SPATIAL AND TEMPORAL SCALING OF NITROGEN CYCLING AND EXPORT: RESOLVING THREE PARADOXES FOR A FORESTED PIEDMONT WATERSHED

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ABSTRACT

Jonathan M Duncan: Spatial and Temporal Scaling of Nitrogen Cycling and Export: Resolving Three Paradoxes for a Forested Piedmont Watershed
(Under the direction of Lawrence E. Band)

Nitrogen is a limiting nutrient in many forest and aquatic ecosystems. Reducing nutrient pollution to downstream receiving waters is an important scientific and management goal. Disproportionate amounts of nitrogen cycling and export occur in small portions of the landscape and over brief periods of time. These “hot spots” and “hot moments” are highly heterogeneous in space and time, making scaling of nitrogen cycling and export a major scientific challenge. This dissertation addresses how linkages between the physical structure of a watershed and related hydrological, ecological, and biogeochemical processes control the spatial and temporal patterns of nitrogen cycling and export.

This work was conducted at Pond Branch, a small, forested watershed in the Piedmont physiographic province in Maryland (USA). This dissertation has three related multiscale questions that are addressed by employing three different views of watershed ecohydrology (plan view, cross sectional, and longitudinal). Detailed observations and analysis at Pond Branch suggest that the ecohydrological processes in the riparian zone (which accounts for 4% of the catchment area) control nitrogen cycling and export at the watershed scale. In particular:

1) Denitrification accounts for approximately 25% of atmospheric N deposition. 99% of watershed scale denitrification occurs in riparian hollows, which comprise less than 1% of the watershed. 2) Water table declines and diurnal variations during the summer likely decrease the retention efficiency of riparian hollows, driving seasonal stream export patterns. Annual stream export is approximately 20% of denitrification, so moderate decreases in the retention in such close proximity to the stream could easily account for stream nitrogen patterns. 3) The ecohydrology of the riparian zone exerts a strong control
on the timing and magnitude of nitrogen export as shown in evolving concentration-discharge relationships.

Overall, this dissertation increases understanding of how the geomorphic template is an important control for nitrogen cycling and export at the watershed scale. It advances our understanding of hot spots and hot moments from a geomorphic perspective that helps link biogeochemical reactions and hydrologic transport mechanisms to explain seasonal patterns in nitrogen export.
To Heather, Benjamin, and Cassidy
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CHAPTER 1. INTRODUCTION

Understanding the spatial and temporal heterogeneity of hydrological and biogeochemical controls on nitrogen cycling and export is a major scientific challenge (Lohse et al., 2009). The heterogeneity in hydrological and biogeochemical processes are themselves controlled by the watershed geomorphology and the variability of the geomorphic template. Stream water quality and quantity are integrated signals of different catchment hydrological and biogeochemical mechanisms, source areas, and flowpaths, all of which are highly nonlinear and can change over time. Changes can occur on timescales ranging from individual storm events to multiple years. My goal is to better understand the mechanisms by which forested watersheds retain and export water and nitrogen. This requires understanding the spatiotemporal variability in complex and interdependent processes. Hydrologic controls on these processes include groundwater levels, soil moisture content, connectivity, and residence times along flowpaths. These processes have characteristic space-time scales that can be useful for hydrological modeling (Blöschl and Sivapalan, 1995). Understanding nitrogen cycling and export also requires knowing the biogeochemical controls along these flowpaths. Biogeochemical controls of terrestrial nitrogen cycling include microbially-mediated transformations that are functions of energy (labile carbon), reactant concentrations, and soil oxygen, moisture, and temperature ranges. Because each of these controls is highly variable in space and time (Figure 1.1), it is important to develop appropriate measurements and models that account for this heterogeneity.

Overarching question: **How does heterogeneity, both in the geomorphic template and in ecohydrological processes control nitrogen cycling and export across a range of spatial and temporal scales?**
General Background

Nitrogen Cycle
The major biological nitrogen cycle processes in a forested watershed include the following: (Figure 1.2):

- Biological fixation - conversion of dinitrogen gas to ammonia
- Assimilation - Incorporation of inorganic nitrogen into amino acids
- Mineralization/Ammonification - production of ammonia by microbial decomposition
- Nitrification - aerobic production of nitrate from ammonium
- Denitrification - anaerobic reduction of nitrate to nitrous oxide and dinitrogen gas

Less common biological processes include:

- Dissimilatory nitrate reduction to ammonium (DNRA) - anaerobic conversion of nitrate to ammonia
- Anammox - anaerobic ammonium oxidation of nitrate produces dinitrogen gas

Physical processes include:

- Sorption and desorption – physical process of binding between bulk phase (liquid or gas) and a surface (soil)
- Volatilization - ammonia gas lost from soil to the atmosphere

My work considers the major biological processes, other processes may warrant further investigation in future research at Pond Branch.

Hydrologic controls
Groundwater levels have been found to be a primary control on nitrogen cycling and dynamics in riparian zones (Hefting et al., 2004). Hefting et al. found that across a set of European catchments with average water tables within 10cm of the soil surface, mineralization is the main nitrogen transformation process. Where average water tables are between 10 and 30cm, denitrification is more dominant; and where water tables are
below 30cm, nitrate accumulates as a result of nitrification. Less work has been done to assess if and how water table fluctuations within a watershed control nitrogen cycling. Soil moisture is the result of interactions among climate, vegetation, and soil and is an important controlling factor of nutrient cycling (Pastor and Post, 1986). Soil moisture can be an important driver of soil oxygen levels, plant nutrient uptake and water stress, and for sustaining microbial communities. Variations in soil moisture at the plot scale could enable coupled denitrification and nitrification. Nitrification could occur during drier oxygenated conditions and denitrification would occur when oxygen levels drop. Coupled nitrification and denitrification is especially plausible when nitrate availability limits denitrification. There is a lack of research on coupled nitrification-denitrification as a result of soil moisture variability.

At landscape scales, the geographic patterns of soil moisture are related to the hydrologic connectivity of a catchment (Western et al., 1997; James and Roulet, 2007). Topography is an important control on soil moisture distributions, especially in non-storm periods or more humid catchments. Topography can also determine the strength of connectivity between hillslopes, riparian zones, and streams (Jencso et al., 2009). Highly connected portions of a watershed can receive or contribute disproportionate amounts of throughflow or groundwater to riparian zones and streams. Many studies have noted the particular importance of riparian zones in controlling denitrification and potentially determining streamflow chemistry (Bishop et al., 2004).

Residence time distributions along flowpaths are an important control on biogeochemistry. A parcel of water that has higher residence time in some locations is more likely to accumulate inputs of reactants and substrate to process. This directly relates to the Damkohler number (the ratio of reaction rate to transport rate). Locations with higher Damkohler numbers are likely to experience higher rates of transformations, relative to the flushing frequency.
Biogeochemical controls

Biogeochemical controls on nitrogen cycling are complex and highly variable in space and time. Reaction rates are dependent upon a combination of microbial, plant, and environmental factors.

Environmental and soil factors are important controls on nitrogen cycling rates. Soil moisture and temperature drive the activity of microbial respiration (Pastor and Post, 1986); (Parton et al., 1996). Soil structure and texture can control how long soil water is available to microbes and the amount of microsites for reactions to take place. Perhaps the most important environmental control is soil oxygen levels, which have considerable control over the rates of nitrification, denitrification, and ammonification (Reddy and Patrick, 1975) (Hedin et al., 1998; Hill, 1996). Oxidation and reduction (redox) reactions are especially important processes that regulate nutrient cycling. Oxic vs. anoxic conditions have been viewed as thresholds for nitrification and denitrification reactions, but recent work has shown that these processes are coupled in many soil environments. Soil oxygen sensors in surficial soils were used to obtain a high temporal resolution dataset and determine the duration and magnitude of anoxic conditions.

Reactant availability (nitrate for denitrification or ammonium for nitrification) is typically a controlling factor (Groffman et al., 2009). These reactants can be produced in situ or transported from upslope areas. In the absence of input or transformation, a given patch of soil will quickly become substrate limited. For example, denitrification in an anoxic region with in situ supplies of nitrate exhausted could only occur through production of new nitrate in the presence of variation in oxygen levels or transport of nitrate from connected patches. Introducing oxygen variability could produce nitrate via nitrification, then revert back to anoxic conditions for denitrification to proceed. Secondly, precipitation-driven advection or some other sort of nitrate addition (e.g., fertilization, deposition) could also stimulate denitrification.

Microbial community composition is an important control on nitrogen cycling. Community composition is structured by long-term environmental drivers (Wallenstein
et al., 2006). Rapid fluctuations in redox potential have also been found to alter community structure (DeAngelis et al., 2010). Anaerobic heterotrophs can alter element cycles by reducing nitrate, iron, manganese, and sulfur.

An energy source for microbial respiration is also necessary. This is typically in the form of labile carbon, but other compounds such as reduced sulfur, reduced iron, or methane can be used. Laboratory measures of microbial respiration were used as a surrogate for carbon availability.

Vegetation can play an important role in the cycling of nitrogen. Different plant species have distinct carbon to nitrogen ratios. The leaves then impart that signature into litter. C:N ratios can effect how quickly nutrients are cycled, mineralization and nitrification rates, and how much is available for hydrologic transport (Lovett et al., 2004).

**Geomorphic controls**

The physical structure of a watershed imparts a fundamental control on where, when, and how long parts of the landscape can transmit, collect, and drain water. There are long-term feedbacks among the pedogenesis, climate drivers which include precipitation and evapotranspiration, and vegetation. Landscape topography and landscape position has long been seen an import control for hydrology and biogeochemistry (Gregory and Walling). The presence of riparian zones and frequently saturated areas such as hillslope hollows are directly related to the frequency of advection of water and solutes. To an extent larger scale land forms co-evolve with vegetation and climate and set the stage for subsequent biogeochemical reactions. Additionally, the microscale geomorphic template of watersheds is an important control for redox sensitive biogeochemical transformations.

**Human Alteration of the N cycle**

2013 marked the 100th year humans have fixed atmospheric nitrogen (N) on an industrial scale via the Haber-Bosch process. Anthropogenic fixation increased the
amount of reactive nitrogen globally by nearly two orders of magnitude from pre-
industrial background levels (Galloway, 2003). Over the last century, there has been a
corresponding and dramatic increase in N loading to receiving waters around the globe.
Even N export from forests where N retention is relatively high is a significant fraction
of overall stream flux. In the Chesapeake Bay, the largest estuary in the country, nearly
20% of the total nitrogen load is estimated to come from forests, despite comprising ~
55% of the watershed area (Jantz et al., 2005).

There is great interest in the ability of forests to serve as “sinks” for atmospheric N,
especially when excess N can stimulate primary production in estuaries which can then
lead to widespread anoxic zones (Boesch et al. 2001, Conely et al. 2009). Understanding
the mechanisms of how ecosystems serve as N sinks through assimilation, storage and
denitrification is especially important given the changing spatial and temporal
distributions of N sources and transport vectors including: a) restoration strategies and
watershed management plans which attempt to restore the form and function of forests),
and b) the periods of time that transport and transform disproportionately high amounts
of N (hot moments) could be altered by the changing climate. As temperatures increase,
there could be higher rates of evapotranspiration and lower water tables leading to a
decrease in denitrification. Additionally, there is mounting evidence for changes in the
frequency of rainfall (Chou et al., 2012) including longer times between storms, and an
increase in the intensity of extreme rainfall events (Westra et al., 2013).

Spatial and temporal scales of variability of hydrological and biogeochemical
controls
Variability of hydrological and biogeochemical drivers can exist at all temporal and
spatial scales. Disproportionate amounts of nitrogen can be transformed or transported
during brief periods of time (hot moments) in discrete patches of the landscape (hot
spots) (McClain et al., 2003). Because there are many intertwined controls,
understanding the structure and dynamics of heterogeneity is crucial for improved
knowledge of water (McDonnell et al., 2007) and nitrogen cycling and export.
Temporal variability of hydrological and biogeochemical controls can be very high at all time scales. At inter-annual scales, there are climatic differences in dry and wet years. Longer timescale variability may also relate to disturbance of ecosystem growth and succession (Aber et al., 1997; Schimel et al., 1996). There are profound differences in nitrogen cycling and export dynamics at seasonal timescales driven by forest cycles. Rates and fluxes can differ markedly between winter and summer months (Miller et al., 2009). In temperate forests, leaf senescence can dramatically increase labile carbon supplies and fuel denitrification (Groffman and Tiedje, 1989; Sebestyen et al., 2008). Plant uptake is typically highest during the summer growth months and lowest during leaf-off (Stoddard, 1994). Causes and sources of diurnal streamflow have been examined for more than 60 years (Troxell, 1936) and have been a recent focus for hydrologic (Bond et al., 2002; Wondzell et al., 2007) and biogeochemical (Rusjan and Mikoš, 2010) research. Episodic events such as rainfall events transport carbon and nitrogen to hot spots where microbial transformations occur. Event sampling of water, carbon, and nitrogen has been the focus of several studies revealing the importance of variable source areas (Inamdar et al., 2004) and groundwater seeps (Burns et al., 1998).

Spatial variability of hydrological and biogeochemical drivers can be highly heterogeneous from watershed to microsite scales. At the catchment scale, the major spatial differences fall out along different landscape positions. In temperate forests, ridges, hillslope hollows, and riparian areas exhibit different frequencies of wetting. Understanding the extent and duration of wetting in these different topographic settings is also important for determining nitrogen cycling and export rates. Within a given landscape unit, there is often considerable microtopography that can account for variation in hydrological and biogeochemical controls. With the advent of high resolution topographic data from LiDAR, exploring high resolution topographic variations is now possible (Tenenbaum et al., 2006). At the smallest scales (mm to m), hydrological variability arises from soil structure and porosity. At these smallest scales, microsites have been shown to host a majority of denitrification reactions in a soil core despite comprising as little as 1% of the volume (Parkin, 1987).
Variability and transport: plot and catchment scale hotspots

Accounting for both hydrologic variability and transport is required for understanding nitrogen cycling and export. Variability in hydrological and biogeochemical drivers is common at the plot scale on diurnal cycles or across space. Part of this dissertation investigates the integrated water table-soil oxygen condition across a range of hydrologic regimes, include baseflow, typically considered a cold moment. In response to diurnal variations of soil moisture and oxygen, nitrification can proceed in aerobic environments producing nitrate for denitrification to occur when oxygen levels drop. Anoxic environments could occur in response to nightly decreases in soil oxygen values. In addition to within plot variations, there are larger differences among plots in different landscape positions. This reflects the geomorphic structure of watersheds and relates to the frequency of hydrologic flushing through different parts of the landscape. Catchment scale hotspots relate to the topography and connectivity that develops during precipitation events and seasonal timescales. Considering plot and catchment scale variability is essential for adequate understanding.

Major Questions and Organization the Dissertation:

This dissertation seeks to advance understanding of nitrogen cycling and export by using distributed measurements and models to scale from cores to the catchment and from minutes to more than a decade. I examine the heterogeneity in water and nitrogen dynamics across a range of spatial and temporal scales in each chapter (Figure 1.3). This work was conducted in Pond Branch, a small, forested watershed in the Piedmont physiographic province in Maryland (USA). The sequence of individual chapters that address these multiscale puzzles are arranged along three major ways to view a catchment (sensu Leopold, 1994): 1) catchment and landscape scale in plan view, 2) longitudinal profile from highest and furthest point in the catchment, down the stream to the outlet, and 3) a cross section from western most ridge to eastern-most ridge, with a focus on the stream and near-stream zone (Figure 1.4).

The following three chapters address specific nitrogen paradoxes of Pond Branch:
Chapter 2 explores how nitrogen cycling regimes change in different landscape positions across seasons and develops a catchment scale denitrification estimate for an entire water year. In many forested catchments, despite large amounts of atmospheric N deposition, there are surprisingly high rates of retention. So, where does all the N go (van Breeman et al., 2002)? The focus of resolving this paradox at Pond Branch was to examine hot spots and hot moments of denitrification and scale denitrification estimates from cores to the catchment. A leading hypothesis is that most sampling and modeling approaches do not properly account for hydrologic processes in both space and time, and may miss a substantial amount of denitrification, the conversion of reactive nitrate and nitrite to nitrogen gases (nitric oxide, nitrous oxide, dinitrogen) (Kulkarni et al, 2008).

Chapter 3 investigates the role of diurnal fluctuations in riparian groundwater, soil moisture, and soil oxygen on summer peaks in streamwater nitrogen concentrations. Paradoxically, the majority of nitrate is exported via the stream at Pond Branch during the summer when the ecosystem should be taking it up. Unlike at some other watersheds- groundwater is depleted in nitrate relative to the stream. Even if the source of summer nitrate is temperature driven mineralization and nitrification, which also peaks in summer- there is still a hydrological puzzle as the geographic sources of nitrate are surface soil- not a region that contributes to baseflow. One of the greatest challenges in watershed science is understanding how the cumulative effects of ecosystem and hydrologic processes occurring throughout terrestrial and in-stream flowpaths collectively control the timing and magnitude of N export. These flowpaths are largely controlled by the geomorphic template, comprised of extensive hillslope hollows and complex fluvial networks characterized by microtopographic variation throughout the riparian zone. A leading hypothesis is that fuller accounting for hydrologic variability is essential for predicting where/when watershed N export from the connected flowpaths within the geomorphic template will occur at any given time.
Chapter 4 uses high-resolution concentration-discharge (c-Q) relationships to examine the evolution of c-Q patterns at storm to seasonal timescales. The paradox in this chapter is that nitrate c-Q patterns are different between those generated by long-term weekly grab samples and storm based c-Q in many other forested watersheds (Inamdar et al., 2004, Sebestyen et al. 2009). Understanding how multiple processes occurring over different temporal and spatial scales control c-Q patterns is important for understanding how much nitrate will be exported during storm events and over the longer timescales.

**Significance of Dissertation**

Scientific importance:
Controls on watershed nitrogen cycling are complex and multi-scale. Linking and integrating ecohydrologic processes across scales is a major scientific challenge (Baird and Wilby, 1999). Nitrogen biogeochemistry is an interesting theoretical example because of numerous nonlinearities that are mediated by biological and hydrological processes. Considering that a disproportionate amount of nitrogen cycling occurs in small portions of a soil core (Parkin, 1987) and small portions of a catchment (McClain et al., 2003), addressing larger scale (regional and river-basin) issues of nitrogen pollution requires improved understanding of controls across scales. A second scientific challenge is the ability to predict N cycling and export in unmonitored locations. Part of this challenge requires deconvolving land use history and landscape change. There are longer-term controls on watershed structure from glaciation millennia ago to human disturbance of deforestation and agriculture centuries ago. With agricultural abandonment in the region in the early part of the 20th century, forests regrew at Pond Branch. Upon this altered landscape, forest ecosystems have been aggrading for nearly a century with anthropogenic N deposition, much of which is generated hundreds of kilometers away and has occurred in significant amounts for the last several decades along with global climate change which has accelerated over the course of the LTER record. Pond Branch is representative of much of the mid-Atlantic Piedmont, which has largely reforested over the last century.
Societal importance:

Altering when and where N transformations and transport will occur requires a more comprehensive understanding that can be operationalized in different watersheds. A major goal of watershed management and pollution mitigation programs such as the total maximum daily load (TMDL) program is to ‘restore’ watershed form and function of disturbed watersheds towards that of forested watersheds. This typically involves trying to reconstruct the function of hot spots and hot moments. Developing resilient management strategies that can provide retention and removal of reactive N have challenges in the spatial optimization of management strategies at a range of scales. Ecosystem services of N removal/retention may occur primarily as denitrification from hot spots and hot moments. The research presented here contributes to the following N management issues:

1. Critical Loads for atmospheric N deposition have been used to quantify soil and stream export thresholds, but depend heavily on the ability for a given watershed to retain, transform, and transport N loads.

2. Spatial optimization of watershed management practices is critical for efficient expenditures of limited resources.

3. Stream restoration and afforestation efforts aimed at restoring the ecosystem form also need to restore ecosystem function.

We note that N export at Pond Branch is very low and similar forest catchments are not a major N source to the Chesapeake Bay. However, this research can be put in the context of pollution sources and management approaches to improve ecosystem retention in other landscapes. The hope is that better understanding of the relationship between the geomorphic template, terrestrial and aquatic ecosystems, and hydrologic regime can shed light on restoration strategies in developed, as well as undeveloped, catchments. These results could help target where in catchments to prioritize management efforts, and where and how to place denitrification enhancements. It could also inform stream and riparian restoration practices by establishing seasonal and storm based functions that need to be better replicated.
Figure 1.1 Characteristic space-time scales for biogeochemical processes.
Figure 1.2 Simplified version of the nitrogen cycle. Adapted from (Trimmer et al., 2003)

Figure 1.3 Spatial and temporal template for dissertation chapters. Scaling Denitrification (Chapter 2), Summer Peaks (Chapter 3), and concentration-discharge (c-Q) patterns in Chapter 4.
Figure 1.4. Three views of watershed ecohydrology presented in this dissertation. Plan view (Chapter 2), Longitudinal (Chapter 3), and Cross-Section (Chapter 4).
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CHAPTER 2: TOWARDS CLOSING THE WATERSHED NITROGEN BUDGET: SPATIAL AND TEMPORAL SCALING OF DENITRIFICATION

2.0 Preface

Denitrification is difficult to estimate at the catchment scale because of a) the spatial distribution soil oxygen/redox status, particularly in small hotspots, is difficult to map, b) the temporal variability of soil oxygen conditions can vary rapidly, and c) observational error of trying to measure N₂ gas in the field given atmospheric contamination. This chapter uses LiDAR topographic data to delineate small features in the riparian zone, soil oxygen sensors to capture temporal variability at sites spanning a topographic gradient and a novel laboratory technique to measure denitrification as N₂ flux from soil cores at different oxygen conditions. Combining these three technological advances enables us to scale denitrification measurements from cores to the entire catchment at daily intervals for an entire water year.

The research in this chapter was conducted in collaboration with Peter Groffman, Cary Institute of Ecosystem Studies and Lawrence Band, University of North Carolina Chapel Hill. The following was published in the Journal of Geophysical Research-Biogeosciences in October 2013.
2.1 Introduction

Enhanced consideration of the hydrogeomorphic template of watersheds is critical to understanding watershed nitrogen budgets. We developed a framework to estimate the spatial distribution and temporal dynamics of soil moisture and soil oxygen in surficial soils to scale nitrogen transformations for a forested watershed (Pond Branch) in Maryland, USA. We sampled soil cores in upland, hillslope hollow, riparian hollow, and riparian hummock landscape positions in different seasons for biogeochemical fluxes including measurement of N$_2$ gas produced via denitrification. We extrapolated these rates in space and time with information derived from in situ soil oxygen and soil moisture probes to scale fluxes from plots to the catchment level. We addressed three questions: 1) How important are seasonal, daily and storm event variations in soil oxygen for denitrification? 2) How is denitrification spatially distributed through the watershed? And 3) How important is denitrification to the watershed nitrogen budget? We found that microtopography within the riparian zone is a significant influence on soil oxygen dynamics and therefore redox sensitive biogeochemical processes such as denitrification. Riparian zone hollows (lower topographic positions) represented 0.5-1.0% of the catchment area, but accounted for >99% of total denitrification. Interestingly, topography was a much stronger controller of oxygen than rainfall, which had little influence on temporal variation in soil oxygen levels. Spatial and temporal extrapolation of measured rates suggests that a minimum of 16 to 27% of atmospheric nitrogen deposition is lost to denitrification. These results suggest that the importance of denitrification in the nitrogen budget of forested watersheds depends fundamentally on the presence of landscape elements such as riparian hollows that function as “hotspots” of activity.

Understanding the processes determining nitrogen cycling in the environment is a major scientific challenge at multiple spatial and temporal scales (Galloway et al. 2003, Davidson et al. 2012). Humans have dramatically increased the amount of reactive nitrogen available to global ecosystems (Vitousek 1997), yet watersheds have been shown to be very retentive of nitrogen and we are unable to resolve where the missing nitrogen goes (Galloway et al. 2003). A leading hypothesis is that most sampling and
modeling approaches do not properly account for hydrologic processes in both space and time, and may miss a substantial amount of denitrification, the conversion of reactive nitrate and nitrite to nitrogen gases (nitric oxide, nitrous oxide, dinitrogen) (Kulkarni et al., 2008).

Denitrification is a function of available nitrate, soil oxygen concentration, temperature and a microbial energy source, e.g., dissolved organic carbon (DOC). This process is difficult to measure, especially in the field (Boyer et al., 2006). Laboratory-based measurements are difficult to extrapolate to the catchment scale in part because many sampling strategies tend to under-sample critical areas, and the analytical environment in the laboratory may be significantly different from field conditions (Groffman et al., 2006a, Wang et al., 2011). A particular challenge is that certain elements of landscape remove a disproportionately high amount of N (hot spots) in response to seasonal and event driven conditions (hot moments) (McClain et al., 2003). Denitrification exhibits spatial variability at scales ranging from soil pores ($10^{-6}$ m$^2$) to watersheds ($10^5$ m$^2$) (Parkin, 1987).

In forested catchments, geomorphic variability influences denitrification within landscape positions ranging from riparian to ridge tops (Vidon and Hill, 2006). Areas with varying slopes and upslope contributing areas can have distinctly different patterns in saturation and biogeochemistry (Creed and Beal, 2008) with redox conditions varying along a catenary sequence. Areas that concentrate shallow subsurface stormflow and zones of deeper groundwater flowpath discharge that contribute to streamflow are called variable source areas (Dunne and Black, 1970). Variable source areas have been shown to be biogeochemically important (McClain et al., 2003, Inamdar and Mitchell, 2006, Harms and Grimm, 2010) as these zones are more frequently anoxic and are likely to have DOC and nitrogen advected in from upslope. In humid watersheds, the relative importance of shallow subsurface flowpaths can often be captured by the topographic wetness index (TWI) (Beven and Kirkby, 1979, Creed and Band, 1998, Tague and Band, 2001), a dimensionless index that accounts for local slope and upslope areas likely to contribute to runoff generation. Areas with high TWI values and located in close proximity to the stream are typically considered variable source areas. Nested within the catchment scale is the presence of microtopography that can have important local scale controls on
saturation frequency. Within riparian zones, hummocks (higher locations) are likely to saturate less frequently than hollows (lower locations) that are more likely to be inundated by rising water tables. Therefore, over very small length scales, biogeochemical processing capacities can vary drastically. Relatively small changes in hydrologic conditions induced by microtopographic variations have been shown to control redox sensitive biogeochemical reactions in geochemical simulations (Frei et al., 2012), peatlands (Waddington and Roulet, 1993), and engineered wetlands (Wolf et al., 2011).

Temporal variability in factors controlling denitrification ranges from storm events ($10^{-3}$ year) to inter-annual variations ($10^1$ year). The extent of temporal variability in denitrification depends on the hydrogeomorphic context; in riparian zones, saturated regions can expand and contract across each of these time scales. Seasonal changes in denitrification are driven by water table fluctuations and are modified by temperature (Hefting et al., 2004). There are also longer term controls on denitrification rates that relate to a) climatic oscillations that produce wetter or drier conditions (Mengistu et al., 2012), b) changes in forest ecosystem processes such as decomposition of fallen trees and changes in vegetation community composition, and c) soil carbon pools and the lability of carbon.

The capacity for quantifying short-term controls on denitrification has improved with the development of sensors that can provide continuous measurements of soil moisture and oxygen (Burgin et al. 2010, Burgin and Groffman 2012) or water table. If these sensors can be deployed in a suitably comprehensive set of geomorphic positions they could provide a strong platform for spatial and temporal extrapolation of point measurements of denitrification to the catchment scale. These extrapolations are facilitated by establishing relationships between denitrification and soil oxygen, which can be accomplished with relatively new soil core incubation systems that allow for quantification of denitrification $N_2$ and $N_2O$ production at different oxygen concentrations (Wang et al. 2011, Groffman and Burgin 2012).

Previous work in Pond Branch, Maryland, USA, the forested reference watershed for the Baltimore urban long-term ecological research (LTER) project, has demonstrated the importance of soil moisture and the associated soil oxygen dynamics to accurately assess
denitrification (Band et al 2001, Tague 2009, Tague et al., 2010). In this study, we improved upon a previous nitrogen budget for this watershed (Groffman et al., 2004) by developing a space/time framework to scale denitrification and associated biogeochemical fluxes in different landscape positions in different seasons to the catchment level by combining denitrification measurements in soil cores with in situ soil oxygen and soil moisture data. We addressed three questions: 1) How important are seasonal, daily and storm event variations in soil oxygen for denitrification? 2) How is denitrification spatially distributed through the watershed? And 3) How important is denitrification to the watershed nitrogen budget?

2.2 Site Description

The Pond Branch watershed is a 37 ha subcatchment of the Baisman Run watershed in the Piedmont physiographic province of Maryland, USA (Figure 2.1) (Lat 39°28'49.1", long 76°41'15.0"). The 1st order stream flows south, with contributing hillslope areas that are dominantly east and west facing. It is the forested reference watershed of the Baltimore Ecosystem Study (BES) Long-Term Ecological Research project (Groffman et al. 2004). Elevation ranges from 140-190m. The entire watershed is underlain by a medium to coarse-grained micaceous schist of the Wissahickon Formation. Depth to saprolite is highest on ridges, thins (<1m) at steep midslope positions, and is 1-2m in bottomland locations (Cleaves et al., 1970). Soils range from silt clay loam to silt loam in the riparian areas to sandy loam on steeper slopes. The upstream (northern) portion of the watershed has gentle slopes with a wide valley bottom. The most upstream portion of the stream emerges from a 1.0m incised headcut, although much of the perennial streamflow emanates from discrete groundwater seeps at the base of the slopes. The riparian zone has two streams draining each side of the catchment with a wetland complex in many locations in between and adjacent to the streams. The valley bottom likely serves as a large storage reservoir of water and nutrients during baseflow conditions. Large portions of the broad valley bottom area are comprised of hummock and hollow microtopography that have likely formed from a combination of tree throw and channel avulsion over time. The terms riparian hummocks
and hollows are used to describe relative high and low topographic positions in the near stream zone. The microtopographic variation is on the order of 10cm in the vertical dimension and the length scale is often about 0.5-1m. To those unfamiliar with Pond Branch, this has left some with the impression that these are self-enclosed depressions and monadnock-like hummocks. In part this is due to the prevalence of these terms in describing boreal peatlands (Bubier et al., 1992). However, there is also broad support for using these terms to describe microtopographic variation in riparian areas (Frei et al., 2010). This microtopographic variation is located within a broad valley-bottom, which has many characteristics of a riparian wetland. We posit that hummocks and hollows have formed through a combination of tree throw and channel avulsion over time. Therefore, these are often long-linear features, consistent with them being abandoned and/or ephemeral channels. In the very headwaters, within 30 m where the main channel is formed at the headcut, there are some hollows that terminate in groundwater seeps. What we do not know about these hummocks and hollows is the extent to which historical erosion after European settlement played a role in their formation. Many of the hummocks have mineral-like soil composition beneath a few cm thick organic horizon, suggesting they’ve been there for some time, which is consistent with the hypothesis that pre-settlement floodplains were broad and contained microtopographic variation (Walter and Merritts, 2008). In general riparian hummocks are found in the middle of the valley bottom, hydrologically disconnected from uplands by hollows or geomorphic incisions on both sides of the valley. These riparian hummocks, typically drain to riparian hollows (Figure 2.2). Slopes become steeper, the riparian zone narrows, and the stream becomes a single channel approximately half way down the catchment. The portion of Pond Branch closer to the gauge is more constrained geologically and the stream transitions into a single threaded channel. Approximately 200m downstream of where the stream becomes a single channel, a bedrock outcropping, which coincides with a small waterfall, acts a local base level. Downstream of this location there is a marked decrease in the extent and depth of riparian soils with the stream flowing over sections of exposed schist bedrock for approximately 200m before reaching the weir pool at the outlet.
2.2.1 Vegetation

Pond Branch is completely forested except for a 20 m wide grass-covered subsurface gasline transect which traverses the watershed. The forest is primarily dominated by *Quercus* spp. (oaks) and *Carya* spp. (hickory) with a stand age of approximately 90 years. There are locations, primarily near the outlet with an understory dominated by *Kalmia* spp. (laurel). In the riparian zones of Pond Branch, the dominant species is *Liriodendron* tulipifera (tulip poplar). *Acer* rubrum (red maple), *Nyssa* sylvatica (black gum), and *Carpinus* caroliniana (ironwood) are also present. The average leaf area index is 4.3 based on 20 sample points within the watershed using a combination of LAI-2000 and Digital Hemispherical Photography measurements. There are some points in the riparian zone where there are gaps created from tree fall in the valley bottom. In some areas the dominant vegetation is skunk cabbage (*Symplocarpus* foetidus) and ferns. The *Symplocarpus* decay quickly in mid summer, leaving little to no trace of their prominence in riparian hollows from spring to early summer, a phenomena common with the species (Small, 1959). Detailed vegetation description can be found in Groffman et al. (2006b).

2.2.2 Climate and N deposition

Pond Branch is in a humid subtropical climate with approximately 1000mm of rainfall annually. Summers are warm with average maximum temperatures of 30°C. Winter temperatures can be cold with mean minimum temperatures of -4°C and snowfall can occur several times per year. Deposition in the Maryland Piedmont is approximately 10 +/- 4 kg N/ha/year (NADP, 2012). During our sampling period, Water Year 2011 spanned near drought conditions in July 2011 to large rainfalls during Hurricane Irene (28-Aug-2011) and Tropical Storm Lee (7-Sept-2011). Irene delivered 86mm of rainfall and Tropical Storm Lee delivered 178mm over a three-day period (6-Sept to 8-Sept).

2.2.3 Land use history

The area was first inhabited in 1729 and logging in the area began in 1776 (Wolman, 1987). Large portions of this land were likely farmed in the eighteenth and nineteenth centuries. From the late 1840s-1857, a large iron-smelting furnace operated approximately 1km to the north of the watershed divide. Around the same time, marble
was mined close to the furnace. In Pond Branch, the remnants of a stone shelter can be found to the southwest of the headcut where the channel begins, just upslope from a distinct groundwater spring. This was likely the base for a small farming operation that consisted of pasture and at least several acres of tobacco and vegetable crops to supply miners (MD Historical Trust Archives, 2002). Current vegetation is thought to have developed on farmland abandoned around 1920, which was the peak of deforestation in Baltimore County (Bain et al, 2012). Selective logging was last conducted in 1958 (Cleaves et al., 1970) and the gas line was installed in the mid 1960s.

2.2.4 Sampling sites
We discretized the watershed into a small number of landscape positions that represent the continuum of the variable source area, and have been shown to exhibit characteristic frequencies of saturation and redox variability. Soil core sampling was conducted in uplands, which saturate rarely, hillslope hollows, which can become saturated seasonally and during storm events (Dunne and Black, 1970), and riparian areas, which are important with respect to streamflow generation and biogeochemical transformations (Burt and Pinay, 2005). Riparian zones were further delineated based on microtopographic variation into binary categories of riparian hummocks and hollows. Because soil moisture variability is highest in riparian zones (Tague et al 2010), we decided to sample in two riparian transects located in contrasting geomorphic regions. One riparian transect was located in the upper portion of the watershed where the valley bottom is wide and there is marked microtopographic variability where multiple channels exist. The active channel is on the west side of the valley. What is now the secondary channel was the primary streambed prior to a tropical storm that felled a large tree 20m upstream of the transect in 2004 and re-rerouted flow to the west. There is an abandoned channel on the east side of the valley. Upland sites in the northern portion of the watershed (Upper Uplands) cores were collected to the west of this riparian transect and Hillslope Hollow cores were collected to the east of the Upper Transect (Figure 2.2). The second riparian transect was located in the lower portion of the watershed with steeper side slopes, a narrower riparian zone, and lower microtopographic variation. There is a deep hollow at the lower riparian transect where water tables are frequently above the
ground surface. The hummocks in this transect are not as pronounced as in the upper transect potentially due to steeper side slopes that lead to higher sediment transport rates through the riparian zone. Upland cores in the southern portion of Pond Branch were taken to the west of the lower transect (Lower Uplands).

2.3 Methods

2.3.1 Sensor locations

Soil moisture and soil oxygen sensors were installed at the upper and lower riparian transects and in a hillslope hollow (Figure 2.2). Four groundwater wells were installed in approximately 5m increments from the stream to the toeslope at each riparian transect. 1m deep wells 5m from either side of the stream were installed in 2001. The transect was expanded in 2009 with ~2m deep wells that were installed 10m from the 2001 channel in another riparian location and 15 m from the channel at the toeslope. Soil oxygen sensors were installed at the upper riparian transect in March 2010. These sensors spanned the hillslope-riparian boundary and were placed in a riparian hummock, a riparian hollow, which is the secondary channel, and at the toeslope. Because there was little difference between hummock and toeslope values after 4 months of data collection, we moved the sensor from the hummock to an intermediate position in July of 2010 (Figure 2.3).

In the hillslope hollow adjacent to the upper transect, approximately 40m from the toeslope location, there were two pairs of soil oxygen and water content probes positioned approximately 20m apart along the trough of the hollow. We collected data from August 2010 to March 2012.

The third datalogger location was in the lower riparian transect. That location had three pairs of soil oxygen and moisture sensors located in riparian hummock, riparian hollow, and toeslope locations. Data were collected at 15-minute intervals from December 2010 to March 2012.

2.3.2 Sensor data

Soil oxygen concentrations were recorded using Apogee SO-111 probes (Apogee Inc., Logan, UT), which utilize a standard galvanic cell to measure the partial pressure of
oxygen in air. The diffusion-head sensors were buried vertically with the heads at 6cm depth. Reported sensor accuracy is < 0.002% O₂ drift per day. Upon removal in March 2012, oxygen sensors showed no signs of biofouling and atmospheric measurements were within 1% of pre-deployment values. Soil moisture was recorded using Campbell Scientific CS 616 (Campbell Scientific Inc., Logan, UT) water content reflectometer probes. Probes were installed vertically into the ground and measured the average water content of the top 20cm of soil. Both types of sensors were calibrated before deployment and set to collect soil oxygen and volumetric water content every 15 minutes (hourly at the upper riparian transect). Soil temperature was measured as part of the BES at hourly intervals in upland locations.

2.3.3 Soil nitrogen cycle measurements
Sets of duplicate 10cm long, 5cm wide soil cores were collected via hand auger to measure rates of N cycling in contrasting landscape positions in different seasons. The landscape positions sampled included: riparian hummock, riparian hollow, hillslope hollow, and upland. Cores were sampled in close proximity to the sensors in four different seasons (March, July, and November of 2010 and March, 2011) except at the upland locations where there were no sensors. Upland cores were collected proximal to long-term biogeochemistry plots where soil moisture was recorded monthly and soil temperature was continuously collected at hourly intervals.

Denitrification rates were measured with the N-Free Atmospheric Recirculation Method (NFARM) flow through core measurement system (Burgin et al., 2010, Burgin and Groffman 2012) at the Cary Institute of Ecosystem Studies. The NFARM system replaces air from the sample core with a synthetic atmosphere free of any nitrogen gas, making it easier to measure small changes in N₂, a central challenge in measuring denitrification rates (Groffman et al. 2006). Each core was analyzed at 20°C for N₂ and N₂O fluxes under varying oxygen concentrations (5%, 0%, then10%).

Net N mineralization and nitrification were measured using an in situ intact core method (Robertson et al., 1999). At each landscape position on each sampling date, two soil cores were taken and returned to the laboratory for extraction (2N KCl) of inorganic N and two soil cores were taken, placed in air tight plastic bags and returned to the plot for in situ
incubation. In situ cores were incubated for approximately four weeks before being returned to the laboratory for analysis. Net nitrification rates were calculated as the increase in nitrate over the course of the incubation period. Net mineralization rates were calculated as the increase in inorganic N (ammonium plus nitrate) over the course of the incubation period. Amounts of ammonium and nitrate were determined by colorimetric analysis with a Lachat Flow Injection Analyzer (Lachat, Loveland, CO). Detection limits for nitrate and ammonium were 0.007 mg/L and 0.002 mg/L N, respectively. The accuracy or average % recovery for nitrate and ammonium were 100.9 and 97.2%, respectively.

Potential net N mineralization and nitrification and microbial respiration were measured from the accumulation of NH$_4^+$ plus NO$_3^-$ and NO$_3^-$ alone during 10 day incubations of field moist, mixed soil in the laboratory (Groffman and Crawford 2003). Mineralization and nitrification rates were calculated as described above and respiration was calculated from the accumulation of CO$_2$ over the course of the incubation period. CO$_2$ was analyzed by gas chromatography.

2.3.4 Water quality analysis
Weekly grab samples were collected at the outlet for the BES LTER site. In addition, longitudinal streamwater samples were collected from a large groundwater seep near the headwaters of the stream at bi-weekly to monthly intervals from April-October 2011. [NO$_3^-$] was analyzed on a Dionex Ion Chromatogram (Dionex Sunnyvale, CA).

2.3.5 Geospatial analysis
Terrain Analysis was conducted to determine the areal extent of hillslope hollows and riparian areas. The extent of the riparian zone was delineated based on field collected GPS points and a hillshaded digital elevation model (DEM). Hillslope hollows were delineated for total contributing area above points located on convergent flowpaths located just outside the riparian zone using a LiDAR generated 0.5m DEM. The percentage of riparian hummocks and hollows were based on topographic wetness index (TWI) calculations that captured the extension or contraction of connected surficial flowpaths (Figure 2.3). While the TWI is sometimes not optimal for capturing the lateral
extent (perpendicular to the direction of flow) of hollows, the objective here was to more accurately capture the distribution of hummocks and hollows throughout the entire riparian area. Hollows were delineated by selecting a threshold TWI value that matched surveyed classifications using a 0.5m LiDAR DEM with a root mean square error of 0.11 in the vertical dimension (Tenenbaum et al., 2006). Accumulation of contributing drainage areas were done by preprocessing the DEM for enclosed depressions (pits) using a breaching algorithm (Lindsay and Creed, 2005), and a routing algorithm that enables flow to be partitioned among all downslope patches ($D_\infty$) (Tarboton, 1997). Because the hummock and hollow sequences are derived largely from fluvial processes, breaching does not substantially alter the outcome of a binary classification. An auto-level was used in the field to measure elevations at least every 0.5m across valley bottom transects that spanned from toeslope to toeslope. This was then compared with a cross-section from the 0.5m LiDAR with minimal differences found (1 point out of 100 that was more than 10cm off). Based on field verification and surveys, the threshold between hummock and hollow was found to be at a TWI 7.0. Using the mean riparian value (TWI=4.7) as a threshold produced a far larger percentage of riparian hollows than the surveyed value (TWI =7). The difference between TWI thresholds of 6 and 8, span field conditions from wet (just after Hurricane Irene (28-Aug-2011 and Tropical Storm Lee (7-Sep-2011) to dry (July 2011 baseflow) (Figure 2.4). In this range of riparian TWI values, the change in riparian hollow area is not large, ranging from 11 to 18% of total riparian area (Figure 2.5).

2.3.6 Scaling to daily watershed fluxes

We scaled nitrogen flux measurements from soil cores collected seasonally in different landscape positions to the entire watershed using a combination of terrain analysis for spatial scaling and in situ soil oxygen and soil moisture content sensors for temporal scaling. We fit NFARM core N$_2$ fluxes measured at 0%, 5%, and 10% O$_2$, with separate curves fit for each landscape position using data collected during all seasons. Soil oxygen concentrations recorded by in situ sensors were then used to produce daily estimates of N$_2$ flux for each landscape position (**Equation 2.1**). We assumed a similar microbial response to oxygen concentration between in situ soils instrumented with soil oxygen
probes and oxygen concentrations in the NFARM setup. A Q_{10} function of 2 (Lloyd and Taylor, 1994) was used to adjust rates for in situ soil temperature. We used upland soil temperature for all landscape positions. Patch flux rates were then extrapolated to the watershed scale based on the total area of each patch type calculated from the terrain analysis.

\[ J = R \times \rho \times v \]  
\textbf{Equation 2.1}

Where \( J \) = N\textsubscript{2} Flux (g/m\textsuperscript{2}/day), \( R \) is the NFARM N\textsubscript{2} rate (g/g soil/day) \( \rho \) is bulk density (g/cm\textsuperscript{3}) \( \times v \) is volume per square meter (cm\textsuperscript{3}/m\textsuperscript{2}) (using a 10cm soil horizon depth).

2.3.7 Statistical Analysis

Mean values and standard deviation of soil core parameters were calculated for duplicate cores collected in each of the 4 seasons. A two-way ANOVA was conducted to test for the differences in N\textsubscript{2} flux between riparian hollow and all other locations and between riparian locations in the upper transects and the lower transect. Because of variance heterogeneity of N\textsubscript{2} flux with oxygen concentration, we used weighted least squares regression. The ANOVA, weighted least squares, and quadratic regression analyses were performed using the software package R (R Development Core Team 2010).

2.4 Results

2.4.1 Soil oxygen

There were marked differences in soil oxygen concentrations among landscape positions and in some locations, across seasons and hydrologic conditions. Soil O\textsubscript{2} probes in toeslope and hillslope hummock positions varied from 15 to 21% (Figure 2.6). Because these were so similar and high, we assumed that these sites respond similarly to upland locations. Soil oxygen concentrations in riparian hollows were at 0% for the majority of the year, but increased to a maximum of 11% in the upper transect hollow and 4% at the lower transect hollow during summer dry periods. The most variable sensor was at the upper transect and was located in an intermediate elevation between a hummock and hollow in a secondary channel along the east side of the valley bottom where concentrations ranged from 17% to 1% (Figure 2.6). There were thus three distinct soil oxygen regimes, one dominated by anoxic conditions (riparian hollows), one dominated
by high oxygen concentrations (hillslope hollows and toeslope locations), and one with higher variability (riparian hummocks/intermediate locations) (Figure 2.7). While the aerobic locations were typically at or near atmospheric oxygen concentrations, there were small (<7%) decreases during storms. Hurricane Irene (27-Aug) and especially Tropical Storm Lee (7-Sep) produced decreases in soil oxygen concentration, but never below 10% in aerobic soils.

2.4.2 Seasonal and spatial patterns in nitrogen dynamics

N$_2$ flux rates from upland locations were low at all oxygen concentrations. Rates were highest (p < 0.001) from the riparian hollow cores with intermediate rates found in hillslope hollow cores (Table 2.1, Figure 2.8). N$_2$O flux rates ranged from 0 to 0.029 µg/g/day and were considerably lower than N$_2$ fluxes (0 – 6.0 µg/g/day) (Figure 2.9). Seasonal differences in soil core denitrification were smaller than variability among landscape positions. A two-way ANOVA using landscape position and sample month as main factors showed there was a significant difference in denitrification rates based on landscape position (F = 56.876, P < 0.001) while sample month was not a significant factor (F = 2.573, p < 0.06). A second two-way ANOVA showed that the lower riparian hollow had significantly higher denitrification rates than hummock and upland sites (F = 12.87, P < 0.001) and that differences in sample month were not significant (F = 2.27, P < 0.10). Denitrification rates were consistently higher at 5% O$_2$ than at 0% or 10% O$_2$ (Figure 2.8). The pattern was especially marked in the sites with the highest denitrification rates (upper hollow, lower hollow, hillslope hollow). We fit quadratic functions between denitrification and O$_2$ for each of these sites (Table 2). While variance of response increased with soil oxygen concentration, this appears to occur as a result of initial soil nitrate concentrations during the March 2010 snowmelt event.

Soil NO$_3$- concentrations were low (< 0.01 g N/kg) for at all sites except during March 2010, which were sampled just after major snowmelt (Table 2.1). In situ net mineralization and nitrification rates ranged from -0.20 g N/kg (net immobilization) to 0.36 g N/kg with significant differences among sites. Potential net N mineralization ranged from -0.71 to 1.24 g N/kg with riparian hollows having significantly higher rates
(Table 2.1). Potential net nitrification ranged from -0.12 to 0.50 g N/kg with no significant differences among sites (Table 2.1).

2.4.3 Annual Potential Mineralization and Nitrification
Estimates of annual in situ net N mineralization and nitrification produced by combining rate and bulk density values in Table 1 and assuming a biologically active season of 270 days ranged from 1.34 to 13.0 g N/m2/y for net N mineralization and from 0.0 to 1.26 g N/m2/y for net nitrification. Estimates of annual potential net N mineralization and nitrification ranged from -3.85 to 8.79 g N/m2/y for net N mineralization and from 0.0 to 17.39 g N/m2/y for potential net nitrification. Potential microbial respiration ranged from 1.01 to 1.67 g C/m2/d with no significant differences among sites.

2.4.4 Scaled denitrification estimates
Estimates of daily N2 flux were produced from the quadratic equations relating denitrification to soil O2 (Figure 8) for each landscape position (Equation 1). Riparian hollows were the dominant source of denitrification in the watershed, although there was a small amount of denitrification in the riparian hummocks and at the lower riparian toeslope location during Tropical Storm Lee (Table 2.2). Riparian hollows had significant denitrification activity throughout the year. Upland locations and hillslope hollows did not produce any N2 flux because oxygen concentrations did not reach sufficiently low levels. The highest rates of denitrification (100-175 mg N/m2/day) occurred in riparian hollow cores when they become partially aerated (Figure 2.10).

2.4.5 Watershed nitrogen budget
Mapping the spatial extent and calculating daily N2 flux from each landscape position using equations in Table 2.2 enabled summation of catchment denitrification for water year 2011 (Figure 2.10). The largest uncertainty with this extrapolation is the spatial extent of riparian hollows. Because rates were so different between riparian hollows at the upper and lower transect, we divided the riparian zone into upper and lower portions at the point where the stream becomes a single threaded channel and the slope of
hillslopes dramatically increases. Similarly, because only the lower upland probe saturated during Tropical Storm Lee, we maintained separate areas for upper (northern and upstream) uplands and lower (southern and downstream) uplands. Because the spatial extent of riparian hollows varies with the selected TWI threshold, we calculated watershed scale fluxes based on the bracketed values (TWI of 6 under wet conditions and 8 under dry conditions) that we observed through frequent visits to the site under hydrologic conditions ranging from drought to floods. Groundwater contributions to the overall nitrogen budget are small. Recurrent sampling of a groundwater seep just above the upper transect had low [NO3] of 0.026 mg/L (± 0.005) Cumulative N2 fluxes ranged from 59 to 98 Kg for WY2011 depending on the extent of riparian hollows (TWI of 6 vs. 8). This denitrification is equivalent to 16-27% of the 370 kg N/year that enters the watershed via atmospheric deposition (Table 2.3).

2.5 Discussion

2.5.1 A daily catchment scale budget of denitrification

We were able to combine intact core measurements of denitrification with data from in situ oxygen sensors and terrain analysis to produce estimates of watershed scale denitrification flux at a daily time step. This analysis highlights the importance of hotspots and hot moments of denitrification activity as drivers of watershed nitrogen budgets and the complexity of assessing this importance. In the Pond Branch watershed, riparian hollows drive the overall denitrification flux and are the critical hot spots for catchment scale fluxes. Variability within riparian hollows was large, but they had far higher N2 fluxes than other landscape positions, suggesting that our spatial discretization captured first order biogeochemical variability within the watershed. Continuous data for in situ O2 sensors allowed us to capture hot moment dynamics. The highest fluxes from riparian hollows occurred during relatively dry periods when the riparian hollows became partially aerated, allowing for maximum rates of coupled nitrification-denitrification (see discussion below). In addition to the hot moments, the O2 data showed that anaerobic conditions, and significant denitrification occurred throughout the year.
As the laboratory conditions of the core analysis preclude any advected supplies of nitrate or labile carbon, it is likely that our denitrification estimates are conservative. Lysimeter data at Pond Branch shows that very little NO$_3^-$ is transported from the uplands (Groffman et al., 2009), it is possible that whatever nitrate is advected from uplands occurs at discrete times that were not sampled, leading to a higher overall denitrification rate than we present here. Our measured rates compare well with other estimates from previous studies in similar ecosystems. We never estimate a positive N$_2$ flux for the relatively dry upland, hillslope hollow, or riparian hummock locations, which is consistent with many previous studies (Bowden 1987, Groffman and Tiedje 1989, Seitzinger et al. 2006). Our estimates of riparian hollow denitrification of 100-175mg N/m²/day were higher than rates from riparian wetlands in New York, USA measured by Burgin et al. (2010) (0-75mg N/m²/day) and from wetlands in New Jersey, USA measured by Watts and Seitzinger (2000) (3-82 mg N/m²/day).

### 2.5.2 Why were N$_2$ fluxes highest at 5% oxygen?

Somewhat surprisingly, N$_2$ fluxes were higher at 5% O$_2$ than at 0% O$_2$, nitrification and denitrification are tightly coupled in Pond Branch soils. When soil NO$_3^-$ levels are low, as is the case in the wet areas at Pond Branch, NO$_3^-$ supply via nitrification is a critical controller of denitrification (Reddy and Patrick 1984, Davidson et al., 2000). The uplands at Pond Branch are dominated by oak-hickory forests that have high C:N ratios and support low rates of nitrification (Lovett et al. 2002) Groffman et al. 2006b, Raciti et al. 2011). Many of our sites showed negative in situ and potential net N mineralization and nitrification supporting the idea that inorganic N availability at our sites was low. We also measured high rates of microbial respiration during the laboratory incubations suggesting that pools of labile carbon, which drive immobilization, were high.

N$_2$ flux might also come from processes other than denitrification including anaerobic ammonium oxidation (annamox) and bacterial N$_2$ fixation. Annamox would require ammonium to be produced in oxygenated soils before proceeding to N$_2$. While this matches our N$_2$ flux data as a function of O$_2$, limited studies have shown that the anaerobic conversion of ammonium to N$_2$ gas is not a large flux in other riparian soils.
despite high annamox bacterial abundance (Wang et al., 2012). The second process that could produce affect our soil core data is nitrogen fixation by non-symbiotic bacteria. However, previous work has shown that rates do not change under aerobic to anaerobic conditions (Limmer and Drake, 1996), a trend not shown in our NFARM data.

Our estimates of in situ and potential net N mineralization and nitrification were similar to previous measurements of these variables at our upland sites (Groffman et al. 2006b, Raciti et al. 2011). Rates of these variables were markedly low at our riparian sites. However, it is likely that denitrification was consuming inorganic N produced during the in situ or laboratory mineralization and nitrification incubations, especially in the hollow sites, contributing to the low net rates. Our results differ markedly from other riparian denitrification studies, where there is a significant exogenous supply of NO$_3^-$ (Mayer et al. 2007). Under these conditions, nitrification is not the key supply of NO$_3^-$ and denitrification declines exponentially with increases in O$_2$ (Burgin and Groffman, 2012).

The low NO$_3^-$ levels and net nitrification rates in our soils are relevant to the validity of our soil core-based estimates of denitrification. Cores in the lab are closed system entities with initial conditions and zero flux boundaries. They are removed from the field and not subject to vertical exchanges with the atmosphere and groundwater or from solutes transported from up-gradient patches. Each core is thus a snapshot in time that inherits the legacy of antecedent conditions in a connected and open system in the field. However, the low net nitrification rates in Pond Branch watershed soils suggest that vertical and horizontal fluxes of NO$_3^-$ from surficial soils are not key drivers of denitrification at our site. This is supported by the low [NO$_3^-$] of soil water collected from upland lysimeters (Groffman et al., 2009), a common finding in more N retentive oak-hickory dominated ecosystems (Lovett et al., 2004).

It is also important to note that the sequence of incubations at different oxygen concentrations took approximately two weeks to complete so there is concern that rates may have declined over that time period. While analysis of CO$_2$ production during the incubation suggests that there was no decrease in general biological activity over the
series of incubations, these long holding times are an inherent challenge with the NFARM method. The inherent limitations of extracted core methods are at least partially overcome by coupling these laboratory measurements with continuous data on volumetric water content and soil oxygen levels that provide temporal context for these point measurements.

Interestingly, many denitrification models (Parton, 1997, Porporato et al., 2003, Band et al., 2001) utilize a scalar function of nitrogen transformation reactions (nitrification, denitrification, and mineralization) based on soil moisture. These models consider separate supply and removal rates based on ambient supply of reactants. By subtracting the relative rates of denitrification from nitrification, a quadratic form similar to our data emerges (Figure 2.11). Our results suggest that these functions may need to be revisited for sites and landscapes where nitrification is low and is the key driver of denitrification.

2.5.3 Why did denitrification peak during baseflow?
Estimated denitrification rates were highest when riparian hollows became partially oxygenated, which occurred during mid summer when hydrologic fluxes were at a minimum. Contrary to the conceptual model presented in McClain et al. (2003), our results show that a significant amount of denitrification can occur during these hydrologically quiescent, non-storm periods. When coupled nitrification-denitrification is likely the dominant mechanism for nitrogen loss, these dry down periods can account for significant amounts of annual denitrification activity.

The importance of hotspot activity during non-storm periods or “cool moments” also raises questions about the spatial and temporal coupling between watershed nitrogen inputs and denitrification outputs. Our analysis suggests that watershed denitrification hotspots remove a significant proportion of atmospheric nitrogen inputs, but the coupling between these inputs and the hotspots is indirect, with a significant time lag, perhaps mediated by downslope movement of plant detritus over many years (Bardgett et al. 2001, Claessens et al. 2010).
We note that groundwater flow, which comprises the majority of baseflow periods, does not appear to play an important role in denitrification or transport to the stream at Pond Branch. Previous studies have shown that denitrification potentials decrease considerably with soil depth and found very low potential at 1m (Groffman et al., 2002 and Gift et al., 2010). Additionally, repeated sampling of a groundwater seep in the upper portion of the watershed shows nitrate and ammonium at or near the detection limit, a condition not seen in other watersheds such as Biscuit Brook, NY where deeper groundwater play an important role in nitrogen transport and transformations (Burns et al., 1998).

2.5.4 Watershed management implications of denitrification hotspots and hot moments. There is great interest in the ability of forests to prevent the movement of atmospheric nitrogen to coastal waters (Boesch et al., 2001). Our results clearly show the importance of microtopographic variation in the near-stream zone as a controller of the ability of forest watersheds to support high rates of denitrification. There is some evidence that artificially created microtopography in engineered wetlands can enhance denitrification (Wolf et al., 2011). Hydrologic connectivity that delivers nitrogen to consistently wet and carbon rich locations such as riparian hollows would be important. Following from variable source area concepts, riparian hollows can be hydrologically connected to upslope areas during storms. As such, these areas can receive subsidies of nutrients and organic material from contributing areas. Successful restoration strategies require understanding these differences and maintaining a balance between saturated riparian denitrification hot spots and nitrate being transported to these zones via storm events. Also of interest are the implications of our findings for stream and riparian restoration efforts. As discussed above, the intermediate location at the upper transect had short-term oxygen variations that were driven by dynamic geomorphic conditions as the proportion of flow in the proximal channel suddenly varied. These dynamic conditions were not captured by terrain analysis. These results suggest that there are locations where oxygen and denitrification hotspot dynamics are likely driven by geomorphic changes. We suggest that future studies consider the potential for the presence of evolving hotspots in the landscape.
2.5.5 Towards closing nitrogen budgets

Many watershed scale mass balances have shown high levels of nitrogen retention, but it is frequently unclear if this “retained” nitrogen is being stored in soils or plants or lost as gas. Here we demonstrate that a significant portion is being lost as N\textsubscript{2} via denitrification. Our results further suggest that very little nitrogen is being lost as N\textsubscript{2}O, which is an important greenhouse gas (Prather et al. 1998). Broader consideration of denitrification by measuring hot spots, hot moments, and cool periods will improve understanding of N retention mechanisms. Our results help to conceptualize controls on nitrogen saturation in forest ecosystems (Aber et al. 1989) by suggesting that watersheds such as Pond Branch, where a significant fraction of nitrogen input is denitrified, may be more resilient to saturation. Pond Branch is primarily oak-hickory forest with a high C:N ratio that is typically more retentive of nitrogen than northern hardwood forests such as sugar maple (Lovett et al. 2004). Our results suggest that in addition to C:N ratios, the hydrogeomorphic context of riparian microtopography that drives watershed denitrification is important for understanding watershed N dynamics with respect to nitrogen saturation. Future research should investigate to what extent structure of the riparian zone enhances denitrification and reduces nitrate export from other forested watersheds. For the remainder of the dissertation, results of this Chapter show that there is a major missing sink from the watershed N budget. Implications of this are revisited in the Conclusion.

Acknowledgements

We thank Dan Dillon for extensive field assistance and Lisa Martel for laboratory analysis. This work was funded by National Science Foundation grants DEB-1027188 (Baltimore LTER) and DEB-0919047 (Ecosystem Studies). We also thank Doug Burns for a helpful and thoughtful review of this paper.
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R Development Core Team (2010), R: A language and environment for statistical computing, reference index version 2.2.1, edited, R Foundation for Statistical Computing, Vienna, Austria.


Table 2.1. Denitrification N\textsubscript{2} fluxes, soil nitrate concentrations, in situ and potential net N mineralization and nitrification, and microbial respiration from cores collected from seven different landscape positions in the Pond Branch watershed. Values are mean and standard deviation of samples taken in March, July and October 2012 and March 2011 in each landscape position.

<table>
<thead>
<tr>
<th></th>
<th>Upper Uplands</th>
<th>Lower Uplands</th>
<th>Hillslope Hollow</th>
<th>Upper Hummock</th>
<th>Lower Hummock</th>
<th>Upper Hollow</th>
<th>Lower Hollow</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Denitrification N\textsubscript{2} Rate (g N/kg soil/day)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
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<td>0.06</td>
<td>0.19</td>
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<td>0.07</td>
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<td>0.1</td>
<td>0.25</td>
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<td>1.64</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td><strong>In situ net Nitrification (g N/kg soil/day)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.05</td>
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<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Potential net Nitrification (g N/kg soil/day)</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>0.00</td>
<td>0.11</td>
<td>0.04</td>
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<tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>0.35</td>
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<td>0.12</td>
<td>0.05</td>
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<td>-0.18</td>
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<td>0.30</td>
<td>0.18</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>12.13</td>
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<td>12.25</td>
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<td>21.77</td>
<td>17.11</td>
<td>29.00</td>
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<td><strong>Soil Moisture (% dry weight)</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>0.03</td>
<td>0.09</td>
<td>0.05</td>
<td>0.05</td>
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<tr>
<td><strong>Bulk Density (g/cm\textsuperscript{3})</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
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<td>0.94</td>
<td>0.82</td>
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<td>0.24</td>
<td>0.12</td>
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Table 2.2. Equations relating denitrification N\textsubscript{2} flux and incubation O\textsubscript{2} levels derived from soil cores from different landscape positions collected at four dates (March, July and October 2012 and March 2011) and incubated at 5\%, 0\%, and 10\% O\textsubscript{2} and the per unit area N\textsubscript{2} fluxes aggregated for the entire water year and the growing season.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Landscape Position</th>
<th>Equation</th>
<th>WY 2011</th>
<th>Summer (Jun Jul Aug)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upland</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper</td>
<td>-0.002[O\textsubscript{2}]\textsuperscript{2} + 0.0165[O\textsubscript{2}] + 0.055</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Lower</td>
<td>-0.0014[O\textsubscript{2}]\textsuperscript{2} + 0.0129[O\textsubscript{2}] + 0.0238</td>
<td>0.002</td>
<td>0</td>
</tr>
<tr>
<td>Riparian Hummock</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper</td>
<td>-0.0037[O\textsubscript{2}]\textsuperscript{2} + 0.0346[O\textsubscript{2}] + 0.0257</td>
<td>0.137</td>
<td>0.029</td>
</tr>
<tr>
<td>Lower</td>
<td>-0.0078[O\textsubscript{2}]\textsuperscript{2} + 0.0779[O\textsubscript{2}] + 0.0043</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Riparian Hollow</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper</td>
<td>-0.0763[O\textsubscript{2}]\textsuperscript{2} + 0.8303[O\textsubscript{2}] + 0.8929\textsuperscript{**}</td>
<td>19.826</td>
<td>6.657</td>
</tr>
<tr>
<td>Lower</td>
<td>-0.0867[O\textsubscript{2}]\textsuperscript{2} + 0.9541[O\textsubscript{2}] + 2.3929\textsuperscript{***}</td>
<td>38.301</td>
<td>10.401</td>
</tr>
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<td>Hillslope Hollow</td>
<td>-0.0176[O\textsubscript{2}]\textsuperscript{2} + 0.173[O\textsubscript{2}] + 0.029\textsuperscript{***}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>58.266</td>
<td>17.087</td>
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\textsuperscript{a} Asterisks indicate the following: 
\textsuperscript{***}, P < 0.01; \textsuperscript{**}, P < 0.05;
Table 2.3. Nitrogen inputs and outputs for the Pond Branch watershed for WY 2011 (October 1, 2010 to September 30, 2011). Atmospheric input and streamflow output estimates are from Groffman (2004) and discharge based statistical (USGS Fluxmaster, Schwarz et al., 2006) model output, respectively. Denitrification fluxes are the sum of daily fluxes multiplied by the total area of each landscape position. The proportion of riparian areas as hummocks or hollows based on topographic wetness index (TWI).

<table>
<thead>
<tr>
<th>Nitrogen Budget</th>
<th>Area (ha)</th>
<th>Rate N (mg/m²) (WY 2011)</th>
<th>Total N Flux (kg/yr)</th>
</tr>
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<tr>
<td></td>
<td>TWI 6</td>
<td>TWI 8</td>
<td>TWI 6</td>
</tr>
<tr>
<td>Input</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Average Deposition</td>
<td>37</td>
<td>37</td>
<td>1000</td>
</tr>
<tr>
<td>Output</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Stream Export</td>
<td>37</td>
<td>37</td>
<td>52.0</td>
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<tr>
<td>Modeled N₂ Flux</td>
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<td></td>
</tr>
<tr>
<td>Upland</td>
<td>24.0</td>
<td>24.0</td>
<td></td>
</tr>
<tr>
<td>Upper</td>
<td>14.4</td>
<td>14.4</td>
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<td>Lower</td>
<td>9.6</td>
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<td>Hillslope Hollow</td>
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<td>Riparian Zone</td>
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<tr>
<td>Lower</td>
<td>0.14</td>
<td>0.08</td>
<td>38301.0</td>
</tr>
<tr>
<td>Total</td>
<td>37</td>
<td>37</td>
<td></td>
</tr>
</tbody>
</table>

Percent Deposition Removed via N₂ Flux

27%  16%
Figure 2.1. LiDAR derived shaded relief image of the Pond Branch watershed, a 37 ha forested subwatershed in Baltimore County, USA. Sensor locations for $O_2$, TDR probes and riparian groundwater wells are shown.
Figure 2.2. Upper and Lower Riparian Transect cross-sections with sensor locations.
Figure 2.3. Topographic Wetness Index of the Pond Branch watershed.
Figure 2.4. Riparian hummock and hollow delineation near the upper riparian transect computed from TWI thresholds selected to match field-based estimation of spatial extents during wet (TWI=6.0) and dry (TWI=8.0) conditions.
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Figure 2.10. Model of daily N$_2$ flux for riparian hollow, toeslope and hillslope hollow landscape positions. The lower riparian toeslope only had a positive flux during Tropical Storm Lee (9/07/11). All other locations had zero flux on all days.
Figure 2.11. Scalar model of net nitrification-denitrification as a function of soil moisture for sandy loam soils [after Hwang et al., 2009]
CHAPTER 3: ECOHYDROLOGIC CONTROLS OF SEASONAL NITRATE EXPORT IN A FORESTED HEADWATER CATCHMENT

3.0 Preface

Stream nitrate flux out of a watershed is an important diagnostic for a combination of ecohydrological processes. Despite early work suggesting that stream export of N should be maximal during the dormant season when ecosystems are not able to retain it, a growing number of sites have shown peak export to occur during the growing season. This chapter examines multiple hypotheses to understand how the combination of terrestrial and in-stream ecological, geochemical, and hydrological processes can control stream N export. While chapter 2 characterized the spatial distribution of nitrogen cycling, and specifically denitrification, in the catchment, chapter 3 focuses on the timing of nitrogen export from the catchment as a result of temporal patterns of the dominant biogeochemical and hydrologic processes.

The research in this chapter was conducted in collaboration with Emily Bernhardt, Duke University, Peter Groffman, Cary Institute of Ecosystem Studies and Lawrence Band, University of North Carolina Chapel Hill. The following was submitted to Water Resources Research in October, 2013.
3.1 Introduction

A major challenge in watershed science is understanding how the cumulative effects of biological and hydrological processes interact to determine the timing and magnitude of nutrient export. Seasonality of nutrient concentration and fluxes exported from headwater catchments have often been viewed as a diagnostic of the terrestrial landscape with attributes of vegetation such as forest age (Vitousek & Reiners, 1975) or forest composition (Lovett et al. 2004) exerting a dominant control on both the magnitude and the patterns of stream nutrient export. Total nitrogen (N) export may be enhanced by additions through anthropogenic N deposition (Aber et al., 1989, Stoddard, 1994), or fertilization (Goodale and Aber, 2001) and may be reduced by physical or biological retention or denitrification in soils (Aber et al 1998), riparian zones (Band et al., 2001, Burt and Pinay, 2005), or in the sediments of receiving streams (Meyer et al., 1988, Peterson et al., 2001, Bernhardt et al., 2005). Predicting the magnitude and timing of N export requires a perspective that is multi-scale and flowpath based that integrates terrestrial and aquatic ecosystems and which considers both biological and physical mechanisms of retention and transformation.

In many early watershed studies in the northeastern US, eastern Canada, and eastern Europe stream N export was found to be highest during the dormant season when microbial and plant uptake is minimal (Stoddard, 1994). For many of these systems N loss is expected to be minimal during the growing season when terrestrial vegetation uptake and soil microbiota immobilization are maximized. However, this pattern is not universal and a growing number of watershed studies have observed peak streamflow
NO$_3^-$ concentrations during the active growing season. Watersheds including Walker Branch (TN), low elevation sites at Coweeta (NC), Pond Branch (MD), and Pine Creek (NY) in the USA have exhibited maximum seasonal concentrations during the summer (Mulholland 1992, Swank and Vose, 1997, Band et al., 2001, Goodale et al., 2009, Brookshire et al., 2011, Ohte et al. 2010, 2012). Despite an approximately even distribution of precipitation over the year, each of these sites have elevated NO$_3^-$ concentrations during summer when baseflow is lowest, a different pattern from some catchments in Japan where elevated NO$_3^-$ concentrations during the growing season coincide with highest periods of discharge (Ohte et al., 2010). Multiple hypotheses have been proposed to explain maximal NO$_3^-$ concentrations coincident with lowest flows. We evaluate five possible controls on the seasonality of streamwater NO$_3^-$ export from watersheds:

1) a shift in flowpaths to groundwaters enriched from bedrock weathering of N. As dominant flowpaths to streams deepen with a summer dry down, it is conceivable that groundwater that has been in contact with a bedrock with a relatively high N content (Halloway and Dahlgreen, 1999) begins to dominate summer flow. While this mechanism has been ruled unlikely in Walker Branch (Mulholland and Hill, 1997) and the Upper Susquehanna (Goodale et al., 2009), this hypothesis is relevant in Pond Branch where the bedrock is a micaceous shist, a similar geology to that shown to be a weathering source of streamwater N in California (Halloway and Dahlgreen, 1999, Morford et al., 2011).

2) Lags between deposition and export to the outlet, in which groundwater is enriched with NO$_3^-$ during winter recharge events when immobilization and uptake are minimal
and enriched groundwater dominates stream flow during the summer, as has been seen in the Catskills, NY (Burns et al. 1998).

3) Lower in-stream uptake of enriched groundwater baseflow due to light limitations with canopy closure. In Walker Branch, TN, a small forested watershed, low light availability and limited summer inputs of terrestrial carbon together constrain in-stream nitrogen uptake during the growing season, while N assimilation can be high during spring algal blooms and following autumn litterfall (Mullholand and Hill, 1997; Roberts et al., 2007).

4) Senescence of riparian herbaceous vegetation during summer. The vernal dam hypothesis suggests that spring ephemeral vegetation takes up nitrogen prior to the overstory leaf out and retains N until summer when the vegetation dies off and releases this N (Muller and Bormann, 1976, Zak et al., 1990). If this temporary biomass sink is alongside or hydrologically connected to receiving streams, there is the potential for these ephemeral plants to contribute significant quantities of N to streamwaters.

5) Net nitrification and transport are greater than denitrification, immobilization, and uptake during the growing season. Previous work in Pond Branch has hypothesized that rates of denitrification decrease and/or that rates of nitrification and mineralization increase as the riparian zone dries and oxygenates during summer (Band et al., 2001). This has also been posited in other catchments with summer NO₃⁻ peaks (Goodale et al., 2009, Brookshire et al., 2010).

We present our conceptual diagram of the system and the potential mechanisms which account for potential sources with nitrogen retention, uptake, and transformations along each of the respective flowpaths (Figure 3.1). The total mass flux of NO₃⁻ at the weir
(export) can then be described by **Equation 3.1** where net loads from each source include gross import or production and are acted upon by vegetation uptake, microbial immobilization, and transformations including denitrification along connected flowpaths to the stream and outlet

\[ E_{\text{weir}} = (L_{\text{geo}} + L_{\text{amt rech}} + L_{\text{eph veg}} + L_{\text{nit}} + L_{\text{str}})(R_{\text{str ret}}) \]  

**Equation 3.1.**

Where:

- \( E_{\text{weir}} \) = Export of NO\(_3^-\) at the weir
- \( L_{\text{geo}} \) = Net load from geochemical weathering
- \( L_{\text{amt rech}} \) = Net load from lagged atmospheric recharge
- \( L_{\text{eph veg}} \) = Net load from ephemeral vegetation
- \( L_{\text{nit}} \) = Net load from soil nitrification
- \( L_{\text{str}} \) = Net load stream sources
- \( R_{\text{str ret}} \) = Net stream retention

\( E \) and \( L \) units (mass/time)

\( R \) is dimensionless ratio of flux in/flux out

In this study, we evaluated the relative importance of each of these five possible controls in driving a summer NO\(_3^-\) export peak at Pond Branch. We combined data from long-term monitoring of stream NO\(_3^-\) levels and discharge, measurements of bedrock N content, groundwater and soil water NO\(_3^-\), and continuous in situ sensor data on stream NO\(_3^-\) and riparian water table and oxygen dynamics to evaluate how the dynamics of production, consumption and transport influence seasonal patterns of NO\(_3^-\) export in this forested watershed. Our objectives were to 1) determine the mechanistic basis for observed summer NO\(_3^-\) peaks that reconciles hydrologic transport with biogeochemical processes and 2) to assess the relevance of these mechanisms in Pond Branch.
3.2 Site Description

Pond Branch is a forested south-facing 37 ha watershed in the Piedmont physiographic province of Maryland, USA (Figure 3.2). It is a subwatershed of Baisman Run, a 370 ha watershed with low-density residential development in an upland headwater portion of the watershed. Pond Branch is the reference watershed of the Baltimore Ecosystem Study (BES), a U.S. National Science Foundation funded Long-Term Ecological Research (LTER) project.

Elevation ranges from 140-190m. The upper (northern) portion of the watershed has gentle slopes with a wide valley bottom. The bottomland has two streams draining each side of the catchment with a wetland complex in many locations in between and adjacent to the streams. The wetland area in the valley bottom likely serves as a large storage reservoir of water and nutrients in baseflow conditions. Large portions of the broad valley bottom area are comprised of hummock and hollow microtopography that have likely formed from a combination of tree throw and channel evulsion over time. Slopes become steeper, the riparian zone narrows, and the stream becomes a single channel approximately half way down the catchment (Figure 3.3). Approximately 200m above the gauge, a bedrock outcropping coincides with a small waterfall below which there is a marked decrease in the extent and depth of riparian soils. The entire watershed is underlain by a medium to coarse-grained micaceous schist of the Loch Raven Formation. Beneath the schist is Cockeysville Marble. Depth to saprolite is highest on ridges, thins (<1m) at steep midslope positions, and is 1-2m in bottomland locations (Cleaves et al., 1970). Soils range from silt clay loam to silt loam in the riparian areas to
sandy loam on steeper slopes. Soils in riparian hollows have extensive organic matter that can extend as deep as 50cm below ground surface.

Vegetation:

Pond Branch is completely forested except for a 20 m wide tall-grass covered subsurface gasoline transect which traverses the entire watershed. The forest is dominated by *Quercus* spp. (oaks), *Liriodendren tulipifera* (tulip poplar), and *Carya* spp. (hickory). There are locations, primarily near the outlet with an understory dominated by *Kalmia* spp. (laurel). Hollows have wetland plant assemblages dominated by *Symplocarpus foetidus* (skunk cabbage), which has a very high foliar N content (McCarty et al., 2007) and quickly decays, in mid-summer.

Climate and N Deposition:

Pond Branch is in a humid subtropical climate with approximately 1000mm of rainfall annually. Summers are warm with average daily maximum temperatures of 30°C. Winter temperatures can be cold with mean daily minimum temperatures of -4°C and snowfall can occur several times per year. Deposition of dissolved inorganic N (DIN) in the Maryland Piedmont is approximately 9 kg N/ha/year (Bettez and Groffman, 2013).

Land Use History:

Logging in the area began in 1776 (Wolman, 1987). Large portions of this land were likely farmed in the eighteenth and nineteenth centuries. Current vegetation in Pond Branch has a stand age of approximately 90 years and is thought to have started on farmland abandoned in the early 20th century. Selective logging was last conducted in 1958 (Cleaves, 1970).
Nitrogen Export Patterns:

Long-term monitoring by BES (Groffman et al. 2004, Kaushal et al. 2008, Shields et al. 2008) has shown that Pond Branch has recurrent summer peaks in NO$_3^-$ concentration (Figure 3.4). Seasonal trends in NO$_3^-$ concentrations are asynchronous from discharge, which is lowest during the growing season when evapotranspiration rates are highest. Despite low discharge, peaks in NO$_3^-$ load also occur during the summer because the increases in concentration compensate for decreases in discharge. Dual isotopic analysis of streamwater NO$_3^-$ suggests that most stream NO$_3^-$ has been processed by microbes and is not directly transported from the atmosphere (Kaushal et al., 2011).

3.3 Methods

3.3.1 Sensor Locations and Descriptions

Soil oxygen concentrations were recorded using Apogee (Logan, UT) SO-111 probes, which utilize a standard galvanic cell approach to measure the partial pressure of oxygen in air. The diffusion-head sensors were buried vertically with the heads at 6cm depth. Soil moisture was recorded using Campbell Scientific (Logan, UT) CS 616 water content reflectometer probes. Probes were installed vertically into the ground to measure the average water content of the top 20cm of soil. Both types of sensors were calibrated before deployment and collected soil oxygen and volumetric water content every 15 minutes (hourly at the upper riparian transect).

Soil moisture and soil oxygen sensors were installed at the upper and lower riparian transects and in a hillslope hollow (Figure 3.2). These sensors spanned the hillslope-
riparian boundary and were placed in a riparian hummock, a riparian hollow, which is the secondary channel (a secondary stream channel), and at the toeslope. In a hillslope hollow adjacent to the upper transect, approximately 40m from the toeslope location, we installed two pairs of soil oxygen and water content probes positioned approximately 20m apart along the trough of the hollow. The third datalogger location was in the lower riparian transect. That location had three pairs of soil oxygen and moisture sensors located in riparian hummock, riparian hollow, and toeslope locations.

3.3.2 Hydrometric Data
Discharge was measured at a USGS gauging station at the outlet of Pond Branch (01583570), but the stage recorder was unable to discern diurnal fluctuations at baseflow. To increase the resolution of stage during periods of baseflow, a Hobo pressure transducer was placed in the weir pool and stage was recorded every 15 minutes. Discharge was calculated for baseflow periods by prorating the Baisman Run USGS record (01583580) by drainage area and by correcting for lag time by using timing from the pressure transducer at the Pond Branch weir. Groundwater levels have been monitored by BES at approximately monthly frequency at two locations along Pond Branch, “upper” and “lower” since 2001 (Groffman et al. 2002, Gift et al. 2010). 1m deep wells 5m from either side of the stream were installed in 2001. The transect was expanded in 2009 with ~2m deep wells that were installed 10m from the 2001 channel in another riparian location and 15 m from the channel at the toeslope. For this study, we expanded these locations to create transects that included toeslope, hummock and hollow locations (Figure 3.1). Four groundwater wells were
installed in approximately 5m increments from the stream to the toeslope at each riparian transect. Water levels in the wells were measured every 15 minutes using a combination of capacitance probes (Odyssey) and pressure transducers (Onset Hobo Water Level Recorders).

3.3.3 Water Quality

Weekly grab samples were collected at the outlet as part of the long term BES LTER sampling. In addition, longitudinal streamwater samples were collected at points along the stream as well as from a large spring near the headwaters of the stream (Figure 3.2). Longitudinal samples were collected at monthly to bi-monthly intervals from September 2001-October 2002 and again at bi-weekly to monthly intervals from April-October 2011. Two samples were collected from each site, one of which was filtered in the field through a 0.7 micrometer GF/F Whatman filter. Samples were placed on ice upon collection and the 2011 samples were frozen as soon as possible (1-3 hours) until analysis. Loads from longitudinal samples were calculated by taking the USGS daily discharge for the Pond Branch outlet and prorating by watershed area for each of the stream locations. Groundwater samples were collected bi-weekly to monthly. Wells were purged and samples were collected from recharge. Ceramic cup tension lysimeters located in upland plots at 10cm and 50cm depths (Groffman et al. 2006, 2009) and at 10cm depth in both riparian transects were sampled monthly from summer 2010 through summer of 2011.

Ammonium was measured using the fluorometric technique (Holmes et al., 1999) on a Turner 10-AU spectrophotometer. Total dissolved nitrogen and dissolved organic carbon (DOC) were measured on a total organic analyzer with a total nitrogen module.
(Shimadzu, Kyoto Japan). NO\textsubscript{3}\textsuperscript{-}, bromide, chloride, and phosphate were analyzed on a Dionex Ion Chromatograph. Total Nitrogen and Total Phosphorus were analyzed by persulfate digestion (Ameel et al. 1993) followed by colorometric analysis using a Lachat Quickchem flow injection analyzer.

A submersible ultraviolet NO\textsubscript{3}\textsuperscript{-} analyzer (SUNA, Satlantic, Halifax, NS), a sensor that utilizes ultraviolet absorption spectroscopy to measure in-situ dissolved NO\textsubscript{3}\textsuperscript{-}, was placed just below the weir to measure NO\textsubscript{3}\textsuperscript{-} concentrations by taking three separate readings 10 seconds apart at 15 minute intervals. The average of each 15 minute interval was then smoothed with a moving mean over a 4-hour window for analysis. Gaps in the data were largely due to sediment transport, which would occasionally fill the sensor window. Data during these periods was discarded from the analysis.

3.3.4 Geologic Samples:

Outcrop samples were collected from a section of exposed bedrock near the stream approximately 50m upstream of the weir. Samples were cut with a slab saw to remove weathered surfaces, treated with 5% hydrogen peroxide for 24 hours to remove any remnant surficial organic matter, and pulverized with a carbide-steel shatter box to pass a 75-mm sieve. Samples were analyzed by the University of California- Davis Stable Isotope Facility with a isotope ratio mass spectrometer for total C and N.

3.4 Results

3.4.1 Climate and Hydrology

2011 was one of the driest years on record while 2010 was significantly wetter. There was a greater than 300% difference in mean monthly discharge between the 2010 and 2011 growing seasons, and nearly a 300% difference among months in 2011 (Table
There were even more marked differences in monthly rainfall with a 10-fold variation between the lowest amount in June 2010 and September 2011. Despite these different hydroclimatic conditions there was a similar response of summer peaks in N export across years.

3.4.2 Geologic weathering

The N content of the Pond Branch watershed bedrock proved to be quite low (112 mg N/kg ± 30 mg N/kg for the Loch Raven Schist and 124 mgN/kg ± 34 mg N/kg for Cockeysville Marble). Importantly, at 0.015% N, bedrock N percentages are approximately two orders of magnitude lower than values of bedrock found to be geologic sources of stream N (Holloway & Dahlgren, 1999). The low rock N content at Pond Branch was within the range of other formations underlying watersheds whose streamwaters also exhibit summer peaks in N concentrations (Mulholland and Hill, 1997, Goodale et al., 2009) where geogenic sources have been ruled as unlikely. We therefore conclude that geogenic sources are unlikely drivers of the observed seasonal N patterns at Pond Branch.

3.4.3 Riparian Understory Phenology

In 2010 and 2011, the rise in NO$_3^-$ concentrations occurred in early June while the skunk cabbage was still at or near peak leaf out and showed no signs of senescence. The hydrologic conditions of the summers of 2010 and 2011 were very different. The early part of the growing season in 2010 was very wet and the mean monthly discharge in 2010 was nearly double the long term mean for Pond Branch (1998-2012), whereas
the summer of 2011 was considerably drier, with mean monthly discharge less than half the long-term mean (Table 3.1). Despite these variable hydrologic conditions between summers, the skunk cabbage did not begin to senesce until mid July in both years, well after the rise in stream NO$_3^-$ concentrations.

3.4.4 Stream chemistry

A combination of weekly BES samples, longitudinal samples, and high frequency sensor data were used to infer spatial and temporal processes driving N export. Weekly grab samples showed increases in concentrations that began in early June 2011, similar to other years of record. Longitudinal stream samples collected in 2011 showed that NO$_3^-$ loads increased monotonically throughout the growing season in the downstream direction, but NH$_4^+$ loads did not (Figure 3.5). NO$_3^-$ concentration data collected at the outlet and the groundwater seep on the same day during 2001/2002 and 2011 show that stream outlet NO$_3^-$ concentrations increased relative to the groundwater source throughout the growing season (Figure 3.6a). The net difference between samples collected from the groundwater seep and the outlet are used to show that for most dates, the outlet had higher concentrations than the seep, particularly during the summer (Julian Day 150 – 250) (Figure 3.6b). Positive values show concentrations that increased from seep to outlet meaning that inputs and instream mineralization outweigh rates of instream uptake during summer months. Although there have been a few isolated dates in the past in which groundwater NO$_3^-$ was higher than NO$_3^-$ concentrations at the watershed outlet (Figure 3.6c), in general the seep has depleted
concentrations relative to the stream, and this is particularly obvious during the summer months (Figure 3.6d).

High temporal resolution in-stream NO$_3^-$ data revealed that an early summer increase from nearly dormant season background levels (0.04mg/L NO$_3^-$-N) to nearly the seasonal maxima (0.14 mg/L NO$_3^-$-N) at baseflow occurred over the course of just 4 days (Figure 3.7). In addition to the strong seasonal signal, we also observed strong diel variation in stream NO$_3$ concentrations over this period. Over a 24-hour period at baseflow, maximum concentrations occurred during the day with minimum concentrations occurring in late afternoon. Cumulative 24-hour NO$_3^-$-N loads at the gauge increased from 15.2 mg/d on the first day to 28.4 mg/d on the last two days of this four-day period.

3.4.5 Groundwater and soil water chemistry

Data from the groundwater seep also shed light on the plausibility of a lagged groundwater delivery from atmospheric deposition input making it to the stream. The seep remained at low concentrations through the year, unlike groundwater seeps in the Catskills Mountains in New York, USA that showed higher summer concentrations that were linked to atmospheric deposition recharged during winter (Burns et al., 1998). Mean riparian groundwater NO$_3^-$ concentrations were consistently lower than summer stream concentrations at 0.07 mg/L NO$_3^-$-N (± 0.07). Riparian groundwater concentrations did not vary consistently between seasons, but rather showed episodic increases in concentration that were likely associated with storms. In the deeper (2m) wells, which extended below a dense cobble layer, NO$_3^-$ concentrations were
consistently at 0.05 mg/L NO$_3^-$-N, consistent with dormant season stream concentrations, with the exception of a single sample in one well (0.59 mg/L NO$_3^-$-N) that increased average concentrations to 0.09 mg/L NO$_3^-$-N.

Tension lysimeter solution chemistry revealed a difference in the seasonal trends between uplands and riparian zones. Riparian lysimeter data showed that concentrations tended to increase during the summer (especially between Julian Days 200 and 250), with concentrations increasing to 0.30 mg NO$_3^-$-N/L, which followed the same seasonal pattern as the stream albeit at slightly higher concentrations. Upland lysimeters showed higher concentrations during winter, spring, and late fall (concentrations frequently above 1.5 mg NO$_3^-$-N/L) and lower concentrations (below 0.5 mg NO$_3^-$-N/L) during the growing season (Figure 3.8). So, despite there being high concentrations in upland tension lysimeters occur only during the dormant season. Given low concentrations in deep groundwater wells and the seep, there is an apparent disconnect between uplands and the riparian zone. Riparian nitrate concentrations increase to maximum stream levels during the summer, suggesting that ecohydrological processes account for this change and suggest that riparian zone serves as a fundamental control on stream concentrations.

3.4.6 Riparian soil oxygen dynamics

Soil oxygen levels varied markedly across the landscape, with near atmospheric levels in the toeslope and hillslope hollows and almost continually anoxic conditions in some of the riparian hollows. There was a seasonal decrease in soil moisture and a corresponding increase in soil oxygen concentrations from 0-3.5% in riparian hollow
Soils of Pond Branch (Figure 3.9). In both of the summers of 2010 and 2011, riparian hollows at the upper and lower transects become oxygenated (Figure 3.10a) going from completely anoxic (0.05 and 0.1%) to (4% and 11%) respectively.

There were marked diel patterns in soil oxygen at the upper transect hollow where concentrations varied by 1.5 to 6% over a 12 hour period (Figure 3.10b). The increase in soil oxygen concentrations in the riparian hollow at the lower transect was coincident with (four days after) the marked increase in stream NO$_3^-$ concentrations observed with the SUNA NO$_3^-$ sensor. The upper transect hollow also had a small increase in soil oxygen (five days after) the increase in stream NO$_3^-$ concentrations and a more marked rise in soil oxygen, and in diurnal variability in soil oxygen (3-4% over 12 hours), just seven days after the increase in stream NO$_3^-$.

3.5 Discussion

3.5.1 Assessing multiple alternative hypotheses

The method of analyzing multiple working hypotheses as we have done here has a long tradition in the geophysical sciences (Chamberlin, 1897). The five alternative hypotheses we evaluated are not mutually exclusive and they could affect nitrogen cycling at different times and in different portions of the landscape. We restrict our discussions to changes that could control N export at the watershed outlet. Our analysis suggests that shifts in dominant groundwater flowpaths that could facilitate transport of either bedrock weathered N (mechanism #1) or atmospheric N (mechanism #2) to the stream during summer are unlikely. The N content of bedrock geology is quite low relative other bedrock types that have been shown to be a significant source of N to aboveground ecosystem processes (Morford et al., 2011). Moreover, the mass flux of
NO$_3^-$ increased as discharge dropped, meaning that a simple ET-driven concentration to a second, more highly concentrated bedrock source is not possible unless the discharge rate of the potential concentrated source increased. These results suggest that upwelling flowpaths or a change in dominant flowpaths that could significantly alter concentrations is highly unlikely.

Groundwater seep chemistry remained near background levels (0.02 mg/L) throughout the growing season suggesting that a lagged transport of atmospheric deposition (mechanism #2) is highly unlikely. In contrast, Biscuit Brook, NY showed distinct increases in groundwater seep NO$_3^-$ concentrations that were isotopically linked to winter deposition. The winter deposition was presumably recharged and transported through a fracture network, out of the seep, and through the stream network during summer. Given that seep N (NO$_3^-$, NH$_4^+$, TDN) concentrations at Pond Branch are nearly constant from April through October 2011 and below growing season streamwater concentrations, temporally lagged atmospheric deposition does not appear to be an important process.

Our third potential mechanism, that senescence of the dense understory of Symplocarpus foetidus (skunk cabbage) contributes to the summer peak in stream NO$_3^-$ also appears to be unlikely. Because the peaks in streamwater concentrations preceded this seasonal decay, we judge the spring ephemeral biomass turnover is unlikely to be driving the recurrent summer peaks in NO$_3^-$ export. However, a reduction in plant uptake of soil water nitrate that precedes the seasonal decay could occur and contribute to the patterns of stream nitrate.
The plausibility of our fourth potential mechanism, a decrease in in-stream retention or denitrification during the growing season is uncertain without detailed tracer additions (including 15N) to yield insights into rates of uptake, in-stream nitrification, and denitrification. Given that N loads increased longitudinally from the incipient channel through the outlet, the sources exceed potential in-stream sinks. Unlike at Walker Branch, the groundwater seep concentrations at Pond Branch are frequently at or below seasonal background concentrations in the stream. In Walker Branch, stream uptake decreases during the growing season due to light limitation allowing enriched groundwater flow through the stream with less net assimilation/removal. Seasonal changes in in-stream processes do not appear to be driving the export pattern at Pond Branch where dormant season groundwater concentrations (0.03±0.01 NO₃⁻-N mg/L in 2001) are equally low to growing season concentrations, suggesting that summer decreases in in-stream retention are unlikely to drive the seasonal export pattern, but could further enhance it.

Additional evidence that in-stream removal or denitrification is not a primary driver of seasonal N export patterns is that high frequency in-stream N concentrations showed increases in NO₃⁻ concentrations during the day, when the majority of autotrophic assimilation and denitrification should occur (Heffernan and Cohen, 2010). Autotrophic assimilation and denitrification would decrease concentrations during the day, a trend not seen at baseflow in Pond Branch during the summer of 2011. Rather than in-stream changes resulting in a sink of N, it might be changes that result in a source of N, presumably via nitrification (Bernhardt et al., 2002), which we discuss below.
The most dramatic seasonal changes that we observed were in riparian soil moisture and shallow groundwater. The fact that these changes were pronounced and coincident with changes in stream NO$_3^-$ suggest that water and redox controlled microbial reactions in the riparian zone (mechanism #5) are driving the observed seasonal changes in stream NO$_3^-$ concentrations. With a seasonal decrease in riparian hollow soil moisture and corresponding increase in soil oxygen, nitrification rates should increase while denitrification rates should decrease. However, complementary work shows that in laboratory core experiments, denitrification increases in Pond Branch riparian hollow soils at mesic oxygen concentrations, presumably via coupled nitrification-denitrification (Duncan et al., 2013). It is also true that the spatial extent of areas with net NO$_3^-$ production would exceed those with sufficiently low oxygen concentrations for denitrification, favoring the aerobic production of NO$_3^-$ at the expense of anaerobic consumption of NO$_3^-$ by denitrification. Thus, we can assume that across the entire stream and riparian zone, rates of nitrification exceed rates of denitrification, making the riparian zone a net source of NO$_3^-$ during the summer period. Separating the roles of riparian hollows and the active flowing stream channel is a difficult and unnecessary task, given the blurred and dynamic boundary. The potential transport mechanism that delivers NO$_3^-$ from the riparian zone to the stream is discussed below.

3.5.2 What, when, and where is the source of summer NO$_3^-$?

Small-scale heterogeneity in the riparian zone has been shown as an important control on bulk N cycling and export (Tague et al., 2010, Duncan et al, 2013). In Pond Branch, stream channels and portions of the near-stream zone including many riparian hollows
are on a continuum of the aquatic-terrestrial nexus that varies in extent daily, with storms, and seasonally. Given that little NO$_3^-$ is exported from Pond Branch during the winter and the vast majority is lost during the summer months, determining the source of the exported NO$_3^-$ is important for management strategies. In regions with shallow water tables, such as riparian zones, these fluctuations can also control the moisture content of surface soils. During certain times of the growing season and in specific catchment positions when microbial conditions are favorable, these diurnal oscillations could facilitate production and transport of both NH$_4^+$ and NO$_3^-$ from the riparian zone to the stream. The hydrologic variability at baseflow could provide sufficiently different redox conditions to facilitate production of NO$_3^-$ via nitrification during the day as soil moisture decreases and soil oxygen increases. This NO$_3^-$ could then be lost via denitrification as water content increases at night, could be incorporated into shallow groundwater with rising water tables (at night), or could be transported through preferential and more transmissive flowpaths to the stream during rainfall events. This sequence of NO$_3^-$ production, consumption and transport could proceed until there is no longer sufficient substrate for mineralization and subsequent nitrification and denitrification to occur or until boundary conditions change, such as leaf abscission in the fall. At some point, for additional nitrogen transformations to occur there would have to be a new source of organic N, NH$_4^+$, and/or NO$_3^-$ to a given patch from either, decomposition, deposition, or rainfall and subsequent advection or diffusion from adjacent (e.g. upslope) sites. Based on the patterns in NO$_3^-$ with concentrations highest during the day and lowest at night, there are three potential sources in the near-stream riparian zone:
1) Stream channel, bed, and banks, a portion of which are exposed could produce NO$_3^-$ which is then transported during the day as groundwater and runoff levels decline. The stream is the most proximal control on NO$_3^-$ concentrations observed at the weir and needs to be carefully considered. Stream stage varies by a few cm over the course of a day. Given the diel oscillations in saturated extent of stream beds and banks it could provide a transport mechanism for recently mineralized NH$_4^+$ which could then be nitrified in the hyporheic zone and/or channel. Future campaigns need to explore the extent and dynamics of N transformations and transport over the microscales at which these processes occur.

2) Deeper riparian hollow soils (on the order of 10-50cm). In Pond Branch, these soils have high organic content and as riparian groundwater tables drop over the growing season there could be additional mineralization and subsequent nitrification occurring from soils between 10 and 50cm. This phenomenon has been documented in Ontario, Canada (Hill, 2011). These deeper riparian soils tend to be in areas with higher topographic wetness index values and are more likely to have connections to the stream (Duncan et al., 2013).

3) Surficial riparian soils within the hydrologically connected source area. At the seasonal scale, summer dry downs are reflected by increases in surficial riparian hollow soil oxygen concentrations, which in turn should increase nitrification. The seasonal evolution of a variable source area with contraction during drier periods (lower
baseflow) and expansion during wetter season (higher baseflow) is an important control of potential sources of N with connectivity to the stream. We argue that summer riparian NO$_3^-$ production is driven by sub-daily variations in surficial soil oxygen caused both by precipitation events and by soil evaporation and transpiration. These events induce diurnal fluctuations in groundwater tables during the summer, which can be several cm during the growing season (Loheide et al., 2005, Schilling et al., 2006, Flewelling et al., 2011).

Previously, Duncan et al. (2013) have estimated that 98-99% of the entire watershed denitrification in Pond Branch is occurring in riparian hollows, which comprise less than 1% of the watershed area. During summer dry downs when riparian hollows drain, there is a large increase in denitrification as more NO$_3^-$, which is a limiting factor in this environment, becomes available, presumably via coupled nitrification-denitrification (Duncan et al., 2013). However, a fraction of that remaining NO$_3^-$ is available for transport to the stream. So despite a drop in N retention efficiency during the summer periods when riparian areas become nominal sources, these zones are critical for being a large nitrogen sink for the majority of the year. During the dormant season, when soil oxygen concentrations are very low, NO$_3^-$ can be limited due to reductions in mineralization and nitrification. In this context, the combination of hydrologic transport and biogeochemical reactions (net nitrification-net denitrification) along flowpaths is critical for assessing the mechanisms for nitrogen retention and export.

The location of the riparian hollow soil oxygen sensors were determined based on the long term well transects, without trying to find locations that were most connected to the stream. Therefore, the fact that soil oxygen trends at these locations respond so similarly
in time to the ~3x increase in stream NO$_3^-$ suggest that these locations are representative of riparian hollow soils. Given the spatial and temporal heterogeneity in near stream soil moisture (Tague et al., 2010) and by extension, soil oxygen, we assume that a set of locations connected to the stream responded just prior to the locations with our sensors. Given the broad valley bottom riparian wetland with threaded channels, we are unable to spatially resolve N mineralization and nitrification in the riparian hollows from stream or hyporheic locations. Further work is necessary to quantify the rates and seasonal variability of in-stream, hyporheic, and near-stream nitrification. Exploring the spatial variance of soil moisture changes within riparian hollows along drainage flowlines is required to test the hypothesis of expansion and contraction of the aquatic-terrestrial nexus driving corresponding changes in stream NO$_3^-$ concentrations.

3.5.3 What is the transport mechanism?

To account for the hydrologic transport necessary for riparian zones to be the source of summer NO$_3^-$ peaks (a modification of hypotheses #5 above), we propose an alternative hypothesis, i.e., that microtopography causes the riparian zone to act as a bioreactor during warmer months, serving as a net producer of NO$_3^-$. Within this microtopography there are local high spots, or hummocks as well as local depressions or hollows. As water tables drop, hummocks become drier and net producers of NO$_3^-$. Denitrification in riparian hollows removes a portion of this NO$_3^-$, but the remainder is transported to streams over diurnal intervals.

Diel streamflow fluctuations induced by evapotranspiration shift the hydraulic gradient and alter the relative depths of riparian soils through which groundwater flow travels.
before entering the stream. These diurnal fluctuations in groundwater have been shown to drive diurnal patterns in stream $\text{NO}_3^-$ concentrations (Flewelling et al., 2013). Further, we argue that summer riparian $\text{NO}_3^-$ production and transport are driven by sub-daily variations in soil oxygen caused both by precipitation events and by soil evaporation and transpiration that induce diurnal fluctuations in groundwater tables during the summer (Loheide et al., 2005, Schilling et al., 2006, Flewelling et al., 2011). The observed groundwater table fluctuations of approximately 10cm per day, when superimposed on the head gradient from variable redox zone to the stream (down gradient) can provide the longitudinal transport necessary to move $\text{NO}_3^-$ (Abit et al., 2008) from the riparian zone to the stream during the growing season. Recent work (Flewelling et al., 2013) showed that fluctuations of riparian water levels over the course of the day changed head gradients, which caused the specific discharge through near-stream sediment to vary at the same time scale. That study was conducted in an agricultural area of coastal Virginia, USA where groundwater $\text{NO}_3^-$ concentrations were quite high and the diel fluctuations affected how much denitrification or removal occurred.

Contrary to what we first expected, our data show than in Pond Branch, stream $\text{NO}_3^-$ concentrations are highest during the day when deeper relatively dilute $\text{NO}_3^-$ groundwater comprises the majority flow. The timing of discharge and $\text{NO}_3^-$ concentrations suggest that the source of stream $\text{NO}_3^-$ concentrations is riparian soils within or close to the contributing source area at baseflow conditions, particularly the region of variable redox conditions in close proximity to the fluctuating water table as well as the stream channel and hyporheic zone. This area varies over the course of the
growing season as evidenced by the hydrologic disconnection of riparian hollows and expansion during extreme events (Duncan et al., 2013).

3.5.4 Implications for predicting the timing of nitrogen export from forested watersheds, landscapes, and regions

A multitude of processes in a complex open system can generate similar responses under different conditions, a concept known as equifinality, which is a hallmark of biological systems (von Bertalanffy, 1950), and has been successfully applied to geomorphologic systems (Chorley, 1962). It is interesting to note the behavioral similarity of NO$_3^-$ export from catchments with marked differences in hydrogeomorphic template, climate, and vegetation like Pond Branch, Walker Branch, Coweeta, the Upper Susquehanna. Our results suggest that rain dominated forested watersheds are likely to exhibit summer peaks in N concentrations and loads. This timing is important for delivery of N to receiving waters that are sensitive to N induced eutrophication. We suggest that summer peaks in N concentrations and loads are driven by a shift in net nitrification (driven ultimately by mineralization) and denitrification dynamics that result in increases in NO$_3^-$ concentrations in riparian soils that are transported to the stream through evapotranspiration induced diel fluctuations in groundwater tables. These results suggest that a fuller consideration of catchment hydrology is necessary to predict streamwater N concentrations. In Pond Branch, we argue that the source of summer NO$_3^-$ is concentrated in the riparian zone and that production and transport of this NO$_3^-$ results
primarily from seasonal decline in near-stream water table and is further enhanced by microtopography in this zone. This microtopography facilitates overall nitrogen retention via coupled nitrification and denitrification in hummocks and hollows (Duncan et al., 2013) but also facilitates a small, but significant increase in NO$_3^-$ export during summer. These dynamics need to be considered in watershed and riparian assessment and restoration programs focused on N delivery to receiving waters.

Our current conceptual model suggests that diel groundwater variations can introduce sufficient redox variability to create zones of nitrification, and also to facilitate transport of recently produced NO$_3^-$ downgradient to the stream (Figure 3.11). A major question is if these micro scale geomorphic (and hydrologic and ecosystem) controls on nitrogen production and transport could also occur in other watersheds. Of the catchments with summer peaks in stream NO$_3^-$ concentrations, low elevation sites at Coweeta, NC and Walker Branch, TN are most similar in terms of vegetation, atmospheric N deposition, and size to Pond Branch, though substantial differences exist. For instance, The stream at Walker Branch is several times the width of Pond Branch and has more rock substrate to support periphyton and algal communities. These in-stream differences have been shown to be a dominant control on seasonal patterns of stream NO$_3^-$ concentrations (Roberts and Mulholland, 2007). There is some question as to whether other small headwater streams have similar in-stream controls as Walker Branch. Coweeta W14 is much steeper and has a considerably smaller riparian zone than Pond Branch. Climate driven variation in mineralization dynamics at Coweeta have been hypothesized to control seasonal NO$_3^-$ export (Brookshire et al, 2011). However, there are expansive areas of saturated organic rich soils near the headcut, which could provide similar
functionality to the riparian zone at Pond Branch. A combination of processes that account for biogeochemical transformations and hydrologic transport could manifest in different catchments and is an interesting area for further research.

These considerable differences in the hydrogeomorphic template and respective differences in the hypothesized controls on seasonal N dynamics suggest that the riparian microtopographic driven dynamics that we observed at Pond Branch are exactly the same other sites. However, this level of process knowledge gives insights as to what set of processes could account for strong seasonal export patterns. Because Pond Branch, low elevation Coweeta catchments, and Walker Branch are warmer than watersheds in the Northeast and Europe that have shown typical winter to early spring peaks in N export, they do not accumulate substantial amounts of atmospheric deposition in snowpack during winter that is exported during snowmelt. We also note that snowpack depth and duration is likely a control given that sites in NY, USA which typically have intermittent snow cover have also exhibited summer peaks (Goodale et al., 2009). Upland lysimeter chemistry at Pond Branch matches the seasonality of many northeastern US and European watershed studies with much higher stream concentrations than Pond Branch. The riparian soil solution chemistry more closely matches stream concentrations. This raises the possibility that evapotranspiration induced groundwater fluctuations may be a fundamental driver of summer N export patterns in rain dominated watersheds. Future work should explore the timing of the onset of diurnal variations in near-stream groundwater and the seasonal rise in stream NO$_3$\textsuperscript{-} at multiple sites with contrasting riparian typologies and topographies.
3.6 Conclusion

By investigating multiple hypotheses, we attribute the recurrent summer peaks in stream NO$_3^-$ in Pond Branch primarily to changes in net nitrification-denitrification dynamics, in the near-stream zone, though a lack of uptake by vernal riparian vegetation and in-stream biota during the peak of the growing season could further enhance this seasonality. The geomorphic template and presence of pronounced microtopography of the riparian zone at this site are important controls on the spatial distribution of redox conditions. The physical structure of the near-stream zone determines the spatial extent (and volume) of hydrologically connected portions of the landscape, in which redox sensitive processes can control stream N concentrations. This hydrologically connected and variable redox volume of the near-stream zone evolves over different hydroclimatic conditions. The N source zone will be largest during drier summer conditions when denitrification is limited by high soil oxygen concentrations. The N source zone is also affected by temperature and moisture controls on microbially mediated N transformations. In terms of transport capacity, mid-summer is typically coincident with largest ET flux, resulting in the largest diel fluctuations in water table. These periods thus have the highest potential to both produce NO$_3^-$ and transport it from the near-stream source volume through the stream network. Diel transport facilitated by groundwater fluctuations could also transport recently produced NO$_3^-$ from riparian hollows and stream segments that have been hydrologically disconnected on the surface. Therefore, even as portions of the stream and near-stream environment would be classified as ephemeral in terms of surface water transport, regions with high organic
matter could still serve as a biogeochemical source area through which subsurface transport still occurs.

In terms the dissertation, this Chapter shows that nearly the entire stream N export originates from the riparian zone.

**Acknowledgements:**
We thank Wil Wollheim and Gopal Mulukutla for help on programming the SUNA sensor and Scott Morford for analyzing rock samples. Thanks to Dan Dillon and many others for field assistance. This work was funded by National Science Foundation grants DEB-1027188 (Baltimore LTER) and DEB-0919047 (Ecosystem Studies).
REFERENCES


Table 3.1. Mean Monthly Discharge at Pond Branch through the growing season

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**Pond Branch Total Monthly Rainfall (mm)**

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<th>June</th>
<th>July</th>
<th>August</th>
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</table>

* from SERCC BWI Normals 1971-2000
Figure 3.1. Conceptual model of summer season nitrate sources. 1) Geochemical weathering of bedrock and saprolite. 2) Delayed transmission of winter precipitation to the stream via fracture flow and groundwater seeps. 3) Senescence of riparian vegetation. 4) Reductions in in-stream uptake. 5) Riparian soils.
Figure 3.2. LiDAR derived shaded relief image of the Pond Branch watershed, a 37 ha forested subwatershed in Baltimore County, USA. Sensor locations for $O_2$, TDR probes and riparian groundwater wells are shown.
Figure 3.3. Riparian topography and active streams channels in the Pond Branch bottomland. The riparian zone is broader in the upper well transect (upper) and narrower at the lower riparian transect (lower panel) where valley slopes are steeper. Microtopographic variation is pronounced throughout the entire riparian zone.
Figure 3.4. Bi-weekly NO$_3$ concentrations generated from weekly BES grab samples from 1999-2010 reveal recurrent summer peaks with increasing concentrations in late May to early June and declines in September and October. Loads increase over the same period during the growing season.
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Figure 3.8. Nitrate concentrations versus day of year in 2010-2011 in tension lysimeters in riparian and upland locations in the Pond Branch watershed.
Figure 3.9. Average daily soil oxygen concentrations measured in toeslope, riparian hummock, and riparian hollow landscape positions Dec 18, 2011 – Oct 11, 2012 at the lower riparian transect in the Pond Branch watershed.
Figure 3.10. Soil oxygen concentrations measured hourly in toeslope, riparian hummock, and riparian hollow landscape positions from June 18 – July 8, 2011 at the lower (a) and upper (b) riparian transects in the Pond Branch watershed.
Figure 3.11. A conceptual model of how seasonal and diel (transpiration-induced) water table fluctuations provide the biogeochemical conditions to produce and transport nitrate from the riparian zone to the stream during the growing season. As net production of nitrate proceeds, there is a greater potential for a portion to be transported to/through the stream network. The area of redox variability changes in response to wetter (winter) and drier (summer, day time, extended drought) conditions as hydrologically connected areas decrease. Complete N cycling processes include: 1. N fixation, 2. Mineralization, 3. Nitrification, 4. Desorption, 5. Absorption, 6. Uptake of ammonium (NH$_4^+$), 7. leaching and exudation of DON, 8. Sorption and assimilation of organic molecules, 9. Biotic assimilation of NO$_3^-$, 10. Leaching and desorption of NO$_3^-$, 11. anaerobic oxidation of ammonium (annamox), and 12. Dissimilatory nitrate reduction to ammonium (DNRA). Processes 10-12 have been shown elsewhere, but are not thought to be important in Pond Branch (see Duncan et al., 2013).
CHAPTER 4. RIPARIAN ECOHYDROLOGIC CONTROLS ON PATTERNS OF STREAM NITRATE EXPORT

4.0 Preface

Chapter 4 examines the seasonal patterns in N export and addresses how the seasonal pattern of inverse c-Q relationships from long-term sampling at Pond Branch reconcile with positive c-Q relationships from many other forested watersheds, particularly during storms. This requires characterization of nitrate export patterns as a function of discharge across time scales. To address the hydrologic and ecological drivers of c-Q patterns, we primarily employed a cross-section view of the watershed. This chapter builds on Chapter 3, which used the rise in nitrate concentrations in June, 2011 and expands the scope through the growing season to specifically investigate the c-Q patterns through time and in comparison to the long-term weekly data.

The research in this chapter was conducted in collaboration with Peter Groffman, Cary Institute of Ecosystem Studies and Lawrence Band, University of North Carolina Chapel Hill and benefitted from review by Martin Doyle, Duke University.
4.1 Introduction

The magnitude and timing of stream nitrogen (N) concentrations is an important diagnostic of ecosystem dynamics, and of critical interest to understanding and controlling impacts on downstream water bodies (Bernhardt et al. 2005). There is significant interest in understanding temporal patterns of stream nitrogen concentrations, which vary with climate and watershed conditions (Bernal et al. 2012). Previous work has examined contrasting seasonal patterns of nitrogen export (e.g. Ohte et al., 2010) and the importance of storm events (McHale et al., 2002), but predicting the magnitude and timing of watershed N export remains difficult.

Nitrate (NO$_3^-$) is often the primary form of dissolved inorganic nitrogen export and is of great concern in estuaries where it is a limiting nutrient that stimulates primary production leading to algal blooms and in some cases to anoxic dead zones. While NO$_3^-$ fluxes from forests are far lower than from agricultural and urbanized watersheds, the goal of watershed, stream, and riparian restoration projects is often to re-create the form and function found in forested reference watersheds. Therefore, understanding the controls on nitrogen cycling and export from forests is critical for optimal watershed management. Additionally, forests are still a sizeable fraction in many parts of the world, and are the dominant land use (56%) in the Chesapeake Bay watershed (Jantz et al., 2005). There is particular interest in forested headwater catchments, which comprise a majority of surface area in large river basins through eastern North America (Alexander et al., 2011). As we restore streams and watersheds to reduce N pollution to receiving
waters, it is important to fully understand the processes by which N is transformed and transported from these headwater areas.

Scientific advances are often driven by new measurement technologies (Kuhn, 1970) including the prospect for higher frequency water quality measurements (Kirchner et al., 2004). Indeed, recent advances in sensor technology are transforming the ability to observe fine temporal scale responses of stream nitrate concentrations with high accuracy and precision (Pellerin et al., 2009, Heffernan and Cohen, 2010). Storm sampling and short periods (hours to days) of autosampling have long been an integral part of watershed science (Bormann et al., 1974). While there is still immense value in collecting long-term low frequency data (Burt et al., 2011), new sensor technologies enable longer duration and higher frequency measurements that could transform our understanding of watershed scale controls on nutrient export.

Concentration-discharge (c-Q) relationships have been a valuable tool for understanding how nutrient export is driven by changing hydrologic conditions and watershed characteristics such as contribution from quick flowpaths from variable source areas. Flushing of solutes during storm events has been classified as “transport limited” where concentrations increase with increasing discharge and “source limited” where concentrations decrease during the event (Burns, 2005). Solutes that have constant concentrations despite changing discharge are termed “chemostatic” (Godsey et al., 2009). While analysis of c-Q relationships has been useful in many watershed studies, generalizable patterns across seasons, storm types, and watersheds has remained elusive.
This is due in part to the many different hydrologic processes that can be responsible for the resultant pattern (Chanat et al., 2003).

The goal of this study was to develop a conceptual model of the controls on stream NO$_3^-$ concentrations in a mid-Atlantic watershed that has maximal export during the growing season. The work extends previous research in the Baltimore Ecosystem Study (BES) based on long term weekly sampling of stream chemistry by including high temporal resolution measurements of stream NO$_3^-$ concentrations to scale and contrast dynamics from sub-daily to seasonal. Previous studies have examined long-term patterns and seasonal dynamics during baseflow (Band et al. 2001, Groffman et al. 2004, Kaushal et al. 2008, 2011, Shields et al. 2008, Duncan et al., In Review). Here we build on that work and use high resolution data to investigate changes in c-Q relationships through time during the growing season. We addressed two questions: 1) are high temporal resolution c-Q patterns the same as patterns developed from long-term weekly grab samples (source limited where c and Q are negatively correlated)? and 2) do c-Q patterns (direction of hysteresis loops and trends) change throughout the growing season?

4.2 Study Site

Pond Branch is a forested south-facing 37 ha (Figure 4.1) subwatershed of Baisman Run, a 370 ha watershed with low-density residential development in the upper third of the watershed. The site has been gauged and sampled by the Baltimore Ecosystem Study since 1998. Elevation ranges from 140-190m. The upper (northern) portion of the watershed has gentle slopes with a wide valley bottom. Extensive portions of the broad
valley bottom area are comprised of hummock and hollow microtopography that have likely formed from a combination of tree throw and channel evulsion over time. We have previously shown that the complex microtopography and soils in riparian areas are hot spots for N cycling, and that the vast majority of denitrification occurs in <1% of the Pond Branch area (Duncan et al. 2013). Slopes become steeper, the riparian zone narrows, and the stream becomes a single channel approximately half way down the catchment (See Duncan et al., 2013 for more information). Riparian hollows have organic rich soils that can extend as deep as 50 cm below ground surface before grading into mineral material. The portion of Pond Branch closer to the gage is more constrained geologically and the stream becomes single threaded. Above the gauge, a bedrock outcropping coincides with a small waterfall below which there is a marked decrease in the extent and depth of riparian soils.

Vegetation:

Pond Branch is completely forested except for a 20 m wide tall-grass covered subsurface gasoline transect which traverses the watershed at about its midpoint. The forest is dominated by Quercus spp. (oaks), Liriodendren tulipifera (tulip poplar), and Carya spp. (hickory) with a stand age of approximately 90 years. There are locations, primarily near the outlet with an understory dominated by Kalmia spp. (laurel). Hollows have wetland plant assemblages dominated by Symlocarpus foetidus (skunk cabbage).

Climate and N Deposition:

Pond Branch is in a humid subtropical climate with approximately 1000 mm of rainfall annually. Summers are warm with average maximum temperatures of 30°C. Winter temperatures can be cold with mean minimum temperatures of -4°C and snowfall can
occur several times per year. Deposition of dissolved inorganic N (DIN) in the Maryland Piedmont is approximately 9 kg N/ha/year (Bettez and Groffman, 2013).

Nitrogen Export Patterns:

Long-term monitoring by BES (Groffman et al. 2004, Kaushal et al. 2008, Shields et al. 2008) has shown that Pond Branch has recurrent summer peaks in NO$_3^-$ concentration (Figure 4.2). Seasonal trends in NO$_3^-$ concentrations are asynchronous with discharge, which is lowest during the growing season when evapotranspiration rates are highest. Despite low discharge, peaks in NO$_3^-$ export also occur during the summer as the increased concentration more than compensate for decreases in discharge.

Initial conceptual model:

To explain an increase in nitrate concentrations and export during the summer, we previously posed a conceptual model suggesting a shift towards higher net nitrate production (increased nitrification and decreased denitrification) in riparian zones and hillslope hollows during the summer months (Band et al., 2001). This pattern is driven by a seasonal drawdown of water tables in the near-stream zone, which reduces riparian saturation levels. Aeration of the organic rich riparian soils and hillslope hollows can promote nitrate production by nitrification. This nitrate flushes to shallow groundwater during storm events and then diffuses to the stream at more steady rates. As water tables and soil moisture levels increase and soil oxygen concentrations decrease in late summer and fall, nitrification decreases while denitrification increases, with net nitrate production tending toward zero. As net nitrate supply declines, stream concentrations decrease until litter fall, which has been shown to stimulate microbial uptake and further decrease
stream nitrate concentrations to the detection limit during the dormant season (Sebestyen et al., 2009).

4.3 Methods

Sensor Locations and Descriptions

Soil oxygen concentrations were recorded using Apogee (Logan, UT) SO-111 probes, which utilize a standard galvanic cell approach to measure the partial pressure of oxygen in air. The diffusion-head sensors were buried vertically with the heads at 6cm depth. Soil moisture was recorded using Campbell Scientific (Logan, UT) CS 616 water content reflectometer probes. Probes were installed vertically into the ground to measure the average water content of the top 20cm of soil. Both types of sensors were calibrated before deployment and collected soil oxygen and volumetric water content every 15 minutes (hourly at the upper riparian transect). Details of sensor deployment and datasets are given in Duncan et al. (In Review).

Soil moisture and soil oxygen sensors were installed at two (upper and lower) riparian transects and in a hillslope hollow. These sensors spanned the hillslope-riparian boundary and were placed in a riparian hummock, a riparian hollow, which is the secondary channel (a secondary stream channel), and at the toeslope. In a hillslope hollow adjacent to the upper transect, approximately 40 m from the toeslope location, two pairs of soil oxygen and water content probes were positioned approximately 20m apart along the trough of the hollow. The third datalogger location in the lower riparian transect had three pairs of soil oxygen and moisture sensors located in riparian hummock, riparian hollow, and toeslope locations.
Hydrometric Data

Discharge was measured at a USGS gauging station at the outlet of Pond Branch (01583570), but the stage recorder was unable to discern diurnal fluctuations at baseflow and fine scale variations during small storm events. To increase the resolution of stage during periods of baseflow, an Onset Hobo pressure transducer was placed in the weir pool and stage was recorded every 15 minutes. Discharge was calculated for baseflow periods by prorating the Baisman Run USGS record (01583580) by drainage area and by correcting for lag time using timing from the pressure transducer at the Pond Branch weir. During storm events, there is much larger uncertainty in discharge and we did not have a sufficient number of velocity measurements to refine the USGS rating curve.

Stage from a baromaretrically corrected pressure transducer was used as a proxy during for c-Q relationships during storm events.

Groundwater levels have been monitored by BES at approximately monthly frequency at two locations along Pond Branch, “upper” and “lower” since 2001 (Groffman et al. 2002, Gift et al. 2010). 1m deep wells 5m from either side of the stream were installed in 2001. The transect was expanded in 2009 with ~2 m deep wells that were installed 10 m from the 2001 channel in another riparian location and 15 m from the channel at the toeslope. Four groundwater wells were installed in approximately 5m increments from the stream to the toeslope at each riparian transect. Water levels in the wells were measured every 15 minutes using a combination of capacitance probes (Odyssey) and pressure transducers (Onset Water Level Recorders).
Water Quality

Weekly grab samples were collected at the outlet as part of the long term BES LTER sampling. Additional grab samples were collected for comparison with high-resolution sensor observations and were filtered in the field through a 0.7 micrometer GF/F Whatman filter and frozen as soon as possible (1-3 hours) until analysis. Groundwater samples were collected bi-weekly to monthly. Wells were purged and samples were collected from recharge. Ceramic cup tension lysimeters located in upland plots at 10 cm and 50 cm depths (Groffman et al. 2006, 2009) and at 10 cm depth in both riparian transects were sampled monthly from summer 2010 through summer of 2011. Ammonium was measured using the fluorometric technique (Holmes et al., 1999) on a Turner 10-AU spectrophotometer. NO$_3^-$, grab samples were analyzed on a Dionex Ion Chromatograph.

A submersible ultraviolet NO$_3^-$ analyzer (SUNA, Satlantic, Halifax, NS) that utilizes ultraviolet absorption spectroscopy to measure in-situ dissolved NO$_3^-$, was placed just below the weir to measure NO$_3^-$ concentrations by taking three separate readings 10 seconds apart at 15 minute intervals. The average of each 15 minute interval was then smoothed with a locally weighted regression (LOESS) filter (Cleveland et al., 1992) for a span of 0.05 of each continuous period of data, uninterrupted by gaps. Gaps in the data were largely due to sediment transport, which would occasionally fill the sensor window, making long continuous records infeasible. Data were occasionally recorded by the sensor during these periods. If the data had a lower signal to noise ratio and were preceded by a decline in nitrate concentrations, consistent with the optical window being blocked, these periods were discarded from the analysis.
Data Analysis:

LOESS regression was performed in R (R Core Team, 2013) and was used to fit relationships between stream stage (finer accuracy than USGS prorated discharge measurements) and nitrate concentrations. Resultant c-stage plots were then treated as c-Q plots and examined for storm periods in early, middle and late growing season.

4.4 Results

4.4.1 Context of 2011 relative to the long-term record

The seasonal trend of summer peaks in stream nitrate concentrations with dormant season values below the detection limit has been consistent from year to year since 1998. The amplitude, or maximal concentrations during the growing season of each year does vary interannually, with higher concentrations correlated with lower summer flow. The 2011 SUNA derived nitrate concentrations were higher during the summer than average concentrations derived from 12-years of weekly sampling, likely due to specific flow conditions during this year. The 15-minute SUNA data captured higher variations in NO$_3$- associated with storm events that are not captured in the long-term weekly sampling (Figure 4.3).

4.4.2 Seasonal nitrate - rising limb characteristics

High resolution SUNA data from Jun 22 to Jun 25, 2011 show that concentrations increased from 0.04 mg NO$_3$ -N/L to 0.16mg NO$_3$ -N/L at baseflow, following a small storm on Jun 21$^{st}$. Using low order fits to detrend this period and examining residuals illustrate the diurnal nature of stream flow and nitrate which are offset from one another with nitrate concentrations higher during the late afternoon with minima during early
morning. The mass flux from Jun 21 to Jun 25 also increased during this period of baseflow, despite an overall decline in discharge (Figure 4.4). Within two days of the increased stream N concentration, marked increases in riparian soil oxygen concentrations were observed at the lower riparian hollow location (Figure 4.5).

4.4.3 c-Q analysis

Patterns from weekly data

An upper envelope of concentration-discharge can be seen with the highest nitrate concentrations occurring at lowest flows, with the exception of one snowmelt event (Figure 4.6). At lowest flows there is the largest range of concentrations from the reported detection limit of 0.01 mg NO$_3^-$ N/L to 0.25 mg NO$_3^-$ N/L. The envelope based on weekly grab samples approximates a negative power function.

Patterns from storm events

SUNA June 21

The earliest storm the SUNA was deployed for was Jun 21$^{st}$. The storm occurred in phase with the diurnal change in discharge, so the effects of the small event were superimposed on diurnal fluctuations. However, concentrations decreased in response to the event (Figure 4.7), showing an overall negative slope. The resultant c-Q hysteresis loop was clockwise in direction.

SUNA July 19

Analysis of a storm on July 19$^{th}$, when nitrate concentrations were higher (nearly the seasonal maxima at 0.17 mg NO$_3^-$ N/L show that concentrations increased with
discharge (Figure 4.8) and peaked just prior to discharge (positive slope). The resultant c-Q hysteresis loop was also clockwise in direction.

SUNA August 3

The period of data from 7/29 to 8/10 captured 5 storm events of varying magnitudes (Figure 4.9). Small events on 8/1 and 8/2 produced large responses in nitrate concentrations. August 3rd had two storm events, both of which produced increases in concentrations during the rising limb of the hydrograph. We note that the second storm, which had a larger change in stream stage had lower peak concentrations than the storm that occurred earlier in the day. In both cases, the c-Q hysteresis loops have clockwise directionality. The storm on 6-Aug produced an increase in nitrate concentrations associated with an increase in discharge.

SUNA September 23

The period of data from 9/18-9/27 captured a range of discharge conditions. Analysis of a storm from September 23rd, which occurred after Tropical Storms Lee and Irene, showed a rise in concentrations with a rise in stream stage (Figure 4.10). There was debris lodged behind the weir, so stage does not drop after the event, nitrate concentrations increased from 0.13 to 0.26 mg/L NO$_3^-$N.

4.5 Discussion

On the ascending limb of the 2011 seasonal nitrate signal (based on weekly samples), SUNA data showed the majority of the rise occurred at baseflow, and that residuals exhibited a strong diel pattern. Based on the weekly sampling in 2011, the period of time is approximately half way through the seasonal rise and accounts for the majority of the rise. This large relative increase during multiple days of baseflow recession suggests
transport from the near stream zone, which is connected during a prolonged drainage sequence. Based on the residual analysis, detrended concentrations were highest during the day and lowest at night, although the mass flux is highest at night when discharge is highest. This timing suggests that the variable source area fluctuates with changes in evapotranspiration and concomitant fluctuations in water table (Duncan et al., in review). The mass flux increases over this relatively short (4 day) period when discharge slightly declines, suggesting that net nitrate production (as the limiting factor) and transport are increasing over this period.

Previous work at Pond Branch examined mass flux of nitrate using the USGS Fluxmaster program based on the weekly grab sample and daily discharge data (Savvas, 2010). Based on that analysis, Savvas (2010) found that discharge was not a significant predictor of nitrate load and because time (seasonality) is so important, there was significant scatter when examining $c$ as a function of $Q$, particularly at low flow. During the period of June 21-25, the marked increase in nitrate (and nitrate mass flux) shown by the SUNA data was likely driven by production and transport of nitrate from increased net nitrification in the riparian zone. This idea is supported by the soil oxygen data, which increased in near-stream riparian hollows, albeit with a two-day lag between the rise in nitrate and the aeration of the lower riparian hollow. It is important to note that the spatial distribution of soil oxygen was undersampled and it quite likely that significant areas of the riparian zone likely became aerobic in the days before the rise in stream nitrate. Given the topographic and soil moisture heterogeneity in the riparian zone, the temporal correlation between stream nitrate and riparian hollow suggests a strong control of near-stream water-table-soil oxygen on stream nitrate concentrations under these conditions.
4.5.1 Why are c-Q patterns for some periods opposite the trend from long-term weekly samples?
The c-Q pattern from weekly grab samples shows a roughly inverse relationship, fit by a power function with a negative exponent. Based on SUNA data, only the 21-June storm 2011, also exhibited source limited flushing (negative c-Q slope). All other storms captured with the SUNA in 2011 exhibited aspects of transport limited flushing behavior (positive c-Q slope). Transport limited flushing is very common with nitrate in forested watersheds (Inamdar, 2004, 2006). In line with previous studies, nitrate responds on the rising limb of the hydrograph, presumably because of near-stream source in response to precipitation, infiltration, and recharge (Iqbal, 2002 and Inamdar et al., 2004). At Pond Branch it is likely due to the extensive riparian wetland complexes throughout the bottomland, which forms labile nitrate in the variable source area.

At Pond Branch, nitrate c-Q patterns vary with sampling frequency. Weekly sampling reveals a negative slope in the c-Q pattern, whereas high-resolution sampling during storms produces variable patterns. These effects of sampling frequency may explain why the Fluxmaster analysis (Savvas, 2010) showed no significant influence of discharge, and that season was the most important explanatory variable. Our analysis suggests that discharge is an important driver of concentration at diel and storm resolution and that groundwater table and soil oxygen conditions, which are also dependent on temperature, are important drivers of concentration at the seasonal scale.

Pond Branch is one of a small (but growing) number of sites that exhibit peak nitrate concentrations and export during the growing season (Swank and Vose, 1992, Mulholland and Hill, 1997, Goodale et al., 2009). Weekly sampling alone appears to be
insufficient to reveal the interactions between hydrologic and ecosystem components that underlie the export behavior of these systems, particularly when relationships are only revealed during storm events. Additional work in Pond Branch and other catchments should include multi-resolution modeling, with long-term infrequent (weekly, monthly) monitoring punctuated by storm sampling across seasons and storm magnitudes. These analyses should also include other forms of dissolved and particulate organic nitrogen to determine how important storm flows are for closing the nitrogen budget.

4.5.2 Do c-Q patterns change over the growing season?

The c-Q relationship for the 21-June storm, which occurred on the rising limb of the seasonal N curve, had a similar form to the seasonal pattern derived from weekly samples. The c-Q pattern exhibited source limited flushing with reductions in concentration over the course of the event. In contrast, other storms in the middle of the growing season (July 19) when nitrate concentrations were higher exhibited transport limited flushing and concentrations remained high after the flush. The storm on 6-Aug produced a combination source/transport limited response where concentrations increased on the rising limb of the hydrograph, but decreased below pre-event conditions following the storm. This event occurred at, and may have been the driver of the decline from the seasonal peak in stream nitrogen concentrations, but there were large data gaps around this period of time. Sampling in future years will be necessary to better capture the point and drivers of when seasonal concentrations begin to decrease. In general, concentrations continued to increase during storm events through late summer and into autumn but in some of those storms, concentrations eventually decreased below pre-event levels. The storm of 23-Sep showed an increase in concentrations, despite large rainfalls during
Hurricane Irene (28 August 2011) and Tropical Storm Lee (7 September 2011). Irene delivered 86mm of rainfall and Tropical Storm Lee delivered 178mm over a 3 day period (6 – 8 September). This could be the result of mobilization of nitrate from the riparian hollows and other distally connected organic rich soils, which comprise a large source of potentially flushable nitrate, even after large rain events.

The lowest correlation between weekly sample concentrations and those from the SUNA were during the period of data from September, likely do to sensor drift that was not corrected until after this time. While the SUNA data were higher than lab derived values, we assume that relative trends were correct even if the absolute value of concentrations are high.

These patterns suggest an evolution from source limitation to transport limitation and back towards source limitation. These results are consistent with the idea that summer seasonal peaks are driven by increases in net nitrification in the stream and near-stream zone (Chapter 3).

Regardless of the trend in c-Q patterns from storm events, whether positive (transport-limited response) or negative (source-limited response), the direction of all hysteresis loops were clockwise. This qualitative similarity among all storm events suggests an important underlying similarity in catchment behavior. An implication of this finding is that runoff generation and nitrate transport are fundamentally driven by a fast contributing variable source area (Butturini, 1999 and Scanlon et al., 2001) in all conditions. The importance of riparian zones for nitrogen cycling and export has been well documented (Lowrance, 1984, McClain et al., 2003), and the high-resolution sensor data illustrate how small differences in riparian soil oxygen concentrations and other
hydrologic factors (such as antecedent moisture conditions) control the amount of nitrate that is exported in streamflow.

Future work at Pond Branch and other catchments that exhibit summer peaks in nitrate concentration should test the hypothesis that purely source limited flushing occurs only during the rising limb of seasonal N concentrations and potentially towards the end of the growing season. The associated hypothesis would test if a combination of transport limited and source limited flushing (increased peak concentrations and decreased baseflow concentration in relation to pre-event conditions) are dominant on the declining limb of the seasonal chemograph. It would also be interesting to examine if periods of source limited flushing occur in snowmelt dominated sites that have late winter/early spring peaks in N concentrations and export. Detailed studies on antecedent conditions, groundwater levels, and end member mixing are required to deconvolve additional temporal controls on the evolution of c-Q patterns.

4.5.3 Revised Conceptual Model

Our revised conceptual model is driven mechanistically by a seasonal shift where water tables and soil moisture levels decline while soil oxygen concentrations and soil temperatures increase. This changes increases the volume of soil where net mineralization and nitrification occur while decreasing the volume of soil where denitrification occurs. The volume of soil where net nitrification increases is large in Pond Branch due to the presence of riparian microtopography and organic rich soils. As mentioned above, there are extensive riparian wetlands at Pond Branch that likely contribute to streamflow both by variable source area where infiltration excess overland flow during storm events and to baseflow during drying conditions. This near-stream
zone at Pond Branch is essentially a bioreactor that grows outward in extent from the stream and riparian hollows during dry downs \((x,y)\), in depth with decreasing water tables \((z)\), and through time \((t)\) with extended dry periods. Storms can reset the system, particularly in the early growing season when the low accumulated supply of recently produced nitrate can be flushed from the system. At this time even small storms can result in concentrations dropping back to the detection limit. As baseflow resumes, nitrate is produced and transported to the stream with groundwater fluctuations at diurnal intervals (Figure 4.11). Nitrate production is maximized in riparian zones by mid summer, during periods of peak ET. During this period, Pond Branch displays transport limited flushing. As supply has been maximized, concentrations do not decrease at all or as much during storms. By later in the summer, storm events can produce a combination of source and transport limited flushing, where concentrations initially increase over pre-event levels and then decrease relative to pre-event concentrations following the storm.

### 4.6 Conclusion

High frequency measurement yields nearly 3 orders of magnitude increase in resolution compared to weekly sampling, enabling much more insight into the processes driving nitrogen export across periods of time ranging from storm events to diel fluctions and sub-seasonal trends that weekly observations are unable to capture. During periods of highest nitrate export, there is marked diurnal timing, which is interspersed by storm events. The c-Q patterns from individual storm events change from source limited to transport limited flushing through the growing season, which is different from the general c-Q response inferred from weekly grab samples, highlighting the importance of higher
temporal resolution measurements. We attribute the change from source limited to transport limited responses to water table fluctuations in a highly organic rich riparian zone during the growing season, suggesting that a more comprehensive conceptual model is needed to account for c-Q patterns for biologically active, redox-sensitive solutes such as nitrate.

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REFERENCES


FIGURES
Figure 4.1. Map of Pond Branch watershed, MD within the larger Baisman Run Watershed.
Figure 4.2. Locally weighted regression (LOESS) fit of nitrate-N concentrations (mg/L) for each year (1998 – 2012) based on weekly grab samples.
Figure 4.3. High resolution nitrate concentration data from 2011 in relation to long-term weekly grab sample concentrations and long-term LOESS fit. Gray bars denote periods of high resolution data in the early (20-Jun to 26-Jun), mid (12-Jul-21-Jul and 29-Jul to 10-Aug), and late (18-Sep to 27-Sep) growing season.
Figure 4.4. Discharge, nitrate concentrations, and mass flux from June 22 – 26, 2011; an ascending limb that accounted for the majority of the seasonal increase in nitrate concentration and flux for the year.
Figure 4.5. Soil oxygen concentrations in toeslope, riparian hummock and riparian hollow landscape positions from June 20 – July 6, 2011. The period denoted within the black box is when stream nitrate concentrations began to increase.
Figure 4.6. Nitrate concentration versus discharge for weekly grab samples collected from October, 1999 to September, 2012.
Figure 4.7. High resolution nitrate concentration versus discharge from June 20 – 26, 2011. Top panel shows time series of stream stage (left Y axis) and stream nitrate (right Y axis). The bottom panel shows nitrate concentration-discharge patterns during ascending and descending limbs of the storm hydrograph.
Figure 4.8. High resolution nitrate concentration versus stage from July 13 - 20, 2011. Top panel shows time series of stream stage (left Y axis) and stream nitrate (right Y axis). The bottom panel shows nitrate concentration-discharge patterns during ascending and descending limbs of the storm hydrograph.
Figure 4.9. High resolution nitrate concentration versus stage from July 29 – August 10, 2011. Top panel shows time series of stream stage (left Y axis) and stream nitrate (right Y axis). The bottom panel shows nitrate concentration-discharge patterns during the period denoted in the gray box.
Figure 4.10. High resolution nitrate concentration versus stage from September 18 - 27, 2011. Top panel shows time series of stream stage (left Y axis) and stream nitrate (right Y axis). The bottom panel shows nitrate concentration-discharge patterns during the period denoted in the gray box.
Figure 4.11. A new conceptual model for controls of stream nitrate concentrations.

Early Summer: Diel increases at baseflow, nitrate concentrations crash during storm events (source-limited) and are lower after the storm.

Mid Growing Season: Concentrations on average are higher, concentrations peak during storms (transport-limited), there are small declines in baseline concentrations following storms, but they never get to dormant season levels.
CHAPTER 5. CONCLUSION

This dissertation sought to explore how heterogeneity in a) the geomorphic template and b) variations in hydroclimate and ecological processes effect nitrogen cycling export across spatial and temporal scales. The overall finding from this work is that the catchment hydrogeomorphic template filters hydroclimate (precipitation, temperature) and nitrogen deposition inputs to produce emergent patterns in nitrogen cycling and export (Figure 5.1).

Each paper in this dissertation uses a multi-scale framework to address how variability in the geomorphic template and soil oxygen controls catchment scale nitrogen biogeochemistry. Three related topics were addressed.

1) Quantification of watershed scale denitrification flux at a daily time step and fine spatial resolution for an entire water year to estimate space/time variation in N cycling and approach closing the nitrogen budget;

2) Determination of ecohydrologic controls on the seasonality of nitrate export by investigating multiple alternative hypotheses, and

3) Characterization of the evolution of nitrate concentration-discharge patterns from dormant through growing season, and their apparent change as a function of data resolution and watershed scale nitrification potential.
Understanding nitrogen transformations and transport across scales is a major scientific challenge. Detailed observations and analysis at Pond Branch suggest that the eohydrological processes in the riparian zone which accounts for 4% of the catchment and riparian hollows which comprise less than 1% of total area control nitrogen cycling and export at the watershed scale. In particular:

1) Denitrification accounts for approximately 25% of atmospheric N deposition. 99% of watershed scale denitrification occurs in riparian hollows, which comprise less than 1% of the watershed. 2) Water table declines and diurnal variations during the summer likely decrease the retention efficiency of riparian hollows, driving seasonal stream export patterns. Annual stream export is approximately 20% of denitrification, so moderate decreases in the retention in such close proximity to the stream could easily account for stream nitrogen patterns. 3) The eohydrology of the riparian zone exerts a strong control on the timing and magnitude of nitrogen export as shown in evolving concentration-discharge relationships.

5.1 Multiscale Approaches and Three Views of Watershed Eohydrology

Borrowing from fluvial geomorphology (sensu Leopold), I employed three different views of watershed eohydrology controls of nitrogen cycling and export across scales. Chapter 2 is the plan view or watershed geographic approach that emphasizes process dynamics between different landscape positions. It is grounded on scaling of denitrification dynamics from soil cores in different landscape positions to the entire watershed. The plan view analytical framework combined information from LiDAR
terrain analysis, soil oxygen sensors, and a novel lab technique to produce the first daily
time-step watershed scale denitrification flux estimate. This chapter aggregates from
daily to an annual timescale and from soil cores (cm²) to the entire watershed (ha).

Chapter 3 examines the seasonality of nitrogen export by examining five alternative
hypotheses drawn from recent literature, essentially from a longitudinal perspective from
surface and subsurface source areas through terrestrial and aquatic flowpaths. Alternative
hypotheses included contributions of deep groundwater from seeps, contributions from
geochemical weathering, the role of in-stream processes, the rapid decay of ephemeral
riparian vegetation, and the oxygen dynamics in surface soils. Soil oxygen concentrations
in the riparian zone are driven by a combination of groundwater levels and respiration.
These ecosystem driven fluctuations create sufficient variability in the redox conditions
to increase net nitrate production and provide a source of hydrologic transport to the
stream. The temporal scales of interest span from diel variations at baseflow to seasonal
patterns in N export. The spatial scales integrate across flowpaths from shallow
throughflow, deeper groundwater draining to seeps, to riparian cross sections to the
catchment.

Chapter 4 extended the cross-section analysis of riparian ecohydrology to examine how
concentration-discharge patterns change through the growing season. The temporal scales
of this chapter range from 15-minute resolution data to resolve storm events to diel
variations. The spatial framework examines watershed integrated concentrations which
are a function of a) antecedent hydroclimate regime, b) seasonal ecosystem dynamics,
including forest ET flux and higher ecosystem respiration rates during the growing season, and c) storm characteristics (magnitude, duration, and intensity).

5.2 Synthesis
One of the unanticipated results of the dissertation was the outsized importance of riparian hollows in the nitrogen budget, even at the catchment scale (Table 5.1). It is a strong hotspot of denitrification throughout the entire year suggesting that the typical definition of hot moments does not apply to these narrow bands of the landscape. In fact, the highest rates of denitrification occur not in response to rainfall events but during dry downs as water tables drop thereby allowing coupled nitrification-denitrification to proceed. There are two important questions that follow from this finding. 1) How much does this help close the watershed N budget and 2) What implications does this have for the riparian N budget?

Watershed Scale:
A simple mass balance was constructed for the catchment:

\[\text{Input} - \text{Output} = \Delta \text{Storage}\]

\[\text{Ndep + Fix} - \text{Denit} - \text{Stream Export} = \Delta \text{Storage}\]

Assumptions include: stream export of DON ~ DIN, biological fixation small and there is not loss to deep groundwater that escapes the weir.

As stated in Chapter 2, the high and sustained rates of denitrification can account for as much as 25% of the catchment scale atmospheric inorganic N deposition. However, given the large atmospheric deposition (370kg) and minor outputs (95 kg from denitrification
and 40kg from stream export), there is a still a major missing sink or large potential increase in storage (Table 5.1). One possible hypothesis is that substantial denitrification occurs in soils deeper than 10cm, which was not specifically measured in the scope of this work. A second hypothesis is that there were changes in storage through the watershed. Nitrogen storage could be in the form of plant assimilation and being adsorbed/incorporated to soil. However, these are traditionally expected to be negligible over the long-term. This watershed scale discrepancy of a missing sink is at odd with the riparian scale budget.

Riparian Scale:

\[ N_{dep, rip} + F_{x, rip} - D_{enit, rip} - S_{tream, rip} = \Delta Storage \]

Because the denitrification rates are so high from riparian hollows, a nitrogen budget of the near stream zone reveals that there is a missing source of N (Table 5.2). Direct litterfall was estimated from data from a set of forest types including high elevation oaks from Coweeta (Knoepp et al., 2009). Because in Pond Branch, much of the canopy directly over the riparian zone is from upslope trees, the conservative assumption is that this is from upslope sources, not nitrogen internally recycled within the riparian zone. The downslope movement of leaf litter from upslope areas to the riparian zone was identified as a potential subsidy in Chapter 2. Data from the Ohio Hills (Boerner et al., 1989) was used to estimate particulate N transfer. From Chapter 3, upland drainage lysimeters suggest that dissolved N is not a significant factor in Pond Branch.
Additionally, results from Chapters 3 and 4 suggest that most of the stream export originates from the riparian zone. To be conservative, we ascribe the export to the full riparian area (4% or 1.48ha), not just the riparian hollows (1% or 0.33ha). While the missing source to the riparian zone is smaller than the catchment scale missing sink, it is still quite large on area weighted basis and demonstrates that fundamental questions about nitrogen biogeochemistry remain unanswered in Pond Branch. One hypothesis, contradictory to the watershed scale budget, is that substantial mineralization and nitrification occur in soils deeper than 10cm. The role of dynamic redox soil volumes is a major research question that emerges from this work; requiring consideration of “hot volumes”, rather than hot spots. One question is to what extent other sources of N transport into the riparian zone have occurred in the past and/or occur under rare conditions. Extreme events have the potential to convey large quantities of particulate N from uplands into the riparian zone. After severe storms in 2010-2013, evidence of overland flow in the headwaters conveyed large amounts of leaf litter into the headcut and ephemeral channels. Additionally, historical erosion that occurred as the watershed was logged and converted to agriculture and pasture 100-300 years ago could have transported organic matter and a large store of N to the riparian zone. This then begs the question, how are the physical structure and biogeochemical rates of riparian hollows maintained?

How sustainable are the high denitrification rates in riparian hollows? And over what timescales? The estimated N losses from riparian hollows are inexplicably large (Table 5.2). There is great interest in determining the N input to these areas and over what
timescales. There has been concern about how stable these systems are both physically and biogeochemically. In terms of the physical stability, there are two major forces that shape the valley bottom geomorphic template: flooding and tree throw. In terms of rainfall-runoff, the highest likelihood for changes to the geomorphic template occur during the largest storms (Wolman and Miller, 1960). However, at Pond Branch, there is a tradeoff because the bulk of hummocks and hollows occur in the upper most portions of the riparian zone, where the stream is much less competent. I posit that they are fairly stable in part because of the magnitude of storms that have passed over Pond Branch within the last four decades, which have not shifted or diminished the hummocks. I base this hypothesis given the observation that current riparian hollows have substantial organic horizons, which takes a much longer time to develop, suggesting that current hollows were not recently hummocks. Similarly, current hummocks have mineral soil beneath a cap of organic matter, suggesting they too have been there for some time.

Tropical Storm Agnes, in June 1972 delivered approximately 375mm of rainfall on top of the 25mm in the previous week and had major geomorphic changes in Western Run (Costa, 1974), very close to Pond Branch. It is a possibility that downcutting of the channel in response to large storms could have slightly exacerbated microtopographic variation, but there is little evidence of this given the high degree of channel-floodplain connectivity. Tree throw on the other hand, has had a measurable impact on the geomorphic template. With the forest approaching a mean stand age of 100 years, there are gaps in the canopy and with high water tables, shallow rooting depths, large trees in the riparian zone appear to have a higher likelihood of wind damage and displacement. During Hurricane Isabel in 2003, there was significant tree throw on the slopes above the
riparian zone. The reworking of advective surface water flowpaths due to storm induced
tree throw has been profound in the three separate areas along the 750m channel. One
example is at the upper transect, when a tree throw (ca. 2004) immediately adjacent to the
channel left a pit and likely some open soil pipes that diverted stream flow approximately
20m downstream and into a relic channel.

In terms of the biogeochemical stability, the main question is how sustainable the rates of
nitrogen cycling are in riparian hollows. There are multiple ways in which these rates are
maintained. One is because the hollows are so rich in organic matter (~ 13% of the top
10cm is actually organic matter), the mineralization, nitrification, and subsequent
denitrification could be derived from in-situ sources. However, it is likely that there are
mechanisms to replenish these stores. A primary source is the longer-term downslope
movement of leaf litter. Previous estimates from oak-hickory sources suggest that low
elevation sites such as riparian hollows could receive 2.2-6.1kg/ha/y (Boerner and
Kooser, 1989). This then, would mean that nitrogen is transported in particulate form via
litter movement and is retained and incorporated into the organic matter of riparian
hollows. There is also a possibility that groundwater of a higher nitrogen concentration
are drained from the hillslopes directly into the riparian zone via upwelling flowpaths.
There is some hydrometric evidence of this from the groundwater well at the lower
transect as piezometric head was above the ground surface in wet conditions. However,
nitrogen concentrations from that well were consistently low, suggesting that upwelling
of N rich groundwater from the uplands into the riparian zone is unlikely to deliver a
sufficient mass of N to sustain consistent denitrification. Although approximate, a simple
mass budget based on atmospheric deposition as the primary input, assuming low dissolved N transport from the surrounding watershed, and the estimate rates of denitrification and stream N export indicates a large missing input. We hypothesize that this is filled by a combination of periodic geomorphic transport of organic debris during major events, and the legacy of historical loading of organic debris from accelerated soil erosion during the agricultural period.

5.3 Significance

This work contributes to understanding how fine scale heterogeneity (space and time) in coupled hydrological and biogeochemical processes operating within the watershed geomorphic template control larger scale patterns in nitrogen cycling and export. The research fits into the framework of hot spots and hot moments (McClain et al., 2003) in watershed ecohydrology, to explain specific high resolution dynamics as controls of catchment-scale behavior.

Key findings from Chapter 2 include:

1. Riparian hollows are less than 1% of the landscape, but provide more than 98% of annual denitrification flux.

2. In the N limited soils at Pond Branch, denitrification peaks at 5% O2 according to the NFARM analysis, presumably due to coupled nitrification-denitrification that
is nitrate limited. Nitrate has to be produced (via nitrification) before it can be removed via denitrification.

3. Catchment scale denitrification flux from surface soils is highest during dry conditions when soil moisture conditions in riparian hollows become sufficiently mesic and produce soil oxygen concentrations that are amenable to coupled nitrification-denitrification.

Key findings from Chapter 3 include:

1. The mass flux of streamflow nitrate peaks during summer when discharge is lowest. Deep groundwater seep contributions and geologic weathering sources were ruled out as causal factors. The role of ephemeral vegetation decay and in-stream processes are plausible, but not primary contributors to the seasonal pattern. Changes in riparian water table and soil oxygen concentration are an important control on the seasonal export pattern.

2. A large portion of the increase in seasonal stream N concentration occurs at baseflow over a period of less than a week in early summer, and corresponds in time to the riparian hollows becoming oxygenated as groundwater tables fall.

3. Diel fluctuations in groundwater can provide the variability in soil redox conditions to increase net nitrate production and can provide the hydrologic transport mechanism to mobilize riparian nitrate to the stream.
Key findings from Chapter 4 include:

1. Nitrate concentration-discharge relationships are a function of data resolution. Long term time series of weekly stream samples show a negative power law relationship of nitrate concentration with flow, but high resolution sensor data of storm events reveals positive trends for storms that occur in mid to late growing season.

2. The trend between concentration and discharge in early summer storms is negative, implying a source limited flushing. The trend quickly transitions to a positive c-Q relationship (to a first order approximation), which persists through the fall.

3. High temporal resolution sensor systems provide concentration data enabling calculation of concentration-discharge and discharge-mass flux relationships that help to infer net nitrate production at the watershed–ecosystem scale.

5.4 Future Work
This dissertation reveals important work to be done in terms of multi-scale analysis of ecohydrologic controls on N cycling and export:

1. Fine Scale 3-D Soil Moisture-Groundwater-Soil Oxygen Patterns in contrasting hillslope-riparian-stream morphologies
Resolving fine-scale riparian-stream interactions to determine the geographic locations of nitrification and denitrification along contributing flowpaths is required. This could be
done by instrumenting riparian–stream transects with nested piezometers, soil moisture sensors, and soil oxygen probes. Increased density of measurements to better resolve heterogeneity over shorter length and time scales is necessary to better characterize the shifting distribution of these processes. It would also require NFARM measurements with cores collected over depth over gradients of antecedent moisture conditions and before and after storm events of varying magnitudes in different seasons. Improving the temporal frequency of NFARM cores would better quantify the roles of transport, percolation, and advection of labile carbon and nitrogen at the core to patch scale.

2. In-Stream Processes

Measuring in-stream processes directly is clearly a major need in addition to terrestrial flowpath sampling. The role of seasonal changes in in-stream uptake would be valuable to quantify. Especially important at Pond Branch is the potential for seasonal changes in in-stream nitrification. As a first approach, the use of photosynthetically available radiation (PAR) sensors above the stream reach, dissolved oxygen, and electrical conductivity measurements in the stream channel could help calculate in-stream metabolism. Eventually calculation of re-aeration coefficients via propane injections and developing in-stream uptake via tracer injections across seasons and hydrologic discharge regimes would dramatically improve the ability to quantify the role of stream ecosystems in controlling N export.
3. **Hydroclimate Variability**

Determining the full influence of inputs can be done in two ways. The first is to extend the length of data collection at Pond Branch. Acquiring better SUNA data through early, mid, and late growing season and in different years with different hydroclimate conditions will help infer how generalizable these patterns are. The second approach would examine the dynamics in a watershed of similar size and forest cover with different hydroclimate conditions.

4. **Changes in Watershed Vegetation**

Vegetation cover and type have profound impacts on the timing and magnitude of streamflow and stream N export. Assessing long-term aggradation is a renewed topic of interest given recent results of continued carbon increases in older trees. (Stephenson et al., 2014)

5. **Changes in Geomorphology**

Extension of these measurements to acquire similar datasets from other watersheds that have very different geomorphic templates yet have similar N export conditions will be essential for testing how generalizable these conceptual models are. Other watersheds that exhibit summer peaks in N export, but have distinct form and climate compared to Pond Branch, include low elevation sites at Coweeta (NC), Walker Branch (TN), and Pine Creek (NY).
Figure 5.1 Hydroclimate (precipitation and temperature) and nitrogen deposition inputs are filtered through the hydrogeomorphic template of watersheds and control the patterns of nitrogen cycling and export at all spatial/temporal scales considered.
Table 5.1 Watershed Scale Nitrogen Mass Balance

<table>
<thead>
<tr>
<th>Total Watershed (ha)</th>
<th>Rate</th>
<th>kg/ha/yr</th>
<th>kg/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Inputs**
- Atmospheric Deposition 10 370
- Nitrogen Fixation
  - symbiotic 0
  - asymbiotic 0
  - lightning 0

Subtotal 370

**Outputs**
- Stream export
  - DIN 18.5
  - DON 18.5
  - Particulate

Denitrification-highest value 95

Subtotal 132

Missing Sink 238
Table 5.2 Riparian Zone Nitrogen Mass Balance

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Riparian Area (ha)</th>
<th>Rate kg/ha/yr</th>
<th>kg/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric Deposition</td>
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<td>14.8</td>
<td></td>
</tr>
<tr>
<td>Nitrogen Fixation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>symbiotic</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>asymbiotic</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direct litterfall</td>
<td>35</td>
<td>51.8</td>
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</tr>
<tr>
<td>Litterfall transport</td>
<td>6</td>
<td>8.88</td>
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</tr>
<tr>
<td>Dissolved</td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td></td>
<td><strong>75.48</strong></td>
<td></td>
</tr>
</tbody>
</table>

| Outputs                          |                    |               |       |
| Stream export                    |                    |               |       |
| DIN                              | 18.5               |               |       |
| DON                              | 18.5               |               |       |
| Particulate                      |                    |               |       |
| Denitrification- lowest value    | 60                 |               |       |
| **Subtotal**                     |                    | **97**        |       |
| **Missing Source**               |                    | **21.52**     |       |
REFERENCES


