incorporating the NO_3^- into microbial biomass (Korom, 1992). Neither immobilization nor DNRA are permanent sinks for N. Microbes die and decompose thereby releasing immobilized N into the soil-water environment. If the NH_4^+ produced in DNRA later encounters aerobic conditions, it may undergo nitrification which recycles NO_3^- back to the soil-water environment (Korom, 1992).

Plant Uptake

An important mechanism of NO_3^- removal is plant uptake. O'Neill and Gordon (1994) examined NO_3^- removal due to plant uptake by setting up a laboratory study with large boxes filled with either soil only or soil with trees planted. When pumping NO_3^- amended water through the boxes, more NO_3^- was removed from the boxes with trees than without any vegetation. Therefore, they attributed the NO_3^- removal to plant uptake.

Carrier proteins help transport NO_3^- across the root cell membrane (Hopkins, 1995). Once inside the plant, the NO_3^- must be reduced to NH_4^+ for assimilation and utilization (Hopkins, 1995). Uptake of NO_3^- by plant roots is affected by 1) low temperatures, 2) inhibitors of respiration and protein synthesis, and 3) anaerobic conditions (Hopkins, 1995). Plant uptake of NO_3^- may experience seasonal patterns with the least amount of plant uptake occurring in winter months (Hopkins, 1995). Plant uptake also declines as plants age (Hopkins, 1995). Nadelhoffer et al. (1995) demonstrated that uptake rates differ between species.

Since the primary rooting zone of many plants extends less than 60 cm into the soil (Harris et al., 1977), plant uptake is not thought to be an important mechanism of NO_3^- removal from deep subsurface soils. However, Huang et al. (1996) found that switchgrass had the capacity to remove a substantial quantity of NO_3^- from soil at depths greater than 120 cm below the soil's surface. Even when plant uptake of NO_3^- occurs, the N may eventually be recycled back into the soil when plant parts senesce and decompose.

Plant uptake of NO_3^- from groundwater may not be constant. Forests may experience "N saturation" after extended periods of N uptake (Aber et al., 1989). N

saturation occurs when availability of N in the soil-water environment exceeds plant and microbial needs, not including denitrification (Aber et al., 1989). As a result of N saturation, there may be an excess of N leached from mature forests. To avoid N saturation in forests, Lowrance et al. (1984) recommend selectively cutting mature trees thereby allowing younger trees, which can utilize more N, to establish. However, N saturation may also be avoided in mature forests if excess NO_3^- stimulates microbiological activity in the soil (Nadelhoffer et al., 1995). This greater microbial activity may increase the need for NO_3^- in the microbial community, and NO_3^- uptake may consequently resume.

Denitrification

Denitrification occurs under the same anaerobic conditions as DNRA. A study by Tiedje et al. (1981) found that the role of DNRA was inferior to denitrification. DNRA is thought to occur in areas dominated by long-term anaerobic conditions while denitrification may occur more frequently in areas where the DO status is transient (Tiedje et al., 1981).

Of all the previous mechanisms of NO_3^- removal mentioned thus far, denitrification is the only mechanism that completely removes NO_3^- from the soil-water environment.

NO_3^- is converted to N_2O or N_2 gas as follows :

In order for denitrification to proceed, the following are needed: 1) NO_3^- , 2) denitrifying bacteria, 3) an energy source (organic C or an inorganic electron donor such as sulfur), and 4) anaerobic conditions (Korom, 1992; Starr and Gillham, 1993).

Nitrate

Perhaps the most basic requirement for denitrification is that NO_3^- be present in the soil to be reduced. A study comparing an enriched N site and a control site found that the enriched site had a greater potential for denitrification (Hanson et al., 1994).

Bacteria

Denitrifying bacteria are essential for denitrification to proceed. In the absence of NO_3^- or anaerobic conditions, a portion of the denitrifying population is able to survive and then utilize NO_3^- once it becomes available again (Schipper et al., 1994).

Anaerobic Conditions

Denitrification only occurs under anaerobic conditions. Oxygen inhibits the formation of N oxide reductases required for denitrification reactions. Oxygen even inhibits the activity of preformed reductase (Knowles, 1981). In order for denitrification to proceed, the DO concentration in the soil needed to be less than 2 mg L^{-1} in a study conducted by Gillham and Cherry (1978). Parkin and Tiedje (1984) found an average two- to four- fold increase in denitrification rates in unsaturated soil as the O_2 concentration was decreased from 20% to 5%.

The water content of soil exhibits great control over the amount of O_2 that is able to diffuse into soil; for example, in wetter soils more pore spaces are filled with water, and less O_2 can diffuse into these pore spaces (Singer and Munns, 1991). Pennock et al. (1992) found that topography influenced denitrification rates by controlling the volumetric water content of soil. Positions lower on the landscape tended to be wetter and thus had lower DO concentrations. Myrold (1988) also found that field denitrification rates were

closely correlated with soil water content. Many studies have concluded that denitrification rates are higher in wetter soil drainage classes. For example, Davidson and Swank (1986) detected the highest denitrification rates in PD surface soils in a North Carolinian study; Groffman and Tiedje (1989a) found that PD surface soils were consistently wetter and had higher denitrification rates than other soil drainage classes in Michigan; Parsons et al. (1991) observed higher denitrification rates in SWPD surface soils than WD surface soils in Kentucky; and Groffman et al. (1992) and Hanson et al. (1994) detected higher denitrifying enzyme activity (DEA) in wetland (PD and VPD) surface soils than in transition zone (MWD and SWPD) surface soils in Rhode Island. Groffman and Tiedje (1989b) concluded that soil drainage is a strong predictor of annual denitrification activity on a landscape scale.

Organic Carbon

Soil moisture also affects the amount of carbon (C) available for denitrification. Under low O₂ conditions, decomposition of organic matter is reduced resulting in an accumulation of organic matter (Donahue et al., 1983). Denitrification has been found to be limited by the amount of available C in soil (Myrold and Tiedje, 1985; Hiscock et al., 1991). When soils were incubated under non-nitrate limiting and anoxic conditions in a study by Bijay-Singh et al. (1988), they suggested that denitrification rates are likely to be controlled by the mineralization of organic C within the soil. C limitation of denitrification was also demonstrated in a laboratory study of aquifer sediments from a golf course in Florida (Bradley et al., 1992); denitrification rates in this study increased once glucose was added to the soil. The quality of the C source has been shown to be an important factor in

denitrification (Schipper et al., 1994; McKenney et al., 1995). A study by Schipper et al. (1994) found that denitrification increased more when fresh plant material was added to laboratory soil slurries than when senescent plant material, with less labile C, was added. Also, different plant species contribute qualitatively and quantitatively different organic matter to soil. For example, soils treated with rye grass residues had greater potential to remove NO_3^- via denitrification than soils treated with legume residues in a study by McKenney et al. (1995).

Denitrifying activity may be unevenly distributed throughout soil with the greatest activity occurring in uppermost horizons (Lind and Eiland, 1989; Ambus and Lowrance, 1991; Lowrance, 1992; McCarty and Bremner, 1992; Starr and Gillham, 1993; Lowrance et al., 1995). In one study, DEA was isolated within the top 10 cm of the soil profile, 80% of this DEA was contained within the top 2 cm of soil (Lowrance, 1992). Spatial variability of denitrification rates has often been explained by the distribution of C in soil. Beauchamp et al. (1980) examined A, B, and C horizons of three different soils and found the highest correlation between denitrification rates and total organic C. Starr and Gillham (1993) reported that denitrification did not occur in deep aquifer sediments due to the declining availability of organic C with depth below the ground's surface. McCarty and Bremner (1992) also observed that the number of denitrifiers decreased with depth; however, substantial populations still existed at a depth of 150-200 cm below the surface. They hypothesized that little organic C was leached into the subsoil and available to denitrifiers since decomposition of plant derived organic matter proceeds so rapidly in surface soils. When glucose was added to subsurface sediments, Lind and Eiland (1989)

noted a substantial increase in denitrifying activity.

Seasonality

Denitrification is affected by soil temperature. Lowering the temperature decreases denitrification rates dramatically. This may be due to a lowering in microbe metabolic activity (Hiscock et al., 1991; Knowles, 1981). As a result, seasonality of denitrification may be expected. In a study of two different cropping systems in Oregon, field denitrification rates were correlated with soil temperature, with the highest rates in spring (Myrold, 1988). Hanson et al. (1994) also observed the highest denitrification rates in the spring and fall in Rhode Island surface soils. Lower rates recorded during warmer summer months in this study may not be attributed to soil temperature but to drier/aerobic conditions. However, a study conducted by Parsons et al. (1991) did not find a correlation between denitrification and soil temperature at two sites. Groffman and Hanson (1997) found inconsistent seasonal patterns over a number of years in another Rhode Island study and suggested that denitrification was not sensitive to changing soil temperatures.

Soil Texture

Soil texture may also influence denitrification rates (Beauchamp et al., 1980; Groffman and Tiedje, 1989a and 1989b). Beauchamp et al. (1980) found that finer textured soils had higher denitrification rates since these soils generally had higher levels of available organic C. Groffman and Tiedje (1989a) observed the same trend. They attributed this trend to smaller pores in finer textured soils which hold water more tightly. The soils therefore become anaerobic more readily.

Denitrification can be influenced by pH. The optimum range for denitrification to proceed is between 7 and 8 (Knowles 1981; Hiscock, 1991). At low pH, denitrification rates may be limited. pH also influences the end products of denitrification (Knowles, 1982). N oxide reductases are inhibited at low pH (around pH 4.0) so that the primary end products of denitrification under such conditions would be NO and N₂O, rather than N₂ (Knowles, 1982). However, Ottow et al. (1985) did not find that pH was correlated with the end products of denitrification. Bradley et al. (1992) also found no significant relationship between potential denitrification and pH in subsurface soils; they suggested this may be due to the narrow range of pH (5.4-6.4) observed at their site. They did find, however, that actual denitrification rates were affected by short-term changes in pH.

Influence of Plants on Denitrification

The role of plants in NO₃⁻ removal is not limited to plant uptake. Plants can also influence denitrification by a few processes: 1) since plants uptake less NO₃⁻ is consequently available to denitrifiers, 2) roots excrete organic substances into the soil which may become substrates for denitrification, and 3) roots may contribute O₂ to rhizosphere soil that may stimulate nitrification, the formation of NO₃⁻ (Christensen et al., 1990). In addition, elevated O₂ consumption by roots and rhizosphere organisms may create anaerobic microsites in the soil that are favorable for denitrification (Woldendorp, 1963; Brar, 1972; Klemetsson et al., 1987).

Bailey (1976) found increased NO₃⁻ removal in the presence of roots. He suggested this was because roots generate C from sloughed-off root cap cells and root

exudates that may be available for microbial activity. The roots of healthy plants naturally shed as part of their development processes, and roots are the primary source of organic matter in deeper soils (Head, 1973; Grineva, 1961). In a *Liriodendron tulipifura* forest, roots accounted for 70% of the total organic matter from above- and below-ground sources in the soil (Cox et al., 1978).

Roots also contribute organic C to the soil when they senesce and decompose. Roots do not have a predetermined life-span, but root hairs have a relatively short life-span, ranging from a few hours to a few months, before they are subjected to decomposition and become a source of available C to microorganisms (Head, 1973). In the northern hardwood Hubbard Brook Experimental Forest, New Hampshire, Fahey and Hughes (1994) found the median longevity of fine roots to be 6 months. These roots also underwent rapid decomposition; 30% of these fine roots disappeared during the period from October to August. Root systems seem to produce localized zones in the soil with anaerobic conditions and ample C supplies thus creating a favorable environment for microbial denitrification activity.

Rhizosphere soil was found to have higher denitrification rates than the matrix soil, with the highest rates closest to the roots (Smith and Tiedje, 1979). Another study suggested that there was 90 times more denitrifying bacteria in the rhizosphere than in the soil matrix (Stefanson, 1972). However, the age and type of plant may determine the effects of root excretions on denitrification (Woldendorp, 1962). For example, a study by Haider et al. (1985) found that root-deposited C from wheat and corn plants was not readily decomposable and therefore not readily used by denitrifying bacteria. Qian and

Doran (1996) found that organic compounds derived from corn roots benefited only 4-11% of the soil microbial biomass. Furthermore, a study by Shamoot et al. (1968) found that only between 30 and 48% of rhizosphere-deposited organic matter was decomposed over 14 weeks of incubation.

There are also distinctions between senescent roots and metabolically active roots. Senescent roots may be resistant to decomposition while active roots may provide less complex and more readily available forms of organic matter to the soil for microbial activity (Volz et al., 1976). For example, the most probable number (MPN) of denitrifiers was higher in flooded soil planted with barley than in a flooded fallow soil that contained senescent plant roots (Volz et al., 1976). Woldendorp (1963) found denitrification was more stimulated by living roots than senescent roots. Whether roots died by natural or artificial means may also influence root effects on denitrification. Roots that have died naturally may have already recycled reserve carbohydrates to the plant. However, roots that are artificially killed may maintain reserve carbohydrates that can be readily excreted to and utilized by microbes in the soil (McClaugherty et al., 1984).

Plants in soil may also influence the major products of denitrification. In soil without plants the main product of denitrification was N_2O while in soils with plants the main product was N_2 gas in studies by Stefanson (1972) and Klemetsson et al. (1987). More work is needed to elucidate the importance of plant roots in inducing microbial processes of groundwater NO_3^- removal.

Denitrification versus Plant Uptake

There is a great deal of uncertainty as to the relative role of plant uptake and

denitrification in removing groundwater NO_3^- in riparian zones (Gilliam et al., 1997; Hill, 1996; Gilliam, 1994). In an ecosystem scale ^{15}N study in a mixed forest, Nadelhoffer et al. (1995) suggested that plant and microbial processes in surface soils have approximately the same potential of removing NO_3^- . In field experiments, it is extremely difficult to determine if NO_3^- removal can be attributed to plant uptake, denitrification, or a combination of the two. In studies where NO_3^- removal was measurable in subsurface soils even though denitrification potential had been demonstrated to be low in these soils, plant uptake is usually assumed to be the dominant mechanism of NO_3^- removal (Lowrance, 1992; Groffman et al., 1992). However, these studies did not directly measure in-situ denitrification. When NO_3^- removal was observed in winter months when plant activity was expected to be low, denitrification was generally suggested as the mechanism of removal (Hanson et al., 1994; Nelson et al., 1995; Groffman et al., 1996). Also, if groundwater was sampled below the major rooting zone, denitrification was generally assumed to be responsible for NO_3^- removal as in a study by Peterjohn and Correll (1984).

Verchot et al. (1997) conducted a field study of subsurface N cycling in grassed and forested vegetated filter zones in which they attempted to eliminate the plant uptake variable. To do so, they dug trenches along the edge of their plots to cut tree roots extending into the area of interest, weeded out saplings and herbaceous plants, and applied herbicide to prevent plant growth. Under these conditions, substantial NO_3^- removal was observed and attributed to denitrification. More research needs to be conducted to determine the relative role plant uptake and denitrification play in removing NO_3^- from

groundwater.

Riparian Zones as Favorable Nitrate Removal Sites

Riparian zones possess many of the properties that favor NO_3^- removal from groundwater. In particular, the PD and VPD sections of riparian zones seem to be particularly favorable sites for denitrification (Nelson et al., 1995). Since these sites are wetter, they tend to be anaerobic for a longer period of time and to have an accumulation of organic matter - conditions favorable for denitrification.

Riparian zones may be "pulsating ecosystems" similar to tidally flushed estuaries (Odum et al., 1995; Gold et al., in review). In such pulsating ecosystems, final steady states do not develop in nature. Rather, spatial or temporal oscillations bring the system to a pulsing steady state. For example, during summer months in riparian zones, the water table drops and roots may extend deeper into the subsurface. These roots shed organic matter and may senesce generating a C source for anaerobic microbial activity to occur when the water table again rises in the dormant season. Therefore, a site favorable for denitrification has been created in this pulsating ecosystem.

Microsites of Microbial Activity

An interesting aspect of riparian zone studies is the discrepancy between companion field and laboratory microcosm studies of groundwater NO_3^- removal. As opposed to counterpart field studies, laboratory studies of shallow aquifer media have found lower denitrification rates and low if any correlation between denitrification rates and soils of different drainage classes (Pennock et al., 1992; Groffman et al., 1996).

Substantial laboratory-detected denitrification potential seems isolated within the top 10 cm of soil (Ambus and Lowrance, 1991; Lowrance, 1992) even though field studies with groundwater well networks have reported groundwater NO_3^- removal deeper in the subsurface (Simmons et al., 1992; Nelson et al., 1995; Lowrance, 1992; Haycock and Pinay, 1993). Laboratory measured microbial activity may not adequately represent field-measured activity because field studies encompass a greater extent of the natural soil heterogeneity (Smith et al., 1996). Differences in sample volume between field and laboratory studies may explain such discrepancies (Groffman et al., 1996).

Organic matter is often distributed unevenly through soil profiles. Starr et al. (1995) suggested that processes, such as denitrification, nitrification, and plant growth, that experience rapid transformations dependent on local conditions may be particularly influenced by sample volume. Parkin et al. (1987) suggest that the bulk of denitrification may occur in microsites or “hotspots” of organic matter. If these microsites occur in irregular patterns, microsites of high activity may be missed in the small samples, i.e. less than 50 grams, typically used in laboratory analysis. Up to a point, the larger the sample volume, the greater chance of capturing these hotspots and the denitrification variability may tend to decrease (Starr et al., 1995). Parkin (1987) found that 25-85% of denitrification potential came from 0.40 - 0.08% of the core's mass while a study by Christensen et al. (1990a) traced the majority of denitrification activity to 8% of the sample's volume. Measurements of microbial activity need to be conducted with methods that take into consideration the heterogeneity in soil and microbial populations (Murray et al., 1995; Starr et al., 1995). Appropriate sample sizes to reflect realistic field conditions

have been suggested, ranging from 5 cm diameter cores (Starr et al., 1995) to 10-15 kg soil samples (Parkin et al., 1987).

Recently, a laboratory mesocosm study (Gold et al., in review; Jacinthe et al., in review) of 12 kg of soil produced NO_3^- removal rates more comparable to a field study than microcosm studies at the same site (Nelson et al., 1995; Groffman et al., 1996). In addition, PD mesocosms exhibited higher NO_3^- removal rates than MWD, the same trend observed in the field studies. When the mesocosms were disassembled, MWD mesocosms did not contain any dark-stained patches of elevated organic matter. However, such patches were found in the PD mesocosms that exhibited high NO_3^- removal rates. These patches appeared to be root-derived biological hotspots of microbial activity.

Nitrate Removal in Forested and Non-Forested Riparian Zones

Most recent riparian zone research has focused on forested areas (Lowrance et al., 1984; Peterjohn and Correll, 1984; Ambus and Lowrance, 1991; Lowrance, 1992; Simmons et al., 1992; Hanson et al., 1994; Nelson et al., 1995; Groffman et al., 1996; Starr et al., 1996). Throughout this work, it is generally accepted that forested riparian zones have the ability to serve as NO_3^- sinks. Fewer studies have examined the role of non-forested riparian zones in removing NO_3^- from groundwater (Haycock and Pinay, 1993; Osbourne and Kovacic, 1993; Lowrance et al., 1995; Schnabel et al., 1996).

In general, trees are thought to uptake more groundwater NO_3^- than grasses because they have a potentially deeper rooting zone (Gilliam et al., 1997). Haycock and Pinay (1993) compared NO_3^- removal in poplar and grass riparian zone subsoils in winter.

The poplar site removed more groundwater NO_3^- . They suggested that C limitation in the grass site was responsible for the lower NO_3^- removal. A study by Osbourne and Kovacic (1993) also found that a forested riparian subsoil removed more groundwater NO_3^- than a grassed riparian subsoil on an annual basis. They suggested that denitrification was the mechanism of NO_3^- removal which was limited by the form of the C source.

However, other studies have shown greater NO_3^- removal in grassed riparian zones than forested riparian zones. It has been suggested that C from grassed areas may be more readily available to microbes as compared to the C from forested biomass (Lowrance et al., 1995). In general, prairie soils contain twice as much organic matter as similar forested soils (Plaster, 1997). Also, organic matter extends deeper into prairie soil where grass roots may decay as opposed to forest soils where most of the soil organic matter originates from surface litter (Plaster, 1997). Even different grass species may contribute different amounts of available C from their roots (Groffman et al., 1991). Schnabel et al. (1996) found greater denitrification rates in subsoils of a grassed riparian area than a forested riparian area in a paired comparison study. Lower denitrification rates in the wooded area were attributed to C limitation. Lowrance et al. (1995) conducted a study in a restored riparian wetland. In this study, the area closest to the stream was replanted with trees while an outer fringe of herbaceous vegetation remained. They concluded that shallow groundwater denitrification rates in grassed riparian buffer zones could equal or exceed denitrification rates in restored buffer zones recently replanted with trees. More studies are needed to determine whether there are any differences in groundwater NO_3^- removal rates between forested and non-forested riparian subsoils.

Nutrient Enrichment of Soil

Hendricks et al. (1993) concluded in their review of fine root research that fine root turnover rates are likely to increase as site quality, i.e. N availability, improves. These roots decompose readily releasing additional N and C into the soil. Therefore, the high site quality is further perpetuated. More research is necessary to explore fine root dynamics.

N-fixing Plants: Alders

N cycling under high-N environments, as in soils planted with N-fixing plants, is of particular interest to research on water quality functions of riparian zones. Alder (*Alnus* sp.) is an example of a genus that forms root nodules and is capable of fixing N from the atmosphere. Beaupied et al. (1990) found that soil mineral N only contributed to 6% of black alder (*Alnus glutinosa*) annual N requirements, the remainder coming from atmospheric N. Flooding can limit N-fixation in alders since this process requires aerobic conditions (Winship and Tjepkema, 1985). However, Winship and Tjepkema (1985) have suggested that red alder (*A. rubra*) root nodules have “compartments of low permeability” that enable some parts of the nodule to remain aerobic for a longer periods of time and thus continue to fix N despite saturation.

Since ancient times, alder has been recognized as improving soil fertility due to their ability to fix N (Yamaya, 1968). Yamaya (1968) studied the role of *A. inokumae* leaves in soil N cycling. In this study, the N content of alder leaves was found to be higher than that of many other broad-leaved and needle-leaved deciduous trees. These leaves were also found to decompose more rapidly than Japanese cedar leaves. This rapid

decomposition may be due to soil fauna being attracted by the high N content. Therefore, alder leaves may recycle more N back into the soil. However, alders also grow very rapidly (Yamaya, 1968). This rapid growth may correlate with a higher rate of N cycling in alder forest soils than other forest soils. As a result, the N content of alder forest soils may not be substantially higher than other forest soils. When alder forests are cut, however, there may be a substantial release of N into the soil (Yamaya, 1968).

The role of alder roots in N dynamics has also been studied. Roots of N-fixers may decompose at different rates than roots of plants that do not fix N. Black alder roots with higher N concentrations decomposed at a slower rate than black alder roots with lower N concentrations in a study by Camire et al. (1991). They suggested that N-lignin derivative compounds, resistant to decomposition, may have formed in these N-rich roots.

Denitrification in soils planted with alders has been explored in a few studies. Binkley et al. (1992) did not find denitrification to be a substantial sink of NO_3^- in red alder forests. As in other forested soil studies (Lind and Eiland, 1989; Ambus and Lowrance, 1991; Lowrance, 1992; McCarty and Bremner, 1992; Starr and Gillham, 1993), the highest denitrification activity was found within the top few cm of the surface soil in an alder stand (Struwe and Kjoller, 1990). Denitrification rates were found to be low overall, but denitrification activity was seasonal with highest rates in the spring and summer months (Struwe and Kjoller, 1990). Duff and Triska (1990) observed substantial denitrification in shallow sediments in the hyporheic zone under a red alder riparian zone. Mander et al. (1997) compared the ability of two grey alder (*A. incana*)/wet meadow riparian zones to remove N from groundwater. They found that even though one site had

greater N inputs (adjacent to a pig farm), the output N concentrations were comparable. This high N removal capacity, between 67 and 96% N removed, was attributed to high rates of denitrification as well as high rates of plant N uptake in both alder stands.

Agricultural Practices

Cultivation

Sotomayor and Rice (1996) compared denitrifier populations between a tallgrass prairie grassland and a cultivated field. They found that denitrifier populations in the cultivated field did not decrease with depth as in the grassland. They suggested that this trend was due to the cultivation process translocating C deeper into the soil profile. Therefore, cultivation alters the surface and subsurface sediments by creating a more favorable denitrifying environment.

Manure Applications

Manure applications to farm land serves two purposes: 1) it is a nutrient source that can replace fertilizer applications and 2) it is way for farmers to dispose of this waste product (Darwish et al., 1995). Manure applications supply nutrients and organic matter to soil (Nat. Res. Council, 1993; Darwish et al., 1995). In a study of surface soils that received manure applications for 15 years, the manure treated soil had a greater organic matter content than control soils- 3% more organic matter in fine sandy loam soils and over 25% for silt loam and clay loam (Darwish et al., 1995). This increase in organic matter may promote denitrification, as evidenced in a study by Rice et al. (1988) where surface soils were treated with fermentation waste.

Alternatively, manure may not contribute to the long-term organic matter content of soil because a large portion of the C may be converted to CO₂ gas (Simpson, 1986). Lovell and Jarvis (1996) found that the application of cattle dung pats on pasture soils did not substantially impact the size or activity of the soil microbial biomass under field conditions. The extent to which denitrification is affected by manure applications depends on the manure composition which is influenced by many factors, such as the type of animal, type of feed the animal received, manner of manure storage, and extent of decomposition in this manure (Paul and Beauchamp, 1989; Nat. Res. Council, 1993). For example, sheep and poultry manure contains high N contents (23-28 lbs ton⁻¹) while manure from cattle, horses, and pigs contains low N contents (10-13 lbs ton⁻¹) (Plaster, 1997).

APPENDIX B: Addendum to Methods

Water Table Well Installation

Water table wells, consisting of slotted 3.8 cm diam. PVC pipe, were installed at the North Kingstown forested vegetated area, at the North Kingstown suburban vegetated area, and midway between the suburban and forested pits at the Charlestown site. I inserted the wells into augered holes to a depth of 1.5 m and then leveled the top of the wells with the ground's surface. Once the wells were in place, I refilled the holes around the outside of the pipes with native material sorted by depth. The top 5 cm of the holes along the outside perimeter of the wells was filled with Bentonite clay pellets mounded slightly to direct runoff away from the wells. The wells were capped to prevent precipitation from directly entering the wells.

Core Extraction

The core extracting apparatus consisted of multiple parts (Fig. 10). It began with a 2-section extendible metal pipe mounted on a metal plate that rested against one wall of the pit. At the other end of the extendible pipe, there was another metal plate on which we attached an 8 ton hydraulic bottle jack. The jack had a metal plate attached to its extension arm that supported the core (15 cm diam., 40 cm long Schedule 35 PVC pipe with one beveled end). We rested this entire apparatus on two scissors jacks.

We randomly selected the side of the pit from which to extract the core. During the extraction procedure, we set the center of the core at least 30 cm below the dormant season water table level of the area. At the North Kingstown site, we extracted cores at a depth of 67.5 cm (midpoint of the core) from the surface. We extracted the Charlestown cores at 57.5 cm (midpoint of the core) from the surface because an elevated water table

prevented deeper extraction at this site. Once we adjusted the scissors jacks to the appropriate height and leveled the apparatus, we began to press the beveled end of the PVC core horizontally into the wall of the pit by pumping the bottle jack. Once the jack's arm was fully extended, we stabilized the PVC pipe by placing blocks of wood below it. Then, we brought the extendible metal pipe out to another extension and reestablished the apparatus. As the core was pushed into the wall of the pit, we excavated the soil around the top and sides of the core with spades in order to relieve pressure on the core and prevent it from bending. We continued this procedure until the back end of the core was flush with the side of the pit.

When pressing of the core was complete, we placed blocks of wood below the core to ensure its stability while we removed the extracting apparatus from the pit. We secured the back face of the core with a sheet of plastic and duct tape. We excavated the core out of the side of the pit by digging around its top and sides and beyond its front end. A piece of wire was used to slice the core cleanly away from the in-situ soil. We carefully lifted the core out of the pit, seated it vertically upright, and secured the other end with a sheet of plastic and duct tape. We brought the cores back to URI and stored them at 4 °C.

As mentioned previously, the water table rose in midsummer which made it necessary for us to extract the cores at that Charlestown site at 57.5 cm rather than at 67.5 cm (midpoints of the core) as at the North Kingstown site. Since the water table at the Charlestown site only dropped to around 45 cm below the surface, we needed to use a pump to remove excess water out of the pits as we dug the pit and extracted the cores.

Mesocosm Set-up

My mesocosm study was not intended to replicate natural, undisturbed field conditions. While I attempted to minimize the disturbance of soil sediments, the state and dynamics of the roots and other organic matter contained within the cores cannot represent natural field conditions over 116 days. Therefore, my results are not equivalent to in-situ rates of groundwater NO_3^- removal from the respective sites. This method should, however, allow us to learn more about NO_3^- removal rates in the absence of plant uptake. In addition, mesocosm results should be more comparable to field conditions than microcosm studies upon which much of our insights into nitrogen dynamics of riparian zones are based.

Figure 13. Schematic of horizontal core extraction. The cores were extracted from depths of 57.5 cm and 67.5 cm (midpoint of 15 cm diam. core) at Charlestown and North Kingstown riparian study sites, respectively.

APPENDIX C: Soil Profile Descriptions

CHARLESTOWN SUBURBAN SOIL PROFILES

Landscape position: Toeslope
Parent material: Glacial Outwash
Landform: Outwash Plain
Classification: Typic Humaquept

Slope: 0-3%
Soil Drainage Class: Poorly Drained
Described by: Kelly L. Addy

Soil Pit #7

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oi	5-0	Fibric organic matter
Ap	0-21.5	Black (10 YR 2/1) with few, small, distinct dark red (2.5 YR 4/8) redox concentrations, sandy loam; friable; clear smooth boundary
Bw1	21.5-34.5	Very dusky red (2.5 YR 2.5/2) sandy loam; friable; clear smooth boundary
Bw2	34.5-48.5	Very dusky red (2.5 YR 2.5/2) sandy loam; streaks of organic matter within horizon; friable; clear smooth boundary
C	48.5+	Dark yellowish brown (10 YR 4/4) sandy loam; friable

Soil Pit #8

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oi	4-0	Fibric organic matter
Ap	0-23	Very dark brown (10 YR 2/2) with few, small, distinct dark red (2.5 YR 4/8) redox concentrations, sandy loam; friable; clear wavy boundary
Bw	23-47	Very dusky red (2.5 YR 2.5/2) sandy loam; friable; clear smooth boundary
C	47+	Dark yellowish brown (10 YR 4/4) sandy loam; friable

Soil Pit #9

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oi	4-0	Fibric organic matter
Ap	0-20	Very dark brown (10 YR 2.2) sandy loam; friable; clear wavy boundary
Bw	20-40.5	Very dusky red (2.5 YR 2.5/2) sandy loam; friable; clear smooth boundary
C	40.5+	Dark yellowish brown (10 YR 4/4) sandy loam; friable

CHARLESTOWN FORESTED SOIL PROFILES

Landscape position: Toeslope
 Parent material: Glacial Outwash
 Landform: Outwash Plain
 Classification: Umbric Endoaquod

Slope: 0-3%
 Soil Drainage Class: Poorly Drained
 Described by: Kelly L. Addy

Soil Pit #10

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oe	2-0	Partially decomposed organic matter
Ap	0-32	Black (10 YR 2/1) fine sandy loam; friable; clear wavy boundary
Bw1	32-37	Very dark brown (10 YR 2/2) fine sandy loam; friable; clear wavy boundary
B2	37-51	Very dusky red (2.5 YR 2.5/2) sandy loam; friable; abrupt smooth boundary
Bh	51-56	Black (10 YR 2/1) silt loam; abrupt smooth boundary
C	56+	Very yellowish brown (10 YR 4/4) sandy loam; friable

Soil Pit # 11

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oe	3-0	Partially decomposed organic matter
Ap	0-40	Black (10 YR 2/1) fine sandy loam; friable; clear wavy boundary
Bw	40-51	Very dusky red (2.5 YR 2.5/2) fine sandy loam; friable; abrupt smooth boundary
Bh	51-56	Black (10 YR 2/1) silt loam; friable; abrupt smooth boundary
C	56+	Dark yellowish brown (10 YR 4/4) sandy loam; friable

Soil Pit #12

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oe	3-0	Partially decomposed organic matter
Ap	0-21	Black (10 YR 2/1) fine sandy loam; friable; clear wavy boundary
Bw1	21-29.5	Dark yellowish brown (10 YR 2/2) fine sandy loam; friable; clear smooth boundary
Bw2	29.5-40.5	Very dusky red (2.5 YR 2.5/2) sandy loam; friable; clear smooth boundary
Bh	40.5-45.5	Black (10 YR 2/1) silt loam; friable; clear smooth boundary
C	45.5+	Dark yellowish brown (10 YR 4/4) sandy loam; friable

NORTH KINGSTOWN SUBURBAN SOIL PROFILES

Landscape position: Depression
 Parent material: Glacial Outwash
 Landform: Outwash Plain
 Classification: Typic Humaquept

Slope: 0-3%
 Soil Drainage Class: Poorly Drained
 Described by: Kelly L. Addy

Soil Pit #4

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oi	2-0	Fibric organic matter
Ap	0-18	Black (10YR 2/1) fine sandy loam; friable; abrupt smooth boundary
Bw1	18-44.5	Dark grayish brown (2.5 Y 4/2) sandy loam; friable; clear wavy boundary
Bw2	44.5-58	Olive brown (2.5 Y 4/3) sandy loam; friable; clear wavy boundary
C	58+	Dark grayish brown (2.5 Y 4/2) sandy loam; friable

Soil Pit # 5

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oi	1.5-0	Fibric organic matter
Ap	0-24	Black (10 YR 2/1) fine sandy loam; friable; abrupt smooth boundary (expect for one ~35 cm drop on one side of pit); few tiny red concentrations
Bw1	24-47	Olive brown (2.5 Y 4/3) sandy loam; friable; clear wavy boundary
Bw2	47-59	Light olive brown (2.5 Y 5/6) sandy loam; friable; clear wavy boundary
BC	59-73.5	Light olive brown (2.5 Y 5/4) sandy loam (slightly coarser than B2 horizon); friable; clear smooth boundary
C	73.5+	Grayish brown (2.5 Y 5/2) sandy loam; friable

Note: When digging pit, found seashells scattered throughout the Ap horizon. Ashes could also be found. the large dip of the Ap on one side of the pit we hypothesize to be from a clam bake

Soil Pit #6

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oi	1.5-0	Fibric organic matter
Ap	0-15	Black (10 YR 2/1) fine sandy loam; friable; abrupt smooth boundary
Bw	15-48	Olive brown (2.5 Y 4/3) sandy loam; friable; clear wavy boundary
C	48+	Grayish brown (2.5 Y 5/2) fine sandy loam; friable

NORTH KINGSTOWN FORESTED SOIL PROFILES

Landscape position: Depression
 Parent material: Glacial Outwash
 Landform: Outwash Plain
 Classification: Typic Humaquept

Slope: 0-3%
 Soil Drainage Class: Poorly Drained
 Described by: Kelly L. Addy

Soil Pit #1

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oi	2.5-0	Fibric organic matter
Ap	0-24	Black (10YR 2/1) fine sandy loam; friable; clear wavy boundary;
Bw1	24-48	Very dark brown (10 YR 2/2) sandy loam; friable; clear wavy boundary; organic streaks throughout
Bw2	48-64	Light olive brown (2.5 Y 5/3) sandy loam; friable; clear smooth boundary that slopes downward toward vernal pool
C	64+	Grayish brown (2.5 Y 5/2) loamy sand (somewhat gravelly, but the side of core extraction was not as gravelly); friable

Soil Pit #2

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oi	8-0	Fibric organic matter
Ap	0-25	Black (10 YR 2/1) fine sandy loam; friable; clear wavy boundary
Bw1	25-40.5	Very dark grayish brown (2.5 Y 3/2) sandy loam; friable; clear wavy boundary; organic streaking throughout
Bw2	40.5-54	Olive brown (2.5 Y 4/3) sandy loam; friable; clear wavy boundary
CB	54-70	Grayish Brown (2.5 Y 5/2) loamy sand; friable; clear smooth boundary
C	70+	Gray (2.5 Y 5/1) loamy sand; gravelly lenses alternated through this media sloping downward toward vernal pool; friable

Soil Pit #3

<u>Horizon</u>	<u>Depth (cm)</u>	<u>Description</u>
Oi	2.5-0	Fibric organic matter
Ap	0-18	Black (10 YR 2/1) fine sandy loam; friable; clear wavy boundary
Bw1	18-29	Very dark brown (10 YR 2/2) sandy loam; friable; clear wavy boundary; organic streaking throughout
Bw2	29-50	Dark grayish brown (2.5 Y 4/2) fine sandy loam; friable; clear wavy boundary that slopes downward toward vernal pool
C	50+	Gray (2.5 Y 5/1) very fine sandy loam layered within yellowish brown (10 YR 5/8) loamy sand; both of these lenses are dense (difficult to shovel with spade); firm

APPENDIX D: Water Table Depths

North Kingstown Suburban Water Table Depths

North Kingstown Forested Water Table Depths

Charlestown Water Table Depths

Appendix E: Outflow Nitrate-N and Bromide Concentrations

North Kingstown Forested Mesocosm #1

North Kingstown Forested Mesocosm #2

North Kingstown Forested Mesocosm #3

North Kingstown Suburban Mesocosm #4

North Kingstown Suburban Mesocosm #5

North Kingstown Suburban Mesocosm #6

Charlestown Suburban Mesocosm#7

Charlestown Suburban Mesocosm #8

Charlestown Suburban Mesocosm #9

Charlestown Forested Mesocosm #10

Charlestown Forested Mesocosm #11

Charlestown Forested Mesocosm #12

Appendix F: Outflow Ammonium-N Concentrations

North Kingstown Forested Mesocosm #1

North Kingstown Forested Mesocosm #2

North Kingstown Forested Mesocosm #3

North Kingstown Suburban Mesocosm #4

North Kingstown Suburban Mesocosm #5

North Kingstown Suburban Mesocosm #6

Charlestown Suburban Mesocosm #7

Charlestown Suburban Mesocosm #8

Charlestown Suburban Mesocosm #9

Charlestown Forested Mesocosm #10

Charlestown Forested Mesocosm #11

Charlestown Forested Mesocosm #12

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