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The controls of watershed nutrient export

Wilfred M. Wollheim

*University of New Hampshire, Durham*

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The controls of watershed nutrient export

Abstract
Anthropogenic nitrogen (N) loading has increased considerably in recent times, yet only a small proportion is generally exported to the coast from most watersheds. This dissertation addresses some of the factors controlling N export from watersheds. The focus is on (1) how N export and N retention change with increased urbanization, and (2) how river networks modify N that is loaded to them.

Urbanization is a major perturbation of the land surface. Chapter 1 uses a budget approach to assess how N retention changes with increased urbanization in small headwater catchments in northeastern Massachusetts, USA. Water runoff, N loading, and N exports were higher in an urban compared to a forested site. N exports increased at a faster rate than N loading, indicating that the capacity of urban catchments to retain nutrients has declined. Impervious surfaces are likely a major factor leading to this decline.

Aquatic systems can store or denitrify a large amount of N, and can therefore potentially buffer increased N loading from terrestrial systems (non-point sources) and point sources. Chapter 2 uses a modeling approach to assess the role of river networks at the global scale. The strength of aquatic N removal varied considerably by watershed, depending on the spatial distribution of N loading, hydraulic characteristics, and biological activity. The representation of biological activity strongly influenced predicted N removal of aquatic systems, pointing out the need to better understand biological controls in different regions of the world.

A great deal of attention has recently been given to the role of river networks in modifying nutrient exports. Chapter 3 is an exploration of the biological and hydrological controls of nutrient removal at the scale of river networks. In particular, the role of stream size and nutrient concentrations are emphasized. The analysis suggests that river network models should clearly separate the biological and hydrological parameters to (1) facilitate understanding of model behavior, (2) facilitate comparability with field measurements, (3) improve the ability to apply/test models across temporal and spatial domains, and (4) improve the ability to explore the relative influences hydrological and biological controls of river network nutrient removal.

Keywords
Biogeochemistry, Environmental Sciences, Hydrology
THE CONTROLS OF WATERSHED NUTRIENT EXPORT

BY

WILFRED M. WOLLHEIM

Bachelor of Science, Cornell University, 1989
Master of Science, University of Wyoming, 1994

DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Doctor of Philosophy
in
Earth Sciences

May, 2005
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Professor of Water Resource Management

May 4, 2005
Date
DEDICATION

To my wife, Maria Niswonger, for all of her support over the years while working towards this degree, and to our daughters, Caroline and Elise, who provide a daily source of inspiration and a reminder for why it is important to understand how the Earth’s ecosystems work, so that we may better ensure safe passage of our world to future generations.
ACKNOWLEDGEMENTS

I would like to thank my advisor Charlie Vörösmarty for his support, advice, and the numerous stimulating scientific discussions we've had over the last six years. He has given me a tremendous amount of freedom to pursue the avenues of research that I am interested in.

I thank everyone in the Water Systems Analysis Group, particularly Balasz Fekete for help with the modeling environment (the superb RGIS system which he developed), Richard Lammers for help with coding and discussions of scientific method, and Pamela Green for laying so much of the groundwork for the global N modeling, as well as Stanley Glidden for help with graphics and Darlene Dube for always being helpful in many ways. Numerous others also contributed to this work including Jocelyn Bradbury, Chris Hunt, Pahlavi Mittal, Corey Lawrence and Hap Garritt who analyzed the nutrient samples and volunteers of the Ipswich R. Watershed Association for helping to collect water samples. Thanks also to my committee members, John Aber, Larry Dingman, Chuck Hopkinson, and Bill McDowell for their help and guidance.

I also would like to thank Brian Pellerin, fellow UNH and LTER graduate student, for many years of enjoyable collaboration. Brian was always willing to talk through ideas and never held back with his comments. Much of the work described here is better for it.

I gratefully acknowledge Bruce Peterson for many years of guidance, insight, and continued collaboration regarding stream ecosystem biogeochemistry.

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Finally, I would like to thank my family: my parents, my sister, and especially my wife and daughters for all their support now and in the past.
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ABSTRACT

THE CONTROLS OF WATERSHED NUTRIENT EXPORT

by

Wilfred M. Wollheim

University of New Hampshire, May, 2005

Anthropogenic nitrogen (N) loading has increased considerably in recent times, yet only a small proportion is generally exported to the coast from most watersheds. This dissertation addresses some of the factors controlling N export from watersheds. The focus is on 1) how N export and N retention change with increased urbanization, and 2) how river networks modify N that is loaded to them.

Urbanization is a major perturbation of the land surface. Chapter 1 uses a budget approach to assess how N retention changes with increased urbanization in small headwater catchments in northeastern Massachusetts, USA. Water runoff, N loading, and N exports were higher in an urban compared to a forested site. N exports increased at a faster rate than N loading, indicating that the capacity of urban catchments to retain nutrients has declined. Impervious surfaces are likely a major factor leading to this decline.

Aquatic systems can store or denitrify a large amount of N, and can therefore potentially buffer increased N loading from terrestrial systems (non-point sources) and point sources. Chapter 2 uses a modeling approach to assess the role of river networks at the global scale. The strength of aquatic N removal varied considerably by watershed, depending on the spatial distribution of N loading, hydraulic characteristics, and biological activity. The representation of biological activity strongly influenced
predicted N removal of aquatic systems, pointing out the need to better understand biological controls in different regions of the world.

A great deal of attention has recently been given to the role of river networks in modifying nutrient exports. Chapter 3 is an exploration of the biological and hydrological controls of nutrient removal at the scale of river networks. In particular, the role of stream size and nutrient concentrations are emphasized. The analysis suggests that river network models should clearly separate the biological and hydrological parameters to 1) facilitate understanding of model behavior, 2) facilitate comparability with field measurements, 3) improve the ability to apply/test models across temporal and spatial domains, and 4) improve the ability to explore the relative influences hydrological and biological controls of river network nutrient removal.
INTRODUCTION

Nitrogen (N) limits biological activity in terrestrial, marine and some freshwater systems (Vitousek and Howarth 1991). Increased N-loading to aquatic systems can lead to eutrophication of freshwater and coastal ecosystems, potentially triggering fish kills and toxic algae blooms (Turner and Rabalais 1994, Carpenter et al. 1998). Long-term impacts are less clear, but could include reduced biodiversity of aquatic systems (Carpenter et al. 1998) and alteration of the biogeochemistry of coastal zones and oceans, potentially affecting carbon sequestration and global climate change (Mackenzie 2002). Understanding factors controlling export of N from watersheds is therefore critical.

The controls of nutrient flux from large complex watersheds are difficult to understand because of numerous interacting factors (Howarth 2000). Major factors include spatially and temporally varying loading rates (either through atmospheric deposition, fertilizer additions, leguminous agriculture, human waste), hydrologic transport, and processing by forests, wetlands, and surface waters. Even watersheds with apparently uniform loading and current land use characteristics can have significantly different nutrient export over annual time scales (Lovett et al. 2000). Yet to effectively manage nutrient levels as humans alter the landscape, an understanding of the relative importance of different controls is critical.

Nitrogen inputs to the biosphere have doubled due to human activity via fertilizer application, fossil fuel use, and agriculture of N fixing plants (Galloway 1995). Despite increased loading, on average only 20-30% of nitrogen entering into North Atlantic watersheds ultimately reaches the ocean (Howarth et al. 1996, Boyer 2002). The fate of...
the other 70-80% is uncertain. Possible mechanisms include storage in regrowing forests (Aber 1989, Goodale 2002) and denitrification in wetlands and streams (Galloway et al. 2003). However, the relative importance of these mechanisms is unclear. In addition, the mechanism for relatively uniform export from a wide range of watersheds with different loading rates has not been determined.

This dissertation addresses two major questions:

1) How do N exports and N retention change with increased urbanization?

2) What is the role of river networks in controlling watershed N exports?

Chapter 1 addresses the first question. N exports and retention are quantified in an urban and a forested headwater catchment over annual time periods during a dry and a wet year. The catchments are located in the Parker and Ipswich watersheds, which drain to the Plum Island Estuary, an important marsh dominated estuarine system in northeastern Massachusetts.

Chapters 2 and 3 address the second question. In chapter 2, a river network model is applied at the global scale to explore the role of heterogeneity of N loading, hydrologic conditions, and biological activity in determining N exports among some of the worlds largest watersheds. In addition to large rivers, lakes and reservoirs, the river network model includes a representation of small rivers, which are difficult to account for at the global scale. Here a statistical approach is used to account for their role. In chapter 3, the hydrological and biological controls of river network nutrient removal are explored in more detail using a theoretical approach combined with a synthesis of literature reports.
The two questions are addressed at different scales. Whereas chapter 1 focuses on urbanization in a particular location (the Plum Island watersheds) and type of catchment (temperate, coastal watershed), chapter 2 focuses on the role of river networks at the global scale, emphasizing large watersheds. The role of river networks was also explored at the scale of the Plum Island watershed, but the results are not included here. However, the principles applied at one scale can be easily applied at another scale, assuming an appropriate representation of the aquatic network.

Each chapter was written in the format for submission to a peer-reviewed journal. Chapter 1 is as of this date (May 2005) in press at the journal Ecosystems with coauthors Brian Pellerin, Charles Vörösmarty, and Charles Hopkinson. Chapter 2 is in revision for eventual resubmission to the journal Global Biogeochemical Cycles with coauthors Charles Vörösmarty, A.F. Bouwman, Pamela Green, John Harrison, Michel Meybeck, Bruce J. Peterson, Sybil P. Seitzinger, James P. Syvitski. Chapter 3 will be submitted shortly to a journal as yet undetermined. All the work in these three chapters was primarily developed, executed, and written by the author of this dissertation.
CHAPTER 1

NITROGEN RETENTION IN URBANIZING HEADWATER CATCHMENTS

Abstract

Urbanization can potentially alter watershed nitrogen (N) retention via combined changes in N loading, water runoff, and N processing potential. We examined N export and retention for two headwater catchments (~4km²) of contrasting land use (16% vs. 79% urban) in the Plum Island Ecosystem (PIE-LTER) watershed, MA. The study period included a dry year (2001-02 water year) and a wet year (2002-03 water year). We generalized results by comparing DIN concentrations from 16 additional headwater catchments (0.6 – 4.2 km²) across a range of urbanization (6 – 90%).

Water runoff was 25-40% higher in the urban compared to the forested catchment, corresponding with an increased proportion of impervious surfaces (25% vs. 8%). Estimated N loading was 45% higher and N flux 6.5 times higher in the urban than in the forested catchment. N retention (1 - measured stream export / estimated loading) was 65-85% in the urban site and 93-97% in the forested site, with lower retention rates during the wetter year. The mechanisms by which N retention stays relatively high in urban systems are poorly known. We show that N retention is related to the amount of impervious surface in a catchment because of associated changes in N loading (maximized at moderate levels of imperviousness), runoff (which continues to increase with imperviousness), and biological processes that retain N. Continued declines in N retention due to urbanization have important negative implications for downstream aquatic systems including the coastal zone.
**Introduction**

Nitrogen (N) export from watersheds is strongly correlated with anthropogenic N loading (Peierls et al. 1991, Caraco and Cole 1999b, Aber et al. 2003). At the same time the proportion of N stored or denitrified in watersheds (1 - N export / N loaded, and henceforth referred to as retention) appears to be relatively constant and high (60 – 90%) in many large northeastern U.S. watersheds (400 – 70,000 km²) experiencing a range of N loading from a variety of sources (Howarth et al. 1996, Boyer et al. 2002, Driscoll et al. 2003). Similarly high retention has been reported for small (14 – 300 km²) agricultural (Jordan et al. 1997) and urban catchments (Valiela et al. 1997, Groffman et al. 2004). A wider range of N retention (40 – 100%) has been reported for small forested catchments (< 20 km²) experiencing a range of atmospheric N loading, but with relatively low N load compared to more anthropogenically modified watersheds (Lovett et al. 2000, Aber et al. 2003). One would expect urban catchments to show at least a similar range in N retention compared with forested sites because disturbance can be severe. However, this range cannot be characterized because of the relatively few N retention studies in urban catchments (but see Valiela et al. 1997, Groffman et al. 2004).

Moreover, although N retention appears to be relatively high in many northeastern watersheds, N retention globally can range between 0 – 100% as a function of hydraulic residence time, mean temperature, and preponderance of point vs. non-point source loads (Green et al. 2004). There is a need to understand the factors controlling watershed N retention because small changes in retention can lead to large changes in N export (Caraco et al. 2003), potentially intensifying coastal eutrophication problems associated with N enrichment.

Urbanization of watersheds invokes a wide range of consequences, both hydrological and biogeochemical. N loading to watersheds generally increases with urbanization due to human waste inputs, increased NOₓ emissions and fertilizer...
applications to lawns (Valiela and Bowen 2002). Increased impervious surface area leads to greater water runoff along altered flow paths compared to undisturbed systems (Dunne and Leopold 1978, Schueler 1994, Arnold and Gibbons 1996, Burges et al. 1998, Paul and Meyer 2001), thereby reducing residence time of water (and N) in the system. Both runoff and residence time of water are major determinants of N export (Caraco and Cole 1999b, Alexander et al. 2000, Peterson et al. 2001, Green et al. 2004). Thus for a given amount of N loading, catchments with higher impervious surface area should show greater N export and reduced N retention. Despite these changes, the impact of urbanization on watershed N retention is poorly known.

Here we address how urbanization influences N export and retention in headwater catchments in northeastern Massachusetts. Our study focuses on the rapidly urbanizing watershed of the Plum Island Ecosystem LTER site located northeast of Boston, MA (Figure 1.1). There are three goals to this paper. First, we construct annual water and N budgets for two headwater catchments (~ 4 km²) of contrasting levels of urbanization (suburban residential vs. forest) for two water years of contrasting moisture conditions (the 2001-02 and 2002-03 Water Years (WY01 and WY02)). Next, we evaluate the generality the results from these two catchments by comparing them with annual DIN concentrations (for WY01) exported from a larger number of less intensively monitored headwater sites across a gradient of urbanization. Finally, we discuss the impact urbanization has on N retention, focusing on changes in water runoff, N concentrations, and N loading associated with impervious surfaces.
Study Area

The headwater catchments are located in the Ipswich River and Parker River watersheds, which drain to the Plum Island Estuary in northeastern MA (Figure 1.1). The watersheds are located on the coastal lowland section of New England and are characterized by low to moderate relief and relatively poor drainage (Baker et al. 1964). The watersheds are underlain by igneous and sedimentary Paleozoic and Precambrian bedrock and have shallow soils developed on surficial till, gravel and sand deposits (Baker et al. 1964). Maximum elevation is about 150 m and mean watershed slope is 24 m km⁻¹. Mean precipitation is about 1150 mm yr⁻¹, and evenly distributed throughout the year.

Two catchments of contrasting land use were intensively studied to characterize runoff and N exports. Sawmill Brook catchment (SB) is a 4.1 km², heavily residential...
watershed that drains a portion of the town of Burlington, MA (Figure 1.1). Residential development is relatively high density, single-family lots (< 0.25 acres), with an abundance of lawns (Table 1.1). Cart Creek catchment (CC) is primarily forest and wetland draining 3.9 km² of the town of Newbury, MA. The forest is primarily oak that has regrown following agricultural abandonment early in the 20th century. SB is roughly 25% impervious surface area, composed primarily of rooftops and roads, with several large parking lots. Although CC is primarily natural vegetation it has a major interstate (I-95) cutting through it, which results in a relatively high % impervious area (8.2%). A purely forested catchment is difficult to find in our region, but CC is on the less impacted end of the urban continuum. SB has a fairly high population density (981 km⁻²), most of whose waste is exported out of the catchment via sewer systems. In contrast, CC has a much lower population density (119 km⁻²), most of whose waste enters the catchment via septic systems. Wetlands represent 18% of CC catchment and only 4% of SB catchment. Both catchments are underlain by similar surficial geology, though CC has more floodplain alluvium (Table 1.1).

A number of additional headwater catchments were studied less intensively to characterize mean annual DIN concentrations. These catchments range in size from 0.6 to 4.2 km² and are distributed throughout the Ipswich watershed (Figure 1.1). Urban development ranges from 7 to 90% and imperviousness from 1 to 29% (Table 1.1). Urban development is primarily residential, but several of the catchments include a large industrial component. Population density ranges from 20 to 1150 km⁻² and is highly correlated with percent residential area ($r^2 = 0.90$). The number of people on septic systems peaks at intermediate levels of residential development (~ 40-50% residential), because as development increases more communities convert from septic to sewage systems. Most of the communities on sewer systems are serviced by the Massachusetts Water Resources Authority (MWRA) and all sewage waste is exported
<table>
<thead>
<tr>
<th>Characteristic</th>
<th>SawMill Br.</th>
<th>Cart Cr.</th>
<th>Other Headwater Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (km²)</td>
<td>4.1</td>
<td>3.9</td>
<td>0.6–4.2 (2.0)</td>
</tr>
<tr>
<td>Surficial Geology (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Floodplain alluvium</td>
<td>6.1</td>
<td>2.9</td>
<td>0–33 (3.6)</td>
</tr>
<tr>
<td>Fine-grained deposits</td>
<td>0.0</td>
<td>12.8</td>
<td>0–15.3 (1.1)</td>
</tr>
<tr>
<td>Sand/Gravel</td>
<td>15.2</td>
<td>12.3</td>
<td>0–92.6 (30.8)</td>
</tr>
<tr>
<td>Till</td>
<td>77.2</td>
<td>68.2</td>
<td>7.3–100 (63.3)</td>
</tr>
<tr>
<td>Land Use (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forest</td>
<td>13.7</td>
<td>55.3</td>
<td>7.7–55.8 (29.9)</td>
</tr>
<tr>
<td>Residential</td>
<td>72.3</td>
<td>10.6</td>
<td>6.6–89.0 (44.3)</td>
</tr>
<tr>
<td>Agricultural/Open Field</td>
<td>4.2</td>
<td>7.5</td>
<td>0–29 (3.9)</td>
</tr>
<tr>
<td>Industrial/Commercial</td>
<td>4.6</td>
<td>5.6</td>
<td>0–28.2 (5.7)</td>
</tr>
<tr>
<td>Wetland</td>
<td>4.3</td>
<td>18.6</td>
<td>1.7–25.5 (13.8)</td>
</tr>
<tr>
<td>Open Water</td>
<td>0.0</td>
<td>0.2</td>
<td>0–20.7 (1.8)</td>
</tr>
<tr>
<td>Impervious Surface Area (%)</td>
<td>24.6</td>
<td>8.2</td>
<td>1.3–28.6 (14.8)</td>
</tr>
<tr>
<td>Population (#/km²)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>981</td>
<td>130</td>
<td>20–1149 (527)</td>
</tr>
<tr>
<td>Waste Treatment via Septic</td>
<td>73</td>
<td>122</td>
<td>20–1050 (231)</td>
</tr>
</tbody>
</table>

Table 1.1. Characteristics of the study catchments during the study period. Range and mean shown for other headwater sites (n = 16).
from the watersheds. Generally, urbanization results in co-varying changes in the
headwater catchments, with % imperviousness, total population density, and %
residential all showing significant positive correlations (Pellerin 2004). Wetland
abundance also tends to decline as % residential increases ($r^2 = 0.28$, $p = 0.03$).

**Methods**

**Water and N Fluxes – Headwater End Member Sites**

Depth was continuously monitored in Sawmill Brook (SB) and Cart Creek (CC)
using YSI-6920 (Yellow Springs Instruments, Yellow Springs OH) or Sigma depth data
loggers (American Sigma, Loveland CO). Depth vs. discharge rating curves were
developed at each monitoring site. Daily runoff (mm d$^{-1}$) was determined from daily
average discharge and watershed area. Our rating curve did not encompass the entire
range of depths so we extrapolated the high end of the rating curve. As a result,
discharge during storm peaks in both SB and CC is subject to uncertainty
(corresponding with runoffs above 2.2 mm d$^{-1}$ in SB and 1.8 mm d$^{-1}$ in CC). To calculate
annual runoff for WY01, some data gaps of several days to several weeks were filled by
interpolating the ratio of headwater runoff to Ipswich R. runoff (USGS gage 01102000)
measured at either end of the gap, and multiplying the daily ratio by the Ipswich R. runoff
during the gap. Because the gaps were relatively short, this approach provided a
reasonable approximation of runoff. For WY02, we used the same approach for
interpolating discharge, despite the much longer data gap occurring in the winter period
because of extremely cold conditions. The annual estimates for WY02 are therefore
subject to greater uncertainty than for WY01. In each year, daily precipitation was based
on interpolated NCDC data for stations in northeastern Massachusetts and southern
New Hampshire.
Nutrients were collected at the discharge monitoring sites using both grab samples and automated samplers (American Sigma). Grab samples were collected roughly every 2 weeks, and automated samples daily during deployment periods. Automated samples were collected only for nitrate + nitrite (NO$_3$-N + NO$_2$-N) and preserved by adding H$_2$SO$_4$ to the bottles prior to deployment. Bottles remained in the field for up to one month before retrieval. Upon retrieval, these samples were filtered and frozen until analysis. Grab samples were filtered through Millipore-HA 0.45 μm filters and frozen until analysis for NO$_3$-N, NO$_2$-N, and ammonium (NH$_4$-N) by flow injection using a Lachat QuikChem 8000 Automated Analyzer (Milwaukee, WI).

Dissolved inorganic nitrogen (DIN) is the sum of NO$_3$-N, NO$_2$-N and NH$_4$-N. Monthly samples were also analyzed for total dissolved nitrogen (TDN) using an Antek High Temperature Total Nitrogen Analyzer. Dissolved organic nitrogen (DON) was derived by subtracting DIN from TDN. PON was not measured in SB and CC during this study; we assume that PON makes a relatively small contribution to N exports from these watersheds (Hopkinson, unpublished data). There was no difference between NO$_3$-N determined from grab or automated samplers, so data from the two methods were combined. Mean annual flow-weighted concentrations were estimated for each constituent using flow from the sample day. Annual fluxes were calculated by linearly interpolating nutrient concentrations between sample days and multiplying by daily discharge. We feel this is valid because generally N concentrations trended over time and because there was no clear relationship between concentration and flow.

**Flow-Weighted DIN Concentration - Spatially Extensive Headwater Sites**

Monthly nutrient samples were collected at 16 additional small headwater catchments (0.6 km$^2$ – 4.2 km$^2$) across a gradient of land use characteristics during WY01. At least 10 samples were collected at each site over the course of the water
year. Additional sites were sampled less frequently and were not included in this study because the reduced frequency was inadequate to characterize annual flow-weighted N concentrations. The samples were analyzed for NO₃+NO₂ and NH₄ as described above. Discharge was not measured at these sites. We calculated annual flow-weighted mean concentrations using discharge reported at the Ipswich USGS gage for the sample day to more heavily weight concentrations from seasonally higher flow periods.

**GIS**

Land use (1:25000) and National Wetland Inventory (NWI) wetland (1:5000) data layers were obtained from MASSGIS (http://www.state.ma.us/mgis/ massgis.htm), and combined into a hybrid land use/wetland coverage. Land use was aggregated to 6 land use features: residential, agricultural/open field, industrial/commercial, forest, wetlands, and open water. Impervious surface area was derived from estimates of percent impervious surface vs. land use type (Arnold and Gibbons 1996). Distributed population was based on Census 2000 Summary File (SF) 1 tabular data and the Topologically Integrated Geographic Encoding and Referencing system (TIGER/line) geographical database, corresponding with the block level. The percent of the population on septic systems was based on census surveys from 1990 (SF3 tables, code HO24) at the census tract level. The census tract scale is relatively coarse. However, most of the variability in waste treatment occurs at the town level (DEP 2002) and generally there are several census tracts per town. Therefore, we believe that our estimates of waste treatment of people in different catchments are reasonable. The waste treatment survey was discontinued after the 1990 survey, necessitating the assumption that the percent of people on septic systems in 1990 could be applied to the updated 2000 population.

Watershed attributes were estimated using a 120 m gridded river network developed for the Plum Island Estuary from 30 m DEM's with USGS stream hydrography.
“burned in”. All spatial data sets were aggregated to 120m grid cells either as percentage grids (land cover), or density grids (population). Upstream average characteristics were calculated using a watershed GIS analysis program, GHAAS/River GIS (Water Systems Analysis Group, University of New Hampshire). At the 120 m grid scale, there are 70 grid cells in each square kilometer.

N Loading Estimates

The major sources of N to the Ipswich and Parker watersheds are atmospheric deposition, waste N inputs via septic systems, and fertilizer applications to lawns (Williams et al. 2004). We assumed N fixation was a relatively small input and did not include it in our budgets. N inputs from leaking sewer lines and pets might be important (Baker et al. 2001), but lacking information we do not include them in our budget. Sewage waste is treated outside the basin and no major point sources exist within the small headwater catchments of our study. Wet deposition was estimated using interpolated daily precipitation from NCDC and monthly precipitation-weighted N concentrations obtained from the NADP site in Lexington MA. Comparison of NADP estimates with atmospheric N deposition collected within the watershed showed similar results for N (Williams et al. 2004). For dry deposition, we assumed constant loading rates over the course of the year based on Ollinger et al. (1993). Dry deposition was assumed constant for all land use types, possibly leading to overestimates of inputs to areas with reduced canopies such as urban areas.

Spatial information described above was used to estimate N inputs via septic waste and fertilizer applications to lawns. Fertilizer N inputs are difficult to quantify, especially at the small catchment scale. Because of uncertainties in the parameters used to calculate these inputs (Valiela et al. 1997), we estimated a high and low N load scenario to determine how these assumptions might affect the results. For the high N
load scenario, septic waste inputs were estimated using population on septic systems and a per capita N loading rate of 4.8 kg N person\(^{-1}\) yr\(^{-1}\) (Valiela et al. 1997). We estimated fertilizer N inputs to lawns from land use estimates of pervious surface areas in human dominated areas (residential + industrial/commercial + agriculture – impervious surface area). We assumed that 75% of pervious surfaces in human dominated areas are potentially fertilized (i.e. are lawns), and that 34% of these areas are actually fertilized (Valiela et al. 1997, Williams et al. 2004). Finally, we assumed that on average 100 kg N ha\(^{-1}\) yr\(^{-1}\) are added to lawns that are fertilized (Valiela et al. 1997) and that fertilizer inputs to agricultural areas are similar to lawns. Agriculture is generally low intensity haying and horse pasture and usually represents a small proportion of land use in our study sites (< 10%). For a low N load scenario, we changed the per capita N loading rate to 1.85 kg N person\(^{-1}\) yr\(^{-1}\) (Caraco et al. 2003), and we reduced the percent of pervious areas that is potentially fertilized to 37.5%. These changes reduce estimated waste N and fertilizer inputs by 62% and 50% respectively. The two scenarios serve to constrain N retention estimates. All N sources were summed together to estimate spatially distributed total annual N load.

**Water Runoff and N Retention Coefficients – Headwater End Member Sites**

Water runoff and N retention coefficients for the two intensively studied sites were determined for the period October 1, 2001 to September 30, 2002 (WY01) and October 1, 2002 to September 30, 2003 (WY02). Water runoff coefficients were determined by dividing measured stream discharge by annual precipitation. N retention was determined by dividing annual TDN export in streams by the estimated annual N load and subtracting from 1. N retention in this calculation includes storage in biomass and soils, denitrification, as well as unmeasured exports (see Discussion).
Results

Water Runoff

During both water years, annual runoff was higher in the urban than in the forested catchment. Precipitation was roughly 200 mm above the long-term average of 1150 mm in WY02 and 200 mm below average in WY01 (Table 1.2). During WY01, annual runoff was 272 mm yr\(^{-1}\) in the urban Sawmill Br. catchment (SB) compared to 194 mm yr\(^{-1}\) in the forested Cart Cr. catchment (CC) (Table 1.2). During WY02, annual runoff increased to 449 mm yr\(^{-1}\) in SB and to 358 mm yr\(^{-1}\) in CC. SB had higher storm runoff especially during the growing season, and generally higher baseflows throughout the year compared with CC (Figure 1.2A). The annual runoff coefficient was roughly the same percentage higher in SB than in CC in both water years (28% vs. 21% in WY01 and 33 vs. 27% in WY02; Table 1.2).

N concentrations

Annual flow-weighted mean DIN concentrations for forested CC and urban SB were 2.8 and 65.1 μM, respectively, in WY01 and 4.3 and 72.4 μM, respectively, in WY02. In SB, DIN was dominated by NO\(_3\)-N (~90% in each year). In CC, NH\(_4\)-N was a larger component of DIN (40-60%). NO\(_3\)-N was lower through most of the year in CC compared to SB (Figure 1.2B). There was an apparent relationship between NO\(_3\)-N and flow in CC and a weak relationship in SB (Figure 1.3). In CC, NO\(_3\)-N was most variable at low runoffs (< 0.05 mm d\(^{-1}\)), ranging between 0 and 10 μM. At moderate runoff (0.05 – 0.5 mm d\(^{-1}\)), NO\(_3\)-N was usually higher (~10 μM), with several extremely high levels.
Table 1.2. Summary of water and N budget results for the 2001-2002 Water Year (WY01) and the 2002-2003 Water Year (WY02). Values in parentheses refer to a low N load scenario to test sensitivity to N loading assumptions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>WY01</th>
<th>WY02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation (mm/yr)</td>
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<td>942</td>
</tr>
<tr>
<td>Total runoff (mm/yr)</td>
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<td>194</td>
</tr>
<tr>
<td>Annual Runoff Coefficient (%)</td>
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</tr>
<tr>
<td>Total N loading (kg/km²/yr)</td>
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<td></td>
</tr>
<tr>
<td>Wet deposition (DIN)</td>
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<td>496</td>
</tr>
<tr>
<td>Dry deposition (DIN)</td>
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<td>290</td>
</tr>
<tr>
<td>Net Waste N</td>
<td>350 (135)</td>
<td>586 (226)</td>
</tr>
<tr>
<td>Fertilizer N</td>
<td>1443 (721)</td>
<td>395 (198)</td>
</tr>
<tr>
<td>Sum</td>
<td>2578 (1641)</td>
<td>1767 (1209)</td>
</tr>
<tr>
<td>River N exports (kg/km²/yr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIN (NO₃ + NH₄)</td>
<td>333</td>
<td>7.5</td>
</tr>
<tr>
<td>DON</td>
<td>51.5</td>
<td>51.6</td>
</tr>
<tr>
<td>Sum</td>
<td>384.5</td>
<td>59.1</td>
</tr>
<tr>
<td>N retention (%)</td>
<td>85 (77)</td>
<td>97 (95)</td>
</tr>
</tbody>
</table>

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Figure 1.2. Measured runoff and nutrient concentrations for the intensively monitored headwater sites during the study period. A) Runoff (mm d\(^{-1}\)), B) NO\(_3\)-N concentrations (\(\mu\text{M}\)), and C) DON concentrations (\(\mu\text{M}\)) for Cart Cr. (forested, area = 3.9 km\(^2\)), Sawmill Br. (residential, area = 4.1 km\(^2\)).
Figure 1.3. $\text{NO}_3^-\text{N}$ concentrations ($\mu$M) vs. runoff (log mm d$^{-1}$) for A) Cart Cr. and B) Sawmill Br. Inset in A) shows the relationship in Cart Cr. at a reduced nitrate scale.

Extremely high concentrations coincided with increasing flows at the end of the growing season. At higher runoffs (> 0.5 mm/d), $\text{NO}_3^-\text{N}$ declined (Figure 1.3A). In SB, $\text{NO}_3^-\text{N}$ showed little relationship with flow, although there was an increased likelihood of higher concentrations at runoffs greater than 1 mm d$^{-1}$ (Figure 1.3B). Although based on many fewer samples, there was no relationship between $\text{NH}_4^-\text{N}$ and DON with runoff in either stream. During both litter fall periods in SB (early WY01 and WY02) when flows were still low, $\text{NO}_3^-\text{N}$ briefly dropped to very low levels (Figure 1.2B), possibly due to immobilization by or denitrification within accumulated leaf litter from the adjacent forested area. Flow weighted mean DON concentrations were higher in CC than SB during WY01 (20.9 $\mu$M vs. 13.9 $\mu$M) but were similar in WY02 (13.5 $\mu$M vs. 12.1 $\mu$M).

DIN concentrations determined for WY01 in the less intensively monitored headwater sites showed similar effects of urbanization. Annual flow-weighted DIN ranged from 1 to 90 $\mu$M and was highly correlated with both % residential land ($r^2 = 0.58$, $n = 16$, $p < 0.001$), and total population density ($r^2 = 0.49$, $n = 16$, $p < 0.01$) (Figure 1.)
Figure 1.4. Annual flow-weighted DIN concentration (µM) for the headwater catchments vs. A) residential area (%), B) impervious area (%), C) total population density (# km²), and D) estimated N loading (kg N km⁻² yr⁻¹, high N load scenario, Table 1.2). Estimates from the Cart Cr. (CC) and Sawmill Br. (SB) are shown for comparison. The two points for SB represent the estimates for each water year. CC concentrations were similar in each year so are not distinguished.

4A,C). DIN concentrations were positively related to impervious surface area, but the relationship was not significant ($r^2 = 0.20$, $p = 0.06$) (Figure 1.4B). A weak relationship occurred between DIN concentration and the high N load scenario ($r^2 = 0.30$, $p = 0.02$; Figure 1.4D) but no significant relationship was found with the low N load scenario ($r^2 = 0.22$, $p = 0.06$). The low $r^2$'s for the N load scenarios were driven in part by a single catchment with high septic N loads that lacked a corresponding increase in DIN concentrations. Multiple regressions did not improve upon the simple regression using
only residential land use (based on adjusted $r^2$). Flow weighted estimates from the more frequently sampled SB and CC from both WY01 and WY02 corresponded well with the relationship for the less intensively studied sites (Figure 1.4).

**N Runoff**

Total dissolved N runoff was much higher from the urbanized SB than from CC because both runoff and N concentrations were higher. In WY01, annual N runoff totaled 385 kg N km$^{-2}$ yr$^{-1}$ in SB vs. 59.1 kg N km$^{-2}$ yr$^{-1}$ in CC (Table 1.2). In WY02, annual N runoff totaled 579 kg N km$^{-2}$ yr$^{-1}$ in SB vs. 89 kg N km$^{-2}$ yr$^{-1}$ in CC. N runoff was dominated by DIN in the urban site, and by DON in the forested site (Table 1.2).

**N Retention**

N retention (1 - TDN export / total N loading) was high in both intensively monitored headwater sites, but was greater in the forested catchment. Whereas the urbanized catchment exported several times more N than the forested catchment, the difference in N loading between the two catchments was relatively small (Table 1.2). For the high N load scenario, total N loads during WY01 were estimated at 2578 and 1767 kg N km$^{-2}$ yr$^{-1}$ in SB and CC, respectively (Table 1.2). Atmospheric deposition, waste N, and fertilizer represented 30%, 14%, and 56% of total N loads in SB, and represented 44%, 33%, and 22% in CC. N loads were similar in WY02 because we assumed fertilizer and waste inputs were the same, and because N inputs via wet deposition were similar despite much higher precipitation. Concentration estimates from the NADP site suggested that a dilution of N in precipitation occurred in the wetter year.

N retention was 85% in SB and 97% in CC (Table 1.2) during WY01. During the wetter WY02, N retention dropped to 78% in SB and only slightly to 95% in CC. For the low N load scenario, waste N and fertilizer N were both considerably reduced (Table...
1.2). The low N load scenario resulted in a greater decrease in N retention in the urban site (85 to 77% in WY01 and 78 to 65% in WY02), than in the forested site (97 to 95% in WY01 and 95 to 93% in WY02). Uncertainty in N loads therefore limits our understanding of the rate at which N retention declines with development.

Discussion

Effect of Urbanization on Water Runoff

Runoff coefficients increase with urbanization due to the impact of impervious surfaces. This phenomenon has long been known for individual storms (Dunne and Leopold 1978, Urbonas and Roesner 1992, Schueler 1994). Recent reports have confirmed that the increase can occur on annual time scales as well (Burges et al. 1998, Grove et al. 2001, Jennings and Jarnagian 2002). Burges et al. (1998) found that annual stream runoff as a percentage of precipitation ranged from 12-30% in a forested catchment (0% impervious) to 44-48% in an urban catchment (30% impervious) over a 3-year period in Washington State. In the Lower Charles R. basin, which includes the city of Boston, annual runoff increased from 20 to 80% across 5 catchments that ranged from 11% to 86% impervious surface (Zarriello and Barlow 2002). Our estimates of annual runoff coefficient are consistent with these other studies, though the rate of increase between our forested and urban catchments was slightly slower (Figure 1.5).

The increased runoff from our urban catchment is due to both greater surface runoff and higher baseflows (Figure 1.2). In SB, hydrograph separations suggest that 4-11% (mean = 5%, n = 12) of rainfall enters the stream immediately as new water, presumably as direct runoff from impervious surfaces (Pellerin 2004). While this is relatively low for an urban catchment, a much smaller percentage enters as new water in the forested CC, despite 8% impervious surfaces. Thus, a large proportion of the
observed 6-7% difference in annual runoff coefficients for SB and CC (Table 1.2) is likely
due to higher surface runoff during storm events. However, baseflow appears to be
more consistent and higher in the urban site relative to the forested site, especially
during the growing season (Figure 1.2). Because SB is 25% impervious and roughly 5%
runs off via surface flowpaths, a significant fraction of rain falling on impervious surfaces
likely enters pervious surfaces. Increased runoff through pervious soils can be an
important factor in urban catchments (e.g. Burges et al. 1998). The different
mechanisms leading to increased runoff (surface vs. subsurface) have different impacts
on biogeochemical cycles. For example, surface flow paths will redirect atmospheric N
inputs away from active retention sites, whereas increased runoff through pervious soils
will increase flushing of accumulated N, thereby reduce residence times and the
effectiveness of biological processes.

Figure 1.5. Proportion of annual precipitation that emerges as stream runoff vs. %
impervious surface area from this and two other studies. Data from this study and
Burges et al. (1998) represent different water years for each level of impervious surface.
Accurately closing the water budget is difficult in small urban catchments. Both inflow and infiltration (I/I) or exfiltration could be occurring (Lemer et al. 2002). Lawn watering imports water during summers in catchments with public water supply. These processes are difficult to quantify for small watersheds. An additional issue for closing the water budget in small headwater catchments in general is potential loss via deep groundwater flow paths that bypass gauging stations (e.g. Jordan et al. 1997). Zarriello and Barlow (2002) found in the Charles River watershed (MA) that up to 40% of rain inputs might be lost to deep groundwater. Based on comparison of runoff coefficients for CC and the Ipswich R. watershed as a whole (both with similar proportion of impervious surfaces), losses via groundwater in our headwater catchments are potentially 10% of annual precipitation (~100 mm). Unmeasured groundwater export is a major challenge when studying small urban catchments, which are selected based on land use and not geological considerations that ensure all runoff exits via streams (Likens and Bormann 1995). Nevertheless, consistent rates of change in the annual runoff coefficient reported by various studies (Figure 1.5) suggest that the effects of impervious surfaces outweigh other changes in urban systems.

Effect of Urbanization on Stream N Concentrations

Elevated DIN concentrations are also a common feature of urbanizing watersheds (Omernik 1976, Wahl et al. 1997, Driscoll et al. 2003, Groffman et al. 2004, Williams et al. 2004). Our intensively monitored sites suggest little inter-annual variability in concentration, despite very different runoff conditions in WY01 and WY02. Because DIN concentrations in the two intensively monitored watersheds correspond well with those from the spatially extensive data set (Figure 1.4), we believe that both sets of DIN results (i.e. temporally intensive and spatially extensive catchments) are representative for our area.
The rate of N loading clearly contributes to elevated N concentrations. However, N loading by itself was a relatively poor predictor of DIN concentrations in our study (Figure 1.4). This is not entirely unexpected since N loading estimation involves many assumptions (e.g. fertilizer application). In addition, we did not account for other potential inputs, such as pet waste (Baker et al. 2001) or leakage from sewer systems (Lerner 2002). High variability in the NO₃-N vs. N loading relationship has also been observed in forested systems (Aber et al. 2003), where the estimate of N loading (via N deposition) is more certain. Factors other than N loading rates, such as the hydrology or biological processing within the catchment, likely influence variability in DIN concentrations (e.g. Stoddard 1994, Lovett et al. 2000, Aber et al. 2003).

The pattern of nitrate vs. runoff in the forested catchment suggests that several mechanisms influence NO₃-N export concentrations. In CC, NO₃-N accumulates during dry periods and is flushed at moderate runoff levels (Figure 1.3). Flushing is a common response in forested watersheds (Creed et al. 1996, Creed 1998). At high runoffs, nitrate is diluted to levels (< 3 µM) much lower than expected based on NO₃-N in precipitation (> 10 µM). Reasons for low NO₃ concentrations at highest discharge are not clear, although riparian zones may be important (Groffman et al. 1996, 2002). In our urban catchment, high runoff events do not lead to dilution as expected based on precipitation N. In fact, concentrations in SB tend to increase with higher runoffs, suggesting flushing and/or additional N sources become a factor (e.g. fertilizer in surface runoff (Morton et al. 1988), sewage leakage). Although sewage is pumped out of the watershed, waste N may be more important than our N budget suggests. Nitrate stable isotopes (δ¹⁵NO₃) sampled in SB were roughly 10 per mil, within the range of wastewater N (Pellerin 2004).
DON concentrations did not differ as dramatically as NO$_3$ in our urban and forest streams. The higher DON concentrations in the forest compared to urban catchment in WY01 correspond with a greater abundance of wetlands, consistent with other studies on the influence of wetlands on DON (Pellerin et al. 2004). During the wetter WY02, DON concentrations were similar in the two catchments. The reason for this is unclear. DON fluxes were similar in the two catchments, suggesting DON sources remain in urban areas.

Effect of Urbanization on N Export and Retention

The relatively few urban N budgets reported in the literature (Groffman et al. 2004; Baker et al. 2001; Valiela et al. 1997) suggest that N retention remains relatively high in heavily modified urban ecosystems. At the same time, comparisons between undisturbed and urban catchments do indicate that N retention declines with urbanization. Groffman et al. (2004) found that whereas N loads increased 2.3 times, N exports were an order of magnitude higher in an urban vs. forested watershed (650 vs. 52 kg N km$^{-2}$ yr$^{-1}$) corresponding with a decline in N retention from 95% to 75%. Our catchments showed similar differences in N exports and retention during the wet year, and smaller differences during the dry year (Table 1.2). Because small declines in N retention lead to proportionally large increases in flux, understanding the mechanisms of N retention is important as urban areas continue to expand.

N retention can result from sequestration in soils or biomass, as well as denitrification in groundwater, wetlands, or streams. Sequestration and denitrification are likely to decline in urban systems. Changes such as increased impervious surface area (with minimal biological activity), reduced wetland abundance, reduced rooting zone depths (lawns vs. forests), increased surface runoff to streams, and increased water inputs to pervious soils (lowering residence times and increasing flushing e.g.
Green et al. 2004) should lead to reduced biological activity. Reductions in stream residence times due to increased water flow will also lower N retention in streams (Peterson et al. 2001, Wollheim et al. 2001, Seitzinger et al. 2002). Our urban catchment displays many of these characteristics (Table 1.2), some combination of which probably contributes to the decline in N retention. Nevertheless overall levels of N retention are apparently high, even in wet years.

Some factors that might be expected to cause large drops in N retention may not have a big impact. For example, in our urban watershed on average 5% of precipitation enters as new water (equivalent to 50-70 mm/yr) (Pellerin 2004). This corresponds to a direct input of ~40 kg N km$^{-2}$ yr$^{-1}$ (5% of wet plus dry deposition), which represents 7-10% of estimated annual N flux and less than 3% of N loads in our urban catchment. Flushing of fertilizer inputs via surface flowpaths is relatively rare (Petrovic 1990, Morton 1998).

Interannual climate variability appears to impact N export and retention in urban systems much more so than in forested systems. The influence of runoff on N fluxes is well known (e.g. Alexander et al. 1996, Jaworski et al. 1992, Donner et al. 2002). The two water years of our study are near the opposite end of the precipitation range in our area. Because N export concentrations were similar in the two years, the higher flux in the wet year is due primarily to increased runoff (Table 1.2). But because flux was so low to begin with in the forested catchment, the change in absolute terms was relatively small and N retention declined little.

The high apparent rates of N retention in the urban watershed could result from unquantified components of the N budget. While we did not measure PON exports as part of this study, past measurements of PON concentrations (12 μM in SB and 4 μM in CC; Hopkinson, unpublished data) suggest that retention would decline only slightly (2-4%) under the high and low N load scenarios. N export via groundwater flow paths
could also be important. N in this water is not truly retained, and is likely to reenter the river network further downstream. If 100 mm of water is exported via groundwater with N concentrations similar to streams, then N retention would decline in SB by 4-5% using the high N load scenario and 7-8% using the low N load scenario.

Several other factors may be important but are difficult to quantify in complex urban watersheds. As mentioned above, infiltration/inflow could lead to unmeasured exports from the basin (Lerner 2002). Other non-hydrologic vectors (volatilization, export of garden waste) might also be important (Baker et al. 2001). During wetter years, it is likely that a greater proportion of fertilizer inputs are washed out prior to incorporation into lawn biomass, contributing to the higher exports. In addition, sewer leaks and pet waste could contribute N inputs to urban catchments (Baker et al. 2001, Groffman et al. 2004), leading to underestimation of N retention. Despite uncertainties in our N budget, however, the net effect of urbanization appears to be increased N exports in surface waters and reduced N retention.

**Impervious Surfaces as Controls on N Retention – A Hypothesis**

Although the mechanisms by which N is retained in urban systems remain poorly understood, it is clear that N retention declines with increasing urbanization. We hypothesize that because impervious surfaces strongly influence the hydrology and biology of urban catchments, the proportion of impervious area drives N retention. We demonstrate this hypothesis using information from our spatially extensive catchments (0-30% impervious) sampled during WY01 (the dry year). We estimated TDN export concentrations in these catchments using measured DIN (Figure 1.4) and assuming DON concentrations are a positive function of wetland abundance ($r^2 = 0.57$; Pellerin et al. 2004). The resulting TDN concentrations increase with impervious surfaces (Figure 1.6A), though the slope is somewhat shallower than for DIN because areas with low
Figure 1.6. Relationship between impervious surface area and A) TDN concentration (μM, calculated using measured DIN and estimated DON), B) Estimated TDN flux (kg N km\(^{-2}\) yr\(^{-1}\); calculated assuming annual runoff vs. impervious relationship), C) Estimated N loading (kg N km\(^{-2}\) yr\(^{-1}\)), and D) N retention, from the headwater catchments during WY01. Estimates from the two intensively monitored headwater sites for each water year (CC01, CC02, SB01, SB02) are shown for comparison. When only one value is shown for the intensively monitored sites, there is little difference between water years.
impervious surface area also correspond with more wetlands and higher DON concentrations (Pellerin 2004).

We estimated annual runoff in each catchment based on reported changes in runoff coefficient as a function of impervious surfaces (Table 1.2, Figure 1.5). We assumed differences in annual runoff are controlled primarily by impervious surface cover (e.g. Arnold and Gibbons 1996, Paul and Meyer 2001), and that the relationship is linear (Corbett et al. 1997). Other factors (septic population density supplied by public water supplies, surficial geology) also affect runoff, but are likely not as important as impervious surfaces (Zarriello and Ries 2000). The resulting TDN export, as would be expected, is strongly related to impervious surface area (Figure 1.6B).

At the same time, N loading is maximized at moderate levels of impervious surfaces (peaking at ~10% impervious in our catchments) because impervious surface abundance is correlated with residential development, septic waste management, and the amount of lawn (Figure 1.6C). This relationship was also confirmed using a larger number of headwater catchments (data not shown). The bell-shaped relationship in N loading vs. impervious cover makes intuitive sense: if a catchment is 100% impervious, N loading would occur only via atmospheric deposition.

As a result of these changes, we calculate that during WY01, N retention remains high across our headwater catchments but trends downward with greater amounts of impervious surfaces. Using the high N load scenario, N retention declines to about 85% at 30% impervious cover (Figure 1.6D). Thus, N retention during the dry year declines by roughly 5% for every 10% increase in impervious area (up to 30%). During wetter years, N retention declines more rapidly (based on SB in WY02). Theoretically, a 100% impervious catchment should approach 0% retention because of increased water runoff and reduction in biologically active surfaces. The trajectory between 30 and 100% during both wet and dry years is unknown. Key questions then are: at what threshold do
TDN exports peak and at what amounts? Are there thresholds of imperviousness at which N retention drops rapidly? Testing this will require synthesis of similar information from sites that span the entire range of impervious surface levels. The relationships between important factors that we think are primary controls on N retention are summarized in Figure 1.7. We present these relationships as a hypothesis to be tested in other urbanizing areas.

Figure 1.7. Conceptual model of how water runoff, N concentrations, and N loading vary in response to impervious surface area. Our findings suggest that these factors are linked in predictable ways to the level of imperviousness in urbanizing catchments. In our study, peak N loading occurs at 10% impervious, with N concentrations continuing to increase, but becoming more variable, at least until 30% impervious. Changes above 30% are hypothesized. Runoff is assumed to continue to increase through the entire range of imperviousness. As a result, N retention declines. During wet years, runoff increases considerably, but N concentrations change relatively little. As a result, N retention declines more rapidly in catchments with moderate amounts of impervious area.
Conclusion

Urbanization results in increased water runoff, N loading, and N exports. N exports increase relatively faster than N loading, corresponding with declines in N retention. Based on our results, we hypothesize that the proportion of impervious surfaces in the catchment controls the decline in N retention. This effect is consistent with earlier suggestions that impervious surface area is a unifying indicator responsible for a suite of environmental changes (Schueler 1994). Moisture conditions interact with impervious surfaces to further reduce N retention in wetter years. Although N retention declines with urbanization, retention remains relatively high. The mechanisms by which N retention remain high in urban systems are poorly known and warrant further study. Studies of N dynamics in small urban catchments face major challenges due to uncertainty in water flow paths, N loading estimates, and difficult-to-measure N transfers. As suburban sprawl with increased impervious surface continues, impacts on downstream aquatic systems are likely to increase. Management of impervious surfaces in these areas will be an important strategy for preventing increased export of N to coastal systems.
CHAPTER 2

A SPATIALLY DISTRIBUTED FRAMEWORK FOR AQUATIC MODELING OF THE EARTH SYSTEM (FrAMES)

Abstract

We present a new system for modeling river network biogeochemical dynamics called the Framework for Aquatic Modeling of the Earth System (FrAMES). FrAMES is cast at the continental to the global scale and links inland waterways (small and large rivers, lakes, and reservoirs), spatially distributed constituent loads from terrestrial systems, space and time varying hydraulic characteristics, and the kinetics of aquatic processes. The framework is applied initially to total N (TN). We find that coupling an existing global terrestrial N process model with simple aquatic N removal (storage plus denitrification) models can explain much of the variation in mean annual observed TN concentrations along river main stems as well as mean monthly concentrations at basin mouths. The strength of aquatic N removal varies by watershed, depending on the spatial distribution of N loading, hydraulic characteristics, and biological activity. The representation of biological activity strongly influences predicted N removal of aquatic systems, pointing out the need to better understand biological controls in different regions of the world. The ability of FrAMES to account for spatial and temporal heterogeneity, both within and across watersheds, will allow for better predictions of changing N fluxes under continued global changes in population, land use, and climate.
Introduction

Aquatic systems are important areas of biogeochemical activity within watersheds. As part of the nitrogen (N) cascade, freshwater aquatic systems are thought to denitrify or store between 30 and 70% of N loads (Galloway et al. 2003). Many large-scale N studies have assumed a uniform proportion of N removal (long term storage plus denitrification) by aquatic systems across a wide variety of watersheds (Seitzinger and Kroeze 1998, Caraco and Cole 1999a, Van Drecht et al. 2003). These studies have not accounted for variability in aquatic N removal caused by interactions between the spatial distribution of N loads, hydraulic conditions, and biological activity within river networks. The position of N loads relative to aquatic N processing locations within basins is potentially an important factor defining N fluxes to the coastal zone, and incorporation of this spatial information is a critical next step in the development of global biogeochemical models (Meybeck and Vörösmarty 2005).

Spatially explicit river network models have recently been applied at the watershed or regional scale to determine factors controlling N exports to the coastal zone (Alexander 2000, Donner et al. 2002, Seitzinger et al. 2002). These modeling studies have found that small rivers have a disproportionate influence on N exports from watersheds, consistent with findings by field researchers (e.g. Peterson et al. 2001). In northeastern United States watersheds, roughly half of the aquatic N removal occurred in small streams and rivers (Seitzinger et al. 2002). As a result of N removal by small rivers, Alexander et al. (2000) found in the Mississippi River Basin that most basin mouth N exports originate near large rivers. Thus, knowledge of both the position of N loads in the watershed and the distribution of aquatic removal strength is needed to understand watershed N exports. At the continental to global scale, data constraints prevent application of regional models with a detailed representation of small rivers, and as a result global models have thus far ignored their role. Here we take a geomorphological
approach to integrate the role of small river systems with large rivers, lakes, and reservoirs to model aquatic N removal at the global scale.

In this paper, we present the Framework for Aquatic Modeling of the Earth System (FrAMES), a spatially explicit system for modeling biogeochemical activity in river networks applicable to both the continental and global scale. A major feature of FrAMES is a representation of small rivers (i.e. those draining areas ~ 1 km²). The modeling framework is the first step in the development of a dynamic aquatic ecosystem model that can predict changing material fluxes as global environmental conditions change. The framework is designed to handle multiple, linked constituents to explore baseline stoichiometry and the impacts of anthropogenic change on constituent:constituent relationships. Here, we use FrAMES to explore how spatial and temporal heterogeneity of both N loads and hydrologic conditions affect aquatic N fluxes both within and across watersheds in a variety of biomes. We also explore how aquatic N removal capacity varies with different assumptions regarding the control of aquatic biological activity, for which there is considerable uncertainty. Finally, we address the value of incorporating spatially and temporally distributed observed nutrient concentration data to test the predictions of linked terrestrial and aquatic process models.
Methods

The Framework for Aquatic Modeling of the Earth System (FrAMES) consists of several components:

Nutrient Removal Model

Although various nutrient-processing algorithms can be included in the framework, we focus on a particular form that clearly describes the interaction between biological and hydraulic characteristics in determining nutrient removal by surface water bodies (Kelly et al. 1987, Stream Solute Workshop 1990, Alexander 2000). We define nutrient removal by any given surface water body as:

\[ R = 1 - \exp\left(-\frac{u_f}{H_L}\right) \]  

(2.1)

where \( R \) is the proportion retained or removed (unitless), \( u_f \) is the vertical velocity, or mass transfer coefficient, of the nutrient molecule of interest (m yr\(^{-1}\)) and \( H_L \) is the hydraulic load (m yr\(^{-1}\)). In the current application we apply Equation (2.1) to Total Nitrogen (TN), but the equation can be applied to other nutrients as well (see Kelly et al. 1987). \( u_f \) is equivalent to \( U/C \) where \( U \) is the areal rate of nutrient removal from the water column (e.g. denitrification plus net storage for N) (mg m\(^{-2}\) yr\(^{-1}\)) and \( C \) is average concentration of the nutrient in the water column (mg m\(^{-3}\)). \( u_f \) can be determined using a variety of empirical approaches (e.g. whole reach tracer additions, core studies), providing abundant information for a priori parameterization of biological activity (e.g. Howarth et al. 1996). Several methods of specifying \( u_f \) globally are described below.
$H_L$ can be derived in several interrelated ways:

$$H_L = \frac{dv}{d} = \frac{\frac{d}{\tau}}{\frac{V}{Q}} = \frac{Q}{A_{sw}} = \frac{Q}{wL}$$

where $d$ is mean water depth (m), $v$ is mean water velocity (m yr$^{-1}$), $w$ is mean width (m), $L$ is length (m), $\tau$ is residence time (yr$^{-1}$), $V$ = volume (m$^3$), $Q$ is discharge (m$^3$ yr$^{-1}$), and $A_{sw}$ is surface area of the water body (m$^2$). $H_L$ over space and time is ultimately derived using $Q$, which can be obtained purely from hydrological models or from composites of observed discharge and model predicted runoff (Fekete et al. 2002). In river channels, hydraulic equations define $w$, $d$, and $v$ as a function of $Q$. An important observation, elaborated further below, is that $H_L$ can be defined based on discharge and surface area of the water body alone, regardless of whether the water body is a river, reservoir, or lake. This proves to be a useful quality when integrating various types of water bodies within river networks.

Equation (2.1) is derived from the river network transfer function $[\exp(-k\tau)]$ used by Alexander et al. (2000) based on the equality $k = \frac{\nu_r}{d}$ (Stream Solute Workshop 1990), where $k$ is the time specific removal rate (yr$^{-1}$), $\tau$ is residence time (yr), and $d$ is depth (m). As a biological parameter, $k$ includes some hydrological information (depth). To facilitate understanding model behavior (e.g. hydrological vs. biological controls of nutrient removal), we prefer to use $\nu_r$ as the biological parameter, and incorporate depth with other hydrological variables to define $H_L$ (Equation 2.2), similar to the approach first suggested by Kelly et al. (1987).
Surface Water Network

The surface water network as currently defined includes a representation of large rivers, small rivers, large lakes, and a major subset of the world’s largest reservoirs.

Large Rivers. A 30 minute simulated topological network (STN-30) defines the flow path of material in large river systems to the coastal zone. The geomorphological attributes of the network are detailed in Vörösmarty et al. (2000). Each individual grid cell in the STN-30 corresponds with a 5th to 6th order river network at the 1:62500 scale (Vörösmarty et al. 2000). We assume that the large river channel within each grid cell is longer than the grid cell length because of meandering (sinuosity) as it flows through the cell. To account for this, we assume a sinuosity factor of 1.3 globally (Vörösmarty et al. 2000).

Small Rivers. We represent small rivers using a statistical, geomorphological approach based on the Geomorphological Unit Hydrograph (GUH) (Rodriguez-Iiturbe and Valdes 1979, Rodriguez-Iiturbe and Rinaldo 1997). We assume each STN-30 grid cell includes a 6th order sub-grid cell river network (Vörösmarty et al. 2000). We use the geomorphological parameters \( R_b \), \( R_l \), and \( R_a \) (bifurcation, length and area ratios) to estimate the proportion of land area in each grid cell draining to a particular stream order, and the probability of a lower order stream draining to any given higher order stream (see below). Based on these probabilities, we can estimate mean \( Q \), \( H_L \), the probability of a nutrient molecule following a particular flow path, and nutrient removal at each step along the flow path. The assumption of uniform distribution of N loading to the aquatic system within the grid cell allows us to calculate the total proportion of N retained by the sub-grid cell river network.

The probability a nutrient molecule will enter the river network in a particular stream order is defined as (Rodriguez-Iiturbe and Rinaldo 1997):

37

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\[
\theta_{\omega} = \begin{cases} 
\frac{N_i A_i}{A_{i2}} & \text{if } \omega = 1 \\
N_{\omega} \left[ A_{\omega} - \frac{\sum_{k=1}^{\omega-2} P_{k,\omega} N_k A_k}{N_{\omega}} \right] & \text{otherwise}
\end{cases}
\]

where \( \theta \) is the proportion of watershed area draining to stream order \( \omega \), \( N \) is number of streams of order \( \omega \), \( A \) is mean watershed area draining each stream order, \( \Omega \) is the order of the network. \( N \) and \( A \) for each stream order are determined using \( R_b \) and \( R_a \).

For example, for a 6th order basin with \( R_b = 4 \), there is \( N = 1 \) stream that is 6th order, \( N = 4 \) streams that are 5th order, \( N = 16 \) that are 4th order, etc. For a 6th order watershed area = 2500 km² and \( R_a = 4.5 \), \( A = 556 \) km² at the mouth of each 5th order stream, 139 km² for each 4th order stream, etc. The probability of a stream of order \( i \) draining to a stream of order \( j \) (\( p_{ij} \)) is determined as

\[
p_{ij} = \begin{cases} 
\frac{2N_{i+1} + (N_i - 2N_{i+1})E(j, \Omega)}{N_i \left[ \sum_{k=i+1}^{\Omega} E(k, \Omega) \right]} & j = i + 1 \\
\frac{(N_i - 2N_{i+1})E(j, \Omega)}{N_i \left[ \sum_{k=i+1}^{\Omega} E(k, \Omega) \right]} & \text{otherwise}
\end{cases}
\]

\[ (2.4) \]
where $E$ is the number of links of order $i$ in the network of order $\Omega$ under the assumption of the random topological model,

$$E_{i,\Omega} = \frac{N_i}{\prod_{j=2}^{i} \frac{N_{j-1}}{2N_j - 1}}$$

In our application we assume $R_a = 2$, $R_s = 4.6$ and $R_b = 3.5$ and that these values are constant globally. The parameters are within the range commonly observed (Dingman 1994). We do not include in the current application any variation in the geomorphic parameters that could arise as a function of local soil, geology, hydrological conditions, or local management (e.g. drainage ditches). The GUH approach requires that $R_a/R_b > 1.2$ (Rodriguez-Iturbe and Rinaldo 1997). Using these geomorphic parameters, and assuming a 6th order watershed (grid cell) with area = 2500 km$^2$, the probability of watershed area (and aquatic nutrient loads) draining directly to each stream order is shown in Figure 2.1. The probability of transfer from a stream of one order to a higher order is given in Table 2.1. For a 6th order network there are 32 possible flow paths for a nutrient molecule to travel to the mouth.
Figure 2.1. Proportion of watershed area that initially drains to a particular stream order in a 6th order watershed, assuming $R_i = 4.6$, $R_b = 3.5$, and $R_c = 2$.

<table>
<thead>
<tr>
<th>Source Stream Order</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.786</td>
<td>0.108</td>
<td>0.055</td>
<td>0.029</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.788</td>
<td>0.110</td>
<td>0.059</td>
<td>0.042</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.795</td>
<td>0.120</td>
<td>0.120</td>
<td>0.085</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.821</td>
<td>0.179</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1. Probability of a stream of a given order entering another stream order, assuming $R_i = 2$, $R_b = 3.5$, $R_a = 4.6$ (Equation 2.4).
The application of Equations (2.3-2.5) in each grid cell requires an estimate of area and length of the 6th order stream from which area and length of all smaller stream orders are derived using $R_a$ and $R_l$. The area draining the 6th order stream is defined by the grid cell area. The length of the 6th order reach ($L_6$) is estimated as

$$L_6 = \sqrt{\text{CellArea}} \left(1 - \frac{1}{R_l}\right)$$

where CellArea is the grid cell area and $R_l$ is the length ratio. The square root of CellArea is used rather than CellLength to ensure that east-west flowing reaches act the same as north-south flowing reaches regardless of latitude. Mean lengths of lower order stream reaches are derived using $R_l$ (Table 2.2).

The 30-minute grid cells that have no upstream inputs consist exclusively of a 6th order local drainage network. Any 30-minute grid cells with inputs from upstream grid cells consist of a large river passing through the cell into which drain on average 3.5 5th order river networks from the local grid cell area (based on $R_b$). Area calculated to drain to 6th order streams (Figure 2.1) in these grid cells is assumed to drain directly into the STN-30 river network. This approach for linking the two river network scales (sub-grid and STN-30) is an approximation. However, the sub-grid scheme is based on sound geomorphic principles, and the combination of the two scales results in consistent changes in numbers, area, and length across the combined scales. Both total lengths and mean watershed area predicted using the approach (with the listed values for the geomorphic parameters) are similar to those estimated by Leopold et al. (1964) for the conterminous United States (Figure 2.2). The transition between local and large river network (5th or 6th order) is smooth, indicating our approach provides a consistent means of linking the two river network scales.
<table>
<thead>
<tr>
<th>Stream Order</th>
<th>Mean Length (km)</th>
<th>Mean Area (km²)</th>
<th>Proportion of Watershed to Order</th>
<th>Q (m³ s⁻¹)</th>
<th>Depth (m)</th>
<th>Velocity (m s⁻¹)</th>
<th>Width (m)</th>
<th>H_L (m yr⁻¹)</th>
<th>Proportion Retained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.78</td>
<td>1.2</td>
<td>0.26</td>
<td>0.023</td>
<td>0.07</td>
<td>0.28</td>
<td>1.19</td>
<td>715.6</td>
<td>0.048</td>
</tr>
<tr>
<td>2</td>
<td>1.56</td>
<td>5.6</td>
<td>0.13</td>
<td>0.106</td>
<td>0.12</td>
<td>0.33</td>
<td>2.61</td>
<td>748.6</td>
<td>0.046</td>
</tr>
<tr>
<td>3</td>
<td>3.13</td>
<td>25.7</td>
<td>0.15</td>
<td>0.489</td>
<td>0.22</td>
<td>0.38</td>
<td>5.75</td>
<td>783.2</td>
<td>0.044</td>
</tr>
<tr>
<td>4</td>
<td>6.25</td>
<td>118.1</td>
<td>0.18</td>
<td>2.248</td>
<td>0.39</td>
<td>0.45</td>
<td>12.64</td>
<td>819.4</td>
<td>0.042</td>
</tr>
<tr>
<td>5</td>
<td>12.50</td>
<td>543.5</td>
<td>0.21</td>
<td>10.340</td>
<td>0.69</td>
<td>0.54</td>
<td>27.78</td>
<td>857.3</td>
<td>0.040</td>
</tr>
<tr>
<td>6</td>
<td>25.00</td>
<td>2500.0</td>
<td>0.08</td>
<td>47.565</td>
<td>1.22</td>
<td>0.63</td>
<td>61.07</td>
<td>896.9</td>
<td>0.038</td>
</tr>
</tbody>
</table>

Table 2.2. Sub-grid cell river network characteristics, assuming 2500 km² watershed (50 x 50 km grid cell), R_b=3.5, R_f=4.6, R_t=2, uniform distribution of runoff (500 mm yr⁻¹), depth = 0.288Q⁰.³⁷⁴⁸, velocity=0.4162Q⁰.¹⁰⁹, width=8.32Q⁰.⁵¹⁶² (where Q is discharge) and \( \nu_r = 35 \text{ m yr}^{-1} \) where \( \nu_r \) is the vertical velocity of TN. N removal within each stream order is calculated by \( R = 1 - \exp(-\nu_r/H_L) \), where R is N removal and H_L is the hydraulic load. Using the probabilities in Table 2.1, and assuming uniform N loading within the grid cell and constant \( \nu_r \), the proportion retained by the entire sub-grid cell river network in this example is 0.131 (Equation 2.9). Note that H_L is relatively constant across stream order because although discharge increases by several orders of magnitude, mean widths and lengths also increase.
Figure 2.2. Total length (A) and mean contributing area (B) as a function of stream order for the river network of the conterminous United States predicted by the combined subgrid cell and STN-30 river networks, assuming $R_s = 4.6$, $R_o = 3.5$, and $R_i = 2$. The subgrid cell river network includes orders 1-6 and the STN-30 network includes orders 6 through 10. Order 6 is represented at both scales. Leopold et al (1964) estimates are for the conterminous United States based on a 1:62500 scale map interpretation.
Using runoff distributed uniformly throughout the grid cell, we can calculate $Q$, $w$, $d$, $v$, and $H_L$ for each stream order and can therefore apply Equation 2.1 to the sub-grid river network. An example of this calculation is shown in Table 2.2.

**Lakes and Reservoirs.** Large lakes and reservoirs were embedded in the STN-30 river network (Figure 2.3 insets). A total of 633 large reservoirs are currently included (Vörösmarty et al. 1997a, Vörösmarty et al. 1997b, Green et al. 2004). Each reservoir includes attributes such as volume, dam height and surface area, which in conjunction with $Q$ are used to calculate $H_L$ (Equation 2.2). We assumed that reservoirs replaced STN-30 river channels (large rivers), but that a sub-grid river network still drains into the reservoir locally. Small reservoirs are not included in this analysis, though in aggregate they can cause considerable hydrological modification in basins (Vörösmarty et al. 2003) that potentially influences N removal.

The distribution and surface area of lakes were obtained from a digital database of 6392 geo-referenced large lakes (1:3 million scale) (Meybeck 1995, Green et al. 2004). Global surface area of lakes in this database is 1.75 million km$^2$, roughly 60% of the extrapolated global lake surface area (2.8 million km$^2$) estimated by Meybeck (1995). Lakes smaller than 10 km$^2$ (~30% of global lake area, Meybeck 1995) are entirely absent in the current analysis. From the lakes database, we calculated the total area of each grid cell covered by lakes. The composite area of lakes in each grid cell was linked to the STN-30 river network as a single body of water. That is, all discharge draining through the grid cell passes through such composite lakes. In first basin cells (those with no upstream inputs), lakes received all the discharge from the sub-grid river network. $H_L$ can then be calculated from discharge and lake surface area (Equation 2.2). In lakes that covered more than one grid cell (e.g. the Great Lakes), the potential
flow path specified by the STN-30 river network was applied within the lake as well (Figure 2.3).

In all grid cells we reduced the estimate of removal by the sub-grid cell river network according to the proportion of the grid cell covered by lakes. This accounts for a reduced sub-grid cell river network due to the presence of lakes. The method of embedding lakes in the river network (i.e. as a single body of water intercepting all Q through the grid cell) allows lakes to intercept a greater amount of N inputs than they would if they were individual lakes, thereby giving lake benthic surface area the maximum opportunity to remove nutrients from overlying water. The role of large lakes in the current framework is therefore likely somewhat greater than in actuality.

**Hydrology and Hydraulics**

Spatially distributed discharge fields are used to determine key hydraulic properties influencing constituent removal. In the current analysis we focus on mean annual and monthly discharges, but the approach can be applied to time series as well. Composite discharge fields integrate Water Balance Model (WBM) predicted local runoffs (Federer et al. 2003) and observed discharges at 663 global stream gauging sites (Fekete et al. 2002). These composite discharge fields, both annual and monthly, result in exact correspondence with observed discharge at gauging sites, and distribute the accumulating discharge between stations based on WBM runoff variability. Outside of gauged regions, the discharge fields rely solely on WBM results. For the sub-grid river network, we first derive local runoff from the composite discharge fields, and calculate discharge for each sub-grid stream order based on mean area (Table 2.2).
Figure 2.3. Global distribution of N loading to the river network predicted by the Bouwman et al. (2005) model (Center Panel). Test basins used in the study are shown in the insets, including A) Yukon, B) Mississippi, C) Rhine and Danube, D) Lena, E) Amazon and Orinoco, F) Chang Jiang. Insets show the STN-30 river network, distribution of large reservoirs (red squares), and lakes (gray shaded areas). For lakes, the darker the shade, the greater percentage of the grid cell taken up by lakes. In FrAMES, each grid cell also has a 5th or 6th order sub-grid cell river network (not shown).
We use the following hydraulic equations to derive mean channel width (w), water depth (d), and water velocity (v):

\[
\begin{align*}
  d &= 0.288Q^{0.3745} & (2.7a) \\
  w &= 8.32Q^{0.5162} & (2.7b) \\
  v &= 0.4162Q^{0.109} & (2.7c)
\end{align*}
\]

The hydraulic equations are based on mean annual Q and dimensions at US stream gauges (Bjerklie et al. 2003, pers. comm.), and assumed valid globally. The hydraulic equations are similar to those used by Alexander et al. (2000) in the Mississippi. When \( H_L \) is calculated, the exponents from Equation (2.7) determine the rate at which \( H_L \) changes with increasing Q, whereas the intercepts set the overall level of \( H_L \) throughout the watershed. The exponent for width tends to vary less than that for depth or velocity across watersheds (Leopold et al. 1964). Therefore, because width can be used to estimate \( H_L \) (\( H_L = Q/A \)), assuming a globally uniform rate of width change in the downstream direction is reasonable. In contrast, the intercept for width appears to be somewhat more variable (Leopold et al. 1964), but factors controlling this variability are less known. In this analysis we assume the mean hydraulic equations can be applied globally. For the monthly scenarios, Equation (2.7) is also applied to changing hydraulics with Q at a station.

We derive \( H_L \) for lakes and reservoirs also using Q/A. An important property of \( H_L \) in lakes and reservoirs is that \( H_L \) can be derived from Q and surface area of the water body alone and is independent of depth. For example, at steady state a 1 km\(^2\) reservoir that is 30 m deep has the same \( H_L \) as a 1 km\(^2\) reservoir that is 100 m deep, assuming both have the same Q inputs. Thus, the relevant hydraulic property controlling N removal in individual river reaches, lakes and reservoirs in our model (Equation 2.1) is
the amount of benthic surface area relative to the incoming discharge. We note that the
\( \nu_f \) parameter as used in this application integrates all biological N transformations in a
specified water body, including water column processes. The key assumption is that in
the long term, benthic processes control N removal (either as loss via denitrification or
storage). Theoretically \( \nu_f \) could also be negative indicating net regeneration of N (e.g.
remineralization, resuspension, or N fixation) by the water body.

N Loading to Aquatic System

FrAMES requires independent model generated predictions of N loading to the
aquatic system as input. We used predictions from a recent global terrestrial N cycle
model (Van Drecht et al. 2003, Bouwman et al. 2005) to load total N (TN) to the river
network (Figure 2.3). TN loading to the aquatic system is spatially distributed at 30-
minute resolution. Inputs to aquatic systems occur via leaching, direct atmospheric
inputs, and point sources (Van Drecht et al. 2003). Direct atmospheric inputs occur
only to grid cells with large surface water bodies (IMAGE-team 2001).

A comparison of four independent N loading data sets shows that there is
considerable disagreement in non-point source systems, especially for estimates of N
deposition and N fixation in natural and semi-natural systems (Van Drecht et al. In
Review). The N loading data used to generate the predictions of aquatic N inputs
(Bouwman et al. 2005) tends to have higher atmospheric N deposition in northern
latitudes compared with other N loading data sets (Van Drecht et al. In Review), and
therefore could affect our model predictions for Arctic systems.

To derive monthly N leaching, we scaled annual leaching based on the
proportion of monthly to annual runoff. N concentrations entering the river network via
leaching are therefore assumed to be constant throughout the year. This approach does
not consider changes in N concentration related to seasonal changes in terrestrial ecosystem processing that can occur in temperate systems (e.g. Likens and Bormann 1995). To derive monthly atmospheric inputs, we scaled the annual estimate based on the proportion of monthly to annual precipitation. For monthly point source inputs, we assigned equal amounts of point loading to each month (i.e. monthly point loading = annual point loading / 12).

System Integration Through FrAMES

In our modeling framework, Equation (2.1) (or any related algorithm) defines N removal by individual surface water bodies, and the surface water network links the various inland water bodies. The routing is accomplished by a flow accumulation routine that incorporates the N loss algorithm. The transfer of materials from each grid cell of the STN-30 river network is given by:

\[
TN_i = (\text{Upstream}_{ln} + (\text{Local}_{ln} \times TE_{local})) \times TE_{large} \times TE_{lake} \times TE_{reservoir} \tag{2.8}
\]

where \( TN_i \) = TN exported from grid cell i, Local\( \text{Grid}_{ln} \) = all N inputs to the aquatic system within the grid cell i, Upstream\( ln \) = TN inputs from all grid cells immediately upstream from grid cell i, \( TE = \) transfer efficiency (TE = 1 – R) associated with the local river network, and large river channels, lakes, or reservoirs.
where, \( v_f \) is vertical velocity of the nutrient (m yr\(^{-1}\)), \( H_L \) is hydraulic load (m yr\(^{-1}\)), \( m \) is unique flow path for \( M = 32 \) possible flow paths in the sub-grid cell 6th order river network, \( n \) is the sub-grid cell stream order in flow path up to \( N \) stream orders in flow path, where \( N = 6 \) in grid cells without upstream inputs, and \( N = 5 \) in all other grid cells. \( Z_m \) is the proportion of grid cell area draining via a particular sub-grid cell flow path, and, LakeArea/GridArea is the proportion of grid cell as lake. Table 2.2 gives an example of how Equation (2.9) is applied to calculate N removal in a 6th order river network.

The scheme for embedding lakes and reservoirs within the river network assumes that 1) small river network removal is reduced based on the proportion of lake area in the grid cell, 2) grid cells with large reservoirs or that are lake dominated have no large river channels, 3) a large river channel remains in grid cells where lake area is less than 50% of the total grid cell area. We assume that all N inputs, including point sources, first enter the local river network according to Figure 2.1 at the upstream end of the stream reach, rather than by a distribution along the stream reach. Similarly, exports from the small river network enter the large river network at the upstream end of the

\[
TE_{\text{localriver}} = \left[ \sum_{m=1}^{M} \left( Z_m \prod_{n}^{N} \exp(-v_f / H_{L,m,n}) \right) \right] \times \text{LakeArea/GridArea} \tag{2.9}
\]

\[
TE_{\text{largeriver}} = \exp(-v_f / H_{L,\text{largeriver}}) \quad \text{if LakeArea/GridArea < 0.5 or no large reservoir present}
\]

\[
= 1 \quad \text{if LakeArea/Grid Area > 0.5 (lakes supercede large river channels), or if large reservoir present} \tag{2.10}
\]

\[
TE_{\text{lake}} = \exp(-v_f / H_{L,\text{lake}}) \tag{2.11}
\]

\[
TE_{\text{reservoir}} = \exp(-v_f / H_{L,\text{reservoir}}) \tag{2.12}
\]
large river reach. Because N inputs that first enter the river network always pass through an entire reach length (i.e. all nutrient molecules experience the entire reach length), aquatic removal at the initial point of entry to the river network is likely to be an overestimate (Lindgren and Destouni 2004). But because residence time at the original point of entry is small in comparison to that of the entire river network, the error is likely to be small.

Oberved Nutrient Data

We test FrAMES predicted TN concentration over space and time using observed TN data from a number of tropical, temperate, and arctic watersheds for which we could locate transect and/or time series (Table 2.3, Figure 2.3). We also compare predictions against the long-term mean TN concentrations for 31 globally distributed watersheds compiled in the GEMS-GLORI data set (Meybeck and Ragu 1997, Van Drecht et al. 2003, Green et al. 2004). Although GEMS-GLORI provides a summary of mean annual N concentrations at the basin mouths of a number of world rivers, no similar data set exists for time series or transects along river main stems, requiring compilation from a variety of sources (Table 2.3).
<table>
<thead>
<tr>
<th>River</th>
<th>Transects</th>
<th>Time Series</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amazon</td>
<td>Average TN from 8 cruises between 1982 and 1984 (CAMREX)</td>
<td>Mean monthly NO₃+PN 1983-93 with average DON at Manaus from CAMREX cruises.</td>
<td>Devol et al. 1995, CAMREX 1998</td>
</tr>
<tr>
<td>Danube</td>
<td>TN, Long term annual</td>
<td>-</td>
<td>EEA 2004-</td>
</tr>
<tr>
<td>Mississippi</td>
<td>TN Long term annual</td>
<td>TN, Long term mean monthly</td>
<td>USGS</td>
</tr>
<tr>
<td>Orinoco</td>
<td>-</td>
<td>TN, Mean monthly 1982-85</td>
<td>Lewis and Saunders 1989</td>
</tr>
<tr>
<td>Rhine</td>
<td>TN, Long term annual</td>
<td>-</td>
<td>EEA 2004</td>
</tr>
<tr>
<td>Yukon</td>
<td>TN, Flow-weighted mean, 2001-03</td>
<td>TN, average from May-Sept, 2002</td>
<td>USGS, Guo et al. 2004</td>
</tr>
<tr>
<td>Lena</td>
<td>TDN, August 2003</td>
<td>TDN collected during 2003</td>
<td>Partners (McClelland, pers. comm.)</td>
</tr>
</tbody>
</table>

Table 2.3. Source of observed N concentration data used for comparison with model predictions. All are TN concentrations unless noted otherwise.
Scenarios – Biology

Relatively little is known about how biological activity varies in space and time at the global scale. As a result, we test the framework using several scenarios of biological activity that vary the controls on \( u_f \). We also include for comparison two models recently described in the literature (Alexander 2000, Seitzinger et al. 2002). Although global variability of certain hydrological characteristics used by FrAMES is also poorly known (e.g. geomorphic parameters \( R_a, R_o, R_i \); intercepts of hydraulic equations), others are fairly well constrained (e.g. distributed Q constrained by observations; exponents of hydraulic equations). In testing the biological scenarios, we assume the hydrological parameters in FrAMES can be considered globally uniform.

We explore six scenarios of biological activity, summarized in Table 2.4. Our initial scenario (VFO) assumes no biological activity (\( u_f = 0 \) m yr\(^{-1} \)). Predicted N concentrations from this scenario reflect conservative mixing of N loads to the aquatic system, and is a useful check of the loading predictions. Scenario two (VF35) assumes the same level of biological activity throughout the world’s aquatic ecosystems. The VF35 scenario assumes TN removal kinetics are 1\(^{st}\) order and uniform (\( u_f = 35 \) m yr\(^{-1} \)) throughout the river network, including lakes and reservoirs. \( u_f \) of 35 was the average suggested by Howarth et al. (1996) for rivers, and is somewhat higher than that suggested for lakes (10 m yr\(^{-1} \)). An important assumption in this scenario, as well as those described below, is that benthic processes dominate N removal. The constant VF scenario is useful to isolate the potential effect of hydraulic and/or N loading variability as factors determining N fluxes and N removal among watersheds. We will therefore use the VF35 scenario as the benchmark for comparison in the analyses below.
<table>
<thead>
<tr>
<th>Scenario</th>
<th>Biology</th>
<th>Loading</th>
<th>Time Step</th>
<th>Source of Biological Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>VF0</td>
<td>Conservative mixing of loads</td>
<td>Distributed</td>
<td>Annual/Monthly</td>
<td>No Biology</td>
</tr>
<tr>
<td>VF35</td>
<td>Vertical velocity constant (first order)</td>
<td>Distributed</td>
<td>Annual/Monthly</td>
<td>Howarth et al. (1996)</td>
</tr>
<tr>
<td>VF35-Q10</td>
<td>Vertical velocity function of air temp.</td>
<td>Distributed</td>
<td>Annual/Monthly</td>
<td>Howarth et al. (1996) with Q_{10}</td>
</tr>
<tr>
<td>MM1</td>
<td>Vertical velocity varies with N conc.</td>
<td>Distributed</td>
<td>Annual/Monthly</td>
<td>Garcia-Ruiz (1998)</td>
</tr>
<tr>
<td>SPARROW</td>
<td>Vertical velocity function of Q, depth</td>
<td>Distributed</td>
<td>Annual</td>
<td>Alexander et al. (2000)</td>
</tr>
<tr>
<td>RIVRN</td>
<td>Vertical velocity function of H_{L}</td>
<td>Distributed</td>
<td>Annual</td>
<td>Seitzinger et al. (2002)</td>
</tr>
<tr>
<td>VF35-UL</td>
<td>Same as VF35</td>
<td>Uniform</td>
<td>Annual</td>
<td>Howarth et al. (1996)</td>
</tr>
</tbody>
</table>

Table 2.4. Model scenarios describing the control of biological activity, N loading and time step.
Scenario three (VF35-Q10) assumes that temperature controls variability in $\nu_f$. In this scenario, we again assume that kinetics are 1st order, but apply a $Q_{10}$ factor as follows:

$$\nu_f = \nu_{f,\text{ref}} Q_{10}^{(T_{air}-T_{ref})/10}$$  \hspace{1cm} (2.12)

where $\nu_{f,\text{ref}}$ is assumed = 35 m yr$^{-1}$, $T_{\text{ref}} = 15$ °C, $T_{air}$ is the mean air temperature for the grid cell and $Q_{10} = 2$. In this scenario, a $\nu_f$ of 35 applies to regions where mean temperature is 15 °C (i.e. temperate regions) and every 10 °C change in air temperature results in a factor of 2 $\nu_f$ change. $\nu_f$ ranges from 6 m yr$^{-1}$ at $T_{air} = -10$ °C to 140 m yr$^{-1}$ at $T_{air} = 35$ °C (Figure 2.4A). $Q_{10} = 2$ is reasonable for denitrification kinetics at particular locations (Seitzinger 1988). Across sites with different mean annual temperature, local microbial communities could potentially adapt to local temperatures keeping N removal high (e.g. Devol et al. 1997), making such a $Q_{10}$ factor less applicable. Nevertheless, we use the $Q_{10}$ approach to explore how N removal might vary with temperature, which could exert control via kinetic effects, dominant form of N loaded to the aquatic system, and/or length of growing season. Using the $Q_{10}$ function, biological activity is higher in tropical systems and reduced in arctic systems, and varies within watersheds based on air temperature. In the monthly time step scenarios, biological activity is greater during warmer months. The use of air temperature in Equation (2.12) results in a greater range in $\nu_f$ than if a water temperature model such as that described by Donner et al. (2002) were used (Figure 2.4A).
Figure 2.4. Control of $\nu_f$ in the scenarios where it is not held constant, including A) $\nu_f$ as a function of air temperature in the VF35Q10 scenario, assuming $Q_{10} = 2$, $T_{ref} = 15^\circ C$ and $\nu_f$ at $15^\circ C = 35 \text{ m yr}^{-1}$. Shown for comparison, but not used as a scenario, is $\nu_f$ assuming the same parameters but instead using modeled water temperature as described in Donner et al. (2002). B) $\nu_f$ as a function of N concentration in the MM1 scenario, assuming $U_{max} = 2.0 \text{ mg m}^{-2} \text{ hr}^{-1}$ and $K_m = 0.25 \text{ mg l}^{-1}$ (Garcia-Ruiz et al. 1998). Using these kinetic parameters, $\nu_f$ ranges from 1 to 70 m yr$^{-1}$. Shown for comparison is the much narrower range in $\nu_f$ assuming an alternative set of kinetic parameters (Garcia-Ruiz et al. 1998): $U_{max} = 16 \text{ mg m}^{-2} \text{ hr}^{-1}$ and $K_m = 9 \text{ mg l}^{-1}$. Inset shows uptake vs. concentration relationship from which $\nu_f$ was calculate ($\nu_f = U/C$). C) $\nu_f$ derived from the $k$ values calibrated using the SPARROW model in the Mississippi (Alexander 2000). In the SPARROW model, a unique $k$ was calibrated for different stream sizes defined by mean annual $Q$. $\nu_f$ was derived from $k$ and water depth. $\nu_f = 35 \text{ m yr}^{-1}$ shown for comparison. D) $\nu_f$ derived from the algorithm used in the RIVRN model (Seitzinger et al. 2002) by setting the RIVRN equation equal to Equation (2.1).
Scenario 4 (MM1) assumes that surface water N concentration controls N removal kinetics. In this scenario, we assume a Michaelis-Menten type function applicable for denitrification can be applied based on TN concentrations alone. Although it is highly unlikely that this is the case, we include this scenario to illustrate how different controlling algorithms can be incorporated into FrAMES. In a recent study, a number of Michaelis-Menten parameters were determined for denitrification within a single basin, and these varied with N concentration, substrate type and/or organic matter content (Garcia-Ruiz et al. 1998). We selected a single set of parameters that would give the greatest range in $\nu_f$ across the N concentration gradient ($U_{\text{max}} = 2 \text{ mg m}^{-2} \text{ hr}^{-1}$, $K_m = 0.25 \text{ mg l}^{-1}$) (Figure 2.4B). Other parameters described by Garcia-Ruiz (1998) would result in narrower range of $\nu_f$'s (e.g. Figure 2.4B). TN concentrations are assumed well mixed in each water body and constant over the time step.

Finally, we included two scenarios using model parameterizations recently published. Scenario 5 (SPARROW) includes the parameters and algorithm from the SPARROW model calibrated for the Mississippi (Alexander et al. 2000). In this model, biological activity as $\nu_f$ varies with discharge as well as water depth (Figure 2.4C). Although we applied the equation as stated in Alexander et al. (2000) (i.e. $R = 1 - \exp[-kx]$), the $k$ values (d$^{-1}$) can be converted to $\nu_f$ (m yr$^{-1}$) as $\nu_f = k*365*h$ where $h$ is water depth (m) (Figure 2.4C). We assume the $k$ parameters for largest rivers (> 850 m$^3$ s$^{-1}$) could be applied to lakes and reservoirs in our study. The original SPARROW parameters were calibrated using the 1:500,000 and therefore the role of extremely small streams was not included (Seitzinger et al. 2002). Nevertheless, we assume here that the parameter calibrated for small rivers in the SPARROW analysis (Q < 28.3 m$^3$ s$^{-1}$) could be applied to the smallest rivers in our analysis (< 0.1 m$^3$ s$^{-1}$).
Scenario 6 (RIVRN) includes the N removal algorithm developed for the RIVRN model recently applied to northeastern US watersheds (Seitzinger et al. 2002). The algorithm, which is based on empirical information, suggests that N removal (R) is a function of hydraulic load ($H_l$):

$$R = 1 - \frac{100 \times 88.5 H_l^{-0.368}}{100}$$  \hspace{1cm} (2.13)

By setting Equation (2.1) equal to Equation (2.13), the underlying this algorithm can be derived (Figure 2.4D). $H_l$ in this function increases with $H_l$.

Scenarios 1 through 6 were applied to mean annual conditions (N loading to the aquatic system, discharge, temperature). Scenarios 1 through 4 were also applied to monthly N loads and discharge. Comparison of results from annual and monthly analyses gives an indication of how variability in hydraulic and/or biological activity within years could affect processing potential of aquatic systems relative to mean conditions. A final scenario (VF35-UL) uses the VF35 biological component, but distributes N loads uniformly throughout the watershed. This scenario tests for the role of spatial heterogeneity of N loading in defining aquatic N removal.

**Results and Discussion**

To demonstrate the utility of FrAMES, we compare model predicted and observed nutrient concentrations in a number of test watersheds from different biomes (Figure 2.3). We focus on nutrient concentration rather than flux because discharge is defined *a priori* in our analysis. We explore how spatial distribution of N loading and aquatic processing determine TN concentrations along large watershed main stems. We explore how sub-annual variation in N loading and aquatic processing determine TN
export concentrations at basin mouths. We next compare for each scenario model-predicted and observed mean annual N concentrations at the 31 GEMS-GLORI basin mouth sample sites. This comparison is similar to that presented by Bouwman et al. (2005) who assumed a uniform aquatic N removal rates across all watersheds. Finally, we quantify the N removal role of the composite aquatic system under each scenario, and break down the role of different aquatic subsystems (small rivers, large rivers, lakes, reservoirs) for one of the scenarios.

**Annual Scenarios - Longitudinal TN Concentration Transects**

Predicted TN concentrations along river main stems assuming conservative mixing of N loads to the aquatic system (VFO scenario) are generally consistent with observations in our test watersheds, both in terms of pattern and levels. That is, the predicted mean annual TN concentrations are usually similar to or higher than those observed and follow the same trends (Figure 2.5). Some exceptions occur, such as along the mid-Mississippi and lower Yukon, where observations are somewhat higher than those expected based on mixing alone. Further downstream in the Mississippi this discrepancy disappears and such discrepancies do not occur in our other test basins. Although tested in only a few basins, the consistency of the N loading data set and observed in-stream concentrations is encouraging given the difficulty of getting good estimates of loading to aquatic systems, and demonstrates the potential of a drainage basin approach as a tool for testing terrestrial ecosystem models.

The VF35 scenario, assuming globally uniform \( v_r \), results in reduced TN concentrations and varying degrees of correspondence with observations in the test watersheds (Figure 2.5). In the VF35 scenario, longitudinal trends in TN concentration set by N loading (VFO scenario) are generally maintained (Figure 2.5). Compared with observations, predicted TN concentrations are too high in the Lena and Chang Jiang,
Figure 2.5. Observed and predicted mean annual N concentrations along the main stem of each test watershed, showing predicted TN concentrations assuming no aquatic biological activity (VF0 scenario, dotted line) and assuming $u_t = 35$ m yr$^{-1}$ globally (VF35 scenario, solid line). Open triangles show long term mean annual TN, open circles show long term mean annual NO$_3$-N. All transects are plotted using upstream contributing area except for the Chang Jiang, for which we used station distance from ocean, as presented in Liu et al. (2003). All scenarios use annual model runs except Chang Jiang and Lena, which were taken from monthly model runs to correspond with months in which the observed transects were collected (May for Chang Jiang, August for Lena). No transect data was found for the Orinoco.
too low in the Danube, Mississippi, and Yukon, and reasonable in the Rhine and Amazon. When predicted concentrations are less than those observed, predicted aquatic removal is too high suggesting that $\nu_l$ on average should be less than 35 m yr$^{-1}$. However, we cannot rule out other possible explanations such as watershed-specific errors in the N loading predictions, or that the hydraulic equations in particular watersheds differ from the averages we used. For example, a lower width intercept (Equation 2.7a) in a particular watershed would result in narrower streams, less benthic surface area, higher $H_i$, reduced N removal and higher concentrations for a given $\nu_l$.

In the Chang Jiang and Lena watersheds, observed data were from single transects (Table 2.3) rather than long term averages, so we used predicted values from the monthly scenario (VF35-Monthly). The ranges of predicted and observed N concentration in the Chang Jiang correspond well, although the point at which N concentrations are predicted to increase is shifted upstream relative to observations (Figure 2.5). On an annual basis, the Yukon data suggest little aquatic processing, as would be expected in DON dominated, cold watersheds. The $\nu_l$ of 35 m yr$^{-1}$ was derived mostly from nitrate studies in temperate regions (Howarth et al. 1996), suggesting that application of this $\nu_l$ to DON dominated systems should result in overestimates of aquatic processing. Differences between the arctic rivers (Yukon and Lena) are due in part to the fact that the Lena transect is from the summer, whereas the Yukon data are flow-weighted averages of samples collected throughout the ice-free period. Time series results from the Yukon suggest some processing could be occurring in the summer.

We demonstrate how the different annual scenarios of biological activity (Table 2.4) influence the predicted TN concentration for the Mississippi R. watershed, a temperate, nitrate dominated system (Figure 2.6). We use the VF35 scenario as the baseline for comparison. TN concentrations from the VF35Q10 are slightly higher than
Figure 2.6. Mean annual TN concentrations along the Mississippi/Missouri main stem predicted for the VFO, VF35, VF35Q10, MM1, SPARROW, and RiVRN scenarios, compared against observed long term mean annual TN concentration measured by the USGS.

those from the VF35 scenario. TN from the SPARROW and RiVRN scenario are slightly lower. The upward shift using the VF35Q10 scenario is because a greater proportion of N loading to the river network occurs in relatively cooler parts of the watershed. The effect is small because mean annual temperatures within the basin vary over a relatively small range. The lower TN concentrations predicted by the SPARROW scenario relative to the VF35 scenario are expected given that $\nu_N$'s derived from the SPARROW parameters tend to be somewhat higher than 35 m yr$^{-1}$ across a range of water depths (Figure 2.4C). The lower TN concentrations predicted by the RiVRN scenario, especially in the lower Mississippi, is consistent with the underlying behavior of $\nu_N$ in the RiVRN model, which increases with $H_L$ (Figure 2.4D). In a gridded river network, $H_L$
increases in the downstream direction because length of river reach is constant (a function of grid size), whereas other hydraulic variables (i.e. width) increase. As a result, N removal in downstream grid cells is relatively high. The greater aquatic processing predicted by the RIVRN relative to the SPARROW scenarios is consistent with the results of an inter-comparison of the two models conducted by Alexander et al. (Alexander 2002). Because we applied the two algorithms within the same framework (i.e. identical river network scale, hydraulics, and N loading), the differences are due to how biological activity is represented by the two algorithms (Figure 2.4 C,D).

Predicted TN from the MM1 scenario \((u_f\) varies with concentration) most closely approximates the observed data throughout much of the Mississippi/Missouri transect, although the predicted rate of concentration decline is somewhat less than observed along the lower Mississippi (Figure 2.6). \(u_f\) in the MM1 scenario is less than 35 m yr\(^{-1}\) for all but the lowest concentrations (Figure 2.4B). The observed decline in N concentration in the lower Mississippi, where TN concentrations are highest, suggests slightly higher biological activity than predicted using the MM1 kinetic parameters. Garcia-Ruiz et al. (1998) determined higher kinetic parameter values \((U_{max} = 16.7 \text{ mg m}^2\text{ yr}^{-1} \text{ and } K_m = 9 \text{ mg l}^{-1})\) in chronically enriched streams, resulting in higher \(u_f\)'s relative to the MM1 scenario in high nitrate streams (Figure 2.4B). Because the lower Mississippi has somewhat higher nitrate concentrations, application of these other Michaelis-Menton parameters to the lower Mississippi would result in greater N removal and more rapid decline of N concentration. However, the discrepancy in the Mid-Mississippi between observed and predicted concentrations (observed TN > predicted TN based on mixing, Figure 2.6) suggests that further work is first needed to evaluate the accuracy of the global N loading and/or discharge data sets before further interpreting the aquatic
biology scenarios. At this point, the comparison of the different scenarios demonstrates how FrAMES can be used to explore the potential role of aquatic systems globally.

**Monthly Scenarios – Time Series of TN Concentrations**

The ability to model time-varying fluxes is an important goal for global models to predict earth system responses to anthropogenic change that in many cases has trends (e.g. climate change) or an episodic character (e.g. precipitation variability) (e.g. Green et al. 2004, Donner et al. 2004). As an initial step, we applied several scenarios at monthly time steps using monthly climatologies to evaluate how seasonal changes in hydraulic characteristics, biological activity, and N loading might affect the processing potential of aquatic systems.

Predicted monthly TN concentrations at basin mouths under the mixing only scenario (VF0 – monthly, no aquatic biology) are generally similar to or greater than the observed time series (Figure 2.7), providing a measure of confidence that the monthly N loading data set is reasonable. In the four temperate watersheds we see two types of mixing patterns. One pattern shows a mid-summer decline in TN concentration (Rhine, Danube, Chang Jiang), and the other a mid-summer increase (Mississippi) (Figure 2.7). A mid-summer decline in predicted TN concentration assuming mixing only can occur when runoff from part of the watershed with low N loads becomes relatively more important at the downstream site (e.g. mountain runoff during summers), causing a dilution (e.g. Rhine). A mid-summer increase can occur in the opposite situation, or where point sources are relatively more important. Thus, the relatively simple assumptions used to disaggregate the monthly from the annual N loading data, placed in a spatially distributed context, can result in variable patterns based on mixing alone.

The tropical watersheds (Amazon, Orinoco) show relatively uniform TN concentrations over the course of the year, assuming mixing only (Figure 2.7). The
Figure 2.7. Predicted long term mean monthly N concentrations at a downstream integrative station, showing predicted TN concentrations assuming no aquatic biological activity (VFO scenario, dotted line) and assuming $u_f = 35 \text{ m yr}^{-1}$ globally (VF35 scenario, solid line). All are at the mouth of the watershed except for the Yukon and Amazon, which are based on time series collected at an intermediate point along the mainstem. The observation in the Chang Jiang corresponds with the farthest downstream site from the single transect shown in Figure 2.5. Time series data were not located for the Rhine and Danube.
Figure 2.8. Predicted long term mean monthly discharge at the locations shown in Figure 2.7. Observed discharges are those reported with the nutrient data, whereas predicted Q's correspond with the long term mean Q.
arctic watersheds (Yukon, Lena) show a different type of mixing pattern, with high concentrations during low flow winters that decline as flow increases (Figure 2.7, 2.8). Clearly a jump in mixing concentrations from December to January in Arctic watersheds is unlikely in reality. The high mixing concentrations early in the winter are a consequence of incongruities between the N loading and runoff data fields in arctic regions that result in non-point N loads in extremely low runoff areas. These incongruities occur in relatively few inter-station areas, but become apparent during the relatively low flow conditions of winter. We believe that concentrations estimated during the higher flow periods (May – Sept) are reasonable because the incongruities become relatively less important with the onset of broad-scale snowmelt.

The introduction of uniform biological processing (VF35-Monthly) reduces N concentrations, sometimes changing the pattern of TN concentration over the course of the year relative to mixing alone (Figure 2.7). Sub-annual TN patterns in the VF35-Monthly scenario can differ from the VF0-Monthly scenario when peak discharge periods with reduced N removal capacity (due to changing hydraulics) coincide with times when mixing alone causes a decline in TN concentration (e.g. May-Sept in Orinoco, Chang Jiang, Figures 2.7,2.8). In the VF35-Monthly scenario, predicted TN concentrations are much lower than observed in the Yukon, moderately lower in the Lena, Mississippi and Amazon, and higher in the Orinoco. Predicted TN in the Chang Jiang, based on the downstream station from a single months transect, are slightly higher than observed. In the Yukon, the VF0 scenario again provides a better fit, suggesting conservative mixing for much of the year.

A comparison of all the scenarios in the Mississippi shows the differential effect of sub-annual variability in hydrology and biology. The VF35-Monthly scenario, in which the hydrology but not biology varies over the course of the year, shows a similar annual TN pattern to that of the VF0-Monthly scenario (Figure 2.9). N removal in the VF35-
Figure 2.9. Mean monthly TN concentrations at the mouth of the Mississippi watershed predicted for the VF0, VF35, VF35Q10, and MM1 monthly scenarios, compared against observed long term mean monthly TN concentration measured by the USGS.

Monthly scenario ranges from 47% of total aquatic loads in March to 66% in September, corresponding with the high and low flow periods. This difference indicates the effect of hydrological changes alone on N removal. A greater concentration range is evident using the VF35Q10-Monthly scenario (Figure 2.9), with removal ranging from 29% in February to 82% in August. The MM1-Monthly scenario tends to overestimate TN concentrations at the mouth, but also follows the observed trend in concentration over the year. The relatively small amount of seasonality in the VF35 and MM1-Monthly scenarios is consistent with observations at the Mississippi mouth. Both scenarios do not vary biological activity over the year, suggesting that hydrological and N loading variability alone can account for intra-annual changes in N concentration in the
Mississippi. However, we controlled seasonal variation in $H_L$ within individual river reaches using hydraulic equations developed for downstream $Q$ increases ($w \sim Q^{0.52}$) rather than at-a-site $Q$ changes ($w \sim Q^{0.25}$) (Leopold et al. 1964). Use of the latter would result in greater fluctuations in $H_L$ and N removal, leading to greater variability of TN concentrations over the year. Interestingly, observed TN export concentrations suggest that large variations in N removal do not occur during the year in the Mississippi.

However, the monthly aquatic N loading estimates do not account for sub-annual variability in, for example, N fertilizer applications and leaching of excess fertilizer to the aquatic system, which probably lead to higher loading concentrations during spring and summer.

Our estimate of monthly N loads is an approximation. The simple assumptions we made in applying an annual loading data set to the monthly time scale result in reasonable predictions of TN concentrations through the year, and correspond with the patterns of concentration change evident among the few test watersheds for which we have time series data (Figure 2.7). As global-scale terrestrial ecosystem models begin to predict temporal variability in N leaching and erosional losses, FrAMES can be linked to these exports to begin to predict how entire watersheds respond to anthropogenic change. However, much more research is first needed to determine the mechanisms controlling $u_r$, including how denitrification rates are influenced by N form and interactions among various N processes (e.g. tight coupling between assimilatory uptake, mineralization, nitrification, and denitrification).

Comparison with Global Data Set of Observed River Chemistry

We compared annual TN concentrations predicted at basin mouths from each annual scenario with those reported in the GEMS-GLORI database ($n = 31$ watersheds, Meybeck and Ragu 1997) to determine which annual aquatic scenario provides the best
Figure 2.10. Predicted vs. observed mean annual TN concentrations for each annual scenario, including VFO, assuming uniform 0.3 N removal (Bouwman et al. 2005), VF35, VF35-Q10, MM1, SPARROW, and RIVRN. Observed data are for 31 rivers with TN concentrations reported in Meybeck and Ragu (1997). Line on each graph is the 1:1 line. The uniform 0.3 N removal scenario is identical to that in Bouwman et al. (2005). Table inset shows the Nash-Sutcliffe Efficiency (NSE, (Nash and Sutcliffe 1970) applied to untransformed and log-log transformed nutrient concentrations. The more positive the NSE, the better the correspondence between observed and predicted data.
fit globally. We include for comparison a scenario where N loss in aquatic systems is a uniform 30% (UR0.3), corresponding with the full global N model presented by Bouwman et al. (2005).

Based on visual inspection, the biological scenario with the least bias across the range of concentrations occurs with the VF35-Q10 scenario (Figure 2.10). At high concentrations (i.e. > 2 mg l\(^{-1}\)), the VF35, SPARROW, and RivN scenarios also do well, but at low concentrations, predicted TN tends to be low (N removal is too high). Predicted TN concentrations are generally too high in the UR0.3, and MM1 scenarios (N loss is too low) (Figure 2.10). The Nash-Sutcliffe Efficiency measure (NSE, Nash and Sutcliffe 1970), which quantifies the relative accuracy of the different model predictions, confirms the visual interpretation (Table inset in Figure 2.10). The NSE using untransformed data, which weights high N data points more heavily, is similar for the SPARROW, RIVRN, VF35 and VF35-Q10 scenarios. The NSE using log-transformed data, which increases the weight of low N points, is highest for the VF35-Q10 scenario (Figure 2.10).

Because TN concentrations from the UR0.3 scenario tend to be high, N removal by river networks is generally greater than 30%. Although the MM1 scenario fits much of the Mississippi transect data better (Figure 2.6), application of this scenario globally on average leads to underestimates of N loss. Considerable scatter remains with the VF35Q10 scenario, but there is little bias, suggesting that temperature is an important control of biological activity globally. A similar effect was recently found by Green et al. (2004) using a whole-watershed regression-based approach that documented the importance of both hydraulics and temperature. The temperature control of aquatic biological activity could be direct, affecting actual reaction rates, or indirect in the sense that aquatic systems in colder regions receive N loads that are less available (e.g. refractory DON in the arctic) than in nitrate dominated or warmer systems. The
dominant form of N loading (DIN, DON, PON) in particular watersheds likely contributes to the scatter.

**N Removal by the Aquatic System**

The proportion of N removed by the aquatic system varies considerably among the different biological scenarios (Table 2.5), demonstrating a need for better understanding the controls of biological activity in aquatic systems in different biomes. The MM1 scenario predicts the lowest aquatic N removal (10-15%, with 40-66% in the low TN arctic watersheds) and the RIVRN scenario predicts the highest (57-94%) (Table 2.5). The VF35-Q10 scenario, which best fit the GEMS-GLORI data set (Figure 2.10) resulted in intermediate TN removal (28-53%).

Some of the variation in aquatic N removal can be attributed to differences in the distribution of hydraulic conditions and/or N loading. The impact of hydraulics alone on N removal can be estimated by comparing % N removal among the test watersheds using the VF35UL scenario (uniform loading), where N loading is uniformly distributed and biological activity is constant (in terms of uf) throughout each watershed. This scenario shows that in our test watersheds, N loss in aquatic systems would vary from 34% in the Orinoco to 76% in the Mississippi due to differences in discharge and hydraulic loads resulting from different runoff conditions. The role of hydrological conditions in determining inter-annual variability in river network N removal was recently demonstrated for the Mississippi watershed (Donner et al. 2004). If the geomorphic parameters and/or hydraulic equations also differed among the watersheds, further variability could occur.
<table>
<thead>
<tr>
<th>Watershed</th>
<th>VF35</th>
<th>VF35-Q10</th>
<th>MM1</th>
<th>SPARROW</th>
<th>RIVRN</th>
<th>VF35-UL</th>
<th>VF35</th>
<th>VF35-Q10</th>
<th>MM1</th>
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<td>0.53</td>
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<td>0.6</td>
<td>0.11</td>
<td>0.62</td>
<td>0.86</td>
<td>0.7</td>
<td>0.6</td>
<td>0.49</td>
<td>0.11</td>
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<td>0.61</td>
<td>0.76</td>
<td>0.76</td>
<td>0.5</td>
<td>0.49</td>
<td>0.11</td>
</tr>
<tr>
<td>ORINOCO</td>
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<tr>
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<td>0.46</td>
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</tr>
<tr>
<td>YUKON</td>
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<td>0.74</td>
<td>0.93</td>
<td>0.75</td>
<td>0.66</td>
<td>0.44</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 2.5. Predicted proportion of N loaded to aquatic systems that is removed in the river network of selected watersheds for each of the scenarios.
Spatial heterogeneity of N loading caused a relatively small change in predicted N removal by the aquatic system. This effect was isolated by comparing the change in aquatic N removal in the VF35-UL scenario (uniform loading) relative to the VF35 scenario (actual loading). The VF35-UL scenario results in 1% higher aquatic N removal in the Yukon up to 22% higher in the Mississippi (Table 2.5). An intermediate percentage increase occurs in the other basins (2-8%). The increase in aquatic N removal using spatially uniform N loading suggests that N loading to the aquatic system is disproportionately greater towards the basin mouth or near river main stems.

However, the effect is relatively small, as also demonstrated by Seitzinger et al. (2002) in northeastern U.S. watersheds. Nevertheless, knowledge of the position of N loads is moderately important for understanding N exports to the coast in some basins, as was suggested for the Mississippi (Alexander 2000).

The predicted effect of seasonal hydrologic variation on annual N loss appears to be relatively small in these watersheds. Annual N loss should be reduced when accounting for flow variability because more flux of material occurs during high discharge periods when N removal is reduced based on hydraulic considerations alone (Equation 2.1). However, we see relatively small declines in annual N removal in the VF35 monthly vs. annual scenario (0-8%) (Table 2.5). A similar small change in annual N removal is evident in the VF35-Q10 monthly vs. annual scenario, showing either increased or decreased N removal depending on whether high discharge periods coincide with high air temperatures (i.e. with higher \( u_t \), Figure 2.4B). The lack of sensitivity results in part from applying the hydraulic equations developed using mean annual Q in the downstream direction (Equation 2.7) to changing Q over time at particular locations. Width tends to vary less at particular sites (\( w \sim Q^{0.25} \)) than in the downstream direction (\( w \sim Q^{0.52} \) (Leopold et al. 1964). If instead we were to incorporate

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at-a-site hydraulic equations to time-varying \( Q \), width would increase more slowly, \( H_L \) would increase faster (Equation 2.2), and N removal would decline faster with increasing \( Q \), resulting in "leakier" watersheds on an annual basis. The climatologies also do not account for greater hydraulic variability that can occur sub-monthly or inter-annually, which could considerably alter aquatic N removal (Donner et al. 2004).

**Removal by different aquatic systems**

The contribution of various aquatic subsystems to total aquatic N removal was partitioned using the VF35 scenario. In the test watersheds, small rivers generally removed the greatest proportion of N loads, followed by large rivers, lakes and reservoirs, though the relative importance can vary (Table 2.6). The importance of small rivers (i.e. those represented by the sub-grid river network) is consistent with results from regional models (Alexander et al. 2000, Seitzinger et al. 2002) and demonstrates the need for including these systems in global models. The statistical approach described here is an attempt to account for their role. N removal by small rivers is large because most N loads first enter the river network through smaller river systems. N removal by large river channels is also relatively important in these large basins because the cumulative length of large river channels is great.
Watershed | Small Rivers | Large Rivers | Large Lakes | Large Reservoirs | Export
--- | --- | --- | --- | --- | ---
AMAZON | 0.15 | 0.16 | 0.01 | 0 | 0.67
CHANG JIANG | 0.21 | 0.16 | 0.09 | 0.03 | 0.52
DANUBE | 0.33 | 0.22 | 0.07 | 0 | 0.38
LENA | 0.37 | 0.30 | 0.01 | 0 | 0.32
MISSISSIPPI | 0.31 | 0.18 | 0.02 | 0.02 | 0.46
NILE | 0.33 | 0.35 | 0.17 | 0.10 | 0.06
ORINOCO | 0.16 | 0.13 | 0 | 0.03 | 0.68
RHINE | 0.25 | 0.13 | 0.08 | 0 | 0.54
SAINT LAWRENCE | 0.22 | 0.03 | 0.59 | 0.01 | 0.15
YUKON | 0.35 | 0.21 | 0.18 | 0 | 0.26

Table 2.6. Proportion of total N loads to the aquatic system predicted to be removed by various aquatic ecosystems and exported using the VF35 scenario. VF35 assumes all aquatic systems have the same biological activity (i.e. constant $v_f$, first order kinetics), but the hydrology, spatial distribution of N loading varies, and abundance of lakes and reservoirs differ. St. Lawrence watershed is included as a lake dominated system. Nile is included as a watershed where reservoirs are relatively more important.

Lakes and reservoirs can be important in specific instances, although from a watershed perspective they often remove a relatively small percentage of TN loads (Table 2.6). For example, predicted N removal by lakes is 59% of aquatic N loads in the lake-dominated St. Lawrence basin, 17-18% in the Nile and Yukon, and < 10% in all other test basins (Table 2.6). N removal by reservoirs is generally lower, though from a coastal perspective (i.e. relative to N exports), the amounts can at times be large. For example, in the Nile basin, reservoir N removal (dominated by the Aswan dam) is 9% of loading to the aquatic network, which is greater than the 6% of predicted export in this scenario. A relatively small role for reservoir N removal was also found by Seitzinger et al. (2002) in northeastern U.S. watersheds, either because $H_r$ does not change much relative to river channels (i.e. because increased depth can compensate for increased residence time) or because reservoirs are located upstream. In our application, large reservoirs are generally located downstream, receiving water that has already passed...
through several upstream aquatic systems that can remove some amount of N. By the
time water reaches a large reservoir, much of the N has already been removed.
However, we stress that in our analysis we have not accounted for the role of small
reservoirs or lakes in the aquatic network. Roughly 40% of the global area of lakes is
not represented in the current framework (Meybeck, 1995). These are generally small
lakes, but their composite role, as with reservoirs (Vörösmarty et al. 2003), could be
large and should be further explored.

Conclusion

The Framework for Aquatic Modeling of the Earth System (FrAMES) allows
integration of spatially distributed nutrient loads, hydraulic conditions and aquatic
biological activity. We applied FrAMES to explore how each of these factors impacts
predictions of aquatic N removal. Spatial heterogeneity in processing potential has been
suggested as an important factor contributing to variability in N exports from various
world watersheds (Meybeck and Vörösmarty 2005). Our results confirm this contention.

We also used FrAMES to demonstrate how coupled terrestrial and aquatic
models can be tested using observed in-stream nutrient concentrations distributed
throughout the basin, and over time. We found that a reasonable N loading data set,
combined with spatially distributed discharge data sets, hydraulic equations and simple
aquatic process models, can explain a relatively large amount of the variability in TN
concentrations both within and across basins. The present analysis provides some
bounds on the role of aquatic systems in determining watershed N exports. These
bounds can be used to constrain the relative role of terrestrial and aquatic N removal in
the watershed N budget. Knowing the relative importance of terrestrial and aquatic
systems is necessary to understand whether most anthropogenic N inputs will continue
to be retained within watersheds as is presently the case (e.g. Howarth et al. 1996), or
whether N exports to coastal systems are expected to increase with the continued large perturbation of the N cycle. To fully address this issue, much more research is required to determine the spatial and temporal variability of νN for different N forms and processes, particularly how denitrification νN varies over a range of conditions and scales (e.g. Böhlke et al. 1997, Garcia-Ruiz et al. 1998, Mulholland et al. 2004).

The ability to account for heterogeneity in Earth System Models will allow for better predictions of changing nutrient fluxes as global change continues. Global changes in population, land use, and climate, are likely to lead to altered nutrient loading, hydrology, and biotic activity. The magnitude and position of these alterations will vary both within and across watersheds. Moreover, various element cycles (C,N,P,Si) may be differentially perturbed resulting in additional layer of complexity. Because FrAMES is being designed as a multiple-element modeling framework, we hope to explore how interactions and feedbacks among constituents, including carbon, also impact nutrient fluxes. Spatially distributed models such as FrAMES are important tools to explore how nutrients will behave in the next decades as global change continues, and what implications these changes have for coastal eutrophication and carbon balances.

Notation

\[
\begin{align*}
A_{sw} & \quad \text{surface area of the water body (L}^2) \\
A & \quad \text{watershed area (L}^2) \\
d & \quad \text{mean water depth (L)} \\
E & \quad \text{link number (-)} \\
H_L & \quad \text{hydraulic load (L T}^{-1}) \\
K_m & \quad \text{half saturation constant (M L}^{-3}) \\
L & \quad \text{channel length (L)}
\end{align*}
\]
N  number of streams (-)
p  probability of stream draining from one order to another (-)
Q  discharge (L³ T⁻¹)
Q₁₀  temperature adjustment (-)
R  proportion of incoming N removed by water body (-)
Rₗ  length ratio (-)
Rₛ  area ratio (-)
Rᵦ  bifurcation ratio (-)
T  air temperature (°C)
TE  transfer efficiency (TE = 1 - R) (-)
θ  proportion of watershed area draining to a particular stream order
τ  residence time (T⁻¹)
U  areal uptake (M L² T⁻¹)
Uₘₐₓ  maximum areal uptake (M L² T⁻¹)
v  mean water velocity (L T⁻¹)
V  volume (L³)
υᵣ  vertical velocity of the nutrient molecule (L T⁻¹)
w  mean width of the water body (L)
Z  proportion of watershed area draining via a particular surface water flow path (-)
CHAPTER 3

HYDROLOGICAL AND BIOLOGICAL CONTROLS OF NUTRIENT REMOVAL IN RIVER NETWORKS

Abstract

Aquatic systems potentially play an important role in controlling nutrient export from watersheds. The ability of entire river networks to remove nutrients (long-term storage or denitrification) will depend on the distribution of both hydrological conditions that control surface to volume ratio and residence times (defined by the hydraulic load, $H_L$) and biological activity that controls the demand for nutrient relative to concentration (defined by vertical velocity of the nutrient, $u_f$). Here, we use a simple nutrient removal algorithm ($R = 1 - \exp(-u_f/H_L)$) to independently explore hydrological and biological factors that influence the intensity and distribution of removal in river networks. We find that hydraulic geometry and river network geomorphology interact to determine whether small or large rivers tend to be more retentive for a given level of biological activity. A synthesis of reported denitrification rates suggests that the demand for nutrients ($u_f$) will depend on concentration in the water column, and that incorporation of more complicated kinetics into river network model will be necessary to fully evaluate how river network nutrient removal has changed with increased anthropogenic loading. We compare several recent river network N removal algorithms by standardizing the biological parameters to $u_f$, revealing large differences in intensity and distribution of removal.
biological activity as a function of stream size. We suggest that river network models should clearly separate the biological and hydrological parameters in order to 1) facilitate understanding of model behavior, including comparison of different model results, 2) facilitate comparability with field measurements, 3) improve the ability to apply/test models outside of the temporal and spatial domains for which they were developed, and 4) improve the ability to explore the relative influences hydrological and biological controls of river network nutrient removal.

Introduction

A large proportion of anthropogenic nutrient loads are not exported from most watersheds (Howarth et al. 1996, Harrison et al. In Press). Aquatic systems are likely major sinks for nutrients, via long-term storage in lake and reservoir sediments (e.g. (Dean and Gorham 1998)) and in the case of nitrogen (N), via denitrification (Galloway et al. 2003). We use the term "removal" throughout this chapter to account for all processes that remove nutrients from surface waters as they flow through the river network, and can include long-term storage as well as denitrification. The ability of individual surface water bodies to remove nutrients is a function of both the hydrology and biology of these systems (Kelly et al. 1987). Hydrology influences nutrient removal via the rate of water passing through the water body relative to its size (surface to volume ratio, residence time). Biology influences nutrient removal by determining the demand for nutrient relative to the available concentration. In surface waters, removal of nutrient over longer time scales (as either storage or denitrification for N) ultimately takes place in the sediments, including the hyporheic zone. The position of individual water bodies, each with unique nutrient removal capacity, relative to the position of nutrient

A number of spatially distributed river network models have incorporated the necessary hydrological and biological information to predict aquatic system influence of watershed nutrient exports (Alexander 2000, de Wit 2001, Donner et al. 2002, Seitzinger et al. 2002, Green et al. 2004). Inter-comparisons of spatially distributed models, though rare, have found differences in the role of river networks and have attributed these to factors such as the resolution of the modeled river network, spatial resolution of N loading to the aquatic system (distributed vs. mean watershed), and whether the models are steady state or time varying (Alexander 2002, Donner et al. 2004). Not assessed in these comparisons is whether differences can be attributed to the level of biological activity represented in the specific algorithms, which differ across the models.

Assessment of biological activity in the various models is difficult because each represents the biological component of nutrient removal differently. Moreover, the biological parameter often includes hydrological information, reducing the ability to independently explore hydrological and biological controls on nutrient removal. Although the hydrological component is often considered well constrained by empirical information (discharge, hydraulic geometry), considerable variability in hydraulic parameters and river network geomorphology occur across watersheds (Leopold et al. 1964, Park 1977, Dingman 1994). The potential effects of this variability on river network nutrient removal have not been evaluated. A biological parameter that includes hydrological information also makes it difficult to incorporate more complicated controls of biological activity, including higher order reaction kinetics. All the models to date assume removal processes are governed by first order kinetics. As spatially distributed river network model are applied globally (e.g. Wollheim et al. In Review) to watersheds experiencing a
range of conditions (Green et al. 2004), the ability to independently explore the influence of various biological and hydrological controls is necessary.

In this paper, we demonstrate how the hydrological and biological controls of river network nutrient removal can be explored using a particular form of the nutrient removal algorithm that clearly separates the hydrological and biological parameters. We first discuss the nutrient removal algorithm and its connection with stream spiraling theory. We then use this algorithm to theoretically explore how hydraulic geometry and river network geomorphology interact to define the hydrologic conditions that control the distribution of removal. In particular, we focus on the issue of whether small or large rivers are likely to be more effective at nutrient removal assuming uniform biological activity. Next, we discuss factors controlling biological activity, focusing on whether N removal capacity is influenced by N concentration, and the implications for river network modeling. Finally, we compare biological activity in several recent river network models, deriving the same biological parameter embedded in each model as the common currency. We identify underlying differences that are not immediately evident from the algorithms and parameterizations originally used. We hope to emphasize that clear separation of biological and hydrological parameters will facilitate the development and application of aquatic models that can be used to explore how the earth system is responding to anthropogenic change.

**Nutrient Removal in Surface Waters**

Nutrient removal in individual water bodies is controlled by the interaction of biological, chemical and hydrological characteristics. The interaction of these characteristics in defining removal is summarized by the exponential form of an equation.
first proposed by Kelly et al. (1987) and recently applied in a spatially distributed global river network model (Wollheim et al. In Review):

\[
R = 1 - \exp\left(-\frac{\nu_f}{H_L}\right)
\]  

(3.1)

where \( R \) is the proportion removed (unitless), \( H_L \) is the hydraulic load (L T\(^{-1}\)), and \( \nu_f \) is the vertical velocity (L T\(^{-1}\)) of the nutrient molecule through the water column (called \( S_n \) in Kelly et al. (1987) and Howarth et al. (1996), but called \( \nu_f \) here to conform with stream spiraling terminology; Stream Solute Workshop 1990). Vertical velocity as applied to dissolved nutrients is defined by the ratio of areal process rate (M L\(^{-2}\) T\(^{-1}\)) and concentration (M L\(^{-3}\)) and is a measure of the demand for nutrient relative to the amount of nutrient available. \( \nu_f \) is therefore a combination of chemical and biological characteristics within the water body. Although the areal process rate is the purely biological component, by itself it does not give an indication of the strength of biological activity relative to the amount of source material available. Assuming a constant \( \nu_f \) implies first order kinetics (process rate varies linearly with concentration). \( \nu_f \) could also vary with concentration, as would occur with Michaelis-Menten type kinetics (process rate becomes saturated) (Dodds et al. 2002). Regardless of how the areal process rate is controlled, to calculate removal, \( \nu_f \) within the water body must be determined so that the demand for nutrient can be related to the hydraulics of the system.

The hydraulic load (\( H_L \)) summarizes the relevant physical characteristics needed to calculate the proportion of incoming nutrient removed by a given water body. \( H_L \) can be estimated in a variety of related ways, but in effect two pieces of information are needed: \( Q \) (L\(^3\) T), the discharge into the water body, and \( A \) (L\(^2\)), the surface area of the water body (\( H_L = Q/A \)). For lakes and reservoirs, \( A \) can be derived from attribute data.
For rivers, $A$ is derived from the length ($I$) of stream reach (defined by grid size in gridded river networks), and mean width ($w$), which is derived from $Q$ using hydraulic equations (Leopold et al. 1964). $H_L$ therefore is a measure of the rate of water passage through the water body relative to the benthic surface area available for nutrient removal. $H_L$ is also equivalent to the mean water depth ($d$, L) (volume to surface ratio) divided by residence time ($\tau$, T) ($H_L = d/\tau$). From a biogeochemical perspective, $H_L$ is the mean distance a nutrient molecule must travel during a given time period before it can be sequestered (e.g. settling) or used by a benthic process. We prefer the $Q/A$ form of deriving $H_L$ because it is easily applied to lakes and reservoirs, and because for rivers only the hydraulic equation for width is required ($w = aQ^b$). With one hydraulic equation, the role of hydraulic and geomorphometric variability in defining nutrient removal can be easily explored (see below).

There are alternative approaches for representing nutrient removal in surface waters that are equivalent to Equation (3.1), but that rearrange the parameters in a way that convolves biological and hydrological characteristics (Table 3.1). We will argue here that these formulations, while valid approaches, make it more difficult to understand how interactions among physical, biological, or chemical characteristics control variability or trends within or among river networks.

The alternative formulations define the biological parameter based on other commonly used stream spiraling descriptors (Stream Solute Workshop 1990), including the first order time-specific ($k_t$, $T^{-1}$) and first order length-specific ($k_l$, $L^{-1}$) nutrient removal rates, where the latter is the equivalent to the reciprocal of the uptake length ($1/S_w$) (Table 3.1). The corresponding removal functions are $R = 1 - e^{(k_t\tau)}$ and $R = 1 - e^{(k_lI)}$, where $\tau$ is residence time (T) and $I$ is reach length (L) (e.g. Alexander 2000, 2002). Both of these parameters include hydrological information, with $k_l$ including depth ($h$, L) ($k_l = \ldots$).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uptake Rate</td>
<td>U</td>
<td>Areal rate of nutrient use</td>
<td>M L^{-2} T^{-1}</td>
<td>Biological information</td>
</tr>
<tr>
<td>Vertical velocity</td>
<td>u_r</td>
<td>Rate at which a nutrient molecule moves through water column</td>
<td>M T^{-1}</td>
<td>Mixture of biological and chemical</td>
</tr>
<tr>
<td>Time-specific loss rate</td>
<td>k_t</td>
<td>Proportion of nutrient removed over specified period of time.</td>
<td>T^{-1}</td>
<td>Mixture of biological, chemical, and hydrological</td>
</tr>
<tr>
<td>Distance-specific loss rate</td>
<td>k_i</td>
<td>Proportion of nutrient removed over specified distance (also reciprocal of uptake length, 1/S_w)</td>
<td>L^{-1}</td>
<td>Mixture of biological, chemical, and hydrological</td>
</tr>
</tbody>
</table>

Table 3.1. Measures of nutrient removal rates in stream reaches.
It has recently been argued in the stream spiraling literature that \( v_f \) is a better parameter when comparing biological activity among streams, because it removes the scale dependant characteristics of the study site (Wollheim et al. 2001, Dodds et al. 2002). Similarly in modeling, use of a biological parameter that is independent of the physics of the system will allow for clearer determination of parameter values based on field studies as well as facilitate model application across systems of different size and hydrological conditions. Any dependence of biological activity on the physics of the system must then be explicitly stated.

As one example, Alexander et al. (2000) found in the Mississippi basin that \( k_t \) declined from 0.455 d\(^{-1}\) in small rivers to 0.0005 d\(^{-1}\) in large rivers. This result was criticized as possibly an artifact of the calibration technique used (Lindgren and Destouni 2004). However, \( k_t \) is by nature scale dependant, and would decline with stream size even if biological activity and nutrient concentration were constant (i.e. constant \( u_f \) (Figure 3.1). \( k_t \) is similarly scale dependant. The use of \( k_t \) may be necessary in systems where processes leading to removal operate in a matrix (e.g. groundwater, soils) or over time scales where temporary storage in the water column is important (e.g. lakes and reservoirs during the stratified growing season). However we suggest here that in surface water networks at longer time scales (monthly or greater), where removal processes ultimately reside in the benthos, approaches relying on \( u_f \) are more generally applicable and provide a better insight into the controls of nutrient removal.
Using the clear separation of biological and physical characteristics in Equation (3.1), we can explore how nutrient removal will tend to vary within and across river networks due to hydrologic variability alone. Because river network models have generally been applied to a single basin or set of basins with similar hydrological characteristics (Alexander 2000, Donner et al. 2002, Seitzinger et al. 2002), the potential role of hydraulic and geomorphological variability among watersheds has not been explored (but see Green et al. (2004) using a whole basin approach and Donner et al. (2004) for the role of interannual runoff variability within a single basin).

For a given $v_r$, hydraulic geometry will define 1) the magnitude of removal, 2) changes in removal with changing flow conditions, and 3) in conjunction with geomorphology, changes in removal in the downstream direction. The relevant parameters that determine these relationships include the intercepts $(a, c)$ and exponents $(b, d)$ of the hydraulic equations both in the downstream direction ($w = aQ^b$)
and at-a-site \( w = cQ^d \) (Stream Solute Workshop 1990), as well as the geomorphometric parameters \( R_a \) (area ratio) and \( R_l \) (length ratio). Although network geomorphometric parameters have been previously applied in river network models (e.g. Garnier et al. 2002), their role in defining nutrient removal has not been explored.

Classical geomorphology describes how stream number, stream length, and mean drainage area change predictably from one order to the next within individual basins (summarized as the Horton ratios \( R_n, R_l, \) and \( R_a, \) respectively) (Horton 1945). Recent analysis showed that there are only two independent Horton ratios, with \( R_l \) and \( R_a \) equivalent (Dodds and Rothman 1999). Because \( H_l \) can be derived from discharge, length of stream reach and width, the change in \( H_l \) with increasing stream order can also be described using a Horton-type of ratio, allowing an a priori description of how nutrient removal should change based on hydrological changes only (i.e. for a constant \( u_l \)).

Figure 3.2 shows an example of how width, \( H_l \) and removal of upstream inputs change with increasing stream order given mean hydraulic and geomorphometric parameter values. Because width tends to change much more slowly at-a-station than in the downstream direction (Figure 3.2A) (Leopold et al. 1964), \( H_l \) and removal are much more variable at-a-site than in the downstream direction (Figure 3.2B,C).

Assuming constant runoff throughout a watershed, discharge will increase from one order to the next according to \( R_a \). Because width is a function of discharge \( w = aQ^b \), mean width increases from one order to the next according to \( R_a^b \). Length increases according to \( R_l \). Using the relationship \( H_l = Q/(tw) \), the change in \( H_l \) for the typical stream of one order to the next (\( R_{HL} \)) can be described as:

\[
R_{HL} = R_a / (R_l ^ * R_a ^ b) \quad (3.2)
\]
Figure 3.2. Changes in A) width (m), B) $H_L$ (m yr$^{-1}$), and C) removal (unitless) with increasing stream order, considering the average stream in each order as a unit. Values are plotted against discharge at the downstream end of each stream order class. Width is based on Q at the downstream end. $H_L$ is based on Q and w at the downstream end, and the mean length of the entire stream reach classified by stream order. Both low and high discharge periods (10 and 200% mean annual Q, respectively) are shown. Mean annual Q is determined assuming runoff = 500 mm yr$^{-1}$, mean drainage area of the 1st order stream = 2.6 km$^2$, and $R_e = 4.85$. Changes in width in the downstream direction are defined by $w = 8.3Q^{0.5}$. Changes in $H_L$ with stream order also assumes mean length of a 1st order stream = 1.6 km and $R_e = 2.4$. Changes in width at-a-site are controlled by $w \sim Q^{0.25}$. To calculate removal, $u_r = 35$ m yr$^{-1}$. Removal calculation assumes nutrient molecules enter the upstream end of each reach.
Depending on the combination of \( R_a, R_i, \) and \( b, H_L \) could either increase or decrease with increasing stream order. Using the widely cited average width exponent \( (b = 0.5) \) (Leopold et al. 1964), \( H_L \) has a tendency to decline with stream order class \( (R_{HL} < 1) \) for most \( R_a \) and \( R_i \), suggesting a tendency for greater removal by the typical high order compared to low order stream (Figure 3.3). This occurs because total benthic surface area \( (A) \) increases faster than the rate of water \( (Q) \) flowing through the typical length stream with increasing order. Although low order streams remove more per unit length due to surface to volume consideration (Peterson et al. 2001), when considered as a unit, high order streams tend to be more effective (assuming constant \( v_i \)) because water spends more time in them, overcoming the decline in surface to volume ratio that occurs (i.e. residence time increases faster than mean depth). Obviously, nutrients entering the river network in low order streams are more likely to be removed within the watershed because they pass through multiple stream orders, each with a removal capacity. The tendency for \( H_L \) to decline across stream orders and the fact that all upstream inputs ultimately pass through higher order streams demonstrates the need to understand the controls of biological activity in larger rivers.

Whether low or high order rivers are more likely to remove nutrients will depend on the combination of \( R_a, R_i, \) and \( b \). The change in \( H_L \) with stream order is more sensitive to \( R_i \) than to \( R_a \). Across watersheds, \( R_i \) ranges between 1.5 and 3.5, whereas \( R_a \) ranges between 3 and 6 (Dingman 1994). The downstream width exponent averages 0.5, with a range of 0.3 to 0.7 (Park 1977). The mean \( R_a \) and \( R_i \) reported for a global river network \( (R_a = 4.6, R_i = 2.6; \) Vörösmarty et al. 2000) results in \( R_{HL} \) usually less than one (Figure 3.3), and therefore a tendency for increasing nutrient removal with stream order. \( R_i \) at the lower reported limit leads to \( R_{HL} > 1 \) across all width exponents, whereas \( R_i \) at the higher reported limit leads to \( R_{HL} < 1 \). In contrast, the reported extremes of \( R_a \) I
Retention declines with stream order

Retention increases with stream order

downstream width exponent

Figure 3.3. Factor change in $R_{nl}$ with increasing stream order ($R_{nl}$) as a function of the downstream width exponent, $R_a$, and $R_l$.

lead to small shifts in $R_{nl}$ (Figure 3.3). $R_a$ has relatively little influence because it affects both the numerator and denominator in Equation (3.2), with increasing Q offset somewhat by increasing $w$.

Overall, the tendency appears to be that, based on hydraulic considerations alone, higher order streams can attenuate N more than lower order streams (Figure 3.3). Alexander et al. (2000) found that terrestrial inputs to large rivers were more likely to be exported, attributing this to reduced biological activity in larger rivers. Another possible reason is that large rivers are capable of greater removal due to greater $H_l$'s and therefore provide a final filtering capacity of material having entered smaller upstream systems. Seitzinger et al. (2002) similarly found that large rivers retain a larger amount of N than small rivers because more material passes through them. Our analysis also suggests that, assuming similar biological activity, higher order rivers as a class will often remove a larger percentage of inputs than lower order rivers. However, variability
across watersheds is expected based on the particular combination of geomorphological and hydraulic parameters.

The factors describing change in $H_L$ with increasing stream order do not address the controls of absolute $H_L$ (i.e. the intercept of $H_L$), which will define the overall level of proportion of nutrients removed by the entire river network. The $H_L$ intercept is controlled by actual discharge, determined by runoff conditions (e.g. Donner et al. 2004), and the width intercept from the downstream hydraulic equation. The factors controlling the width intercept have not been well explored in the hydrological literature. Based on a small number of mid-western streams originally reported by Leopold et al. (1964), the width intercept is likely to be more variable than the exponent, varying from 4 to 12 m (mean = 8.4m). Across this range of width intercepts, nutrient removal would vary by a factor of 2 assuming constant $\nu_f$ (Figure 3.4). Because of its importance in defining $H_L$ throughout the river network, characterization of intercept variability is important for understanding nutrient removal across watersheds.

Based on hydraulic and geomorphological relationships typical of many river networks (Figure 3.3), large rivers can potentially remove a greater proportion of upstream inputs than small rivers. However, if biological activity in the form of $\nu_f$ also changes with increasing stream size (e.g. see discussion in Wollheim et al. 2001), trends in removal could either be offset or magnified. Although such changes are theorized to occur (Vannote 1980), trends in biological activity leading to permanent nutrient removal (denitrification, storage) as a function of stream size have not yet been identified based on field measurements. In the next section, we explore some of the factors that could control $\nu_f$, focusing on nitrogen.
Biological Controls of Removal

Over longer time scales, nutrient exports can be removed via sedimentation and burial (storage) in various water bodies along the river network (Dean and Gorham 1998), and in the case of nitrogen by dissimilatory removal via denitrification (Seitzinger 1988). In surface waters, both of these processes occur primarily in benthic habitats. Many other processes can transform or temporarily store nutrients in the water column over shorter time scales, but over longer time scales burial and denitrification control net nutrient removal (Figure 3.5). This section will discuss some factors that might control net uptake of denitrification and nitrogen (N) burial relevant to river network models.

Nitrogen can enter the river network as nitrate (NO$_3$), ammonium (NH$_4$; NO$_3$+NH$_4$ = DIN), dissolved organic N (DON), and allochthonous particulate N (PN).

Autochthonous production and microbial assimilation can convert DIN into DON and PN.
Figure 3.5. Approach for determining $\nu_I$ relevant for calculating removal (long term storage + denitrification) of upstream inputs for various N species. Letters define the proportion of source following a particular pathway, where $A$ = long term PN storage in sediments, $B$ = PN resuspension, $C$ = net PN remineralization ($A+B+C = 1$), $D$ = release of mineralized NH$_4$ back to the water column, $E$ = nitrification in sediments ($D+E = 1$), $F$ = release of sediment-produced NO$_3$ to water column, and $G$ = denitrification of sediment-produced NO$_3$ ($G+F = 1$). Total denitrification is defined by denitrification of surface water NO$_3$ ($NO_3^{-\nu_I}_{denitr}$) and the coupling of remineralization and denitrification within the sediments (pathway $C-E-G$). $A$ is likely to be smaller in rivers than in lakes and reservoirs. For simplicity, we assume DON behaves conservatively, there is minimal nitrification of surface water NH$_4$, and lability of PN is uniform for various sources (i.e., allochtonous and autochtonous PN behave similarly). The equations in the lower half of the figure standardize all $\nu_I$'s to incoming concentrations for the particular N form. Net $\nu_I$'s will depend on the time scale of interest.
Conversely, aquatic processes can convert organic N back to inorganic forms (Figure 3.5). Spiraling theory combines all these transformations to describe transport of nutrients downstream (Newbold et al. 1981). Of interest at the scale of entire river networks is the proportion of this spiraling N that is permanently removed via long-term burial or denitrification, en route from point of entry in the river network to the basin mouth. In terms of Equation (3.1), what controls the $v_f$ of denitrification ($v_{fract}$) and long term N burial? Numerous processes interact to define net transformation of incoming N to N$_2$ and long-term burial of PN (Figure 3.5).

Because $v_f$ is the ratio of the areal process rate and concentration, the first consideration is whether water column N concentrations control net $v_f$. Is the net result of all processes leading to nutrient removal described by first-order reactivity with respect to incoming N concentrations, or are more complicated kinetics involved? Most river network models to date have assumed a first order control of nutrient removal.

Denitrification is controlled by numerous factors, including the amount of nitrate available, presence of anoxic conditions, the amount of organic matter available to denitrifiers, and temperature (Seitzinger 1988). Denitrification rates often follow Michaelis-Menten type kinetics, resulting in declining $v_f$ with increasing concentration (Figure 3.6, Garcia-Ruiz et al. 1998). In a study of denitrification along a river continuum, the Michaelis-Menten parameters themselves ($K_n$, the half saturation constant and $U_{max}$, the maximum areal denitrification rate) were primarily a function of the water column nitrate concentration to which the sediments were chronically exposed and secondarily of substrate type and organic matter content (Garcia-Ruiz et al. 1998). Although kinetic parameters in that study varied substantially ($K_n$ 0.18 – 9.0 mg N L$^{-1}$, $U_{max}$ 0.5 – 16.7 mg N m$^{-2}$ hr$^{-1}$), $v_{fract}$ calculated from these is always less than 100 m yr$^{-1}$. The $v_{fract}$ measurements from whole reach $^{15}$NO$_3$ addition studies to date are
remarkably consistent with the Michaelis-Menten parameters determined using core measurements (Figure 3.6).

Synthesis of a variety of denitrification field studies using various techniques where both areal denitrification rate and water column concentration are reported (Howarth et al. 1996, Böhlke et al. 2004, Mulholland et al. 2004, Royer et al. 2004) Peterson, pers. comm.) suggests that declining $u_{f-denitr}$ with increasing concentration occurs across sites ($r^2 = 0.5$, $p < 0.01$, Figure 3.7B). The regression from these field studies is of the same order as the Michaelis-Menten kinetics described above (Figure 3.6). As concentrations increase, the ability of the water body to permanently remove N via denitrification declines. The considerable remaining scatter could be due to variability in other factors controlling denitrification, as well as to the different techniques used.

If the concentration dependence of $u_{f-denitr}$ applies generally, there are important implications regarding how entire river networks respond to elevated N loading. First, if nitrate concentrations are positively correlated with discharge, as for example in agricultural streams (Royer et al. 2004), a decline in nitrogen removal capacity occurs during the period of highest fluxes by both increased $H_L$ (Figure 3.2) and by reduced $u_f$. Second, at the whole river network scale, the low removal capacity in high nitrate upstream reaches will be somewhat buffered by higher order stream reaches where dilution results in higher $u_f$ and where $H_L$ for the average higher order stream are often lower (Figures 3.2, 3.3). Third, despite any large-river buffering capacity, if anthropogenic N loading has increased over time, the overall capacity of river network to denitrify this material (i.e. $u_f$) must have declined. Heavily N loaded watersheds have been shown to maintain a similar rate of nutrient removal as those less impacted (e.g.
Figure 3.6. Change in A) areal denitrification rate (mg N m\(^{-2}\) hr\(^{-1}\)) and B) \(v_t\) (m yr\(^{-1}\)) with increasing water column concentration (mg N L\(^{-1}\)) based on sediment core experiments (Garcia-Ruiz et al. 1998). MM1: \(K_n = 0.25\) mg N L\(^{-1}\), \(U_{max} = 2.0\) mg N m\(^{-2}\) hr\(^{-1}\); MM2: \(K_n = 9.0\) mg N L\(^{-1}\), \(U_{max} = 16.7\) mg N m\(^{-2}\) hr\(^{-1}\); MM3: \(K_n = 1.3\) mg N L\(^{-1}\), \(U_{max} = 4.5\) mg N m\(^{-2}\) hr\(^{-1}\). Estimates of denitrification parameters from whole reach \(^{15}\)NO\(_3\) tracer additions (Bohike et al. 2004, Mulholland et al. 2004, Peterson personal comm.) shown for comparison.
Figure 3.7. Change in A) areal denitrification rate (mg N m\(^{-2}\) hr\(^{-1}\)) and B) \(v_r\) (m yr\(^{-1}\)) with increasing water column concentration (mg N L\(^{-1}\)) based on ambient field conditions, including measurements using sediment cores and whole reach tracer additions. \(R^2\) for regression in B) is on log transformed \(v_r\) data.
Howarth et al. 1996). Assuming a similar rate of terrestrial removal, then if denitrification of surface water nitrate declines with increasing N concentrations, the aquatic system must be responding with increased longer-term storage of N in the sediments or denitrification of remineralized organic matter (as opposed to surface water nitrate).

It is important to stress that different techniques for measuring denitrification quantify different denitrification pathways. For example, whole reach $^{15}$N tracer techniques measure denitrification of water column nitrate whereas core studies could include some amount of sediment-produced nitrate (i.e. via mineralization/nitrification) (Howarth et al. 1996). At the same time, whole reach tracer techniques incorporate hyporheic denitrification, whereas core measurements do not.

The data used in Figure 3.7 mainly include techniques quantifying surface water denitrification ($\text{NO}_3^{-}-\nu_{\text{denitr}}$ in Figure 3.5). New techniques using changes in $\text{N}_2$:Ar ratio in surface waters (Laursen 2002, McCutchan et al. 2003), which are not included in the synthesis in Figure 3.7, include all denitrification pathways, including denitrification of surface water nitrate, tightly coupled remineralization/nitrification/denitrification in sediments, and hyporheic processes. These techniques have generally resulted in much higher measurements of areal denitrification rates than other techniques (Laursen 2002, McCutchan et al. 2003). These techniques will allow better estimation of the proportion of assimilated DIN and deposited PN that is ultimately denitrified (Figure 3.5), and whether this pathway is also related to the concentration of upstream N inputs.

It is noteworthy that $\nu_{\text{denitr}}$ appears to be constrained to 150 m yr$^{-1}$ or less based on the studies included in Figures 3.6 and 3.7, with most reported measurements less than 70 m yr$^{-1}$, regardless of water body type (i.e., lake, stream). Over annual time scales, $\nu_{\text{denitr}}$ will likely be lower than those in Figure 3.7 because most studies have focused on the periods of warmer temperature. In contrast, gross assimilatory $\nu_{\text{f (NH}_4^{-})}$
\( \text{NO}_3^-_{\text{assim}} \) can be several orders of magnitude higher in low N streams during the growing season (Peterson et al. 2001). Much of this N is quickly returned to the water column as PN, NH\(_4\) or NO\(_3\) (parameters B,D, and F in Figure 3.5; Peterson et al. 2001; Wollheim et al. 2001). But if only a small proportion of assimilated N is ultimately stored or denitrified via tight coupling (parameters A, and C*E*G), then the nitrogen removal capacity of river networks will be greatly increased relative to denitrification of surface water nitrate alone. As an example using the equations and parameters in Figure 3.5, if \( \text{NO}_3^-_{\text{denitr}} = 35 \text{ m yr}^{-1} \), \( \text{NO}_3^-_{\text{assim}} = 200 \text{ m yr}^{-1} \), A = 0.2, C = 0.5, E = 0.4, and G = 0.3, net \( \text{NO}_3^- \) will equal 87 m yr\(^{-1}\). Obviously, these parameters would need to be determined from long enough time periods to provide a true estimate of N removal rather than temporary storage. Several field techniques deployed simultaneously will likely be required to determine the relative importance of this pathway.

N burial will be the net result of numerous processes, including DIN assimilation, sedimentation/resuspension (of both allothonous and autochthonous PN), and remineralization rates (Figure 3.5). A discussion of all the factors controlling these processes is beyond the scope of this paper. However, because Michaelis-Menten kinetics are likely to operate for the initial assimilatory process due to stoichiometric factors (e.g. high N:P ratios will result in a reduced capacity to convert DIN to PN) (Dodds et al. 2002), net \( \nu_f \) as burial will likely decline with increasing DIN concentrations. Conversely, if primary production due to nutrient enrichment has increased, with subsequent high respiration and increased anoxic conditions, then denitrification rates could have increased (von Gunten and Lienert 1993). These interactions suggest that incorporating coupled C, P, and N cycling in river network models is necessary to fully understand how human activities are impacting river network processing. We suggest
that use of $v_f$ as the biological parameter provides a useful approach by which more complicated dynamics can be summarized for use in river network removal models.

**Comparison of Model Algorithms**

Comparison of biological activity among various river network models has been difficult because each model uses a different removal algorithm with different biological parameters. Recent models include the SPARROW model (Alexander et al. 2000, 2002), RivN model (Seitzinger et al. 2002), Green et al. (2004) model, Donner et al. (2002) model, and the POLFLOW Model (de Wit 2001). As with field studies where $v_f$ can be used to compare streams of different sizes, here we derive the $v_f$'s implicit (and explicit in Donner et al. 2002, 2004) in each modeling study to compare biological activity. All the models assume $v_f$ is constant with respect to nutrient concentration, but each shows a different type of scale dependence of $v_f$ that is not always evident in the original formulation.

In the original models, the parameters governing biological activity were either calibrated using observed river N concentrations and modeled inputs to the river network (SPARROW, Green et al., POLFLOW) or based on empirical information (RivN, Donner et al.). The Green et al. model was calibrated from whole watershed characteristics, whereas the other models were calibrated and/or applied in spatially distributed form. Nutrient removal was calculated for either TN (SPARROW, RIVN, Green et al.) or NO$_3$ (Donner et al., POLFLOW).

The central algorithms describing nutrient removal from each model are listed in Table 3.2. For purpose of the comparison, we have omitted the temperature modifier used in Donner et al. (2002) and the slope modifier used in the POLFLOW model (de Wit 2001). $v_f$ can be derived directly from the parameters (SPARROW, Green et al.,...
<table>
<thead>
<tr>
<th>Equation</th>
<th>N Form</th>
<th>Source</th>
<th>Parameter value</th>
<th>Derivation of $\nu_f$</th>
</tr>
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</table>
| $R = 1 - \exp(-ktT)$ | TN | Alexander et al. (2000) | $k_t = 0.455 \text{ d}^{-1}$, $Q < 28.3 \text{ m}^3 \text{ s}^{-1}$
$k_t = 0.118 \text{ d}^{-1}$, $28.3 < Q < 283 \text{ m}^3 \text{ s}^{-1}$
$k_t = 0.051 \text{ d}^{-1}$, $283 < Q < 850 \text{ m}^3 \text{ s}^{-1}$
$k_t = 0.005 \text{ d}^{-1}$, $Q > 850 \text{ m}^3 \text{ s}^{-1}$ | $\nu_f = k_t h$
| $R = \frac{\nu_f}{H}$ | NO$_3$ | Donner et al. (2002) | $\nu_{f_0} = 14.6 \text{ m yr}^{-1}$ at $0 \degree \text{C}$ (Empirical) | $\nu_f = \max(\nu_{f_0}, \nu_{f_0} \cdot 120/Q)$
| $R = 1 - \exp(-T_{adj}a_{riv})$ | TN | Green et al. (2004) | $a_{riv} = 0.086 \text{ (yr}^{-1} \text{ C}^{-1})$
$T_{adj} = \text{temperature} + 30 \degree \text{C}$ | $\nu_f = T_{adj}a_{riv}h$
| $R = 0.8845 H^{(-0.3688)}$ | TN | Seitzinger et al. (2002) | Empirical | $\nu_f = -H_L \ln[1 - (0.8845H_L^{-0.3688})]$ |
| $R = 1 / (1 + m_0 Q^{m_2})$ | TN | De Wit (2000) | $m_0 = 50 \text{ s m}^{-3}$
$m_2 = 0.5$ (-) | $\nu_f = -H_L \ln[1 - (1 / (1 + m_0 Q^{m_2})]$

Table 3.2. Recently used river network N removal algorithms and derivation of $\nu_f$. 
Donner et al.) or by setting the original form equal to Equation (3.1) (POLFLOW, RivN) (Table 3.2).

$v_f$ behaves differently in each model, tending to decline with increasing depth in the SPARROW and Donner et al. models, increase with depth in Green et al. (Figure 3.8), and is relatively constant in the POLFLOW model (not shown). It tends to increase with $H_L$ in the RivN model (Figure 3.9A). Because $H_L$ is arbitrarily defined based on choice of reach length, the RivN model is difficult to compare based on depth. However, the original field data converted to $v_f$ does not show a relationship against depth (Figure 3.9B).

Some of the $v_f$ behavior is an artifact of the approach used to determine the biological parameter. In the SPARROW calibration (Alexander 2000), the underlying $v_f$ declines across $Q$ classes, but increases within $Q$ class (Figure 3.8A). This $v_f$ pattern occurs because during the calibration procedure, $k_r$ was assumed constant while depth increases continuously within each $Q$ class. Nevertheless, the overall decline of $v_f$ (on average) across $Q$ classes is an outcome of the calibration. This relationship will be further discussed below.

The Donner et al. (2002) model uses $v_f$ and $H_L$ to calculate N removal, though the equation is not in exponential form (Table 3.2). $v_f$ was assumed to decline with increasing discharge above 120 m$^3$s$^{-1}$ (scale factor = 120 /Q) (Figure 3.8B). The $Q$-based $v_f$ modifier was included to account for reduced contact time between bottom sediments and water column due to increasing depth. But because the physical parameter $H_L$ (Q/A) is already included in the algorithm used in this study (Table 3.2), inclusion of a $v_f$ modifier for this purpose is redundant. A decline in $v_f$ with increasing $Q$ assumes that biological activity per unit benthic surface area declines with increasing $Q$. 

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Figure 3.8. Relationship between $u_f$ and depth of water body from A) SPARROW calibration of mean annual river processing in the Mississippi watershed (Alexander et al. 2000), B) Donner et al. (2002) model applied to the Mississippi, and C) Green et al. (2004) calibration based on whole watershed attributes. Dashed line shows $u_f = 35$ m yr$^{-1}$ suggested by Howarth et al. (1996).
Such a relationship may exist, for example, due to natural changes in the River Continuum (Vannote 1980) or even at a site (e.g. temporarily flooded areas where microbial communities are not established). However, an in situ dependence of $\nu_f$ with $Q$ has yet to be demonstrated.

In contrast, the Green et al. (2004) calibration suggests that $\nu_f$ increases with stream depth (Figure 3.8c). The Green et al. parameterization was based on whole watershed hydrologic characteristics (residence time) rather than spatially distributed estimates within watershed. Although not intended for this purpose, application of the calibrated Green et al. parameters in spatially distributed form within basin would imply lower $\nu_f$'s in smaller compared to larger streams (Figure 3.8c). Applied at the whole watershed scale, the implication is that larger watersheds with greater mean depths have greater biological activity (higher $\nu_f$) than smaller watersheds with on average shallower rivers.

Two models (POLFLOW, RivN) have important scale considerations that suggest they must be carefully applied beyond their original studies. In both, nitrogen removal is a function of a parameterization against a hydrologic variable ($Q$ for POLFLOW, $H_L$ for RivN). Embedded within the empirical relationship of RivN is an increasing $\nu_f$ with $H_L$ (Figure 3.9A). The relationship is apparently driven by observed retention at two sites from a single study (Burns 1998), for which the derived $\nu_f$'s are greater than 100 m yr$^{-1}$ (Seitzinger et al. 2002). All other sites in the RivN synthesis have $\nu_f$'s of 40 or less. The increasing biological activity with $H_L$ suggests that this algorithm must be carefully applied because $H_L$ is not a scale independent parameter for river reaches. A 100 m reach will have a much greater $H_L$ than a 1000 m reach, assuming uniform discharge and width. In spatially distributed aquatic models, river networks are arbitrarily broken into individual reaches (either gridded or vector). Because $\nu_f$ increases with $H_L$, a large
Figure 3.9. Relationship between A) $v_l$ and hydraulic load ($H_L$) and B) $v_f$ and water depth derived from the synthesis of Seitzinger et al. (2002) [$v_l = -H_L \ln(1-R)$], with results from denitrification in cores and mass balance studies distinguished.
Figure 3.10. Effect of element size (i.e. choice of reach length) on removal estimates using various removal algorithms. Shown is the proportion of upstream N inputs exported from the same 50 km reach as a function of whether the stream reach is represented as a single 50 km reach, two 25 km reaches, five 10 km reaches and 50 one km reaches. Kelly et al. (1987) removal is $R = \frac{u_f}{(u_f + H_L)}$, Donner et al. (2002) is $R = \frac{u_f}{H_L}$ and RivN is $R = 0.8845H_L^{-0.3689}$. The number of small reaches will have inflated removal in the aggregate than a small number of long reaches (Figure 3.10). The Donner et al. (Table 3.2) and original Kelly et al. (1987) equation ($R = \frac{u_f}{(u_f + H_L)}$) also have a slight scale-dependence that is a function of river reach length (Figure 3.10). The exponential form (Equation 3.1) does not have this scale dependence.

The POLFLOW model (de Wit 2001) results in a relatively constant $u_f$ with increasing discharge for a given set of hydraulic relationships. The POLFLOW calibration was based on a gridded river network with 1 km resolution. Because the POLFLOW algorithm (Table 3.2) itself includes no information regarding the dimensions of the water body (e.g. reach length or residence time), the calibrated parameters are valid only for the 1 km resolution river networks used in that study. However, $u_f$ derived from these parameters using reasonable hydraulic parameters is scale independent and can be used to compare biological activity of other river network models. The $u_f \sim 76$ m
yr⁻¹ derived from POLFLOW is within the range of reported denitrification υᵣ's (Figure 3.7B).

Comparison of Nutrient Removal Using the Algorithms on a Model Reach

The various algorithms and their parameterizations result in very different patterns of N removal moving from small to large rivers. To demonstrate the differences, we applied all the algorithms to a linear sequence of stream reaches ("model watershed"). We include an additional model assuming constant υᵣ = 35 m yr⁻¹ as originally suggested by Howarth et al. (1996). The model watershed consists of a linear set of 200 grid cells, each 400 km² (20x20 km) with a 25 km stream reach, resulting in total river length of 5000 km. Runoff is 500 mm yr⁻¹ in each grid cell. Mean annual depth, velocity, and width vary according to relationships for USGS gauges (w = 8.3Q⁰.⁵¹, h=0.29Q⁰.³⁷⁴⁵, v=0.416Q⁰.¹⁰⁹; Dave Bjerklie, pers. comm.). The biological parameters are as described in the original papers (Table 3.2), with the exception of POLFLOW for which we applied the derived υᵣ directly. The model watershed is not meant to reflect an actual watershed but demonstrates how the different parameterizations manifest themselves with increasing stream size.

For each model, local removal in individual river reaches declines in the downstream direction (Figure 3.11A), reflecting the impact of hydraulic gradients in controlling the proportion removed (note that here we considering constant length stream segments rather than stream reaches defined by order as discussed above). The rate of decline, however, is controlled by the biological parameterization (Figure 3.11B). With the exception of the Green et al. model, which was parameterized at the whole basin scale, all the models start at similar levels of removal in small rivers, with
Figure 3.11. Comparison of A) removal and B) $v_t$ in constant length river reaches with increasing discharge in the downstream direction using different algorithms with the same hydraulic assumptions. See text for description of hydrologic conditions. Donner et al. (2002) and Green et al. (2004) models assume water temperature = 10 °C, roughly the mean annual temperature in the Mississippi basin.
the SPARROW parameters resulting in somewhat higher removal in the upstream reaches (Figure 3.11A).

With increasing stream size, the models begin to diverge. Local removal remains high in the downstream direction in the RivN model, declines rapidly in the SPARROW and Donner et al. models and declines moderately in the POLFLOW and uf 35 model. High N removal is maintained in the RivN model because $\nu_f$ increases with $H_l$ (Figure 3.8A, 11B), partially offsetting the effect of increasing $H_l$ that occurs in local river reaches with constant length. In the SPARROW model, local removal is nearly constant within the discharge classes selected for the calibration because velocity (which controls residence time with uniform reach lengths) increases slowly.

Alexander et al. (2002) in a comparison of the SPARROW and RivN model applied to northeastern US watersheds found that SPARROW generally predicted less river network nutrient removal than RivN. They suggested that this difference could be due to the scale of the river network used (i.e. inclusion of small rivers), or to whether aquatic N loads were spatially distributed. Our comparison suggests that interacting with these factors are differences in biological activity (Figure 3.11B). Donner et al. (2004) noted that the fraction of NO$_3$ removed in their model was less than that of SPARROW or RivN. These comparisons are consistent with different patterns of biological activity embedded in the algorithms. As river network models are applied more widely, it will become important to understand how underlying biological activity and hydrological characteristics interact to define predicted patterns of nutrient removal, and how these patterns influence watershed nutrient exports (e.g. Wollheim et al. In Review).
Comparison of Model and Field Measured Vertical Velocities

Standardization of the biological parameter as $v_t$ is also useful for comparing model-calibrated parameters and results from various field measurements. The ability to remove any underlying relationship caused by the physics of the system (e.g. Figure 3.1) will increase the power of such comparisons. Such standardization is necessary because field approaches themselves are sometimes applied to only certain stream scales, while at the same time measuring different processes. As watershed-scale biogeochemical models begin to incorporate more sophisticated biological controls, it will become critical to distinguish information obtained from different field approaches.

Recent reports have suggested that biological activity declines with increasing stream size. Model-calibrated parameters ($k_i$) from the Mississippi declined with stream channel depth and were in good correspondence with a synthesis of field data (Alexander et al. 2000, 2002). The decline in $k_i$ would be expected assuming constant biological activity (Figure 3.1). However, after standardizing both model and field results to $v_t$, the decline in biological activity with increasing stream depth remains (Figure 3.12A). In contrast, the synthesis of Seitzinger et al. (2002), does not suggest a relationship between $v_t$ and depth (Figure 3.9B). Comparison of $N_\text{O}_3\^{\text{vol}}$ alone, as opposed to estimates that could include assimilatory processes as well, also suggest no relationship with depth (Figure 3.12B). Field studies that actually compare different stream size are rare. A comparison of $N\text{H}_4$ dynamics in Alaskan streams found no relationship between stream size and $N\text{H}_4\^{\text{vol}}$ (Wollheim et al. 2001). Garcia-Ruiz et al. (1998) found greater denitrification rates in downstream systems, but $N_\text{O}_3$ concentrations co-varied with stream size and were likely the driver of changing rates.
Figure 3.12. Comparison of $v_f$ as a function of depth A) derived from data reported in the Alexander et al. (2000) synthesis from various field studies, with SPARROW calibrated parameters shown for comparison, and B) with additional studies that have focused on N assimilation and/or denitrification. NH$_4$-LINX and NO$_3$-LINX are means and error bars from sites reported in Peterson et al. (2001). NH$_4$-Alaska is mean and error bar from sites reported in Wollheim et al. (2001). Results from whole reach $^{15}$NO$_3$ additions include simultaneous measurement of total NO$_3$-$v_f$ and denitrification NO$_3$-$v_f$, which are circled. Denitrification rates with error bars are from Royer et al. (2004). Other denitrification estimates are from Seitzinger et al. (2002).
A variety of field approaches were included in these various syntheses, including some that combine modeling elements at the whole watershed scale (e.g. Behrendt (1996) in Alexander et al. (2000, 2002)). Field methods vary in the information they provide. They measure different processes (e.g. denitrification, total N removal, assimilatory N removal) for different N species (NO$_3$, DIN, TN) over different time scales (e.g. annual, growing season, month, day). Moreover, some methods can only be applied to certain stream sizes (e.g. $^{15}$N tracer additions only in small streams). These are important considerations when exploring relationships against stream size.

Standardization of the biological parameter in the form of $\nu_f$ will facilitate comparison of results across different field approaches that are often stream size (and water body) dependant.

Nevertheless it is interesting to speculate that when all N processes are considered (Figure 3.5) gradients in N removal as a function of stream size could occur. Natural downstream gradients in controlling factors such as light, sediment organic matter, substrate size, habitat permanence, mean temperatures, and hyporheic connectivity could all be factors. Artificial gradients might also occur, such as higher nitrate concentrations downstream due to distribution of anthropogenic loading (Garcia-Ruiz et al. 1998). If denitrification of surface water NO$_3$ ($\nu_{d,denitr}$ in Figure 3.5) is constant with increasing depth, and total NO$_3$ removal declines with increasing depth (as suggested in Figure 3.12A), then the implication is that storage and/or indirect denitrification processes are more important in smaller systems. Because small streams are not thought to store considerable amounts of material over longer time scales, the more likely hypothesis is that indirect denitrification of remineralized N, which has not been measured by whole stream addition and acetylene block methods, is an important
factor in determining overall denitrification rates. The use of N2:Ar techniques, in conjunction with \(^{15}\)N tracer approaches, could help address this issue.

**Conclusions**

A clear separation of biological and physical parameters (e.g. Equation 3.1) will allow for a better understanding of the controls of river network nutrient removal. Here, we demonstrated the usefulness of this approach by independently exploring some of the hydrological and biological factors influencing removal that would be difficult to evaluate using other nutrient processing algorithms. Based on this analysis, we found that interactions between hydraulic and geomorphometric characteristics control the potential strength of nutrient removal both within and across watersheds. As spatially distributed river network models are applied globally (e.g. Wollheim et al. In Review), it will be necessary to better assess how hydraulic characteristics influence removal across watersheds of different world biomes. The impact of anthropogenic changes to the hydrologic cycle can then be better addressed.

Although physical characteristics set the potential for nutrient removal in river networks, biological activity ultimately determines actual removal for reactive nutrients such as nitrogen. We showed that, with respect to certain nitrogen processes, reaction rates are unlikely to be controlled by first order kinetics, but are instead concentration dependant. The current generation of spatially distributed models has mainly assumed first order reactivity (but see Wollheim et al. in review). To better assess how ecosystem services provided by aquatic systems are changing, the impact of higher aquatic concentrations resulting from anthropogenic loads should be considered. Moreover, because different nutrient processes may have been affected differently by human
activity, the ability to include different pathways of nutrient removal (e.g. Figure 3.5) will further enhance our ability to predict changes. The influence of coupled biogeochemical cycles (C-N-P interactions) should therefore also be integrated.

A scale independent parameter of biological activity ($\omega$) can be used to standardize and compare biological activity in different model calibrations and from field results that were based on water bodies of diverse size, using different techniques, and focusing on different processes. Controlling for physical variability among various field and modeling studies will remove a confounding factor that might mask the role of important biological controlling factors. Uncovering these and incorporating them into river network models will greatly improve our ability to model watershed nutrient exports as human modifications of the earth system continue to increase.
SUMMARY

This dissertation focuses on one of the major perturbations currently driven by human activity, that of an accelerated nitrogen cycle. Nitrogen loads to continental surfaces are anthropogenically elevated for multiple reasons, including basic sustenance of human populations (fertilizer -> agriculture -> protein) and to satisfy lifestyle choices (fertilization of lawns, motor vehicle use, meat intensive diet). Increased N loading is often coupled with other anthropogenic changes associated with land use (agriculture, residences, impervious surfaces).

The first part of this dissertation evaluates how increased N loading interacts with a particular type of land use change, that of relatively low-density urbanization (suburbanization). Suburbanization is in many ways a lifestyle choice, reflecting the desire for free-standing homes with large yards. Supporting urbanization is an extensive road network and building infrastructure (impervious surfaces), and green lawns requiring fertilization. As a result of the popularity of suburban living, impervious surfaces in the United States are at present equivalent in area to the state of Ohio (Elvidge et al. 2004) and lawn area is greater than the combined cultivation of barley, cotton, and rice in the United States (Robbins and Birkenholz 2003), and is also roughly equivalent to the size of Ohio. The suburban lifestyle shows every indication of continued popularity and is expected to increase in extent (e.g. Schneider and Pontius 2001).

The results described in Chapter 1 show that suburbanization leads to greater small catchment N export, and that these N exports increase at a faster rate than do N loads. The implication is that N removal by the watershed has declined. N removal occurs via storage in biomass or permanent removal via denitrification. I hypothesize
impervious surfaces, because they are biologically inert and lead to reduced water residence times, are the mechanism for a decline in N removal. Nevertheless, this and other studies (Groffman et al. 2004, Valiela et al. 2002) have noted that urban watersheds continue to have a fairly sizeable removal capacity (> 70%). Removal might be maintained because of storage in soils or because flow paths containing high nutrient loads continue to intersect systems where N is denitrified (groundwater, riparian zone, streams). More work is needed to characterize the removal capacity of urban watersheds. The threshold of imperviousness where rapid drops in N removal occurs has important management implications.

Clearly, the N removal capacity of some terrestrial systems is reduced, whether they are urban systems with high levels of imperviousness or forested systems that have reached N saturation. But at the large watershed-scale, many basins show similar N removal capacity based on estimates of total mobilizable N loads and observed N exports at basin mouths (Boyer et al. 2002, Howarth et al. 1996). One possible explanation for this discrepancy is that aquatic systems act as a buffer preventing excess N loads from reaching the coast. The removal could occur as storage in lakes and reservoirs, or via denitrification in all aquatic systems, which is a permanent removal from the system.

The second part of this dissertation addresses the role of aquatic systems in attenuating N exports at the global scale. This global scale analysis takes into account the distribution of lakes and reservoirs as well as the role of small rivers, which represent a large proportion of the global river network but have not been previously represented at the global scale. This dissertation presents a first such global analysis of the integrated role of all aquatic systems.

The analysis of river network N removal shows that the capacity of river networks to modify N exports will vary depending on the distribution of hydrological characteristics.
and biological activity. Representing biological activity at the global scale is difficult because most research on biological controls has taken place in temperate systems. Application of several approaches for representing biological activity (constant, or using temperature, concentration, and depth dependencies) results in a wide range of predicted aquatic N removal. Much more research is needed to characterize the biological controls, and to determine methods for scaling these controls globally.

Although biological activity clearly determines the potential for aquatic N removal, hydrological characteristics control the impact biological activity can have on the flux of materials through the river network (e.g. Vörösmarty and Loder 1994, Donner et al. 2004). Hydrological characteristics include the abundance of lakes and reservoirs, moisture conditions that determine discharge, and size of the river network.

The analysis in chapter 2 shows that variability in hydrologic characteristics alone would lead to considerable variability in N removal by river networks (e.g three-fold difference in % removal in the Nile vs. Amazon rivers). The importance of hydrology is significant because human activities are greatly altering hydrological characteristics via reservoir construction, channelization, water withdrawals for public consumption and irrigation, and global climate change. To investigate how N exports will vary due to both natural climate variability as well as watershed specific human activities it will be important to adequately characterize hydrological characteristics. Because many of the human impacts are localized, a spatially distributed framework such as the one presented in chapter 2 will be necessary.

To fully understand the controls of watershed N export, a modeling approach where the biological and hydrological characteristics are separately described will be necessary. Chapter 3 demonstrates the importance of such an approach using a model algorithm that easily allows exploration of hydrological and biological controls. The approach reveals that large rivers are, because of hydraulic considerations, likely to be
as important as small rivers in controlling N exports, assuming similar biological activity. The assumption of 1st order dependence (i.e. independent of nutrient concentration) of N removal processes common in river network removal models was also called into question using the model algorithm described in chapter 3. This is an important consideration, since human activities have led to increased N concentrations in many aquatic systems, and suggests that the removal capacity of aquatic systems could be declining. Such a decline has important implications for future change in N export to the coastal zone and should be further explored. Overall, the clear separation of biological and hydrological parameters will allow for a better dialogue between field researchers and modelers, better synthesis of field information, and better tests of models developed for particular areas in other watersheds.

The results from the river network analyses have important management implications that are directly relevant to declines in N removal observed in urban small catchments. The analysis in chapter 2 suggests that roughly 30-50% of aquatic removal in large watersheds could occur in rivers larger than 6th order. The potential importance of large rivers suggests that smaller catchments should be "leakier" than large catchments that have longer river networks. Because urbanization often occurs in relatively small coastal watersheds (most people live within 100 km of the coast), declining watershed N removal due to urbanization is more likely to impact coastal systems. Therefore, in small coastal watersheds management of N inputs to coastal systems will need to place a greater emphasis on influencing lifestyle choices. In urban areas with extensive aquatic systems intervening between them and the coast, greater emphasis could potentially be placed on ensuring adequate aquatic processing (e.g. no channelization).

The disturbance of the N cycle starts in terrestrial systems. How this disturbance is transferred to coastal systems will depend in part to the response of the intervening
aquatic network. N loads to aquatic networks occur across the scales represented by the river continuum. At the same time the hydraulics of aquatic systems behaves predictably along the continuum. Factors contributing to N removal therefore can be evaluated if the spatial structure of N loading relative to aquatic system scale is adequately represented. The distributions of N loading, hydraulic characteristics, and biological activity ultimately determine the N removal capacity of river networks. The topological structure of these three factors is therefore an important determinant of N exports to coastal systems.

In conclusion, the perturbation of the N cycle is large, and ecosystems are responding to this perturbation. Knowledge of this response is necessary if we are to understand how changes in one system impact another and manage the impacts of the perturbation into the future. The results presented in this dissertation are a small step towards a better understanding of how the Earth System functions and how the activities of the Earth’s dominant species, Homo sapiens, is altering these functions.
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