Influences of Mountainside Residential Development to Nutrient Dynamics in a Stream Network

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Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
In
Biological Sciences

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December 2, 2013
Blacksburg, Virginia

Keywords: mountainside development, exurbanization, nutrient dynamics, decomposition, stream network

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ABSTRACT

Forested mountain watersheds provide essential resources and services (e.g., water supply) to downstream ecosystems and human communities. Fast-growing mountainside residential development not only modifies the terrestrial system but also aquatic systems by changing the nutrient input from the terrestrial to aquatic. However, the impacts of mountainside residential development on stream ecosystems are complex because interactions between in-stream process and hillslope soils control in-stream nutrient dynamics, and it is difficult to experimentally study these interactions at broad spatial scales. In my dissertation research, I first developed models for leaf decomposition in a forested headwater stream by synthesizing several important ecological concepts, including ecological stoichiometry, microbial nutrient mining, and microbe-substrate interaction. I then extended the single stream model to a stream network model and further linked the stream network model with a terrestrial model that simulates nutrient processes and hydrology in hillslope soils. With this complete modeling framework, I conducted a global sensitivity analysis to evaluate the importance of terrestrial nutrient input versus in-stream processes in modifying nitrogen export. I also conducted a simulation to investigate the impacts of housing density, buffer zone protection, and stream travel distance from the residential development to the catchment outlet on nitrogen export at the local and regional scale. The model for leaf decomposition performed better for predicting detritus decay and nutrient patterns when microbial groups were divided into immobilizers and miners and when leaf quality was included as a variable. The importance of terrestrial nutrient input versus

in-stream nutrient processes greatly depended on the level of terrestrial nutrient input. When terrestrial nitrate input was low, nitrogen export was more sensitive to in-stream net microbial nitrogen flux (mineralization - immobilization) than nitrate input. However, when terrestrial nitrate input was high, nitrate input was more important than in-stream net nitrogen flux. Greater impacts, i.e., higher nitrogen export at the local scale or greater change in nitrogen export at the regional scale, were associated with higher residential density, a lack of buffer zone protection, and shorter stream travel distance from the residential development to the catchment outlet. Although subject to model assumptions and further validation through field experiments, this research provides a general modeling framework for in-stream processes and aquatic-terrestrial linkages and expands an understanding of interactions between terrestrial and in-stream nitrogen dynamics and the impacts of mountainside development on stream ecosystems, identifies directions for further research, and provides insights for land and river management in mountainous areas.

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my Ph.D. advisor Dr. Webster for taking me as his graduate student knowing that I had little background in biology and ecology. Over the five and half years of my Ph.D. study, Dr. Webster has given me opportunities to learn many ecological concepts and participate field experiments, and guided me on developing mathematical models that would benefit the field of ecology. I also thank Dr. Webster offering me lots of help on scientific writing and presentation. I am so lucky to have had the opportunity to work with him.

I am highly indebted to my advisory committee for their constant support and valuable advice over past five and half years. Dr. Benfield offered me great opportunities to learn and to teach ecology. Dr. Barrett introduced me many ecological concepts related to global change. Dr. Claessens offered me great advices on model development and simulation. Dr. Jiao brought me lots of fresh perspectives on how to improve model performance and how to integrate knowledge from different disciplines.

I extend my acknowledgement to my M.S. advisor Dr. Peckham and one of my M.S. committee members Dr. Pastor at University of Minnesota. I got my M.S. degree in Mathematics, and Drs. Peckham and Pastor introduced me to the world of ecology. Influenced by them, I decided to take on the journey to ecology and join the Stream Team at Virginia Tech.

When I accepted the Ph.D. offer at Virginia Tech, I also became a member of the Stream Team, organized by Drs. Webster, Benfield, Barrett and Valett. The article discussion at our weekly Stream Team meeting has benefited me immensely. The diverse and strong expertise of our group allowed me to develop as an ecologist. I would especially like to thank my previous and current Stream Teamers Dr. Northington, Dr. Cheever, Jeff Norman and Kevin Geyer,

Katlyn Amos, Kristen Muller, James Skelton and Brett Tornwall for helping me throughout my Ph.D. experience with less pain and more fun. Additional thanks go to the Virginia Tech Computational Center for providing computational facility (Hokieone) for some of my dissertation work.

Lastly, I give my deep gratitude to my family. My parents gave me great support to pursue my career in scientific research. My wife Yan offered me lots of care and love in my life and also great help improving my academic writing and perspectives. Most importantly, our daughter Mavis joined our family six weeks ago, which is the sweetest gift for my graduation that I could never imagine.

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Chapter 1

Introduction

1.1 Mountainside Residential Development and Its Impacts on Stream Ecosystems

In this research, mountainside residential development refers to construction of residential housing on the sides and tops of mountains, typically far away from cities. As one type of exurbanization, it contributes to the fastest-growing landscape in the U.S., extending far into the countryside but within the commuting range to urban / suburban areas (Beale 1982, Herbers 1986, Nelson and Dueker 1990, Brown et al. 2005, Hansen et al. 2005). Many social, economic and environmental concerns have arisen as exurbanization has accelerated since the 1950-60s (Burchell 1998, Sutton et al. 2006).

In mountainside development, people convert forest landscapes into residential communities by developing housing on mountainsides, which has far-reaching impacts on ecosystem services (e.g., water supply) provided by forest and streams to people living in both rural and urban areas. Many studies have shown that exurbanization changes land cover and land use (e.g., Pearson et al. 1998, Webster et al. 2012), alters ecosystem processes and biodiversity (e.g., Marzluff 2001, Maestas et al. 2003, Hansen et al. 2005), and most especially modifies nutrient dynamics in streams (Fig. 1-1) via changing nutrient input to streams (e.g., Garrison and Wakeman 2000, Viviroli et al. 2007, Webster et al. 2012).

Impacts of exurbanization on ecosystems have only recently been studied (Hansen et al. 2005). Manipulation of large-scale mountainside development through experiments could be challenging in practice. Comparing reference areas and areas subject to exurbanization (e.g., Garrison and Wakeman 2000) or synthesizing changes in existing land cover and land use over years or over space (Cifaldi et al. 2004, Theobald 2005, Webster et al. 2012) are the alternative

approaches but they provide a limited understanding of impacts of exurbanization such as a correlation between land cover/ land use changes and ecosystem dynamics. Considerably more research on how residential home density, spatial distribution, and homeowner behavior affect ecosystems is needed (Hansen et al. 2005).

1.2 Nutrient Dynamics in Forested Mountain Streams

Forested mountain streams in the southern Appalachians are heavily shaded (Webster et al. 1997) and support low rates of primary production (Mulholland et al. 1997, Bernot et al. 2010). Headwater and low order streams integrate the nutrient and hydrological budgets of terrestrial and aquatic systems and provide important resources to downstream reaches (Vannote et al. 1980). Both nutrient input from hillslope soils and in-stream nutrient processes may greatly influence nutrient dynamics in streams (Bernhardt et al. 2005, Sudduth et al. 2013). In-stream nutrient processes include nitrification, denitrification, immobilization and mineralization. Immobilization and mineralization are particular important in streams because they involve exchange of nutrients between inorganic and organic materials. In forest mountain streams, in-stream immobilization and mineralization are often associated with in-stream detritus decomposition. Allochthonous input of detritus provides the major energy source to many streams (Minshall 1967, Fisher and Likens 1973, Wallace et al. 1997) and this detritus modifies nutrient dynamics (Fig. 1-1) (Kaushik and Hynes 1971, Gregory 1978, Meyer 1980, Triska and Buckley 1978, Mulholland et al. 1984, Webster et al. 2001, Webster et al. 2009). Factors influencing in-stream detritus decomposition and its associated nutrient processes (Fig. 1-1) may include detritus carbon:nutrient ratio (Howarth and Fisher 1976, Melillo et al. 1984, Taylor et al. 1989, Manzoni et al. 2008, Webster et al. 2009), detritus substrate quality (e.g., % lignin and

cellulose, Taylor et al. 1989, Gessner and Chauvet 1994, Royer and Minshall 2001), and microbial carbon : nutrient ratio (Cross et al. 2005, Webster et al. 2009). Many studies have shown that nutrient input from hillslope to streams (Fig. 1-1) could also influence detritus decomposition (e.g., Findlay and Tenore 1982, Suberkropp and Chauvet 1995, Gulis and Suberkropp 2003, Gessner et al. 2007). In this dissertation, nutrient input from hillslope to streams is referred as lateral nutrient input.

1.3 Model Studies on Hillslope Nutrient Processes and In-Stream Nutrient Processes

There are well developed and widely used terrestrial models of nutrient processes , but few of these models specifically include streams. For example, the Regional Hydro-Ecologic Simulation System (RHESSys, Tague and Band 2004) is a process-based hydro-ecological model, which has been widely used in landscape and hydrological studies. It simulates water, carbon and nitrogen cycling, and transport over spatially variable terrains. Its forest biogeochemical processes and soil organic matter decomposition are based on the BIOME-BGC framework (Running and Hunt 1993) and the CENTURY model (Parton et al. 1987, 1996). RHESSys also incorporates land cover to simulate water and nitrogen flux in non-forested areas within a catchment. Despites surface and sub-surface water and dissolved nitrogen flux being explicitly routed in the model, streams are not included in the RHESSys.

Many stream models (e.g., Alexander et al. 2000, Seitzinger et al. 2002, Wollhiem et al. 2006) focus on denitrification. For example, SPAtially Referenced Regressions On Watershed attributes (SPARROW, Smith et al. 1997, Alexander et al. 2000) is a hybrid statistical and process-based watershed model. It applies a statistical modeling approach for estimating nitrogen sources and transport in streams. In-stream nitrogen processes are modeled as first-

order uptake and removal. Nitrogen uptake rate and removal rate are empirically derived from channel geometry, stream flow, or channel slope. However, in mountain streams, immobilization and mineralization associated with detritus decomposition could be more important in controlling nutrient dynamics (Newbold et al. 1981, Mulholland et al. 1985, Elwood et al. 1988, Webster et al. 2000, 2009). Stream ecologists have attempted to model immobilization by using a first order decay rate equation (Runkel 1998) or a Monod kinetic equation (Cleassen et al. 2009, Lin and Webster 2012, while mineralization largely remains unknown (Webster et al. 2009). Webster et al. (2009) investigated both immobilization and mineralization using a detritus decomposition model because both processes are tightly related to decomposition in forested headwaters. Continuing the approach used by Webster et al. (2009), I developed stream models that focused on in-stream detritus decomposition.

1.4 Research Goal and Approaches

Given fast-growing mountainside development observed in recent decades and projected into the future, the overall goal of this dissertation was to improve our understanding of its influences on nutrient dynamics in a stream network (Fig. 1-1). There were three research questions that I addressed. First, given the importance of immobilization and mineralization in modifying nutrient dynamics in forested mountain streams, I asked how to model these processes for better nutrient concentration prediction. Second, in-stream nutrient dynamics are not only driven by in-stream nutrient processes but are also affected by terrestrial nutrient input. Thus I compared the relative roles of in-stream nutrient processes versus hillslope nutrient input in controlling nitrogen export. Third, because exurbanization changes hillslope nitrogen input to streams, I asked how these changes influence nitrogen dynamics in headwater streams (the local

scale) and further downstream (the regional scale). This research expands our understanding of in-stream decomposition-nutrient interaction by considering immobilizers and miners as different microbial functional groups, contributes to the literature on exurbanization influences on stream ecosystems through a simulation approach, and provides insights for land and river management in mountainous areas.

My approach to address these research questions was to develop a stream network model, to link the developed stream network model with a terrestrial model (the Regional Hydro-Ecologic Simulation System, RHESSys, Tague and Band 2004) and to simulate the terrestrial and in-stream nutrient processes under different scenarios in which the density and spatial distribution of residential development on hillslopes within a regional basin were manipulated. Specifically, in Chapter 2, I developed three models for leaf decomposition in a forested headwater stream. I synthesized several important ecological concepts from previous studies, including ecological stoichiometry, microbial nutrient mining, and microbe-substrate interaction. I used the models to estimate in-stream nutrient dynamics during decomposition, and I evaluated model performance with observed data. The best stream model that I selected in this chapter was extended to a stream network model and applied to the analyses in the following two chapters. In Chapter 3, I investigated the effects of terrestrial nutrient input and in-stream nutrient processes on nitrogen export and compared the relative importance of these two processes. I used the stream model developed in Chapter 2 expended to a stream network, and linked it with the terrestrial RHESSys model. I then applied a global sensitivity analysis, a method that can account for interactions among factors when focusing on a single factor of interest. In Chapter 3, I also investigated factors (e.g., detritus stoichiometry and substrate quality and nutrient availability) that affect nutrient immobilization and mineralization, two important in-stream

processes. Finally in Chapter 4, I used this model to investigate effects of mountainside residential development. Based on the upper Little Tennessee basin, I simulated water and nutrient fluxes from terrestrial ecosystem with the terrestrial RHESSys model under different scenarios. These scenarios represented residential development at different densities, development with or without buffer zones, and development at different locations in terms of steam travel distances to the catchment outlet.

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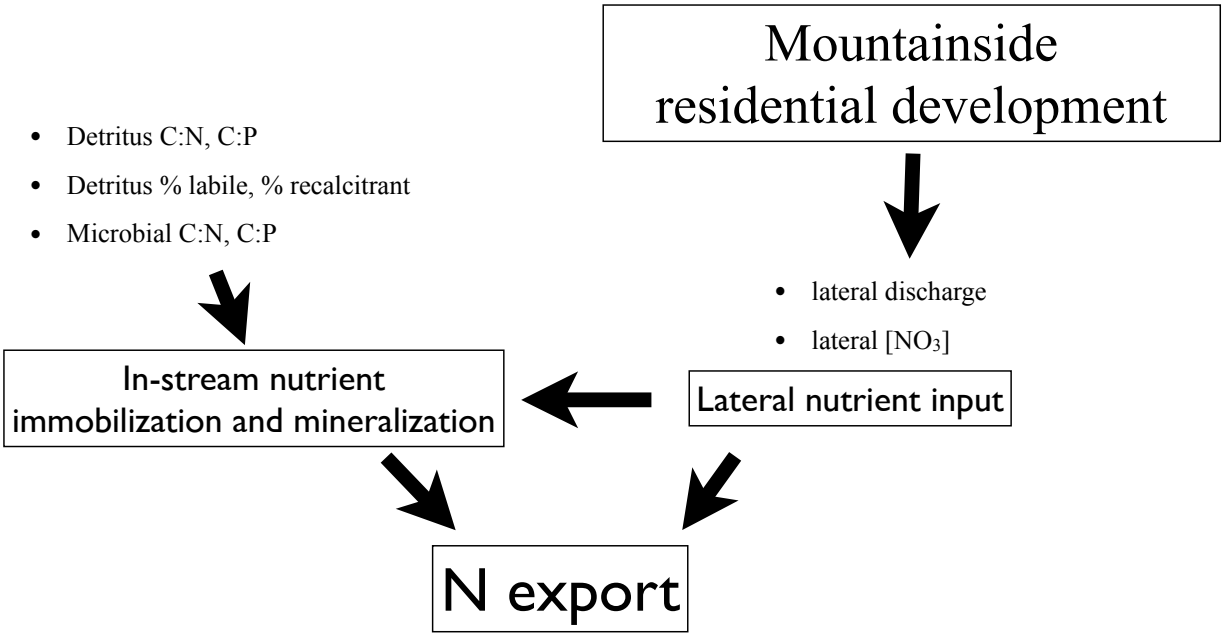

Figure 1-1. Factors influencing nitrogen dynamics in streams

Chapter 2

Detritus Decomposition and Nutrient Dynamics in a Forested Headwater Stream

2.1 Introduction

Detritus breakdown in streams involves leaching (Nykvist 1961), microbial colonization (Suberkropp and Klug 1974, Cummins 1974), animal-microbial conversion, and fragmentation (Petersen and Cummins 1974). During detritus breakdown, microbial-involved nutrient processes, i.e., immobilization and mineralization, are important in the changes of nutrient content of detritus and nutrient concentrations in stream water (Gulis and Suberkropp 2003, Mulholland 2004). Based on their nutrient acquisition strategy, there are two important microbial assemblages, immobilizers and miners. What I am calling immobilizers use detritus as their primary carbon source and use nutrients from both detritus and from stream water as their nutrient sources, especially when nutrients obtained from detritus are insufficient to satisfy the microbial demand for growth (Kaushik and Hynes 1971, Suberkropp and Chauvet 1995, Mulholland et al. 1985). Miners grow more slowly (Moorhead and Sinsabaugh 2006) and rely on detritus for both their carbon and nutrient sources without dissolved nutrients as a secondary nutrient source. Miners respire a large amount of carbon to reduce the C:N and C:P ratios of detritus to match their own biomass C:N and C:P ratios. This is the definition of miners used by Berg and McClaugherty (2008), Fontaine and Barot (2005), Moorhead and Sinsabaugh (2006), and Craine et al. (2007). I use the term miners more generally for microbes that acquire carbon and nutrients from detritus.

Several studies of decomposition using modeling have been conducted. Schimel and Weintraub (2003) modeled soil organic matter decomposition and incorporated extracellular

enzyme activity with first-order decay. Moorhead and Sinsabaugh (2006) developed a model for leaf decomposition in forests in which they included interactions of substrate types and microbial assemblage. Webster et al. (2009) modeled leaf decomposition in streams using a first-order decay function modified by available nutrients. Manzoni et al. (2008, 2010) synthesized data from previous decomposition studies and formulated a relationship between detritus carbon and detritus nutrients based on ecological stoichiometry (Sterner and Elser 2002) with an assumption of unlimited nutrient supply. Except for Webster et al. (2009), the other studies focused on terrestrial decomposition and used their models to predict the change of nutrient content in detritus throughout decomposition. Manzoni et al. (2008, 2010) did not explicitly provide the calculation of decay rate; the other three studies assumed that decomposition depends on detritus standing crop and incorporated a decay rate modified by factors such as enzyme activity, substrate type, or nutrients in soil or water. In this study, I modified the model of Webster et al. (2009) for modeling aquatic decomposition and predicting annual nutrient patterns in streams. I assumed that microbial metabolism is the primary driver of decomposition and calculated decay rate based on microbial production. Previous models have only considered immobilizers; although Moorhead and Sinsabaugh (2006) mentioned "miners" in their study, they modeled miners similarly to immobilizers. In my study, I considered both immobilizers and miners, and modeled them separately based on their nutrient acquisition strategies. Data from Hugh White Creek (Coweeta Hydrologic Laboratory, NC), have shown that nutrient concentrations vary seasonally in this heavily shaded catchment (USDA Forest Services data). I propose that these seasonal dynamics may be largely explained by the processes of microbes associated with detritus decay.

The goals of this study were to (1) simulate benthic detritus decomposition in hardwood forested headwater streams, using models that account for microbial metabolism driven decomposition, microbial nutrient immobilization and mining, and leaf substrate quality (labile vs.refractory); (2) use these models to estimate in-stream nutrient concentrations, detritus standing crop, detritus nutrient dynamics, microbial biomass, and nutrient fluxes between stream and detritus; and (3) compare model estimates with observed data and general expectations based on previous research to evaluate model performance.

2.2 Methods

Data description

Hugh White Creek (HWC) is a second-order stream at Coweeta Hydrologic Laboratory, North Carolina, USA. Phosphorus and nitrogen dynamics in this stream have been studied extensively (e.g., Golladay and Webster 1988, Webster et al. 1991, Mulholland et al. 1997, Crenshaw et al. 2002, Valett et al. 2008, Brookshire et al. 2005, 2010, Cheever et al. 2012). This has also been a site of extensive studies of leaf decomposition (e.g., Benfield et al. 2001, 1991, Hagen et al. 2006, Webster et al. 2009, Cheever et al. 2012). HWC drains a reference forested catchment. The climate at Coweeta is mild and humid (Swift et al. 1988). Annual precipitation is 188 cm for the watershed drained by Hugh White Creek. Rainfall occurs fairly evenly throughout the year. On average 133 storms occur annually. Only 2-10% of annual precipitation occurs as snow (Webster et al. 1997). Stream channels are heavily shaded and, therefore, primary production within the channel (periphyton production) is very low (Mulholland et al. 1997, Bernot et al. 2010). Annual leaf-fall to the channel averages about 327 g ash-free-dry-mass/m2 (AFDM) (Webster et al. 2001). Leaf types and their proportions in annual leaf-fall in

HWC were measured by Webster et al. (2001). The dominant riparian leaf species are Betula spp. and Rhododendron maximum (Table 2-2). Leaf stoichiometric mass ratios (C:N:P) of most leaf species (fresh leaves) found in HWC range from 54 to 165 for C:N and from 444 to 634 for C:P (Table 2-2). Proportions of cellulose and lignin of most leaf species found in HWC range from 0.1 to 0.4 and from 0.1 to 0.3, respectively (Table 2-2). Groundwater and springs that drain into HWC have low nutrient concentrations (Webster et al., 2009), averaging 25 µgNO3-N L-1 and 2 µgPO4-P L-1.

Based on discharge records of HWC (annual average discharge 16.4 L s-1), I calculated daily median discharge (Fig. 2-1, top panel). Discharge increases through the winter because of reduced transpiration in the deciduous forest. Coarse benthic organic matter (CBOM) standing crop is high in mid-autumn and decays through time (Fig. 2-1, middle panel), while nitrate concentration at HWC is low in autumn and winter and increases in early spring and summer (Fig. 2-1, bottom panel). The rapid decrease in nitrate concentration in autumn occurs when discharge remains fairly constant (Fig. 2-1, top from Sept to Nov), suggests that this nitrate pattern is not driven by dilution alone. In spring (Mar - Jun), nitrate concentration increases while discharge also gradually decreases. If the increase in nitrate concentration was caused by decrease in discharge, I would expect an increase in ammonium concentration as well. However, ammonium concentration (Fig. 2-1, bottom) remains constantly low throughout the year. Changes in nitrate concentration are affected not only by discharge but also by in-stream microbial immobilization and mineralization.

I used data from HWC for my model development (Table 2-1). All models have a single 1125-m channel that represents the HWC main channel (Webster et al., 1999), with average velocity and width. Discharge in my model simulation varies daily according to the observed

daily discharge in HWC (Fig. 2-1). Water depth varies according to discharge while velocity and width are held unchanged. The channel drains from a spring with constant nutrient concentrations, 25 μgN/L as nitrate and 2 μgP/L as phosphate. I did not include lateral inflow or groundwater input explicitly in this model. Instead I assumed the same discharge (annual average 19 L/s) over the 1125 m. I included transient storage using values estimated by Brookshire et al. (2005) because transient storage can affect residence time of nutrients in the channel. In my single channel model, I included nitrification in the water column and denitrification in the transient storage because both processes can affect the nitrogen availability to immobilizers. In the model, initial leaf standing crop in stream is zero. Leaf input varies monthly (Webster et al. 1999, 2001) but is the same spatially over the 1125 m. Fallen leaves (CBOM) leach 15% of their mass within 24 hours once they are in the stream channel (Cummins 1974, Peterson and Cummins 1974). CBOM fragmentation to FBOM is the result of macroinvertebrate CBOM consumption, and its rate is constant starting 14 days after autumnal leaf-fall begins (Sept 22 in my models; Cummins 1974, Peterson and Cummins 1974). I used the weighted averages of leaf stoichiometric ratios and leaf substrate qualities for my simulations.

Model development

In the following sections, I define gross production as the sum of biomass production, basal respiration, and respiration for growth. I developed a general model (Fig. 2-2) based on the decomposition model of Webster et al. (2009). I separated detritus (leaf material and microbial biomass) into different pools: coarse benthic organic matter (CBOM, ≥ 1 mm), fine benthic organic matter (FBOM, < 1 mm), seston, and dissolved organic matter (DOM). Both CBOM and FBOM are stationary, while seston and DOM are carried downstream by flow. Leaf

materials from leaf fall enter the stream as CBOM. The leached material from fresh leaves becomes DOM. Fragmentation of leaves becomes FBOM. Entrained FBOM becomes seston, and the deposited seston becomes FBOM. I use detritus to refer to leaf material and accumulated dead microbial biomass on the leaf material. Live microbial biomass is considered separately.

Model I

Within the general model framework, I first focused on the interactions between CBOM and immobilizers, that is, microbes that can get nutrients from the water. Webster et al. (2009) assumed that CBOM decomposition depends on detritus standing crop and calculated detritus decomposition using a stream nutrient corrected decay rate. Instead, I assumed that CBOM decomposition was driven by gross production of the microbes, and gross production was determined by the availability of carbon in detritus and nutrients in both detritus and water column (Fig. 2-3, Model I). I constrained immobilizer nutrient uptake by Monod kinetics using parameter values estimated by Payn et al. (2005; Table 2-1). For immobilizers, all assimilated materials are for gross production. Potential gross production follows an exponential growth curve with a specific growth rate (μ_i):

$$pgp_i = \mu_i m_i, \qquad (1)$$

where pgp_i is potential gross production for immobilizers, and m_i is immobilizer biomass. When nutrient availability is low, actual gross production is determined by the nutrient in least relative abundance:

$$agp_i = \min\left(pgp_i, \frac{DIN}{(N:C)_i - (N:C)_{om}}, \frac{DIP}{(P:C)_i - (P:C)_{om}} \right), \qquad (2)$$

where agp_i is the actual gross production for immobilizers, DIN and DIP are available nitrogen

and phosphorous in the stream water, $(N:C)_i$ and $(P:C)_i$ are N:C and P:C ratios of immobilizers, $(N:C)_{om}$ and $(P:C)_{om}$ are N:C and P:C ratios of detritus. The nutrient content of detritus is generally lower than that of immobilizer biomass (Sterner and Elser 2002). Thus, the difference of $(\text{nutrient:carbon})_i$ - $(\text{nutrient:carbon})_{om}$ is positive, and it represents how much additional nutrient is needed by immobilizers for making a unit of gross production out of a unit of leaf material. Nutrients in the water column supply the additional nutrients needed by the immobilizers. Available nutrient divided by the difference of $(\text{nutrient:carbon})_i$ - $(\text{nutrient:carbon})_{om}$ yields the maximum gross production given the available nutrient. The actual gross production is constrained by biological production and available nutrients and is the minimum of the three terms: potential gross production, maximum gross production given available nitrogen, and maximum gross production given available phosphorous. Decay of CBOM is then equal to agp_i.

Live microbial biomass on detritus rarely exceeds 10% of detritus mass (Petersen and Cummins 1974, Paul and Clark 1997, Adl 2003, Berg and McClaugherty 2008). Hence, I used an increasing mortality rate to constrain the microbial biomass to the carrying capacity:

$$\text{Mortality} = \left(\frac{\mu_i m_i}{K}\right) m_i \ , \qquad (3)$$

where m_i is immobilizer biomass, μ_I is the specific growth rate (Eq. 1), and K is carrying capacity (10% of detritus mass). Immobilizer respiration consists of basal respiration and growth-associated respiration:

$$\text{Respiration} = b\ m_i + e\ agp_i \ , \qquad (4)$$

where basal respiration (b) is proportional to microbial biomass, and growth-associated respiration is determined using a carbon-use efficiency (e). I used a carbon-use efficiency of 0.5

in this study, as was also used by Schimel and Weintraub (2003). This value falls within the range that Manzoni et al. (2008, 2010) estimated, although I used this efficiency differently, i.e., Manzoni et al. (2008, 2010) used it to calculate total respiration while I used it to calculate growth-associated respiration, which is a part of the total microbial respiration (the sum of growth-associated, basal respiration, and respiration of mining) in my models. As immobilizers respire, nutrients are released to the water column, nitrogen as ammonium and phosphorus as phosphate, to maintain microbial C:N:P homeostasis. Ammonium was then converted to nitrate by nitrification in the channel.

Model II

In the second model (Fig. 2-3, Model II) I added miners, i.e., microorganisms that get both their carbon and nutrients from detritus and respire carbon to reduce the C:N and C:P ratios of assimilation to match their own biomass C:N and C:P ratios. The process of "mining" in this study includes not only decaying detritus to obtain carbon for gross production but also decaying additional detritus to obtain nutrients for gross production. Detritus generally has lower nutrient content than microbes (Sterner and Elser 2002). Therefore, assimilated material by miners includes extra material for mining respiration other than the material for gross production. The actual gross production of miners is not limited by nutrients in the water column and is, hence, the same as the potential gross production:

$$agp_m = \mu_m m_m \,, \qquad (5)$$

where agp_m is the actual gross production of miners, μ_m is the specific growth rate of miners, and m_m is the miner biomass. The actual gross production of miners is also not constrained by nutrients in the detritus because miners decay large amount of detritus to obtain detrital nutrients

to meet their nutrient demands for gross production. To achieve actual gross production, needed nutrient is $agp_m(nutrient:carbon)_m$. In detritus, there is $(carbon:nutrient)_{om}$ of carbon per unit of nutrient. Therefore, miners have to decompose $agp_m(nutrient:carbon)_m(carbon:nutrient)_{om}$ amount of leaf material to obtain enough nutrients. Considering both nitrogen and phosphorus, I derived Eq. 6 for the amount of detritus decomposed by miners:

$$decay_m = agp_m \max\left(\frac{(C:N)_{om}}{(C:N)_m}, \frac{(C:P)_{om}}{(C:P)_m}\right), \tag{6}$$

where $decay_m$ is the amount of detritus decomposed by miners, $(N:C)_m$ and $(P:C)_m$ are the N:C and P:C ratios of miners, $(C:N)_{om}$ and $(C:P)_{om}$ are C:N and C:P ratios of detritus. Respiration of miners consists of basal respiration, growth-associated respiration, and respiration for microbial mining:

$$\text{Respiration} = b\, m_m + e\, agp_m + decay_m\left(1 - \min\left(\frac{(C:N)_m}{(C:N)_{om}}, \frac{(C:P)_m}{(C:P)_{om}}\right)\right), \tag{7}$$

where b is basal respiration rate, and e is the carbon-use efficiency.

Total microbial biomass (immobilizer biomass + miner biomass) in this model is regulated to the carrying capacity by mortality:

$$Mortality_i = \mu_i\left(\frac{m_i + m_m}{K}\right)m_i\ , \tag{8}$$

$$Mortality_m = \mu_m\left(\frac{m_i + m_m}{K}\right)m_m\ , \tag{9}$$

where $Mortality_i$ and $Mortality_m$ are mortality of immobilizers and miners, respectively, m_i is immobilizer biomass, μ_i is the specific growth rate of immobilizers, m_m is miner biomass, μ_m is the specific growth rate of miners, and K is carrying capacity (10% of detritus mass).

Model III

In the third model (Fig. 2-1), I further partitioned detritus into three substrate groups, labile (Lab), intermediate (Int), and recalcitrant (Rec); immobilizers and miners consume each of the three substrate groups but at different rates. Moorhead and Sinsabaugh (2006) modeled these rates using Michaelis–Menten kinetics:

$$r_{x,y} = \frac{r_y m_y}{k_{x,y} + C_x} \ , \tag{10}$$

where $r_{x,y}$ is the decay rate of substrate type x by microbe y; x refers to intermediate (Int), recalcitrant (Rec), or labile (Lab); y can be either immobilizers or miners; r_y is the maximum carbon uptake rate by microbe y, m_y is biomass of microbe y, $k_{x,y}$ is the half-saturation coefficient for substrate x with microbe y, and C_x is the mass of substrate x. With these rates incorporated in Model III, I defined decay rate ratios as follows:

$$R_{\mathrm{Lab/Rec},y} = \frac{r_{\mathrm{Lab},y}}{r_{\mathrm{Rec},y}} \text{ and } R_{\mathrm{Int/Rec},y} = \frac{r_{\mathrm{Int},y}}{r_{\mathrm{Rec},y}} \ , \tag{11}$$

I used cellulose content in leaf material to approximate the pool size of intermediate material, lignin content for the pool size of recalcitrant material, and the rest of leaf material for the pool size of labile material (Table 2-2). Total detritus is the sum of these three pools. Taking different decay rates into account, the accessible detritus for microbe y is ($R_{\mathrm{Lab/Rec},y}$ Lab + $R_{\mathrm{Int/Rec},y}$ Int + Rec). Using this accessible detritus estimate in Model II, I calculated decomposition for immobilizers and miners respectively. Using the decay rate ratios (Eq. 11), I converted the decomposition of accessible detritus to the decomposition of actual detritus, i.e., the decay rates of Lab, Int, and Rec material by microbe y are:

$$\text{decay rate of Lab} = decay_y \frac{R_{\mathrm{Lab/Rec},y}}{R_{\mathrm{Lab/Rec},y} L + R_{\mathrm{Int/Rec},y} I + R}, \tag{12}$$

$$\text{decay rate of Int} = decay_y \frac{R_{\text{Int/Rec},y}}{R_{\text{Lab/Rec},y}L + R_{\text{Int/Rec},y}I + R}, \quad (13)$$

$$\text{decay rate of Rec} = decay_y \frac{1}{R_{\text{Lab/Rec},y}L + R_{\text{Int/Rec},y}I + R}, \quad (14)$$

where $decay_y$ is the decomposition of accessible detritus by microbe y.

Model calibration and simulation

I ran 8-year simulations at a 30-second time scale and a 3-m spatial scale. This short time step in my simulations was need for the numerical stability and precision over the space-time integration. I also tested a larger time step (up to 3 minutes) for simulations and the numerical solutions of my models were not greatly affected. Model output stabilized after 4 years, and I present the results of the 8th year of the simulation. I first calibrated my models using only the observed benthic organic matter. Second, I simulated CBOM breakdown and the corresponding dynamics of in-stream nutrient concentrations using the calibrated model. I also tracked detritus carbon to nutrient ratios and nutrient fluxes between microbes and dissolved inorganic nutrients in stream water. Third, I compared the simulated nutrient patterns at the downstream end of the stream to the observed nutrient patterns at HWC.

Most of my model parameters, e.g., stoichiometric ratios of detritus and microorganisms, were based on published values (Table 2-1). Annual average water depth, discharge and leaf-fall varied following the observed annual patterns (i.e., discharge, Fig. 2-1, top; leaf-fall, Webster et al. 2001). The specific growth rates of immobilizers and miners were calibrated by fitting my model to the observed benthic detritus standing crop (Fig. 2-1, middle) using mean absolute error (MAE). I used fixed constants for the other parameters based on previous studies. The model with the smallest MAE was judged to be the best model.

All models were computed using the fractional-steps numerical technique (Yanenko 1971, Lin and Webster. 2012). The hydrological flow component of the model was numerically solved using a Lagrangian approach that is more stable and allows for spatial variations in flow velocity compared to the Crank-Nicolson finite difference method (Tsai et al. 2001). The Euler method was applied to solve the decomposition component. I programed in JAVA and used parallel processing to increase simulation speed.

2.3 Results

Model III fit the benthic detritus data best (MAE = 15.2, Fig. 2-4), followed by Model II (MAE = 28.9) and Model I (MAE = 49.7). The best fits to the benthic detritus were achieved by adjusting the specific growth rates of immobilizers and miners. Specific growth rate of immobilizers in Model I was 1.73 day^{-1}. Specific growth rates of immobilizers and miners were 0.43 day^{-1} and 0.08 day^{-1} in Model II respectively, and 0.41 day^{-1} and 0.07 day^{-1} in Model III respectively. Model I had the poorest prediction to observed nutrient dynamics (MAE = 13.7 for nitrate and 12.6 for ammonium, Fig. 2-4). Model III performed better in predicting nitrate (MAE = 9.7) and Model II did slightly better in predicting ammonium (MAE = 6.0). However, the simulated pattern of nitrate by Model III better than Models I and II captured the observed nitrate pattern during the net mineralization phase (March to Sept). Other than total detritus standing crop, Model III also predicted the changes of pool sizes of different detritus components (i.e., liable, intermediate, and recalcitrant). The simulated microbial biomass accumulation (including live and dead microbial biomass) decreased from Model I to Model III, especially for the late stage of decomposition (March to June). Average accumulated microbial biomass for Models I, II, and III were 32.3%, 31.5%, and 18.2% of the remaining detritus, respectively.

The patterns of detritus C:N were similar to those of detritus C:P in all three models (Fig. 2-5, left column). In all three models, detritus C:N and detritus C:P increased during autumn leaf-fall (Sept to Nov). In Models II and III, detritus C:N and C:P declined near the end of autumn leaf-fall while in Model I detritus C:N and C:P continued to rise until February. At the late stage of decomposition (Mar to Sept), detritus C:N and C:P in Models I and II remained low, while those in Model III curved up. At the late stage of decomposition, dead microbial biomass accumulated as intermediate material. This intermediate material was rich in nutrients since it was microbial biomass and it decayed at a higher rate than recalcitrant material (i.e., has higher carbon-to-nutrient ratios) in Model III, leading to an increase in the carbon to nutrient ratio of detritus.

I tracked nutrient immobilization and mineralization as fluxes between microbal and dissolved inorganic nutrients. I defined net flux as nutrient mineralization minus nutrient immobilization. Net immobilization occurred when the net flux was negative, and net mineralization occurred when the net flux was positive. Net immobilization occurred first and was then followed by net mineralization in all three models (Fig. 2-5). The net flux of total N (sum of nitrate and ammonium) showed similar patterns to the net flux of P but had a higher magnitude. Net immobilization in Model I did not start until after December due to nutrient depletion (Fig. 2-5, Model I) and yielded the highest net immobilization and net mineralization of N and P, compared to Model II and III. Model III had higher net mineralization during the later stage of decomposition than Model II. Net mineralization of P occurred earlier than that of N in Model II and III, suggesting that immobilizers may need relatively more N than P for growth. Miners were not included in Model I (Fig. 2-5, right column). Net mineralization by miners was similar in Models II and III. Net mineralization of N was higher than net

mineralization of P during decomposition by miners. The peak of P net mineralization occurred earlier than that of N net mineralization, suggesting that miners also need P more than N. The average N:P ratio of net immobilization by immobilizers in Models I, II, and III were 51.7, 74.3, and 75.3, respectively. The average N:P ratio of net mineralization by miners in Models II and III were both 25.0.

In my simulations, dissolved inorganic nutrients came from the spring. Upstream detritus decomposition changed the availability of nutrients downstream and affected downstream detritus decomposition. To explore this effect, I calculated monthly average total nitrogen concentrations and net nitrogen flux in Models I, II, and III at upstream, midddle, and downstream reaches (Fig. 2-6). During and after leaf-fall (from Sept to Dec), nitrogen in stream water was depleted downstream. At that time, net immobilization was high upstream in all three models. Net immobilization also occurred downstream but was very low due to low available nitrogen downstream. In Model I, immobilizer growth was limited, primarily by nitrogen. Thus, little decomposition of detritus occurred downstream (Fig. 2-4, Model I from Sept to Feb).

After December, upstream net mineralization occurred, and nitrogen became available downstream. In Model I, net immobilization greatly increased mid-reach and then downstream a few months later. Immobilizers grew rapidly as nutrients become available in Model I. Rapid growth of immobilizers led to high nutrient immobilization (Fig. 2-5, Model I, Immobilizers), resulting in high microbial biomass accumulation (Fig. 2-4, Model I) and high nutrient mineralization (Fig. 2-5, Model I, June). In Models II and III, net immobilization increased mid-reach and downstream much less than in Model I. The time when net immobilization at middle and downstream reaches increased was similar in Models II and III. In Models II and III, miners were not affected by nutrient depletion. Miners mineralized nutrients, particularly nitrogen (N:P

of mineralization flux = 25, N:P of miner biomass = 4) (Fig. 2-5, Models II and III). Nutrients generated via mineralization by miners upstream support immobilizer growth downstream although their growth might not be at the potential growth rate (Fig. 2-5, Models II and III, Immobilizers from Sept to Feb). Because of miners, Models II and III predicted lower nutrient immobilization downstream where nutrients were limiting to immobilizers (Fig. 2-5, Models II and III Immobilizers, Fig. 2-6, Models II and III) while Model I predicted no nutrient immobilization downstream (Fig. 2-5, Model I Immobilizers).

Net mineralization was very high in Model I compared to Models II and III. Net mineralization in Model I at upstream, middle, and downstream reaches occurred successively, while net mineralization in Models II and III occurred roughly at the same time. With limited nutrient supply downstream, miners contribute to the net mineralization at least as great as immobilizers (Fig. 2-5). Net mineralization by immobilizers lasted for four months, while that of miners lasted year round.

2.4 Discussion

In this study, I synthesized several ecological concepts related to decomposition and nutrient dynamics in streams. For Model I, I used ecological stoichiometry and microbial nutrient immobilization (Manzoni et al. 2008, 2010, Webster et al. 2009), while I emphasized microbial metabolism driven decomposition rather than detritus standing crop driven decomposition (first order decay). The use of decay rate has been widely adopted in many detritus decomposition models because one can easily calculate decay rate from the time series of standing crop of detritus in fine-mesh litter bag experiments. Decay rate, hence, is an average rate of decay in a given environment where experiments are conducted. To generalize the use of

decay rate in different environments and to better describe the change of decay rate throughout the course of decomposition, ecologists have used temperature (e.g., Webster et al. 2001), nutrient concentration (e.g., Webster et al. 2009), and enzyme activity (Schimel and Weintraub 2003, Moorhead and Sinsabaugh 2006) to modify the decay rate to make their models more general and more precise. Since detritus decomposition is a consequence of microbial processes, I used the idea of Parnas (1975) and developed a decomposition model that focuses on microbial processes, i.e., microbial metabolism drives the decay process and decay rate. For Model II, I incorporated microbial nutrient mining into the model, in which miners compete for detritus with immobilizers. Recent detritus decomposition models (e.g., Manzoni et al. 2008, 2010, Webster et al. 2009) emphasize coupling carbon and nutrient processes through ecological stoichiometry (Sterner and Elser 2002). A common assumption is that the assemblage of microbial decomposers can obtain nutrients from both the detritus and the environment. Result from Model I suggest that in downstream areas microbial decomposers did not obtain enough nutrients from detritus or from stream water in downstream reaches during and after leaf-fall. Nutrients were depleted downstream. As a consequence, the downstream detritus decomposition rate remained low but rapidly increased when nutrient mineralization began occurring upstream. This result suggests that availability of nutrients downstream might heavily depend on upstream mineralization. In Model II, I separated the assemblage of microbial decomposers into two groups, immobilizers and miners, and redesigned the nutrient acquisition strategy for miners based on published studies (Moorhead and Sinsabaugh 2006, Craine et al. 2007). For Model III, a number of previous studies have used decomposition models with consideration of subtrate quality (e.g., Lousier and Parkinson 1976, Couteaux et al. 1998, Moorhead and Sinsabaugh, 2006). I incorpporated substrate quality and microbial-substrate interactions to further explore

the potential for improving model predictions, and the result of Model III confirmed the importance of considering substrate quality.

Live microbial biomass in my models was constrained by the carrying capacity of 10% of the remaining detritus mass, as was also used by Moorhead and Sinsabaugh (2006). Moorhead and Sinsabaugh (2006) used increasing respiration to regulate microbial biomass (no mortality was explicitly calculated in their model), but I used increasing mortality. My approach provided a mechanism for cycling nutrients between detritus and microorganisms. Stream inorganic nutrients taken up by immobilizers became organic nutrients and later become a part of detritus via mortality of immobilizers, and this detritus was then again available to immobilizers and miners.

Model II and Model III predictions of nutrient patterns showed a longer net immobilization period for total nitrogen than that of Webster et al. (2009) and Model I. In Model I, a high immobilizer specific growth rate led to a short period of immobilization and a high peak of mineralization because the detritus C:N ratio quickly reached the critical ratio (Manzoni et al. 2010). When the detritus C:N ratio was larger than the critical ratio, nutrient immobilization occurs; otherwise net nutrient mineralization occurred (Manzoni et al. 2010). Microbial specific growth rates in my study were calibrated using the time series of detritus standing crop. Without miners, Model I had a much higher immobilizer specific growth rate than that in Models II and III. A higher immobilizer specific growth rate in Model I was needed to compensate for the decomposition by miners. Half of the decayed material was counted as microbial growth by Webster et al. (2009) with the carbon-use efficiency assumed to be 0.5. Without considering miners, the full proportion of microbial growth in the model was counted as

the growth of immobilizers, i.e., growth of immobilizers was higher than that of Model II and Model III.

My models predicted higher dissolved ammonium concentration than was observed. Particularly, Model I predicted a large peak around Jun, and Models II and III predicted a relatively constant ammonium concentration during decomposition. The discrepancy between predicted and observed ammonium patterns may have been a result of underestimating nitrification rate. The nitrification rate used in my models was from the Lotic Intersite Nitrogen eXperiment (LINX) study for Upper Ball Creek, Coweeta, NC, rather than HWC. Additionally, I did not include ammonium uptake by sorption, which may have contributed to this discrepancy (Triska et al.s 1994). Predicted nitrogen uptake rates, on the other hands, were within the range of measured nitrogen uptake rates in forested streams (Fig. 2-5, Model III, Fig. 2-6, Model III, Valett et al. 2008).

Through the mechanistic modeling approach, I provided a framework linking in-stream detritus decomposition and in-stream nutrient dynamics. I increased model complexity from Model I to Model III by integrating microbial nutrient mining and substrate quality. Although the model complexity increased from Model I to Model III, the only parameters involved in model calibrations were the microbial growth rates, i.e., Model I had one parameter, Model II and Model III had two parameters, while all other parameters were fixed. Besides better fitting to observed data, Model III had several advantages over Models I and II. First, Model III included three substrate types with each type being decomposed at a different rate, which made detritus pool composition vary as decomposition proceeded. By contrast, all different substrate types were decomposed at the same rate in Models I and II. Second, the processes of detritus decomposition, nutrient immobilization, nutrient mineralization, and microbial metabolism were

interdependent in Model III. Microbial-substrate interactions influence detritus decomposition, which further affected nutrient immobilization, nutrient mineralization, and microbial metabolism. I suggest that microbial-substrate interaction may lead to a succession of microbial types (e.g., Fontaine et al. 2003) due to the change in resources that favor one microbial type over the other. Third, Model III also better captured the microbial biomass pattern described in previous studies (Peterson and Cummins 1974, Paul and Clark 1997, Adl 2003, Berg and McClaugherty 2008). Model III predicted less accumulated microbial biomass on detritus than previous studies (e.g., Webster et al. 2009). Webster et al. (2009) predicted over 50% of the remaining detritus as total microbial biomass (live and dead microbial biomass) after 90 days, while my Model III yielded an average of 18.2% over a year.

My models could be further extended in many ways – I suggest four directions that might be most useful. First, temperature effects on detritus decomposition could be included. One way to incorporate temperature effects would be to apply a Q10 temperature response to microbial growth rate and respiration rate. For example, water temperature in temperate zones is generally colder in winter and warmer in summer. Based on a Q10 temperature response, microbial process rate would be faster in summer than in winter. If I were to include temperature effects in my models, I would expect a relatively longer net immobilization period and a shorter net mineralization period than in current models because growth of immobilizers would slow down in winter and speed up in summer.

Second, decomposition of FBOM and DOM is not well understood. In my current study, focusing only on headwater streams, FBOM and DOM may be less important than CBOM. If I were to extend my models to higher order streams where FBOM and DOM relatively more

important, it would be essential to incorporate the decomposition of FBOM and DOM for a more complete picture of detrital dynamics.

Third, macroinvertebrates (shredders) consume detritus and associated microbial biofilms which modifies the pool size of dead and living microbes, microbial basal respiration flux, indirect nutrient mineralization flux, nutrient immobilization flux, and population dynamics of immobilizers and miners. Additionally, Small et al. (2009) illustrated that how consumer stoichiometry could also affect nutrient spiraling as consumers have lower excretion rates of limiting nutrients and higher excretion of non-limiting nutrients. In my study, macroinvertebrates and their consumption of detritus were not explicitly modeled. I modeled macroinvertebrate CBOM consumption as CBOM fragmentation with a fixed rate, and did not include macroinvertebrate nutrient excretion. More explicit inclusion of macroinvertebrate mediated processes is a logical extension of my models.

Fourth, stream width and flow velocity were fixed in simulations. In nature, stream width and flow velocity change with discharge (e.g., Leopold and Maddock 1953), resulting in changing solutes concentration and water residence time within a reach, possibly affecting nutrient immobilization (Cleassen et al. 2009). Wider stream also includes more detritus near stream bank, changing the in-stream detritus pool size. A more detailed hydrology model incorporating changes of width and velocity would benfit studying in-stream detritus decomposition and nutrient dynamics in high hydrological variation environments and during storms.

This study illustrated the importance of opening the microbial black box in nutrient processes in streams. Compared to Model I, which did not include miners and did not specify different leaf qualities, Models II and III yielded better prediction of nutrient dynamics. These

findings suggest that for better understanding of nutrient process in streams, it is essential to consider both immobilization and mining as different microbial processes and to consider different leaf qualities with their corresponding decay rates. A long-term comprehensive leaf decomposition experiment would be helpful to further validate my models and lead to a better understanding of the ecological functions of immobilizers and miners and their impacts on decomposition in streams.

2.5 Acknowledgement

This study was part of the Coweeta Long Term Ecological Research study funded by National Science Foundation, DEB0823293. I also thank Virginia Tech Computation Center for providing the facility for model computations. Some of the results of this study were presented at the symposium on Systems Ecology: A Network Perspective and Retrospective in April 2013 in honor of Dr. Bernard C. Patten. As branches and twigs of Dr. Pattern's academic tree, I celebrate his contributions to ecology in general and especially his impetus to the field of ecological modeling.

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Table 2-1. Parameters used in simulations.

Parameters	Values	Sources
Channel length	1125 m	Webster et al. 1997
Annual average water depth	0.05 m	Webster, unpublished data
Channel average cross-sectional area	0.087 m^2	Webster, unpublished data
Annual average discharge	16.4 L s^{-1}	USDA Forest Services, Coweeta Hydrologic Laboratory
A_s/A	0.8	Brookshire et al. 2005
Transient storage exchange rate	0.00019 s^{-1}	Brookshire et al. 2005
Initial SRP concentration in water	2 µgP L^{-1}	Webster et al. 1991, 2009
Initial nitrate concentration in water	25 µg-N L^{-1}	Webster et al. 2009
Initial ammonium concentration in water	0 µg L^{-1}	USDA Forest Services, unpublished data
Annual leaf-fall	327 g AFDM m^{-2}	Webster et al. 2001

Half saturation constant for phosphorus	1 μgP L^{-1}	Webster et al. 2009
Half saturation constant for nitrogen	6 μgN L^{-1}	Payn et al. 2005, Webster et al. 2009
Maximum areal uptake for phosphorus	0.31 μgN m^{-2} s^{-1}	calculated from Payn et al. 2005 and Webster et al. 2009
Maximum areal uptake for nitrogen	1.88 μgN m^{-2} s^{-1}	Payn et al. 2005
Leaching loss proportion - carbon	0.15	Petersen and Cummins 1974
Leaching loss proportion - nitrogen	0.48	calculated using median values of Cross et al. 2005
Leaching loss proportion - phosphorus	0.66	calculated using median values of Cross et al. 2005
Macroinvertebrate CBOM consumption rate	7.69×10^{-9} s^{-1}	calculated using observed detritus standing stock in HWC
Macroinvertebrate assimilation efficiency (%)	40	Petersen and Cummins 1974
Miner C:N	5	Cross et al. 2005
Miner C:P	20	Cross et al. 2005
Immobilizer C:N	7	Cross et al. 2005

Immobilizer C:P	188	Cross et al. 2005
Carbon-use efficiency (%)	50	Moorhead and Singsabaugh 2006
Basal respiration	$1.16\times10^{-7}s^{-1}$	Moorhead and Singsabaugh 2006
Nitrification rate	$2.34\times10^{-4}\ s^{-1}$	Valett and Webster, unpublished data
Denitrification rate	$4.78\times10^{-5}\ s^{-1}$	Valett and Webster, unpublished data

Table 2-2. Composition of leaf detritus in HWC, NC.

Leaf type	Proportion of annual leaf-fall[a]	Mass C:N	Mass C:P	Mass Prop. Cellulose	Mass Prop. Lignin	Sources
Betula spp.	0.240	84.03	634.58	0.2125	0.2835	Johansson 1995
Rhododendron maximum	0.182	165.40	[b]444.45	0.2112	0.1101	Hunter et al. 2003
Liriodendron tulipifera	0.145	90.33	[b]444.45	0.1837	0.0957	Hunter et al. 2003
Quercus alba	0.045	120.72	[b]444.45	0.1839	0.1220	Suberkropp et al. 1976
Quercus prinus	0.045	87.00	[b]444.45	0.1795	0.1157	Hunter et al. 2003
Tsuga canadensis	0.068	103.27	[b]444.45	0.3960	0.2060	Moorhead and Sinsabaugh 2006
Carya spp.	0.064	57.92	[b]444.45	0.1506	0.1001	Suberkropp et al. 1976
Acer rubrum	0.059	68.40	[b]444.45	0.1038	0.0976	Carreiro et al. 2000

Quercus rubra	0.044	54.70	[b]444.45	0.2002	0.2607	Carreiro et al. 2000
Others	0.108	[†]33.26	[b]444.45	[c]0.1839	[c]0.1157	Cross et al. 2005
Weighted average		93.48	490.12	0.2038	**0.1628**	

[a]From Webster et al. 2001.

[b]Median value of Cross et al. 2005.

[c]A median value based on the rows above.

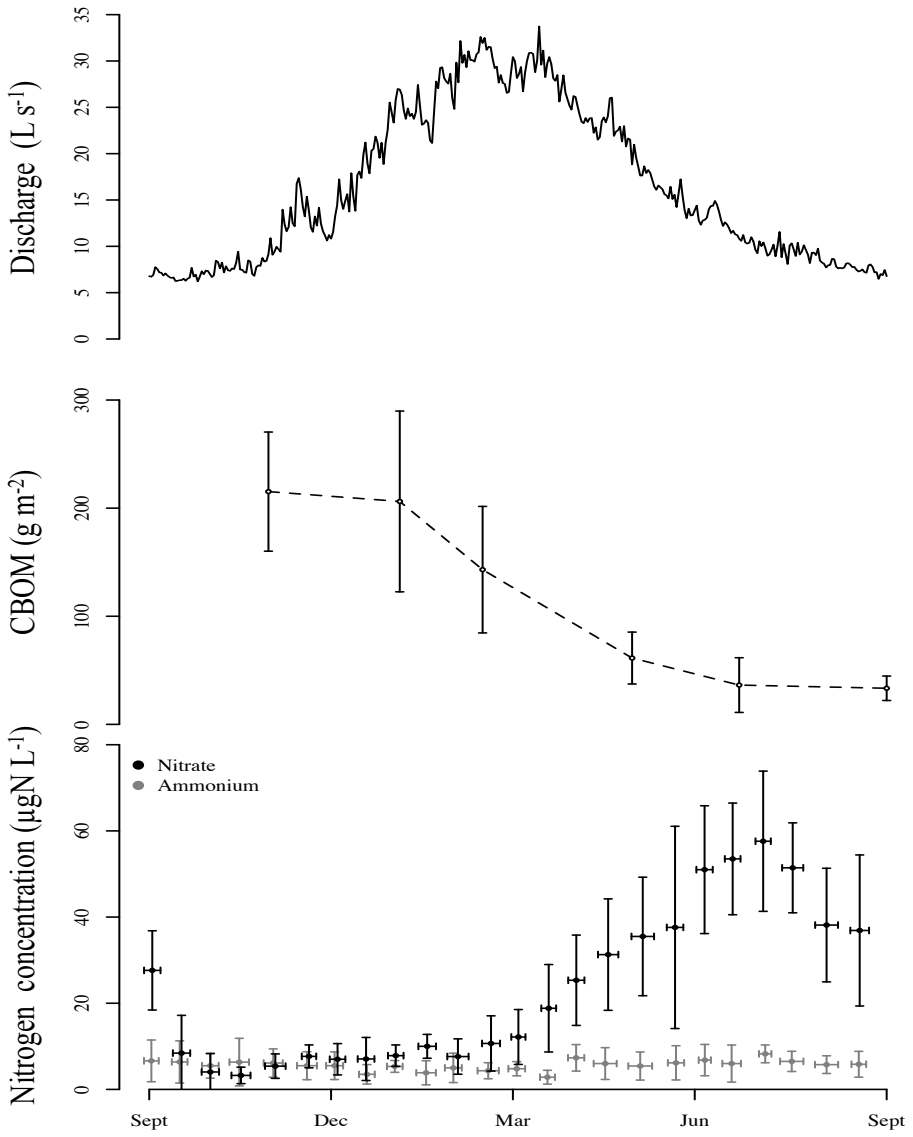


Figure 2-1. Annual patterns of discharge (daily median), coarse benthic organic matter (CBOM) standing stock, and nitrogen concentrations in HWC. Discharge was monitored from 1971 to 2002. Nitrate and ammonium concentrations were measured from 2005 to 2008. Hydrology and nutrient data are from USDA Forest Services, Coweeta Hydrologic Laboratory. CBOM standing crop was measured by Webster et al. (2001) from 1993 to 1994.

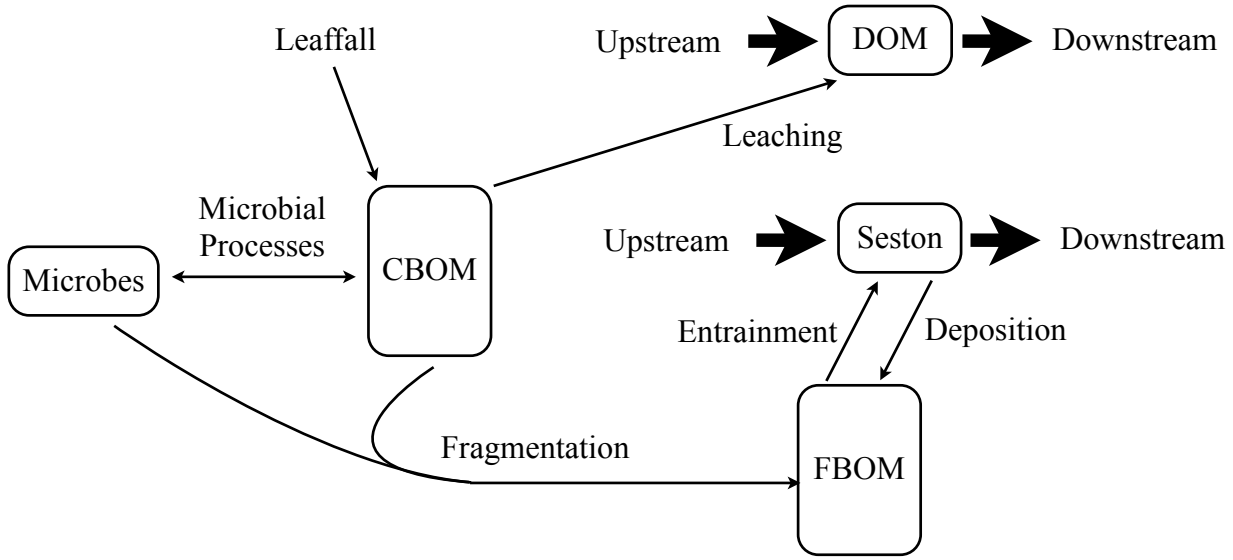
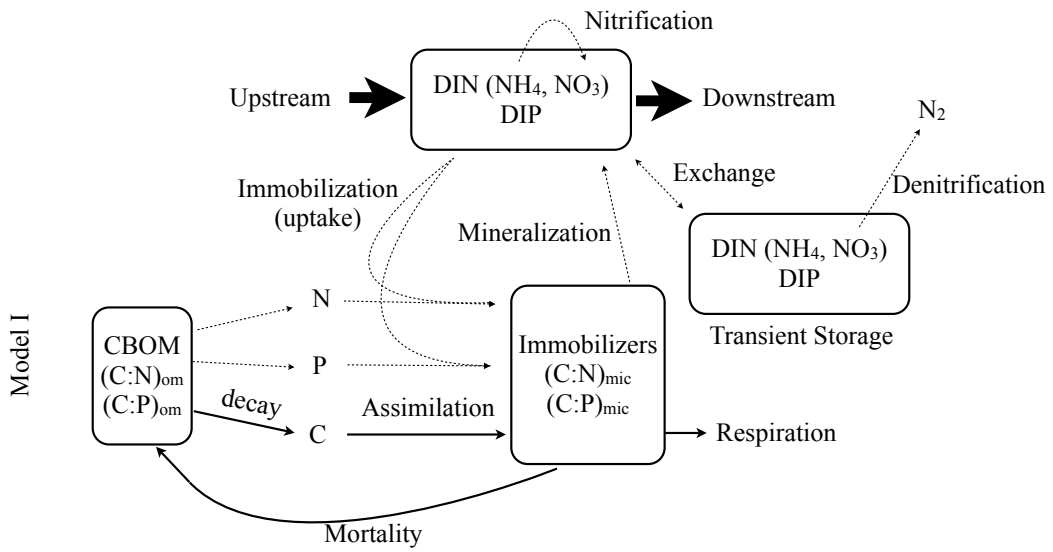
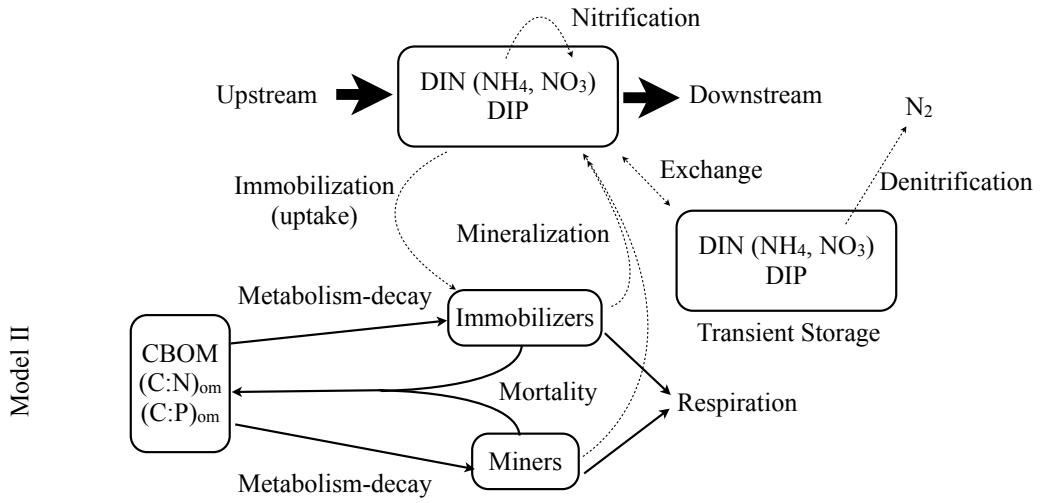


Figure 2-2. A conceptual diagram of a general model for leaf decomposition in streams. Large arrows represented the flow of dissolved organic matter (DOM) and seston in stream water; solid arrows represented carbon fluxes among the organic matter pools. CBOM and FBOM are coarse and fine benthic organic matters, respectively.


Model I
Nitrification
Upstream
DIN (NH_4, NO_3)
DIP
Downstream
N_2
Exchange
Denitrification
Immobilization
(uptake)
Mineralization
DIN (NH_4, NO_3)
DIP
Transient Storage
N
P
CBOM
$(C:N)_{om}$
$(C:P)_{om}$
decay
C
Assimilation
Immobilizers
$(C:N)_{mic}$
$(C:P)_{mic}$
Respiration
Mortality


Model II
Nitrification
Upstream
DIN (NH_4, NO_3)
DIP
Downstream
N_2
Exchange
Denitrification
Immobilization
(uptake)
Mineralization
DIN (NH_4, NO_3)
DIP
Transient Storage
Metabolism-decay
Immobilizers
CBOM
$(C:N)_{om}$
$(C:P)_{om}$
Mortality
Respiration
Miners
Metabolism-decay

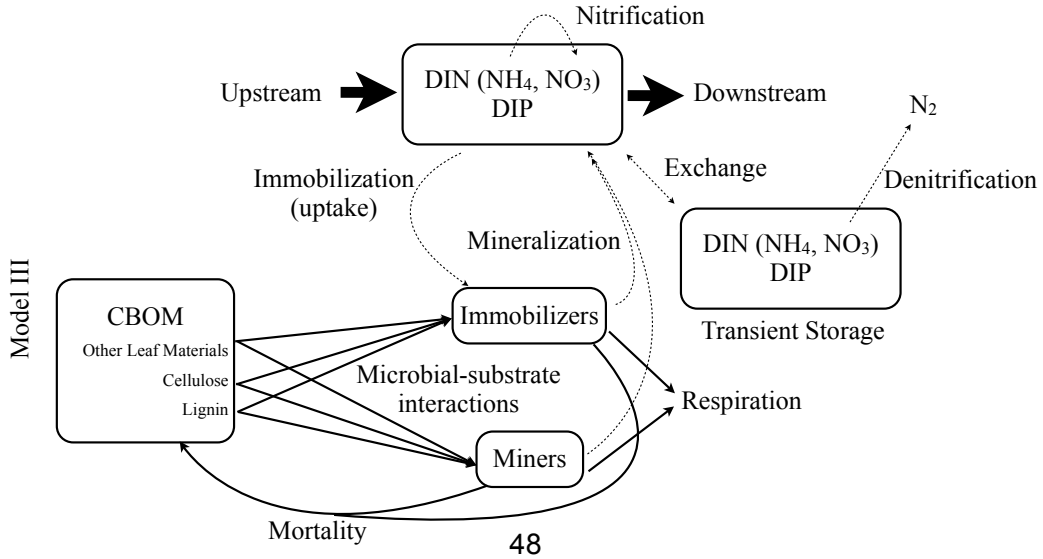

Model III
Nitrification
Upstream
DIN (NH_4, NO_3)
DIP
Downstream
N_2
Exchange
Denitrification
Immobilization
(uptake)
Mineralization
DIN (NH_4, NO_3)
DIP
Transient Storage
CBOM
Other Leaf Materials
Cellulose
Lignin
Immobilizers
Microbial-substrate
interactions
Respiration
Miners
Mortality

Figure 2-3. Conceptual diagrams of Model I, II, and III. Large arrows represented the flow of dissolved nutrient in stream water, solid arrows represented carbon fluxes, and dashed arrows represented nutrient fluxes. Model I diagrams show the details of decomposition. The decomposition portions of Model II and III diagrams were simplified. CBOM is coarse benthic organic matter. DIN and DIP are dissolved inorganic nitrogen and phosphorus. In my models, DIN has two forms, ammonium and nitrate, and DIP is phosphate.

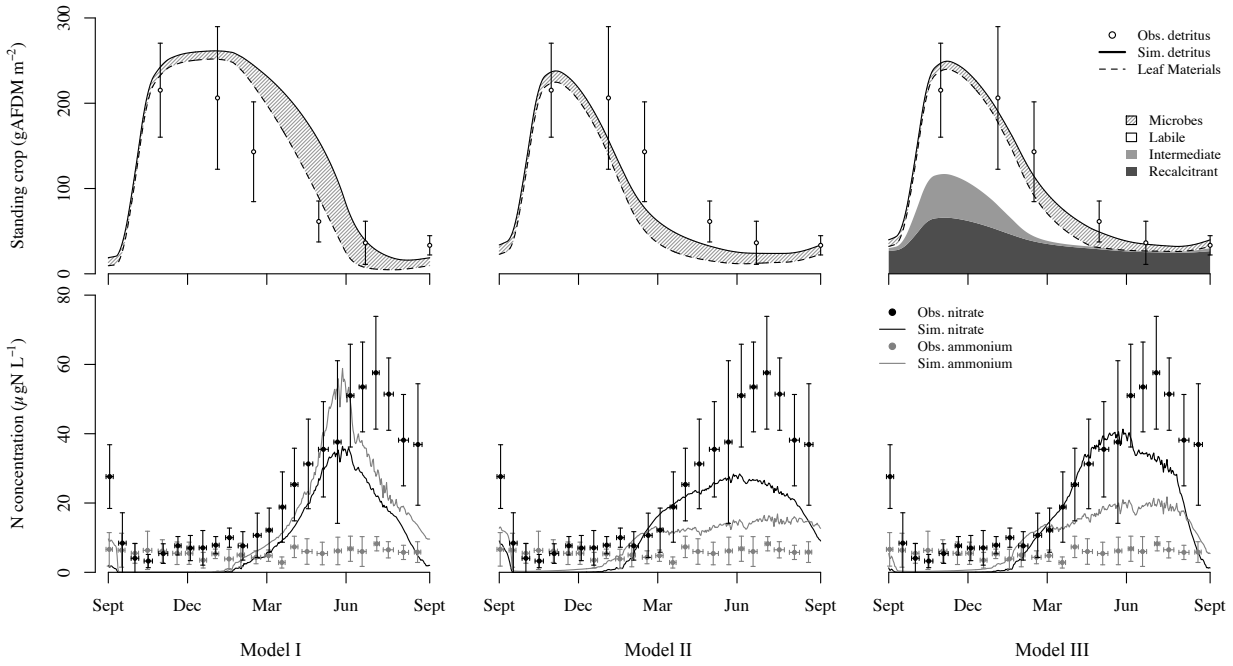


Figure 2-4. Observed patterns of detritus (top), nitrate and ammonium (bottom), and their simulated patterns by Models I, II, and III. Circles are the mean observed patterns in HWC. MAE of detritus by Models I, II, and III were 49.7, 28.9, and 15.2, respectively. MAE of nitrate and ammonium concentrations by Models I, II, and III were (13.7, 12.55), (11.63, 5.99), and (9.69, 7.46), respectively.

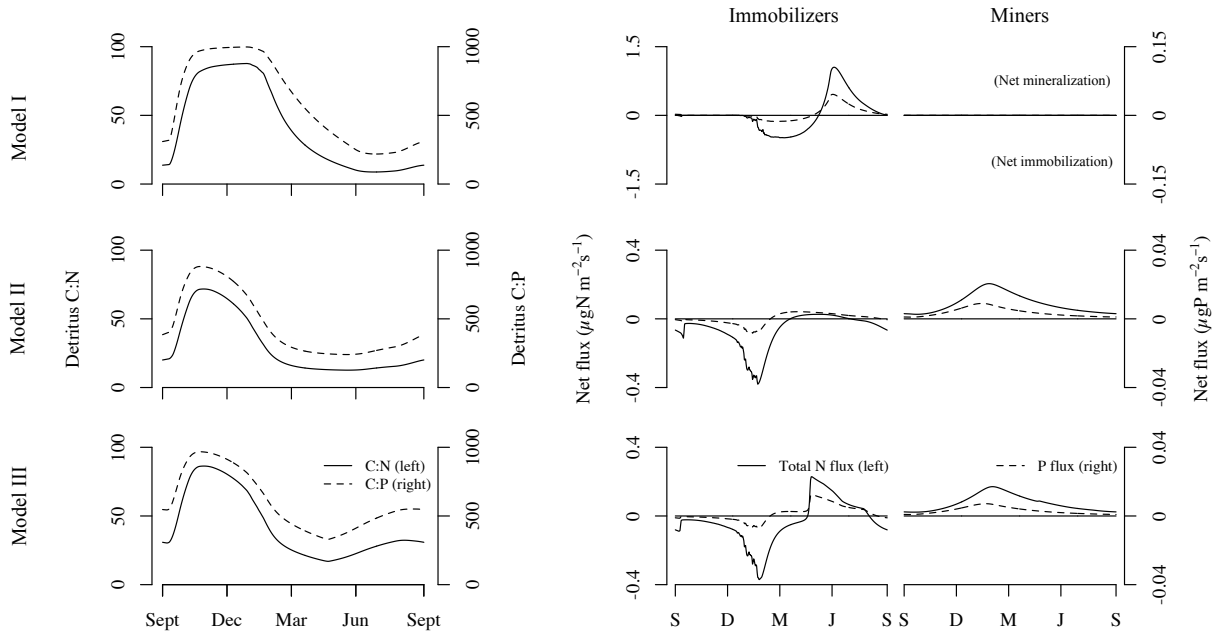


Figure 2-5. Prediction of detritus carbon to nutrient ratios (left column) and nutrient net flux by immobilizers (middle column) and miners (right column). Solid lines are for nitrogen, and dashed lines are for phosphorus.

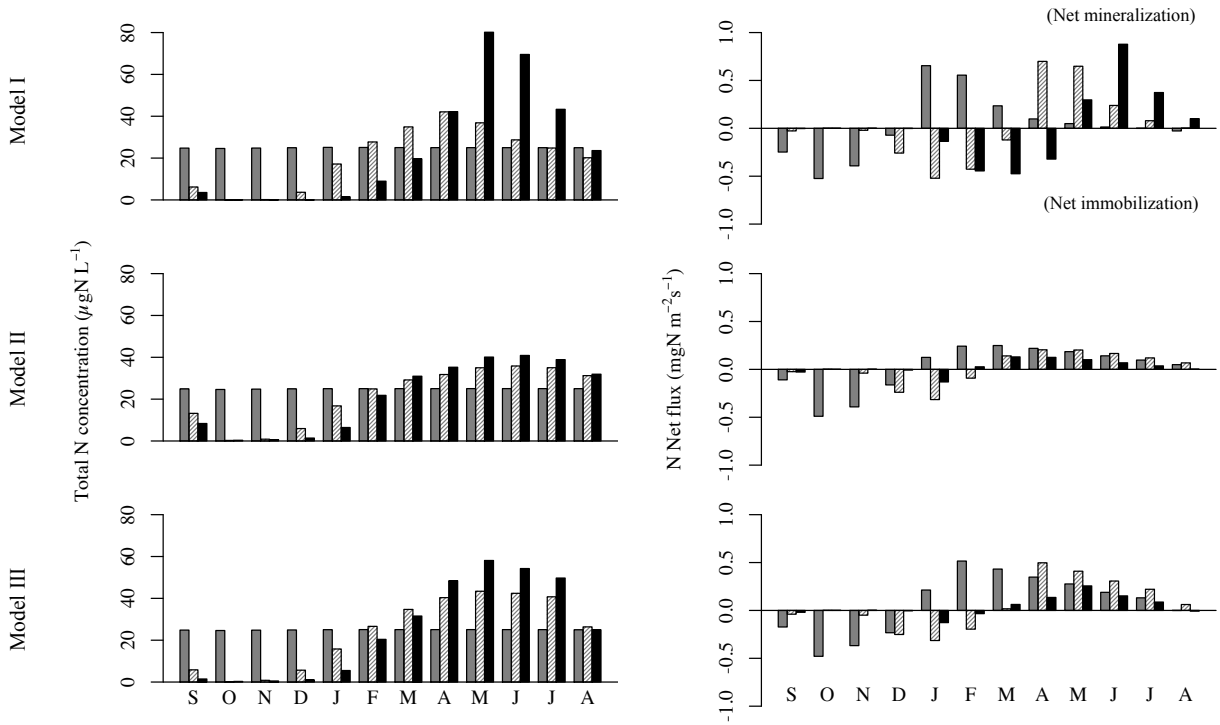


Figure 2-6. Monthly averaged total nitrogen (NO_3 + NH_4) concentration and total nitrogen net flux from microbes (immobilizers + miners) to stream water, predicted by Models I, II, and III. Dark gray is upstream, light gray pattern is mid-reach, and black is downstream.

Chapter 3

Effects of Lateral Nutrient Input and In-Stream Nutrient Processes on Nitrogen Export in a Forested Catchment

3.1 Introduction

Forested mountain headwater streams, e.g., streams in the southern Appalachian Mountains, are heavily shaded (Webster et al. 1997) and characterized by low in-stream primary production (Mulholland et al. 1997, Bernot et al. 2010). Allochthonous input of detritus is the major energy source in many streams (Minshall 1967, Fisher and Likens 1973, Wallace et al. 1997) and also an influential factor for nutrient spiraling (Kaushik and Hynes 1971, Gregory 1978, Meyer 1980, Triska and Buckley 1978, Mulholland et al. 1984, Webster et al. 2001, Webster et al. 2009).

Both lateral nutrient input from terrestrial ecosystems and in-stream nutrient process may play important roles in modifying nutrient concentrations in streams (Fig. 3-1, Bernhardt et al. 2005, Sudduth et al. 2013). Classical studies supported the idea that terrestrial processes and lateral nutrient input control nutrient export from watersheds (e.g, Bormann and Likens 1967, Vitousek and Reiners 1975, McGroddy et al. 2008, Brookshire et al. 2009). In contrast, recent studies have shown that in-stream processes play a major role in controlling nutrient balance and export (e.g., Peterson et al. 2001, Bernhardt et al. 2005, Webster et al. 2009).

In this study, I focused on microbial nutrient immobilization (i.e., nutrient uptake) and mineralization, two critical in-stream nutrient processes that are closely associated with detritus decomposition and may substantially modify stream nutrient concentrations. Investigation of the importance of microbial nutrient immobilization and mineralization can be traced back to

Kaushik and Hynes (1971) and Hynes (1960). Although nutrient immobilization has been a major focus of studies on nutrient dynamics in streams, there is less understanding of how mineralization influences in-stream nutrient processes because quantification of mineralization has been limited to whole-stream tracer studies (Beever and Burns 1980, Jennings 1995) or animal excretion experiments (Vanni 2002, Hood et al. 2005, McIntyre et al. 2008). Webster et al. (2009) used a model to illustrate and emphasize the importance of both nutrient immobilization and mineralization in modifying nutrient concentrations in streams.

Because microbial nutrient immobilization and mineralization are closely related to detritus decomposition, factors driving decomposition such as detritus carbon : nutrient ratio, detritus substrate quality (e.g., % lignin and cellulose) and microbial carbon : nutrient ratio, may also substantially influence these two in-stream processes and as a result, modify stream nutrient concentrations (Fig. 3-1). Some studies have shown that detritus with high initial carbon : nitrogen ratio (C:N) decayed slower than detritus with low initial C:N ratio (Howarth and Fisher 1976, Melillo et al. 1984, Taylor et al. 1989). Manzoni et al. (2008) found initial nutrient content of detritus to be an important factor controlling mineralization. Some studies have suggested lignin content in detritus to be the major factor limiting decay rate (Melillo et al. 1984, Taylor et al. 1989, Gessner and Chauvet 1994, Royer and Minshall 2001). Cross et al. (2005) showed the important roles of microbial carbon : nutrient ratio on detritus decomposition and further on nutrient spiraling in streams. Webster et al. (2009) showed that both the initial nutrient content of detritus and nutrient composition of microbes affected nutrient dynamics in streams. Lateral nutrient input may also interact with in-stream processes (Fig. 3-1) because it contributes to the nutrients in streams available to microbes (Cross et al. 2005, Webster et al. 2009). Many nutrient enrichment experiments (e.g., Elwood et al. 1981, Gulis and Suberkropp 2003) and

decomposition studies (e.g., Meyer and Johnson 1983, Webster and Benfield 1986, Suberkropp and Chauvet 1995, Gessner et al. 2007) found that detritus decay and fungal activity were correlated with nutrient concentrations in streams. More clear evidence was provided by Findlay and Tenore (1982) who directly demonstrated through experimentation that microbes growing on decaying *Spartina* grass acquired nitrogen primarily from the water column. Using isotopic nitrogen (^{15}N), Cheever et al. (2013) also found that microbes associated with leaf decomposition in streams acquired nitrogen primarily from the water column.

Although extensive studies have been conducted to investigate the factors involved in nutrient dynamics in streams, most of these factors were examined independently (Royer and Minshell 2001). Royer and Minshell (2001) extended the focus from exploring the individual factors to investigating their interactions. They also emphasized the importance of interaction among factors across spatial and temporal scales and of understanding decomposition processes within a global framework. Following their argument of extension from investigating individual factors to incorporating their interactions, I applied a global sensitivity analysis to a stream network model that I developed in this chapter to examine the impacts of lateral nutrient input and in-stream nutrient process on nitrogen export in streams. Global sensitivity analysis (Sobol 2001, Nossent et al. 2011, Glen and Isaacs 2012) provides a framework to analyze the sensitivity of a complex non-linear model to its parameters. This technique is different from the generalized likelihood uncertainty estimation (GLUE) method (Beven and Binley 1992) for estimating the uncertainty and distribution of parameter values in a given set of observation, because it takes known ranges of parameters and yields an index for each of the parameters to indicate their strength of influence to the model outcomes. Global sensitivity analysis also differs from

traditional sensitivity analysis in that it allows other factors to vary and interact simultaneously as the single factor of interest is varied.

The overall goal of this study was to explore the effects of lateral nutrient input and in-stream nutrient process on nitrogen export through a global sensitivity analysis and to evaluate their relative importance in contributing to nutrient export. In Chapter 2, I developed a stream model that synthesized microbial processes associated with detritus decomposition. In this study, I calibrated the model based on a forested reference stream and used this calibrated model to conduct global sensitivity analysis. Thus, the specific purposes of this study were to (1) examine the effects of lateral nitrate input on nitrogen export; (2) investigate the effects of in-stream nutrient processes, i.e., nitrogen immobilization and mineralization on nitrogen export; (3) explore the factors driving nutrient immobilization and mineralization, including detritus carbon : nutrient ratio, detritus substrate quality, microbial carbon : nutrient ratio, and lateral nitrate input; and (4) identify the most important factors that may regulate nitrogen export in a forested catchment. Instead of annual nitrogen export, I focused on seasonal nitrogen export to explore the temporal patterns of the effects.

3.2 Methods

Model description and calibration

I developed a stream network model based on the stream model in Chapter 2. The stream network model is a geographic information system (GIS) based model. The stream network and its segments were derived from elevation data (GRASS 6.0). Each stream segment in the stream network was modeled as Model III in Chapter 2 with additional ecological and hydrological features, including water temperature effects on process rates and hillslope nutrient inputs. To

estimate hillslope nutrient inputs (lateral nutrient inputs), I used the Regional Hydro-Ecologic Simulation System (RHESSys, Tague and Band 2004), a terrestrial model simulating forest ecosystem and hillslope hydrology. The modified Model III used for each stream segment included two components, hydrological processes such as downstream transportation, transient storage, and lateral inflow, and biological processes such as detritus breakdown, nutrient immobilization, mineralization, nitrification, and denitrification. In the model, detritus was broken down by two mechanisms, fragmentation via current forces and macroinvertebrate consumption and decomposition driven by microbial processes. I included two microbial groups in the model, immobilizers and miners. Immobilizers use detritus as their primary carbon source and use nutrients from both detritus and stream water as their nutrient sources, especially when nutrients obtained from detritus are insufficient for the microbial demand for growth (Kaushik and Hynes 1971, Suberkropp and Chauvet 1995, Mulholland et al. 1985). Miners grow more slowly (Moorhead and Sinsabaugh 2006) and rely on detritus for both their carbon and nutrients. Nitrification occurred in the water column, and denitrification occurred in the transient storage. I assumed the same detritus stoichiometry (C:N and C:P) and the same substrate quality (i.e., % labile, % cellulose, and % lignin) for all detritus in the model. Details of the decomposition-nutrient interaction model development was described in Chapter 2.

The stream network model was first initiated based on studies of Hugh White Creek (HWC, Coweeta Hydrologic Laboratory, North Carolina, USA). Major relationships and parameter values (Tables 3-1 and 3-2) were derived from previous research or assigned to achieve realistic initial simulations. I included climate data (i.e., daily temperature and precipitation) from 1971 to 2012, which were provided by U.S. Forest Service, Coweeta Hydrologic Laboratory, to calibrate and initiate RHESSys for HWC.

I programmed the model as a stream network composed of 17 stream segments, each of which had a single channel with hill-slopes on both sides (Fig. 3-2). Stream segments were extracted using the geographic information system (GIS) watershed calculation (GRASS GIS version 6.4), and I used an elevation map with 10 m × 10 m resolution and 2.5 ha as the minimum basin size. Within each segment, channel morphology and detritus inputs were calculated based on drainage area (Table 3-1). Water runoff and nitrogen flux from the forest sub-model were used as inputs to the stream channel. If a segment was a headwater segment, I split the water and nitrogen inputs into spring and lateral inflow based on the proportion of the drainage area at the origin of this segment relative to the total drainage area of the segment. If a segment was a downstream segment, the water and nitrogen inputs were treated as lateral input.

Global sensitivity analysis

I applied the Sobol global sensitivity analysis method (Sobol 1967, 1976, 1990, 2001) to examine the effects of lateral input and in-stream microbial processes on nitrogen export. I randomized all parameters within their ranges (Table 3-2) simultaneously using the Sobol sequence randomization method (Sobol 1967, 1976, 1990, 2001). I adopted the Glen and Isaacs (2012) method to calculate indices of both direct and indirect effects for those parameters of interest, and I applied the bootstrapping method to estimate the uncertainty in index calculation. Because nutrient immobilization and mineralization are associated with detritus decomposition, I randomized detritus decomposition related parameters in the Sobol sequence randomization. I used net microbial nitrogen flux (i.e., mineralization - immobilization) to represent the overall effects of these two processes. Therefore, my parameters of interest in this study included lateral nitrate input, detritus stoichiometric parameters (detritus C:N mass ratio, detritus C:P mass ratio),

detritus substrate quality parameters (% cellulose and % lignin), and microbial stoichiometric parameters (immobilizer C:N, immobilizer C:P, miner C:N, and miner C:P).

I conducted the global sensitivity analysis under two scenarios based on the annual patterns of terrestrial lateral water and nitrate input to streams that were calculated by RHESSys (Fig. 3-3 top). Randomization of lateral nitrate input was achieved by scaling these annual patterns with a randomized scalar. In the first scenario, I used a scalar randomly selected from the range 0-1, so that variation in lateral nitrate input was at most equivalent to the level of RHESSys output. In the second scenario, I increased the scalar to be within the range 1-4, thus increasing the lateral nitrate input to streams. With the analyses under these two scenarios, I attempted to explore the conditions under different contributions of lateral nitrate input and in-stream nitrogen processes.

Here, I present the results in two parts. First, I show the sensitivity of nitrogen export to lateral nitrate input and net microbial nitrogen flux. Second, I present the direct and indirect effects of detritus stoichiometry parameters, detritus substrate quality parameters, microbial stoichiometry parameters and lateral nitrate input on net microbial nitrogen flux. I also organize the outcomes by season to explore the possible seasonal patterns on the effects of these parameters.

The forest sub-model was executed using RHESSys software (version 5.15), the stream sub-model was programmed in JAVA (version 7), and the Sobol sensitivity analysis was programmed in R (version 3.0.1).

3.3 Results

Direct effects of lateral nitrate input and in-stream net microbial nitrogen flux on nitrogen export

When lateral nitrate input to streams was low, in-stream net microbial nitrogen flux consistently had more impact on nitrogen export than lateral nitrate input over all four seasons (Fig. 3-4). The influences of lateral input in fall and winter tended to be higher than that in spring and summer. By contrast, with higher lateral nitrate and higher nitrate in streams, the impacts of in-stream net microbial nitrogen flux were less than lateral input over all four seasons. The influences of in-stream net microbial nitrogen flux showed some seasonal pattern, i.e., slightly higher influences in spring and summer than in fall and winter.

Direct effects of lateral input and decomposition factors on in-stream net microbial nitrogen flux

The importance of lateral input and decomposition factors and the seasonal pattern of their impacts greatly depended on the lateral nitrate input level (Fig. 3-5). Lateral nitrate input was one of the most influential factors determining net microbial nitrogen flux in the low lateral nitrate input scenario while under high lateral input, the impact of lateral input was negligible.

With low lateral nitrate input, detritus C:N substantially affected net microbial nitrogen flux in winter while its impact in other three seasons was slight. In contrast, with high lateral nitrate input, detritus C:N had much greater impact on net microbial nitrogen flux in winter than in other seasons. Detritus C:P substantially affected net microbial nitrogen flux in all seasons when lateral nitrate input was low. However, when lateral input was higher, its impacts was lower.

Detritus cellulose (%) had large influences to net microbial nitrogen flux in all seasons when lateral nitrate input was low. However, when lateral nitrate input was raised, it had little

impact. Detritus lignin (%) was an influential factor to net microbial nitrogen flux in all seasons except spring under low terrestrial nitrate input scenario. In contrast, under high lateral input scenario, % lignin had a substantial impact in spring whereas its impact in other seasons was slight.

Immobilizer C:N and miner C:N played an important role in modifying net microbial nitrogen flux under low lateral nitrate input scenario, but their impacts were dramatically less under high terrestrial input scenario. Net microbial nitrogen flux was more sensitive to immobilizer C:P in spring and summer than in fall and winter when lateral nitrate input from terrestrial was low whereas when lateral nitrate input was high, this seasonal pattern reversed, i.e., greater impacts in fall and winter than in spring and summer. Miner C:P was an influential factor in all four seasons in modifying net microbial nitrogen flux with low lateral nitrate input. However with high lateral nitrate input, its effect started to show seasonal patterns, i.e., higher impacts in winter than other seasons.

Indirect effects of lateral input and decomposition factors on in-stream net microbial nitrogen flux

The indirect effects of lateral input and decomposition factors on in-stream net nitrogen flux were less variable than their direct effects. Interaction between nutrients, detritus, and microbes in the model may have contributed to the lower variability of indirect effects. However, regardless of lateral nitrate input level, in-stream net microbial nitrogen flux was more sensitive to detritus C:N and immobilizer C:P than other factors in fall and winter (Fig. 3-6). In spring and summer, detritus C:N also played the most important role in regulating in-stream net microbial nitrogen flux, followed by detritus lignin content.

3.4 Discussion

There has been a debate between classical models that emphasize the importance of terrestrial nutrient processes in controlling stream nutrient exports (e.g., Vitousek and Reiners 1975, McGroddy et al. 2008) versus recent studies that have shown the importance of in-stream process in modifying steam nutrient concentrations (e.g., Bernhardt et al. 2005, Webster et al. 2009). In response to such a debate, Brookshire et al. (2009) evaluated in-stream contribution through a modeling approach and concluded that under many conditions, longitudinally static stream nutrient concentration reflected the balance between terrestrial input and in-stream process. I re-evaluated this debate with a more complete modeling framework (i.e., linking a stream network model and a terrestrial model), and my results suggested that the importance of terrestrial input versus in-stream process to nitrogen export may depend on levels of lateral input and may have seasonal patterns.

The influences of nitrogen saturation on in-stream processes have been well documented (e.g., Bernot and Dodds 2005, O'Brien et al. 2007, Claessen et al. 2009). High nitrogen loading to streams may override in-stream process and therefore influence the ability of streams to transport, retain, and remove nitrogen (Dodds and Welch 2000, Bernot and Dodds 2005). My results supported previous studies in that high nitrate input changed the importance of those factors that I evaluated and their seasonal patterns (Figs. 3-4 and 3-5). In this study, for the low lateral nitrate input scenario, I limited the maximum lateral input to be equivalent to the nitrate level generated by the RHESSys model by using a randomized scalar from zero to one. Actually, the nitrate level output from the RHESSys model (e.g., the annual average nitrate concentration of 54 mg NO_3-N m^{-3}, Fig. 3-3 bottom) already doubled the nitrate level that was

measured in streams. For example, the average nitrate concentration reported by Webster et al. (2009) was 25 mg NO_3-N m^{-3}. It is likely that nitrogen saturation of microbial immobilization occurred at high lateral nitrate input because lateral nitrate input had little impact on net microbial nitrogen flux at high nitrate loading (Fig. 3-5). This result indicates that the available nitrogen in streams may already exceed or be near to exceeding the demand by microbes, and in-stream processes associated with decomposition may start to be limited by other factors (Bernot and Dodds 2005).

I observed a prominent seasonal pattern of the impacts of lateral nitrate input on nitrogen export under the scenario with low lateral nitrate input (Fig. 3-4). Lateral nitrate input had greater influences on nitrogen export in fall and winter than in spring and summer. This seasonal pattern may not be driven by lateral nitrate input itself because the lateral nitrate flux showed little seasonal pattern (Fig. 3-3, top). Instead, such a seasonal pattern of lateral nitrate input effect was very likely the result of seasonal variation in in-stream process. In fall and winter, potential nitrogen immobilization is greater than potential nitrogen mineralization because of the allochthonous input of detritus. Although potential nitrogen immobilization is high, the actual nitrogen immobilization depends on nitrogen availability, which is controlled by the lateral nitrate input. Therefore, the direct effect of lateral nitrate input was relatively higher in fall and winter because of great potential nitrogen immobilization. Net nitrogen mineralization generally occurs in spring and summer and is not affected by nitrogen availability at that time. When lateral nitrate input remains low (less than nitrogen mineralization), nitrogen export is greatly controlled by net nitrogen mineralization. Therefore, the direct effect of lateral nitrate input was low in spring and summer.

Many studies have found that decay rate is related to detritus C:N (e.g., Melillo et al. 1984, Taylor et al. 1989, Manzoni et al. 2008). As detritus is decomposed by microbes, nutrient immobilization and mineralization occur. Microbes can obtain nitrogen for growth from two sources, either assimilating nitrogen from detritus or immobilizing nitrogen from water (Findlay and Tenore 1982, Cheever et al. 2013). Although detritus C:N plays an essential role in decay, my results showed that detritus C:N was relatively less important than other factors in modifying net microbial nitrogen flux in streams when lateral nitrate input was low (Fig. 3-5). Cheever et al. (2013) suggested that stream water may be the predominant source of nitrogen for meeting microbial requirements even when nitrogen concentration was low. This finding may explain the relative minor role of detritus C:N in controlling net microbial nitrogen flux with low terrestrial nitrate input. My results also showed that when lateral nitrate input was high, detritus C:N played an important role in modifying net microbial nitrogen flux (Fig. 3-5). This result may be explained by the important role of detritus C:N in determining the microbial nitrogen flux switching from net immobilization to net mineralization. Various studies suggest that this shift depends on the stoichiometry of microbes relative to the stoichiometry of remaining detritus (Moore et al. 2006, Manzoni et al. 2008, 2010). When nitrogen supply in streams is low, I would expect that it would take longer for microbes to accumulate enough nitrogen to reach the switching point. In contrast, when nitrogen supply in streams is high, I would expect that this shift may not be limited by water nitrogen but detritus C:N, i.e., lower detritus C:N may become more similar to microbial C:N and result in earlier switching and more intense net mineralization.

In this chapter, parameter values were randomly selected from the uniform distribution defined by their range for the global sensitivity analysis. Although some of the parameters (e.g.,

detritus C:N and immobilizer C:P) may be skewed, I used uniform distribution due to limited understanding of the distributions of these parameters. Obtaining more information on the distribution of these parameters and incorporating this information into the global sensitivity analysis would further enhance this analysis.

Although my results are subject to model assumptions and the limited number of scenarios that I explored, they may help identify hypotheses that can be tested through well-designed field and laboratory studies to improve our understanding of the impacts of lateral nutrient input and in-stream process on nitrogen export. First, I found that nitrogen export was more sensitive to net microbial nitrogen flux in spring and summer than in fall and winter regardless of lateral nitrate input levels (Fig. 3-4). This seasonal pattern corresponds to that of the two in-stream processes, i.e., net mineralization in spring and summer and net immobilization in winter and fall (previous chapter). Therefore, I hypothesize that periods of net mineralization may have greater influence on nitrogen export than periods of net immobilization.

Second, immobilizer C:P and miner C:P were always identified, although not for all seasons, as important factors in controlling net microbial nitrogen flux under both low and high lateral nitrate input scenarios (Fig. 3-5). This result may indicate that phosphorus cycling may greatly interact with nitrogen cycling in streams. However, few studies have demonstrated how these two nutrients interact.

Finally, net microbial nitrogen flux in streams was sensitive to detritus cellulose and lignin content when lateral nitrate input was low (Fig. 3-5). Both substrates are relatively refractory, and thus I suggest that their importance may be positively related to miner activity because miners have greater ability to process less labile substrate than immobilizers (Moorhead and Sinsabaugh 2006). However, when lateral nitrate input was high, the impacts of detritus

cellulose and lignin contents, especially lignin content, were substantially less (Fig. 3-5). This reduction in the importance of detritus cellulose and lignin contents may be associated with increased immobilizer activity suppressing mining activity (Craine et al. 2007). Immobilizers can use both detritus and stream water nutrients as their nutrient sources (Findlay and Tenore 1982, Webster et al. 2009, Cheever et al. 2013). When the nitrogen supply in streams is high, immobilizers can obtain sufficient nitrogen and dominate microbial processes. Immobilizers have limited ability to process less labile substrate, and thus substrates such as cellulose and lignin have little impacts on immobilizer activity.

In summary, the application of global sensitivity analysis with a modeling framework that links a stream network model and a terrestrial model allowed exploration of direct and indirect effects of lateral nitrate input and in-stream net microbial nitrogen flux on nitrogen export. The importance of lateral input and decomposition factors and their seasonal patterns were greatly dependent on the lateral nitrate input level. Net microbial nitrogen flux was more important than lateral nitrate input in modifying nitrogen export in streams when the lateral nitrate input level was low. However, with high lateral nitrate input, lateral nitrate input was more important than in-stream net microbial nitrogen flux. Those factors that had high impacts on net microbial nitrogen flux under the low nitrate input scenario were less important under the high nitrate input scenario.

3.5 Acknowledgement

This study was part of the Coweeta Long Term Ecological Research study funded by National Science Foundation grant, DEB0823293. I thank Dr. Rhett Jackson for helping with

bankfull channel morphology estimates using drainage area and Drs. Lawrence Band and Taehee Hwang for providing information and helping with RHESSys simulation.

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Table 3-1. Equations for channel bankfull width, depth, and in-stream CBOM annual input.

A = drainage area (km^2)

Equations	References
Channel bankfull width (m) = $1.97\ A^{0.44}$ if $A \geq 10$	Faustini et al. 2009
Channel bankfull width (m) = $2.328\ A^{0.266}$ if $A < 10$	Leigh 2010
Channel depth (m) = $0.0305\ A^{0.507}$	Webster 2007
CBOM annual input (mgC m^{-2} yr^{-1}) = $184382\ e^{(-0.0021*A)}$	Webster 2007

Table 3-2. Model parameter values for initiating stream network model and ranges of model parameter values for Sobol sequence randomization used in global sensitivity analysis.

Parameters	Value for initiation	Min value	Max value	References
Spring [NH_4] µg/L	0	-	-	Webster et al. 2009
Spring [NO_3] µg/L	25	-	-	Webster et al. 2009
Spring [PO_4] µg/L	2	-	-	Webster 2001, 2009
Detritus mass C:N	93.5	34	95	Cross et al. 2005
Detritus mass C:P	490.1	490	1830	Cross et al. 2005
Detritus cellulose %	20.3	10	40	Berg and McClaugherty 2008
Detritus lignin %	16.3	8	30	Berg and McClaugherty 2008
Immobilizers mass C:N	7.2	2.4	10	Cross et al. 2005
Immobilizers mass C:P	188.1	18	385	Cross et al. 2005
Miner mass C:N	4.7	2.4	10	Cross et al. 2005
Miner mass C:P	20.2	18	385	Cross et al. 2005

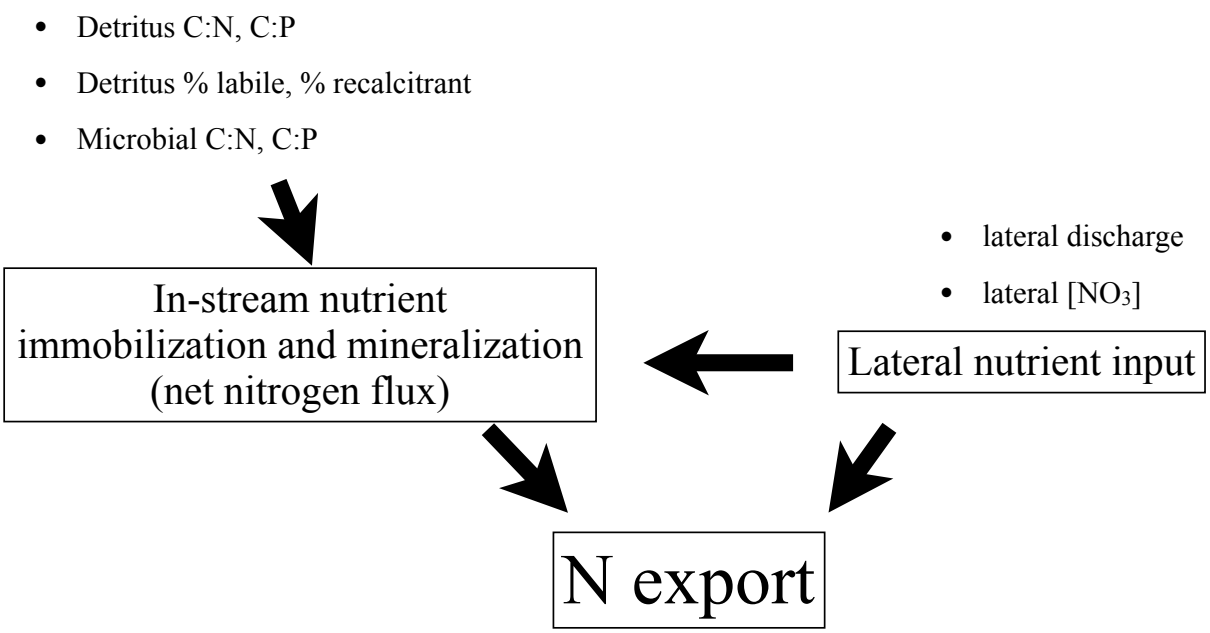

Figure 3-1. Factors influencing nitrogen export in streams.

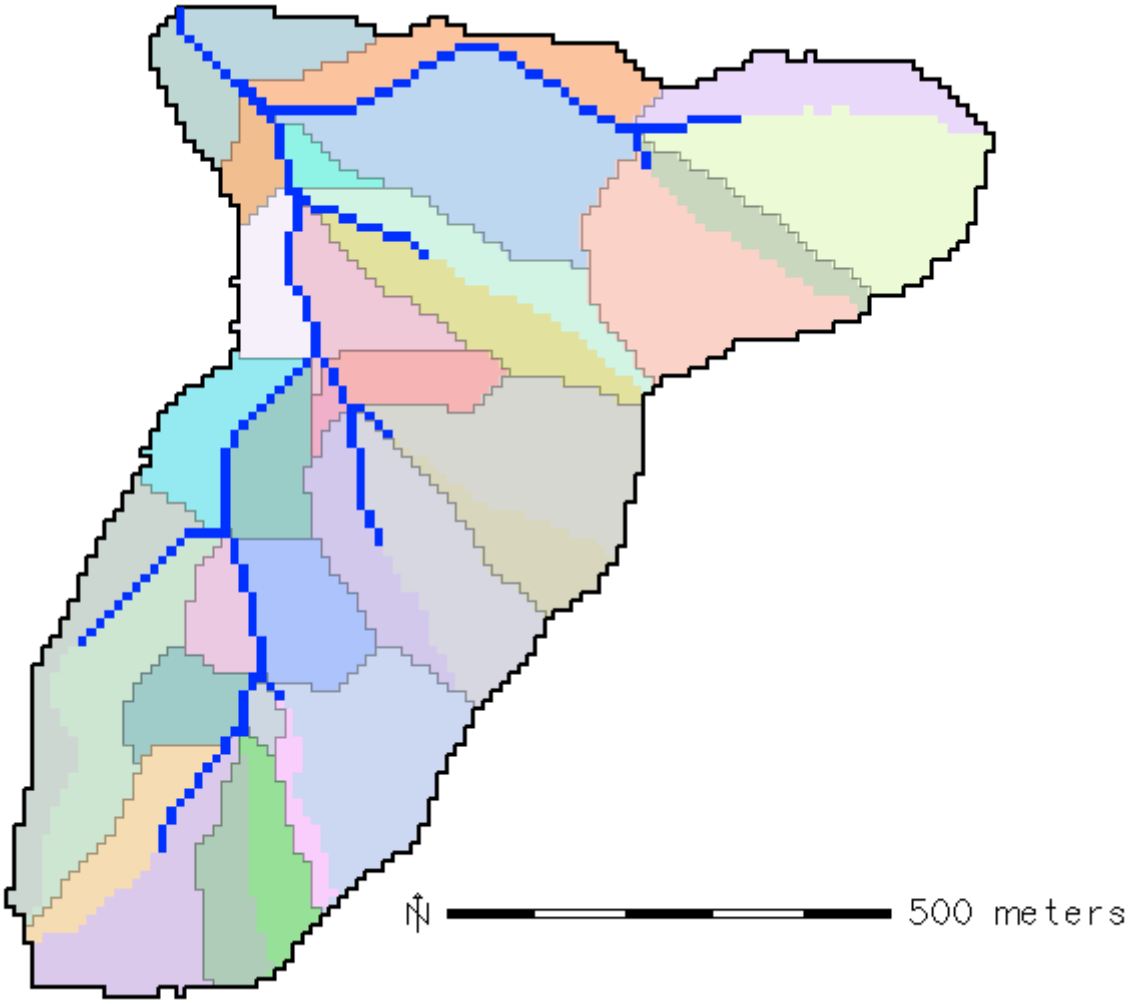

Figure 3-2. Subcatchments, hillslopes, stream segments, and stream network extracted from GRASS GIS with a 10 m × 10 m spatial resolution DEM at HWC, Coweeta. Gray boundaries indicate subcatchments and two colors in each subcatchment indicate two hillslopes, one on each side of a stream segment. There are 17 stream segments labelled by number IDs. The stream generally flows north.

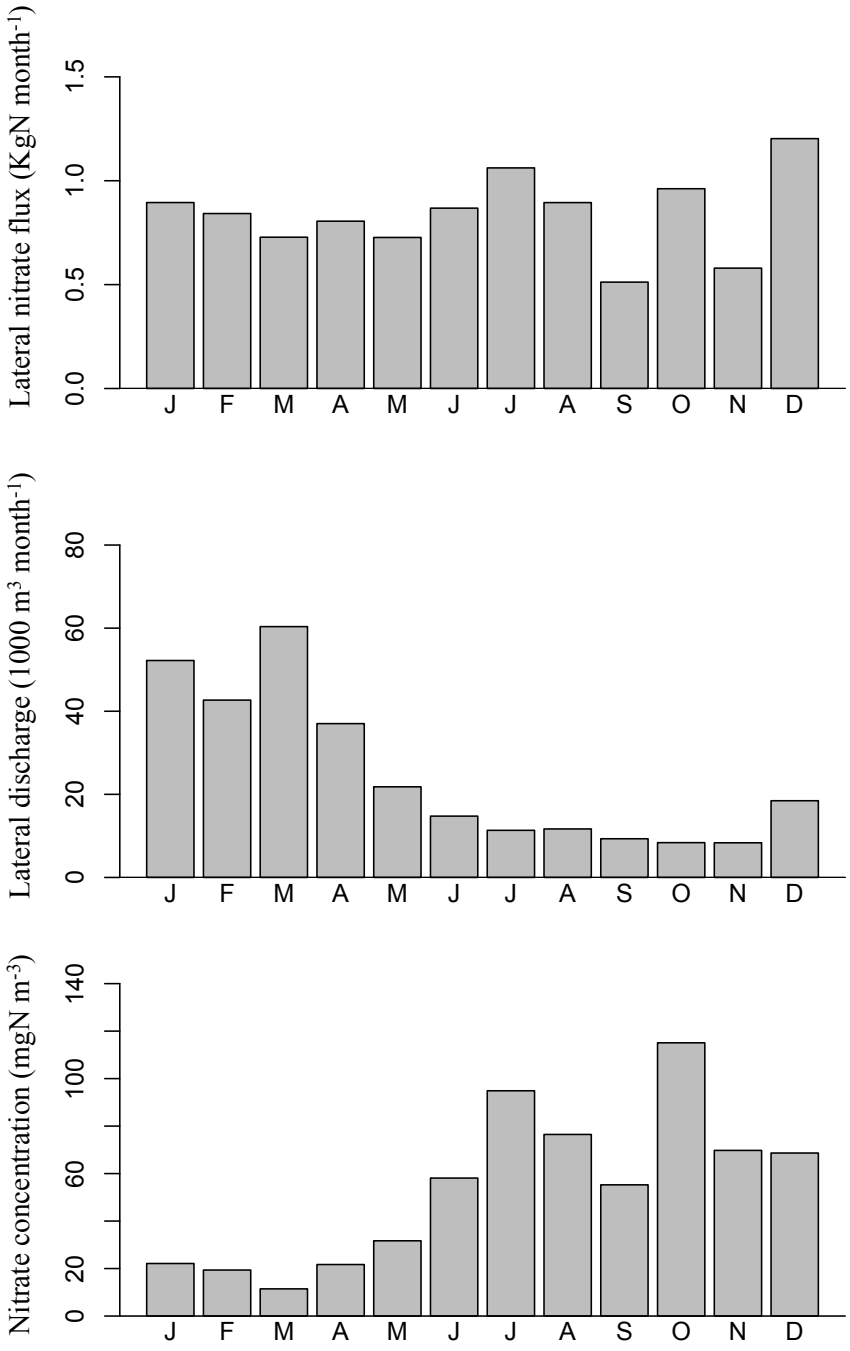

Figure 3-3. Monthly lateral nitrate flux (top), lateral discharge (middle), and nitrate concentration (bottom) from the Regional Hydro-Ecologic Simulation System (RHESSys).

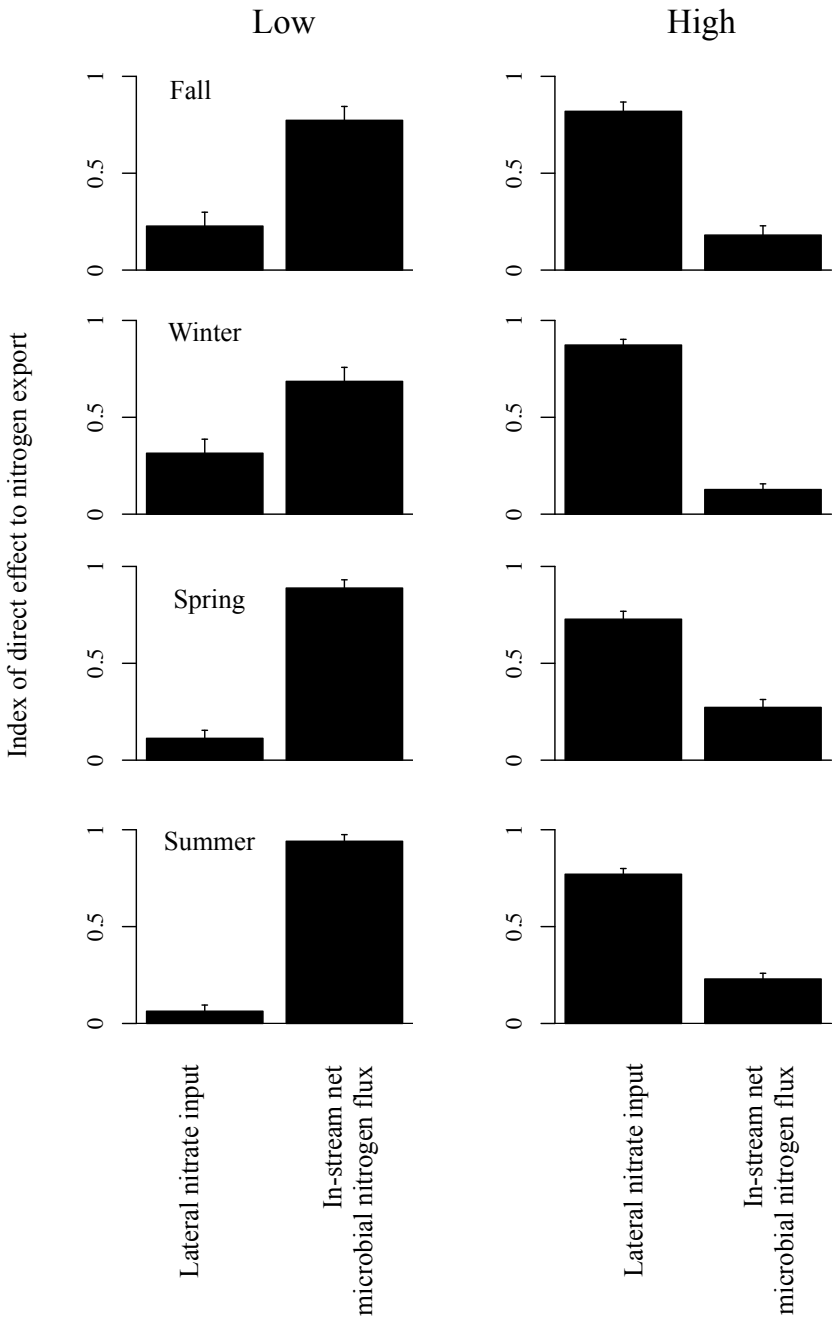

Figure 3-4. Index of direct effects of lateral nitrate input and in-stream net microbial nitrogen flux on nitrogen export under scenarios with low (low) and high (high) lateral nitrate input.

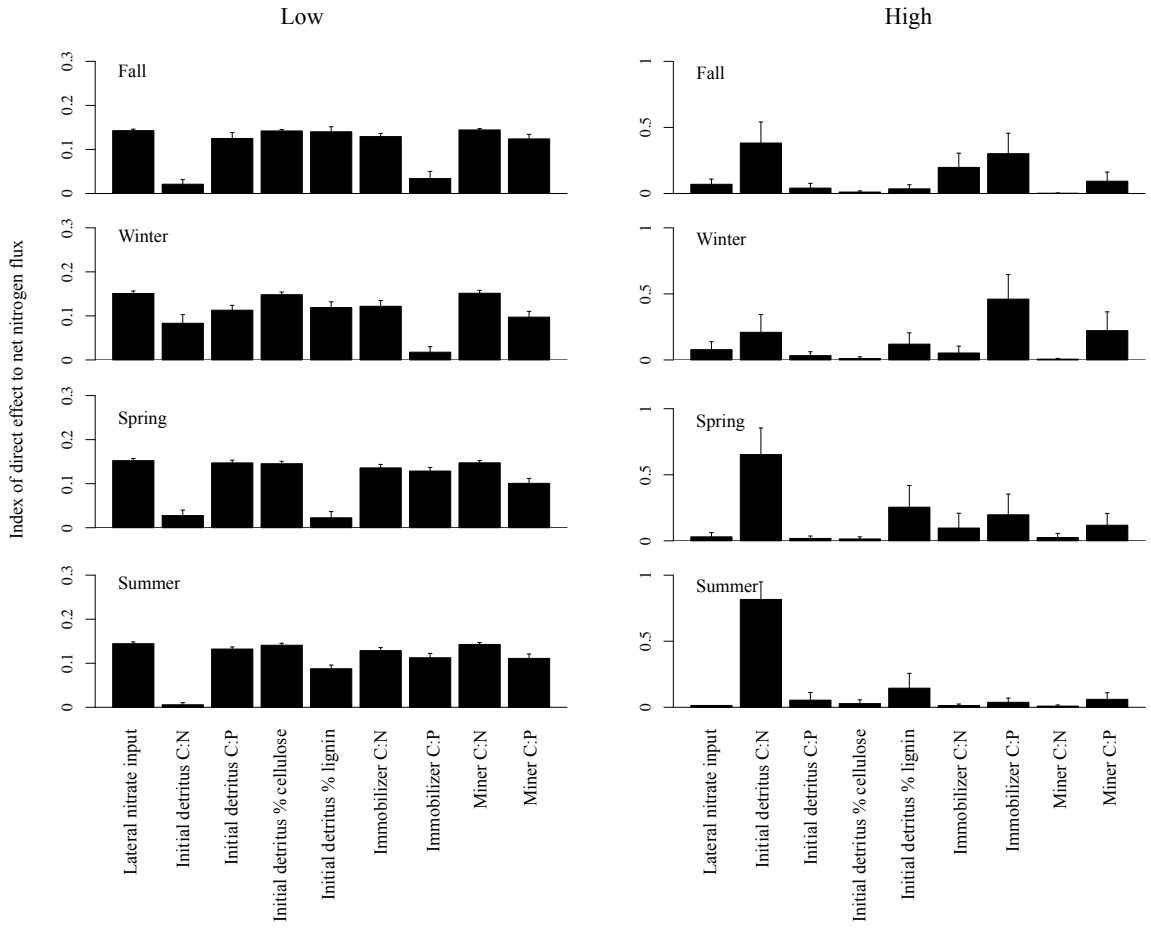

Figure 3-5. Index of direct effects of lateral nitrate input, detritus and microbial stoichiometry, and detritus substrate quality on in-stream net microbial nitrogen flux under scenarios with low (low) and high (high) lateral nitrate input from terrestrial.

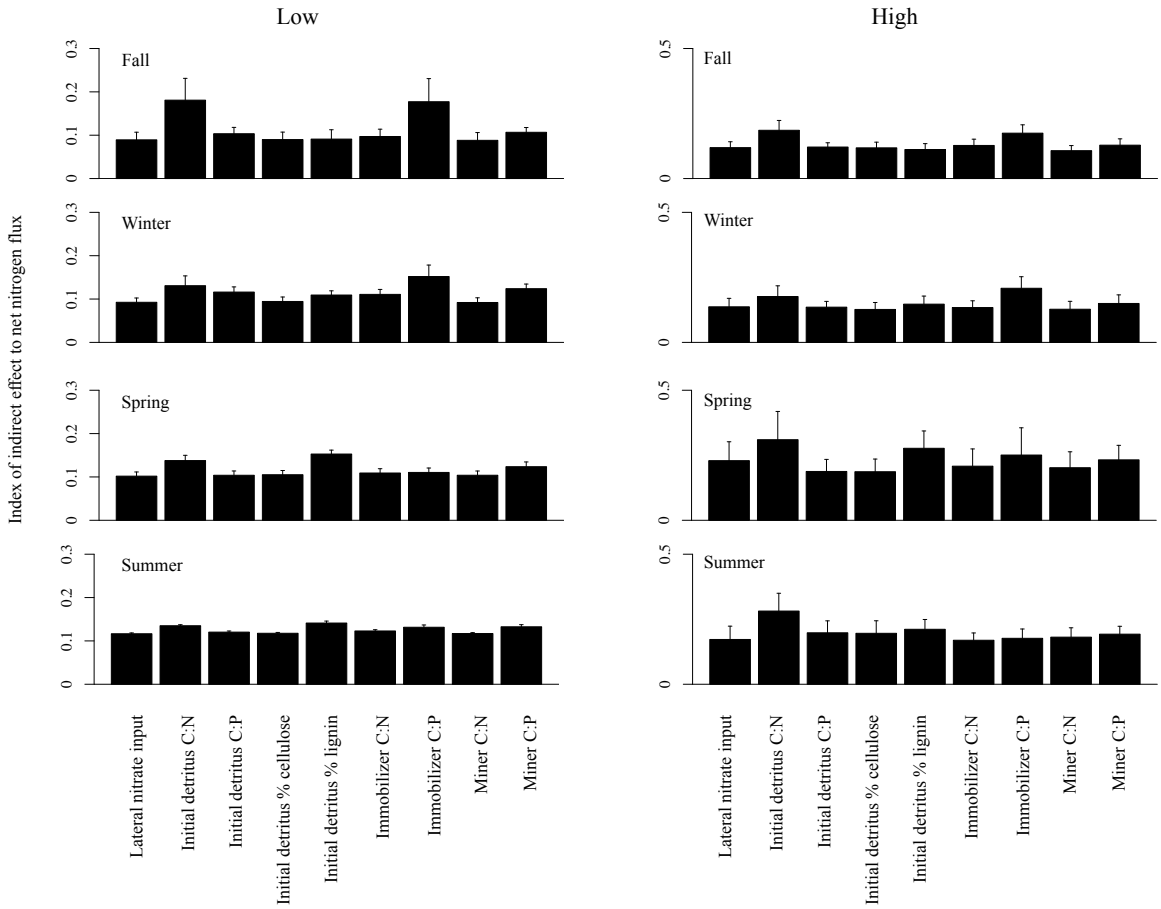

Figure 3-6. Index of indirect effects of lateral nitrate input, detritus and microbial stoichiometry, and detritus substrate quality on in-stream net microbial nitrogen flux under scenarios with low (low) and high (high) lateral nitrate input from terrestrial.

Chapter 4

Influences of Mountainside Residential Development to Dissolved Inorganic Nitrogen Dynamics in a Stream Network: A Simulation Study

4.1 Introduction

The term "exurbanization" was originated by Spectorsky (1955). Beale (1982) and Herbers (1989) described exurbanization as development extending far into the countryside but within commuting range to urban and suburban areas. Exurbanization has accelerated across the U.S. since the 1950s-60s and has been estimated to be the fastest-growing component of the U.S. landscape (Nelson and Dueker 1990, Brown et al. 2005, Hansen et al. 2005). During the period of 1960 to 1985, approximately 24-25% of the U.S. population lived in exurban areas (Nelson and Dueker 1990), while the exurban population increased to 37% by 2000 (Sutton et al. 2006). Exurban area within the conterminous U.S. increased fivefold from 1950 to 2000 (Brown et al. 2005).

Growth in exurbanization has raised many challenges for society, economics, and the environment (Burchell 1998, Sutton et al. 2006). In this study, I focused on mountainside residential development, which is one type of exurbanization and specifically refers to people building houses on the side and tops of mountains far away from cities. Mountainside residential development may not only substantially affect the forest and stream ecosystems where people build new homes and enjoy natural landscapes but also has far-reaching impacts on ecosystem services provided by forest and streams to people living in both rural areas and cities (Webster et al. 2012). Pearson et al. (1998) showed the impacts of exurbanization on landscape fragmentation. Agricultural, urban, and suburban development have resulted in a landscape

consisting of a mosaic of forest patches interspersed with agricultural and suburban land. Pearson et al. (1998) showed that density and distribution of plant species in such fragmented forest patches depended on patch size and isolation. Viviroli et al. (2007) demonstrated the threats of mountainside development to stream systems in the southern Appalachian Mountains and emphasized that such threats extend beyond the mountain itself and into low-lying urban areas that depend on the mountains for water supply. With long-term and basin-wide data, Webster et al. (2012) showed that exurbanization is changing land cover and land use in the Upper Little Tennessee Basin and found that mountainside development can be a major contributor to elevated stream nitrate concentration. Garrison and Wakeman (2000) showed that exurbanization around four Wisconsin lakes affected water quality and diatom communities.

Impacts of exurbanization have only recently been the topic of ecological studies (Hansen et al. 2005). Investigation of these impacts has been limited to comparison between reference areas and the areas subject to exurbanization (e.g., Garrison and Wakeman 2000), synthesies of existing land cover/land use information (Cifaldi et al. 2004, Theobald 2005, Webster et al. 2012), or analysis across multiple studies (e.g., Marzluff 2001, Hansen et al. 2005). Thus, our understanding of impacts of exurbanization has been limited to the correlation between land cover/ land use changes and ecosystem responses. Webster et al. (2012) suggested that a more predictive understanding of how rapid changes in land cover and land use affect water quality in traditional rural areas is a major challenge for future research. Hansen et al. (2005) emphasized that considerable research is urgently needed to better understand the impacts of residential home density, spatial distribution, and homeowner behavior during ex-urbanization. However, manipulation of large-scale mountainside development through experiments would be difficult and costly. Therefore in this study, I used simulation to extend our understanding from

correlation to more detailed and quantitative information of how density and spatial distribution of mountainside development influence nutrient dynamics in a regional stream network.

Ecological research has shifted from site-based science to regional and global scales (Peters et al. 2008) and has shifted from conceptual scope to multidisciplinary integration (Liu et al. 2007, Collins et al. 2010). Many studies have shown that spatial scale matters when predicting stream water chemistry using land cover (reviewed by Allan 2004). For example, whole catchment land cover can be useful for in-stream nitrate prediction (e.g., Omernik et al. 1981, Jones et al. 2001, Strayer et al. 2003), while riparian land-cover can be a better predictor for phosphorus prediction (e.g., Osborne and Wiley 1988, Johnson et al. 1997, Jones et al. 2001). Webster et al. (2012) emphasized the importance of considering impacts of mountainside development at a basin-wide level in making management decisions to protect water resources. In this study, I simulated the whole stream network, extending from local riparian to catchment and further to regional basin scale, and I coupled terrestrial and stream models that integrate climate, forest processes, hydrology, water chemistry, and in-stream nutrient processes.

The overall goal of this study was to expand our understanding of the influences of mountainside development on dissolved inorganic nitrogen dynamics in a stream network and to provide insights for land and river management in mountainous areas. Specifically, I explored how (1) mountainside housing density, (2) protective buffer zones, and (3) stream travel distance from houses to catchment outlet affect dissolved inorganic nitrogen export within local catchments and through the whole regional network. I constructed a regional basin based on the drainage area above the Prentiss gage on the Little Tennessee River in southwestern North Carolina and north Georgia (Fig. 4-1). I then conducted the simulation by coupling a terrestrial

model, the Regional Hydro-Ecologic Simulation System (RHESSys, Tague and Band 2004) with a stream network model that I developed in Chapters 2 and 3.

4.2 Methods

Model description

I conducted the simulation study by linking forest and stream models through water and nitrogen fluxes. I used RHESSys as the forest model to simulate forest hydrologic and nitrogen processes. I modified the nitrogen processes in the RHESSys model to better approximate nitrate export to streams (personal communication with Dr. Band and Dr. Hwang, University of North Carolina, Chapel Hill, NC). These modifications allowed plants and soil microbes to access surface accumulated nitrate and ammonium when the nutrients within soil were depleted. I calibrated the hydrological parameters in the RHESSys model based on studies of Watershed 8 at Coweeta Hydrologic Laboratory, NC. I adopted the soil hydrological and plant physiologic parameters from White et al. (2000), Dingman (2002), and Hwang et al. (2009) with additional personal communication with Dr. Band and Dr. Hwang (University of North Carolina, Chapel Hill, NC).

The stream model that simulated in-stream process was developed in previous chapters. This model is geographic information system (GIS) based and includes both hydrological processes such as downstream transportation, transient storage, and lateral inflow from hill-slopes, and biological processes such as detritus breakdown, nutrient immobilization, mineralization, nitrification, and denitrification. The stream model assumes two mechanisms for detritus breakdown, fragmentation via current forces and macro-invertebrate consumption, and decomposition driven by microbes that immobilize and mineralize nitrogen. Nitrification occurs

in the water column and denitrification occurs in transient storage. The model also specifies detritus stoichiometry (C:N and C:P) and substrate quality (% labile, % intermediate, and %refractory). Details of the stream model development were described in Chapters 2 and 3. Calibration of the stream model was based on studies of Hugh White Creek (HWC, Coweeta Hydrologic Laboratory, NC, USA).

Simulation

The impacts of mountainside residential development on nutrient dynamics in streams were simulated in a regional basin (Fig. 4-1). This regional basin was based on the drainage area of the Little Tennessee River above the Prentiss gage near Franklin, NC. The majority of this drainage area is forested with most urban developed areas located along the 5-6 order main channel in the valley. Some pasture and crop lands may extend from valley to headwater areas. Land cover within the basin was based on the land cover derived from 2001 NASA Landsat Thematic Mapper Image and classified by Jeff Hepinstall and Hunter Allen (Warnell School of Forestry and Natural Resource, University of Georgia, Athens, GA 30602). The road network was derived from the Macon County GIS by Dr. John Chamblee (University of Georgia, Athens, GA 30602). Forest cover and surface impermeability were based on the National Land Cover Database (NLCD) 2001. Soil properties were derived from USDA NRCS Soil Data and classified by Dr. Teahee Hwang (University of North Carolina, Chapel Hill, NC). The stream network within the basin comprised 5443 stream segments, each of which had a single channel with hillslopes on both sides. Stream segments were extracted using an elevation map with 10 m × 10 m resolution and 4 ha as the minimum drainage area using GRASS GIS (version 6.4).

Within each segment, water runoff and nitrogen flux from the RHESSys model were then used as input from hillslopes to the stream channel.

Climate in my simulation varies spatially within basin. I obtained daily climate data (precipitation, maximum and minimum air temperature) from 2000 to 2010 at climate stations (Coweeta, Franklin, Highlands, and Mountain City) within or near to the basin. I assumed nitrogen deposition to be spatially uniformed over the regional basin with a value of 0.001 kgN m^{-2} yr^{-1} (Knoepp et al. 2008). With additional information on fertilizer use (personal communication with Dr. Band and Dr. Hwang, University of North Carolina, Chapel Hill, NC), I also estimated nitrate-fertilizer use based on land cover (Table 4-1).

Before manipulating residential development in the basin, I calibrated both the RHESSys model and the stream model, and I ran both models for a sufficient number of years to have their outcomes reach the current leaf area index (LAI) of the forests and the current detritus standing crop in streams. Specifically, I first calibrated RHESSys hydrologic parameters based on Watershed 8 in Coweeta and used it for the whole basin. Long-term precipitation and stream flow records were available for Watershed 8. I then ran the calibrated RHESSys model for 300 years until forest biomass reached the current forest stage. With the initialized RHESSys model, I additionally simulated 20 years of hillslope hydrology and nitrogen flux, and then used these outcomes as input to the stream model for initializing the stream model. Biological parameters in the stream model were calibrated based on Watershed 14 data (Hugh White Creek) in my previous studies. Manipulation of mountainside residential development in my simulation was based on these initialized models.

In the manipulation of mountainside residential development, I restricted the residential development to areas that satisfied three criteria (highlighted in red in Fig. 4-1): (1) more than

80% forest cover, (2) at least 500 m away from third-order streams, and (3) in the upper 60% of the catchment elevation. I developed three simulations in this study and set the basin without residential development as the baseline scenario for each simulation. In the first simulation, I used three different densities of residential development based on currently observed housing densities within the region. The three residential development densities were 14,213 m^2 residential area (high), 7169.5 m^2 residential area (medium), and 126 m^2 residential area (low) per km^2, with the assumption of each residential development occupied an area of 30×30 m^2 (nine grid cells). Of the nine gird cells that each residential development occupied, I defined the center grid cell to be a house and the surrounding grid cells to be garden and drive way. In the second simulation, I had two scenarios, allowing residential development within a 30-m buffer zone adjacent to streams versus protecting the buffer zone from residential development. In the third simulation, I had residential development occur 0-26 km, 26-39.5 km or 39.5-49 km away from the catchment outlet in terms of stream travel distance (Fig. 4-1). Locations of residential development in all simulations were randomly assigned within the designated areas. With the initialized models, I conducted each of the three simulations for eight years and presented results from the last four years. Because I incorporated climate information during the simulations, variability (error bars) in outcomes reflected annual climate variation.

To reduce computing time and improving calculation efficiency, I divided the whole basin into 1633 small regions based on stream network structure. I initialized the RHESSys (version 5.15) model on Virginia Tech high performance computer cluster (HokieOne). The stream model was programmed in JAVA (version 7) with parallel processing. All simulation results were organized and analyzed in R (version 3.0.1).

In this study, I present the results from both the local scale and the regional scale for my simulations. For the local scale results, I show the areal nitrogen export (i.e., the nitrogen export corrected by drainage area) under each of the first two simulations (simulations for residential density and buffer zone protection) for one local catchment (Fig. 4-1) as an example. Within this local catchment, I traced the areal nitrogen export along the main stream, and I selected five sites for detailed information. These five sites were 592 m (A), 726 m (B), 1116 m (C), 1429 m (D), and 3950 m (E) downstream of the origin of the main stream (0 m), respectively. At each of the sites from A to D, stream branches subject to residential development join the main stream. From site D to E, the main stream runs through patches of agriculture. For the regional scale results, I show the change in areal nitrogen export at the outlet of the regional basin relative to the baseline scenario for each of the three simulations.

4.3 Results

Areal nitrogen export and net nitrogen flux at local scale

At the local scale, baseline annual areal nitrogen export showed little longitudinal variation (Fig. 4-2). As stream branches joined the main stream at sites A, B, and C, I observed spikes of nitrogen export at these sites. Areal nitrogen export increased from site D to E in baseline scenario when passing patches of agriculture along the main stream in between these two sites. Residential development resulted in higher areal nitrogen export (Fig. 4-2). The differences among simulations became less further from the stream origin as the influence of housing density on nitrogen export decreases downstream.

The monthly patterns of areal nitrogen export and net nitrogen flux (mineralization - immobilization) for sites A, B, and C were similar, and thus I only reported the results for sites

A, D, and E under different housing density scenarios at the local scale (Fig. 4-3). At these three sites, monthly areal nitrogen export increased at higher housing density, with more variation in late summer and early fall. The seasonal pattern in areal nitrogen export tended to diminish with higher housing densities. Regardless of housing density, the magnitudes of net nitrogen immobilization and mineralization became higher as long as residential development occurred, which may indicate nutrient saturation effect (i.e., nutrient in streams was sufficient for immobilization) so that additional nutrient introduced by higher housing densities did not further increase immobilization. Net nitrogen flux in May was an exception in that the net flux for the baseline scenario was higher than that for housing development scenarios.

In the simulation with different buffer zone management strategies, the annual areal nitrogen export under both scenarios (i.e., the scenarios with and without buffer zone protection) produced spikes at sites A, B, and C where stream branches subject to housing development joined the main stream and was less variable downstream (Fig. 4-4). Areal nitrogen export in this local catchment was higher when residential development occurred within the buffer zone, and such impacts became less obvious downstream.

Areal nitrogen export at the regional scale

Similar to results at the local scale, at the regional scale (Fig. 4-5), higher housing density led to an increase in areal nitrogen export relative to the baseline scenario. Greater nitrogen export was observed when houses were built within the buffer zone compared to when the buffer zone was protected from residential development. Also when houses were built closer to the catchment outlet in terms of stream travel distance, there was higher areal nitrogen export. In all

three simulations, I observed similar seasonal patterns of the percentage change in areal nitrogen export, with greater difference in winter and spring and less difference in summer and fall.

4.4 Discussion

Since the wave of exurban development in the 1950-60s, many questions have arisen. One of the questions is how housing density and spatial distribution affect the impacts of exurbanization. It has been believed that these impacts are proportional to housing density (Hansen et al. 2005), and residential development is often associated with areas of natural and cultural amenities rather than being randomly distributed (Cromartie and Wardwell 1999, McGranahan 1999, Nelson 1999). However, investigation of exurbanization impacts on water quality has been limited to correlation between land cover/land use and water quality (e.g., Webster et al. 2012) because large-scale land cover manipulation on forested mountains are impractical. Additionally, the impacts of exurbanization may be manifest for several decades and ecosystems are likely still responding to it, which may make experimentation even more difficult. With a simulation approach such as this study, I can synthesize our existing understanding of forest and stream ecosystems and incorporate climate, soil biogeochemistry, hill-slope and groundwater hydrology, and in-stream nutrient processes to explore the causation between exurbanization and ecosystem responses at a large spatial scale and a high temporal resolution (e.g, daily variation). Although I provided limited insights for addressing several aspects of this question through the present study, I demonstrated an application of simulation approach to investigate complicated ecological questions.

My results showed that upstream net nitrogen flux (both net immobilization and net mineralization) increased under mountainside residential development but such increase was not

proportional to development density. These results suggest that upstream immobilization was nitrogen limited in the baseline scenario and became nitrogen saturated under housing development. I calculated the percent increases in nitrogen flux from hillslopes to streams for different density scenarios relative to the baseline scenario and found the percent increase to be proportional to housing density (Table 4-2). I also estimated the in-stream nitrogen retention efficiency (i.e., 100% × (1 – nitrogen export / lateral nitrogen input)) and found that the retention efficiency generally declined as nitrogen input increased in the density scenarios (Table 4-3). This decline in retention efficiency further supports my suggestion of upstream nitrogen saturation with housing development. In medium and high housing density scenarios, the retention efficiency in the local catchment became slightly negative for some years, indicating that nitrogen export was greater than lateral nitrogen input. The lateral nitrogen input used in the retention efficiency calcualtions includes only inorganic nitrate in the lateral water input. I did not include the input of organic nitrogen in leaf-fall. One reason of nitrogen export being higher than nitrogen input(negative retention efficiency) is that higher lateral nitrate input stimulated detritus decomposition. Consequently, more detritus nitrogen was mineralized and exported.

Additionally, I calculated the contribution of denitrification to nitrogen retenetion (Table 4-2). Denitrification contributed approximately 2% to nitrogen retention in the baseline scenario and up to 8% in the high housing density scenario. Mulholland et al. (2008, 2009) found denitrification highly variable in streams within the Little Tennessee basin. Denitrification contributed to the total nutrient uptake (k_{den} / k_{total} ×100%) ranged from 3 to 100% with average 49%.

I also found that with increased nitrogen input to streams, the immobilizer:miner ratio increased from 64.2 in the baseline scenario to 81.3 in the high density scenario, the benthic

detritus pool increased from 285 gAFDM/m^2 301 gAFDM/m^2, and detritus C:N declined from 46.1 for CBOM and 40.3 for FBOM to 43.7 for CBOM and 36.8 for FBOM. In an annual basis, nitrogen retention by immobilization is temporary because microbes eventually mineralize the detrital nitrogen and the previously immobilized nitrogen. I found that with more nitrogen available, microbes immobilized more nitrogen via three mechanisms: (1) a greater uptake rate; (2) immobilizers becoming more dominant in the microbial assemblage; and (3) increased detritus pool size due to nitrogen suppression of nutrient mining, which further resulted in an overall higher microbial density on detritus. With a higher density of immobilizers and a higher detritus pool size, the C:N of detritus was lower, as was the C:N of FBOM and seston.

At sites A to D, patterns of areal nitrogen export and net nitrogen flux in the baseline scenario reflected seasonal patterns in typical forested mountain streams (Fig. 4-3). As leaf-fall began at the end of September, net immobilization occurred through winter, i.e., immobilization was greater than mineralization. In the later stages of leaf decomposition, net immobilization declined and net mineralization (i.e., mineralization greater than immobilization) gradually dominated in-stream process during spring and summer. Correspondingly, I observed higher areal nitrogen export in spring and summer in the baseline scenario due to net mineralization and lower areal nitrogen export in fall and winter due to net immobilization. By contrast, at site E in the baseline scenario, there was little seasonal pattern of areal nitrogen export and net nitrogen flux probably due to nitrogen saturation of microbial processes as a result of high nitrogen input from nearby agriculture areas between sites D and E.

Seasonal pattern of nitrogen export became less obvious as housing density became higher (Fig. 4-3). Due to saturation of nitrogen immobilization, nitrogen export during fall and winter increased under mountainside residential development. Although mineralization cannot

become saturated by nitrogen, higher nitrogen immobilization may lead to higher nitrogen mineralization. Thus, nitrogen export was also elevated but not as much as during the net mineralization period (spring and summer) under mountainside residential development.

The influence of mountainside residential development was greatest near the headwaters but was diluted downstream (Figs. 4-2 and 4-4) and became undetectable at the regional scale. At the regional scale, nitrogen input to streams caused by the highest housing density only increased by 0.5% compared to the baseline scenario (Table 4-4). Although only this slight increase in nitrogen input to streams occurred with mountainside residential development, nitrogen retention efficiency at the regional scale decreased from 8% (baseline scenario) to 6.8% (high density scenario). This result suggested that the impact of mountainside residential development may depend on spatial scale. Many studies have demonstrated the importance of spatial scale in investigating relationship between land cover and stream water chemistry (e.g., Johnson et al. 1997, Jones et al. 2001, Allan 2004). At the regional scale, although I would expect impacts to be diluted, I were still able to detect these impacts (Fig. 4-5). In a simulation study, it is more appropriate to focus on relative change rather than absolute output due to the hypothetical setup, especially in a situation where information is limited and/or with large uncertainty.

My simulation results showed that mountainside residential development influenced nitrogen export and in-stream processes. Residential development increased terrestrial nitrogen input to streams, leading to an increase in microbial nitrogen flux and modified nitrogen export. These results may provide directions and hypotheses for future comparative and experimental studies. Additionally, this study has implications for land and river management in mountainous areas. For example, regulation for lower density housing is often used to protect ecological

resources because it is believed that impact of exurban development is proportional to housing density (Hansen et al. 2005). My results supported this lower housing density strategy. Alternatively, many local planners often recommend clustered residential development (urban sprawl) to reduce the total road density and to increase the overlap of impacts from each home, which will further reduce the ecological impacts of exurbanization and the costs of government services (Daniels 1998). High intensity development might also have centralized waste treatment and generate a less fragmented landscape. Although I did not explore the scenario with different cluster patterns, my results with scenarios of buffer zone protection and stream travel distance suggest that spatial distribution of residential development needs to be considered in land management.

As to the seasonal pattern of net microbial nitrogen flux at the five sites (Fig. 4-3), the net nitrogen flux in the baseline scenario was higher than that in all density scenarios in May, which was different from the patterns in other months. I suggest that high nutrient input to stream associated with residential development may delay the switch from net immobilization to net mineralization. According to the simulations, this switch generally occurs in May in forested mountain streams. At this time, immobilization decreases while at the same time mineralization increases. My results seemed to indicate that although the switch still started in May, at those streams subject to residential development, mineralization did not increase fast or intensively enough to override immobilization, which led to the switch occurring later than in the baseline scenario. Thus I observed lower net nitrogen mineralization in residential development scenarios than in the baseline scenario in May, but starting in June net mineralization in residential development scenarios consistently became higher.

There are two major improvements that could be made for this simulation study in the future. First, the fertilizer use in agriculture and urban lawns was roughly estimated based on previous studies, and a sensitivity analysis to explore the influences of different fertilizer levels to simulation outcomes would be valuable. Results showed that headwater streams quickly became nitrogen saturated in residential development scenarios, resulting in higher nitrogen export (Fig. 4-3, site A). At higher nitrogen input associated with higher housing density, downstream areas also became nitrogen saturated (Fig. 4-3, site B). I would expect that manipulation of the fertilizer level might influence this nitrogen saturation. Second, Webster (2007) suggested that primary production further downstream could be a significant component at a regional scale. However, I did not include primary production in the stream network model.

This study could be extended by exploring more scenarios of ecological and management interest. For example, region specific information could be incorporated in the model for better prediction for a particular region. Questions related to where to build a house (e.g., at borders of national forests or at areas with easy access to towns and cities) and how to arrange houses (e.g., more clustered or more scattered) could also be explored by constructing corresponding scenarios.

In conclusion, with the simulation modeling approach that integrated our existing understanding of exurbanization and terrestrial and stream ecosystems, I explored the influences of mountainside residential development on nitrogen export in streams at local and regional scales. Results showed that higher residential density, house development closer to streams, and residential development closer to the catchment outlet led to higher nitrogen export at both the local and regional scales. Although my conclusions are based on many model assumptions and need to be further validated through well-designed field and laboratory studies, my hope is that

this study will expand our understanding of impacts of exurbanization on stream ecosystems, identify directions for further research, and provide insights for land and river management in mountainous areas.

4.5 Acknowledgement

This study was part of the Coweeta Long Term Ecological Research study funded by National Science Foundation grant, DEB0823293.

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Table 4-1. Estimated fertilizer use for different land covers.

Land cover types	Estimated fertilizer use (kg N m^{-2} yr^{-1})
Crops	0.013
Pasture	0.013
Low urban	0.008
Medium urban	0.065
High urban	0.065
Mountainside residential housing	0.008
Mountainside residential garden / grassland	0.013

Table 4-2. Percent change in nitrogen flux at different mountainside residential densities relative to nitrogen flux in the baseline scenario at the local catchment.

Housing density	% increase in annual nitrogen flux from hillslope to stream	% increase in annual nitrogen export from the local catchment
Low	0.69	3.24
Medium	8.95	9.35
High	11.34	16.08

Table 4-3. Retention efficiency (mean± standard error) of nitrogen at the local catchment and the regional basin. Retention efficiency = 100% × (1 - nitrogen export / nitrogen input from hillslopes to streams).

	Local catchment		Regional basin
Housing density	Retention (%)	Denitrification contribution to retention (%)	Retention (%)
Baseline	5.18±0.63	2.4±0.2	8.03
Low	2.77±0.67	6.2±2.4	7.94
Medium	4.77±0.90	2.9±0.4	7.24
High	1.08±0.86	8.6±2.7	6.81

Note: Negative retention efficiency indicated that nitrogen export was greater than nitrogen input from hillslopes to streams.

Table 4-4. Percent change in nitrogen flux at different mountainside residential densities relative to nitrogen flux in baseline scenario at regional basin.

Housing density	% increase in annual nitrogen flux from hillslope to stream	% increase in annual nitrogen export from local catchment
Low	0.04	0.09
Medium	0.38	0.86
High	0.54	1.32

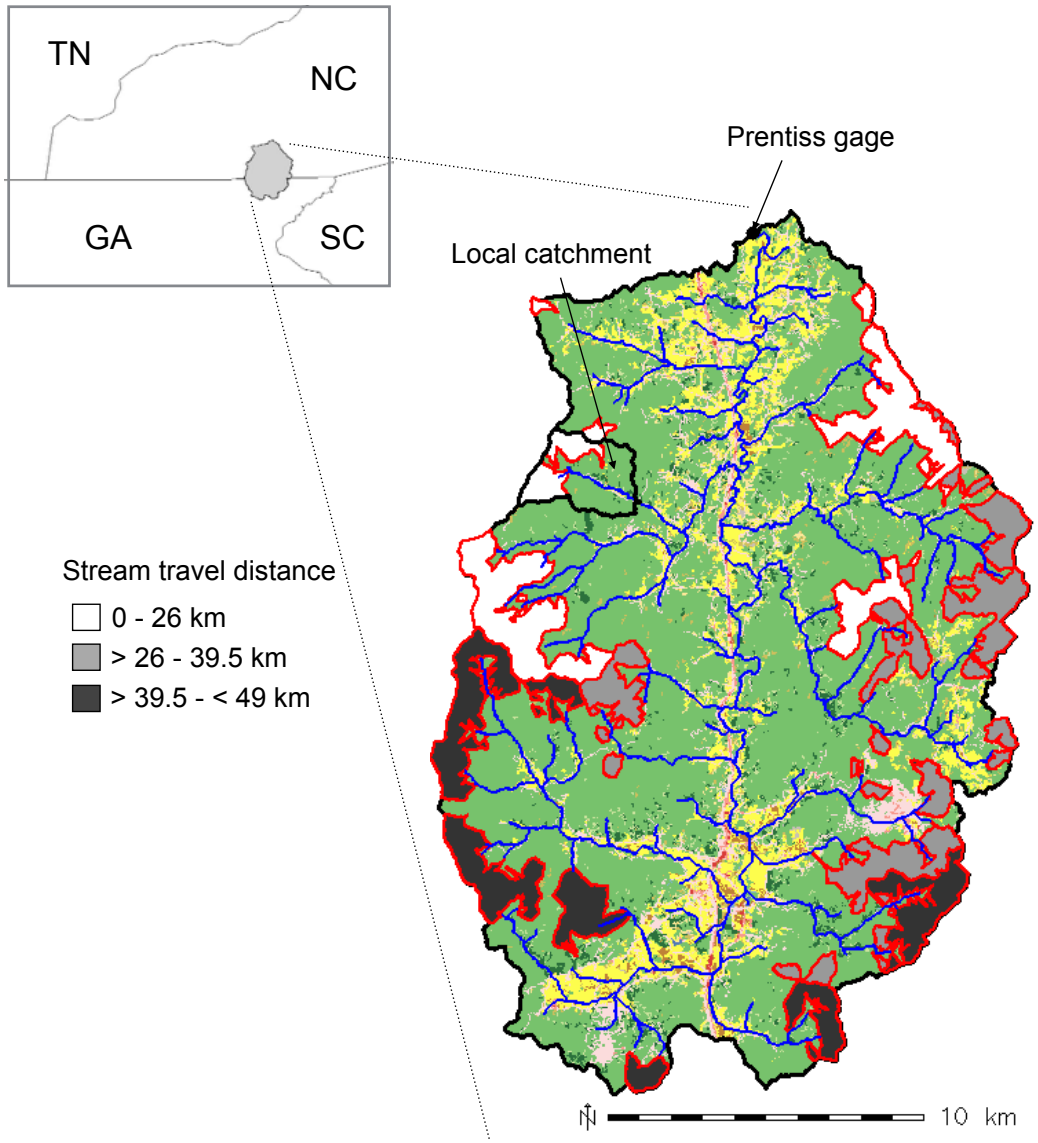

Figure 4-1. The basin that I used for this simulation study was based on the upper Little Tennessee basin in the southern Appalachians. The basin boundary is the drainage area above Prentiss, NC. Its area is about 524 km^2 (52355 ha). Blue lines represent streams and rivers. Black lines outline the smaller catchment used for demonstrating the effects of mountainside residential development at the local scale. Red lines highlight potential areas for mountainside residential development based on the three criteria. These areas are further classified into three

groups by stream travel distance. The total areas of these three groups are 2360 ha, 2296 ha, and 2358 ha respectively.

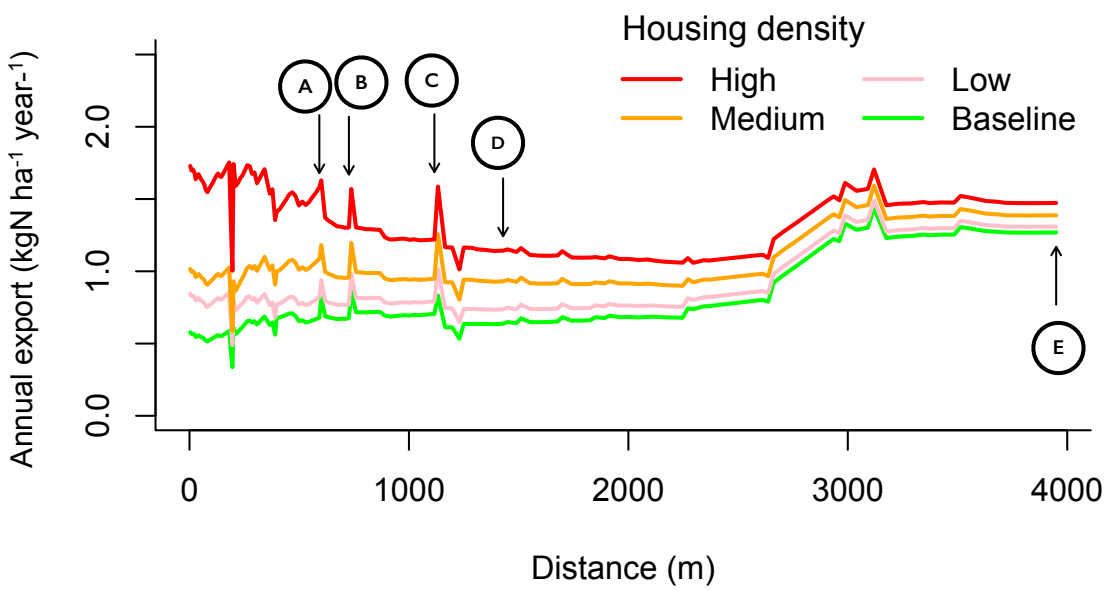

Figure 4-2. Annual areal nitrogen export along the main stream within the local catchment for the simulation with different residential development densities. Five sites (A-E) were selected within this local catchment for detailed information. These five sites are 592 m (A), 726 m (B), 1116 m (C), 1429 m (D), and 3950 m (E) away from the origin of the main stream.

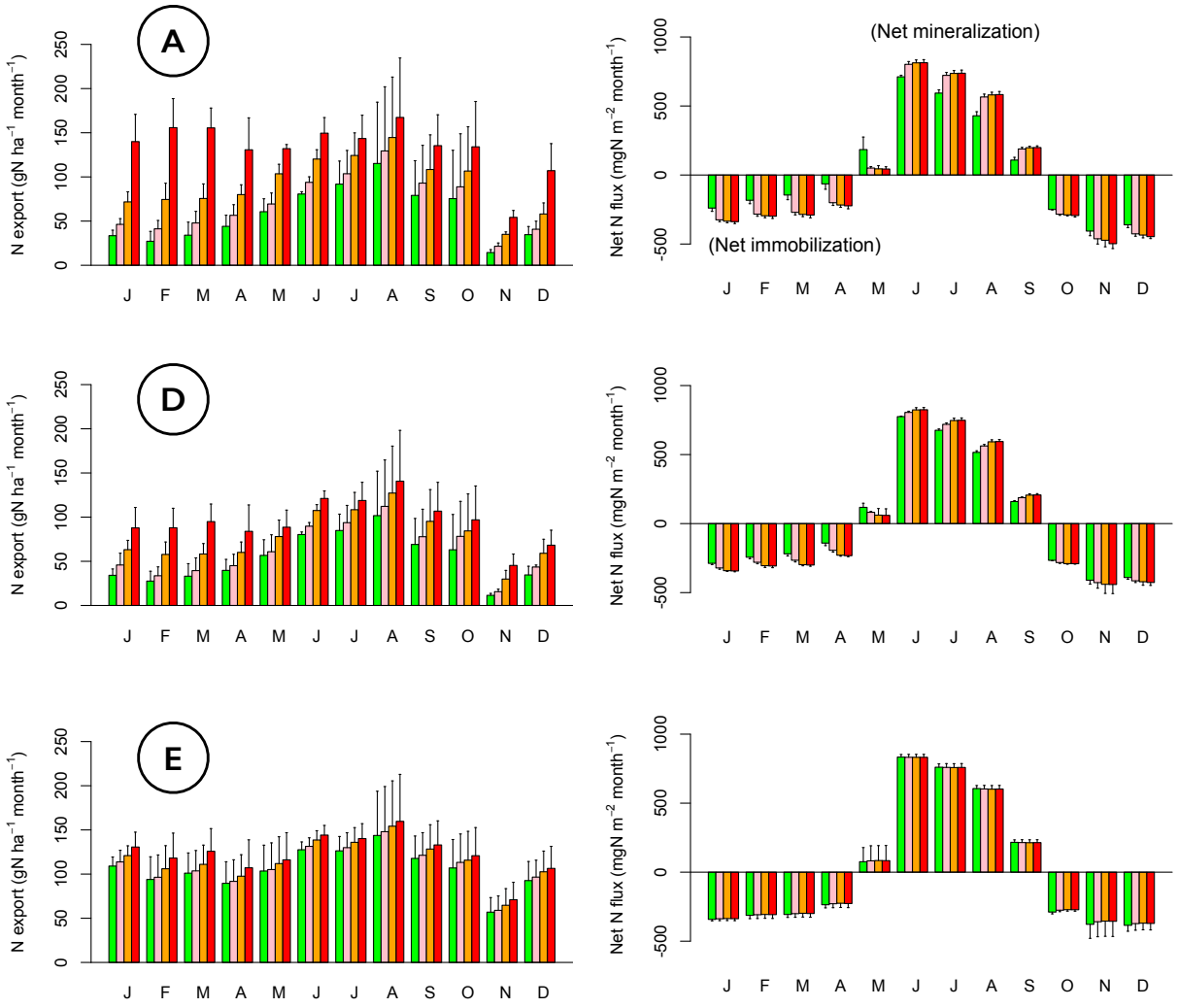

Figure 4-3. Monthly areal nitrogen export and net nitrogen flux (mineralization – immobilization) at sites A, D, and E within the local catchment for the simulation with different residential development densities.

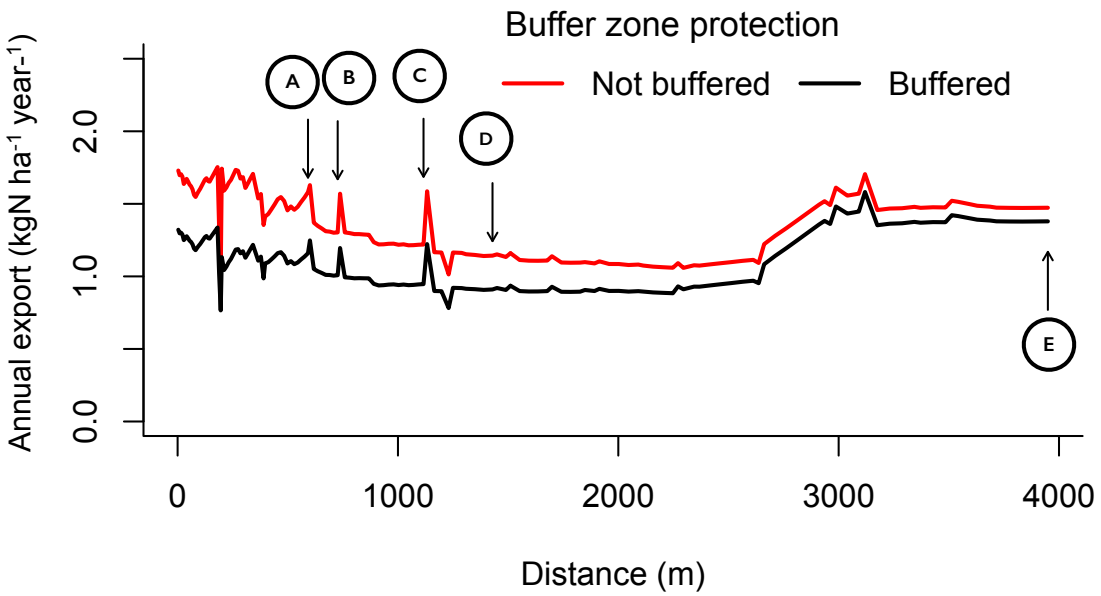

Figure 4-4. Annual areal nitrogen export along the main stream within the local catchment for the simulation with different buffer zone protection strategies.

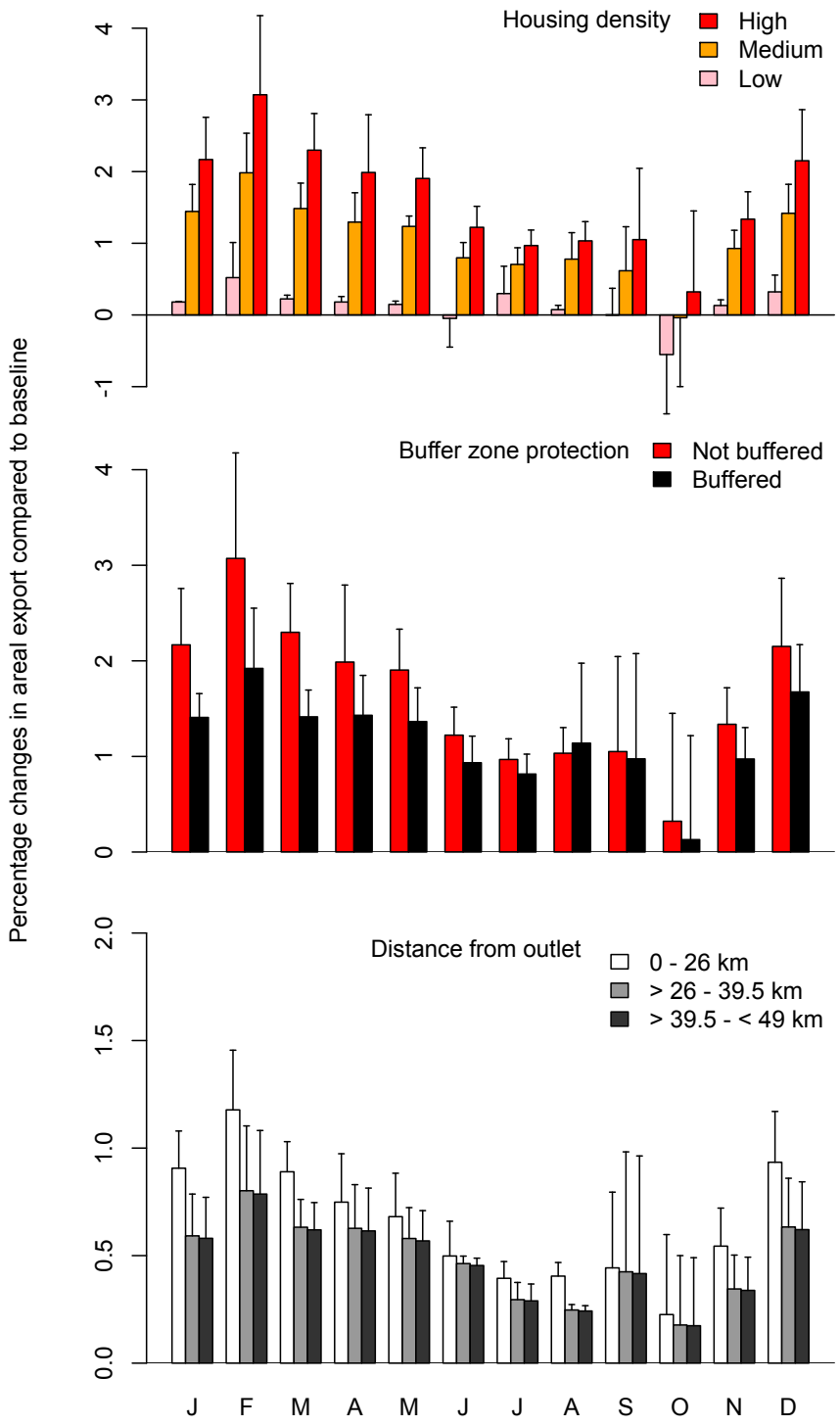

Figure 4-5. Percentage change in areal nitrogen export relative to baseline scenario at the regional scale for the three simulations, different residential development densities (top),

different buffer zone protection strategies (middle), and different stream travel distances from residential development to the catchment outlet (bottom).

Chapter 5

Conclusions

Forested mountain streams play an important role in integrating terrestrial and aquatic ecosystem and also provide essential resources and services (e.g., water supply) to downstream ecosystems and human communities (Vannote et al. 1980, Viviroli et al. 2007). The fast-expanding mountainside development occurring in the southern Appalachian Mountains not only modifies terrestrial systems but also aquatic systems by changing the terrestrial input to streams (Garrison and Wakeman 2000, Hansen et al. 2005, Viviroli et al. 2007, Webster et al. 2012). The impacts of mountainside development on stream ecosystems are complex due to the interactions of terrestrial and in-stream processes that control catchment nutrient export.

In this study, starting with the attempt to better understand in-stream processes, I synthesized several important ecological concepts, including ecological stoichiometry, microbial nutrient mining, and microbial-substrate interaction, and I developed models for leaf decomposition in forested headwater streams (Chapter 2). I then extended this single stream model to a stream network model and linked the network model with a terrestrial model. Using the results of these linked models, I then explored the relative importance of in-stream process and lateral terrestrial nutrient input in modifying nutrient dynamics in streams (Chapter 3). Specifically, I investigated the effects of lateral nutrient input and in-stream nutrient process on nitrogen export. Finally, with the linked stream network and terrestrial models, I investigated the influences of mountainside residential development on nitrogen export through a simulation in which the impacts of housing density, buffer zone protection, and various stream travel distances from housing location to catchment outlet were varied (Chapter 4).

By comparing the performance of three candidate models, the model including both immobilizers and miners as different microbial groups and including different leaf qualities yielded better prediction of nutrient dynamics (Chapter 2). The importance of terrestrial nutrient input versus in-stream nutrient process and their interactions greatly depended on the terrestrial nutrient input level (Chapter 3). With low lateral nitrate input, net microbial nitrogen flux played a more important role than lateral nitrate input in controlling nitrogen export in streams. However, with high lateral nitrate input, lateral nitrate input was more important than in-stream net microbial nitrogen flux. Greater impacts, i.e., higher nitrogen export at a local scale or higher percentage change in nitrogen export at a regional scale, were found with higher residential density, without buffer zone protection, and with shorter stream travel distance from residential development to catchment outlet (Chapter 4).

This research was conducted primarily using a modeling approach, including mathematical models (Chapter 2), model simulation (Chapters 3 and 4), and global sensitivity analysis (Chapter 3). Model quantification was based on previous studies and field data. Although conclusions obtained via modeling are subject to model assumptions and need to be further validated through well-designed field and laboratory studies, this research may provide significant insights in three major ways. First, this study may help expand our understanding of detritus decomposition in streams (Chapter 2), interaction of in-stream process with terrestrial input (Chapter 3), and impacts of exurbanization on stream ecosystems (Chapter 4). Second, this study may help identify directions for further research and provide insights for land and river management in mountainous areas. For example, a long-term comprehensive leaf decomposition experiment would be helpful to further validate my models and to better understand the ecological functions of immobilization and mining and their impacts on decomposition in

streams (Chapter 2). Sensitivity analyses (Chapter 3) may help identify potential important factors that directly and indirectly influence nutrient immobilization and mineralization, which may further provide guidance for developing field experiments. Third, I demonstrated an application of the modeling approach to investigate complicated ecological questions, especially in cases where large-scale and long-term experiments are difficult and costly such as residential development manipulation in forested mountains (Chapter 4).

5.1 Literature Cited

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