

## ABSTRACT

Title of Document: NITROGEN UPTAKE AND  
DENITRIFICATION IN RESTORED AND  
DEGRADED-URBAN STREAMS: IMPACTS  
OF ORGANIC CARBON AND INTEGRATED  
STORMWATER MANAGEMENT

Tamara Ann Newcomer Johnson  
Doctor of Philosophy, 2015

Directed By: Associate Professor Sujay S. Kaushal  
Department of Geology and  
Earth System Science Interdisciplinary Center

Managing the N cycle and restoring urban infrastructure are major challenges especially in urban ecosystems. Organic carbon is important in regulating ecosystem function and its source and abundance may be altered by urbanization. My research focused on urban-degraded, restored, and forested watersheds at the Baltimore LTER in the Chesapeake Bay watershed.

In Chapter 2, I investigated shifts in organic carbon quantity and quality associated with urbanization and ecosystem restoration, and its potential effects on denitrification at the riparian-stream interface. Denitrification enzyme assay experiments showed carbon was limiting in hyporheic sediments and variable carbon sources (grass clippings, decomposing leaves, and periphyton) stimulated

denitrification differently. Evidence from stable isotopes, molar C:N ratios, and lipid biomarkers suggested that urbanization can influence organic carbon sources and quality in streams, which may have substantial downstream impacts on ecosystem services such as denitrification.

In Chapter 3, I investigated whether stormwater best management practices (BMPs) integrated into restored and degraded urban stream networks can influence watershed N loads. I hypothesized that hydrologically connected floodplains and stormwater BMPs are “hot spots” for N retention through denitrification because they have ample organic carbon, low dissolved oxygen levels, and high residence time. I used reach-scale nitrogen mass balances, in-stream tracer injection studies, and  $^{15}\text{N}$  *in situ* denitrification to measure N retention in stormwater BMPs and their larger stream networks. There were high rates of *in situ* denitrification in both stormwater BMPs and floodplain features. Hydrologically connected floodplains can be important “hot spots” for N retention at a watershed and stream network scale because these areas likely receive perennial flow through the groundwater-surface water interface during both baseflow and storm events, while BMPs only receive intermittent flow associated with storm events.

In Chapter 4, I conducted a literature review of N retention within hydrologically reconnected streams and floodplains. I reviewed 79 stream and floodplain restoration empirical studies from North America, Europe, and Asia and found that methods for measuring N retention varied considerably. I found many diverse strategies for promoting the ecosystem function of N retention in urban and agricultural watersheds.

NITROGEN UPTAKE AND DENITRIFICATION IN RESTORED AND  
DEGRADED-URBAN STREAMS: IMPACTS OF ORGANIC CARBON AND  
INTEGRATED STORMWATER MANAGEMENT

By

Tamara Ann Newcomer Johnson

Dissertation submitted to the Faculty of the Graduate School of the  
University of Maryland, College Park, in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy  
2015

Advisory Committee:

Professor Sujay S. Kaushal, Chair

Professor Walter R. Boynton

Professor Jeffrey C. Cornwell

Dr. Peter M. Groffman, Cary Institute

Dr. Paul M. Mayer, US Environmental Protection Agency

Professor David R. Tilley, Dean's Representative

© Copyright by  
Tamara Ann Newcomer Johnson  
2015

## **Dedication**

*To my parents,*

*Joan and Joseph Newcomer,*

*I am so grateful for your endless love, support, and  
encouragement.*

## Acknowledgements

*I would like to express my deep appreciation and gratitude to my advisor, Dr. Sujay Kaushal, for the patient guidance and mentorship he provided to me, ever since I started working on a summer Research Experience for Undergraduates (REU). Dr. Kaushal's intellectual intensity is matched only by his genuinely good nature and down-to earth humility, and I am truly fortunate to have had the opportunity to work with him.*

*I would also like to thank my committee members, Paul Mayer, Walter Boynton, Peter Groffman, and Jeffrey Cornwell, for the friendly guidance, thought provoking suggestions, and the general collegiality that each of them offered to me over the years. In a similar vein, I'd like to recognize Dr. Alan Berkowitz and Michael Liffmann for the contributions that each of them made to my intellectual growth.*

*Finally, I'd be remiss if I didn't acknowledge my wonderful and loving husband, Mike. We have so many wonderful adventures to look forward to!*

# Table of Contents

|  |     |
|--|-----|
| List of Tables .....   | v   |
| List of Figures .....  | vii |
| List of Appendices .....   | xii |
| Chapter 1: Introduction and Overview.....  | 1   |
| Chapter 2: Influence of Natural and Novel Organic Carbon Sources on Denitrification in Forested, Degraded-Urban, and Restored Streams..... | 7   |
| Chapter 3: Effects of Stormwater Management and Stream Engineering on Watershed Nitrogen Retention.....                                    | 51  |
| Chapter 4: Nutrient Retention in Restored Streams and Floodplains: A Review and Synthesis.....   | 129 |
| Chapter 5: Conclusions.....  | 201 |
| Bibliography.....  | 212 |
| Curriculum Vitae .....   | 212 |

## List of Tables

|  |     |
|--|-----|
| Table 2.1. Dissolved organic carbon (DOC) and nitrate concentration (mg/L) in forested, restored, and degraded-urban Baltimore streams from April 2008 – April 2010. ....  | 33  |
| Table 2.2. Lipid biomarker data from two locations at forested Pond Branch, two locations at restored Spring Branch, and three locations at restored Minebank Run streams (Canuel and Martens 1993, Canuel et al. 1995). ....  | 34  |
| Table 2.3. Estimation of potential nitrate load reduction through denitrification based upon available DOC and literature ranges for DOC bioavailability (from Petrone et al. 2009). ....  | 36  |
| Table 3.1. Study site characteristics of Pond Branch, Spring Branch, and Gwynns Run watersheds. Land use data from (Baltimore City 2005, 2005, DEPRM 2008b). ....  | 84  |
| Table 3.2. <i>In situ</i> groundwater denitrification rates (means $\pm$ SE, $n = 3$ replicates per well). ....  | 85  |
| Table 3.3. Concentrations of TDN and DOC from stream network groundwater wells... ..   | 86  |
| Table 3.4. Calculation of areal denitrification rates (mg N/m <sup>2</sup> /day) and estimation of feature denitrification (g/day) within the SCMs and the stream network. ....  | 87  |
| Table 4.1. The 79 empirical nutrient studies were divided into 4 strategies used to increase hydrologic connectivity. We recorded the number of results for each strategy as well as percentage of nutrient results that were positive, neutral, and negative. Note the total number of results is higher than the total number of studies because many studies used multiple strategies and many studies had multiple results based upon seasonality and nutrient species. .... | 161 |
| Table 4.2. We recorded the nutrient spiraling tracers (NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , and/or SRP) and uptake metrics [k (uptake rate coefficient; sec <sup>-1</sup> ), S <sub>w</sub> (uptake length; m), U (areal uptake; µg/m <sup>2</sup> /sec), and V <sub>f</sub> (uptake velocity; mm/min)] that were recorded as well as a summary for each study. ....  | 162 |
| Table 4.3. The 15 nutrient spiraling studies measured 45 diverse potential controlling variables. We divided these variables into 5 categories: watershed, reach, water  |     |

chemistry, transient storage, and metabolism characteristics. Shaded boxes indicate that a variable was measured in the specific study. The two columns on the right show the total number and percent of studies that recorded each variable. ....164

Table 4.4. Mean, median, range, and number of studies reporting each nutrient spiraling metric by stream type (restored, degraded, and reference). Uptake metrics included:  $S_w$  (uptake length in m),  $U$  (areal uptake in  $\mu\text{g}/\text{m}^2/\text{sec}$ ), and  $V_f$  (uptake velocity in mm/min). P values are listed for ANOVA comparisons between stream types that are significant or marginally significant. ....166

Table 4.5. The 15 nutrient spiraling studies measured 45 diverse potential controlling variables. We found 12 significant relationships between each controlling variable and nutrient spiraling metrics ( $p \leq 0.05$ ). Yellow boxes with a plus sign (+) indicate a significant positive relationship and the blue box with the minus sign (-) indicates a significant negative relationship. Relationships that were marginally significant ( $P > 0.05$ ) are lighter colored. \*Nitrate  $S_w$  relationships were only significant after a high winter value of 2,668 m from McMillan et al. (2014) was excluded. ....167

Table 5. Comparison of 10 studies that measure denitrification ( $\mu\text{g N}/\text{kg soil}/\text{day}$ ) using the  $^{15}\text{N}$  *in situ* push-pull method. ....206

# List of Figures

|   |    |
|---|----|
| <u>Figure 1.</u> Stormwater system N cycle.....   | 5  |
| <u>Figure 2.1.</u> Land cover map of study sites at the Baltimore Ecosystem Study Long-Term Ecological Research Site. Coloration is from the 2001 National Land Cover Database (red indicates urban areas and green indicates forested areas).....  | 37 |
| <u>Figure 2.2.</u> Photographs showing (A) forested Pond Branch and Baisman Run; (B) restored Spring Branch and Minebank Run; (C) degraded-urban Dead Run and Scotts Level Branch. ....   | 37 |
| <u>Figure 2.3.</u> Seasonal DOC and nitrate concentrations ( $\text{mg}\cdot\text{L}^{-1}$ ) from (A) forested, (B) restored, and (C) degraded-urban watersheds. ....   | 37 |
| <u>Figure 2.4.</u> Daily loads of DOC and nitrate ( $\text{g}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$ ) versus log daily runoff ( $\text{mm}\cdot\text{day}^{-1}$ ) from (A) forested, (B) restored, and (C) degraded-urban watersheds. Daily loads of DOC and nitrate increased with log daily runoff according to a power function.....   | 37 |
| <u>Figure 2.5.</u> Comparison of C:N molar ratios for leaves, periphyton, grass, sediment, and POM across forested (N=20), restored (N=14), and degraded-urban sites (N=13). Values are means $\pm$ 1 SE. Letters represent comparisons (lowercase is inter-site type and uppercase is intra-site type) that are significant at an alpha of 0.05 according to Tukey's Studentized Range (HSD) Test.....   | 37 |
| <u>Figure 2.6.</u> Comparison of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic ratios in periphyton, leaves, grass, and water from (A) forested (N=20), (B) restored (N=14), and (C) degraded-urban sites (N=13). Values are means $\pm$ 1 SE. ....  | 38 |
| <u>Figure 2.7.</u> Relative importance of nitrate versus glucose on denitrification potential rate across sites. (A) Hydrograph of mean daily runoff of the storm that was sampled as part of the denitrification experiments ( $\text{L}\cdot\text{sec}^{-1}\cdot\text{km}^{-2}$ ). Comparison of denitrification potential rates associated with the glucose amendment (B) and nitrate amendment (C) produced from 2 forested, 2 restored, and 2 degraded-urban streams using baseflow and stormflow water. Values are means $\pm$ 1 SE. Letters represent comparisons between site types that are significant at an alpha of 0.05 according to Tukey's Studentized Range (HSD) Test..... | 38 |
| <u>Figure 2.8.</u> Comparison of denitrification potential rates associated with different naturally occurring organic carbon sources at 2 forested (Pond Branch and Baisman Run), 2 restored (Spring Branch and Minebank) and 2 degraded-urban streams (Dead Run and Scotts Level Branch). Values are means $\pm$ 1 SE. Letters represent comparisons (lowercase is carbon source and uppercase is site type) that are significant at an alpha of 0.05 according to Tukey's Studentized Range (HSD) Test. (A) Results from all 6 sites are averaged and divided into categories of organic carbon sources, and (B) data is divided by site type and organic carbon source.....             | 38 |

Figure 3.1. Land cover map of Spring Branch, Gwynns Run, and Pond Branch watersheds at the Baltimore Long-Term Ecological Research Site (LTER) in MD, USA. Coloration was from the 2006 National Land Cover Database (red indicates urban areas and green indicates forested areas). White Xs indicate location of stormwater control measures (SCMs) in urban sites or the forested reference pond..... 88

Figure 3.2. Conceptual diagram of the Spring Branch, Gwynns Run, and Pond Branch watersheds. Red lines indicate locations of monthly surface water chemistry and discharge measurements. Blue “W”s indicate locations of mini-piezometer wells used for <sup>15</sup>N in situ denitrification measurements and seasonal groundwater monitoring. At each site, 4 wells were located in the floodplain and 4 wells were located in the SCM or reference pond. Wells were numbered in the order they were sampled which is from downstream to upstream to avoid tracer cross contamination. This diagram is not to scale. .... 88

Figure 3.3. Photos showing Spring Branch before restoration when it was lined in concrete (a) and (b) afterward when the channel was reconnected to the floodplain. (c) The stream restoration construction process..... 88

Figure 3.4. Flow duration curves (liters/second) for mean daily flow from April 2008 to September 2010 with synoptic sampling dates labeled according to the associated flow values for A) Spring Branch at 3,005 m (continuous discharge modeled from USGS gage 01589464), B) Gwynns Run at 138 m (continuous discharge modeled from USGS gage 01589352), and C) Pond Branch at 0 m (continuous discharge from USGS gage 01583570). .... 89

Figure 3.5. Box-and-whisker plot of denitrification rates from <sup>15</sup>N in situ push-pulls in the floodplain and SCMs or reference pond (n = 72). The center vertical line of the box-and-whisker plot marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall. Box edges indicate the first and third quartiles. Circles (o) represent outside values..... 89

Figure 3.6. A comparison of denitrification rates ( $\mu\text{g N}\cdot\text{kg soil}^{-1}\cdot\text{day}^{-1}$ ) versus (a) dissolved oxygen (mg/L), (b) temperature ( $^{\circ}\text{C}$ ), (c) mean nitrate (mg/L), and (d) mean DOC (mg/L) from mean values for the present study and similar sites from the literature. Sample size was 72 measurements for DO and temperature and 12 measurements for nitrate and DOC, which were averaged from seasonal measurements for each well. .... 89

Figure 3.7. Spring Branch longitudinal variation in mean ( $\pm$  SE) A) discharge (L/s), B) TDN concentrations (mg/L), and DOC concentrations (mg/L) along 15 sampling points. .... 90

Figure 3.8. Gwynns Run longitudinal variation in mean ( $\pm$  SE) A) discharge (L/s), B) TDN concentrations (mg/L), and DOC concentrations (mg/L) along 7 sampling points (n = 23-25 sampling dates). .... 90

Figure 3.9. Pond Branch longitudinal variation in mean ( $\pm$  SE) A) discharge (L/s), B) TDN concentrations (mg/L), and DOC concentrations (mg/L) along 4 sampling points (n = 23-25 sampling dates). ..... 90

Figure 3.10. Water Budgets (%) for Spring Branch, Gwynns Run, and Pond Branch stream networks. Water budgets are composed of the surface water from the mainstem at the sampling point furthest upstream, tributary inputs, and groundwater seepage. There is positive groundwater seepage at Spring Branch and Gwynns Run (gaining reaches) and negative groundwater seepage at Pond Branch (losing reach)..... 90

Figure 3.11. Box-and-whisker plot of Spring Branch longitudinal variation in reach export and retention A) TDN (mg/m<sup>2</sup>/day), B) DOC (mg/m<sup>2</sup>/day), C) TDN (%), D) DOC (%) along 7 stream reaches. SCM 1 is from 0-50 m, SCM 2 is from 50-121 m, phase 1a is from 121-604 m, phase 1b is from 604-1860 m, phase 1c is from 1860-2265 m, phase 2 is from 2265-3005 m, and the unrestored reach is from 3005-3516 m. The center vertical line of the box-and-whisker plot marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall. Box edges indicate the first and third quartiles. Circles (o) represent outside values, which are provided in the Supporting Information. .... 90

Figure 3.12. Box-and-whisker plot of Gwynns Run longitudinal variation in reach export and retention A) TDN (mg/m<sup>2</sup>/day), B) DOC (mg/m<sup>2</sup>/day), C) TDN (%), D) DOC (%) along 5 stream reaches (n = 23-25 sampling dates). SCM 1 is from 0- 50 m, SCM 2 is from 50-121 m along the oxbow. The center vertical line of the box-and-whisker plot marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall. Box edges indicate the first and third quartiles. Circles (o) represent outside values, which can be found in the Supporting Information. .... 91

Figure 3.13. Net flux per streambed area (g/m<sup>2</sup>/day) versus instantaneous discharge (liters/second) at Spring Branch, Gwynns Run, and Pond Branch in the stormwater control measures (SCMs) and reference pond and the overall stream networks. A negative value indicates retention and a positive value indicates release. .... 91

Figure 3.14. Feature-scale denitrification (g N/day) versus surface area (m<sup>2</sup>) at Spring Branch, Gwynns Run, and Pond Branch. Comparisons are between the stream reach surface areas versus the surface areas for SCMs or reference pond. .... 92

Figure 4.1. (a) Based on our search criteria, we found 550 publications about stream restoration since 1978 and (b) 79 empirical nutrient studies about stream restoration since 1997. (c) The 79 empirical nutrient studies were located in the United States (45 studies), Austria (6), Denmark (6), Germany (4), England (3), Spain (3), China (3), France (2) and the following countries each had 1 study: Canada, Iraq/Iran, Japan, Korea, Poland, Taiwan, and Mexico/USA. American states with studies were Maryland (11), North Carolina (7), Indiana (2), Michigan (2), Mississippi (2), Nevada (2), New York (2), Ohio (2), Virginia (2), Wisconsin (2), and the following states each had 1 study: Arkansas, California, Florida, Georgia, Illinois, Kentucky, Tennessee, Wyoming, Washington, Texas and there was a study comparing sites in Maryland, Illinois, and Iowa. ....168

Figure 4.2. Pie chart representing methods used for evaluating stream and floodplain restoration. The primary methods used were changes in water chemistry, mass balances, denitrification, and nutrient spiraling. Alternative methods were sediment dynamics, plant dynamics, nitrification, stable isotope ratios, dissimilatory nitrate reduction to ammonium (DNRA), anammox, microbial biomass nitrogen (MBN) and potentially mineralizable nitrogen (PMN). The percentage of the 79 studies using each method is listed along with the total number of studies. The total percentages do not add up to 100% because many studies used multiple methods. ....168

Figure 4.3. Restoration projects were divided into 9 typologies: (A) raise stream bottom, (B) lower floodplain, (C) raise water levels with drainage control structures, (D) reconnect wetlands, (E) remove concrete liner, and (F) daylighting urban streams buried in pipes, (G) increase sinuosity, (H) add in-stream wetlands, and (I) reconnect oxbow wetlands.....169

Figure 4.4. Meta-analysis of nutrient spiraling showed that nitrate uptake length (m) had a positive correlation with (a) watershed area (ha) and (b) discharge (L/s). Nitrate uptake length relationships were only significant after a high winter value of 2,668 m from McMillan et al. (2014) was excluded (this high value has been circled).....169

Figure 4.5. Meta-analysis of nutrient spiraling showed that in restored streams, nitrate areal uptake rate (U;  $\mu\text{g}/\text{m}^2/\text{s}$ ) had a positive relationship with impervious surface coverage (%). ....169

Figure 4.6. In restored streams, ammonium areal uptake rate (U;  $\mu\text{g}/\text{m}^2/\text{s}$ ) was negatively correlated with (a) disturbance intensity (%) and (b) ammonium concentration ( $\mu\text{g}/\text{L}$ ).....169

Figure 4.7. In restored streams, ammonium uptake velocity ( $V_f$ ; mm/min) has a significant negative relationship with (a) disturbance intensity (%) and (b) ammonium concentration ( $\mu\text{g}/\text{L}$ ) and a significant positive relationship with (c) discharge and (d) velocity. There was also a marginally significant positive correlation with (e) the relative extent of transient storage ( $A_s/A$ ) and (f) the median travel time due to transient storage over a standardized 200 m reach (%). ....169

Figure 4.8. Meta-analysis of nutrient spiraling showed that SRP uptake length (m) had a positive correlation with (a) watershed area (ha) and (b) discharge (L/s). ....170

Figure 4.9. Meta-analysis of nutrient spiraling showed that SRP uptake velocity (mm/min) had a positive correlation with (a) discharge (L/s), (b) Chl-a ( $\text{mg}/\text{m}^2$ ) and (c) SRP concentration ( $\mu\text{g}/\text{L}$ ), and a negative correlation with (d) ammonium concentration ( $\mu\text{g}/\text{L}$ ).....170

Figure 4.10. Top panel: As the number of typologies per study increased from 1 to 5, the number of studies declined exponentially from 45 to 1. Bottom panel: In contrast, as the number of typologies per study increased from 1 to 5, the % of positive results increased from 59% to 100%.....170

Figure 5. A comparison of denitrification rates ( $\mu\text{g N}\cdot\text{kg soil}^{-1}\cdot\text{day}^{-1}$ ) versus dissolved oxygen (mg/L), temperature ( $^{\circ}\text{C}$ ), nitrate (mg/L), and DOC (mg/L) from mean values for the present study and the available literature.....210

## List of Appendices

|   |     |
|---|-----|
| Appendix A. Different organic C sources affect denitrification rates. ....  | 48  |
| Appendix B. Aerial photographs of sampling locations at (A) forested Pond Branch, (B) forested Baisman Run, (C) restored Minebank Run, (D) restored Spring Branch, (E) unrestored urban Scotts Level Branch, and (F) unrestored urban Dead Run..... | 50  |
| Appendix C. Information on in-stream tracer studies, mass balance calculations, and continuous discharge. ....  | 107 |
| Appendix D. Method, land use, management action, nutrient retention effectiveness, location, and source for 79 empirical nutrient case studies. ....  | 181 |

# Chapter 1: Introduction and Overview

## Overview

The aim of my dissertation research was to investigate rates of nitrogen removal in forest, restored, and degraded-urban streams in the Maryland piedmont region. I also examined linkages between nitrogen (N) and carbon (C) cycles in these streams. A secondary goal was to develop a decision support tool for reducing nitrogen flux based on my research and other available studies. The second chapter examined the effect of organic carbon quantity and quality on potential denitrification rates across a land use and restoration gradient. The third chapter examined measurements of stream nitrogen and carbon mass balances, uptake rates from tracer studies, and in situ denitrification rates. The fourth chapter reviewed of nitrogen retention within hydrologically restored streams & floodplains.

## Background

Managing the nitrogen cycle is listed as one of fourteen “Grand Challenges for Engineering” by the National Academy of Engineering of the National Academies. This challenge exists because fertilizer production, cultivation of N-fixing crops, and

combustion of fossil fuels have led to a doubling of terrestrial nitrogen inputs (Vitousek et al. 1997). Excess amounts of reactive nitrogen have led to water quality problems like contamination of drinking water supplies and eutrophication in coastal bodies like the Chesapeake Bay (Boesch et al. 2001). The Chesapeake Bay is particularly sensitive to increased nitrogen loading because it is a relatively small and shallow basin compared to its watershed area (Kemp et al. 2005). The Chesapeake Bay has been experiencing problems with nutrient over-enrichment leading to eutrophication, algal blooms, and summertime anoxic zones that can cover as much as a third of its mainstem (Howarth et al. 2002, Weller et al. 2003, Wazniak and Glibert 2004, Kemp et al. 2005). Such water quality problems are detrimental to the ecology and economy of the region as they decrease the productivity of fisheries and reduce recreational appeal (Boesch et al. 2001).

Management efforts like the current Chesapeake Bay total maximum daily load (TMDL) have been implemented to reduce eutrophication by managing nutrient loads from various sources (Boesch et al. 2001, Carstensen et al. 2006). Though the largest nutrient contributor is agriculture, the Chesapeake Bay Program reports that in 2008, urban and suburban land use contributed 16% of the nitrogen load, 32% of the phosphorus load, and 24% of the sediment load (CBT 2009). Suburban and urban land use is rapidly spreading globally (Grimm et al. 2008) and especially in the Chesapeake Bay watershed (Jantz et al. 2005). Over 80% of the United States' and over 50% of the world's populations live in urban areas, and the number of cities is growing (Pickett et al. 2011). Urban watersheds often receive greater nitrogen inputs than nearby natural landscapes (Groffman et al. 2004, Kaushal et al. 2008a). Urbanized watersheds can be effective at retaining nitrogen at low to moderate flows (Groffman et al. 2004), and they

can be less effective at retaining it during high flows (Kaushal et al. 2008a). Sources of nitrogen pollution to streams include septic system effluent, leaky sanitary lines, pet waste, fertilizer, and runoff of atmospheric deposition from fossil fuel combustion (Groffman et al. 2004, Kaushal et al. 2006, Elliott et al. 2007, Cadenasso et al. 2008, Davidson et al. 2009).

Many of the streams in the Chesapeake Bay watershed have elevated  $\text{NO}_3^-$  concentrations as a result of increasing urbanization, and there is a growing need to improve N management within watersheds to prevent downstream delivery of N to sensitive coastal waters and drinking water bodies (Kemp et al. 2005, Kaushal et al. 2008a). Nitrogen in urban aquatic systems can undergo either temporary assimilation by biota or removal by microbial denitrification, the transformation of  $\text{NO}_3^-$  to  $\text{N}_2$  and  $\text{N}_2\text{O}$  gases (Davidson and Schimel 1995) Fig. 1). Denitrification is a process relevant to water quality, particularly where anthropogenic nitrogen from urban sources can contribute to eutrophication (Kemp et al. 2005). Heterotrophic anaerobic bacteria perform this biogeochemical process, which requires anoxic conditions, a carbon source, and nitrate to be reduced (Groffman et al. 2005, Boyer et al. 2006). The riparian-stream interface is thought to be a “hot spot” for denitrification because bioavailable carbon and low oxygen conditions may exist along flow paths (Hedin et al. 1998, Kaushal et al. 2008b, Mayer et al. 2010). Substantial N removal can also occur within stream and river networks. For example, (Seitzinger et al. 2002a) estimate that 37 - 76% of N entering northeast US waterways is removed by streams.

Urban stream reaches may have impaired N retention and removal ability compared with restored stream reaches (Brush 2008, Kaushal et al. 2008b, Klockner et al.

2009, Sivorichi et al. 2011). The “urban stream syndrome” is characterized by increased impervious cover, reduced vegetation, a flashier hydrograph, increased concentrations of nutrients and pollutants, altered geomorphology (channel incision), and reduced biotic richness (Walsh et al. 2005). Streams are often straightened or buried in underground pipes (Elmore and Kaushal 2008). Such alterations can decrease floodplain connectivity, groundwater–riparian interactions, residence time, and labile carbon availability, and limit the effectiveness of stream ecosystem functions like nitrogen removal via denitrification (Kaushal et al. 2008b, Mayer et al. 2010, Harrison et al. 2011).

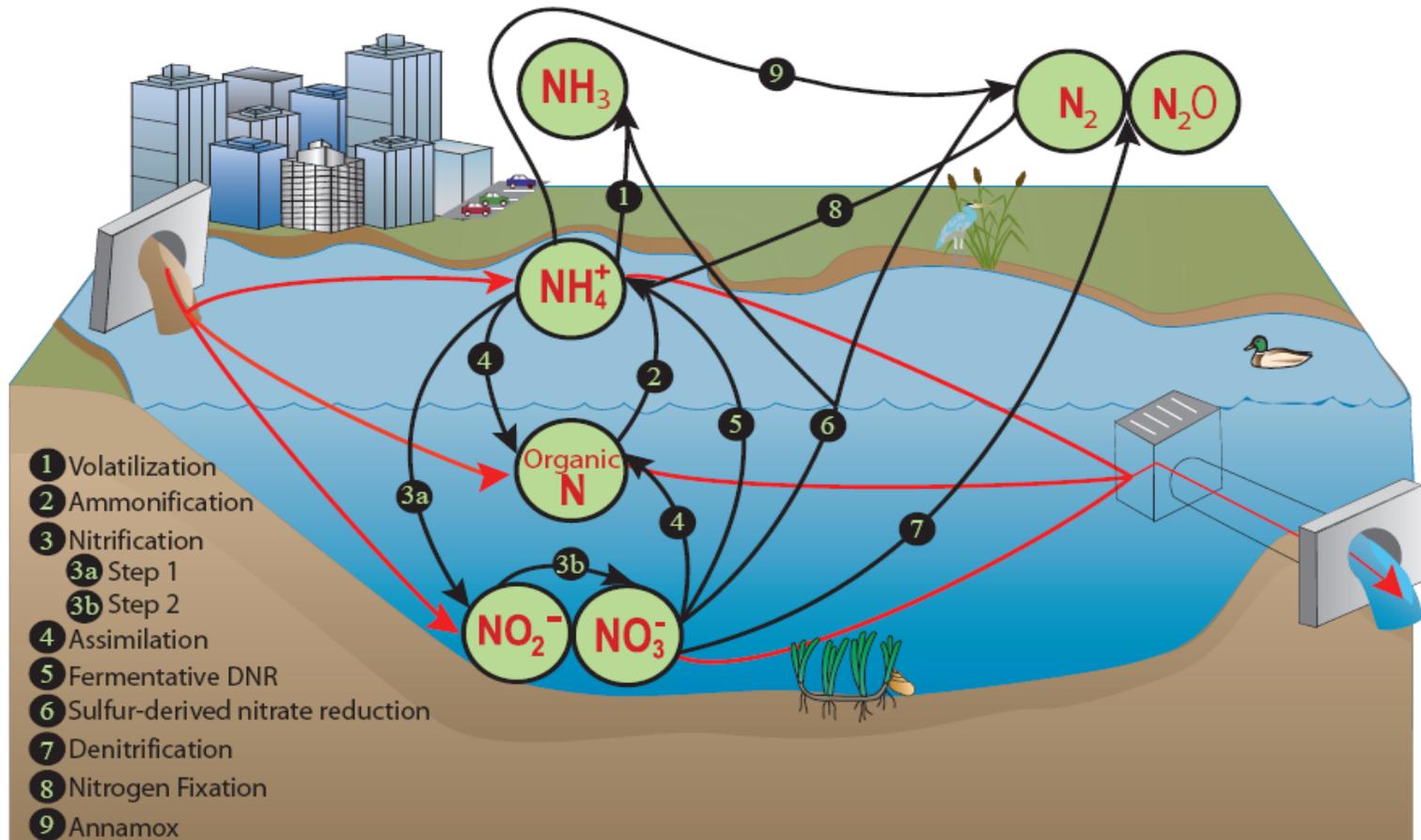
Stream restoration can be employed as a strategy to offset these anthropogenic impacts and restore ecosystem function. Stream restoration has become particularly common within the Chesapeake Bay watershed within the past several decades (Hassett et al. 2005). Empirical studies measuring the effectiveness of stream restoration practices on water quality improvement are limited, but growing ( e.g., Bukaveckas 2007, Roberts et al. 2007, Klocker et al. 2009, Harrison et al. 2011, Sivorichi et al. 2011).

The aim of my dissertation research was to expand knowledge of how restored streams and integrated stormwater management networks transport and transform nitrogen, and how such transformation can be coupled with the carbon cycle. The second chapter examined how different natural organic carbon sources can affect denitrification rates in forest, restored, and degraded-urban streams. The third chapter quantified rates of N and C fluxes, N and C uptake, and N removal via *in situ* denitrification in streams with integrated stormwater management practices. The fourth chapter reviewed nitrogen retention within hydrologically restored streams & floodplains.

## Figure Caption

Figure 1. Stormwater system N cycle: nitrogen enters the stormwater system in the form of ammonium ( $\text{NH}_4^+$ ), nitrate/nitrite ( $\text{NO}_3^-/\text{NO}_2^-$ ), and organic nitrogen. Inorganic N can be assimilated into organic N and temporally stored in biomass. Organic N can then undergo ammonification to ( $\text{NH}_4^+$ ) and nitrification to ( $\text{NO}_2^-$  and then to  $\text{NO}_3^-$ ). Inorganic N can be permanently removed from the system via volatilization of ammonium ( $\text{NH}_4^+$ ) to ammonia gas ( $\text{NH}_3$ ) or through respiratory denitrification (oxidizing  $\text{NO}_3^-$  and organic C to release  $\text{CO}_2$  and  $\text{N}_2$  gas), iron-derived denitrification (oxidizing  $\text{NO}_3^-$  and  $\text{Fe}_2^+$  to release  $\text{Fe}_3^+$  and  $\text{N}_2$  gas), anammox ( $\text{NO}_2^-$  and  $\text{NH}_4^+$  are oxidized to  $\text{N}_2$  gas), or sulfur-driven nitrate reduction. (Created by T.A. Newcomer from Collins et al. 2010)

Fig. 1.



## **Chapter 2: Influence of Natural and Novel Organic Carbon Sources on Denitrification in Forested, Degraded-Urban, and Restored Streams**

### *Abstract*

Organic carbon is important in regulating ecosystem function and its source and abundance may be altered by urbanization. I investigated shifts in organic carbon quantity and quality associated with urbanization and ecosystem restoration, and its potential effects on denitrification at the riparian-stream interface. Field measurements of streamwater chemistry, organic carbon characterization and lab-based denitrification experiments were completed at 2 forested, 2 restored, and 2 degraded-urban streams at the Baltimore Long-Term Ecological Research site. Daily dissolved organic carbon (DOC) and nitrate loads increased with log daily runoff according to a power function that varied across sites. Evidence from stable isotopes and molar C:N ratios suggested that stream particulate organic matter (POM) was a mixture of periphyton, leaves, and grass that varied across site types. Stable isotope signatures and lipid biomarker analyses of sediments suggested that terrestrial organic carbon sources in streams varied as a result of riparian vegetation. Laboratory experiments indicated that organic carbon

availability significantly increased rates of denitrification ( $35.1 \pm 9.4 \text{ ng N} \cdot \text{g dry sediment}^{-1} \cdot \text{hr}^{-1}$ ; mean  $\pm$  SE) more than nitrate availability ( $10.4 \pm 4.0 \text{ ng N} \cdot \text{g dry sediment}^{-1} \cdot \text{hr}^{-1}$ ) across streamflow conditions and sites ( $p < 0.05$ ). Denitrification rates associated with stormflow conditions were consistently but not significantly higher than rates associated with baseflow conditions. Denitrification experiments with naturally occurring carbon sources showed that denitrification was significantly higher with grass clippings from home lawns ( $1,244 \pm 331 \text{ ng N} \cdot \text{g dry sediment}^{-1} \cdot \text{hr}^{-1}$ ;  $p < 0.05$ ) and degraded-urban sites showed significantly higher denitrification rates than restored and forest sites overall ( $p < 0.05$ ). My results suggest that urbanization can influence organic carbon sources and quality in streams, which may have substantial downstream impacts on ecosystem services such as denitrification. Stream restoration and riparian management should consider the differential effects of riparian vegetation and organic carbon quality on in-stream N processing.

### Introduction

Organic carbon plays a key role in regulating ecosystem functions (Fisher and Likens 1973, Vannote et al. 1980). In headwater streams, dissolved organic carbon (DOC) serves as an energy source for microorganisms (Edwards and Meyer 1987), influences nutrient cycling (McDowell and Likens 1988, Bernhardt and Likens 2002), forms complexes with metals (Perdue et al. 1976), absorbs ultraviolet light (Frost et al. 2005), and can stimulate production of disinfection by-products in drinking water during chlorination (Krasner et al. 1989, Kraus et al.

2008). Availability of dissolved and particulate organic carbon can limit denitrification, a microbial process critical to maintaining water quality (Sobczak et al. 2003, Mayer et al. 2010). In this project, I investigated the relative importance of different organic carbon sources to denitrification at the riparian-stream interface of forested, restored, and degraded-urban streams.

Many streams and rivers in the U.S. have elevated concentrations of nitrogen (Carpenter et al. 1998, Howarth et al. 2006). In the Chesapeake Bay watershed, there are elevated regional  $\text{NO}_3^-$  concentrations in streams and rivers because of agricultural and urban land use (Boesch et al. 2001, Kemp et al. 2005, Kaushal et al. 2008b). There is also a corresponding regional need to improve N management within watersheds to prevent downstream delivery to sensitive coastal waters (Boesch et al. 2001, Kemp et al. 2005, Kaushal et al. 2008b). Denitrification is a microbial process that removes N and is performed by heterotrophic anaerobic bacteria that require labile organic carbon (Davidson and Schimel 1995, Groffman et al. 2005, Boyer et al. 2006). The riparian-stream interface is thought to be a “hot spot” for denitrification because this interface is a site where streamwater and groundwater mix and there are low dissolved oxygen and high DOC (e.g., (Hedin et al. 1998, Kaushal et al. 2008b, Mayer et al. 2010).

Dissolved organic carbon in streams is a mixture of both recalcitrant and labile fractions, with the labile fraction being important to biogeochemical processes (Findlay and Sinsabaugh 1999, Kaushal and Lewis, Jr. 2003). Therefore, it is critical to understand which watershed organic carbon sources actually enter streams and how these sources may subsidize denitrification, metabolism, and organic carbon export. In forest ecosystems, riparian vegetation surrounding streams can influence DOC and comprise a substantial proportion of stream organic

carbon budgets (Fisher and Likens 1973, McDowell and Likens 1988). The effects of differential organic carbon sources on ecosystem functions have been quantified for forested streams (McDowell and Likens 1988, McCutchan Jr and Lewis Jr 2002) and agricultural streams (Schaller et al. 2004, Royer and David 2005, Griffiths et al. 2009, Warrner et al. 2009).

However, there has been little assessment of the relative importance and sources of natural and anthropogenic organic carbon sources in urban streams (Paul and Meyer 2001, Paul et al. 2006).

Variations in organic carbon from autochthonous (in-stream) and allochthonous (watershed) sources can be pronounced in urban streams due to flashy hydrology, wastewater input, and anthropogenically enhanced sources (Hook and Yeakley 2005, Kaushal et al. 2010, Petrone 2010). Urban watersheds and riparian zones may also have extensively modified vegetation such as home lawns, and this vegetation may have a strong effect on the supply of organic carbon to streams (Pouyat et al. 2009). Therefore, there is a need to elucidate how denitrification in sediments may vary in response to stormflow vs. baseflow conditions and changes in the relative importance of terrestrial vs. aquatic sources.

My study objectives were to: (1) determine the influence of land use and restoration status on amounts and sources of organic carbon, (2) measure the denitrification potential rates associated with baseflow and stormflow conditions, (3) conduct experiments to evaluate whether nitrate or carbon availability produced a greater denitrification potential response, and (4) characterize the relative importance of naturally occurring organic carbon sources (leaves, grass, and periphyton) for denitrification across land use and restoration status.

## Methods

My project design included six Baltimore County, Maryland, USA streams (two forested, two urban restored, and two degraded-urban). At each site, I monitored discharge and concentrations of nitrate and dissolved organic carbon for 2 years. I examined how particulate organic matter (POM) and organic carbon sources varied across land use and restoration status with molar C:N ratios and stable isotope ratios. I also conducted laboratory experiments to measure microbial responses to differing organic carbon sources typical of the study systems: grass clippings from home lawns, decomposed leaves taken from debris dams, and periphyton which was a mixture of filamentous algae and terrestrial detritus. Laboratory experiments examined changes in denitrification potential rates in sediments from the riparian-stream interface with water taken at baseflow vs. stormflow conditions and in response to varying organic carbon sources.

Site description: forest, degraded-urban, and restored streams

Study sites included six low order streams (two forested, two restored, and two degraded-urban) in the Baltimore metropolitan area, which is situated in the Piedmont region of Maryland USA in the watershed of Chesapeake Bay (Fig. 1, Fig. 2). These sites have been studied as part of the Baltimore Ecosystem Study (BES), one of two urban study sites in the US National Science Foundation Long Term Ecological Research network.

Pond Branch (39°28'49"N, 76°41'16"W, 32.3 ha) is a forested, 1<sup>st</sup>-order stream with no impervious surfaces. It is a tributary of Baisman Run (39°28'45"N, 76°40'42"W, 381 ha), which is a 3<sup>rd</sup>-order stream within a watershed that was 66% forested, 1% agriculture, 34% residential with septic systems, and 1% impervious surface coverage (Groffman et al. 2004). Discharge in both streams was monitored continuously by US Geological Survey (USGS) gaging stations.

The two restored streams, Spring Branch (39°26'43.9" N, 76°37'12.9"W) and Minebank Run (39°24'36" N, 76°33'23"W), are low order streams in close proximity to the Loch Raven drinking water reservoir. Both restorations incorporated a combination of standard natural channel design techniques (Rosgen 1994) and integrated stormwater management such as hydrologically connected floodplains (Minebank Run; e.g., (Kaushal et al. 2008b, Klocker et al. 2009) or stormwater management areas including sequential ponds after a storm drain outfall (Spring Branch; (DEPRM 2008a, 2008b, EPA 2011). Spring Branch (407 ha) was the first restoration site in Baltimore County and 3.2 km of stream length were restored during 1994-97. My study reach at Spring Branch was restored by removal of concrete channels, creation of a series of step-pools, tree and shrub plantings for bank stabilization, and creation of multiple cell stormwater management areas in the headwaters (DEPRM 2008a, 2008b, EPA 2011). The Spring Branch watershed has an impervious surface coverage of 18.6% and land use composition is 91.5% residential with varying degrees of density (33% low, 54.8% medium, and 3.7% high), 1.7% institutional (a school) and 6.7% forest (DEPRM 2008). At Minebank Run (207 ha), 2.4 km of stream length were restored during 1998-99 and 2.9 km were restored from 2004-05 (EPA 2006). Land use in Minebank Run is 17% forested, 2% agriculture, and 81% urban/suburban,

including 30-35% impervious surface coverage (Doheny et al. 2006). Discharge is continuously monitored at Minebank Run by the USGS.

The two degraded-urban streams are Scotts Levels Branch (39°21'41.8"N, 76°45'42.3"W) and Dead Run (39°17'45.2"N, 76°44'38.7"W) on the boundary of urban Baltimore City and suburban Baltimore County. In contrast to the forested streams, Scotts Level Branch (836.5 ha) and Dead Run (204.6 ha) have sections where the riparian zone is forested and reaches where lawns are managed to the edge of the stream. Discharge at both streams is monitored continuously by USGS gaging stations.

#### Temporal changes in $\text{NO}_3^-$ and DOC concentrations and daily fluxes

From April 2007 to April 2010, I collected monthly surface water samples to characterize temporal changes in nitrate ( $\text{NO}_3^-$ ) and quantify DOC concentrations at all six streams over a range of hydrologic conditions. Samples were collected in HDPE Nalgene bottles, filtered within 24 hours with pre-combusted Whatman 0.45  $\mu\text{m}$  glass fiber filters (GF/F), and kept frozen until analysis at the University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, Maryland, USA. Analysis of  $\text{NO}_3^-$  was performed with a Dionex Ion Chromatography System (ICS-1500) and analysis of DOC was performed with a Shimadzu Total Organic Carbon Analyzer (TOC-272 V CPH/CPN; (Kaushal and Lewis, Jr. 2003, 2005). Daily fluxes were calculated by multiplying concentration (mg/L) by stream flow (L/day) to get mass transport per day. I used mean daily stream flow recorded at sites with USGS gages (forested

Pond Branch is gage 01583570, forested Baisman Run is 01583580, degraded-urban Scotts Level Branch is 01589290, degraded-urban Dead Run is 01589312, and restored Minebank Run is 0158397967) and measured instantaneous stream flow at Spring Branch with a Marsh McBirney 2000 (Hach Co., Loveland, CO, USA) velocity meter.

Organic matter sources: C:N ratios,  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  isotopic analysis, lipid biomarkers  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  isotopic ratios and molar C:N ratios were analyzed on triplicate samples of sediment, grass, periphyton, leaves, and POM that were collected at two locations at 5 streams: forested Pond Branch and Baisman Run, restored Spring Branch and Minebank Run, and degraded-urban Dead Run. For POM analysis, 750-1000 mL streamwater was filtered through a 125- $\mu\text{m}$  sieve and onto pre-combusted 25-mm diameter Whatman GF/F filters. The filters were placed on combusted foil and frozen at  $-80\text{ }^{\circ}\text{C}$  until subsequent analysis. Sediment and vegetation samples were collected in 125 ml jars. Before final analysis, filters, sediment, and vegetation samples were rinsed, dried, milled, and acidified according to Stable Isotope Facility, University of California, Davis (UC Davis), California, USA protocol. Samples were shipped to UC Davis for analysis on a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). The ratios  $^{13}\text{C}:^{12}\text{C}$  and  $^{15}\text{N}:^{14}\text{N}$  are reported in delta ( $\delta$ ) units as per-mil difference between the ratio of the sample to the standard (PDB and air, respectively).

Lipid biomarker analyses were conducted to further investigate the sources of organic carbon in stream sediments. Two sediment samples were collected from each of three sites:

forested Pond Branch, restored Spring Branch, and restored Minebank Run during May and June 2008. Sediment samples were extracted in a 2:1 solution of CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH (DCM:MeOH) using an Accelerated Solvent Extraction-200 (ASE) (Dionex®) at 80°C and 1800 psi (2 x 10 minute cycles) following a modification of the Bligh and Dyer (1959) method. Frozen sediments were thawed, homogenized and dried with hydromatrix prior to extraction. Surrogate standards including a fatty acid methyl ester (FAME), methyl nonadecanoate (C<sub>19</sub> FAME), nonadecanol, a wax ester (myristyl arachidate) that yielded a C<sub>14</sub> alcohol and a C<sub>20</sub> FAME following saponification, and androstanol were added to each sample prior to extraction. Extracts were partitioned into two phases and the lower organic phase collected. The aqueous phase was back-extracted into hexane and the combined organic phases placed over anhydrous Na<sub>2</sub>SO<sub>4</sub> overnight to reduce traces of H<sub>2</sub>O. The samples were concentrated to 1 ml using turbo-evaporation (Zymark Turbo Vap 500). The weight of each total lipid extract (TLE) was determined gravimetrically using aliquots representing ~10% of the TLE. A portion of the extract was saponified using 1N KOH in aqueous methanol (110°C for 2 hours). Neutral and acidic lipids were extracted into hexane from the saponified sample following Canuel and Martens (1993). Fatty acids were converted to methyl esters using BF<sub>3</sub>-MeOH. Both fatty acids (as methyl esters) and neutral lipids were separated from other lipid classes by silica gel chromatography following published methods (Canuel and Martens 1993). Sterols were derivatized to trimethylsilyl (TMS) ethers using BSTFA and acetonitrile and heating at 70°C for 30 minutes. Fatty acids (as methyl esters) and alcohols/sterols (as TMS ethers) were analyzed using gas chromatography (GC) (Hewlett Packard 5890 Series II Plus) with flame ionization detection

using a 40 m x 0.18 mm DB5 column (J&W Scientific). Peak areas were quantified relative to the C21 FAME internal standards; C21 FAME was used for fatty acids and 5( $\alpha$ )-H-cholestane for alcohols/sterols. A GC- interfaced to a mass selective detector (Hewlett Packard 6890 GC-MSD) operated in electron impact mode was used to verify the identification of individual compounds using similar conditions as for GC analysis.

### Experimental design for denitrification experiments

Denitrification experiments were related to three of my four overall study objectives: (1) evaluate whether nitrate or carbon availability produced a greater denitrification potential response, (2) measure the denitrification potential rates associated with baseflow and stormflow, and (3) characterize the relative importance of naturally occurring organic carbon sources to denitrification across land use and restoration status.

I conducted two types of denitrification experiments: the first involved amending sediment and water with glucose or nitrate to determine how denitrification potential rates were affected by N and C availability, hydrologic conditions (stormflow and baseflow), and restoration status. The second experiment involved incubating sediment and water with naturally occurring organic carbon sources (grass, periphyton, or leaves) to assess their differential impacts on denitrification. The first experiment had a factorial design with three factors: (1) site type (forested, restored, and degraded-urban), (2) water type (collected during baseflow and stormflow conditions), and (3) amendment type (glucose and nitrate). The second experiment

had a factorial design with two factors: (1) site type (forested, restored, and degraded-urban) and (2) naturally occurring organic carbon source type (control, periphyton, grass, and leaves).

#### Sample collection for denitrification experiments

Sediments were collected from each stream at the riparian-stream interface using a gas-powered auger to drill down to a depth of approximately 0.5 meter below the stream level. The sediment samples were taken from each stream on each bank at a distance of 1 meter from the main channel. All samples were refrigerated less than 2 weeks before analysis. Organic carbon sources (grass, periphyton, and leaves) were collected from the riparian zone at each site and refrigerated in zip-lock bags for less than 2 weeks before the experiments. Grass samples were typically cut from as near the stream as possible; leaves were collected from debris dams within the stream channel; and periphyton samples were collected from within the stream. Leaves, periphyton, and grass clippings were rinsed in the lab with deionized water to remove possible silt or debris. In a few cases, periphyton or grass were not available from a particular study site, and were used from a different site or location. Samples were collected during June 2006. I collected stormflow water during a storm on June 25, 2006 and baseflow water 4 days later.

## Denitrification potential rate methodology

Denitrification enzyme activity assays are widely used to compare sites and treatments (Smith and Tiedje 1979, Groffman et al. 1999, 2005, 2006). Briefly, I amended 5.0 grams of sediment and 10 mL of streamwater with a media made of organic carbon (glucose), nitrate ( $\text{KNO}_3^-$ ), and chloramphenicol (Groffman et al. 1999). I added enough organic carbon and nitrate to ensure denitrification was not limited and chloramphenicol to block the production of new enzymes during incubation. This mixture was sealed in 125 ml Erlenmeyer flasks using rubber stoppers and the headspace was evacuated and replaced with  $\text{N}_2$  gas. Acetylene was added to each flask to block the final step of denitrification, the transformation of  $\text{N}_2\text{O}$  to  $\text{N}_2$ . Gas samples were taken at 30 and 90 minutes. Samples were stored in evacuated glass vials and  $\text{N}_2\text{O}$  concentrations were analyzed by gas chromatography using a Shimadzu GC 14 gas chromatograph outfitted with an electron capture detector at the Cary Institute for Ecosystem Studies, Millbrook, New York, USA.

## Denitrification experiment #1: glucose versus nitrate amendment

In this first experiment, I conducted denitrification enzyme assays where I amended sediments with either glucose or nitrate. For glucose amendments, glucose concentrations were increased by 500 mg/L so that I could measure denitrification potential rates associated with ambient nitrate in water samples collected under different hydrologic conditions (baseflow or

stormflow) across study sites. For the nitrate amendment experiment, I increased the  $\text{KNO}_3$  concentration by 720 mg/L so that I could measure denitrification potential rates associated with ambient organic carbon. My experimental design for comparing glucose, nitrate and stormwater included 96 sample jars (6 stream sites x 2 locations per stream x 2 amendment types [organic carbon and nitrate] x 2 hydrologic conditions [baseflow and stormflow] x 2 duplicates).

Denitrification experiment #2: effects of naturally occurring C sources on denitrification

A second denitrification enzyme activity experiment was conducted to investigate how different naturally occurring organic carbon sources affected denitrification potential rates. This experiment used media that included nitrate but omitted glucose to induce carbon limitation. The dry mass equivalent of 0.2 gram of grass, periphyton, and leaves were made into slurries in a blender and added to the incubations in place of glucose as an organic carbon source. These slurries were incubated with sediment, streamwater, and media in half-pint mason jars. Controls contained only sediment, streamwater, and media. My experimental design for comparing the effects of naturally occurring organic carbon sources on denitrification rates across streams included 96 samples (6 stream sites x 2 locations per stream x 4 organic carbon sources [control, grass, periphyton, or leaves] x 2 duplicates).

## Statistical analysis

Statistical analyses were performed using SAS Analyst (version 9.1, SAS Institute, Cary, North Carolina, USA). Differences in streamwater chemistry, denitrification potential rates, and C:N ratios, and lipid biomarkers were evaluated using an analysis of variance (ANOVA) followed by Tukey's test with a significance level ( $\alpha$ ) of 0.05. I evaluated differences in denitrification potential rates across stream site (forest, restored, and degraded-urban), organic carbon source (periphyton, leaves, and grass), and flow rate (baseflow water and stormflow water).

## Results

### Concentrations and fluxes of $\text{NO}_3^-$ and DOC

Forested Pond Branch had significantly lower and restored Spring Branch had significantly higher mean nitrate-N concentrations than other sites ( $F = 94.33$ ,  $N = 159$ ,  $P < 0.0001$ ; Fig. 3, Table 1). The low-density residential forested site, Baisman Run, had significantly lower and degraded-urban Dead Run had significantly higher mean DOC concentrations than other sites ( $F = 14.14$ ,  $N = 204$ ,  $P < 0.0001$ ; Fig. 3, Table 1).

At all six streams, the daily loads of DOC and nitrate ( $\text{mg}\cdot\text{day}^{-1}$ ) increased according to a power function with runoff (Fig. 4). There were substantial differences in mean daily runoff

normalized by watershed area between the different stream types during the June 25, 2006 storm event when denitrification was measured (Fig. 9a). The forested sites, Pond Branch and Baisman Run, displayed low peak flows that were an order of magnitude lower than the flashy peak flows at the degraded-urban sites, Dead Run and Scotts Level Branch. Minebank Run, a restored site, had a flashy peak ( $230 \text{ L} \cdot \text{sec}^{-1} \cdot \text{km}^{-2}$ ) that was intermediate between forested and degraded-urban streams.

#### Organic carbon source characterization

Overall, there was a significant difference in molar C:N ratios among site types ( $F = 23.14$ ,  $N = 245$ ,  $P < 0.0001$ ) and organic carbon sources ( $F = 21.89$ ,  $P < 0.0001$ ), and there was a significant interaction between site type and organic carbon source ( $F = 3.25$ ,  $P < 0.0016$ ; Fig. 5; Table 2). The forested sites had a significantly higher mean C:N ratio,  $22.9 \pm 1.1$ , than the restored sites,  $16.4 \pm 0.8$  ( $t = 5.99$ ,  $P < 0.0001$ ), and the degraded-urban sites,  $16.6 \pm 0.9$  ( $t = 5.44$ ,  $P < 0.0001$ ). Mean C:N ratios associated with leaves,  $26.5 \pm 1.7$ , were significantly higher than for periphyton,  $19.3 \pm 1.5$  ( $t = 4.67$ ,  $P < 0.0001$ ), or grass,  $18.3 \pm 0.8$  ( $t = 4.90$ ,  $P < 0.0001$ ), and stream POM,  $11.9 \pm 0.4$  ( $t = 9.32$ ,  $P < 0.0001$ ). Mean C:N ratios associated with stream POM were significantly lower than for grass ( $t = 4.41$ ,  $P < 0.0001$ ), periphyton ( $t = 4.64$ ,  $P < 0.0001$ ), and sediment ( $t = 5.26$ ,  $P < 0.0001$ ).

Isotopic C and N signatures of grass clippings, leaf litter, and periphyton showed distinct separation with no overlap among sources in all 5 streams besides the overlap of POM and

sediment at forested Baisman Run and the overlap of POM and leaves at restored Minebank Run (Fig. 6). Across sites, mean  $\delta^{13}\text{C}$  signatures for grass clippings ranged from -32.01‰ at forested Baisman Run to -28.76‰ at degraded-urban Dead Run and mean  $\delta^{15}\text{N}$  ranged from -1.69‰ at forested Pond Branch to 4.96‰ at restored Minebank Run. Mean  $\delta^{13}\text{C}$  of leaf litter ranged from -29.47‰ at forested Pond Branch to -25.10‰ at restored Spring Branch and mean  $\delta^{15}\text{N}$  ranged from -0.86‰ at forested Pond Branch to 2.69‰ at restored Spring Branch. Mean  $\delta^{13}\text{C}$  of periphyton ranged from -29.75‰ at forested Pond Branch to -23.68‰ at restored Minebank Run and mean  $\delta^{15}\text{N}$  ranged from -2.63‰ at forested Pond Branch to 7.87‰ at degraded-urban Dead Run. The isotopic signatures for POM and sediment were intermediate between the grass, leaf, and periphyton sources indicating a mixture of sources. Mean  $\delta^{13}\text{C}$  of POM ranged from -28.15‰ at restored Minebank Run to -27.07‰ at degraded-urban Dead Run and mean  $\delta^{15}\text{N}$  ranged from -0.62‰ at forested Pond Branch to 3.25‰ at degraded-urban Dead Run. Mean  $\delta^{13}\text{C}$  of sediment ranged from -28.22‰ at forested Pond Branch to -26.34‰ at degraded-urban Dead Run and mean  $\delta^{15}\text{N}$  ranged from 0.40‰ at forested Pond Branch to 8.29‰ at restored Minebank Run. Isotope biplots showed that at forested Pond Branch and Baisman Run, the POM and sediment were closest to the  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values of the leaf litter, suggesting that decayed leaves were an important source for POM and sediment among all site types but especially at the forested sites (Fig. 6). At restored Minebank Run, the isotopic signature for POM was also close to the leaf source. Isotopic signatures at restored Spring Branch and degraded-urban Dead Run also suggested that POM appeared to be a mixture of grass,

periphyton, and decayed leaf isotope signatures. At most sites, the POM signature was similar to the sediment signature except at Minebank Run.

Lipid biomarker results showed that the source and quality of organic matter varied across sites (Table 3). Long-chain alcohols and plant sterols serve as proxies for vascular plant (terrestrial) sources (Canuel and Martens 1993, Waterson and Canuel 2008). Percent long-chain alcohols were higher at forested pond branch than at restored Minebank Run ( $t = 2.23$ ,  $P = 0.028$ ) while % plant sterols was higher at restored Spring Branch than at forested Pond Branch ( $t = 2.68$ ,  $P = 0.0089$ ) and restored Minebank Run ( $t = 3.89$ ,  $P = 0.0002$ ). Percent diatom sterols were lower at forested Pond Branch than at restored Minebank Run ( $t = 2.09$ ,  $P = 0.0392$ ).

#### Denitrification potential rates

Denitrification potential was significantly higher when sediments were amended with glucose ( $35.1 \pm 9.4$  ng N·g dry sediment<sup>-1</sup>·hour<sup>-1</sup>) than when amended with nitrate ( $10.4 \pm 4.0$  ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>;  $F = 94.33$ ,  $N = 48$ ,  $P = 0.0194$ ; Fig. 7bc). Denitrification potential was too low to detect in the nitrate amendment experiment at the forested site.

Denitrification potential rates at forested streams ( $2.2 \pm 1.0$  ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>) were significantly lower than at restored streams ( $36.0 \pm 12.3$  ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>) and urban streams ( $30.1 \pm 8.8$  ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>) but the rates measured at the restored and the degraded-urban sites were not significantly different ( $F = 4.29$ ,  $N = 48$ ,  $P = 0.0198$ ; Fig. 7bc).

Denitrification potential rates associated with incubating sediments with stormflow water ( $29.6 \pm$

9.4 ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>) were consistently higher than with baseflow water (15.9 ± 5.1 ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>) but the difference was not statistically significant (F = 1.67, N = 48, P = 0.2030; Fig. 7bc).

Denitrification potential rates from the experiment comparing the effects of naturally occurring organic carbon sources (control, periphyton, leaves, and grass), differed across site type (F = 3.79, N = 86, P = 0.014, Fig. 8b) and organic carbon source (F = 8.78, N = 86, P < 0.001, Fig. 9a). There was also a significant interaction between site type and organic carbon source (F = 2.33, N = 86, P = 0.0232, Fig. 8).

Denitrification potential rates (ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>) were greatest when grass clippings were added as the naturally occurring organic carbon source (1 200 ± 300) compared to periphyton (410 ± 110; t = 2.9, P = 0.0049), leaves (170 ± 30; t = 4.21, P = <0.0001), and control treatments (3.1 ± 1.7; t = 4.63, P = <0.0001; Fig. 8a). The highest denitrification potential rates were observed when sediments from degraded-urban Scotts Level Branch were incubated with the grass extract (7,200 ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>). In addition, mean denitrification potential rates at the urban sites (1 000 ± 470 ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>) were significantly higher than denitrification potential rates from the forested sites (92 ± 36 ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>; t = 3.20, P = 0.002) and the restored sites (290 ± 90 ng N·g dry sediment<sup>-1</sup>·hr<sup>-1</sup>; t = 2.51, P = 0.0145; Fig. 8b). Mean denitrification potential rates across naturally occurring organic carbon sources, were not significantly different between the forested and restored sites.

## Discussion

### Variations in organic carbon amounts and sources across land use

My results suggest that urbanization may cause shifts in organic carbon quantity, sources, and quality. I observed higher organic carbon concentrations and daily fluxes in urbanized streams than in forest streams. Urban streams can receive inputs from natural and/or anthropogenically enhanced organic carbon sources including leaf litter, autochthonous production, materials deposited on impervious surfaces, human and animal waste, and grass clippings from home lawns (Kaushal et al. Submitted, (Lofton et al. 2007, Sickman et al. 2007). Furthermore, urbanization can decrease canopy cover (Paul and Meyer 2001), and canopy coverage of riparian flow paths can then influence the quantity and character of DOC delivered to streams and alter DOC bioavailability in some cases (Findlay et al. 2001, Pernet-Coudrier et al. 2010).

Molar C:N ratios served as a second organic carbon source tracking method; higher values indicate potential terrestrial sources (Kaushal and Binford 1999). Stable isotope signatures and C:N ratios suggested that particulate organic carbon sources and quality varied with watershed land use. Mean C:N ratios of organic carbon samples at the forested site were found to be significantly higher than at the restored and the degraded-urban sites indicating that organic matter at the forested sites may be lower in quality and more recalcitrant. A shift in C:N ratios suggests that the forested site receives terrestrial organic matter like leaves while the

restored and the degraded-urban sites receive a mixture of higher quality organic matter sources like grass clippings, periphyton, and wastewater. Ratios of C:N in streams may influence ecosystem functions like N cycling (Dodds et al. 2004) and increasing the quantity of available DOC can enhance whole-stream N uptake (Johnson et al. 2009). Furthermore, these differential C:N ratios may affect denitrification and respiration rates in streams. Isotopic signatures suggested that terrestrial leaf sources provided significant contributions to POM in forested streams. In contrast, the POM in restored and degraded-urban streams was a mixture of periphyton, leaves, and grass. The  $\delta^{15}\text{N}$  of the sediment in Minebank Run was considerably higher than other sites – these high values may indicate denitrification or contamination from previous  $\delta^{15}\text{N}$  tracer studies (Kaushal et al. 2008b). Theoretically, the stable isotope signatures of sources can be used to indicate organic matter sources but additional tracers like lipid biomarkers can provide more quantitative evidence.

Lipid biomarker data provided another line of evidence that the source and amount of organic matter varied across land use and restoration status. Forested Pond Branch and Spring Branch (the older restoration) showed higher contributions from terrestrial sources than Minebank Run (the newer restoration). I speculate that Minebank showed lower contributions from terrestrial sources because trees planted in the restored the riparian zone have not yet matured to full canopy coverage. This reach of Minebank Run, which, was restored in 2004 to 2005, had a significantly higher relative abundance of diatom carbon. Higher concentrations of diatom biomarkers suggest that streamwaters may receive more sunlight due to the open canopy. Though lipid biomarker data were only available for a limited number of sites, these data provide

further evidence that urbanization may influence the source and quality of organic carbon in streams and the proportion of terrestrial vs. aquatic contributions.

Residential landscaping decisions like replacing forested areas with mowed lawns can also lead to considerable variability in riparian vegetation (Larson et al. 2009). For example, some riparian zones at my study sites consisted of managed lawns near streams with little or no tree canopy. Previous work analyzing stable isotopes from streams draining nonforested sites at the BES LTER site suggested a potential contribution of organic carbon from home lawns (Kaushal et al. 2011). There may be shift from organic carbon inputs to streams from C3 plants (trees) to C4 plants (grasses) and/or changes in carbon quality with increasing urbanization (Kaushal et al. 2011). My results from stable isotopes and C:N ratios suggested that grass clippings may play some role as a carbon source in urban streams. The total estimated area of urban lawns for the contiguous US is  $163,800 \pm 35,850 \text{ km}^2$ , 3x greater than the area covered by irrigated corn (Milesi et al. 2005), making lawns the single largest agricultural land use in the US. Natural grasses have been shown to be an important allochthonous resource in open-canopy agricultural headwater streams (Menninger and Palmer 2007). Home lawns may have altered organic carbon dynamics when compared to native ecosystems (Kaye et al. 2005, Golubiewski 2006, Yesilonis et al. 2008, Groffman and Pouyat 2009). Relatively little is known regarding how increasing suburbanization and conversion of landscapes to home lawns potentially influences stream ecosystem functions.

## Relative importance of organic carbon sources to denitrification in urban streams

Urbanized streams are more likely to have flashy hydrology (Striz and Mayer 2008) and storm events that carry nutrient and DOC rich water to the stream (Paul and Meyer 2001, Allan 2004). Surprisingly, I did not observe a significant difference in denitrification rates between stormflow vs. baseflow. My laboratory experiments suggested that labile organic carbon availability was relatively more important in limiting denitrification than nitrate availability during baseflow and stormflow conditions.

My results also suggest that shifts in natural organic matter may influence denitrification in urbanized and restored streams (Mayer et al. 2010, Dosskey et al. 2010). I found that the organic carbon sources that stimulated the highest denitrification rates were grass clippings from urban areas. Periphyton produced intermediate rates across sites. Higher denitrification rates occurred in the urban sites, intermediate denitrification in the restored sites, and relatively lower denitrification in the forested sites. Possible reasons for higher denitrification potential rates in urban areas are elevated nitrate concentrations and organic carbon quality (Groffman et al. 2005).

In order to understand how changes in organic carbon sources might influence the mass balance of a stream, I multiplied measured DOC loads by published bioavailability values to estimate the amount of denitrification that could be potentially supported at each site.

Reported ranges for DOC bioavailability in forested streams included 0-40% in the Rocky Mountains of Colorado (Kaushal and Lewis, Jr. 2005) and  $21 \pm 7\%$  in New Jersey

(Wiegner and Seitzinger 2001). Based on these studies I used a midrange value of 21% as an assumption. In urban streams, DOC bioavailability ranged from 16-17% with a mode of 16% (Petroni et al. 2009). I used a value of 16% DOC bioavailability for the urban streams as well as for the restored streams since I could not find any literature values of DOC bioavailability in restored streams. I estimated the percent daily nitrate load reduction ( $\text{kg}\cdot\text{day}^{-1}$ ) that may be possible with bioavailable DOC from each stream using the following formula:

$$\%NO_3^- \text{ load reduction} = 100 * \frac{\% \text{bioavailability} * \text{DOC load}}{NO_3^- \text{ load} * 4}$$

Where % bioavailability is the percent of DOC that is assumed to be bioavailable, DOC load is the mean daily DOC load ( $\text{kg}\cdot\text{day}^{-1}$ ), and  $NO_3^-$  load is the mean daily nitrate load ( $\text{kg}\cdot\text{day}^{-1}$ ). The equation is divided by 4 because 4 mg of CBOD are needed for each mg of nitrate removed (EPA 1993). Results show that forested Pond Branch has ample carbon for complete removal of nitrate by denitrification while bioavailable DOC loads at the other sites can limit denitrification (Table 4). It is important to note that I typically see very low concentrations of nitrate in forested Pond Branch (average concentration is  $0.045 \text{ mg}\cdot\text{L}^{-1}$ ), so other factors must also influence N removal in addition to carbon availability.

#### Implications for riparian management and restoration

Studies of stream restoration effects on ecosystem functions like N cycling are limited but growing (Roberts et al. 2007, Bukaveckas 2007, Kaushal et al. 2008a, Klockner et al. 2009, Svirichi et al. 2011). Previous work has shown linkages between DOC and nitrate (Mayer et al.

2010, Svirichchi et al. 2011) and results suggested that management efforts to increase groundwater residence time and increase DOC availability may improve N removal capacity (Striz and Mayer 2008, Mayer et al. 2010). Integrated stormwater management and stream restoration may be a means to improve N removal capacity by enhancing denitrification in some cases (Kaushal et al. 2008a, Mayer et al. 2010, Collins et al. 2010). Denitrification rate potentials in restored streams have been shown to increase with increasing amounts of organic carbon in riparian zone sediments (Gift et al. 2010) and debris dams (Groffman et al. 2005). Surprisingly, organic carbon from residential lawns was shown to impact the N cycle of streams in unanticipated ways. Given that C:N stoichiometry can be important in fostering denitrification, management strategies that increase organic carbon relative to N may increase denitrification (Park et al. 2008, Taylor and Townsend 2010). Therefore, an improved understanding of coupled carbon and nitrogen biogeochemical cycles in urban watersheds may be critical to enhancing denitrification and N removal along stream networks (Svirichchi et al. 2011).

### Conclusions

I found that concentrations and loads of nitrate and DOC varied with runoff and there was flashy delivery at urban sites. Stable isotope and lipid biomarker data suggest that urbanization alters the amount and source of organic carbon delivered to streams. Management of riparian vegetation may influence denitrification rates at the riparian-stream interface.

Managing amounts, sources, and quality of organic carbon may be critical for managing nitrogen flux in stormwater management systems and urban restoration stream projects. Since DOC, nitrate, and other biogeochemicals can be delivered in pulses, future work should investigate how specific restoration and stormwater management features like connected pond and wetland systems may affect organic carbon sources and hydrologic residence times, which are both important to denitrification.

### *Acknowledgements*

This research was supported by Maryland Sea Grant Award SA7528085-U, Maryland Sea Grant Award NA05OAR4171042, NSF Award DBI 0640300, NSF Award CBET 1058502, EPA NNEMS Award 2010-308, the U.S. EPA Office of Research and Development, and Baltimore Ecosystem Study LTER project (NSF DEB-0423476). E. Canuel was supported by NSF Award OCE 0962277. I thank Melissa Grese, Katie Delaney-Newcomb, Gwen Sivirichi, and Ashley Sides for assisting with DOC and nitrate data collection and Elizabeth Lerberg for assistance with lipid biomarker analyses. I also thank Michael Pennino and Frank Siewerdt for their help in choice of statistical analysis. And, I thank Michael Johnson, Carolyn Klocker, Pete Bogush, Joseph Newcomer, and Dan Dillon for their help with fieldwork and Stewart Findlay, Kristine Hopfensperger, Dave Lewis, and Casey Sperling for their help with lab work. I thank Victor Kennedy for help with editing. The research has not been subjected to U.S. Environmental Protection Agency review and therefore does not necessarily reflect the views of

any of the funding agencies, and no official endorsement should be inferred. This paper is  
Contribution 3236 of the Virginia Institute of Marine Science, The College of William and Mary.

Table 2.1. Dissolved organic carbon (DOC) and nitrate concentration (mg/L) in forested, restored, and degraded-urban Baltimore streams from April 2008 – April 2010.

| Restoration status and stream | Analysis                     | Tukey comparison | Mean $\pm$ SE     | Range       | Sample size ( <i>N</i> ) |
|-------------------------------|------------------------------|------------------|-------------------|-------------|--------------------------|
| <b>Forested</b>               |                              |                  |                   |             |                          |
| Pond Branch                   | DOC                          | a                | 2.13 $\pm$ 0.14   | 0.62–5.07   | 47                       |
|                               | NO <sub>3</sub> <sup>-</sup> | A                | 0.045 $\pm$ 0.010 | 0.001–0.188 | 31                       |
| Baisman Run                   | DOC                          | b                | 1.23 $\pm$ 0.13   | 0.20–2.87   | 28                       |
|                               | NO <sub>3</sub> <sup>-</sup> | B                | 1.374 $\pm$ 0.089 | 0.323–2.215 | 28                       |
| <b>Restored</b>               |                              |                  |                   |             |                          |
| Spring Branch                 | DOC                          | a, b, c          | 1.50 $\pm$ 0.16   | 0.71–3.74   | 25                       |
|                               | NO <sub>3</sub> <sup>-</sup> | C                | 2.898 $\pm$ 0.222 | 0.704–4.218 | 22                       |
| Minebank Run                  | DOC                          | b, c             | 1.38 $\pm$ 0.12   | 0.40–5.72   | 48                       |
|                               | NO <sub>3</sub> <sup>-</sup> | B, D             | 1.083 $\pm$ 0.060 | 0.470–1.532 | 22                       |
| <b>Unrestored urban</b>       |                              |                  |                   |             |                          |
| Dead Run                      | DOC                          | d                | 3.42 $\pm$ 0.43   | 1.33–12.42  | 27                       |
|                               | NO <sub>3</sub> <sup>-</sup> | E                | 0.568 $\pm$ 0.076 | 0.007–1.469 | 27                       |
| Scotts Level Branch           | DOC                          | a, c             | 2.14 $\pm$ 0.20   | 0.80–5.50   | 29                       |
|                               | NO <sub>3</sub> <sup>-</sup> | D                | 0.982 $\pm$ 0.062 | 0.316–1.717 | 29                       |

*Notes:* Values are means  $\pm$  SE. Letters represent comparisons that are significant ( $\alpha = 0.05$ ) according to Tukey's studentized range (HSD) test; lowercase letters correspond to DOC concentration, and uppercase letters correspond to nitrate concentration.

Table 2.2. Lipid biomarker data from two locations at forested Pond Branch, two locations at restored Spring Branch, and three locations at restored Minebank Run streams (Canuel and Martens 1993, Canuel et al. 1995).

| Site                      | Lipid biomarkers                          |                               |                               |                     |               |                     |
|---------------------------|---|-------------------------------|-------------------------------|---------------------|---------------|---------------------|
|                           | Terrestrial : aquatic<br>fatty acid ratio | Long-chain<br>fatty acids (%) | Terrestrial-source indicators |                     |               |                     |
|                           |   |                               | Long-chain alcohols           |                     | Plant sterols |                     |
|                           |   |                               | Percentage                    | Tukey<br>comparison | Percentage    | Tukey<br>comparison |
| <b>Pond Branch</b>        |   |                               |                               |                     |               |                     |
| Forested site 1           | 0.17 ± 0.11                               | 3.99 ± 2.34                   | 29.40 ± 11.88                 | A                   | 47.68 ± 11.29 | A                   |
| Forested site 2           | 0.36 ± 0.07                               | 7.10 ± 0.29                   | 37.56 ± 8.45                  |                     | 56.44 ± 16.23 |                     |
| <b>Spring Branch</b>      |   |                               |                               |                     |               |                     |
| Restored 1994–1997 site 1 | 0.56 ± 0.27                               | 11.67 ± 3.90                  | 45.68 ± 2.62                  | AB                  | 76.49 ± 0.85  | B                   |
| Restored 1994–1997 site 2 | 0.05 ± 0.01                               | 1.36 ± 0.37                   | 16.06 ± 2.24                  |                     | 68.36 ± 1.63  |                     |
| <b>Minebank Run</b>       |   |                               |                               |                     |               |                     |
| Restored 1998–1999 site 1 | 0.04 ± 0.02                               | 0.83 ± 0.46                   | 28.98 ± 4.31                  | B                   | 38.93 ± 8.22  | A                   |
| Restored 1998–1999 site 2 | 0.05 ± 0.05                               | 1.16 ± 1.16                   | 19.00 ± 3.23                  |                     | 66.02 ± 3.07  |                     |
| Restored 2004–2005 site 3 | 0.01 ± 0.01                               | 0.29 ± 0.29                   | 5.978 ± 0.54                  |                     | 31.27 ± 0.16  |                     |

*Notes:* Values are means ± SE. Letters represent comparisons between the three streams that are significant ( $\alpha=0.05$ ) according to Tukey's studentized range (HSD) test.

Table 2.2. Extended.

| Lipid biomarkers          |                |                  |
|---------------------------|----------------|------------------|
| Aquatic-source indicators |                |                  |
| Short-chain alcohols (%)  | Diatom sterols |                  |
|                           | Percentage     | Tukey comparison |
|                           |                | <b>A</b>         |
| 32.62 ± 13.27             | 0.89 ± 0.89    |                  |
| 17.59 ± 8.48              | 6.30 ± 1.76    |                  |
|                           |                | <b>AB</b>        |
| 11.92 ± 1.24              | 1.92 ± 0.18    |                  |
| 9.84 ± 0.97               | 9.69 ± 0.35    |                  |
|                           |                | <b>B</b>         |
| 17.31 ± 3.60              | 6.68 ± 0.52    |                  |
| 25.34 ± 6.05              | 7.30 ± 0.25    |                  |
| 9.51 ± 0.59               | 40.41 ± 3.36   |                  |

Table 2.3. Estimation of potential nitrate load reduction through denitrification based upon available DOC and literature ranges for DOC bioavailability (from Petrone et al. 2009).

| Stream                                 | Discharge<br>(L/d) | Mean<br>DOC<br>(kg/d) | Estimated<br>bioavailability<br>(%) | Bioavailable<br>DOC (kg/d) | Bioavailable<br>DOC<br>(kg/d) ÷ 4 | Mean<br>nitrate<br>(kg/d) | Potential<br>nitrate load<br>removal (%) |
|--|--------------------|-----------------------|-------------------------------------|----------------------------|-----------------------------------|---------------------------|--|
| Pond Branch (forested)                 | 345 279            | 108                   | 2                                   | 2.16                       | 0.54                              | 1                         | 54                                       |
| Baisman Run (forested)                 | 4 653 736          | 874                   | 2                                   | 17.48                      | 4.37                              | 747                       | 1  |
| Spring Branch (restored)               | 23 608             | 5                     | 16                                  | 0.80                       | 0.22                              | 9                         | 2  |
| Minebank Run (restored)                | 5 261 577          | 1 319                 | 16                                  | 211.04                     | 52.76                             | 859                       | 6  |
| Dead Run (unrestored urban)            | 18 192 911         | 7 430                 | 16                                  | 1 188.80                   | 297.19                            | 2 497                     | 12                                       |
| Scotts Level Branch (unrestored urban) | 8 103 227          | 3 415                 | 16                                  | 546.40                     | 136.60                            | 1 029                     | 13                                       |

## Figure Captions

Figure 2.1. Land cover map of study sites at the Baltimore Ecosystem Study Long-Term Ecological Research Site. Coloration is from the 2001 National Land Cover Database (red indicates urban areas and green indicates forested areas).

Figure 2.2. Photographs showing (A) forested Pond Branch and Baisman Run; (B) restored Spring Branch and Minebank Run; (C) degraded-urban Dead Run and Scotts Level Branch.

Figure 2.3. Seasonal DOC and nitrate concentrations ( $\text{mg}\cdot\text{L}^{-1}$ ) from (A) forested, (B) restored, and (C) degraded-urban watersheds.

Figure 2.4. Daily loads of DOC and nitrate ( $\text{g}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$ ) versus log daily runoff ( $\text{mm}\cdot\text{day}^{-1}$ ) from (A) forested, (B) restored, and (C) degraded-urban watersheds. Daily loads of DOC and nitrate increased with log daily runoff according to a power function.

Figure 2.5. Comparison of C:N molar ratios for leaves, periphyton, grass, sediment, and POM across forested (N=20), restored (N=14), and degraded-urban sites (N=13). Values are means  $\pm$  1 SE. Letters represent comparisons (lowercase is inter-site type and uppercase is intra-site type) that are significant at an alpha of 0.05 according to Tukey's Studentized Range (HSD) Test.

Figure 2.6. Comparison of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotopic ratios in periphyton, leaves, grass, and water from (A) forested (N=20), (B) restored (N=14), and (C) degraded-urban sites (N=13). Values are means  $\pm$  1 SE.

Figure 2.7. Relative importance of nitrate versus glucose on denitrification potential rate across sites. (A) Hydrograph of mean daily runoff of the storm that was sampled as part of the denitrification experiments ( $\text{L}\cdot\text{sec}^{-1}\cdot\text{km}^{-2}$ ). Comparison of denitrification potential rates associated with the glucose amendment (B) and nitrate amendment (C) produced from 2 forested, 2 restored, and 2 degraded-urban streams using baseflow and stormflow water. Values are means  $\pm$  1 SE. Letters represent comparisons between site types that are significant at an alpha of 0.05 according to Tukey's Studentized Range (HSD) Test.

Figure 2.8. Comparison of denitrification potential rates associated with different naturally occurring organic carbon sources at 2 forested (Pond Branch and Baisman Run), 2 restored (Spring Branch and Minebank) and 2 degraded-urban streams (Dead Run and Scotts Level Branch). Values are means  $\pm$  1 SE. Letters represent comparisons (lowercase is carbon source and uppercase is site type) that are significant at an alpha of 0.05 according to Tukey's Studentized Range (HSD) Test. (A) Results from all 6 sites are averaged and divided into categories of organic carbon sources, and (B) data is divided by site type and organic carbon source.

Fig. 2.1

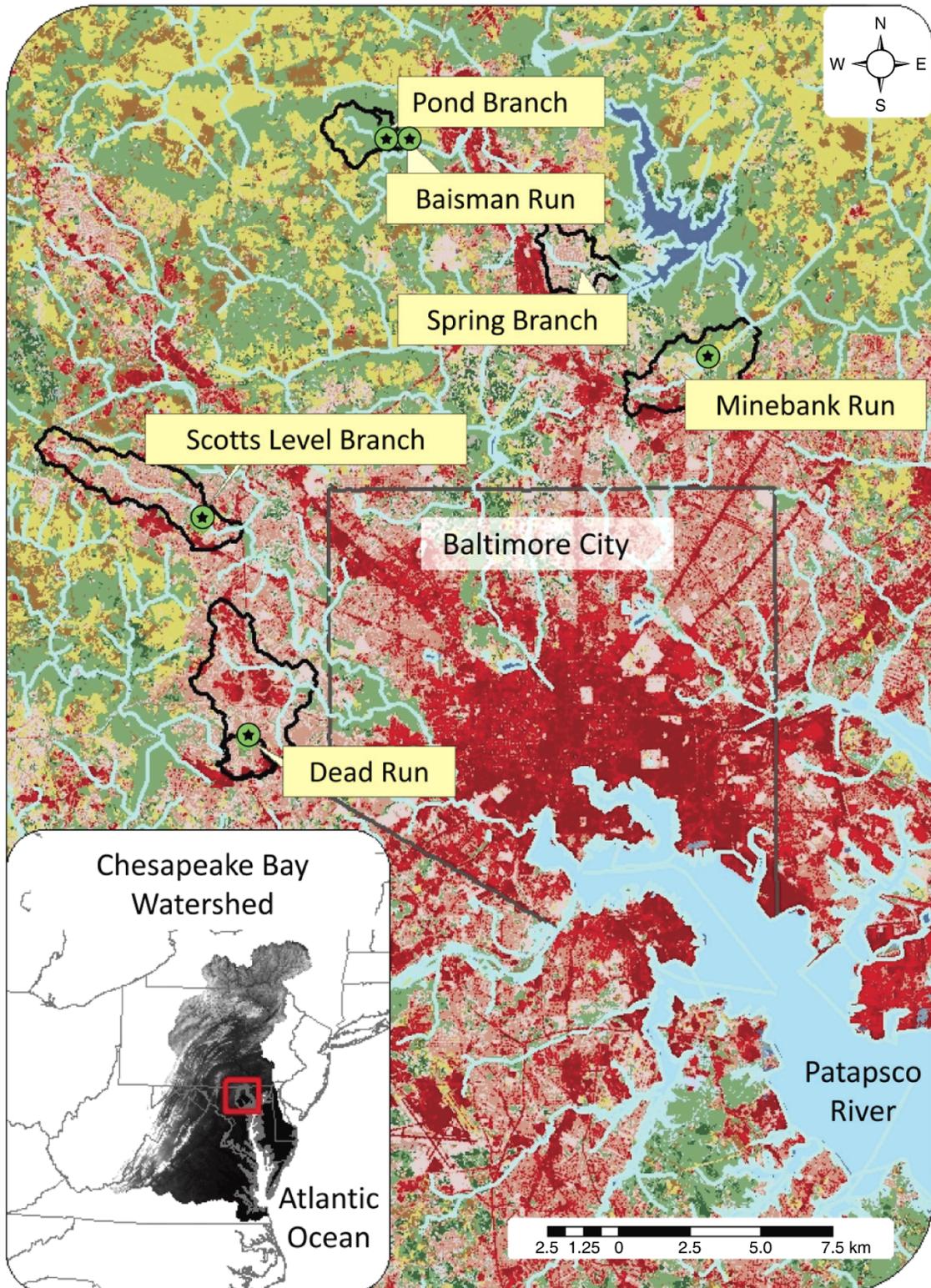


Fig. 2.2

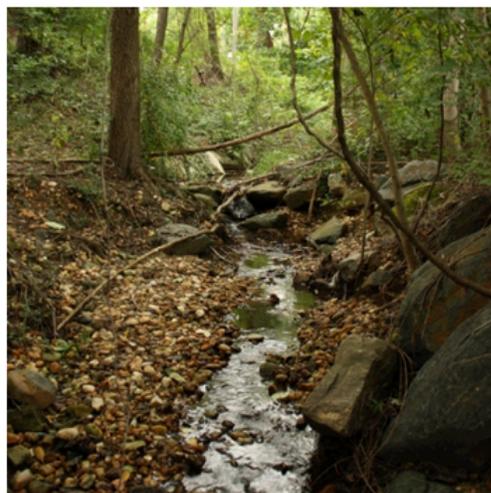
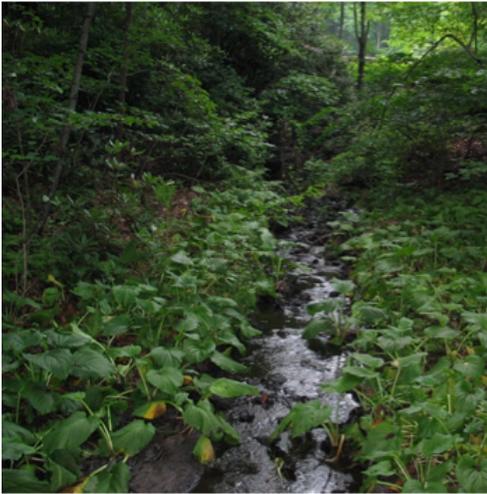


Fig. 2.3

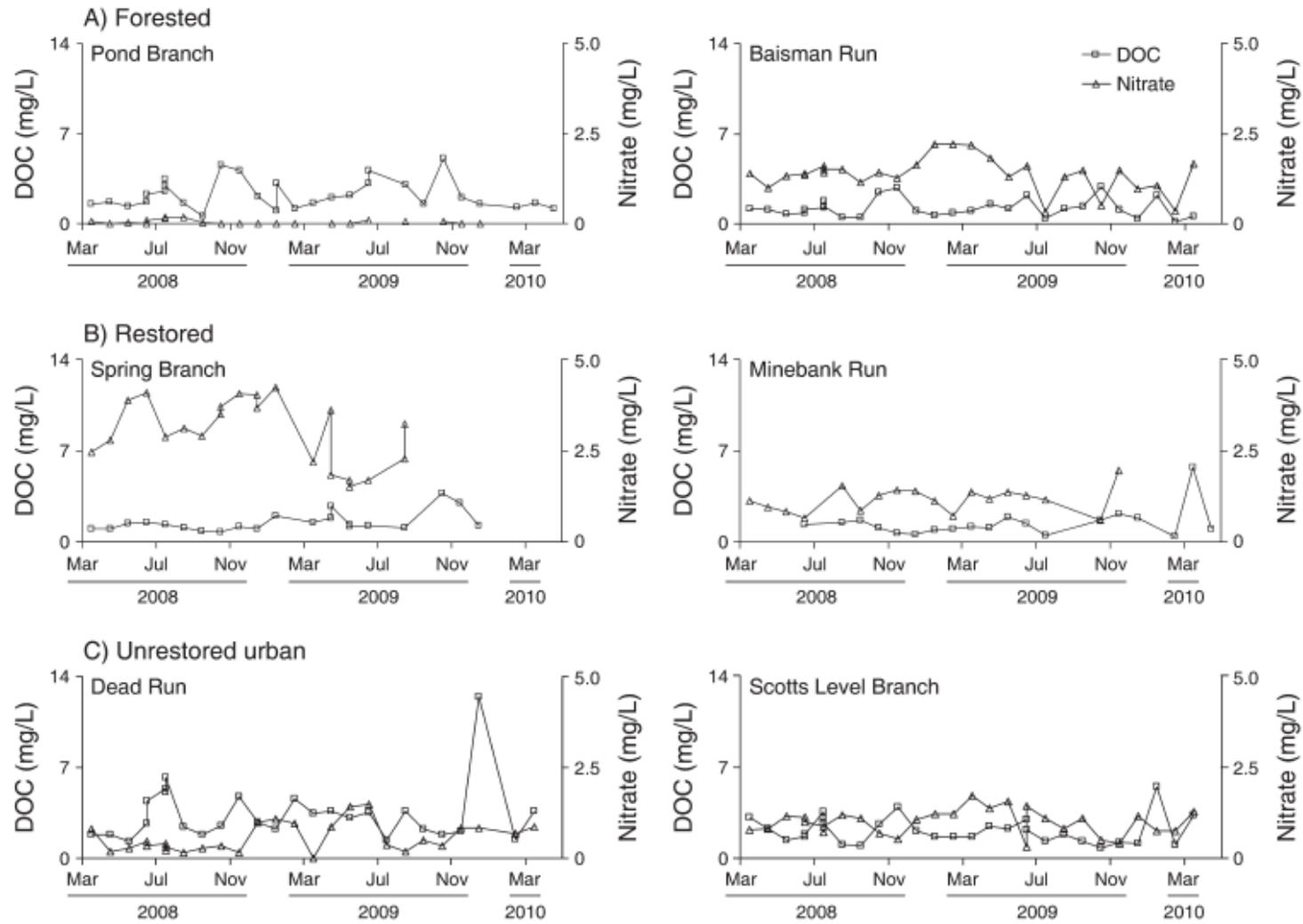


Fig. 2.4

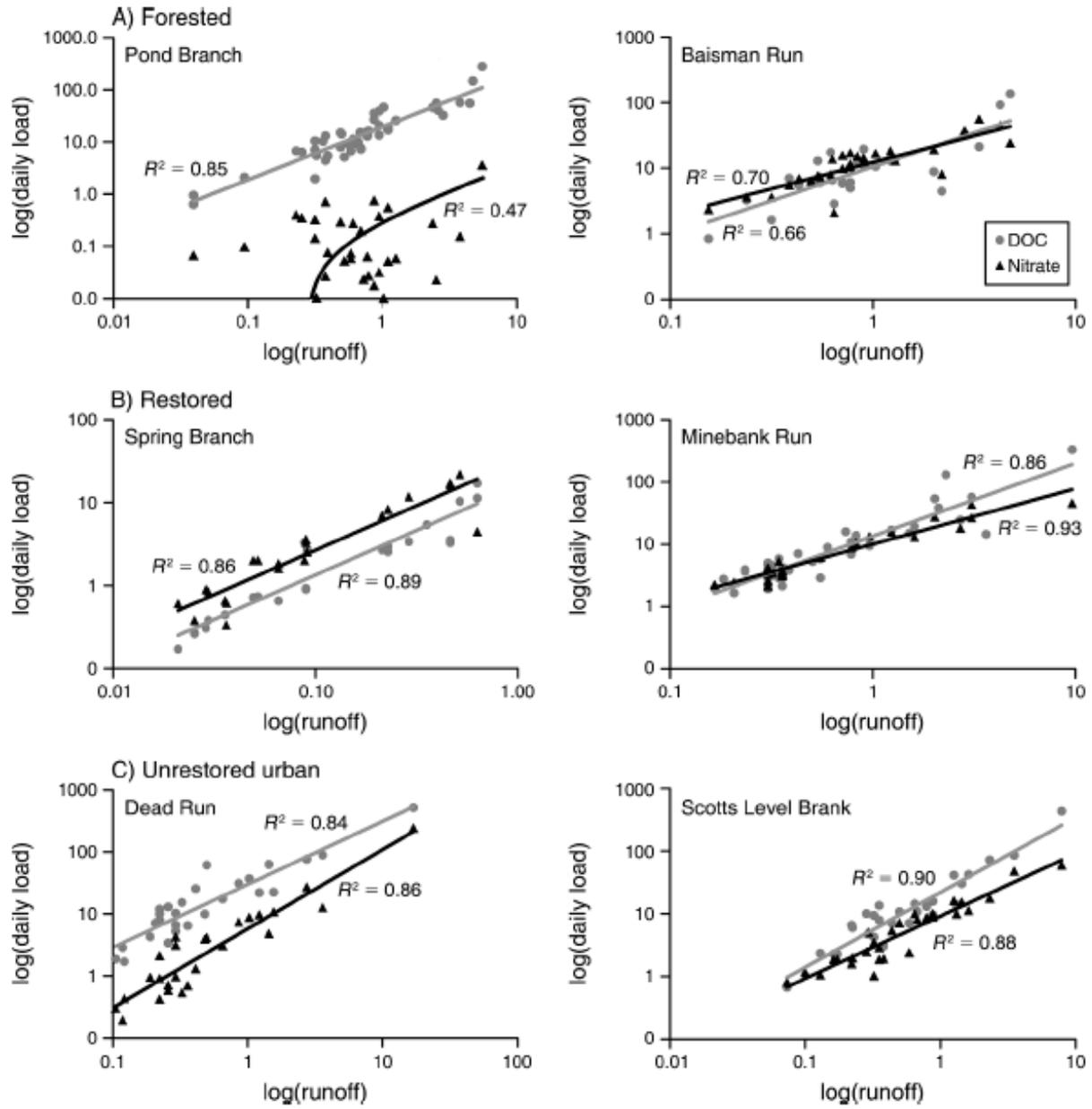


Fig. 2.5

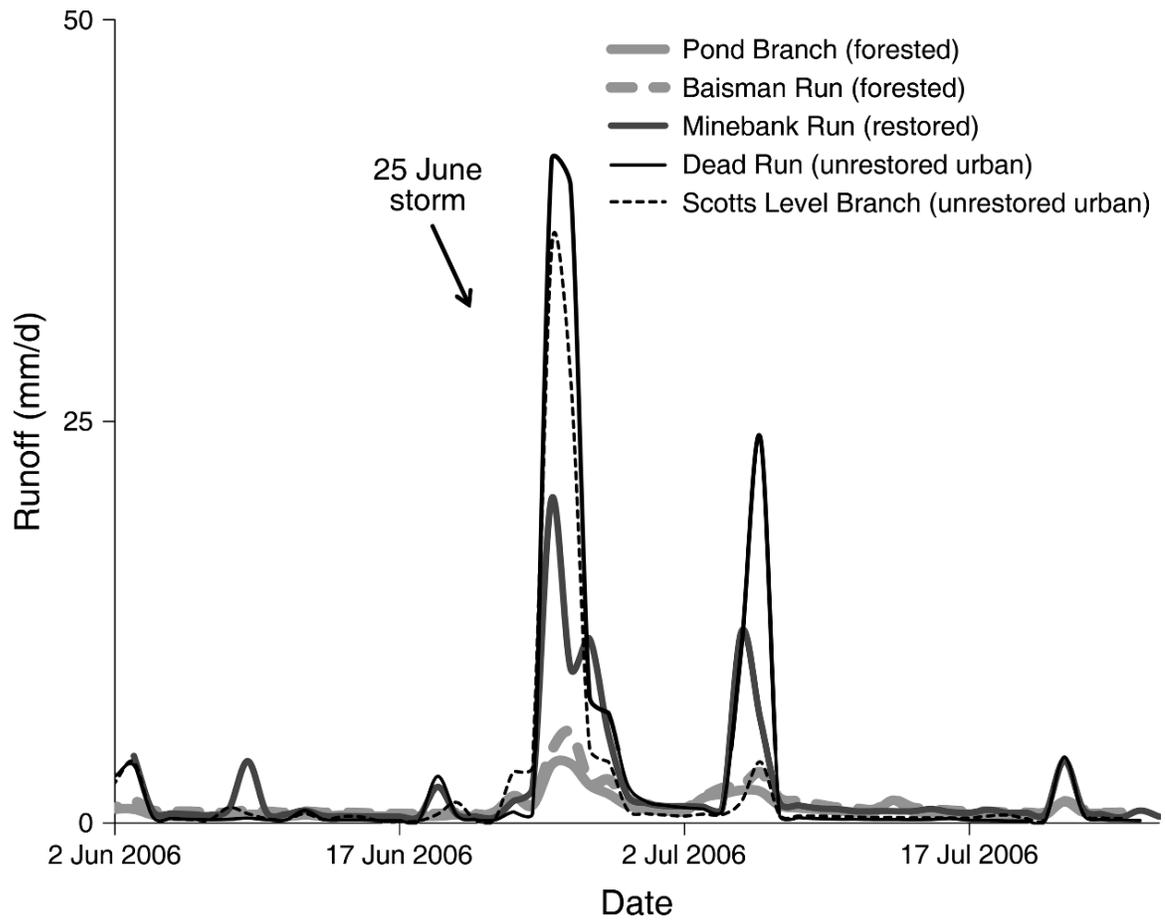


Fig. 2.6

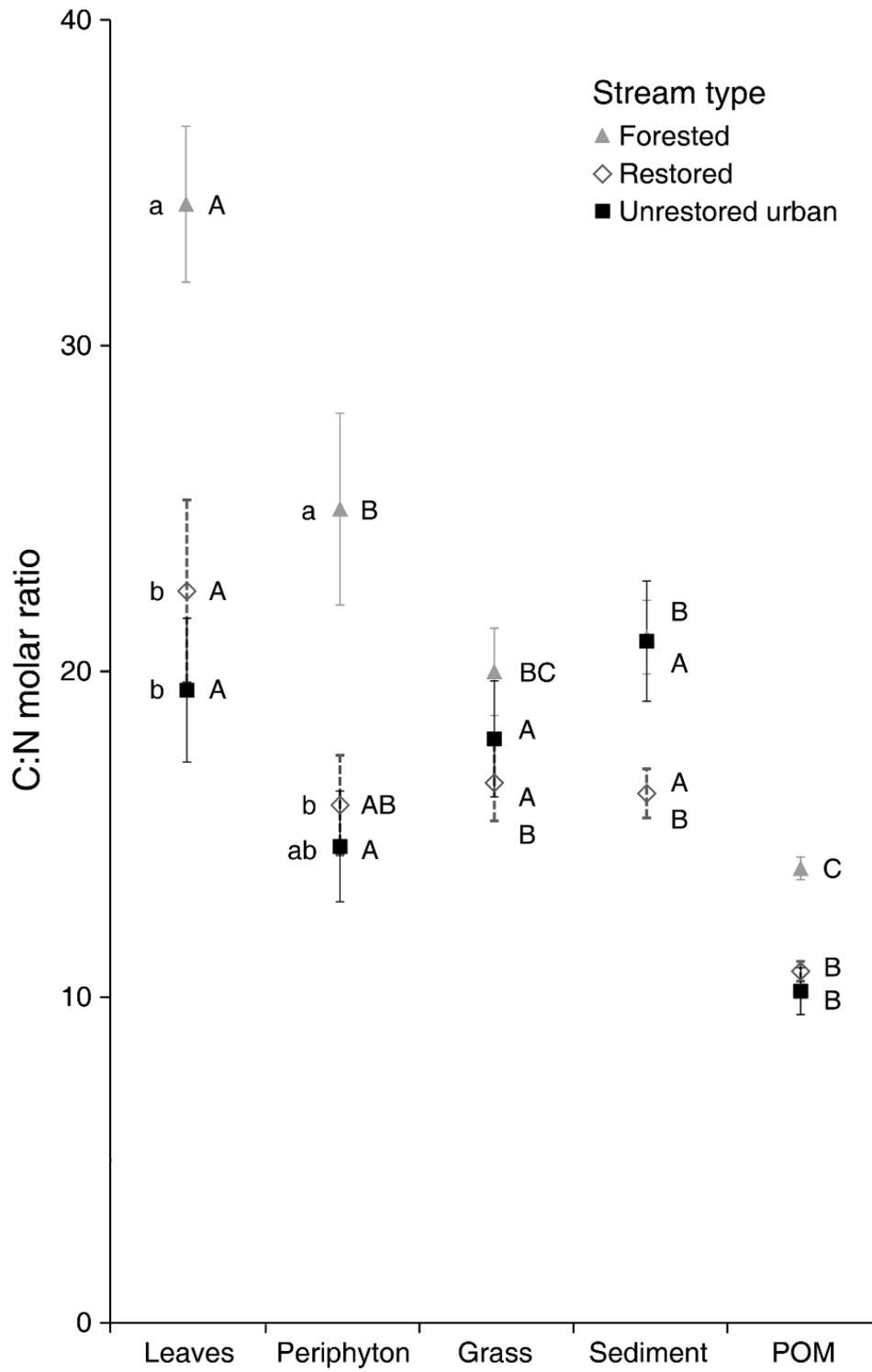


Fig. 2.7

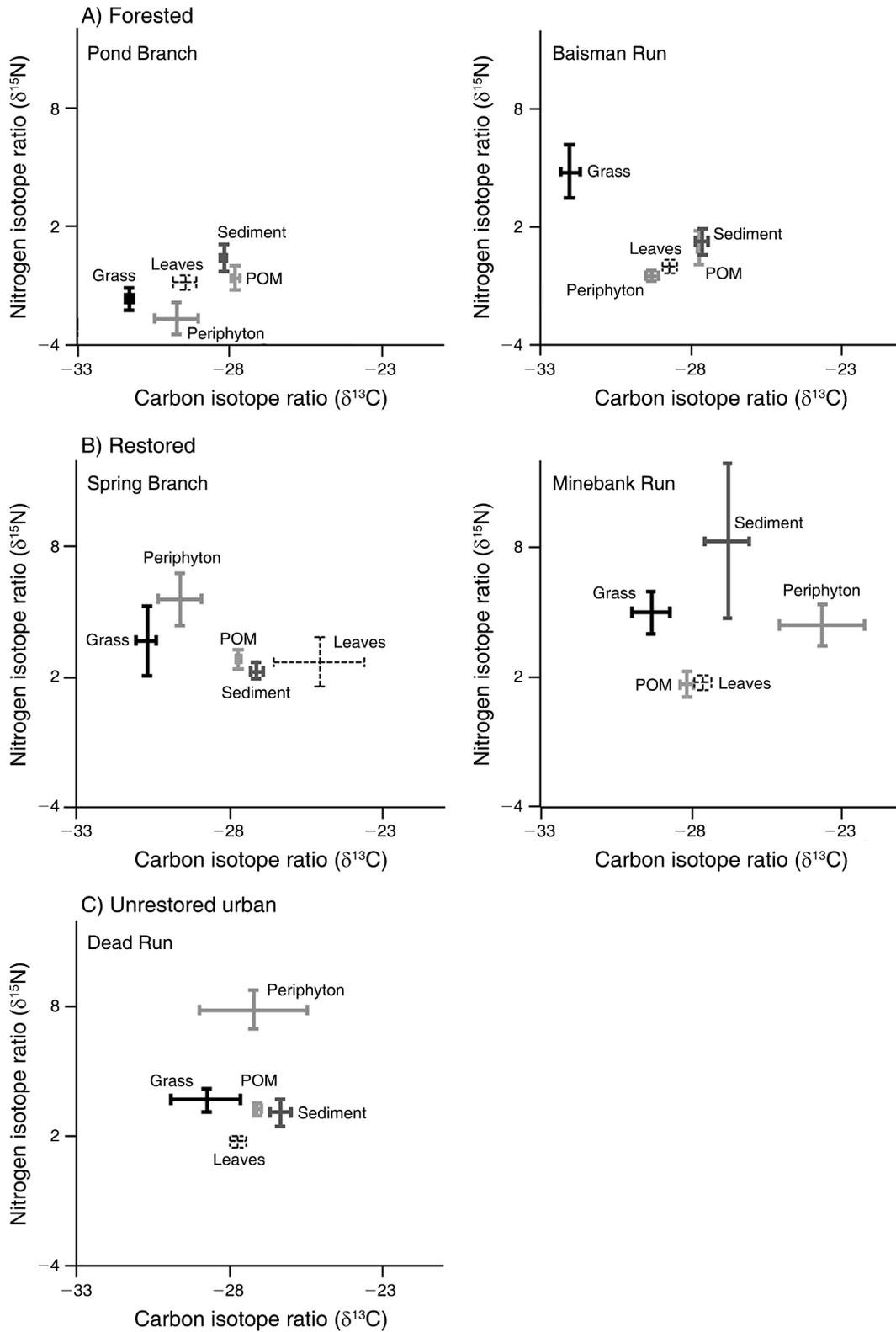


Fig. 2.8

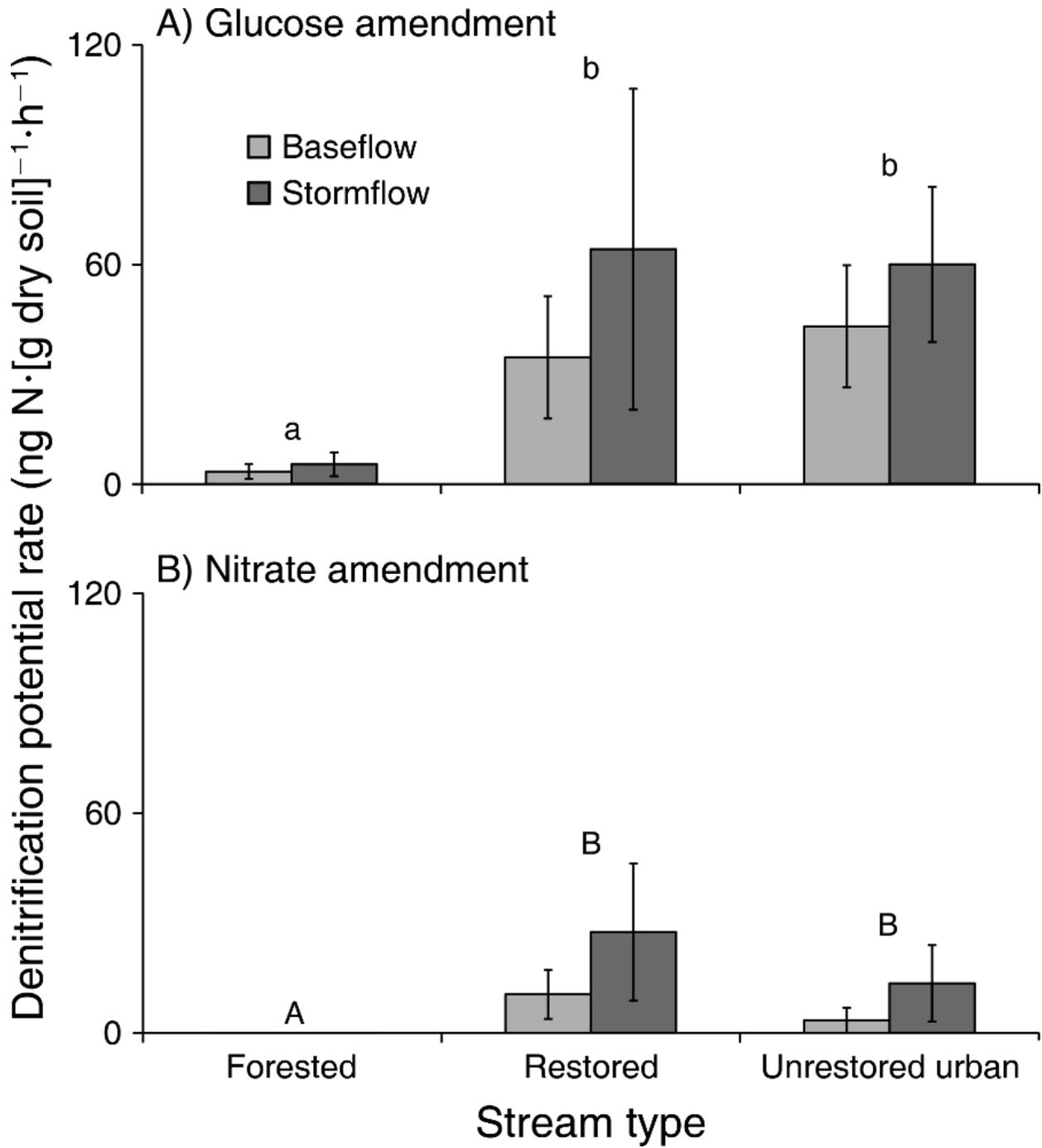
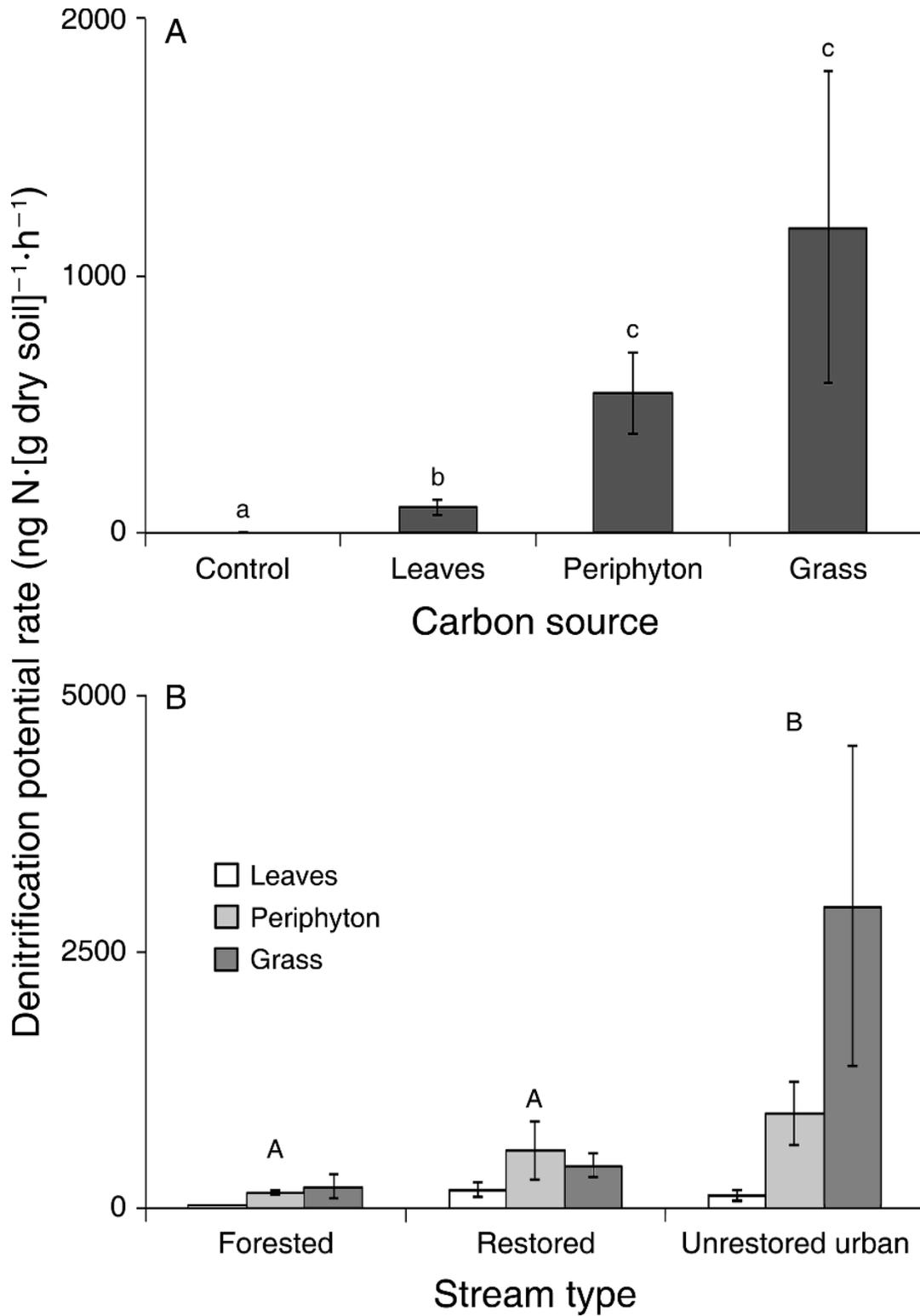


Fig. 2.8



Appendix A. Different organic C sources affect denitrification rates.

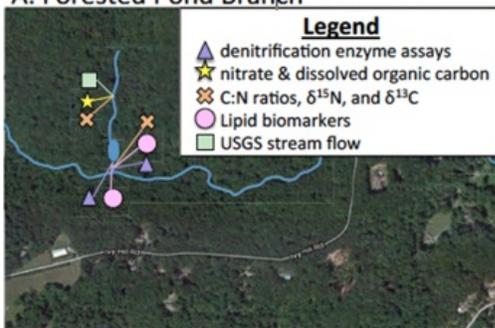
| Study  | Land use/context                      | Organic carbon source(s) examined  |
|--|---------------------------------------|--|
| Harrison et al. 2012<br>& Groffman et al. 2005 | Baltimore LTER                        | organic debris dams<br>pools<br>riffles<br>gravel bar sloughs  |
| This Study                                     | Baltimore LTER                        | grass clippings<br>decomposed leaves<br>periphyton<br>stormflow water<br>baseflow water  |
| Arango et al. 2007                             | agricultural streams<br>in midwest US | sand<br>fine benthic organic matter (FBOM)<br>coarse benthic organic matter (CBOM)<br>biofilm  |
| Chao and Young 1995                            | agricultural soils                    | 34 materials:<br>- 27 chemical compounds<br>- 4 crop residues<br>- 3 composted animal manures  |
| Kemp and Dodds 2002                            | prairie streams                       | fine benthic organic matter (FBOM)<br>coarse benthic organic matter (CBOM)<br>suspended particulate organic matter<br>filamentous green algae<br>bryophytes<br>epilithic diatoms |
| Park et al. 2008                               | hydroponic<br>wastewater              | 5 waste plant material liquors<br>methanol (control)   |
| Li et al. 2008                                 | wastewater<br>treatment               | glucose<br>sucrose<br>sodium acetate   |
| Shivran et al. 2005                            | wastewater<br>treatment               | glucose<br>sodium acetate  |
| Ilies and Mavinic 2001                         | wastewater<br>treatment               | methanol   |
| Kulikowska and Dudek<br>2010                   | wastewater<br>treatment               | untreated molasses<br>molasses after pretreatment<br>(hydrolyzed molasses)   |
| Fernandez-Nava et al.<br>2010                  | wastewater<br>treatment               | wastewater from a sweet factory<br>residue from a soft drinks factory<br>residue from a dairy plant  |
| Liu et al. 2011                                | wastewater<br>treatment               | agriculture wastes:<br>- corncob<br>- rice hull<br>- rice straw<br>- sawdust   |

## Literature Cited

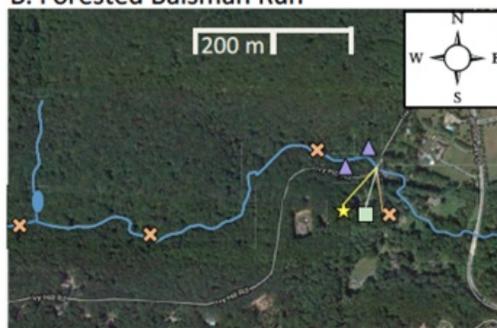
- Arango, C. P., J. L. Tank, J. L. Schaller, T. V. Royer, M. J. Bernot, and M. B. David. 2007. Benthic organic carbon influences denitrification in streams with high nitrate concentration. *Freshwater Biology* 52:1210–1222.
- Chao, C.-C., and C.-C. Young. 1995. The enhancement of organic carbon substrate on the denitrification of soil. *Journal of the Chinese Agricultural Chemical Society* 33:468–481.
- Fernandez-Nava, Y., E. Maranon, J. Soons, and L. Castrillon. 2010. Denitrification of high nitrate concentration wastewater using alternative carbon sources. *Journal of Hazardous Materials* 173:682–688. doi: 10.1016/j.jhazmat.2009.08.140.
- Groffman, P. M., A. M. Dorsey, and P. M. Mayer. 2005. N processing within geomorphic structures in urban streams. *Journal of the North American Benthological Society* 24:613–625.
- Harrison, M. D., P. M. Groffman, P. M. Mayer, and S. S. Kaushal. 2012. Microbial biomass and activity in geomorphic features in forested and urban restored and degraded streams. *Ecological Engineering* 38:1–10.
- Ilies, P., and D. Mavinic. 2001. Biological nitrification and denitrification of a simulated high ammonia landfill leachate using 4-stage Bardenpho systems: system startup and acclimation. *Canadian Journal of Civil Engineering* 28:85–97. doi: 10.1139/cjce-28-1-85.
- Kemp, M. J., and W. K. Dodds. 2002. The influence of ammonium, nitrate, and dissolved oxygen concentrations on uptake, nitrification, and denitrification rates associated with prairie stream substrata. *Limnology and Oceanography*:1380–1393.
- Kulikowska, D., and K. Dudek. 2010. Molasses as a carbon source for denitrification. *Archives of Environmental Protection* 36:35–45.
- Li, Q., P. Li, P. Zhu, J. Wu, and S. Liang. 2008. Effects of exogenous organic carbon substrates on nitrous oxide emissions during the denitrification process of sequence batch reactors. *Environmental Engineering Science* 25:1221–1228. doi: 10.1089/ees.2007.0172.
- Liu, W., G. Liu, and Q. Zhang. 2011. Influence of Vegetation Characteristics on Soil Denitrification in Shoreline Wetlands of the Danjiangkou Reservoir in China. *Clean-Soil Air Water* 39:109–115. doi: 10.1002/clen.200900212.
- Park, J., R. Craggs, and J. Sukias. 2008. Treatment of hydroponic wastewater by denitrification filters using plant prunings as the organic carbon source. *Bioresource Technology* 99:2711–2716. doi: 10.1016/j.biortech.2007.07.009.
- Shivran, H., D. Kumar, S. Kumar, and R. Singh. 2005. The effect of different carbon sources as an energy source for biological denitrification through *Pseudomonas stutzeri* and impact on other water quality parameters. *Journal of the Indian Chemical Society* 82:978–980.

Appendix B. Aerial photographs of sampling locations at (A) forested Pond Branch, (B) forested Baisman Run, (C) restored Minebank Run, (D) restored Spring Branch, (E) unrestored urban Scotts Level Branch, and (F) unrestored urban Dead Run. Sediment, organic matter, and water samples for the denitrification enzyme assay experiments were collected from 2 locations at each stream (▲), nitrate and dissolved organic carbon were monitored monthly at each stream (★), sediments, water and organic matter samples were collected for C:N ratios and  $\delta^{15}\text{N}/\delta^{13}\text{C}$  isotopic signatures (✕), sediments were collected for lipid biomarker analysis at 3 sites (●), and discharge was taken at USGS Gages (■). All images were taken from Google Maps and are identical in scale.

A. Forested Pond Branch



B. Forested Baisman Run



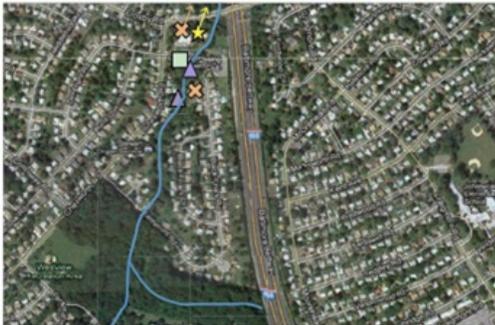
C. Restored Minebank Run



D. Restored Spring Branch



E. Unrestored urban Dead Run



F. Unrestored urban Scotts Level Branch



## Chapter 3: Effects of Stormwater Management and Stream Engineering on Watershed Nitrogen Retention

### Abstract

Restoring urban infrastructure and managing the nitrogen cycle represent emerging challenges for urban water quality. I investigated whether stormwater control measures (SCMs), a form of green infrastructure, integrated into restored and degraded urban stream networks can influence watershed nitrogen loads. I hypothesized that hydrologically connected floodplains and SCMs are “hot spots” for nitrogen removal through denitrification because they have ample organic carbon, low dissolved oxygen levels, and extended hydrologic residence times. I tested this hypothesis by comparing nitrogen retention metrics in 2 urban stream networks (1 restored and 1 urban degraded) with SCMs and a forested reference watershed at the Baltimore Long-Term Ecological Research (LTER) site. At all 3 sites, I used a combination of: (1) longitudinal reach-scale mass balances of nitrogen and carbon conducted over 2 years during baseflow and storms ( $n = 360$ ) and (2)  $^{15}\text{N}$  push-pull tracer experiments to measure *in situ* denitrification in SCMs and floodplain features ( $n = 72$ ). The SCMs consisted of inline wetlands installed below a storm drain outfall at one urban site (restored Spring Branch) and a wetland/wet pond configured in an oxbow design to receive water during high flow events at another highly urbanized site

(Gwynns Run). The SCMs significantly decreased total dissolved nitrogen (TDN) concentrations at both sites and significantly increased dissolved organic carbon (DOC) at one site. At Spring Branch, TDN retention estimated by mass balance (g/day) was ~150 times higher within the stream network than the SCMs. There were no significant differences between mean *in situ* denitrification rates between SCMs and hydrologically connected floodplains. Longitudinal N budgets along the stream network showed that hydrologically connected floodplains were important sites for watershed nitrogen retention due to groundwater-surface water interactions. Overall, my results indicate that hydrologic variability can influence nitrogen source/sink dynamics along engineered stream networks. My analysis also suggests that: (1) surface area, (2) hydrologic residence time, and (3) streamwater and groundwater flux are major predictors of the potential for stream/wetland restoration features to retain nitrogen at the watershed scale.

### Introduction

Nitrogen inputs to watersheds have doubled globally (Vitousek et al. 1997), and urbanizing landscapes are becoming important sources of nonpoint source pollution to streams and rivers (Grimm et al. 2005). Nitrogen inputs can contribute to coastal eutrophication (Howarth et al. 1996) and contamination of major drinking-water supplies (Kaushal et al. 2006). Likewise, increased organic carbon from bioavailable sources can also contribute to coastal hypoxia (Mallin et al. 2004, Sickman et al. 2007). Urban watersheds receive a mix of nitrogen and carbon inputs from external sources such as atmospheric deposition, fertilizer, and food (Bernhardt et al. 2008, Fissore et al. 2012), which supply internal nitrogen and carbon loading

from human and pet waste, leaky septic systems, and aging sanitary infrastructure (Kaushal et al. 2011).

In urban watersheds, above and belowground modifications of hydrologic connectivity contribute to impaired water quality. Aboveground human modifications of the land surface like impervious surfaces, gutters, and storm drains collect and convey carbon and nutrients in ways that can bypass natural flow paths (Kaushal and Belt 2012). These modifications can disconnect the riparian zone from the drainage network and contribute to decreased opportunities for retention and removal of nitrogen from surface runoff (Walsh et al. 2005). Belowground modifications to urban hydrology include a complex, patchy network of buried streams, storm drains, sanitary lines, and potable water supply pipes known as the "urban karst" (Kaushal and Belt 2012). As part of the "urban karst," leaky piped infrastructure and groundwater table height fluctuations can cause streams to gain or lose water (Bhaskar and Welty 2012, Kaushal and Belt 2012, Janke et al. 2013).

Given that urbanization contributes to water quality impairments, considerable amounts of public funds have been spent on stream restoration strategies to reduce river nitrogen loads (Bernhardt et al. 2005). Urban stream restoration can involve hydrologic reconnection of streams with floodplain wetlands, geomorphic channel stabilization approaches, and addition of carbon sources (e.g., riparian vegetation and large woody debris). However, there can be variability in the effectiveness of restoration approaches intended to enhance denitrification (Kaushal et al. 2008b). Stream restoration strategies like concrete channel removal and daylighting buried streams may increase nitrogen retention and removal by restoring hydrologic

connection between the channel and the floodplain (Bukaveckas 2007, Kaushal et al. 2008b, Klockner et al. 2009, Roley et al. 2012b). Areas of enhanced hydrologic connectivity like floodplains with low stream banks can have high rates of denitrification (Roley et al. 2012b, Mayer et al. 2013). This is because groundwater is in contact with carbon rich surface soils, and mixing of groundwater and stream water with variable oxygen and redox levels can promote coupled nitrification-denitrification (Mayer et al. 2010).

In addition to stream restoration, there is also growing interest in the potential for stormwater management to reduce nitrogen loads, but there are still many uncertainties (Collins et al. 2010). SCMs, a form of green infrastructure, may be effective at nitrogen retention at smaller spatial scales (Collins et al. 2010), but less is known about how SCMs can potentially affect watershed scale N budgets. The primary aim of stormwater management is actually not related to water quality improvement, but it is to intercept runoff from developed areas and discharge it to surface waters at a more controlled rate (Rosenzweig et al. 2011). In the United States, stormwater discharges are now regulated under the U.S. Environmental Protection Agency (EPA) 1987 amendments to the National Pollutant Discharge Elimination System and the Phase I (1990) and Phase II (1999) stormwater permitting program (NRC 2008). There is increased interest in determining if SCMs may have the ancillary benefit of improving water quality because urban stormwater can transport high loads of nitrogen and organic carbon (Paul and Meyer 2001, Galloway et al. 2003, Walsh et al. 2005, Taylor et al. 2005).

More work is needed to determine how effective stream restoration and stormwater management are at retaining nitrogen loads (Lowrance et al. 1995, Clausen et al.

2000). Here, I investigated the extent to which stream restoration and SCMs integrated into urban stream networks can influence nitrogen and carbon retention across multiple spatial scales. My specific objective was to investigate if and how stream restoration involving hydrologic floodplain reconnection and integrated SCMs may enhance nitrogen retention and removal through denitrification. I hypothesized that hydrologically connected floodplains and SCMs can have substantial denitrification rates because they should have ample organic carbon, low dissolved oxygen levels, and extended hydrologic residence times. I also hypothesized that surface area of hydrologically connected features and hydrologic flux through SCMs can constrain their role in influencing nitrogen removal at the watershed scale. I tested these hypotheses by comparing nitrogen retention metrics such as *in situ* denitrification and patterns in nitrogen loads and retention rates along 2 urban stream networks with SCMs and a forested reference watershed at the Baltimore Long-Term Ecological Research (LTER) site (Figs. 3.1, 3.2). My study builds upon previous work at the Baltimore LTER site examining the effects of stream restoration and stormwater management on nitrogen dynamics (Kaushal et al. 2008b, Mayer et al. 2010, Harrison et al. 2011, Svirichni et al. 2011, Bettez and Groffman 2012, Newcomer et al. 2012).

### Methods

My study sites are located within the Chesapeake Bay watershed, where there is interest in reducing downstream nitrogen delivery to sensitive coastal waters (Boesch et al. 2001, Kemp

et al. 2005, Kaushal et al. 2008a). I compared nitrogen retention metrics in 2 urban stream networks with SCMs and a forested reference watershed at the Baltimore LTER site (Table 3.1; Figs. 3.1, 3.2). At all 3 sites, I used a combination of: (1) stream reach scale mass balances of nitrogen and carbon conducted monthly for 2 years across stream flow (24 monthly synoptic samplings [April 2008 to April 2010] across 15 reaches [7 reaches at Spring Branch; 5 reaches at Gwynns Run; and 3 reaches at Pond Branch]  $n = 360$  mass balance calculations), and (2)  $^{15}\text{N}$  push-pull tracer experiments to measure *in situ* denitrification rates in SCMs and floodplain features ( $n = 72$  denitrification measurements).

#### Site description and sampling design

Spring Branch is a restored, low-order stream with a drainage area of 407 ha in Baltimore County, MD (39°26'43.9" N, 76°37'12.9"W; Table 3.1; Figs. 3.1, 3.2). The Spring Branch watershed has 18.6% impervious surface cover, 6.37 km of stream channel, and 37.8 km of sewer lines (Table 3.1; DEPRM 2008b). The headwaters originate from a storm drain in a medium-density residential neighborhood, and the stream passes through confined areas of residential development into Loch Raven reservoir, a major source of drinking water for Baltimore, MD. Development occurred during the 1950-1970s before current stormwater regulations were in place, and the entire watershed is served by public sewer (DEPRM 2008a). Approximately 61% of the watershed drains directly to storm drains and only 7.2% of the watershed is served by stormwater management (DEPRM 2008a). Spring Branch has a

relatively low drainage density (1.57 km of stream/km<sup>2</sup> of drainage area) because some sections were straightened and other sections were buried in underground pipes (DEPRM 2008a). The stream restoration project repaired leaking infrastructure, removed 0.5 km of concrete channel liner, created a series of step pools, and planted trees and shrubs for bank stabilization (Klocker et al. 2009, EPA 2011, Svirichich et al. 2011). During Phase I (1994-1997), \$2.25 million was spent to restore 3.2 km of stream length, create 2.9 ha of riparian buffer, and install dissipative structures at storm drain outfalls like the inline headwater SCMs that are a focus of this study. The inline headwater SCMs consist of a 4-cell headwater-settling basin that drains 18.4 ha (4.5% of the watershed; Fig. 3.2; DEPRM 2008a). During Phase II (2008), \$1.3 million was spent to restore 0.8 km of additional stream length (DEPRM 2008a). The project incorporated a combination of standard natural channel design restoration techniques (Rosgen 1994), in-stream structures (vortex rock weirs, step pools), bank stabilization (root wads, rock toe protection), and bioengineering using native plantings (DEPRM 2008a, 2008b, Klocker et al. 2009).

Gwynns Run is a highly urbanized, low-order stream with a drainage area of 557 ha (39°16'41.3"N, 76°39'07.2"W) and the stream has been heavily impacted by sewage leaks (Halden and Paull 2005, Belt et al. 2007, Kaushal et al. 2011). I used zonal statistics to estimate an impervious surface coverage of 61.2% using a 30 m raster dataset from MD Department of Planning for the year 2000. The majority of the stream network was buried in underground pipes during development. This site has a long history of industrial use and pollution, and was identified by Baltimore City as one of its two most degraded streams (Fisher 2001). Baltimore City was required by a 1999 consent decree (Civil Action No. Y-97-4185) to construct Gwynns

Run Pollution Control Facility, a lowland oxbow SCM system, at a cost of \$1.7 million. The purpose of the lowland oxbow SCMs was to reduce downstream transport of suspended solids, metals, oil, grease, nitrogen, and phosphorus. The lowland oxbow SCMs were completed in 2004 and consisted of a reinforced concrete flow diverter, forebay, oxbow wetland (SCM 1), and wet pond (SCM 2; Fig. 3.2). The SCMs were designed to treat 40% of flow during 1.4 to 3.2 cm rain events (capacity of 7,380 m<sup>3</sup>; (Baltimore City 2005). However, I have observed that smaller amounts of precipitation generate sufficient runoff to enter the lowland oxbow SCMs. The lowland oxbow SCMs transitioned between wetlands and ponds and were filling with sediment and progressing towards a more wetland state during the study period (T. Newcomer Johnson pers. observation).

Finally, because restoration projects often aim to mimic natural conditions, it is useful to know how urban systems function in comparison to rural counterparts. I also made comparisons with Pond Branch, a reference stream with an in-line engineered pond at the Baltimore LTER site. Pond Branch is a completely forested, 1st-order stream with a watershed area of 37 ha located within Oregon Ridge State Park in the Maryland Piedmont physiographic province (39°28'49"N, 76°41'16"W, Table 3.1, Figs. 3.1, 3.2). This watershed has no impervious surfaces and has been widely used as the reference watershed for Baltimore Ecosystem Study (Groffman et al. 2004, Kaushal et al. 2008a, Newcomer et al. 2012, Duncan et al. 2013). Pond Branch has a single inline pond that was constructed several decades ago for recreational purposes. Discharge was monitored continuously by USGS gaging station 01583570.

Flow duration curves were constructed from USGS gage flow records during the study period (Fig. 3.4). At Spring Branch, the site with the headwater inline SCMs, continuous discharge from April 2008 to September 2010 was modeled based upon a logarithmic relationship between nearby USGS gage 01589464 and my measurements along the stream reach located at 3,005 m downstream from the headwaters ( $y = 17.7 \ln(x) + 30.2$ ;  $R^2 = 0.61$ ; Appendix C Figure 1). At Gwynns Run, the site with the lowland oxbow SCMs, continuous discharge from April 2008 to September 2010 was modeled based upon a logarithmic relationship between nearby USGS gage 01589352 and my measurements in the stream reach located at 138 m downstream from the concrete flow diverter ( $y = 26.3 \ln(x) - 41.1$ ;  $R^2 = 0.70$ ; Appendix C Figure 1). At Pond Branch, continuous discharge was obtained from USGS gaging station 01583570. Dates of synoptic sampling events were labeled according to the flow associated with each date (Appendix C).

#### *In situ* denitrification rates from $^{15}\text{N}$ tracer experiments

I used  $^{15}\text{N}$  *in situ* push-pull tracer additions to measure spatial and temporal variability in *in situ* denitrification rates in features such as hydrologically connected floodplains versus SCMs and a forested pond (during summer 2008, winter 2008, and summer 2010, Fig. 3.2). This groundwater tracer method provides an integrated estimate of denitrification because it aggregates soil microsites; each pulled sample represents 1 L of groundwater that occupied approximately 4.37 kg of sediment (assuming a bulk density of  $1.65 \text{ g/cm}^3$ , a particle density of

2.65 g/cm<sup>3</sup>, and a porosity of 0.38; (Addy et al. 2002, Kaushal et al. 2008a, Harrison et al. 2011). Briefly, I added <sup>15</sup>N-labeled nitrate to quantify the amount of <sup>15</sup>N-labeled N<sub>2</sub> and N<sub>2</sub>O produced and used SF<sub>6</sub> as a conservative tracer. I used similar methods to previous push-pull studies and further details can be found elsewhere (Addy et al. 2002, Kaushal et al. 2008b, Harrison et al. 2011). Concentrations and isotopic composition of N<sub>2</sub> and N<sub>2</sub>O gases were determined on a PDZ Europa 20-20 continuous flow isotope ratio mass spectrometer coupled to a PDZ Europa TGII trace gas analyzer (Sercon, Cheshire, UK) at the Stable Isotope Facility, University of California, Davis, California, USA. Concentrations of N<sub>2</sub>O and SF<sub>6</sub> gases were analyzed by electron-capture gas chromatography on a Tracor Model 540 (ThermoFinnigan, Austin, Texas) at the Institute of Ecosystem Studies in Millbrook, New York, USA (summer 2008 and winter 2008) and US EPA, National Risk Management Research Lab in Ada, OK, USA (summer 2010) following standard methods.

#### Water chemistry and discharge monitoring

I conducted monthly monitoring of water chemistry and discharge at Spring Branch, Gwynns Run, and Pond Branch for over 2 years at multiple longitudinal points along each stream network (Figs. 3.1, 3.2). At Spring Branch, I initially sampled from 0-604 m (Fig. 3.2); after the first 5 months, I included additional sampling points downstream to the drinking water reservoir (3,512 m) in order to better characterize stream network retention and the effect of the Phase 2

restoration. At Gwynns Run, I sampled along 7 longitudinal points on all dates. At Pond Branch, I sampled along 4 longitudinal points on all dates (Fig. 3.2).

During the study period, samples spanned a range of hydrologic conditions (baseflow and storms; Fig. 3.4). The synoptic sampling effort was intended to be a snapshot of water chemistry at each stream. Adjacent water samples were collected approximately 10–25 min apart. Each of the synoptic sampling events lasted no more than four hours for an individual stream and each monthly campaign lasted no more than three days (the majority occurred on a single day). My sampling efforts occurred over time frames that were less than observed diurnal and daily cycles for parameters such as nitrate and DO (Klocker et al. 2009, VerHoef et al. 2011). Therefore, the synoptic sampling event was assumed to have been a simultaneous sampling of water throughout the entire stream network (Sivirichi et al. 2011).

I collected grab samples for streamwater chemistry using HDPE bottles rinsed 5 times with streamwater, and measured discharge with a Marsh-McBirney 2000 flow meter (Hach Co., Loveland, CO, USA) using the 60% depth method with a 5-second averaging interval (Sivirichi et al. 2011). In the field, dissolved oxygen (mg/L) and temperature (°C) were measured using the YSI 550A (YSI Inc., Yellow Springs, OH) and pH was measured using an Oakton Multiparameter PCS Tester 35 (OAKTON Instruments, Vernon Hills, IL). Water samples were filtered through pre-combusted 0.45 micron glass fiber filters within 24 hours of collection and then frozen until further analysis with a Shimadzu Total Organic Carbon Analyzer (TOC-V CPH/CPN) for total dissolved nitrogen and dissolved organic carbon.

## Stream network scale mass balances

Longitudinal sampling for mass balances was conducted for each stream network as described above (Fig. 3.2). Information from this surface water chemistry was used in conjunction with groundwater chemistry and hydrologic data to estimate monthly mass balances for TDN and DOC along each stream network. Mass-balance calculations were used to determine net retention or net release of TDN and DOC per unit area of stream for each reach (Fig. 3.2). Fluxes were calculated by multiplying concentration (mg/L) by the stream flow rate (L/day) to obtain mass transport per day (mg/day). Differences between upstream and downstream fluxes were then used as an estimate of retention/release. “No net change” in instantaneous fluxes does not imply that nitrogen transformations are absent between stations, but that uptake processes balance release processes.

I calculated mass balances for TDN and DOC using equation (1) modified from (Burns 1998, Sivirichi et al. 2011, Kaushal et al. 2014):

$$(1) M_D - (M_U + M_T + M_S) = \Delta M$$

Where

$M_D$  = mg/day at downstream end of reach

$M_U$  = mg/day at upstream end of reach

$M_T$  = mg/day from tributaries contributing at least 5% of streamflow

$M_S$  = mg/day from groundwater seepage

$\Delta M$  = mg/day of net transformation (net retention if (-); net release if (+))

Rates of net flux per streambed area ( $\text{mg}/\text{m}^2/\text{day}$ ) were calculated by dividing  $\Delta M$  by reach surface area. Surface area was estimated by measuring stream cross sections at 2-3 points along each reach to determine wetted width of the channel and multiplying by the length of each reach. On dates that I did not sample tributaries, I substituted data from the closest available sampling date (data taken from Sivorichi et al. 2011). A negative net transformation ( $\Delta M$ ) indicated net removal of the constituent (retention), whereas a positive  $\Delta M$  indicated net generation (release) of the constituent. This approach assumes no change in storage within the reach and no gains or losses via atmospheric exchange (net DOC retention could include mineralization processes and  $\text{CO}_2$  loss to the atmosphere). Percent retention or release of a constituent for each reach was calculated using equation 2 ( $[\text{outputs} - \text{inputs}] / \text{inputs}$ ):

$$(2) 100 * (\Delta M / [M_U + M_T + M_S]) = \% \text{ retention } (-) \text{ or release } (+)$$

Groundwater seepage ( $M_S$ ;  $\text{mg}/\text{day}$ ) was calculated by combining estimates of groundwater TDN and DOC concentrations ( $\text{mg}/\text{L}$ ) with groundwater discharge ( $\text{L}/\text{day}$ ). Each longitudinal site had 8 mini-piezometer wells that were installed 0.5 m below the stream surface (during baseflow) in hydrologically connected floodplains and 0.3 m below the surface in the SCMs/pond (Fig. 3.2). For the mass balance, I used average TDN and DOC concentrations from groundwater samples collected during June 2008, July 2008, August 2008, November 2008, December 2008, February 2009, May 2009, August 2009, and November 2009 ( $n = 67-68$  groundwater samples per stream or  $n = 203$  for all 3 streams). Rates of net groundwater input for each stream were determined based on the differences in flow from each sampling point to the next, according to equation 3:

$$(3) F_D - (F_U + F_T) = F_S$$

Where

$F_D = \text{m}^3/\text{day}$  at downstream end of reach

$F_U = \text{m}^3/\text{day}$  at upstream end of reach

$F_T = \text{m}^3/\text{day}$  of major tributaries

$F_S = \text{m}^3/\text{day}$  of groundwater seepage

From the perspective of characterizing hydrologic budgets, it is important to note that Baltimore does not have any combined sewer overflows (CSOs) because the city's infrastructure was rebuilt to include separate sanitary sewer lines and stormwater drains after the Great Baltimore Fire of 1904 (Boone 2003); however, there are still leaks from separate storm, sanitary, and drinking water pipes that vary in age and condition (Kaushal et al. 2011, Bhaskar and Welty 2012, Kaushal and Belt 2012).

### Statistical analyses

I used R (R Core Team 2013) and lme4 (Bates et al. 2013, Winter 2013) to perform stepwise multiple linear regression to test for significant relationships between longitudinal and temporal patterns in TDN (mg/L) and DOC (mg/L). All non-significant interactions were removed from the model first, followed by all non-significant main effects until only significant interactions or main-effects remained in the model. Visual inspection of residual plots did not reveal any obvious deviations from homoscedasticity or normality. Once the best model was

selected, I calculated the coefficient of partial determination (partial  $R^2$ ) for each predictor variable left in the model. I did this by partitioning the sums of squares, to estimate the contribution of each predictor variable to the total variance explained by the model. I used likelihood ratio tests of the full model with the effect in question against the model without the effect in question to obtain  $p$  values.

I examined candidate variables that could predict *in situ* denitrification rates ( $\mu\text{g N}\cdot\text{kg soil}^{-1}\cdot\text{day}^{-1}$ ) including groundwater chemistry (temperature ( $^{\circ}\text{C}$ ), dissolved oxygen (mg/L), nitrate (mg/L), and DOC (mg/L)) using linear regression. Linear regressions with temperature ( $^{\circ}\text{C}$ ) and dissolved oxygen (mg/L) used all available denitrification measurements ( $n = 72$ ). Linear regressions with nitrate (mg/L) and DOC (mg/L) were performed for the average value for each groundwater well ( $n = 24$ ) because parameters were measured seasonally instead of concurrently with the denitrification measurements.

Differences in TDN (mg/L) and DOC (mg/L) concentrations between longitudinal sampling points along each stream network were evaluated using a 2-way analysis of variance (ANOVA) followed by Tukey's test with a significance level ( $\alpha$ ) of 0.05. A 2-way ANOVA followed by Tukey's test was also used to evaluate differences in groundwater input (L/day, L/day/m, and %), incoming TDN and DOC loads (g/day), outgoing TDN and DOC loads (g/day), tributary TDN and DOC loads (g/day), groundwater incoming TDN and DOC loads (g/day), groundwater outgoing TDN and DOC loads (g/day), and export of TDN and DOC (g/day,  $\text{g}/\text{m}^2/\text{day}$ , and %) between stream reaches along each stream network. Differences in denitrification rates between sites, seasons, and feature types (floodplain, SCM, and reference

pond) were evaluated using a three-way analysis of variance (ANOVA) followed by Tukey's test.

## Results

### *In situ* denitrification rates

Denitrification rates ranged from 0.2 to 1,360.5  $\mu\text{g N}\cdot\text{kg soil}^{-1}\cdot\text{day}^{-1}$  (Figs. 3.5, 3.6; Table 3.2). Based on 3-way ANOVA, the reference pond at Pond Branch had significantly lower *in situ* denitrification rates than the other sites ( $F_{7,64} = 3.0$  (subscripts indicate degrees of freedom between and within groups, respectively),  $n = 72$ ,  $p = 0.01$ ; Fig. 3.5) with significantly lower rates during summer 2010 than the other seasons ( $p = 0.01$ ). There was not a significant difference for *in situ* denitrification rates between the SCMs and the hydrologically connected floodplains. Based on linear regression, there was a significant positive relationship between temperature and *in situ* denitrification rate (Fig. 3.6;  $F_{1,66} = 5.0$ ,  $n = 68$ ,  $p = 0.01$ ) and a significant negative relationship between dissolved oxygen concentrations and *in situ* denitrification rate (Fig. 3.6;  $F_{1,69} = 6.7$ ,  $n = 71$ ,  $p = 0.01$ ) and no relationship between dissolved oxygen and temperature ( $F_{1,65} = 0.0007$ ,  $n = 67$ ,  $p = 0.98$ ). Mean nitrate concentrations ranged from 0.005 to 4.52 mg/L (Fig. 3.6; Appendix C Table), and there was a significant positive relationship between mean groundwater nitrate concentrations and mean *in situ* denitrification rates (Fig. 3.6;  $F_{1,22} = 5.9$ ,  $n = 24$ ,  $p = 0.02$ ; Appendix C Table). Mean DOC ranged from 0.58 to 10.83 mg/L, but there was no significant relationship between mean DOC concentrations and

mean *in situ* denitrification rates (Fig. 3.6;  $F_{1,22} = 0.56$ ,  $n = 24$ ,  $p = 0.46$ ; Appendix C Table).

There was also no significant relationship between mean nitrate and mean DOC concentrations ( $F_{1,22} = 1.9$ ,  $n = 24$ ,  $p = 0.19$ ; Fig. 3.6; Appendix C).

### Longitudinal trends in concentrations along the stream network

*Spring Branch (the site with headwater inline SCMs):* Stepwise multiple linear regression analysis of TDN concentration (mg/L) from all monthly samples produced a model ( $F_{36,204} = 4.8$ ,  $R^2 = 0.36$ ,  $p < 0.001$ ), using distance downstream as a fixed effect and date and DOC concentration as random effects (Fig. 3.7). Concentration of TDN decreased with distance downstream ( $\chi^2(1) = 24.6$ ,  $p < 0.001$ ) by about  $1.09 \pm 0.21$  mg/L along the 3,512 m length of the stream network. I found that the positive relationship between TDN and DOC concentrations was driven by a single sample taken at the storm drain outlet (0 m) on 9/1/08 with 12.7 mg/L TDN and 8.7 mg/L DOC; this sample was likely influenced by a sewage leak, and when I removed this sample from the analysis, DOC concentration was no longer a significant predictor for TDN concentration.

Within the SCMs, stepwise multiple linear regression analysis of TDN concentration (mg/L) from all monthly samples at SCMs sampling points produced a model for TDN concentration using distance downstream as a fixed effect and date and DOC concentration as random effects ( $F_{35,54} = 4.856$ ,  $R^2 = 0.60$ ,  $p < 0.001$ ). The model showed that concentration of

TDN significantly decreased with distance downstream ( $\chi^2(1) = 28.0, p < 0.001$ ) by about  $1.53 \pm 0.24$  mg/L along the 121 m length of the SCMs (Fig. 3.7).

Gwynns Run (the site with lowland oxbow SCMs):

Stepwise multiple linear regression analysis of TDN concentration (mg/L) along longitudinal sampling locations within the stream reach parallel to the SCMs produced a model ( $F_{25, 73} = 6.6, R^2 = 0.59, p < 0.001$ ), using discharge as a fixed effect and date as a random effect. Concentration of TDN decreased by about  $0.0016 \pm 0.0050$  mg/L for each 1 L/s increase in discharge ( $\chi^2(1) = 4.5; p = 0.03$ ; Fig. 3.8). Likewise, stepwise multiple linear regression analysis of DOC concentration (mg/L) along sampling locations within the stream reach parallel to the SCMs produced a weak model ( $F_{2, 96} = 3.1, R^2 = 0.04, p < 0.05$ ), using discharge as a fixed effect and TDN concentration and distance downstream as random effects. Concentration of DOC increased by about  $0.018 \pm 0.008$  mg/L for each L/s increase in discharge ( $\chi^2(1) = 5.0, p = 0.03$ ).

Stepwise multiple linear regression analysis of TDN concentration (mg/L) along sampling locations within the SCMs produced a model ( $F_{25, 46} = 6.1, R^2 = 0.64, p < 0.001$ ), using time in days and distance downstream as a fixed effect and individual date as a random effect. Concentration of TDN significantly decreased over time in days ( $\chi^2(1) = 6.3, p = 0.03$ ) by approximately  $-1.63 \pm 0.53$  mg/L over 739 days and TDN concentration significantly decreased with distance downstream ( $\chi^2(1) = 8.9, p = 0.03$ ), by approximately  $-0.97 \pm 0.32$  mg/L across the 177 m length of the SCMs (Fig. 3.8). The significant decrease in TDN concentration over

time was accompanied by a significant decrease in surface flow through the SCMs as the oxbow SCMs aged and filled with sediment (Appendix C). DOC concentration tended to increase with distance downstream in the SCMs, but the linear regression model was not significant ( $p = 0.14$ ). A two-way ANOVA was used to test for differences in DOC concentrations among sampling stations and sampling dates. Concentrations of DOC in samples taken at the BMP 2 outlet (177 m;  $5.842 \pm 0.270$  mg/L) were significantly higher than concentrations in the parallel stream reach ( $3.894 \pm 0.160$  mg/L,  $p < 0.01$ ; Fig. 3.8).

*Pond Branch (reference site with pond):* Linear regression analysis of all monthly samples showed that there were no significant changes longitudinally or temporally in TDN or DOC.

Hydrologic mass balance: Importance of groundwater inputs

*Spring Branch (the site with headwater inline SCMs):* Along the outlet of the SCMs to the bottom of the phase II restoration (3,005 m), the stream network gained an average of  $15.6 \pm 3.2$  L/s, which was a  $41\% \pm 4\%$  increase due to groundwater (Fig. 3.9; Table 3.3). On 3 Dec 2008, there was a suspected potable water pipe leak just downstream of 2,374 m in a concrete lined channel the size of mainstem Spring Branch. This normally dry channel had a flow of 22.2 L/s, which is considerably higher than the mainstem flow just upstream of that point (13.3 L/s).

The amount of water released from the potable water leak was higher than the average groundwater inputs from all other sampling dates.

*Gwynns Run (the site with lowland oxbow SCMs):* The stream gained an average of  $9.6 \pm 2.8$  L/s due to groundwater ( $14\% \pm 4\%$ ; Fig. 3.10; Table 3.3).

*Pond Branch (reference site with constructed pond):* In the stream reach upstream of the constructed pond, the stream lost an average of  $-1.02 \pm 0.55$  L/s due to groundwater recharge ( $-47\% \pm 13\%$ ; Table 3.3).

TDN and DOC mass balance results along each stream network

*Spring Branch (the site with headwater inline SCMs):* At Spring Branch, TDN retention estimated by mass balance (g/day) was ~150 times higher within the stream network than the SCMs. On average, there was net TDN retention in all reaches (except phase 1a of the restoration). Across the entire stream network, average TDN retention was  $-0.94 \pm 0.13$  g/m<sup>2</sup>/day ( $-59\% \pm 6\%$  of incoming load; Fig. 3.11; Appendix C Table 4). Based on 2-way ANOVA, TDN retention (g/day) was significantly higher in phase 2 ( $-953.8 \pm 304.7$  g/day;  $p = 0.001$ ) than SCM 1 ( $-41.4 \pm 18.8$  g/day;  $p = 0.001$ ), SCM 2 ( $-30.7 \pm 22.5$  g/day;  $p = 0.001$ ), phase 1a ( $146.2 \pm 74.5$  g/day;  $p < 0.001$ ), and the unrestored reach ( $-19.1 \pm 376.8$  g/day,  $p = 0.010$ , Figs. 3.2, 3.10). TDN release (mg/m<sup>2</sup>/day and %) was significantly higher in phase 1a than in all other reaches besides the unrestored reach ( $p = 0.03$ ).

DOC retention and release varied along all reaches and along the entire stream network. Average DOC retention was  $0.03 \pm 0.20 \text{ g/m}^2/\text{day}$  ( $-4\% \pm 23\%$  of incoming load; Fig. 3.11; Appendix C Table 4). Based on 2-way ANOVA, there were no significant differences in DOC retention/release ( $\text{mg/m}^2/\text{day}$ ; %) between reaches (Fig. 3.11).

*Gwynns Run (the site with lowland oxbow SCMs):* Along the entire stream network, there was variable retention and release with an average TDN release of  $0.03 \pm 0.29 \text{ g/m}^2/\text{day}$  ( $29\% \pm 28\%$  of incoming load; Fig. 3.12; Appendix C Table 5). Based on 2-way ANOVA, incoming TDN load varied by reach ( $F_{28, 94} = 13.3$ ,  $n = 123$ ,  $p < 0.001$ ) and was significantly lower ( $p < 0.001$ ) in SCM 1 ( $1,280 \pm 465 \text{ g/day}$ ) and SCM 2 ( $780 \pm 396 \text{ g/day}$ ) than in the stream reach (average is  $14,768 \pm 1,271 \text{ g/day}$ ). There were no significant differences in TDN retention/release ( $\text{mg/m}^2/\text{day}$ ; %) between reaches (Fig. 3.12).

Average DOC retention was  $-1.36 \pm 0.39 \text{ g/m}^2/\text{day}$  ( $-25 \pm 7\%$  of incoming load; Fig. 3.12; Appendix C Table 5). Incoming DOC load varied by reach ( $F_{28, 94} = 12.6$ ,  $n = 123$ ,  $p < 0.001$ ) and was significantly lower ( $p < 0.001$ ) in SCM 1 ( $1,567 \pm 501 \text{ g/day}$ ) and SCM 2 ( $1,885 \pm 649 \text{ g/day}$ ) than in the stream reach (average is  $21,938 \pm 1,794 \text{ g/day}$ ).

*Pond Branch (reference site with constructed pond):* Average TDN retention was  $-0.14 \pm 0.04 \text{ g/m}^2/\text{day}$  ( $-40\% \pm 10\%$  of incoming load; Appendix C Table 6). At Pond Branch, in the stream reach upstream of the reference pond, TDN retention/release ranged from  $-45.1\%$  to

58.8% with a median of 4.2% and a mean of  $3.5 \pm 5.6\%$ . In the pond, TDN retention/release ranged from -63.8% to 66.4% with a median of 5.1% and a mean of  $3.5 \pm 7.1\%$ .

Average DOC retention was  $-0.02 \pm 0.03 \text{ g/m}^2/\text{day}$  ( $-6\% \pm 4\%$  of incoming load; Appendix C Table 6). DOC retention/release ranged from -57.4% to 31.4% with a median of -1.1% and a mean of  $-2.9 \pm 3.7\%$  (mean  $\pm$  SE;  $n = 25$  sampling dates). In the pond, DOC retention/release ranged from -19.3% to 84.6% to with a median of 18.2% and a mean of  $21.1 \pm 4.8\%$ . The pond served as a net source of DOC on most dates.

#### Relationships between streamflow and retention/release per unit area

Along the Spring Branch stream network, TDN retention ( $\text{g/m}^2/\text{day}$ ) increased with discharge whereas DOC retention or release ( $\text{g/m}^2/\text{day}$ ) was variable (Fig. 3.13). Within the Spring Branch headwater inline SCMs, TDN retention and DOC release tended to increase with discharge to a level of about 2 L/s then declined and even switched at higher levels indicating that retention capacity may have been saturated at higher flows. Within the Gwynns Run stream there was variable TDN and DOC retention or release, and no relationship with discharge. Within the Gwynns Run lowland oxbow SCMs, TDN retention and DOC release increased with discharge (Fig. 3.13). Within the Pond Branch forest reference stream and constructed pond there was no significant relationship between retention/release and discharge.

## Discussion

My overall objective was to investigate if and how stream restoration and integrated SCMs can enhance watershed nitrogen retention. I hypothesized that hydrologically connected floodplains and SCMs can have rates of *in situ* denitrification rates because they have ample organic carbon and nitrate, low dissolved oxygen levels, and extended hydrologic residence times. I also hypothesized that (1) streamwater and groundwater flux through stream restoration or stormwater management controls, (2) hydrologic residence times, and (3) surface area are major predictors for N retention at the watershed scale.

I found high denitrification rates in both floodplains and SCMs and determined that surface area of hydrologically connected features plays a key role in controlling watershed nitrogen retention and removal. Other studies have also suggested that stream restoration projects that include floodplain reconnection may foster nitrogen retention (Bukaveckas 2007, Kaushal et al. 2008b, Klockner et al. 2009, Filoso and Palmer 2011, Roley et al. 2012a). Previous work in urban stream channels has shown that nitrogen retention can be considerable in urban streams with high nitrogen levels (Grimm et al. 2005), and stream metabolism can show patterns with increasing watershed urbanization (Meyer et al. 2005, Paul et al. 2006, Kaushal et al. 2014). Channel incision, lining stream channels with concrete, and stream burial can diminish N retention in urban streams because these practices quickly carry nitrogen enriched water away

and decrease interaction with hyporheic and riparian zones containing roots and soil organic matter (Elmore and Kaushal 2008, Beaulieu et al. 2014, Pennino et al. 2014).

Recent studies examining the effects of stream restoration on nitrogen and carbon dynamics have shown there can be net nitrogen retention and carbon release (Bukaveckas 2007, Klocker et al. 2009, Filoso and Palmer 2011, Svirichni et al. 2011), while others have shown there can be less of an effect (Sudduth and Meyer 2006). Various and diverse stream restoration designs currently are being employed globally. Specific stream restoration strategies that have been shown to influence nitrogen retention include hydrologically connected floodplains (Kaushal et al. 2008b), stream wetland complexes (Rücker and Schrautzer 2010, Filoso and Palmer 2011), and remnant oxbow wetlands (Bukaveckas 2007, Harrison et al. 2011). These restoration features can increase hydrologic residence times, carbon availability, and hydrologic connectivity between surface water and groundwater. When used appropriately these restoration features may improve water quality in highly degraded urban streams that are concrete-lined, buried in pipes, and/or channelized with high-incised banks.

#### Influence of SCMs on DOC and TDN

I found that SCMs could influence DOC fluxes, nitrogen retention, and mass removal through denitrification. The Gwynns Run SCMs significantly increased DOC concentrations, a finding consistent with other work showing that wetlands tend to leach DOC into streams (Mann and Wetzel 1995). In contrast to Gwynns Run, my other sites did not increase average DOC

concentrations; this is likely because the smaller Spring Branch SCMs (750 m<sup>2</sup>) were almost fully shaded while the larger Gwynns Run SCMs (3,775 m<sup>2</sup>) received direct sunlight.

Additionally, Pond Branch received lower TDN and DOC inputs than urban Gwynns Run.

Urban SCMs at both my sites significantly decreased average TDN concentrations. Several other mass balance studies have shown that there can be considerable removal of nitrogen in stormwater management areas (Mallin et al. 2002, Rosenzweig et al. 2011, Chen et al. 2013). A stormwater bioretention system in Kansas, USA, removed 33% of influent nitrate and 56% of influent total nitrogen concentrations (Chen et al. 2013). This study also found high concentrations of denitrifying organisms in the uppermost sediments of the stormwater system (Chen et al. 2013). A study in New Jersey, USA, found that a detention pond removed 68% of nitrate during summer whereas nitrate concentrations increased during winter (Rosenzweig et al. 2011). Similarly, a study of 3 wet detention ponds in North Carolina, USA measured variable rates of nitrogen retention (0-63% removal of nitrate; Mallin et al. 2002). Mallin et al. (2002) recommended SCM designs with high length to width ratios to increase water residence time. In addition, they suggested designs to support the presence of macrophytes, which assimilate nitrogen and whose roots oxygenate soil and foster coupled nitrification-denitrification (Mallin et al. 2002). Overall, my results are consistent with other research on SCMs, which shows that they can be sources and sinks of carbon and nitrogen.

Are restored floodplains and SCMs important for denitrification at landscape scales?

I found that there was considerable denitrification in SCMs, but there was no significant difference between denitrification rates in SCMs and low connected floodplain areas. Several laboratory-based denitrification enzyme assay (DEA) studies have shown that SCMs can be denitrification “hot-spots” (Zhu et al. 2004, Roach and Grimm 2011, Bettez and Groffman 2012). A study at the Baltimore LTER found that potential denitrification rates were 3 times higher in stormwater control structures than in riparian areas (Bettez and Groffman 2012); potential denitrification rates were positively correlated with soil moisture, soil organic matter, and microbial biomass. Two studies at the Arizona urban LTER found high rates of potential denitrification in stormwater retention basins that were positively correlated with soil organic matter content, net nitrogen mineralization rates, and nitrification rates (Zhu et al. 2004). High denitrification rates in stormwater lakes at the Arizona urban LTER were limited by nitrate availability (Zhu et al. 2004, Roach and Grimm 2011). A laboratory mesocosm study in Australia showed that inclusion of a saturated zone in stormwater designs can optimize nitrogen removal (Zinger et al. 2013).

At a feature scale, denitrification has been shown to be important in stormwater management areas, but questions remain regarding the watershed scale impacts of these features. Laboratory studies are useful for determining controlling factors and relative rates throughout the landscape (Groffman et al. 2006). However, there is considerable uncertainty associated with scaling laboratory measurements to make predictions at the larger scales of management and

environmental policy (Urban 2005). I used *in situ*  $^{15}\text{N}$  push-pull tracer additions because this method aggregates a larger volume of soil and is more representative of field conditions (Addy et al. 2002). This method integrates groundwater, and my mass balances and tracer studies demonstrated that groundwater inputs are an important source of water, nitrogen, and carbon. It is especially important to include groundwater in urban studies because cracked, leaky infrastructure like sanitary, drinking water, and stormwater pipes can make urban groundwater systems more complex than rural systems (Pouyat et al. 2007, Ryan et al. 2010, Kaushal and Belt 2012). Elevated concentrations of fluoride and chloride indicate that leaky pipes influence stream chemistry at Spring Branch and Gwynns Run (Appendix C Table 2, Kaushal et al. 2011, Kaushal and Belt 2012).

#### Importance of groundwater inputs at watershed scales

The water mass balance complicates interpretation of longitudinal data, particularly in Spring Branch. More information regarding hydrologic connectivity of floodplains to stream channels is necessary. Nonetheless, I found that groundwater seepage was more important than typically considered in studies of urban streams (Fig. 3.10; Table 3). Additional work at my site using dilution gauging with a conservative tracer suggested that during summer baseflow 70% and 34% of the streamflow was from groundwater inputs at Spring Branch and Gwynns Run, respectively (Appendix C). Water inputs from leaky pipe infrastructure were also important on certain dates like 3 Dec 2008, when a potable water pipe leak accounted for 74% of flow.

Additional work using nitrate tracer injections also showed that nitrate uptake rates were 0.16 and 1.27 g/m<sup>2</sup>/day at Spring Branch, 6.9 and 33.6 g/m<sup>2</sup>/day at Gwynns Run, and 0.13 and 1.43 g/m<sup>2</sup>/day at Pond Branch which were in the same range as mass balance results (Appendix C). The degree of hydrologic connectivity of floodplains varied year-round, but my mass balance results suggested that groundwater seepage was a consistent source of water, nitrogen, and carbon to the stream channel across sampling dates and streamflow distribution. My study confirms that groundwater-surface water exchange is significant and important in floodplains (Brunke and Gonser 1997, Hefting et al. 2004, Wriedt et al. 2007, Fan et al. 2013).

#### Managing denitrification and nitrogen retention at a stream network scale

It may be useful to scale up processing rates in order to evaluate their potential impacts at the stream network and watershed scale. Here, I scale up my <sup>15</sup>N *in situ* denitrification rates and mass balance results in order to understand how features like floodplains and SCMs can influence nitrogen removal and retention at both the feature scale and the stream network scale. One of the fundamental challenges with this type of approach is that the majority of the nitrogen load is delivered during stormflow conditions when advective flow greatly impacts hydrologic residence times and the potential for removal in either SCMs or floodplains. Because I conducted routine *in situ* denitrification measurements along multiple longitudinal points and across baseflow and stormflow, my results can be used to investigate potential impacts at the watershed scale.

For the denitrification rates, I scaled-up my measurements for SCMs and low connected floodplain areas and compared them with scaled up measurements of high, disconnected banks (Kaushal et al. 2008b). I compare the scaled-up effect of low connected floodplain banks versus high, disconnected banks in order to explore the potential retention associated with floodplain restoration. As a caveat, streams usually do not have all low connected or high disconnected banks; instead there is a range of variability of channel complexity in urban, restored and forested reference streams (Laub et al. 2012).

In order to scale up results, measured denitrification rates ( $\mu\text{g N} \cdot \text{kg sediment}^{-1} \cdot \text{day}^{-1}$ ) were converted to areal rates ( $\text{mg} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ ) and used to estimate the load (g/day) of nitrogen removed through denitrification by each feature. Denitrification (g/day) in floodplains and SCMs was then compared to the average incoming load (g/day) from the monthly mass balances. I calculated areal denitrification rates ( $D_A$ ;  $\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ ) according to equation 4:

$$(4) D_S \times \rho_b \times d \div 1,000 = D_A$$

Where:

$D_S = \mu\text{g N} \cdot \text{kg sediment}^{-1} \cdot \text{d}^{-1}$   $^{15}\text{N}$  *in situ* sediment denitrification rate

$\rho_b = \text{kg/m}^3$  bulk density (1,650  $\text{kg/m}^3$ ; (Kaushal et al. 2008b)

$d = \text{m}$  mini-piezometer well depth (floodplain: 0.5 m & SCMs/pond: 0.3 m)

1,000 = conversion from  $\mu\text{g N}$  to  $\text{mg N}$

$D_A = \text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$  areal denitrification

by multiplying the mean  $^{15}\text{N}$  *in situ* denitrification rate ( $\mu\text{g N} \cdot \text{kg soil}^{-1} \cdot \text{d}^{-1}$ ) for each site and feature by bulk density and mini-piezometer well depth.

The areal rates ( $D_A$ ) I measured in urban SCMs and floodplains ranged from 0.5 to 1,122  $\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$  (Table 3.4). My denitrification rates were typically higher than rates in (Mulholland et al. 2009). Mulholland et al. (2009) measured areal denitrification rates that ranged from 2 to 220  $\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$  in streams across the U.S. (including 24 urban streams) with a median of approximately 48  $\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ . I may expect that the rates in my study would be higher. This is because proximate controls in SCMs and floodplains (e.g., variable  $\text{O}_2$  levels and sufficient organic carbon) can support higher denitrification rates than in a typical urban stream.

Next, I scaled up the areal denitrification to feature denitrification (g/day) by multiplying the areal rates by the estimated surface area of the SCM system or the stream network (consisting of all stream reaches but excluding SCMs; Fig. 3.14; Table 3.4). Surface area was calculated by multiplying SCM/stream length by width. Google Earth<sup>TM</sup> was used to measure the total stream length at each site. Width was measured in the field and 0.5 meter was added to each side of the baseflow, wetted width to estimate the width of the hyporheic zone. I chose 0.5 m because my mini-piezometer wells were installed 0.5 m from the edge of the channel. I calculated stream network denitrification for 2 different scenarios: a floodplain consisting entirely of high-disconnected banks versus a floodplain consisting entirely of low connected banks (Table 3.4).

I found that the Spring Branch stream network was able to denitrify a nitrogen load 6-52 times greater than the SCMs (depending upon whether the stream banks were assumed to be high and disconnected or low and connected) because the stream network covers a surface area ~33 times greater than the SCMs (Fig. 3.14; Table 3.4). If the current stream network consisted of all

high hydrologically disconnected banks, then I estimated 2.5% of the mean load could be removed through denitrification. In contrast, if the stream banks were all low hydrologically connected floodplains then 20% of the TDN load could be removed through denitrification. I estimated that the Spring Branch SCMs could denitrify 5% of the incoming load to the SCMs. If the SCMs had a greater surface area and/or if there were more SCMs distributed throughout the watershed, denitrification could remove a greater proportion of the overall watershed nitrogen load.

My scaling up exercise shows the importance of hydrologically connected surface area in maximizing denitrification along stream networks. This is similar to previous work demonstrating that surface area influences nitrogen retention in larger rivers and impoundments (Seitzinger et al. 2002b). Similarly, other work has shown that headwater streams play an important role in N retention due to their extensive surface area along stream networks (Alexander et al. 2000, Peterson et al. 2001). Unless watershed restoration is conducted over broader watershed and stream network spatial scales, it may have minimal impacts on N retention.

### *Management Implications and Future Research Needs*

There is considerable interest in managing the amount of nitrogen leaving watersheds and entering coastal zones (Boesch et al. 2001, Rabalais 2002). Urban stormwater is one of the fastest growing forms of nitrogen pollution in many coastal zones globally (NRC 2008). My

results show that hydrologic fluxes must be integrated with process level measurements when evaluating effectiveness of management activities at the watershed scale. My results also suggest that understanding groundwater hydrology of a region is important for managing fluxes, flowpaths, and sources of nitrogen. I found that only a small portion of the water budget was moving through the SCMs at Spring Branch, that the majority of water fluxes occurred along the stream network, and that groundwater was a significant source of nitrogen and carbon. Nitrogen retention was influenced by the interaction of feature surface area, retention rates per area, hydrologic residence times, and flow through a feature. My study demonstrates that groundwater inputs and surface area of hydrologically connected features like SCMs and floodplain-wetland complexes are major determinants of a stream network's capacity to retain N loads. Additionally I found that discharge levels (baseflow and storm events) can influence N and C retention and release rates. In order to meet nitrogen load reduction goals (e.g. Total Maximum Daily Loads), there is a need to determine the minimum critical surface area requirements for green infrastructure features like restored streams and SCMs.

### *Acknowledgments*

This research was supported by MD Sea Grant Awards SA7528085-U, R/WS-2 and NA05OAR4171042, NSF Awards DBI 0640300 and CBET 1058502, EPA NNEMS Award 2010-308, NASA grant NASA NNX11AM28G, the U.S. EPA Office of Research and Development, and Baltimore Ecosystem Study LTER project (NSF DEB-0423476). I thank

Melanie Harrison, Jeff Campbell, Katie Newcomb, Gwen Sivrichi, Michael Pennino, Dan Dillon, Shuiwang Duan, Casie Smith, and Rich Foot for assistance in the lab and field. Steve Stewart, Prakash Mistry, and Bill Stack provided help with selection of field sites and logistical support. The research has not been subjected to U.S. Environmental Protection Agency review and therefore does not necessarily reflect the views of any of the funding agencies, and no official endorsement should be inferred.

Table 3.1. Study site characteristics of Pond Branch, Spring Branch, and Gwynns Run watersheds. Land use data from (Baltimore City 2005, 2005, DEPRM 2008b).

| Site          | Location                     | Context | Drainage area (ha) | Impervious cover (%) | Land use (%) |                          |                                    |            |
|---------------|------------------------------|---------|--------------------|----------------------|--------------|--------------------------|------------------------------------|------------|
|               |                              |         |                    |                      | Forested     | High-density residential | Low and medium-density residential | Commercial |
| Spring Branch | 39°26'43.9"N<br>76°37'12.9"W | Urban   | 407 ha             | 18.6                 | 6.7          | 3.7                      | 87.8                               | 0          |
| Gwynns Run    | 39°16'41.3"N<br>76°39'07.2"W | Urban   | 557 ha             | 61.2                 | 1.5          | 63                       | 0                                  | 18.5       |
| Pond Branch   | 39°28'49"N<br>76°41'16"W     | Forest  | 37 ha              | 0                    | 100          | 0                        | 0                                  | 0          |

Table 3.2. *In situ* groundwater denitrification rates (means  $\pm$  SE,  $n = 3$  replicates per well).

| Site             | Well ID     | Site description | Groundwater denitrification rate ( $\mu\text{g N/kg/soil/day}$ ) |                   |                       |                        |
|------------------|-------------|------------------|--|-------------------|-----------------------|------------------------|
|                  |             |                  | Summer 2008  | Winter 2008       | Summer 2010           | Average across seasons |
| Spring Branch    | 1           | Low Floodplain   | 199.5 $\pm$ 19.6   | 231.3 $\pm$ 98.9  | 442.6 $\pm$ 47.1      | 291.1 $\pm$ 76.3       |
| Headwater        | 2           | Low Floodplain   | 355.1 $\pm$ 84.2   | 50.6 $\pm$ 5.0    | 1,360.5 $\pm$ 1,148.6 | 588.7 $\pm$ 395.8      |
| Inline           | 3           | Low Floodplain   | 111.2 $\pm$ 26.4   | 1.2 $\pm$ 0.2     | 322.5 $\pm$ 83.6      | 145.0 $\pm$ 94.3       |
| SCMs             | 4           | Low Floodplain   | 18.3 $\pm$ 9.0   | 0.6 $\pm$ 0.1     | 6.7 $\pm$ 3.5         | 8.5 $\pm$ 5.2          |
|                  | 5           | SCM              | 166.0 $\pm$ 13.3   | 122.9 $\pm$ 2.7   | 289.8 $\pm$ 14.6      | 192.9 $\pm$ 50.0       |
|                  | 6           | SCM              | 61.3 $\pm$ 41.1  | 22.2 $\pm$ 6.8    | 17.1 $\pm$ 16.2       | 33.5 $\pm$ 13.9        |
|                  | 7           | SCM              | 31.2 $\pm$ 2.8   | 64.8 $\pm$ 6.7    | 928.6 $\pm$ 38.5      | 341.5 $\pm$ 293.7      |
|                  | 8           | SCM              | 20.0 $\pm$ 11.4  | 16.8 $\pm$ 2.1    | 184.0 $\pm$ 95.0      | 73.6 $\pm$ 55.2        |
| Gwynns Run       | 1           | Low Floodplain   | 14.6 $\pm$ 0.4   | 39.9 $\pm$ 2.0    | 75.3 $\pm$ 4.2        | 43.3 $\pm$ 17.6        |
| Lowland          | 2           | Low Floodplain   | 84.9 $\pm$ 11.6  | 16.3 $\pm$ 2.9    | 185.1 $\pm$ 19.9      | 95.4 $\pm$ 49.0        |
| Oxbow            | 7           | Low Floodplain   | 139.3 $\pm$ 46.3   | 1135.7 $\pm$ 54.0 | 197.4 $\pm$ 16.5      | 490.8 $\pm$ 322.9      |
| SCMs             | 8           | Low Floodplain   | 179.9 $\pm$ 24.6   | 47.6 $\pm$ 5.7    | 123.1 $\pm$ 69.4      | 116.9 $\pm$ 38.3       |
|                  | 3           | SCM              | 610.2 $\pm$ 34.9   | 29.6 $\pm$ 7.1    | 630.4 $\pm$ 63.4      | 423.4 $\pm$ 197.0      |
|                  | 4           | SCM              | 192.2 $\pm$ 14.5   | 0.9 $\pm$ 0.3     | 407.6 $\pm$ 13.4      | 200.2 $\pm$ 117.5      |
|                  | 5           | SCM              | 9.9 $\pm$ 3.7  | 49.1 $\pm$ 25.8   | 942.9 $\pm$ 123.0     | 334.0 $\pm$ 304.7      |
|                  | 6           | SCM              | 114.7 $\pm$ 17.8   | 15.0 $\pm$ 13.7   | 608.3 $\pm$ 124.6     | 246.0 $\pm$ 183.4      |
|                  | Pond Branch | 1                | Low Floodplain   | 233.4 $\pm$ 145.3 | 180.4 $\pm$ 10.7      | 538.1 $\pm$ 60.1       |
| Forest Reference | 2           | Low Floodplain   | 199.2 $\pm$ 10.8   | 167.3 $\pm$ 4.2   | 62.9 $\pm$ 10.9       | 143.1 $\pm$ 41.2       |
| Pond             | 7           | Low Floodplain   | 124.4 $\pm$ 39.3   | 30.5 $\pm$ 5.7    | 143.5 $\pm$ 27.0      | 99.5 $\pm$ 34.9        |
|                  | 8           | Low Floodplain   | 45.5 $\pm$ 7.5   | 29.1 $\pm$ 8.9    | 246.3 $\pm$ 26.4      | 107.0 $\pm$ 69.8       |
|                  | 3           | Reference Pond   | 43.3 $\pm$ 3.2   | 20.8 $\pm$ 3.0    | 108.7 $\pm$ 6.7       | 57.6 $\pm$ 26.4        |
|                  | 4           | Reference Pond   | 2.0 $\pm$ 0.1  | 4.9 $\pm$ 0.7     | 33.8 $\pm$ 15.9       | 13.6 $\pm$ 10.1        |
|                  | 5           | Reference Pond   | 2.1 $\pm$ 0.5  | 6.3 $\pm$ 3.8     | 42.9 $\pm$ 14.9       | 17.1 $\pm$ 13.0        |
|                  | 6           | Reference Pond   | 85.7 $\pm$ 83.1  | 22.8 $\pm$ 3.1    | 0.2 $\pm$ 0.0         | 36.2 $\pm$ 25.6        |

Table 3.3. Concentrations of TDN and DOC from stream network groundwater wells.

| Stream                                    | Feature ( <i>n</i> = 4 wells per feature per stream) | Mass balance groundwater concentrations |   | Estimated seepage rate  |  |
|---|--|---|---|---|--|
|   |  | TDN (mg/L)<br>Mean ± SE<br>(range)      | DOC (mg/L)<br>Mean ± SE<br>(range)      | L/s<br>Mean ± SE<br>(range)   | %<br>Mean ± SE<br>(range)  |
| Spring Branch<br>Inline headwater<br>SCMs | Floodplain   | 2.84 ± 0.37<br><i>n</i> = 35<br>samples | 0.98 ± 0.09<br><i>n</i> = 35<br>samples | 15.6 ± 3.2<br>(-4.2 to 43.3)<br><i>n</i> = 4 reaches * 18<br>dates    | 41 ± 4 %<br>(-14 to 76 %)<br><i>n</i> = 4 reaches * 18<br>dates        |
|   | Stormwater Control Measures (SCMs)                   | 3.10 ± 0.42<br><i>n</i> = 28<br>samples | 1.62 ± 0.41<br><i>n</i> = 28<br>samples | -0.9 ± 0.3<br>(-6.1 to 1.4)<br><i>n</i> = 2 reaches * 25<br>dates     | -273 ± 116 %<br>(-3,600 to 71 %)<br><i>n</i> = 2 reaches * 25<br>dates |
| Gwynns Run<br>Lowland Oxbow<br>SCMs       | Floodplain   | 1.97 ± 0.53<br><i>n</i> = 36<br>samples | 4.43 ± 0.40<br><i>n</i> = 36<br>samples | 9.6 ± 2.8<br>(-15.4 to 56)<br><i>n</i> = 3 reaches * 29<br>dates      | 17 % ± 4 %<br>(-27 to 51 %)<br><i>n</i> = 3 reaches * 29<br>dates      |
|   | Stormwater Control Measures (SCMs)                   | 5.89 ± 1.04<br><i>n</i> = 35<br>samples | 6.61 ± 1.24<br><i>n</i> = 35<br>samples | -1.28 ± 1.46<br>(-29.8 to 12.4)<br><i>n</i> = 2 reaches * 25<br>dates | -8 ± 23 %<br>(-100 to 476 %)<br><i>n</i> = 2 reaches * 25<br>dates     |
| Pond Branch<br>Forest Reference<br>Pond   | Floodplain   | 0.36 ± 0.06<br><i>n</i> = 39<br>samples | 1.42 ± 0.13<br><i>n</i> = 39<br>samples | -1.02 ± 0.55<br>(-11.1 to 3.4)<br><i>n</i> = 2 reaches * 25<br>dates  | -47 ± 13 %<br>(-200 to 68 %)<br><i>n</i> = 2 reaches * 25<br>dates     |
|   | Reference pond                                       | 3.10 ± 0.66<br><i>n</i> = 30<br>samples | 2.54 ± 0.58<br><i>n</i> = 30<br>samples | 0.13 ± 0.24<br>(-2.2 to 2.8)<br><i>n</i> = 1 reach * 25<br>dates      | 2 ± 9 %<br>(-130 % to 65 %)<br><i>n</i> = 1 reach * 25<br>dates        |

Table 3.4. Calculation of areal denitrification rates (mg N/m<sup>2</sup>/day) and estimation of feature denitrification (g/day) within the SCMs and the stream network.

| Feature                             | Length (m) | Mean width (m) | Surface area (m <sup>2</sup> ) | Floodplain scenario                      | Areal denitrification mg N/m <sup>2</sup> /day<br>Mean ± SE<br>(range) | Feature denitrification g/day<br>Mean ± SE<br>(range) | % Mean BMP load<br>Mean ± SE<br>(range) | % Mean watershed load<br>Mean ± SE<br>(range) |
|-------------------------------------|------------|----------------|--------------------------------|--|--|---|---|---|
| Spring Branch Headwater Inline SCMs | 37         | 13.7           | 507                            | n/a                                      | 132.3 ± 61.1<br>(13.9–766.1)   | 67.1 ± 31.0<br>(7.0–388.6)                            | 5.4 ± 2.4<br>(0.6–31)                   | 0.09 ± 0.04<br>(0.01–0.55)                    |
| Spring Branch Stream Network        | 4,970      | 3.3            | 16,580                         | High banks with disconnected floodplains | 26.2 ± 4.4<br>(0.1–84.5)   | 434 ± 73<br>(1.4–1,401)                               | n/a                                     | 2.5 ± 0.4<br>(0.01–8.1)                       |
|                                     |            |                |                                | Low banks with connected floodplain      | 213.1 ± 90.4<br>(0.5–1,122)  | 3,534 ± 1,499<br>(8.2–18,610)                         | n/a                                     | 20.4 ± 8.7<br>(0.05–100)                      |
| Gywms Run Lowland Oxbow SCMs        | 139        | 24.9           | 3,454                          | n/a                                      | 248.2 ± 77.4<br>(0.7–777.9)  | 857.5 ± 267.4<br>(2.6–2,687)                          | 67 ± 21<br>(0.2–100)                    | 0.21 ± 0.07<br>(0.00–0.67)                    |
| Gywms Run Stream Network            | 400        | 7.6            | 3,027                          | High banks with disconnected floodplains | 26.2 ± 4.4<br>(0.1–84.5)   | 79 ± 13<br>(0.3–256)                                  | n/a                                     | 0.06 ± 0.01<br>(0.00–0.21)                    |
|                                     |            |                |                                | Low banks with connected floodplain      | 153.9 ± 72.9<br>(12.0–937.0)   | 465.9 ± 220.5<br>(36.5–2,836)                         | n/a                                     | 0.38 ± 0.18<br>(0.03–2.3)                     |

We examined potential stream network watershed removal through denitrification under the scenario that the entire floodplain is composed of high banks with disconnected flood plains versus low banks with connected floodplains. For the high banks with disconnected floodplains scenario, we used denitrification rates from Kaushal et al. 2008b

## Figure Captions

Figure 3.1. Land cover map of Spring Branch, Gwynns Run, and Pond Branch watersheds at the Baltimore Long-Term Ecological Research Site (LTER) in MD, USA. Coloration was from the 2006 National Land Cover Database (red indicates urban areas and green indicates forested areas). White Xs indicate location of stormwater control measures (SCMs) in urban sites or the forested reference pond.

Figure 3.2. Conceptual diagram of the Spring Branch, Gwynns Run, and Pond Branch watersheds. Red lines indicate locations of monthly surface water chemistry and discharge measurements. Blue “W”s indicate locations of mini-piezometer wells used for  $^{15}\text{N}$  *in situ* denitrification measurements and seasonal groundwater monitoring. At each site, 4 wells were located in the floodplain and 4 wells were located in the SCM or reference pond. Wells were numbered in the order they were sampled which is from downstream to upstream to avoid tracer cross contamination. This diagram is not to scale.

Figure 3.3. Photos showing Spring Branch before restoration when it was lined in concrete (a) and (b) afterward when the channel was reconnected to the floodplain. (c) The stream restoration construction process.

Figure 3.4. Flow duration curves (liters/second) for mean daily flow from April 2008 to September 2010 with synoptic sampling dates labeled according to the associated flow

values for A) Spring Branch at 3,005 m (continuous discharge modeled from USGS gage 01589464), B) Gwynns Run at 138 m (continuous discharge modeled from USGS gage 01589352), and C) Pond Branch at 0 m (continuous discharge from USGS gage 01583570).

Figure 3.5. Box-and-whisker plot of denitrification rates from  $^{15}\text{N}$  *in situ* push-pulls in the floodplain and SCMs or reference pond ( $n = 72$ ). The center vertical line of the box-and-whisker plot marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall. Box edges indicate the first and third quartiles. Circles (o) represent outside values.

Figure 3.6. A comparison of denitrification rates ( $\mu\text{g N}\cdot\text{kg soil}^{-1}\cdot\text{day}^{-1}$ ) versus (a) dissolved oxygen (mg/L), (b) temperature ( $^{\circ}\text{C}$ ), (c) mean nitrate (mg/L), and (d) mean DOC (mg/L) from mean values for the present study and similar sites from the literature. Sample size was 72 measurements for DO and temperature and 12 measurements for nitrate and DOC, which were averaged from seasonal measurements for each well.

Figure 3.7. Spring Branch longitudinal variation in mean ( $\pm$  SE) A) discharge (L/s), B) TDN concentrations (mg/L), and DOC concentrations (mg/L) along 15 sampling points.

Figure 3.8. Gwynns Run longitudinal variation in mean ( $\pm$  SE) A) discharge (L/s), B) TDN concentrations (mg/L), and DOC concentrations (mg/L) along 7 sampling points ( $n = 23$ -25 sampling dates).

Figure 3.9. Pond Branch longitudinal variation in mean ( $\pm$  SE) A) discharge (L/s), B) TDN concentrations (mg/L), and DOC concentrations (mg/L) along 4 sampling points ( $n = 23-25$  sampling dates).

Figure 3.10. Water Budgets (%) for Spring Branch, Gwynns Run, and Pond Branch stream networks. Water budgets are composed of the surface water from the mainstem at the sampling point furthest upstream, tributary inputs, and groundwater seepage. There is positive groundwater seepage at Spring Branch and Gwynns Run (gaining reaches) and negative groundwater seepage at Pond Branch (losing reach).

Figure 3.11. Box-and-whisker plot of Spring Branch longitudinal variation in reach export and retention A) TDN ( $\text{mg}/\text{m}^2/\text{day}$ ), B) DOC ( $\text{mg}/\text{m}^2/\text{day}$ ), C) TDN (%), D) DOC (%) along 7 stream reaches. SCM 1 is from 0-50 m, SCM 2 is from 50-121 m, phase 1a is from 121-604 m, phase 1b is from 604-1860 m, phase 1c is from 1860-2265 m, phase 2 is from 2265-3005 m, and the unrestored reach is from 3005-3516 m. The center vertical line of the box-and-whisker plot marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall. Box edges indicate the first and third quartiles. Circles (o) represent outside values, which are provided in the Appendix C.

Figure 3.12. Box-and-whisker plot of Gwynns Run longitudinal variation in reach export and retention A) TDN ( $\text{mg}/\text{m}^2/\text{day}$ ), B) DOC ( $\text{mg}/\text{m}^2/\text{day}$ ), C) TDN (%), D) DOC (%) along 5 stream reaches ( $n = 23\text{-}25$  sampling dates). SCM 1 is from 0- 50 m, SCM 2 is from 50-121 m along the oxbow. The center vertical line of the box-and-whisker plot marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall. Box edges indicate the first and third quartiles. Circles (o) represent outside values, which can be found in the Supporting Information.

Figure 3.13. Net flux per streambed area ( $\text{g}/\text{m}^2/\text{day}$ ) versus instantaneous discharge (liters/second) at Spring Branch, Gwynns Run, and Pond Branch in the stormwater control measures (SCMs) and reference pond and the overall stream networks. A negative value indicates retention and a positive value indicates release.

Figure 3.14. Feature-scale denitrification ( $\text{g N}/\text{day}$ ) versus surface area ( $\text{m}^2$ ) at Spring Branch, Gwynns Run, and Pond Branch. Comparisons are between the stream reach surface areas versus the surface areas for SCMs or reference pond.

Fig. 3.1

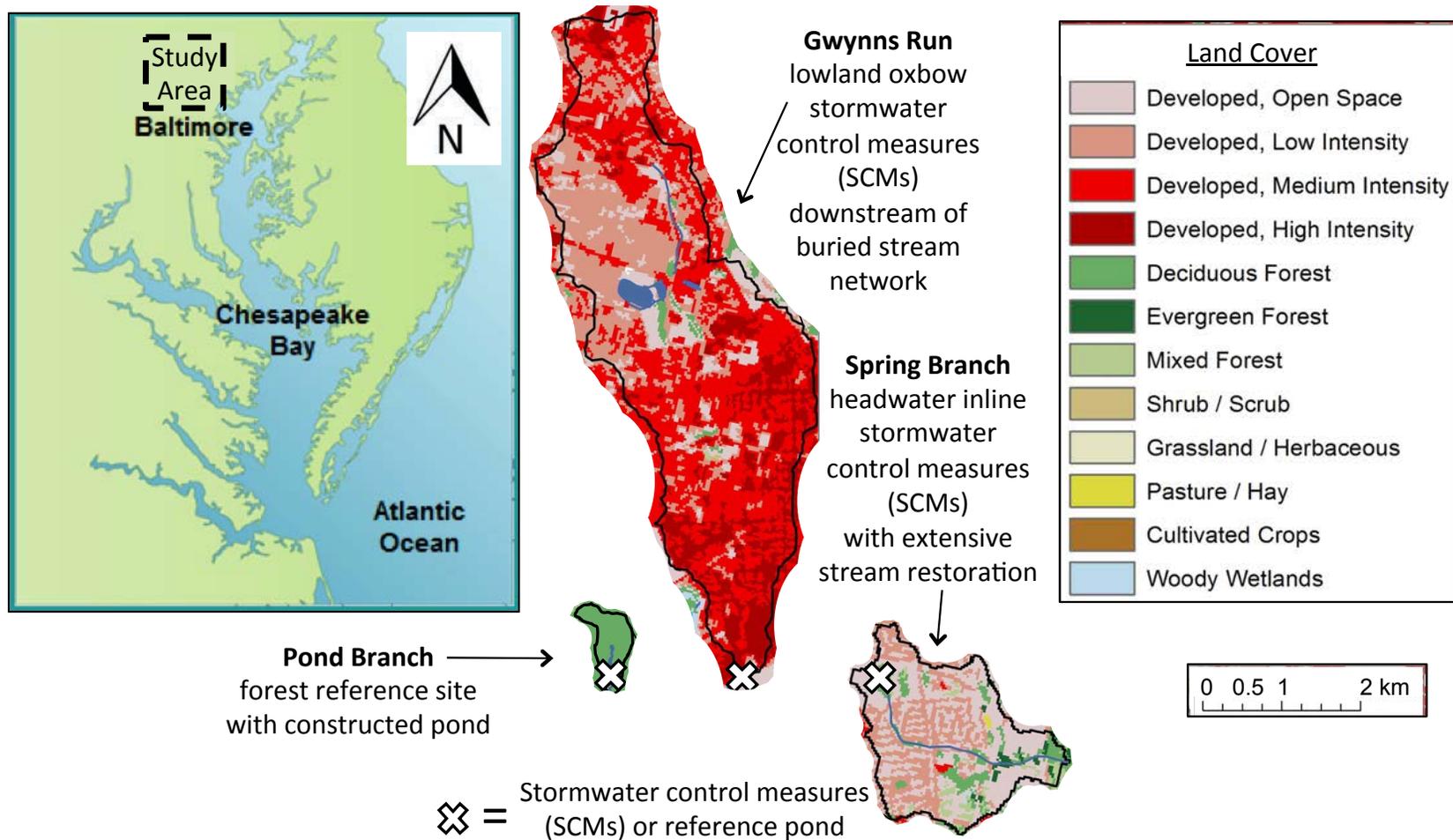


Fig. 3.2

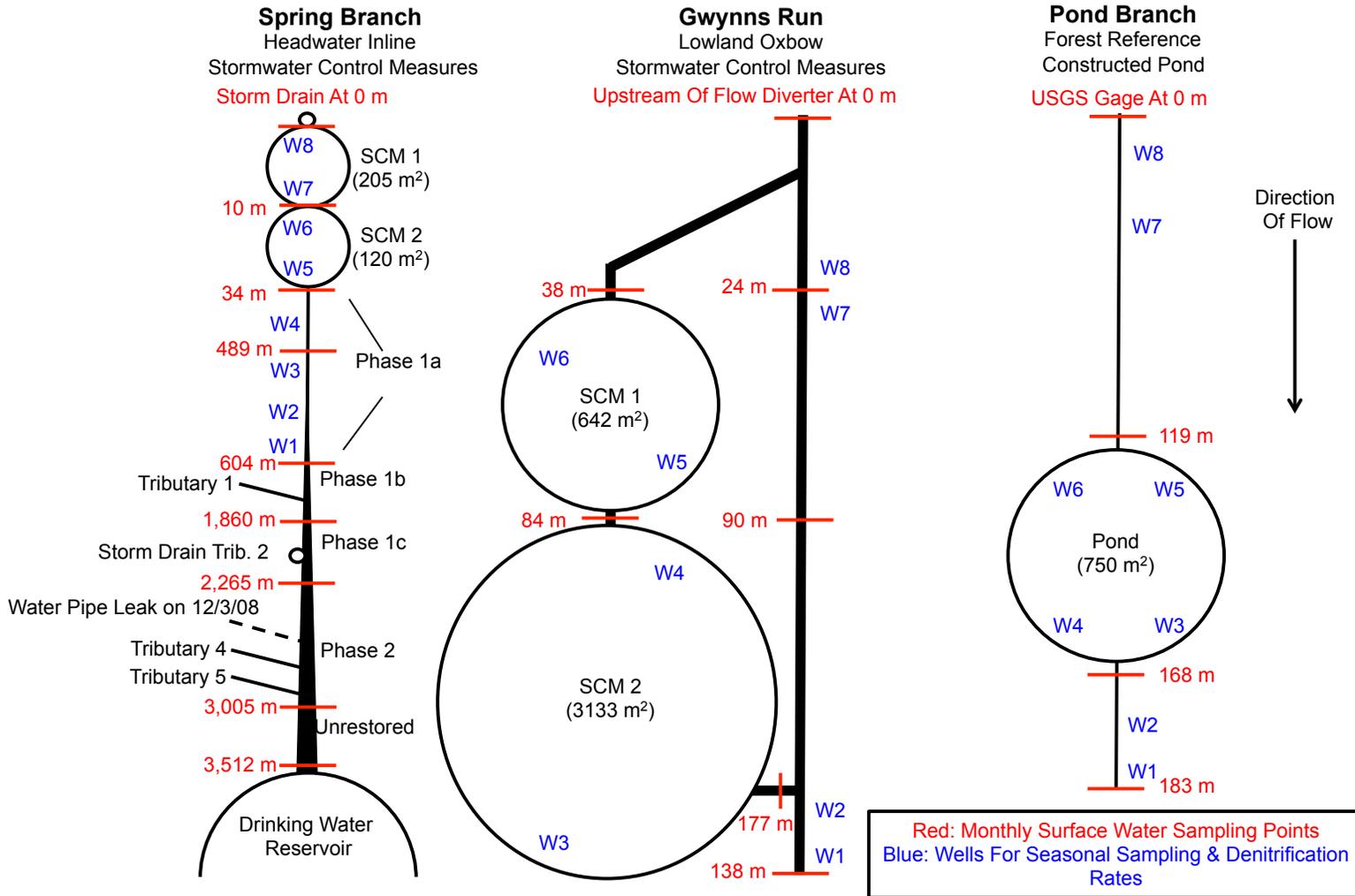


Fig. 3.3



Fig. 3.4

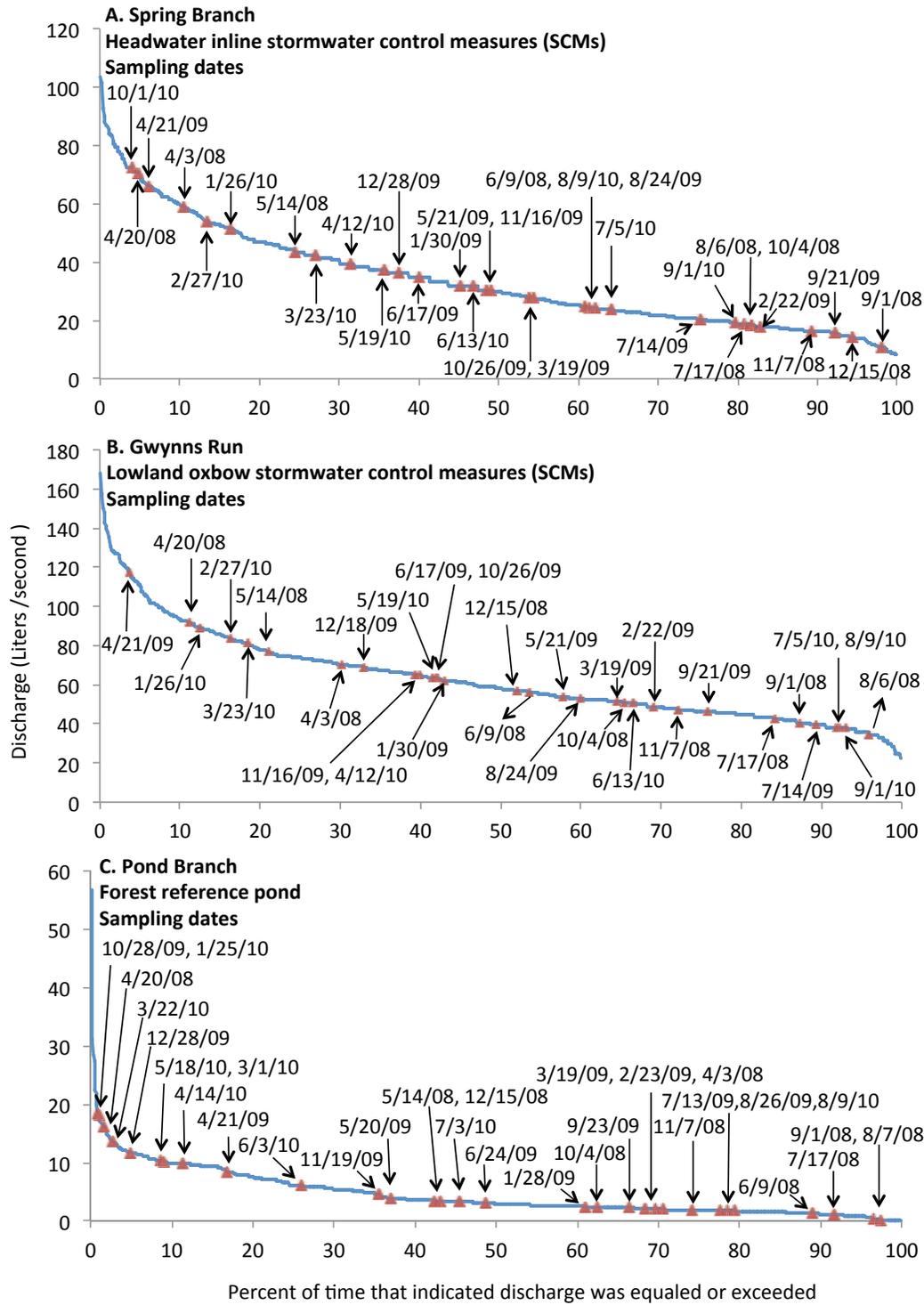


Fig. 3.5

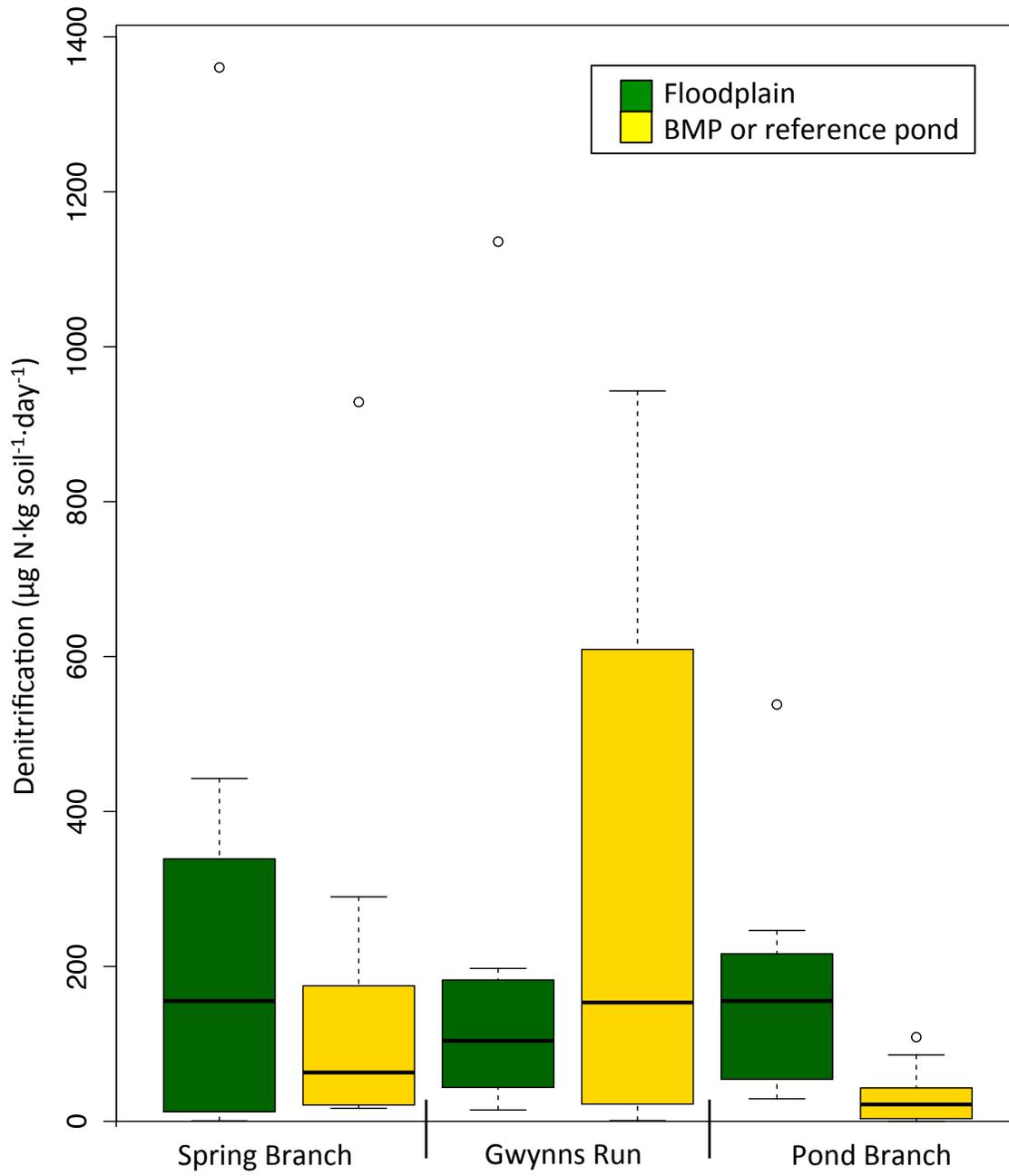


Fig. 3.6

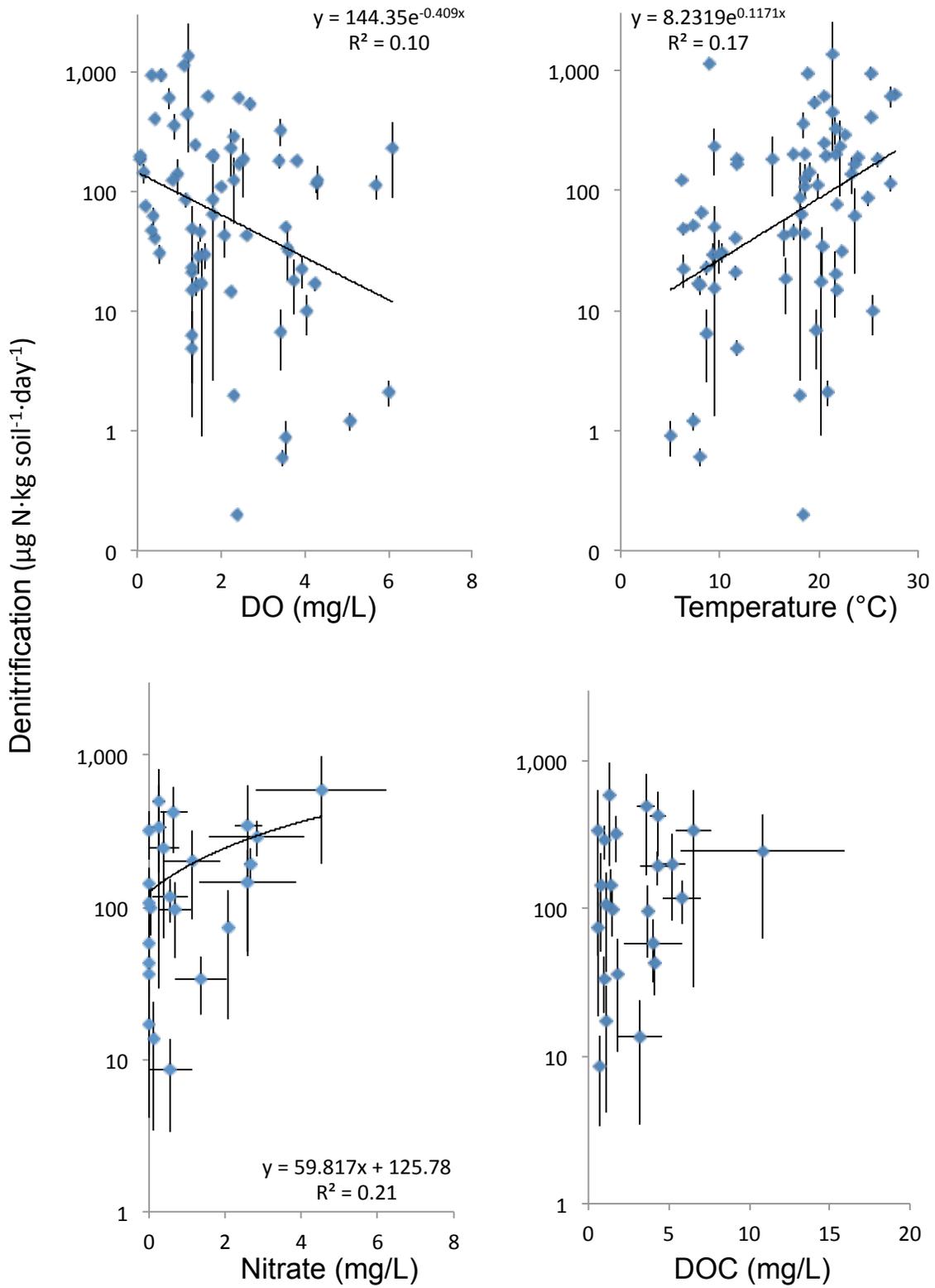


Fig. 3.7

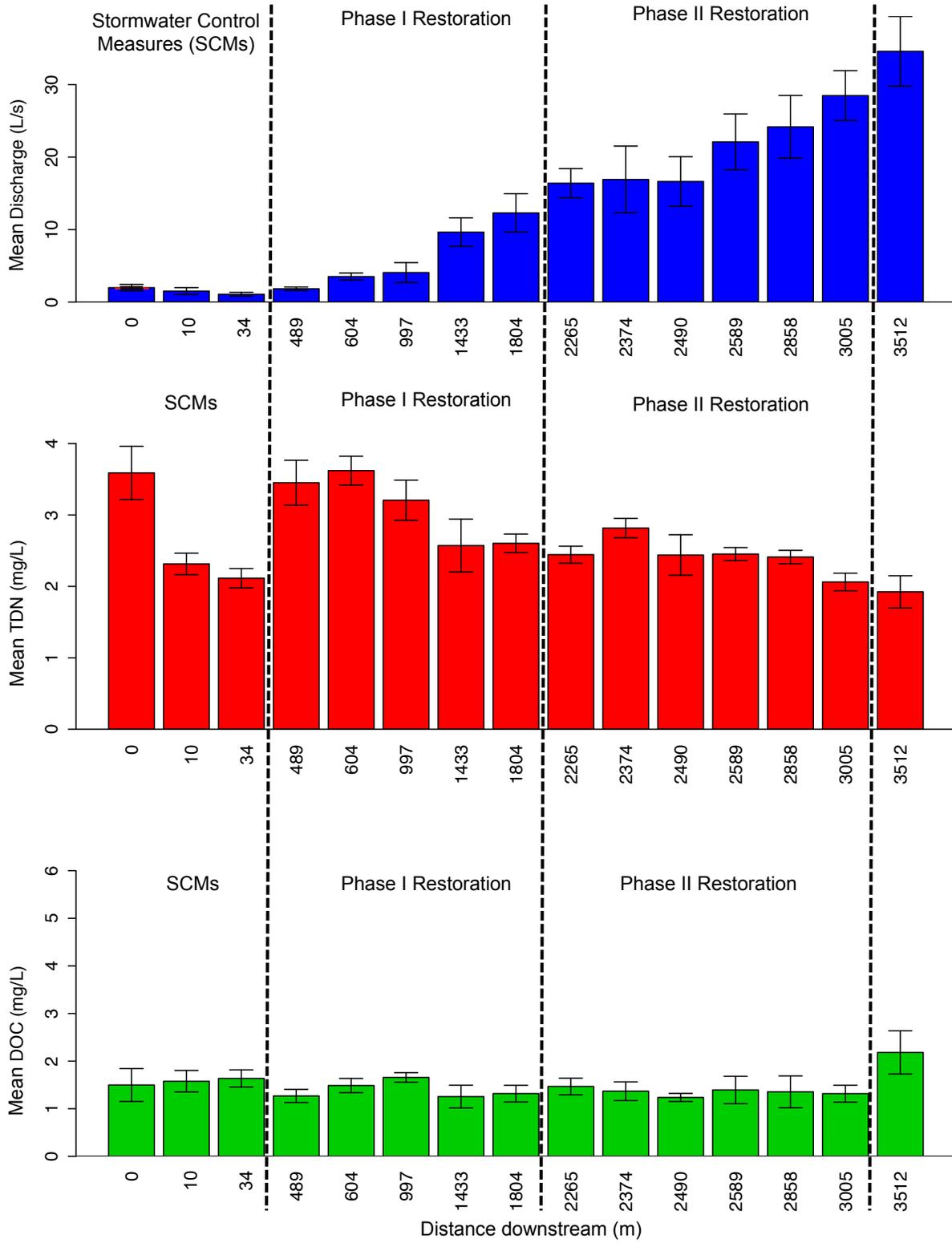


Fig. 3.8

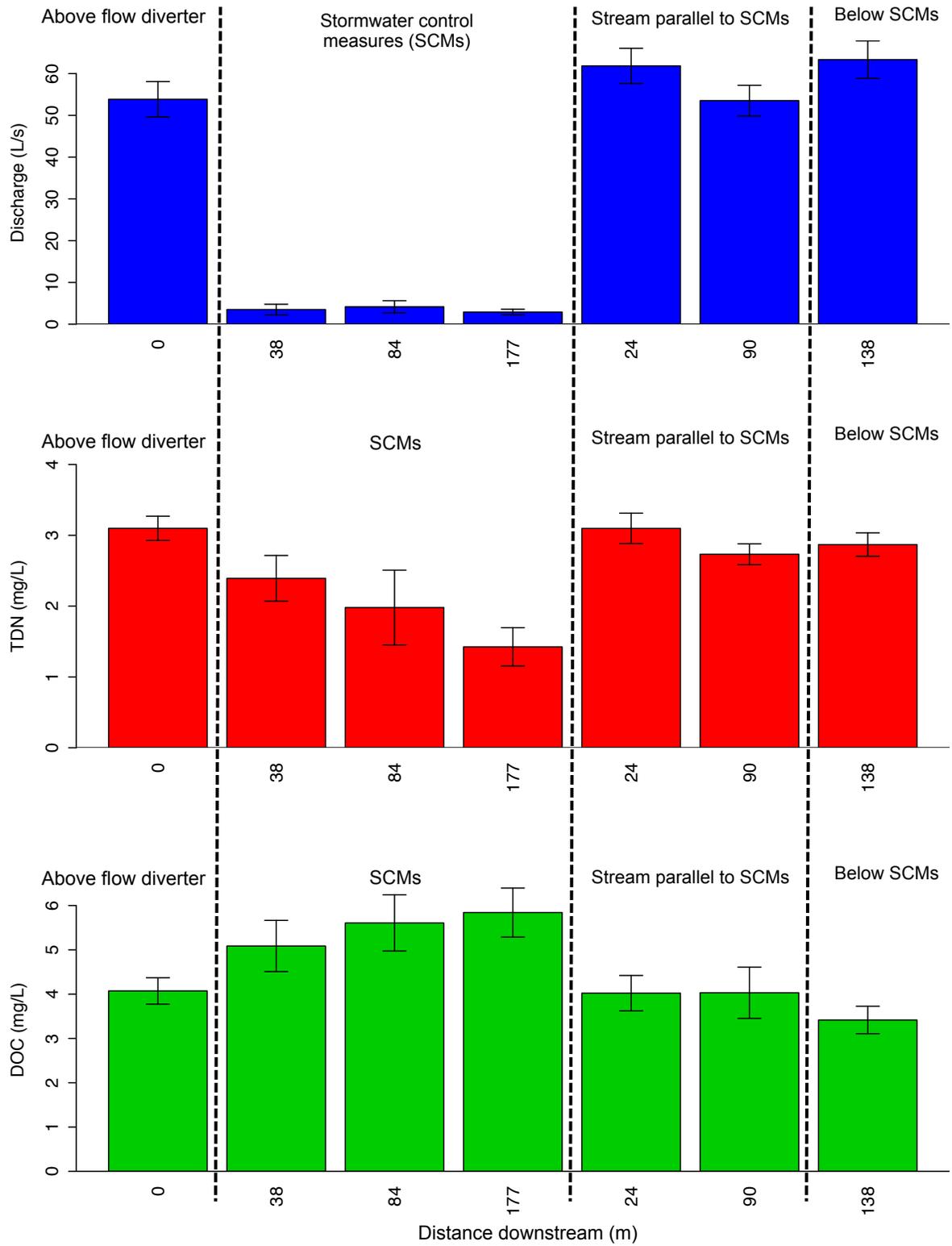


Fig 3.9

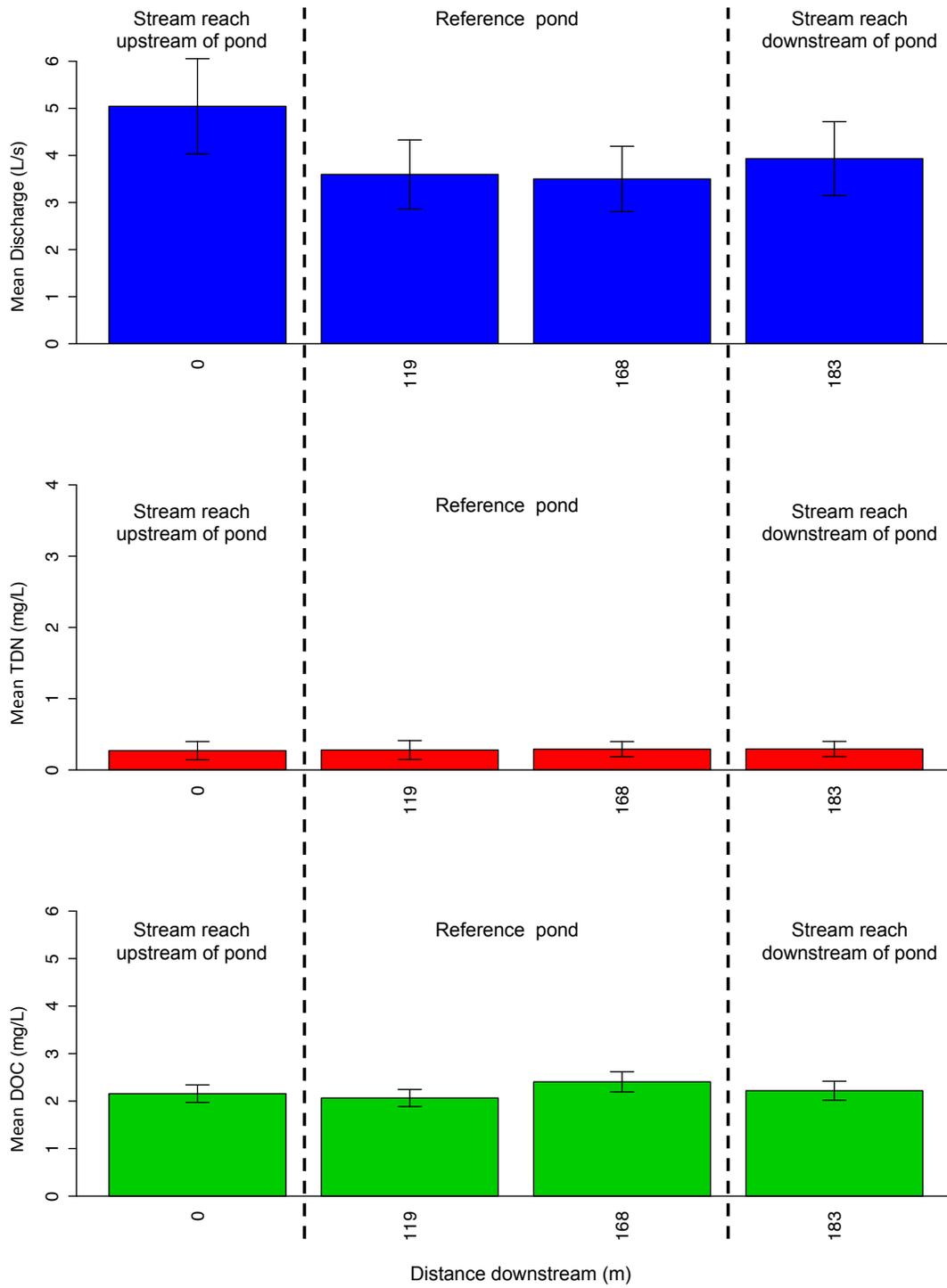


Fig. 3.10

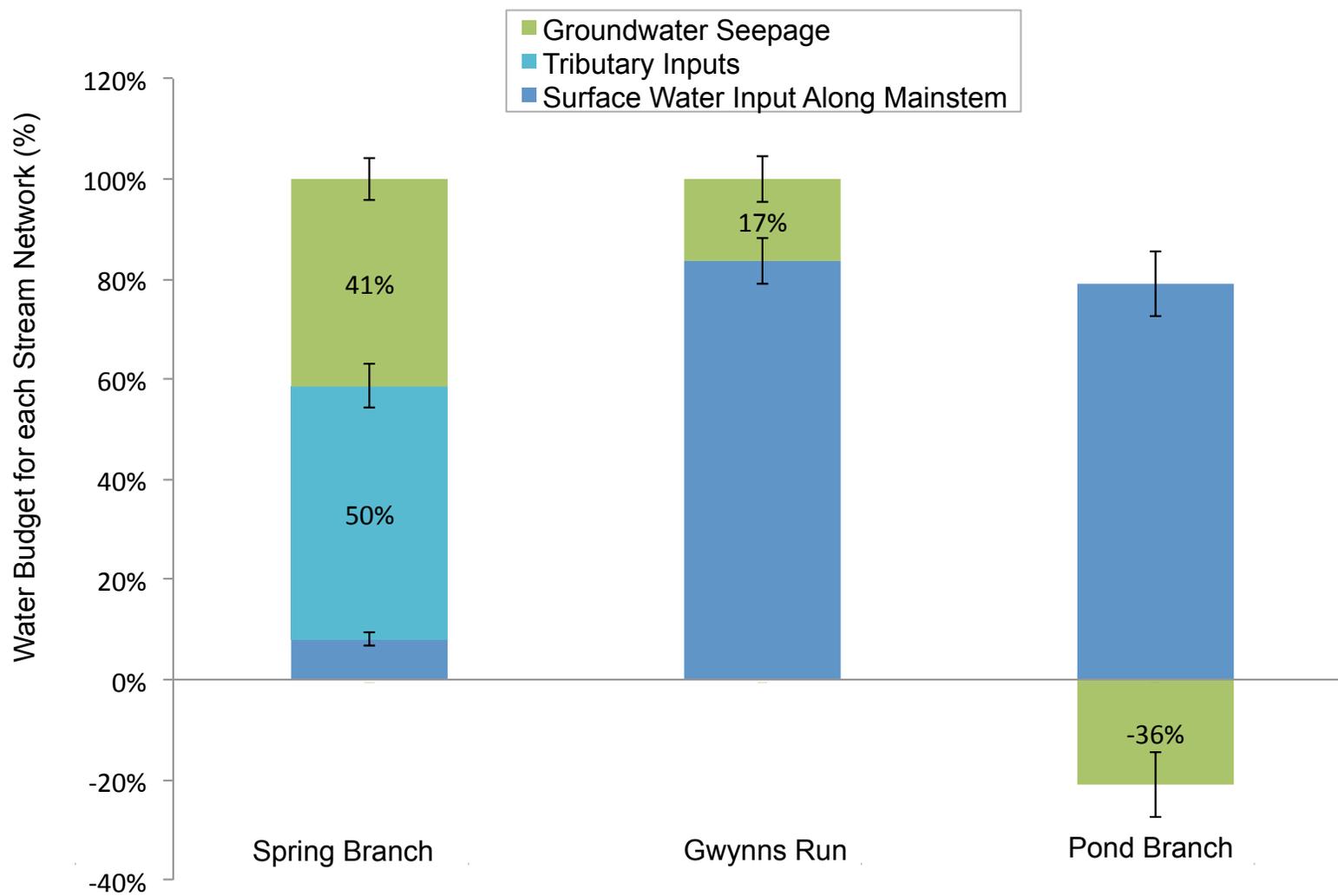


Fig. 3.11

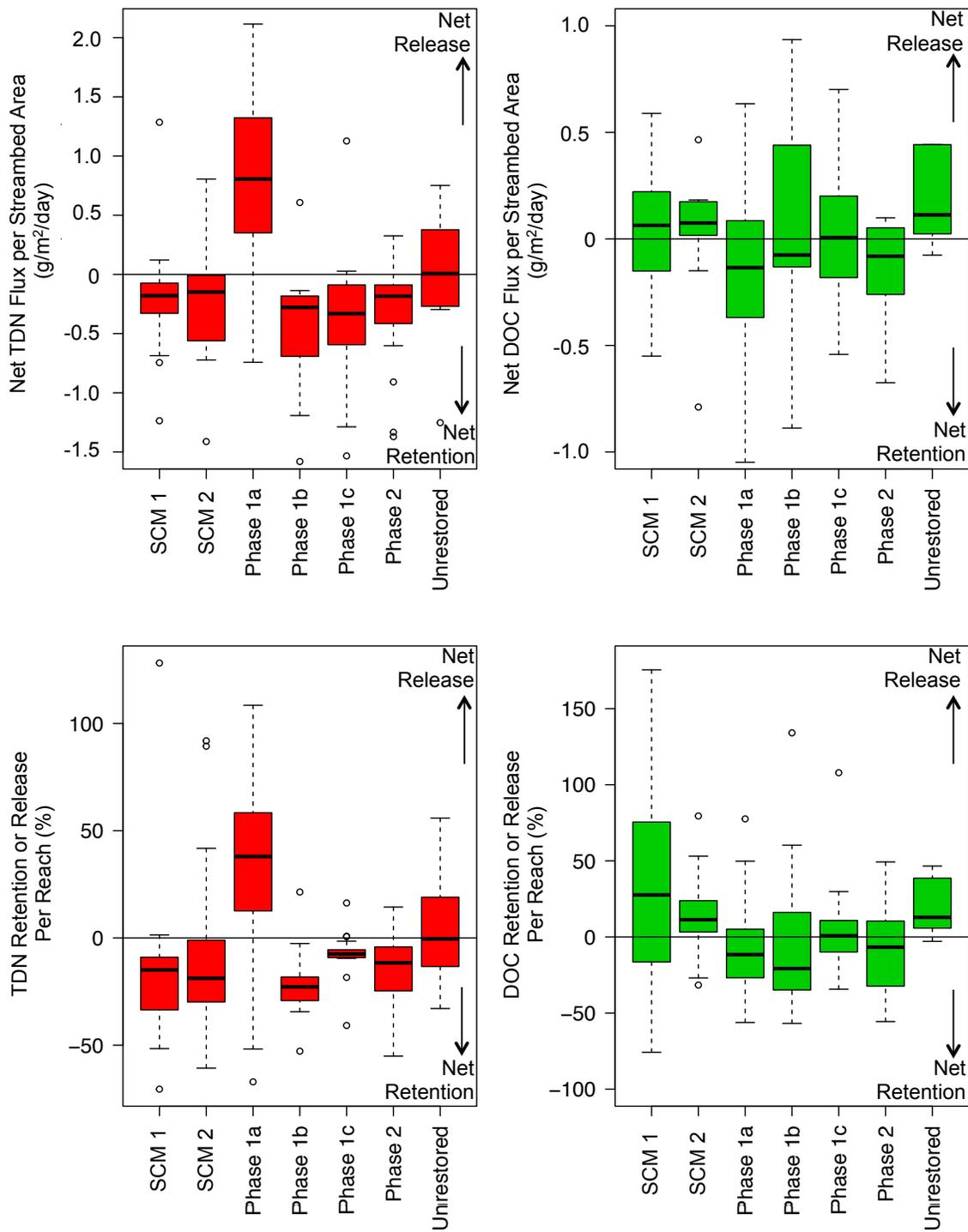


Fig. 3.12

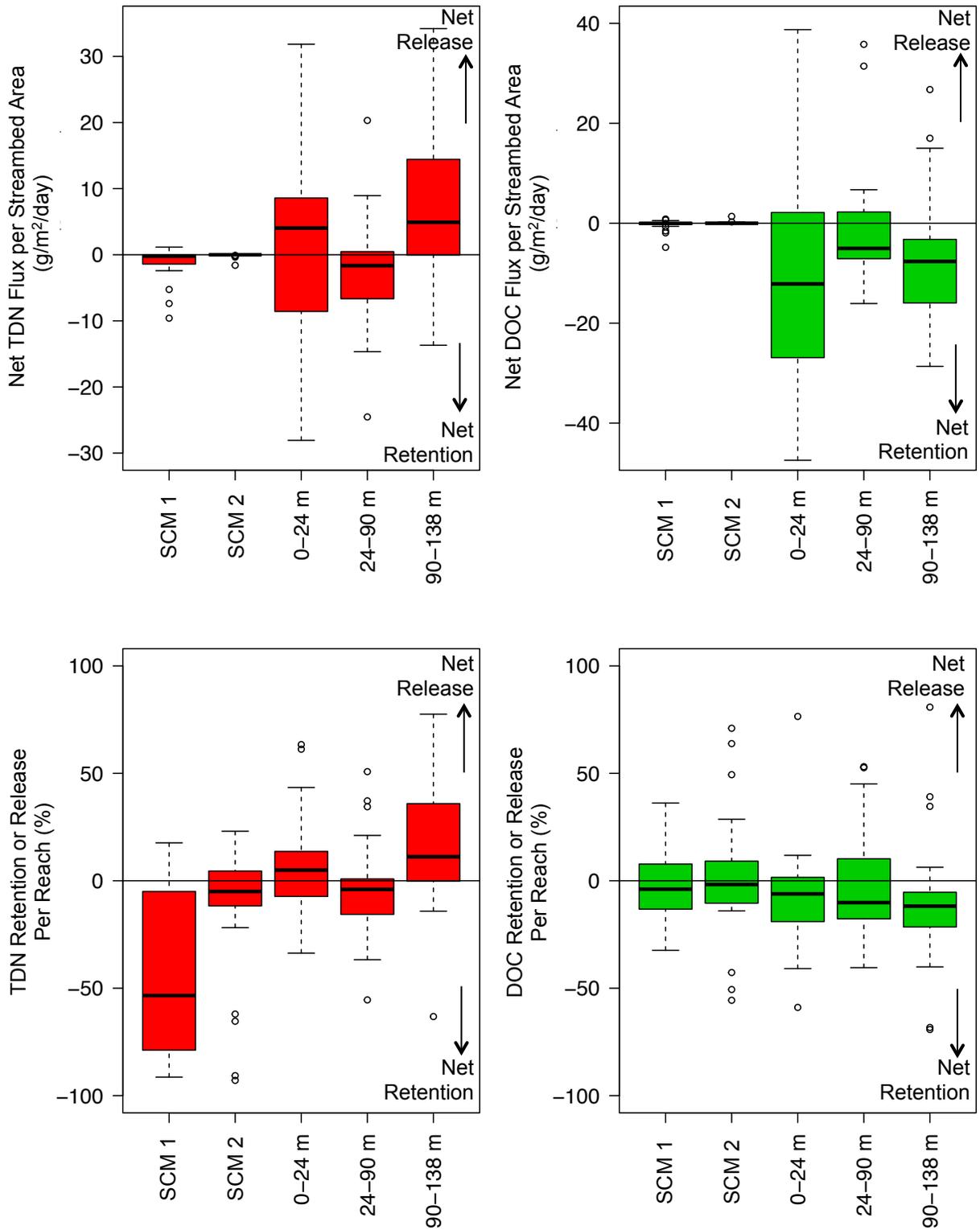


Fig. 3.13

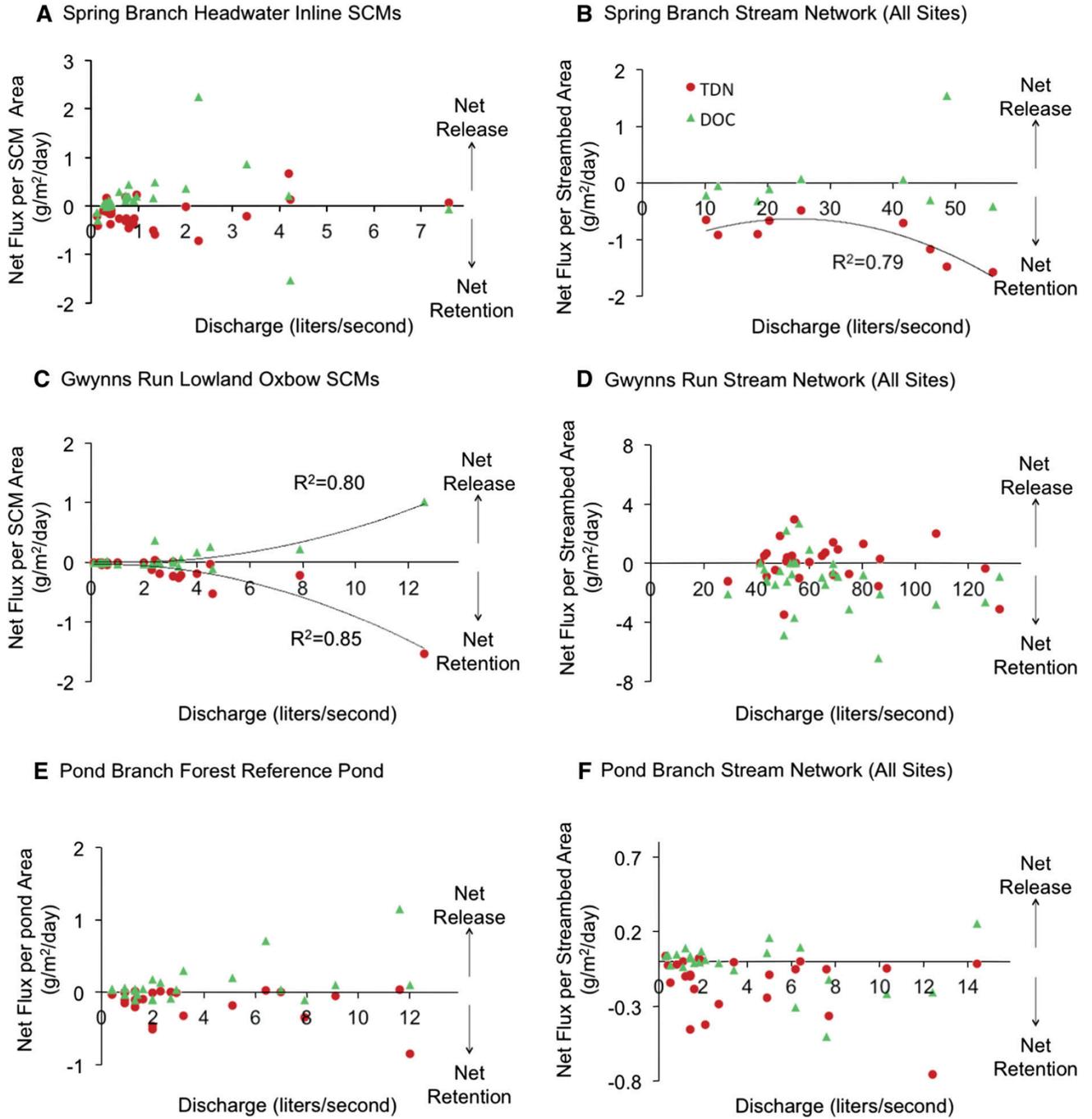
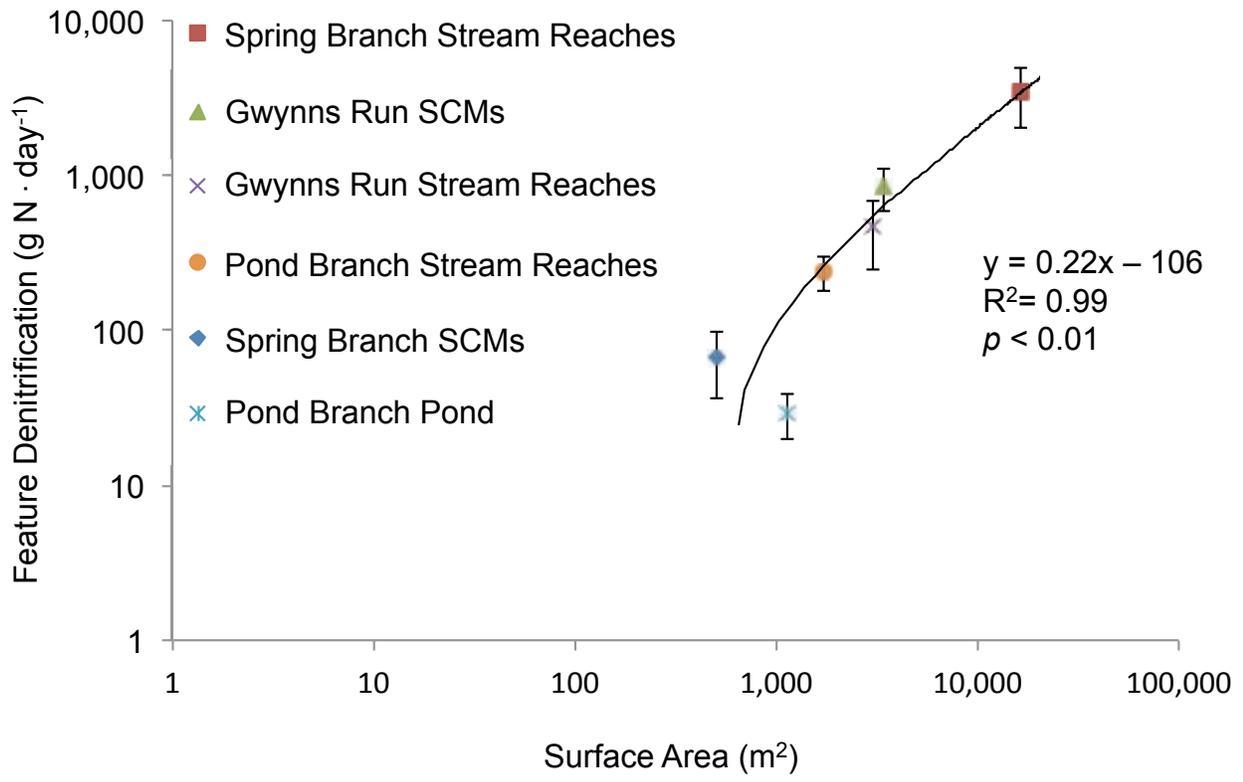


Fig. 3.14



Appendix C. Information on in-stream tracer studies, mass balance calculations, and continuous discharge.

## Methods

### In-stream Tracer Studies

Tracer studies were conducted by injecting a reactive nitrate tracer ( $\text{KNO}_3$ ) and a conservative tracer ( $\text{NaBr}$ ) at a known rate (100 ml/min) into the stream and sampling along the reach over a period of hours to days to determine residence time, transient storage, groundwater seepage, and nitrate uptake (Webster and Valett 2006; Klocker et al. 2009). At restored Spring Branch, a tracer experiment was conducted at the storm drain pipe upstream of the SCMs and samples were taken after the first SCM at 45 m, after the second SCM at fixed distances of 64 m, 78 m, 84 m, and 346 m downstream. The ambient concentrations of  $\text{NO}_3^-$  and  $\text{Br}^-$  were elevated by approximately 1 mg/L and 5 mg/L, respectively. At the Gwynns Run stormwater treatment facility, the 5-hour tracer study was conducted 5 m upstream of a trash diversion structure in a location where the flow was confined and well mixed. Samples were collected at 61 m, 80 m, 119 m, 138 m, and 155 m downstream. The ambient concentrations of nitrate and bromide were elevated approximately 0.3 mg/L and 5 mg/L, respectively. At forested Pond Branch, a 48 hour tracer study was conducted at the USGS gage and samples were taken at fixed distances of 30 m, 61 m, 91 m, 122 m, and 168 m downstream using ISCO automated samplers. The Pond Branch pond was located between 122 m and 168 m. The ambient concentrations of  $\text{NO}_3^-$  and  $\text{Br}^-$  were elevated by 0.1 mg/L and 1 mg/L, respectively.

Stream discharge was estimated using the following equation:

$$Q = \frac{Q_{\text{pump}} * (Br_{\text{injection}} - Br_{\text{background}})}{Br_{\text{plateau}} - Br_{\text{background}}}$$

where  $Q_{\text{pump}}$  was the release rate (100 ml/min);  $Br_{\text{injection}}$  was the bromide concentrations of injection solution (mg/L),  $Br_{\text{plateau}}$  was the plateau bromide concentrations (mg/L); and  $Br_{\text{background}}$  was the background (i.e., prerelease) bromide concentration.

Uptake length ( $S_w$ ) was estimated as follows; first calculated the normalized nitrate concentrations ( $NO_3^-N$ ):

$$NO_3^-N = \frac{NO_3^-_x - NO_3^-_{\text{background}}}{NO_3^-_{\text{injection}}}$$

where  $NO_3^-_x$  was the plateau nitrate concentrations at “x” distance downstream from the release site;  $NO_3^-_{\text{background}}$  was the background nitrate concentration; and  $NO_3^-_{\text{injection}}$  was the bromide concentrations of injection solution (mg/L). The normalized nitrate concentrations ( $NO_3^-N$ ) were plotted against distance downstream (x) and the slope of the regression line was an estimate of the fractional decline of nitrate ( $K_w$ ). Uptake length ( $S_w$ ) was calculated as the negative inverse of  $K_w$ .

## Results

Table 1. In-stream tracer study nitrate uptake metrics.

| Site                      | Kw<br>(1/m) | Sw<br>(m) | Vf<br>(mm/hr) | U<br>(g/m <sup>2</sup> /day) |
|---------------------------|-------------|-----------|---------------|------------------------------|
| Pond Branch stream 2009   | -0.0029     | 344.8     | 21.1          | 0.13                         |
| Pond Branch pond 2009     | -0.0029     | 344.8     | 0.3           | 0.00                         |
| Spring Branch stream 2009 | -0.0023     | 434.8     | 3.6           | 0.16                         |
| Spring Branch pond 2009   | -0.0023     | 434.8     | 1.3           | 0.07                         |
| Gwynns Run stream 2009    | -0.0041     | 243.9     | 146.7         | 6.95                         |
| Pond Branch stream 2011   | -0.0042     | 238.1     | 35.2          | 1.43                         |
| Gwynns Run stream 2011    | -0.0093     | 107.5     | 279.1         | 33.64                        |
| Spring Branch stream 2011 | -0.0227     | 44.1      | 6.7           | 1.27                         |

Table 2. In-stream tracer study anion concentrations (means  $\pm$  SE, N = 10). Nitrite was below detection limit at Spring Branch and Pond Branch.

| Site          | In-stream tracer study anion concentrations (mg/L) |                   |                 |                   |                 |                |
|---------------|--|-------------------|-----------------|-------------------|-----------------|----------------|
|               | Bromide  | Nitrate           | Nitrite         | Fluoride          | Chloride        | Sulfate        |
| Spring Branch | 0.15 $\pm$ 0.05                                    | 2.09 $\pm$ 0.33   | BQL             | 0.15 $\pm$ 0.01   | 102.1 $\pm$ 3.7 | 13.1 $\pm$ 0.6 |
| Gwynns Run    | 0.20 $\pm$ 0.06                                    | 1.76 $\pm$ 0.10   | 2.11 $\pm$ 0.71 | 0.32 $\pm$ 0.01   | 127.0 $\pm$ 4.7 | 41.2 $\pm$ 3.0 |
| Pond Branch   | 0.064 $\pm$ 0.011                                  | 0.076 $\pm$ 0.007 | BQL             | 0.086 $\pm$ 0.020 | 2.7 $\pm$ 0.3   | 1.6 $\pm$ 0.2  |

Table 3. Average reach-scale characteristics for mass balance studies.

| Stream   | Reach Name        | Distance<br>Downstream<br>(m) | Reach<br>Length<br>(m) | Average<br>Reach<br>Width<br>(m) | Reach<br>Area<br>(m <sup>2</sup> ) |       |
|--|-------------------|-------------------------------|------------------------|----------------------------------|------------------------------------|-------|
| (headwater<br>inline<br>stormwater<br>control<br>measures<br>(SCMs)) | Spring<br>Branch  | SCM 1                         | 0-10                   | 10                               | 20.5                               | 205   |
|  |                   | SCM 2                         | 10-34                  | 24                               | 5.0                                | 120   |
|  |                   | Restoration Phase 1a          | 34-604                 | 570                              | 0.4                                | 222   |
|  |                   | Restoration Phase 1b          | 604-1,860              | 1256                             | 1.2                                | 1482  |
|  |                   | Restoration Phase 1c          | 1,860-2,265            | 405                              | 2.0                                | 810   |
|  |                   | Restoration Phase 2           | 2,265-3,005            | 740                              | 4.0                                | 2960  |
|  | Unrestored        | 3,005-3,512                   | 507                    | 4.1                              | 2084                               |       |
| (lowland<br>oxbow<br>SCMs)   | Gwynns<br>Run     | SCM 1                         | 38-84                  | 46                               | 14.0                               | 642   |
|  |                   | SCM 2                         | 84-177                 | 93                               | 33.7                               | 3,133 |
|  |                   | Stream above SCMs             | 0-24                   | 24                               | 6.4                                | 154   |
|  |                   | Stream parallel SCMs          | 24-90                  | 66                               | 6.4                                | 422   |
|  | Stream below SCMs | 90-138                        | 48                     | 6.9                              | 331                                |       |
| (forest<br>reference<br>pond)  | Pond<br>Branch    | Stream above pond             | 0-119                  | 119                              | 0.6                                | 65    |
|  |                   | Reference Pond                | 119-168                | 49                               | 15.3                               | 750   |
|  |                   | Stream below pond             | 168-183                | 15                               | 0.6                                | 9     |

Table 4a-d. Mass balance transformation rates (g/m<sup>2</sup>/day; %) from Spring Branch, the site with headwater inline SCMs. Negative values represent net retention, positive values represent net release.

| Table 4a.                                  |        |        |             |               |                 |                 |                 |             |
|--|--------|--------|-------------|---------------|-----------------|-----------------|-----------------|-------------|
| Spring Branch<br>TDN g/m <sup>2</sup> /day | SCM 1  | SCM 2  | Phase<br>1a | Phase<br>1b   | Phase<br>1c     | Phase<br>2      | Un-<br>restored | Total       |
| Distance<br>downstream (m)                 | 0-10   | 10-34  | 34-604      | 604-<br>1,860 | 1,860-<br>2,265 | 2,265-<br>3,005 | 3,005-<br>3,512 | 0-<br>3,512 |
| Width (m)                                  | 20.5   | 5.0    | 0.4         | 1.2           | 2.0             | 4.0             | 4.1             | 2.2         |
| 3-Apr-08                                   | -0.09  | -0.19  | -0.60       | -             | -               | -               | -               | -           |
| 14-May-08                                  | -      | -      | 0.07        | -             | -               | -               | -               | -           |
| 9-Jun-08                                   | -0.24  | -0.30  | 1.23        | -             | -               | -               | -               | -           |
| 23-Jun-08                                  | -      | -      | 1.42        | -0.34         | -0.60           | -1.93           | -0.25           | -0.89       |
| 17-Jul-08                                  | -0.18  | -0.14  | 1.02        | -             | -               | -               | -               | -           |
| 7-Aug-08                                   | -0.22  | -0.46  | 0.18        | -             | -               | -               | -               | -           |
| 1-Sep-08                                   | -0.74  | -0.04  | 0.66        | -             | -               | -               | -               | -           |
| 15-Sep-08                                  | -      | -      | 1.76        | -0.33         | -0.69           | -1.36           | -0.24           | -0.67       |
| 4-Oct-08                                   | -0.27  | 0.00   | -           | -             | -1.55           | -               | -               | -           |
| 8-Oct-08                                   | -      | -      | 3.49        | -0.36         | -0.32           | -1.34           | 0.09            | -0.48       |
| 3-Nov-08                                   | -      | -      | -           | -             | 0.16            | -0.91           | -               | -           |
| 7-Nov-08                                   | -0.07  | -0.14  | 0.79        | -             | -               | -1.46           | -               | -           |
| 3-Dec-08                                   | -0.22  | -      | -           | -             | -1.21           | -7.14           | -               | -           |
| 15-Dec-08                                  | -0.07  | -0.13  | 1.86        | -             | -               | -               | -               | -           |
| 9-Jan-09                                   | -      | -      | -           | -             | -1.19           | -1.55           | -               | -           |
| 28-Jan-09                                  | -0.65  | 0.17   | 2.11        | -             | -               | -               | -               | -           |
| 11-Feb-09                                  | -      | -      | 0.88        | -0.21         | -2.61           | -2.55           | -               | -           |
| 23-Feb-09                                  | -0.02  | 0.47   | 0.41        | -             | -               | -               | -               | -           |
| 11-Mar-09                                  | -0.17  | 1.47   | -0.40       | -             | -               | -               | -               | -           |
| 19-Mar-09                                  | -0.07  | -0.58  | 1.33        | -             | -               | -               | -               | -           |
| 9-Apr-09                                   | -0.11  | 0.97   | -           | -             | -               | -               | -               | -           |
| 21-Apr-09                                  | -0.11  | -1.38  | 0.05        | -             | -               | -               | -               | -           |
| 6-May-09                                   | -      | -      | 1.29        | -0.78         | -1.95           | -2.54           | -               | -           |
| 20-May-09                                  | -0.36  | -0.41  | 0.37        | -             | -               | -               | -               | -           |
| 24-Jun-09                                  | -0.04  | -0.02  | 1.29        | -0.35         | -0.55           | -2.03           | -               | -           |
| 26-Aug-09                                  | -0.45  | -0.05  | 0.88        | -0.19         | -0.49           | -1.85           | -0.54           | -0.91       |
| 23-Sep-09                                  | -0.05  | -0.16  | 0.71        | -0.26         | -0.57           | -1.62           | 0.20            | -0.65       |
| 28-Oct-09                                  | -0.16  | -1.67  | 0.82        | -             | -               | -2.31           | -               | -           |
| 20-Nov-09                                  | -0.29  | -0.72  | 0.10        | -1.16         | -1.39           | -2.07           | -1.21           | -1.47       |
| 28-Dec-09                                  | 0.12   | 0.00   | 0.70        | -0.03         | -6.98           | -2.38           | 0.08            | -1.57       |
| 27-Jan-10                                  | -      | -2.42  | -           | -             | -2.06           | -2.81           | 0.38            | -           |
| 17-Feb-10                                  | 1.29   | 0.09   | -3.33       | 0.63          | -2.59           | -2.38           | -               | -           |
| 24-Mar-10                                  | -0.69  | -0.64  | 4.32        | -0.30         | -3.17           | -2.14           | -0.29           | -1.16       |
| 15-Apr-10                                  | -0.13  | 0.81   | 2.28        | -0.91         | -0.17           | -2.14           | 0.81            | -0.70       |
| <i>Mean</i>                                | -0.16  | -0.22  | 0.92        | -0.35         | -1.55           | -2.24           | -0.10           | -0.94       |
| <i>(± SE)</i>                              | ± 0.07 | ± 0.16 | ± 0.26      | ± 0.12        | ± 0.39          | ± 0.30          | ± 0.17          | ± 0.13      |

Table 4b. Mass balance transformation rates for TDN (%) from Spring Branch, the site with headwater inline SCMs. Negative values represent net retention, positive values represent net release.

| Table 4b.<br>Spring Branch<br>TDN % | SCM<br>1 | SCM<br>2 | Phase<br>1a | Phase<br>1b   | Phase<br>1c     | Phase<br>2      | Un-<br>restored | Total       |
|-------------------------------------|----------|----------|-------------|---------------|-----------------|-----------------|-----------------|-------------|
| Distance<br>downstream (m)          | 0-10     | 10-34    | 34-604      | 604-<br>1,860 | 1,860-<br>2,265 | 2,265-<br>3,005 | 3,005-<br>3,512 | 0-<br>3,512 |
| Width (m)                           | 20.5     | 5.0      | 0.4         | 1.2           | 2.0             | 4.0             | 4.1             | 2.2         |
| 3-Apr-08                            | -11%     | -21%     | -16%        | -             | -               | -               | -               | -           |
| 14-May-08                           | -        | -        | 3%          | -             | -               | -               | -               | -           |
| 9-Jun-08                            | -26%     | -22%     | 47%         | -             | -               | -               | -               | -           |
| 23-Jun-08                           | -        | -        | 57%         | -30%          | -20%            | -68%            | -14%            | -69%        |
| 17-Jul-08                           | -32%     | -18%     | 64%         | -             | -               | -               | -               | -           |
| 7-Aug-08                            | -50%     | -52%     | 16%         | -             | -               | -               | -               | -           |
| 1-Sep-08                            | -70%     | -15%     | 56%         | -             | -               | -               | -               | -           |
| 15-Sep-08                           | -        | -        | 66%         | -39%          | -18%            | -55%            | -13%            | -61%        |
| 4-Oct-08                            | -50%     | 0%       | -           | -             | -39%            | -               | -               | -           |
| 8-Oct-08                            | -        | -        | 116%        | -28%          | -8%             | -44%            | 3%              | -38%        |
| 3-Nov-08                            | -        | -        | -           | -             | 25%             | -84%            | -               | -           |
| 7-Nov-08                            | -18%     | -20%     | 43%         | -             | -               | -65%            | -               | -           |
| 3-Dec-08                            | -8%      | -        | -           | -             | -25%            | -82%            | -               | -           |
| 15-Dec-08                           | -15%     | -16%     | 36%         | -             | -               | -               | -               | -           |
| 9-Jan-09                            | -        | -        | -           | -             | -17%            | -51%            | -               | -           |
| 28-Jan-09                           | -32%     | 4%       | 77%         | -             | -               | -               | -               | -           |
| 11-Feb-09                           | -        | -        | 42%         | -24%          | -65%            | -61%            | -               | -           |
| 23-Feb-09                           | -6%      | 91%      | 21%         | -             | -               | -               | -               | -           |
| 11-Mar-09                           | -4%      | 37%      | -8%         | -             | -               | -               | -               | -           |
| 19-Mar-09                           | -14%     | -34%     | 79%         | -             | -               | -               | -               | -           |
| 9-Apr-09                            | -3%      | 14%      | -           | -             | -               | -               | -               | -           |
| 21-Apr-09                           | -10%     | -60%     | 1%          | -             | -               | -               | -               | -           |
| 6-May-09                            | -        | -        | 36%         | -23%          | -27%            | -47%            | -               | -           |
| 20-May-09                           | -34%     | -26%     | 17%         | -             | -               | -               | -               | -           |
| 24-Jun-09                           | -7%      | -2%      | 63%         | -31%          | -17%            | -64%            | -               | -           |
| 26-Aug-09                           | -49%     | -12%     | 60%         | -24%          | -31%            | -78%            | -54%            | -88%        |
| 23-Sep-09                           | -10%     | -20%     | 35%         | -35%          | -27%            | -58%            | 12%             | -71%        |
| 28-Oct-09                           | -7%      | -32%     | 18%         | -             | -               | -44%            | -               | -           |
| 20-Nov-09                           | -22%     | -40%     | 2%          | -34%          | -25%            | -54%            | -32%            | -68%        |
| 28-Dec-09                           | 1%       | 0%       | 7%          | 0%            | -34%            | -36%            | 1%              | -53%        |
| 27-Jan-10                           | -        | -38%     | -           | -             | -57%            | -72%            | 24%             | -           |
| 17-Feb-10                           | 128%     | 3%       | -50%        | 22%           | -36%            | -68%            | -               | -           |
| 24-Mar-10                           | -12%     | -12%     | 64%         | -8%           | -28%            | -37%            | -5%             | -46%        |
| 15-Apr-10                           | -10%     | 42%      | 42%         | -25%          | -2%             | -48%            | 17%             | -33%        |
| <i>Mean</i>                         | -15%     | -10%     | 35%         | -21%          | -25%            | -59%            | -6%             | -59%        |
| <i>(± SE)</i>                       | ± 7%     | ± 6%     | ± 7%        | ± 5%          | ± 5%            | ± 3%            | ± 7%            | ± 6%        |

Table 4c. Mass balance transformation rates for DOC ( $\text{g}/\text{m}^2/\text{day}$ ) from Spring Branch, the site with headwater inline SCMs. Negative values represent net retention, positive values represent net release.

| Table 4c.<br>Spring Branch<br>DOC $\text{g}/\text{m}^2/\text{day}$ | SCM<br>1   | SCM<br>2   | Phase<br>1a | Phase<br>1b   | Phase<br>1c     | Phase<br>2      | Un-<br>restored | Total       |
|--|------------|------------|-------------|---------------|-----------------|-----------------|-----------------|-------------|
| Distance<br>downstream (m)   | 0-10       | 10-34      | 34-604      | 604-<br>1,860 | 1,860-<br>2,265 | 2,265-<br>3,005 | 3,005-<br>3,512 | 0-<br>3,512 |
| Width (m)  | 20.5       | 5.0        | 0.4         | 1.2           | 2.0             | 4.0             | 4.1             | 2.2         |
| 3-Apr-08   | 0.24       | -0.15      | -0.01       | -             | -               | -               | -               | -           |
| 14-May-08  | -          | -          | 0.22        | -             | -               | -               | -               | -           |
| 9-Jun-08   | 0.14       | 0.19       | 0.29        | -             | -               | -               | -               | -           |
| 23-Jun-08  | -          | -          | 0.41        | -0.03         | 0.22            | -0.99           | 0.09            | -0.32       |
| 17-Jul-08  | 0.06       | 0.09       | 0.10        | -             | -               | -               | -               | -           |
| 7-Aug-08   | 0.09       | 0.10       | -0.07       | -             | -               | -               | -               | -           |
| 1-Sep-08   | -0.55      | -0.01      | -0.06       | -             | -               | -               | -               | -           |
| 15-Sep-08  | -          | -          | -0.21       | 0.01          | 0.44            | -0.50           | 0.15            | -0.10       |
| 4-Oct-08   | -0.02      | 0.03       | -           | -             | -0.62           | -               | -               | -           |
| 8-Oct-08   | -          | -          | 1.07        | -0.15         | -0.05           | -0.16           | 0.52            | 0.08        |
| 3-Nov-08   | -          | -          | -           | -             | 0.11            | -0.23           | -               | -           |
| 7-Nov-08   | 0.14       | 0.07       | 0.01        | -             | -               | -0.31           | -               | -           |
| 3-Dec-08   | 0.05       | -          | -           | -             | -0.10           | -2.99           | -               | -           |
| 15-Dec-08  | 0.01       | 0.10       | 0.07        | -             | -               | -               | -               | -           |
| 9-Jan-09   | -          | -          | -           | -             | -0.28           | -0.34           | -               | -           |
| 28-Jan-09  | -3.00      | 4.92       | -1.82       | -             | -               | -               | -               | -           |
| 11-Feb-09  | -          | -          | 0.10        | -0.03         | -0.75           | -0.72           | -               | -           |
| 23-Feb-09  | 0.02       | -0.10      | 0.00        | -             | -               | -               | -               | -           |
| 11-Mar-09  | 0.07       | 0.73       | -0.22       | -             | -               | -               | -               | -           |
| 19-Mar-09  | -0.33      | 1.30       | -0.68       | -             | -               | -               | -               | -           |
| 9-Apr-09   | 0.08       | 1.50       | -           | -             | -               | -               | -               | -           |
| 21-Apr-09  | 0.63       | 0.23       | 1.66        | -             | -               | -               | -               | -           |
| 6-May-09   | -          | -          | 0.62        | 1.30          | -0.78           | 0.99            | -               | -           |
| 20-May-09  | 0.09       | 0.16       | 2.01        | -             | -               | -               | -               | -           |
| 24-Jun-09  | 0.11       | 0.02       | 0.14        | -0.16         | -0.10           | -0.29           | -               | -           |
| 26-Aug-09  | -0.31      | 0.02       | -0.04       | -0.11         | -0.09           | -0.75           | 1.03            | -0.05       |
| 23-Sep-09  | 0.03       | 0.02       | -0.07       | -0.09         | -0.19           | -0.13           | -0.47           | -0.21       |
| 28-Oct-09  | 1.82       | 2.97       | 1.50        | -             | -               | 1.35            | -               | -           |
| 20-Nov-09  | 0.42       | 0.46       | 2.90        | 2.95          | -1.77           | 0.92            | 2.73            | 1.54        |
| 28-Dec-09  | -0.27      | 0.18       | -0.23       | 1.01          | -2.46           | -1.01           | 0.14            | -0.42       |
| 27-Jan-10  | -          | -0.79      | -           | -             | -0.64           | -1.09           | 7.27            | -           |
| 17-Feb-10  | 0.47       | -0.06      | -1.12       | 0.66          | -1.75           | -1.07           | -               | -           |
| 24-Mar-10  | 0.28       | 0.15       | 0.91        | 0.41          | -0.84           | -0.85           | -0.05           | -0.31       |
| 15-Apr-10  | 0.21       | 0.18       | 0.63        | -0.15         | 0.17            | -0.17           | 0.42            | 0.06        |
| <i>Mean</i>  | 0.02       | 0.49       | 0.29        | 0.43 $\pm$    | -0.53           | -0.44           | 1.18            | 0.03        |
| <i>(<math>\pm</math> SE)</i>                                       | $\pm 0.15$ | $\pm 0.23$ | $\pm 0.18$  | $0.25$        | $\pm 0.18$      | $\pm 0.21$      | $\pm 0.73$      | $\pm 0.20$  |

Table 4d. Mass balance transformation rates for DOC (%) from Spring Branch, the site with headwater inline SCMs. Negative values represent net retention, positive values represent net release.

| Table 4d.<br>Spring Branch<br>DOC % | SCM<br>1 | SCM<br>2 | Phase<br>1a | Phase<br>1b   | Phase<br>1c     | Phase<br>2      | Un-<br>restored | Total       |
|-------------------------------------|----------|----------|-------------|---------------|-----------------|-----------------|-----------------|-------------|
| Distance<br>downstream (m)          | 0-10     | 10-34    | 34-<br>604  | 604-<br>1,860 | 1,860-<br>2,265 | 2,265-<br>3,005 | 3,005-<br>3,512 | 0-<br>3,512 |
| Width (m)                           | 20.5     | 5.0      | 0.4         | 1.2           | 2.0             | 4.0             | 4.1             | 2.2         |
| 3-Apr-08                            | 108%     | -21%     | -1%         | -             | -               | -               | -               | -           |
| 14-May-08                           | -        | -        | 17%         | -             | -               | -               | -               | -           |
| 9-Jun-08                            | 64%      | 27%      | 25%         | -             | -               | -               | -               | -           |
| 23-Jun-08                           | -        | -        | 39%         | -7%           | 18%             | -66%            | 11%             | -55%        |
| 17-Jul-08                           | 49%      | 23%      | 15%         | -             | -               | -               | -               | -           |
| 7-Aug-08                            | 54%      | 15%      | -10%        | -             | -               | -               | -               | -           |
| 1-Sep-08                            | -75%     | -8%      | -15%        | -             | -               | -               | -               | -           |
| 15-Sep-08                           | -        | -        | -18%        | 3%            | 32%             | -59%            | 24%             | -34%        |
| 4-Oct-08                            | -31%     | 29%      | -           | -             | -51%            | -               | -               | -           |
| 8-Oct-08                            | -        | -        | 102%        | -32%          | -4%             | -20%            | 48%             | 23%         |
| 3-Nov-08                            | -        | -        | -           | -             | 56%             | -77%            | -               | -           |
| 7-Nov-08                            | 201%     | 17%      | 1%          | -             | -               | -39%            | -               | -           |
| 3-Dec-08                            | 7%       | -        | -           | -             | -5%             | -74%            | -               | -           |
| 15-Dec-08                           | 15%      | 48%      | 4%          | -             | -               | -               | -               | -           |
| 9-Jan-09                            | -        | -        | -           | -             | -11%            | -36%            | -               | -           |
| 28-Jan-09                           | -35%     | 81%      | -31%        | -             | -               | -               | -               | -           |
| 11-Feb-09                           | -        | -        | 12%         | -10%          | -57%            | -52%            | -               | -           |
| 23-Feb-09                           | 13%      | -32%     | 1%          | -             | -               | -               | -               | -           |
| 11-Mar-09                           | 8%       | 49%      | -12%        | -             | -               | -               | -               | -           |
| 19-Mar-09                           | -28%     | 98%      | -38%        | -             | -               | -               | -               | -           |
| 9-Apr-09                            | 14%      | 62%      | -           | -             | -               | -               | -               | -           |
| 21-Apr-09                           | 132%     | 11%      | 64%         | -             | -               | -               | -               | -           |
| 6-May-09                            | -        | -        | 38%         | 92%           | -12%            | 35%             | -               | -           |
| 20-May-09                           | 35%      | 23%      | 201%        | -             | -               | -               | -               | -           |
| 24-Jun-09                           | 71%      | 5%       | 19%         | -33%          | -8%             | -29%            | -               | -           |
| 26-Aug-09                           | -63%     | 19%      | -8%         | -41%          | -24%            | -78%            | 263%            | -11%        |
| 23-Sep-09                           | 32%      | 9%       | -9%         | -36%          | -28%            | -9%             | -24%            | -64%        |
| 28-Oct-09                           | 200%     | 58%      | 28%         | -             | -               | 27%             | -               | -           |
| 20-Nov-09                           | 74%      | 27%      | 107%        | 164%          | -18%            | 27%             | 41%             | 166%        |
| 28-Dec-09                           | -4%      | 2%       | -5%         | 35%           | -25%            | -29%            | 4%              | -38%        |
| 27-Jan-10                           | -        | -27%     | -           | -             | -40%            | -57%            | 618%            | -           |
| 17-Feb-10                           | 78%      | -3%      | -47%        | 64%           | -51%            | -66%            | -               | -           |
| 24-Mar-10                           | 27%      | 9%       | 36%         | 32%           | -17%            | -32%            | -2%             | -31%        |
| 15-Apr-10                           | 87%      | 24%      | 34%         | -12%          | 7%              | -12%            | 18%             | 9%          |
| <i>Mean</i>                         | 41% ±    | 22% ±    | 20% ±       | 17% ±         | -13%            | -34%            | 100% ±          | -4% ±       |
| <i>(± SE)</i>                       | 14%      | 6%       | 10%         | 17%           | ± 7%            | ± 8%            | 63%             | 23%         |

Table 5a-d. Mass balance transformation rates (g/m<sup>2</sup>/day; %) from Gwynns Run, the site with lowland oxbow SCMs. Negative values represent net retention, positive values represent net release.

| Table 5a.<br>Gwynns Run<br>TDN g/m <sup>2</sup> /day | SCM<br>1     | SCM<br>2      | Stream<br>above<br>SCMs | Stream<br>parallel<br>SCMs | Stream<br>below<br>SCMs | Total        |
|--|--------------|---------------|-------------------------|----------------------------|-------------------------|--------------|
| Distance<br>downstream (m)                           | 38-84        | 84-177        | 0-24                    | 24-90                      | 90-138                  | 0-138        |
| Reach width (m)                                      | 14           | 33.7          | 6.4                     | 6.4                        | 6.9                     | 33.9         |
| 3-Apr-08   | -0.21        | -             | 31.30                   | 12.01                      | -14.68                  | 0.65         |
| 14-May-08  | 1.16         | -             | -22.96                  | 8.74                       | 20.24                   | 1.32         |
| 9-Jun-08   | -7.26        | -0.09         | 51.79                   | 4.73                       | 0.52                    | 2.95         |
| 17-Jul-08  | -9.43        | -0.05         | -18.24                  | 6.89                       | -0.81                   | -0.74        |
| 6-Aug-08   | -0.08        | -0.02         | 82.32                   | 28.29                      | -44.77                  | 1.40         |
| 1-Sep-08   | -0.29        | -0.20         | -21.26                  | -0.59                      | 5.26                    | -0.46        |
| 4-Oct-08   | -2.35        | 0.00          | 3.75                    | 4.53                       | 8.91                    | 0.92         |
| 7-Nov-08   | -            | -0.05         | 7.06                    | -0.98                      | 0.02                    | 0.12         |
| 15-Dec-08  | -1.41        | -0.34         | -8.39                   | -0.66                      | -1.48                   | -0.76        |
| 28-Jan-09  | -5.12        | 0.06          | -6.39                   | 2.09                       | -1.88                   | -0.98        |
| 21-Feb-09  | -0.32        | 0.02          | -1.89                   | 0.65                       | -0.02                   | 0.07         |
| 19-Mar-09  | -0.51        | 0.00          | -27.92                  | -1.56                      | 2.21                    | -0.90        |
| 21-Apr-09  | -1.47        | -1.56         | -47.83                  | 5.32                       | -5.87                   | -3.09        |
| 21-May-09  | -0.97        | 0.00          | -113.18                 | -51.45                     | 43.08                   | -3.47        |
| 17-Jun-09  | -1.61        | 0.00          | 5.75                    | 17.95                      | -5.90                   | 0.73         |
| 14-Jul-09  | -1.30        | 0.02          | -9.04                   | -13.94                     | 2.99                    | -1.22        |
| 24-Aug-09  | -0.01        | 0.01          | 6.33                    | -1.72                      | 4.48                    | 0.49         |
| 21-Sep-09  | -0.20        | 0.00          | 5.09                    | 14.20                      | -7.34                   | 0.48         |
| 26-Oct-09  | -0.08        | 0.00          | 10.42                   | 4.24                       | -1.66                   | 0.50         |
| 16-Nov-09  | -0.02        | 0.00          | 78.95                   | 20.75                      | -24.54                  | 1.86         |
| 18-Dec-09  | -0.06        | 0.00          | 8.20                    | 33.67                      | -7.30                   | 2.00         |
| 26-Jan-10  | 0.00         | 0.00          | 3.10                    | -5.92                      | -13.61                  | -1.55        |
| 27-Feb-10  | -0.03        | 0.00          | 8.28                    | -0.40                      | -6.54                   | -0.35        |
| 23-Mar-10  | -0.01        | -0.01         | 3.04                    | 7.27                       | -3.39                   | 0.31         |
| 12-Apr-10  | 0.00         | 0.00          | 20.81                   | -1.47                      | -2.15                   | 0.39         |
| <i>Mean</i>  | <i>-1.32</i> | <i>-0.10</i>  | <i>1.96 ±</i>           | <i>3.71 ±</i>              | <i>-2.17</i>            | <i>0.03</i>  |
| <i>(± SE)</i>  | <i>±0.51</i> | <i>± 0.07</i> | <i>7.62</i>             | <i>3.12</i>                | <i>± 3.04</i>           | <i>±0.29</i> |

Table 5b. Mass balance transformation rates for TDN (%) from Gwynns Run, the site with lowland oxbow SCMs. Negative values represent net retention, positive values represent net release.

| Table 5b.<br>Gwynns Run<br>TDN % | SCM<br>1 | SCM<br>2 | Stream<br>above<br>SCMs | Stream<br>parallel<br>SCMs | Stream<br>below<br>SCMs | Total |
|----------------------------------|----------|----------|-------------------------|----------------------------|-------------------------|-------|
| Distance<br>downstream (m)       | 38-84    | 84-177   | 0-24                    | 24-90                      | 90-138                  | 0-138 |
| Reach width (m)                  | 14       | 33.7     | 6.4                     | 6.4                        | 6.9                     | 33.9  |
| 3-Apr-08                         | -5%      | -        | 24%                     | 60%                        | -25%                    | 42%   |
| 14-May-08                        | 18%      | -        | -17%                    | 14%                        | 50%                     | 36%   |
| 9-Jun-08                         | -34%     | -3%      | 43%                     | 11%                        | 1%                      | 673%  |
| 17-Jul-08                        | -68%     | -5%      | -16%                    | 15%                        | -2%                     | -16%  |
| 6-Aug-08                         | -1%      | -6%      | 63%                     | 62%                        | -55%                    | 37%   |
| 1-Sep-08                         | -65%     | -61%     | -34%                    | -2%                        | 35%                     | -19%  |
| 4-Oct-08                         | -85%     | 5%       | 6%                      | 9%                         | 37%                     | 32%   |
| 7-Nov-08                         | -        | -84%     | 18%                     | -4%                        | 0%                      | 8%    |
| 15-Dec-08                        | -79%     | -65%     | -7%                     | -1%                        | -4%                     | -18%  |
| 28-Jan-09                        | -81%     | 23%      | -4%                     | 5%                         | -5%                     | -22%  |
| 21-Feb-09                        | -14%     | 8%       | -3%                     | 2%                         | 0%                      | 3%    |
| 19-Mar-09                        | -83%     | 15%      | -24%                    | -3%                        | 7%                      | -27%  |
| 21-Apr-09                        | -91%     | -90%     | -21%                    | 7%                         | -9%                     | -36%  |
| 21-May-09                        | -80%     | 4%       | -100%                   | -86%                       | 1091%                   | -100% |
| 17-Jun-09                        | -68%     | 2%       | 5%                      | 35%                        | -13%                    | 17%   |
| 14-Jul-09                        | -74%     | 19%      | -19%                    | -64%                       | 21%                     | -68%  |
| 24-Aug-09                        | -1%      | 2%       | 12%                     | -5%                        | 20%                     | 25%   |
| 21-Sep-09                        | -84%     | -7%      | 10%                     | 55%                        | -37%                    | 20%   |
| 26-Oct-09                        | -40%     | 16%      | 13%                     | 9%                         | -5%                     | 16%   |
| 16-Nov-09                        | -33%     | -8%      | 60%                     | 76%                        | -32%                    | 120%  |
| 18-Dec-09                        | -69%     | 0%       | 7%                      | 53%                        | -16%                    | 41%   |
| 26-Jan-10                        | -10%     | -10%     | 2%                      | -14%                       | -25%                    | -38%  |
| 27-Feb-10                        | -53%     | -22%     | 13%                     | -1%                        | -25%                    | -11%  |
| 23-Mar-10                        | -4%      | -13%     | 2%                      | 10%                        | -5%                     | 6%    |
| 12-Apr-10                        | 0%       | -10%     | 17%                     | -2%                        | -4%                     | 13%   |
| <i>Mean</i>                      | -46%     | -13%     | 2%                      | 10%                        | 40%                     | 29%   |
| <i>(± SE)</i>                    | ± 7%     | ± 7%     | ± 6%                    | ± 7%                       | ± 44%                   | ± 28% |

Table 5a-d. Mass balance transformation rates for DOC (g/m<sup>2</sup>/day) from Gwynns Run, the site with lowland oxbow SCMs. Negative values represent net retention, positive values represent net release.

| Table 5c.<br>Gwynns Run<br>DOC g/m <sup>2</sup> /day | SCM<br>1 | SCM<br>2 | Stream<br>above<br>SCMs | Stream<br>parallel<br>SCMs | Stream<br>below<br>SCMs | Total |
|--|----------|----------|-------------------------|----------------------------|-------------------------|-------|
| Distance<br>downstream (m)                           | 38-84    | 84-177   | 0-24                    | 24-90                      | 90-138                  | 0-138 |
| Reach width (m)                                      | 14       | 33.7     | 6.4                     | 6.4                        | 6.9                     | 33.9  |
| 3-Apr-08   | -0.70    | -        | -44.68                  | 13.80                      | -8.78                   | -1.24 |
| 14-May-08  | 0.69     | -        | -34.79                  | -35.11                     | 35.75                   | -0.81 |
| 9-Jun-08   | -1.97    | 0.24     | -146.06                 | -7.98                      | 1.30                    | -3.67 |
| 17-Jul-08  | -4.90    | 0.26     | -34.76                  | -24.76                     | -4.62                   | -3.09 |
| 6-Aug-08   | 0.42     | 0.21     | -4.08                   | 2.43                       | -6.51                   | -0.03 |
| 1-Sep-08   | -0.08    | 0.08     | -36.41                  | -5.16                      | 4.23                    | -1.41 |
| 4-Oct-08   | -0.02    | -0.10    | -3.21                   | -15.22                     | 6.20                    | -0.89 |
| 7-Nov-08   | -        | 0.01     | 12.49                   | -14.11                     | 31.44                   | 2.21  |
| 15-Dec-08  | -0.28    | -0.08    | 3.41                    | -1.87                      | -2.96                   | -0.63 |
| 28-Jan-09  | -1.59    | 0.09     | 16.99                   | 27.67                      | 6.84                    | 2.68  |
| 21-Feb-09  | 0.84     | 0.16     | -2.03                   | -12.06                     | -4.92                   | 0.90  |
| 19-Mar-09  | -0.04    | -0.01    | -12.12                  | -2.92                      | -4.90                   | -1.09 |
| 21-Apr-09  | -0.64    | 1.35     | 555.96                  | -360.37                    | 86.67                   | -0.89 |
| 21-May-09  | 0.45     | 0.00     | -152.54                 | -67.39                     | 52.71                   | -4.85 |
| 17-Jun-09  | 0.66     | -0.02    | -16.42                  | -3.70                      | -7.10                   | -1.42 |
| 14-Jul-09  | -0.15    | 0.01     | -13.72                  | -22.65                     | 2.25                    | -2.08 |
| 24-Aug-09  | -0.01    | 0.04     | 39.12                   | -7.28                      | -13.12                  | -0.41 |
| 21-Sep-09  | 0.09     | -0.01    | -12.39                  | 3.50                       | -6.47                   | -0.75 |
| 26-Oct-09  | -0.22    | 0.00     | 2.87                    | -8.63                      | -4.98                   | -0.97 |
| 16-Nov-09  | 0.00     | -0.01    | -9.33                   | 15.13                      | -14.41                  | -0.54 |
| 18-Dec-09  | -0.02    | -0.02    | -25.90                  | -19.96                     | -5.58                   | -2.78 |
| 26-Jan-10  | 0.01     | 0.00     | -123.14                 | -28.68                     | -3.34                   | -6.41 |
| 27-Feb-10  | -0.03    | -0.01    | -3.11                   | -22.65                     | -10.06                  | -2.62 |
| 23-Mar-10  | -0.01    | -0.03    | -17.15                  | -5.36                      | -12.30                  | -2.06 |
| 12-Apr-10  | -0.07    | -0.03    | 10.79                   | -1.53                      | -15.88                  | -1.19 |
| <i>Mean</i>  | -0.31    | 0.09     | -2.01                   | -24.2                      | 4.06                    | -1.36 |
| <i>(± SE)</i>  | ±0.24    | ± 0.06   | ± 25.1                  | ± 14.5                     | ± 4.74                  | ±0.39 |

Table 5d. Mass balance transformation rates for DOC (%) from Gwynns Run, the site with lowland oxbow SCMs. Negative values represent net retention, positive values represent net release.

| Table 5d.<br>Gwynns Run<br>DOC % | SCM<br>1 | SCM<br>2 | Stream<br>above<br>SCMs | Stream<br>parallel<br>SCMs | Stream<br>below<br>SCMs | Total |
|----------------------------------|----------|----------|-------------------------|----------------------------|-------------------------|-------|
| Distance<br>downstream (m)       | 38-84    | 84-177   | 0-24                    | 24-90                      | 90-138                  | 0-138 |
| Reach width (m)                  | 14       | 33.7     | 6.4                     | 6.4                        | 6.9                     | 33.9  |
| 3-Apr-08                         | -16%     | -        | -25%                    | 66%                        | -18%                    | -34%  |
| 14-May-08                        | 9%       | -        | -16%                    | -32%                       | 53%                     | -13%  |
| 9-Jun-08                         | -8%      | 5%       | -41%                    | -14%                       | 2%                      | -51%  |
| 17-Jul-08                        | -28%     | 10%      | -21%                    | -34%                       | -10%                    | -47%  |
| 6-Aug-08                         | 8%       | 49%      | -3%                     | 4%                         | -12%                    | -1%   |
| 1-Sep-08                         | -11%     | 18%      | -58%                    | -16%                       | 45%                     | -43%  |
| 4-Oct-08                         | 0%       | -14%     | -3%                     | -20%                       | 16%                     | -17%  |
| 7-Nov-08                         | -        | 10%      | 8%                      | -11%                       | 53%                     | 40%   |
| 15-Dec-08                        | -15%     | -10%     | 2%                      | -3%                        | -6%                     | -11%  |
| 28-Jan-09                        | -22%     | 8%       | 12%                     | 38%                        | 14%                     | 61%   |
| 21-Feb-09                        | 35%      | 29%      | -3%                     | -26%                       | -19%                    | 15%   |
| 19-Mar-09                        | -5%      | -4%      | -12%                    | -7%                        | -13%                    | -34%  |
| 21-Apr-09                        | -33%     | 63%      | 159%                    | -72%                       | 26%                     | -8%   |
| 21-May-09                        | 28%      | 0%       | -100%                   | -86%                       | 594%                    | -100% |
| 17-Jun-09                        | 14%      | -2%      | -10%                    | -5%                        | -13%                    | -23%  |
| 14-Jul-09                        | -7%      | 3%       | -19%                    | -68%                       | 10%                     | -73%  |
| 24-Aug-09                        | -3%      | 71%      | 79%                     | -23%                       | -41%                    | -19%  |
| 21-Sep-09                        | 35%      | -10%     | -16%                    | 8%                         | -28%                    | -18%  |
| 26-Oct-09                        | -13%     | 0%       | 2%                      | -12%                       | -10%                    | -17%  |
| 16-Nov-09                        | 1%       | -10%     | -5%                     | 40%                        | -21%                    | -12%  |
| 18-Dec-09                        | -10%     | -43%     | -20%                    | -20%                       | -15%                    | -33%  |
| 26-Jan-10                        | 6%       | -13%     | -39%                    | -38%                       | -5%                     | -66%  |
| 27-Feb-10                        | -26%     | -56%     | -4%                     | -40%                       | -36%                    | -52%  |
| 23-Mar-10                        | 0%       | -6%      | -7%                     | -6%                        | -15%                    | -26%  |
| 12-Apr-10                        | -4%      | -9%      | 9%                      | -3%                        | -29%                    | -33%  |
| <i>Mean</i>                      | -3%      | 4%       | -5%                     | -15%                       | 21%                     | -25%  |
| <i>(± SE)</i>                    | ± 4%     | ± 6%     | ± 9%                    | ± 7%                       | ± 24%                   | ± 7%  |

Table 6a-d. Mass balance transformation rates (g/m<sup>2</sup>/day; %) from Pond Branch, the site with the forest reference pond. Negative values represent net retention, positive values represent net release.

| Table 6a.                 |                    |                     |                     |                     |
|---------------------------|--------------------|---------------------|---------------------|---------------------|
| Pond Branch               | Stream             | Reference           | Stream Below        |                     |
| TDN g/m <sup>2</sup> /day | above pond         | Pond                | Pond                | <i>Total</i>        |
| Distance                  |                    |                     |                     |                     |
| downstream (m)            | 0-119              | 119-168             | 168-183             | <i>0-119</i>        |
| Reach width (m)           | 0.6                | 15.3                | 0.6                 | <i>4.5</i>          |
| 3-Apr-08                  | -0.39              | 0.00                | -5.09               | <i>-0.09</i>        |
| 14-May-08                 | -0.39              | -0.18               | -4.70               | <i>-0.24</i>        |
| 9-Jun-08                  | -0.01              | -0.11               | 0.25                | <i>-0.10</i>        |
| 17-Jul-08                 | -0.03              | -0.15               | 0.10                | <i>-0.14</i>        |
| 7-Aug-08                  | 0.83               | -0.03               | 0.03                | <i>0.04</i>         |
| 1-Sep-08                  | -0.01              | -0.03               | 0.35                | <i>-0.03</i>        |
| 4-Oct-08                  | -0.03              | -0.11               | 0.12                | <i>-0.10</i>        |
| 7-Nov-08                  | 0.01               | 0.00                | -0.20               | <i>0.00</i>         |
| 15-Dec-08                 | 0.01               | -0.47               | -0.06               | <i>-0.43</i>        |
| 28-Jan-09                 | 0.00               | -0.11               | 0.40                | <i>-0.09</i>        |
| 23-Feb-09                 | 0.05               | -0.20               | -0.60               | <i>-0.18</i>        |
| 19-Mar-09                 | 0.01               | -0.51               | 0.40                | <i>-0.46</i>        |
| 21-Apr-09                 | 0.18               | 0.00                | -5.91               | <i>-0.05</i>        |
| 20-May-09                 | 0.22               | -0.32               | -0.78               | <i>-0.29</i>        |
| 24-Jun-09                 | 0.03               | 0.02                | 0.35                | <i>0.02</i>         |
| 13-Jul-09                 | -0.07              | -0.10               | -0.27               | <i>-0.10</i>        |
| 26-Aug-09                 | -0.01              | -0.01               | -0.69               | <i>-0.02</i>        |
| 23-Sep-09                 | 0.13               | 0.01                | -1.69               | <i>0.01</i>         |
| 28-Oct-09                 | -0.35              | 0.03                | 0.00                | <i>0.00</i>         |
| 19-Nov-09                 | 0.05               | 0.00                | -1.04               | <i>-0.01</i>        |
| 28-Dec-09                 | 0.47               | -0.06               | -3.65               | <i>-0.05</i>        |
| 25-Jan-10                 | 0.17               | 0.04                | -5.99               | <i>-0.02</i>        |
| 1-Mar-10                  | -0.28              | -0.34               | -2.96               | <i>-0.37</i>        |
| 22-Mar-10                 | 0.13               | -0.85               | 0.42                | <i>-0.76</i>        |
| 14-Apr-10                 | 0.00               | 0.01                | -4.99               | <i>-0.05</i>        |
| <i>Mean (± SE)</i>        | <i>0.03 ± 0.05</i> | <i>-0.14 ± 0.04</i> | <i>-1.45 ± 0.45</i> | <i>-0.14 ± 0.04</i> |

Table 6b. Mass balance transformation rates for TDN (%) from Pond Branch, the site with the forest reference pond. Negative values represent net retention, positive values represent net release.

| Table 6b.<br>Pond Branch<br>TDN % | Stream<br>above pond | Reference<br>Pond | Stream Below<br>Pond | <i>Total</i>     |
|-----------------------------------|----------------------|-------------------|----------------------|------------------|
| Distance<br>downstream (m)        | 0-119                | 119-168           | 168-183              | <i>0-119</i>     |
| Reach width (m)                   | 0.6                  | 15.3              | 0.6                  | <i>4.5</i>       |
| 3-Apr-08                          | -43%                 | -7%               | -57%                 | -68%             |
| 14-May-08                         | -42%                 | -61%              | -51%                 | -84%             |
| 9-Jun-08                          | -5%                  | -78%              | 9%                   | -74%             |
| 17-Jul-08                         | -6%                  | -85%              | 4%                   | -90%             |
| 7-Aug-08                          | 155%                 | -19%              | 0%                   | 78%              |
| 1-Sep-08                          | -9%                  | -71%              | 30%                  | -63%             |
| 4-Oct-08                          | -10%                 | -87%              | 5%                   | -78%             |
| 7-Nov-08                          | 7%                   | 13%               | -14%                 | -2%              |
| 15-Dec-08                         | 6%                   | -96%              | -3%                  | -95%             |
| 28-Jan-09                         | 0%                   | -79%              | 18%                  | -76%             |
| 23-Feb-09                         | 24%                  | -93%              | -26%                 | -91%             |
| 19-Mar-09                         | 8%                   | -96%              | 23%                  | -96%             |
| 21-Apr-09                         | 18%                  | -4%               | -36%                 | -31%             |
| 20-May-09                         | 35%                  | -86%              | -18%                 | -90%             |
| 24-Jun-09                         | 5%                   | 34%               | 7%                   | 79%              |
| 13-Jul-09                         | -9%                  | -61%              | -5%                  | -68%             |
| 26-Aug-09                         | -2%                  | -15%              | -13%                 | -30%             |
| 23-Sep-09                         | 24%                  | 31%               | -28%                 | 12%              |
| 28-Oct-09                         | -15%                 | 49%               | 0%                   | -1%              |
| 19-Nov-09                         | 16%                  | 0%                | -26%                 | -19%             |
| 28-Dec-09                         | 20%                  | -21%              | -21%                 | -31%             |
| 25-Jan-10                         | 4%                   | 13%               | -16%                 | -5%              |
| 1-Mar-10                          | -15%                 | -76%              | -32%                 | -85%             |
| 22-Mar-10                         | 7%                   | -79%              | 2%                   | -77%             |
| 14-Apr-10                         | 0%                   | 6%                | -24%                 | -21%             |
| <i>Mean (± SE)</i>                | <i>7 ± 7%</i>        | <i>-39 ± 10%</i>  | <i>-11 ± 4%</i>      | <i>-40 ± 10%</i> |

Table 6c. Mass balance transformation rates for DOC ( $\text{g}/\text{m}^2/\text{day}$ ) from Pond Branch, the site with the forest reference pond. Negative values represent net retention, positive values represent net release.

| Table 6c.                            |                                   |                                    |                                    |                                    |
|--------------------------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|
| Pond Branch                          | Stream                            | Reference                          | Stream Below                       |                                    |
| DOC $\text{g}/\text{m}^2/\text{day}$ | above pond                        | Pond                               | Pond                               | <i>Total</i>                       |
| Distance                             |                                   |                                    |                                    |                                    |
| downstream (m)                       | 0-119                             | 119-168                            | 168-183                            | <i>0-119</i>                       |
| Reach width (m)                      | 0.6                               | 15.3                               | 0.6                                | <i>4.5</i>                         |
| 3-Apr-08                             | 0.56                              | 0.04                               | 7.46                               | <i>0.16</i>                        |
| 14-May-08                            | 0.96                              | 0.20                               | -18.82                             | <i>0.06</i>                        |
| 9-Jun-08                             | -0.07                             | 0.05                               | -1.78                              | <i>0.02</i>                        |
| 17-Jul-08                            | 0.08                              | -0.02                              | 0.05                               | <i>-0.03</i>                       |
| 7-Aug-08                             | 0.29                              | 0.03                               | -1.21                              | <i>0.04</i>                        |
| 1-Sep-08                             | -0.04                             | 0.05                               | -0.12                              | <i>0.04</i>                        |
| 4-Oct-08                             | -0.48                             | 0.06                               | 4.00                               | <i>0.09</i>                        |
| 7-Nov-08                             | -0.02                             | -0.02                              | 1.78                               | <i>-0.03</i>                       |
| 15-Dec-08                            | -0.04                             | -0.10                              | -3.21                              | <i>0.01</i>                        |
| 28-Jan-09                            | -0.01                             | -0.02                              | 1.08                               | <i>0.04</i>                        |
| 23-Feb-09                            | 0.14                              | -0.10                              | -0.49                              | <i>-0.01</i>                       |
| 19-Mar-09                            | 0.08                              | -0.11                              | 1.88                               | <i>0.02</i>                        |
| 21-Apr-09                            | 2.08                              | 0.18                               | -28.51                             | <i>-0.31</i>                       |
| 20-May-09                            | 0.19                              | 0.30                               | -28.51                             | <i>-0.01</i>                       |
| 24-Jun-09                            | -1.50                             | 0.13                               | -0.86                              | <i>0.00</i>                        |
| 13-Jul-09                            | -0.41                             | 0.05                               | 0.40                               | <i>0.02</i>                        |
| 26-Aug-09                            | -0.02                             | 0.06                               | 0.15                               | <i>0.05</i>                        |
| 23-Sep-09                            | 1.16                              | 0.02                               | -0.77                              | <i>0.07</i>                        |
| 28-Oct-09                            | -7.05                             | 0.71                               | -12.90                             | <i>0.09</i>                        |
| 19-Nov-09                            | 0.70                              | -0.09                              | 2.05                               | <i>-0.06</i>                       |
| 28-Dec-09                            | -2.25                             | 0.10                               | -40.86                             | <i>-0.50</i>                       |
| 25-Jan-10                            | -3.85                             | 1.15                               | 0.12                               | <i>0.26</i>                        |
| 1-Mar-10                             | -6.61                             | -0.11                              | 33.26                              | <i>-0.12</i>                       |
| 22-Mar-10                            | -3.52                             | 0.10                               | -1.69                              | <i>-0.21</i>                       |
| 14-Apr-10                            | -1.54                             | 0.04                               | -12.08                             | <i>-0.22</i>                       |
| <i>Mean (<math>\pm SE</math>)</i>    | <i>0.85 <math>\pm</math> 0.45</i> | <i>-0.11 <math>\pm</math> 0.05</i> | <i>-3.89 <math>\pm</math> 2.82</i> | <i>-0.02 <math>\pm</math> 0.03</i> |

Table 6d. Mass balance transformation rates for DOC (%) from Pond Branch, the site with the forest reference pond. Negative values represent net retention, positive values represent net release.

| Table 6d.          |                |                |                |               |
|--------------------|----------------|----------------|----------------|---------------|
| Pond Branch        | Stream         | Reference      | Stream Below   |               |
| DOC %              | above pond     | Pond           | Pond           | <i>Total</i>  |
| Distance           |                |                |                |               |
| downstream (m)     | 0-119          | 119-168        | 168-183        | <i>0-119</i>  |
| Reach width (m)    | 0.6            | 15.3           | 0.6            | <i>4.5</i>    |
| 3-Apr-08           | 5%             | 3%             | 10%            | <i>21%</i>    |
| 14-May-08          | 8%             | 16%            | -15%           | <i>5%</i>     |
| 9-Jun-08           | -1%            | 12%            | -4%            | <i>6%</i>     |
| 17-Jul-08          | 2%             | -8%            | 0%             | <i>-7%</i>    |
| 7-Aug-08           | 42%            | 28%            | -10%           | <i>80%</i>    |
| 1-Sep-08           | -5%            | 48%            | -1%            | <i>42%</i>    |
| 4-Oct-08           | -10%           | 40%            | 19%            | <i>24%</i>    |
| 7-Nov-08           | 0%             | -8%            | 7%             | <i>-6%</i>    |
| 15-Dec-08          | -1%            | -21%           | -10%           | <i>2%</i>     |
| 28-Jan-09          | 0%             | -11%           | 7%             | <i>14%</i>    |
| 23-Feb-09          | 4%             | -39%           | -3%            | <i>-4%</i>    |
| 19-Mar-09          | 2%             | -20%           | 5%             | <i>5%</i>     |
| 21-Apr-09          | 9%             | 15%            | -25%           | <i>-18%</i>   |
| 20-May-09          | 2%             | 41%            | -33%           | <i>-2%</i>    |
| 24-Jun-09          | -11%           | 17%            | -1%            | <i>0%</i>     |
| 13-Jul-09          | -8%            | 13%            | 1%             | <i>6%</i>     |
| 26-Aug-09          | 0%             | 20%            | 0%             | <i>13%</i>    |
| 23-Sep-09          | 25%            | 5%             | -2%            | <i>19%</i>    |
| 28-Oct-09          | -5%            | 16%            | -4%            | <i>1%</i>     |
| 19-Nov-09          | 6%             | -10%           | 3%             | <i>-6%</i>    |
| 28-Dec-09          | -9%            | 7%             | -32%           | <i>-25%</i>   |
| 25-Jan-10          | -6%            | 27%            | 0%             | <i>5%</i>     |
| 1-Mar-10           | -41%           | -16%           | 70%            | <i>-9%</i>    |
| 22-Mar-10          | -17%           | 5%             | -1%            | <i>-9%</i>    |
| 14-Apr-10          | -11%           | 4%             | -10%           | <i>-16%</i>   |
| <i>Mean (± SE)</i> | <i>-1 ± 3%</i> | <i>-7 ± 4%</i> | <i>-1 ± 4%</i> | <i>6 ± 4%</i> |

Table 7. Dissolved oxygen and temperature of ambient groundwater in push-pull wells from summer 2008, winter 2008, and summer 2010 (means  $\pm$  SE, N = 3 sampling dates).

| Site          | Well ID | Site Description | Dissolved Oxygen (mg/L) | Temperature (°C) |
|---------------|---------|------------------|-------------------------|------------------|
| Pond Branch   |         |                  |                         |                  |
|               | 1       | Low Floodplain   | 4.2 $\pm$ 1.0           | 17.8 $\pm$ 3.1   |
|               | 2       | Low Floodplain   | 1.5 $\pm$ 0.6           | 16.2 $\pm$ 2.2   |
|               | 7       | Low Floodplain   | 1.3 $\pm$ 0.7           | 16.4 $\pm$ 2.4   |
|               | 8       | Low Floodplain   | 3.4 $\pm$ 2.0           | 16.8 $\pm$ 2.6   |
|               | 3       | Reference Pond   | 3.1 $\pm$ 1.4           | 16.1 $\pm$ 3.7   |
|               | 4       | Reference Pond   | 2.2 $\pm$ 0.7           | 15.7 $\pm$ 3.6   |
|               | 5       | Reference Pond   | 2.3 $\pm$ 1.1           | 15.1 $\pm$ 2.5   |
|               | 6       | Reference Pond   | 1.8 $\pm$ 0.3           | 15.3 $\pm$ 2.7   |
| Spring Branch |         |                  |                         |                  |
|               | 1       | Low Floodplain   | 1.8 $\pm$ 0.3           | 16.1 $\pm$ 3.5   |
|               | 2       | Low Floodplain   | 1.9 $\pm$ 0.8           | 15.7 $\pm$ 4.3   |
|               | 3       | Low Floodplain   | 4.7 $\pm$ 0.7           | 16.3 $\pm$ 4.5   |
|               | 4       | Low Floodplain   | 3.5 $\pm$ 0.1           | 14.8 $\pm$ 3.5   |
|               | 5       | Stormwater SCM   | 2.6 $\pm$ 0.3           | 17.5 $\pm$ 5.7   |
|               | 6       | Stormwater SCM   | 2.7 $\pm$ 1.2           | 16.7 $\pm$ 5.3   |
|               | 7       | Stormwater SCM   | 1.9 $\pm$ 0.9           | 16.4 $\pm$ 4.3   |
|               | 8       | Stormwater SCM   | 3.4 $\pm$ 0.9           | 14.9 $\pm$ 4.0   |
| Gwynns Run    |         |                  |                         |                  |
|               | 1       | Low Floodplain   | 0.9 $\pm$ 0.6           | 18.4 $\pm$ 3.4   |
|               | 2       | Low Floodplain   | 0.9 $\pm$ 0.4           | 19.0 $\pm$ 5.5   |
|               | 7       | Low Floodplain   | 0.6 $\pm$ 0.5           | 17.9 $\pm$ 4.5   |
|               | 8       | Low Floodplain   | 2.0 $\pm$ 0.9           | 16.1 $\pm$ 9.8   |
|               | 3       | Stormwater SCM   | 1.9 $\pm$ 0.3           | 19.2 $\pm$ 5.4   |
|               | 4       | Stormwater SCM   | 2.0 $\pm$ 1.6           | 17.0 $\pm$ 6.1   |
|               | 5       | Stormwater SCM   | 2.0 $\pm$ 1.1           | 20.0 $\pm$ 5.3   |
|               | 6       | Stormwater SCM   | 2.1 $\pm$ 1.1           | 21.3 $\pm$ 5.9   |

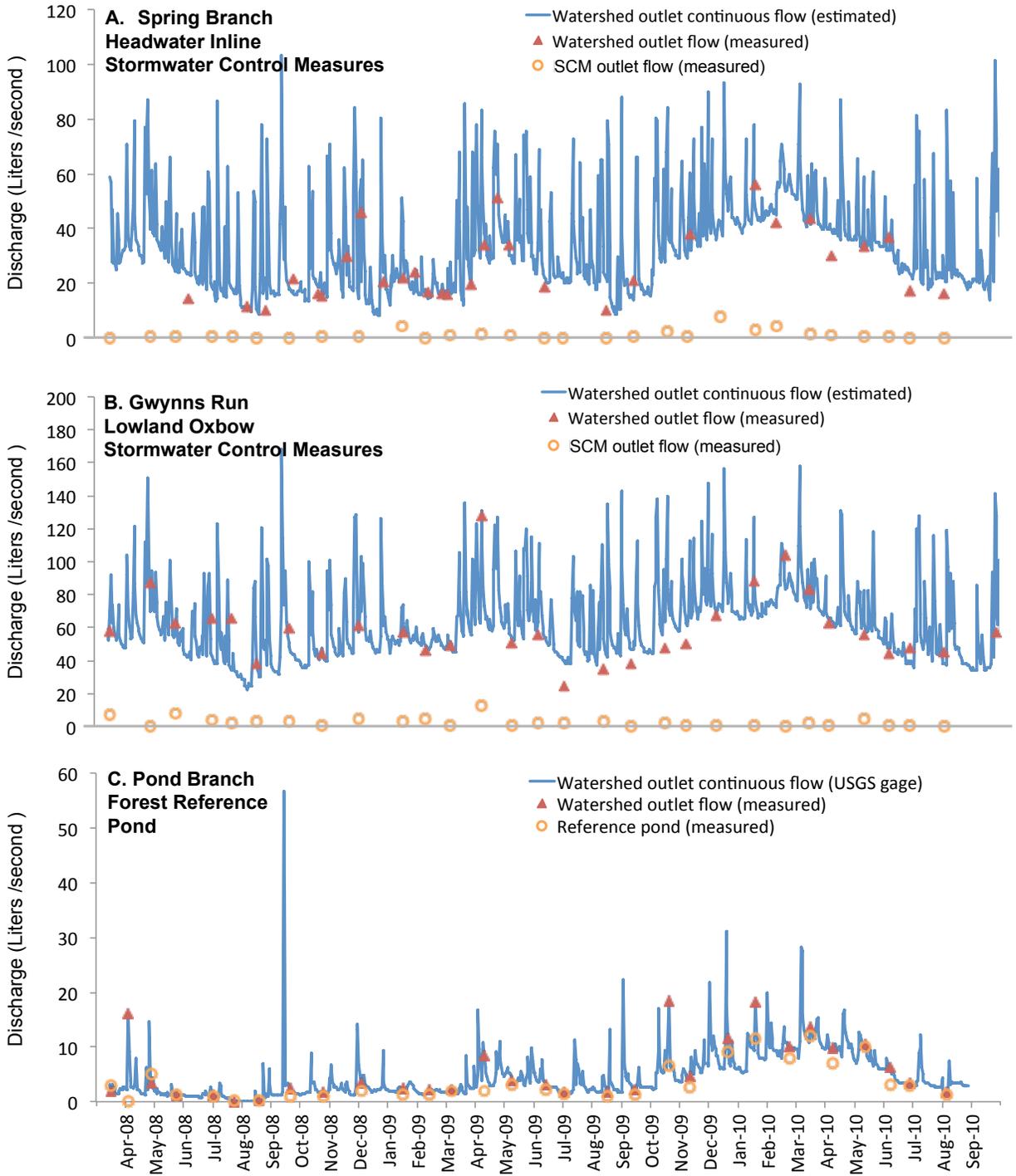
Table 8. Nitrate and DOC of ambient groundwater in push-pull wells from seasonal sampling that does not correspond to the same dates as the *in situ* denitrification measurements (means  $\pm$  SE, N =1-5 for nitrate and N = 6-12 for DOC).

| Site          | Well ID | Site description | Nitrate (mg/L)    | DOC (mg/L)       |
|---------------|---------|------------------|-------------------|------------------|
| Pond Branch   |         |                  |                   |                  |
|               | 1       | Floodplain       | 0.019 $\pm$ 0.007 | 1.74 $\pm$ 0.19  |
|               | 2       | Floodplain       | 0.007 $\pm$ 0.003 | 1.38 $\pm$ 0.34  |
|               | 7       | Floodplain       | 0.044 $\pm$ 0.025 | 1.47 $\pm$ 0.19  |
|               | 8       | Floodplain       | 0.007 $\pm$ 0.006 | 1.12 $\pm$ 0.23  |
|               | 3       | Reference Pond   | 0.016 $\pm$ 0.007 | 4.02 $\pm$ 1.85  |
|               | 4       | Reference Pond   | 0.112 $\pm$ 0.107 | 3.19 $\pm$ 1.39  |
|               | 5       | Reference Pond   | 0.006 $\pm$ 0.002 | 1.13 $\pm$ 0.12  |
|               | 6       | Reference Pond   | 0.005 $\pm$ 0.001 | 1.84 $\pm$ 0.26  |
| Spring Branch |         |                  |                   |                  |
|               | 1       | Floodplain       | 2.827 $\pm$ 1.262 | 0.99 $\pm$ 0.16  |
|               | 2       | Floodplain       | 4.523 $\pm$ 1.704 | 1.35 $\pm$ 0.15  |
|               | 3       | Floodplain       | 2.583 $\pm$ 1.286 | 0.76 $\pm$ 0.15  |
|               | 4       | Floodplain       | 0.569 $\pm$ 0.563 | 0.71 $\pm$ 0.14  |
|               | 5       | Stormwater SCM   | 2.656 $\pm$ 0.145 | 4.28 $\pm$ 1.10  |
|               | 6       | Stormwater SCM   | 1.374 $\pm$ 0.681 | 0.96 $\pm$ 0.40  |
|               | 7       | Stormwater SCM   | 2.607 $\pm$ 0.371 | 0.58 $\pm$ 0.15  |
|               | 8       | Stormwater SCM   | 2.069 (N=1)       | 0.63 $\pm$ 0.19  |
| Gwynns Run    |         |                  |                   |                  |
|               | 1       | Floodplain       | 0.008 $\pm$ 0.003 | 4.10 $\pm$ 0.27  |
|               | 2       | Floodplain       | 0.693 $\pm$ 0.421 | 3.67 $\pm$ 0.18  |
|               | 7       | Floodplain       | 0.256 $\pm$ 0.186 | 3.60 $\pm$ 0.55  |
|               | 8       | Floodplain       | 0.550 $\pm$ 0.476 | 5.83 $\pm$ 1.16  |
|               | 3       | Stormwater SCM   | 0.654 $\pm$ 0.357 | 4.34 $\pm$ 0.52  |
|               | 4       | Stormwater SCM   | 1.127 $\pm$ 0.747 | 5.20 $\pm$ 0.87  |
|               | 5       | Stormwater SCM   | 0.254 $\pm$ 0.199 | 6.55 $\pm$ 1.12  |
|               | 6       | Stormwater SCM   | 0.399 $\pm$ 0.391 | 10.83 $\pm$ 5.10 |

Appendix C Figure 1. Discharge (liters/second) at Spring Branch, Gwynns Run, and Pond Branch. Continuous discharge (blue) is shown along with discharge from mass balance sampling events at the watershed outlets (red triangle) and SCM or reference pond outlets (orange circles).

(A) At Spring Branch, continuous discharge was modeled based upon a logarithmic relationship between nearby USGS gage 01589464 and my measurements in the stream reach at 3,005 m from April 2008 to September 2010 ( $y = 18 \cdot \ln(x) + 30$ ;  $R^2 = 0.61$ ). (B) At Gwynns Run, continuous discharge was modeled based upon a logarithmic relationship between nearby USGS gage 01589352 and my monthly measurements in the stream reach at 138 m from April 2008 to September 2010 ( $y = 26 \cdot \ln(x) - 41$ ;  $R^2 = 0.70$ ). Discharge decreased over time in the Gwynns Run SCMs as they filled with sediment and on some dates it was not possible to measure discharge with a flow meter. (C) At Pond Branch, continuous flow is from USGS gage 01583570 located at 0 m. Pond Branch flowed through a wetland upstream of the pond and discharge frequently decreased in this section due to groundwater recharge.

Appendix C Figure 1.



## Notes

### Figure 11

We narrowed the y-axis range so the following high values were not shown: A) TDN (g/m<sup>2</sup>/day): SCM 2 (-1.7, -2.4, 2.4), phase 1a (-5.8, -3.5, 2.1, 2.1, 3.4, 4.1), phase 1b (-1.6), and phase 1c (-1.6); B) DOC (g/m<sup>2</sup>/day): SCM 1 (-4.2, -1.2, 1.7), SCM 2 (1.1, 2.8, 2.9), phase 1a (-1.8, -1.6, -1.0, 1.2, 1.3, 2.4), phase 1b (2.7), and phase 1c (-1.1), phase 2 (1.2, 1.3), unrestored (2.6, 7.2); and D) DOC Export (%): SCM 1 (175%) and unrestored (617%)

### Figure 12

We narrowed the y-axis range so the following high values were not shown: A) TDN (g/m<sup>2</sup>/day): 0-24 m (-48, 52, 80, 83) and 24-90 m (-45); B) DOC (g/m<sup>2</sup>/day): 0-24 m (-146, -125, -47, 558), 24-90 m (86.7), and 90-138 m (-364); C) TDN export (%): SCM 1 (462%); and D) DOC export (%): SCM 1 (203%) and 0-24 m (158)

### Spring Branch Tributary Mass Balance Sampling

We regularly sampled tributaries 2 and 3; sometimes tributary 1 was dry, tributary 4 only had measurable flow on one date, and tributary 5 was discovered later into the study period because it was a near-channel spring that was not on any of the local maps so we had to back-calculate data for tributary 5.

# Chapter 4: Nutrient Retention in Restored Streams and Floodplains: A Review and Synthesis

## *Abstract*

Excess nitrogen (N) and phosphorus (P) from human activities have contributed to degradation of coastal waters globally. A growing body of work suggests that hydrologically restoring streams and floodplains in agricultural and urban watersheds has potential to increase nitrogen and phosphorus retention, but rates and mechanisms have not yet been synthesized and compared across studies. I conducted a review of nutrient retention within hydrologically reconnected streams and floodplains including 79 studies. Overall, 62% of results were positive, 26% were neutral, and 12% were negative. The studies I reviewed used a variety of methods to analyze nutrients cycling. I did a further intensive meta-analysis on nutrient spiraling studies because this method was the most consistent and comparable between studies. A meta-analysis of 240 experimental additions of ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and soluble reactive phosphorus (SRP) was synthesized from 15 nutrient spiraling studies. Overall, I found that rates of uptake were variable along stream reaches over space and time. My results indicate that the size of the stream restoration (total surface area) and hydrologic residence time can be key drivers in influencing N and P uptake at broader watershed scales or along the urban watershed continuum.

## Introduction

Managing nutrient pollution, restoring urban infrastructure, and providing clean drinking water are recognized as grand challenges for human society (National Academy of Engineering 2014). Excess nitrogen (N) and phosphorus (P) from urban and agricultural areas contributes to freshwater and coastal eutrophication (Conley et al. 2009). This paper is a review of how effective stream and floodplain restoration projects have been at reducing N and P loads. N and P can be important limiting nutrients in aquatic systems. N is required for protein synthesis and P is required for DNA, RNA, and energy transfer. Human activities have severely altered N and P global biogeochemical cycles. Currently, the amount of N and P transported through streams and rivers to the ocean has increased by 2 to 20-fold (Caraco 1993, Green et al. 2004). This increase in aquatic N has resulted from the doubling of terrestrial N inputs from a mixture of fertilizer production, cultivation of N-fixing crops, and combustion of fossil fuels (Vitousek et al. 1997, Galloway et al. 2003). Likewise, P levels have increased because P-rich rock deposits have been mined to produce fertilizer and detergents which are transported with runoff and wastewater inputs (Caraco 1993, Conley 1999, Bennett et al. 2001). In the United States, nearly two-thirds of coastal rivers and estuaries have been significantly impacted by excess nutrients (Howarth et al. 2002, Kemp et al. 2005). Excess N and P have contributed to contamination of drinking water supplies and the proliferation of harmful algal blooms (HABs) and over 400 hypoxic “dead zones” in coastal waters (Boesch et al. 2001, Kaushal et al. 2008a, Diaz and Rosenberg 2008, Yang et al. 2012). Such water quality problems can impact the ecology and economy of coastal regions by decreasing the productivity of fisheries and reducing recreational appeal (Boesch et al. 2001).

Increasing urbanization, agricultural intensification, and climate variability will likely exacerbate future N and P loads to coastal areas (Howarth et al. 2006, Kaushal et al. 2014). The increasing environmental impacts of N and P pollution have motivated efforts to track sources and manage nitrogen loads in rivers and streams (Collins et al. 2010, Kaushal et al. 2011, Duan et al. 2012, Stets et al. 2015). Watershed N and P loads can be reduced through multiple solutions such as reducing fertilizer inputs, fixing leaky sewer systems, and phosphate detergent bans (Lee and Jones 1986, Moomaw 2002, Dinnes et al. 2002, Maxted et al. 2009). Unfortunately, in many regions there are social, political, and economic difficulties associated with reducing sources and inputs to watersheds (Howarth 2008). Thus, there is increasing interest in restoring the ability of streams, rivers, wetlands, and floodplains to retain and process watershed N and P inputs. Stream restoration is not a panacea for watershed nutrient management. Tracking and managing watershed sources are essential. Stream restoration is a practice that is likely to continue for the primary goals of bank stabilization, upgrading aging infrastructure, and repairing property damage. In order to sustainability manage watersheds, it is important to determine whether stream restoration practices can also improve water quality by controlling the flux of both N and P. Thus, realistically efforts must be placed towards empirically understanding the possibilities and limitations of restoration across a range of environmental conditions (e.g., land use, watershed size, stream flow, restoration type).

### Stream processes driving nutrient cycling

Restoration practices such as stream and floodplain reconnection may enhance N and P retention processes such as temporary storage through assimilation and adsorption or permanent

removal through coupled nitrification and denitrification. Plants, fungi, and certain bacteria in the stream and riparian zone can temporarily assimilate inorganic N and P into biomass (Søvik and Syversen 2008, Weigelhofer et al. 2012). Assimilation rates increase with retention time and the availability of sunlight and nutrients (Bukaveckas 2007, Klockner et al. 2009, Pennino et al. 2014).  $\text{NH}_4^+$  and SRP are readily assimilated forms of inorganic N and P because of highly reduced redox states (Melzer and Exler 1982).  $\text{NH}_4^+$  and SRP can also be retained through adsorption onto negatively charged soil particles. Under aerobic conditions, water column P concentrations are kept low because of strong bonds to natural clay particles (Froelich 1988). Thus, P is typically transported in particulate form. Biomass assimilation and sediment adsorption are temporary forms of N retention. N and P in assimilated biomass may be recycled back into the environment through excretion or death and decomposition. Likewise, N and P adsorbed to sediments can be resuspended due to turbulence and mixing or remobilized from anaerobic sediments (House and Denison 2002, Duan and Kaushal 2013). Another possible fate for N and P that has been assimilated into biomass or adsorbed to sediment particles may be long-term burial in sediments.

Coupled microbial nitrification and denitrification is a more permanent form of removal because inorganic compounds ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ ) are transformed to biologically inert gaseous products ( $\text{N}_2\text{O}$  and  $\text{N}_2$ ) (Davidson and Schimel 1995). The first step, nitrification oxidizes ammonium to nitrite and then nitrate ( $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$ ) and this process requires aerobic conditions. The second step, denitrification reduces nitrate to nitrous oxide and nitrogen gas ( $\text{NO}_3^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$ ). Denitrification requires anoxic conditions and an electron donor such as organic carbon (Groffman et al. 2005, Boyer et al. 2006). Saturated soils with oxygenating root surfaces promote coupled nitrification and denitrification. Thus, restored streams and floodplains may have high rates of nitrogen retention and removal because conditions are favorable for both

coupled nitrification-denitrification and assimilation (Hedin et al. 1998, Kaushal et al. 2008b, Mayer et al. 2010). As the mechanisms controlling N and P retention are different, the inclusion of macrophytes in restoration designs may be beneficial for retention of both N and P because roots can oxygenate soil for coupled nitrification–denitrification and P immobilization (Forshay and Dodson 2011, Roley et al. 2012b).

### Stream impairment in human dominated watersheds

Anthropogenic activities have hydrologically disconnected streams and rivers from floodplains and impacted their ability to retain N and P (Kaushal and Belt 2012). In both urban and agricultural watersheds, rivers and streams have been straightened and channelized which also increases how efficiently water is transported away. Furthermore, increased N and P inputs from fertilizer and sewage can saturate in-stream demand (Mulholland et al. 2008). Overall, human activities have dramatically altered the plumbing and nutrient inputs of many urban and agricultural watersheds contributing to amplified pulses of water and nutrient export from watersheds (Kaushal et al. 2014). Below, I discuss the nature of stream degradation from an agricultural and urban perspective and its relevance to restoration.

Agricultural practices have led to both physical and chemical alterations to streams globally. In the eastern United States, the legacy of 19th-century sediment erosion can be a defining feature of stream channel geomorphology. During this time, clearing, burning, tilling, and grazing of hillsides led to soil erosion and filled valley bottoms with fine sediment (Costa 1975, Magilligan 1985, Knox 1987). In some valleys, layers of post-settlement alluvium eventually filled in floodplains with as much as 3 meters of “legacy” sediments, which are being transported

downstream in places where stream incision occurs (Parola et al. 2007, Walter and Merritts 2008). Fine sediments can clog interstitial voids within a gravel bed and obstruct groundwater-surface water hydrologic connectivity (Kasahara and Hill 2008, Nogaro et al. 2010). In addition to raising the elevation of the floodplain surface, transport of fine sediments from land development for agriculture and residential use has led to a massive loss of wetlands globally (Verhoeven et al. 2006). Furthermore, ditching, diking, and tile drains have been used to artificially lower groundwater levels in former wetlands in order to increase agricultural productivity and efficiently transport water away. This reduction in groundwater levels decreases hydrologic connectivity between surface water and groundwater in floodplains and decreases hydrologic residence time.

Similarly, urban drainage networks have been re-plumbed with storm drains to efficiently transport runoff away (Walsh et al. 2005, Kaushal and Belt 2012). In some urban areas, natural streams have been either lined in concrete or buried in underground pipes (Elmore and Kaushal 2008, Pennino et al. 2014). These artificial drainage networks can limit hydrologic connectivity between streams and floodplains and increase the flashiness of runoff events and promote erosion and downcutting of stream banks. After decades of trying to quickly move runoff away from urban landscapes, perceptions regarding managing urban runoff have changed. There can be important water quality and flood safety benefits associated with “slowing down” runoff events and retaining water on the landscape (Roley et al. 2012a).

Stream restoration and floodplain reconnection have been employed as potential strategies to restore ecosystem functions, although degradation may be difficult or impossible to reverse (Bernhardt and Palmer 2011). Stream restoration and floodplain reconnection has been used in an attempt to influence water quality by slowing stream flow by altering channel/floodplain

morphology and riparian vegetation (Mayer et al. 2007, 2010, Roberts et al. 2007, Bukaveckas 2007, Kaushal et al. 2008b). The objective of this review and synthesis was to evaluate how effective stream restoration and floodplain reconnection practices have been at restoring ecosystem functions such as N and P retention. I address this question by reviewing and synthesizing peer-reviewed literature studies that provide N and P retention data for projects that restore streams and reconnect floodplains. I found that stream restoration and floodplain reconnection projects encompass a plethora of designs and take place at a wide range of scales from headwater streams to large rivers like the Mississippi (Theriot et al. 2013). Additionally, there were many different methods used to evaluate the effects of restoration on water quality. My objectives were to 1) develop a typology of different forms of restoration, 2) examine the methods used for evaluating stream and floodplain restoration and 3) estimate the effectiveness of various restoration practices and use this information to inform future restoration and monitoring efforts. This review and synthesis is intended to evaluate factors contributing to restoration outcomes across various scales.

### *Database Review of Empirical Nutrient Studies*

#### Selection criteria and typology development

The goal of this review was to identify N and P retention studies that used hydrologic and/or geomorphic manipulations to increase stream-floodplain hydrologic connectivity. I performed a systematic search using literature database search engines, primarily *ISI Web of Knowledge*, to amass potentially relevant studies published from 1970 to 2014. I also searched for technical papers and examined reference lists within selected papers. My initial search identified papers

containing at least one key word from each of three areas of interest: (1) study ecosystem (*river, wetland, ditch, stream, floodplain*); (2) management actions (*restor\*, engineering, rehabilitation*); and (3) nutrients measured (*nitr\* or phos\**). An initial screening of titles and abstracts for relevance yielded 550 papers after excluding (1) those not meeting basic selection criteria (e.g. explicitly examining stream/floodplain restoration projects), (2) studies of isolated wetlands and of systems that are tidally influenced because my focus was on restoration of flowing waters connected to a stream or river network. I examined these results and recorded the number of restoration studies over time (Figure 4.1).

For the remainder of this review, I restricted my scope so that it only includes empirical case studies with nutrient monitoring data. After excluding any review papers or modeling studies that did not include new empirical nutrient data, I ultimately included 79 peer-reviewed studies. For each study, I documented the following: monitoring method, land use, management action, summary of results (e.g., uptake metrics, denitrification rates, etc.), and geographic location. Additionally, I developed a typology (classification according to general type) for the restoration projects and evaluated the diversity of methods used to examine how these projects influenced N retention (Appendix D). I standardized metric units for retention rates across studies and regions in order to analyze and compare studies with common methods.

#### Evaluating diversity of methods and determining standard metrics

An initial screening of the studies included in Supplementary Table 4.1 revealed that the most frequently used methods were nutrient spiraling tracer studies, denitrification studies, mass balance studies, and changes in water chemistry (Fig. 4.2). Further examination revealed that a

diversity of methods were used for measuring denitrification and mass balances which made it challenging to compare them. Thus, I chose to focus a more intensive meta-data analysis on the nutrient spiraling results. For the nutrient spiraling meta-data analysis, I reviewed the results from each study and recorded the potential controlling factors and removal metrics for N and P. I plotted the potential controlling factors vs. the removal metrics in order to discover trends. WebPlotDigitizer (Version 3.6) was used to extract data from graphs when it was not available in text form (Rohatgi 2015). Statistical analyses were performed using R (R Core Team 2013).

### Growth in Stream Restoration Studies Over Time

Based on my analysis of peer-reviewed literature, the average number of articles regarding stream restoration in general (nutrient retention, biodiversity, hydrology etc.) published each year increased from 0.3 studies per year in the 1980s, to 5 per year in the 1990s, to 24 per year in the 2000s, to 51 per year during 2010-2014 (Fig. 4.1a). Out of these 550 publications, I determined that 79 studies contained empirical nutrient monitoring data for stream restoration projects that implemented hydrologic and/or geomorphic changes to increase stream-floodplain hydrologic connectivity. The average number of empirical nutrient studies published each year increased from 0.3 in the 1990s, to 2.5 in the 2000s, to 10 during 2010-2014 (Fig. 4.1b).

### Geographic Distribution of Study Sites

The majority of the studies were located in North America (47 studies), Europe (25), and Asia (7), and there were no studies that I found that matched my criteria on any other continent (Fig. 4.1c). Studies were conducted in: United States (45 studies), Austria (6), Denmark (6),

Germany (4), England (3), Spain (3), China (3), France (2), and one each in Canada, Japan, Korea, Poland, Taiwan, and along the Mexico/USA border and the Iraq/Iran border.

Distribution of studies in the United States was: Maryland (11), North Carolina (7), Indiana (2), Michigan (2), Mississippi (2), Nevada (2), New York (2), Ohio (2), Virginia (2), Wisconsin (2), and the following states each had 1 study: Arkansas, California, Florida, Georgia, Illinois, Kentucky, Tennessee, Wyoming, Washington, Texas and there was a study comparing sites in Maryland, Illinois, and Iowa.

### Comparison of Methods used for Evaluating Stream Restoration Effectiveness

There were many diverse methods used to evaluate the effects of stream and floodplain restoration on nutrient retention (Fig. 4.2). The most common methods were mass balance, nutrient spiraling, denitrification measurements, and changes in water chemistry. Alternative methods used for evaluating stream and floodplain restoration included: sediment dynamics, plant dynamics, nitrification, stable isotope ratios, dissimilatory nitrate reduction to ammonia (DNRA), anammox, microbial biomass nitrogen (MBN) and potentially mineralizable nitrogen (PMN). Nutrient retention associated with sediment dynamics were measured by 9% of studies and ranged from measuring concentrations (Garcia-Linares et al. 2003) to nitrogen sedimentation and turnover rates (Wolf et al. 2013), and experimentally evaluating changes like N release from sediments deposited on the floodplain (Audet et al. 2011). Nutrient retention rates associated with plant dynamics were measured by 6% of studies and included measurements of biomass, plant uptake, and nutrient utilization efficiency (Troxler Gann et al. 2005, Akamatsu et al. 2008). Nitrification rates were measured by 4% of the studies (Forshay and Dodson 2011, Harrison et al.

2012, Wolf et al. 2013). Stable isotope ratios were measured in 4% of the studies and used to determine composition and microbial utilization of particulate organic material (Aspetsberger et al. 2002, Akamatsu et al. 2008, Newcomer et al. 2012).

### Restoration Typologies that Increase Hydrologic Connectivity

Based upon the practices I found in the literature, stream and floodplain restoration practices were divided into 9 typologies that increase hydrologic connectivity: **(A)** raise stream bottom, **(B)** lower floodplain, **(C)** raise water levels with drainage control structures, **(D)** reconnect wetlands, **(E)** remove concrete liner, and **(F)** daylighting urban streams buried in pipes, **(G)** increase sinuosity, **(H)** add in-stream wetlands, and **(I)** reconnect oxbow wetlands. I also grouped these typologies into strategies based on how they increase hydrologic connectivity: typologies **ABCD** lead to floodplain reconnection; typologies **EF** lead to streambed reconnection; typology **G** increases stream surface area; and typologies **HI** lead to increased wetland surface area (Table 4.1).

When I analyzed the 79 empirical nutrient studies I found that there were 27 unique combinations of the 9 typologies (Supplementary Table 4.1; Fig. 4.3). Overall, 62% of results were positive, 26% were neutral, and 12% were negative. The most common combinations of restoration typologies were reconnect oxbow wetlands (**I**; 11 studies), raise stream bottom (**A**; 9 studies), raise water levels with drainage control structures (**C**; 8 studies), and lower floodplain (**B**; 7 studies). Most studies listed a single restoration typology (N = 45 studies) or two typologies (N = 20 studies). There were also studies that listed 3, 4, and 5 typologies (N = 6, 7, and 1

studies, respectively). The % positive results increased from  $59 \pm 3\%$  when the study had a single typology to 100% when there were 5 typologies.

#### Examination of common methods used to monitor restoration projects

*Changes in water chemistry:* Most studies (96%) examined changes in water chemistry (pre and post restoration and/or compared restored and degraded streams), and there was considerable variety in how changes in streamwater chemistry were examined. N species monitored included one or more of the following: nitrate, nitrite, ammonium, inorganic nitrogen, organic nitrogen, total dissolved nitrogen, particulate nitrogen, total Kjeldahl nitrogen, and total nitrogen. If P was monitored, it was one or more of the following: total phosphorus (TP), total dissolved phosphorus (TDP), and soluble reactive phosphorus (SRP). Some studies compared concentrations pre-restoration to post-restoration (Orr et al. 2007, Kim et al. 2007, Pedersen et al. 2007, Akamatsu et al. 2008, Hoffmann et al. 2012, Gordon et al. 2013, Sheng et al. 2013). Other water chemistry studies compared restored and reference reaches. Reference reaches were usually either in neighboring watersheds or a reach upstream of the restoration. References were either “natural” reaches which are nearby streams of similar size and geology that are considered to be good ecological condition (Evans et al. 2007, Daniluk et al. 2013, Wolf et al. 2013, Theriot et al. 2013) or unrestored, degraded reaches (Troxler Gann et al. 2005, Hines and Hershey 2011, Welti et al. 2012b, Hoellein et al. 2012). Some studies compared concentrations in restored reaches with concentrations in both natural and unrestored degraded reference reaches (Pedersen et al. 2006, Harrison et al. 2012, Newcomer et al. 2012, Meyer et al. 2013, Newcomer Johnson et al. 2014). Additionally, several studies used a before-after-control-impact (BACI, citation) design to

evaluate changes in water chemistry (Hoffmann et al. 1998, Roberts et al. 2007, Bukaveckas 2007, Filoso and Palmer 2011). Lastly, another approach was to examine changes in water chemistry through detailed mapping of hyporheic porewater dynamics around individual restoration structures ((Lautz and Fanelli 2008); Kasahara and Hill 2006). Most water chemistry studies examined surface water dynamics but there were several that examined porewater and groundwater as well (Clilverd et al. 2013, Daniluk et al. 2013, Gordon et al. 2013).

*Mass Balance:* Mass balances were conducted in 22% of the studies. Mass balance complexity ranged from measuring inlet and outlet flux (Comin et al. 1997, Mitsch et al. 2005, Kieckbusch and Schrautzer 2007, Evans et al. 2007, Rücker and Schrautzer 2010, Huang et al. 2010, Passy et al. 2012) to projects across broader spatial scales that incorporated longitudinal sampling, groundwater, and tributaries (Richardson et al. 2011, Sivirichi et al. 2011, Newcomer Johnson et al. 2014). A limitation of the mass balance approach is that it represents a “black box” approach where it is difficult to distinguish between N plant uptake (temporary removal unless vegetation is harvested) and denitrification. This differentiation requires moving beyond N mass balance approaches and conducting direct measurements of nutrient spiraling and *in situ* denitrification in these systems.

*Denitrification:* Denitrification rates were measured in 29% of the studies. Denitrification was measured using denitrification enzyme assays,  $^{15}\text{N}$  denitrification capacity assays,  $^{15}\text{N}$  laboratory mesocosms, and  $^{15}\text{N}$  *in situ* push-pulls. Denitrification enzyme assays are laboratory methods that use acetylene to block the microbial conversion of  $\text{N}_2\text{O}$  to  $\text{N}_2$ , allowing more easily measured  $\text{N}_2\text{O}$  to accumulate in assay bottles. Denitrification enzyme assays were used in 75% of the

denitrification studies evaluating stream and floodplain restoration. The denitrification enzyme assays methods are useful for conducting simultaneous measurement of numerous replicates over both space and time. Some of the denitrification enzyme assay studies used ambient levels of nitrogen and carbon (Comin et al. 1997, Roley et al. 2012b, 2012c). Other denitrification enzyme assay studies added sufficient levels of nitrogen and carbon so that denitrification was not limited and rates measured were considered potential denitrification rates (Comin et al. 1997, Orr et al. 2007, Klocker et al. 2009, Gift et al. 2010, Harrison et al. 2012, Wolf et al. 2013, Gabriele et al. 2013). Additionally, other studies using denitrification enzyme assays added nitrate but not carbon in order to examine the influence of carbon sources (Sheibley et al. 2006, Ullah and Faulkner 2006, Newcomer et al. 2012).

The  $^{15}\text{N}$  *in situ* push-pulls were used by 15% of the denitrification studies (Kaushal et al. 2008b, Harrison et al. 2011, Newcomer Johnson et al. 2014). The  $^{15}\text{N}$  *in situ* push-pull method involved drawing 10 L of water from a shallow well, amending the sample water with  $^{15}\text{N}$  enriched nitrate and a conservative tracer ( $\text{SF}_6$ ), injecting the solution back into the well for an incubation and then drawing the water back up and analyzing dissolved gas concentrations in the water samples. The push-pull method allows measurement of denitrification in restored streams under ambient conditions, but is labor intensive.

The  $^{15}\text{N}$  denitrification capacity assay is a method that incubated anoxic samples of soil with  $^{15}\text{NO}_3^-$  in 3 mL vials without any addition of organic carbon (Sgouridis et al. 2011); This method avoids the complications of acetylene block (Groffman et al. 2006). The  $^{15}\text{N}$  laboratory mesocosm experiments manipulated undisturbed floodplain sediment under controlled conditions to separate the effects of the riverine nitrate input and changes in DOM composition on the rate of denitrification, DNRA, and anammox (Welti et al. 2012a).

### Nutrient Spiraling Meta-Data Analysis

Results are based on 240 individual experimental additions of ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and soluble reactive phosphorus (SRP) from 15 published studies (Tables 2-3). Nutrient uptake was measured by 19% of the studies reviewed here. All of the studies that measured nutrient uptake took place within the channel of a restored stream (except for Bukaveckas 2007, which occurred in a backwater oxbow of a remnant channel).

Nutrient spiraling is a term that describes the cycling of nutrients as they are assimilated from the water column into benthic biomass, temporarily retained, and mineralized back into the water column (Stream Solute Workshop 1990). Nutrient spiraling rates are influenced by a variety of abiotic and biotic factors. Geomorphic physical properties such as channel size and the surface area to channel volume ratio are abiotic factors that influence the duration (residence time) that water is exposed to biochemically reactive substrates. Biotic factors such as bacteria, fungi, algae, and macrophytes control nutrient uptake. Stream restoration and other restoration projects are able to modify both abiotic (e.g., channel width, transient storage, temperature, and sunlight availability) and biotic factors (by altering flow, substrate composition, and plantings) important to nutrient spiraling.

Urban and agricultural watersheds can have less geomorphic complexity than natural systems because of some of the following alterations: straightening meanders, armoring banks with stone gabions, removal of woody debris and bank vegetation, lining channels in concrete, and burying channels in underground pipes (Allan 2004). Such actions decrease geomorphic complexity and can reduce temporary retention of water in pools, eddies, channel margins, and

other backwater transient storage zones (Roberts et al. 2007). I hypothesized that stream restoration projects that increase transient storage and organic carbon availability can significantly increase nutrient uptake rates.

Out of the 15 nutrient spiraling studies I reviewed, various study designs were employed to identify factors controlling nutrient flux (Tables 2-3). Some studies injected a single nutrient while others injected multiple nutrients. There were 66 single nutrient ammonium injections (Roberts et al. 2007, Hines and Hershey 2011, Northington et al. 2011, Weigelhofer et al. 2013), 45 single nutrient nitrate injections (Kasahara and Hill 2006, Klockner et al. 2009, Filoso and Palmer 2011, Newcomer Johnson et al. 2014), 38 combined ammonium and phosphate experiments (Argerich et al. 2011, Arango et al. 2015), 59 combined nitrate and phosphate experiments (Bukaveckas 2007, McMillan et al. 2014), and 30 combined ammonium, nitrate and phosphate experiments (Hoellein et al. 2012, Bott et al. 2012). Based on the type of nutrient injection, the total number of experiments was 134 ammonium, 134 nitrate, and 127 phosphate injections. Hines and Hershey (2011) explained that they were interested in the impact of nitrate transport downstream but they measured ammonium uptake as a metric of water quality restoration because ammonium's lower ambient concentrations and more rapid removal in the streambed make it more cost-effective than nitrate.

Nutrient spiraling is typically described by 4 terms: uptake rate coefficient ( $k$ ), uptake length ( $S_w$ ), areal uptake ( $U$ ), and uptake velocity ( $V_f$ ). Uptake rate coefficient ( $k$ ) describes uptake on a volumetric basis in units of  $\text{sec}^{-1}$ . Uptake length ( $S_w$ ) is the average downstream distance that a nutrient atom travels in meters in its dissolved form in the water column before it is consumed by biota or sorbed onto sediments. Areal uptake ( $U$ ) is the nutrient uptake rate per unit area of stream bottom in  $\mu\text{g}/\text{m}^2/\text{sec}$ . Uptake velocity ( $V_f$ ) is the vertical velocity of nutrient

molecules through the water column towards the benthos in mm/min.  $V_f$  is useful for measuring the absolute demand by a stream's benthos for a nutrient because, in contrast to  $S_w$  and  $U$ , it is independent of hydrologic characteristics and concentration (Ensign and Doyle 2006). The most commonly reported metric was  $V_f$  which was reported by 80% of nutrient spiraling studies reviewed, followed by  $U$  (60%),  $S_w$  (47%),  $k$  (27%), and % removal (20%). Additional metrics measured were amount of nutrient removed in g/day (Kasahara and Hill 2006) and uptake coefficient in the main channel ( $\lambda$ ) vs. uptake coefficient in the transient storage zone ( $\lambda_s$ ;  $\text{sec}^{-1}$ ; (Argerich et al. 2011)). Nutrient spiraling studies can represent a "snapshot" of nutrient retention in a particular stream at a specific time and discharge (Ensign and Doyle 2006).

#### Evaluating potential controlling factors of nutrient uptake

I examined 34 different possible controlling factors to determine potential drivers of nutrient spiraling rates (Table 4.3). There were substantial inconsistencies from study to study in terms of what was measured, recorded, and reported. Some of the potential controlling factors were commonly available (e.g., discharge) while others were only recorded in a single study (e.g., % woody debris). Thus my meta-data analysis of nutrient spiraling controlling factors required that I draw upon different studies and sites for different metrics and therefore, sample size for each variable was highly variable. I divided these variables into 5 categories: watershed scale variables, reach characteristics, water chemistry, transient storage, and stream productivity.

*Watershed Scale Variables:* I examined four watershed scale variables: watershed area, % impervious surface coverage, % disturbance intensity, % developed. Watershed drainage area, the

most common variable, ranged from 80 to 1,620 ha with a median value of 407 ha, and was recorded by 47% of studies. Percent impervious surface coverage varied from 16.8 to 38% in restored streams and was recorded in 27% of studies. Percent watershed disturbance intensity was defined as the % of watershed area covered by unpaved roads or bare ground on slopes >5% (Roberts et al. 2007). Percent development in both the watershed and the riparian area (defined as a 30 m stream buffer) was calculated by reclassifying 2001 National Land Cover Dataset (NLCD) into four categories: developed, agriculture, undeveloped, and water (Sudduth et al. 2011).

*Reach Scale Variables:* I examined 11 reach scale variables: study reach length, reach average width, reach average depth, discharge (Q), velocity, flashiness (estimated from changes in mean hourly discharge (Sudduth et al. 2011)), longitudinal slope, % canopy cover, % coarse woody debris, above-water photosynthetically active radiation (PAR) in ( $\text{mol quanta photons m}^{-2} \text{ d}^{-1}$ ), and % substrate. Stream width ranged from 0.06 to 7 m with a median value of 2 m. Discharge was recorded for all of the studies and varied from 3 to 344 L/s with a median value of 11.5 L/s. Stream velocity ranged from 0.042 to 5 m/s with a median value of 0.24 L/s.

*Water Chemistry Variables:* I examined 6 water chemistry factors: concentration, temperature, dissolved  $\text{O}_2$  (mg/L), dissolved  $\text{O}_2$  (%), specific conductance ( $\mu\text{S/cm}$ ), and pH. There were over 15 different concentration variables measured that could influence nutrient spiraling rates; the most commonly listed ones were  $\text{NH}_4^+$  (80%),  $\text{NO}_3^-$  (67%), and SRP (27%).

*Transient Storage Variables:* I examined 7 transient storage factors:  $F_{\text{med}}^{200}$ , stream area (A), storage area (As), the ratio of storage to stream area (As/A), dispersion coefficient (D), exchange

coefficient ( $\alpha$ ), and Rh Factor ( $A_S/Q$ ).  $F_{med}^{200}$  is the fraction of the median travel time attributable to transient storage calculated over a standardized length of 200 m (Runkel 2002). Area-based measurements included the main channel cross-sectional area ( $A$ ;  $m^2$ ), transient storage zone cross-sectional area ( $A_S$ ;  $m^2$ ), and the relative size of the transient storage zone ( $A_S/A$ ). Transient storage coefficients include the dispersion coefficient ( $D$ ;  $m^2/sec$ ) and the exchange coefficient between the main channel and the transient storage zone ( $\alpha$ ;  $sec^{-1}$ ). The hydraulic retention factor (Rh) represents the time water spends in the transient storage zone for each meter advected downstream and is calculated as  $A_S/Q$  (Morrice et al. 1997).

*Metabolism Variables:* I examined 6 stream metabolism factors: production (GPP), respiration (ER), net daily metabolism (NDM), P:R, Chl-*a*, and U/Chl-*a*. Stream gross primary production (GPP;  $g/m^2/day$ ) is the total production of energy within a stream and is primarily driven by nutrient, light, and stable habitat availability. Ecosystem respiration (ER;  $g/m^2/day$ ) is a stream's total consumption of energy including both autotrophic and heterotrophic respiration. Net daily metabolism (NDM;  $g/m^2/day$ ) is the net production or consumption of energy, which is calculated as the difference between production and respiration (GPP minus ER). Some studies also report the photosynthesis to respiration ratio (P:R). Benthic algal abundance was measured as chlorophyll-*a* (Chl-*a*). Nutrient uptake per unit Chl-*a* was determined by dividing areal uptake by biomass, measured as U/ Chl-*a*.

## Nutrient spiraling results

### Nitrate

### Nitrate Uptake Length ( $S_w$ )

Nitrate uptake lengths ( $S_w$ ) in restored streams ranged from 34 to 2,668 m (mean: 316 m, median: 136 m,  $N = 25$  measurements, Table 4.4). In comparison to restored streams, nitrate molecules had to travel 10x further ( $p = 0.03$ ) before being assimilated in the degraded streams, which ranged from 108 to 18,632 m (mean: 3,107 m; median: 1,341 m;  $N = 13$  measurements).

Likewise, nitrate molecules tended to travel further before being assimilated in larger and faster rivers (Ensign and Doyle 2006). I found that nitrate  $S_w$  was best correlated with watershed area ( $R^2 = 0.13$ ; Fig. 4.4; Table 4.5). When a winter value of 2,668 m from McMillan et al. (2014) was excluded, linear regression showed a significant positive relationship between nitrate uptake length (m) and two factors related to size: watershed area (ha,  $F_{1,19} = 5.0$ ,  $n = 21$ ,  $p < 0.001$ ) and channel width (m,  $F_{1,19} = 13.7$ ,  $n = 21$ ,  $p = 0.002$ ).

### Nitrate Areal Uptake Rate ( $U$ )

Areal nitrate uptake rates ( $U$ ) in restored streams ranged from 0.15 to 32.3  $\mu\text{g}/\text{m}^2/\text{s}$  (mean: 5.2  $\mu\text{g}/\text{m}^2/\text{s}$ ; median: 1.8  $\mu\text{g}/\text{m}^2/\text{s}$ ;  $N = 32$  measurements). There was a significant positive relationship between areal nitrate uptake rate ( $\mu\text{g}/\text{m}^2/\text{s}$ ) and % impervious surface coverage (Fig. 4.5,  $F_{1,28} = 4.9$ ,  $n = 30$ ,  $p = 0.04$ ). As imperviousness is often used as a proxy for urbanization (Schueler et al. 2009), this relationship may indicate higher rates in urban streams receiving nutrient higher loads.

### Nitrate Uptake Velocity ( $V_f$ )

In the restored reaches, nitrate uptake velocity ( $V_f$ ) ranged from 0.0 to 8.9 mm/min (mean: 2.2 mm/min; median: 1.1 mm/min; N = 36 measurements). The two lowest values were from restored acid mine drainage (AMD) impacted streams (Bott et al. 2012).

### Ammonium

#### Ammonium Uptake Length ( $S_w$ )

Ammonium uptake lengths ( $S_w$ ) averaged 70 m and 421 m in restored streams based on a total of 43 experiments from Weigelhofer et al. (2013) and Hines and Hersey (2011).

#### Ammonium Areal Uptake Rate ( $U$ )

Areal ammonium uptake rates ( $U$ ) in restored streams ranged from 0.0 to 1.4  $\mu\text{g}/\text{m}^2/\text{s}$  (mean: 0.6  $\mu\text{g}/\text{m}^2/\text{s}$ ; median: 0.5  $\mu\text{g}/\text{m}^2/\text{s}$ ; N = 9 measurements) which were marginally significantly lower than rates in degraded streams ( $p = 0.07$ ), which ranged from 0.0 to 2.2  $\mu\text{g}/\text{m}^2/\text{s}$  (mean: 0.7  $\mu\text{g}/\text{m}^2/\text{s}$ ; median: 0.6  $\mu\text{g}/\text{m}^2/\text{s}$ ; N = 17 measurements).

There was a significant negative relationship between areal ammonium uptake rate ( $\mu\text{g}/\text{m}^2/\text{s}$ ) and disturbance intensity (Fig. 4.6;  $F_{1,6} = 7.6$ ,  $n = 8$ ,  $p = 0.03$ ) and a marginally significant negative relationship with ammonium concentration ( $\mu\text{g}/\text{L}$ ; Fig. 4.6;  $F_{1,6} = 4.7$ ,  $n = 8$ ,  $p = 0.07$ ). This relationship is based on Roberts et al. (2007) which studied 8 streams at Fort Benning

Military Installation that had some of the smallest transient storage zones and lowest ammonium uptake rates in the literature (Roberts et al. 2007). They found that disturbance intensity ranged from 3-14% and when they experimentally added coarse woody debris they observed a short-term (within 1 month) increase in transient storage and increase in ammonium uptake.

### Ammonium Uptake Velocity ( $V_f$ )

In the restored reaches, ammonium uptake velocity ( $V_f$ ) ranged from 0.2 to 48.9 mm/min (mean: 9.4 mm/min; median: 4.1 mm/min; N = 18 measurements). The highest values of  $V_f$  occurred in Arango et al. (2015) directly after reconstruction of a new channel. Ammonium uptake velocities were marginally significantly higher in restored streams than in the degraded streams ( $p = 0.11$ ), which ranged from 0.0 to 22.8 mm/min (mean: 3.5 mm/min; median: 1.0 mm/min; N = 23 measurements).

In restored streams, ammonium uptake velocity has a negative linear relationship with disturbance intensity (%),  $F_{1,13} = 14.3$ ,  $n = 15$ ,  $p = 0.002$ ), median travel time due to transient storage over a standardized 200 m reach ( $F_{med}^{200}(\%)$ ),  $F_{1,6} = 2.0$ ,  $n = 8$ ,  $p = 0.20$ ), and a negative power function relationship with ammonium concentration ( $\mu\text{g/L}$ ),  $F_{1,16} = 178$ ,  $n = 18$ ,  $p < 0.001$ , Fig. 4.7). There was also a positive linear correlation with discharge (L/s),  $F_{1,13} = 14.3$ ,  $n = 15$ ,  $p = 0.002$ ), velocity (m/s),  $F_{1,7} = 25.1$ ,  $n = 9$ ,  $p = 0.002$ ) and the ratio of transient storage area to stream area ( $A_S/A$ ),  $F_{1,5} = 5.1$ ,  $n = 7$ ,  $p = 0.07$ ). The positive relationship between ammonium uptake velocity and discharge (which ranged from 5-161 L/s in restored streams) was heavily influenced by the high uptake velocity values reported by Arango et al. (2015) directly after restoration.

## Soluble Reactive Phosphorus (SRP)

### SRP Uptake Length ( $S_w$ ) and Areal Uptake Rate ( $U$ )

SRP uptake lengths ( $S_w$ ) ranged from 12.4 to 1,403 m (mean: 229 m; median: 90 m; N = 20 (Bukaveckas 2007, McMillan et al. 2014)). The highest value was for a channelized stream prior to restoration (Bukaveckas 2007). Based on linear regression, there was a significant positive relationship between phosphate uptake length (m) and two factors related to size: watershed area (ha,  $F_{1, 16} = 8.5$ ,  $n = 18$ ,  $p = 0.01$ ) and discharge (L/s,  $F_{1, 16} = 7.6$ ,  $n = 18$ ,  $p = 0.01$ , Fig. 4.8).

SRP areal uptake rate ( $U$ ) ranged from 0.3 to 117  $\mu\text{g}/\text{m}^2/\text{s}$  (mean: 14  $\mu\text{g}/\text{m}^2/\text{s}$ , median: 3  $\mu\text{g}/\text{m}^2/\text{s}$ ,  $n = 17$ , (Bukaveckas 2007)). Based on such a small sample size, there was not enough data to determine the influence of other potential controlling factors on SRP areal uptake rates.

### SRP Uptake Velocity ( $V_f$ )

In the restored reaches, SRP uptake velocity ( $V_f$ , mm/min) ranged from 0.1 to 32.9 mm/min (mean: 5.7 mm/min; median: 1.9 mm/min;  $n = 28$  measurements). The degraded streams, which ranged from 1.4 to 87.4 mm/min (mean: 19.9 mm/min; median: 11.8 mm/min;  $N = 8$  measurements) has significantly higher SRP  $V_f$  than restored ( $p = 0.03$ ) and reference streams ( $p = 0.05$ ), which ranged from 2.2 to 5.9 mm/min (mean: 4.2 mm/min; median: 4.9 mm/min;  $N = 9$  measurements). The highest values of  $V_f$  occurred in Bott et al. (2012) in a degraded AMD

impacted anthracite stream, a value higher than any other in the literature (Ensign and Doyle 2006).

There were significant positive linear relationships between phosphate uptake velocity and discharge (L/s,  $F_{3,6} = 3.6$ ,  $n = 25$ ,  $p < 0.001$ ), chlorophyll *a* concentration ( $\text{mg/m}^2$ ,  $F_{1,8} = 21.6$ ,  $n = 10$ ,  $p = 0.09$ ), and SRP concentration ( $\mu\text{g/L}$ ,  $F_{1,8} = 19.6$ ,  $n = 10$ ,  $p = 0.002$ , Fig. 4.9). There was also a negative correlation between phosphate uptake velocity and ammonium concentration ( $\mu\text{g/L}$ ,  $F_{1,8} = 3.2$ ,  $n = 10$ ,  $p = 0.11$ ). When chlorophyll *a*, SRP concentration, and ammonium concentration were used for a multiple linear regression analysis, only SRP concentration remained a significant predictor ( $\mu\text{g/L}$ ,  $F_{1,8} = 19.6$ ,  $n = 10$ ,  $p = 0.002$ ). It also appears that for a given concentration of SRP or Chl-*a*, there was higher  $V_f$  in the restored streams than in the reference streams.

### Discussion

Some of the highest uptake rates seen in nutrient spiraling literature were measured shortly after a restoration project that converted Wilson Creek in Okanogan-Wenatchee National Forest of Central Washington, USA from a narrow, high velocity stream devoid of wood to a wide, low velocity channel with large wood and boulder structures (Arango et al. 2015). This study was unique in that it captured the immediate ecosystem response to restoration (Arango et al. 2015). A common aim of restoration is to stabilize streams to reduce erosion of sediments and infrastructure (Doyle et al. 2015). However, the physical process of bringing in heavy machinery like bulldozers to restore a stream can be a major disturbance. Some other possible restoration related disturbances include redirecting the channel to a new location, bringing in new rock and

other substrate, and removing large canopy trees that used to shade the channel. After the physical disturbance of restoration, there can be rapid succession as periphyton and other biota rapidly recover (Grimm 1987). Overall, I found highest rates in newly restored sites, high rates in urban (Knust and Warwick 2009, Klocker et al. 2009, Hines and Hershey 2011, Sudduth et al. 2011, Newcomer Johnson et al. 2014, McMillan et al. 2014, Arango et al. 2015) and agricultural watersheds (Ensign and Doyle 2005, Kasahara and Hill 2006, Bukaveckas 2007, Argerich et al. 2011, Weigelhofer et al. 2013) (which are likely linked to positive relationships with nutrient and Chl-*a* concentrations (Filoso and Palmer 2011), lower rates in forested and acid mine drainage watersheds, shorter uptake lengths in smaller streams (which have higher surface-to-volume ratios), and some conflicting trends with transient storage.

#### High rates in newly restored agricultural and urban streams

Several studies linked elevated uptake rates in newly restored streams to increased light availability and coarser substrate composition (Hines and Hershey 2011, Sudduth et al. 2011, McMillan et al. 2014). Increased light availability from reduced canopy cover can temporarily increase stream temperature and the abundance of algal biofilms. The notably high rates in Wilson Creek are attributed to rapid algal growth causing a transient spike in whole system nutrient demand which leveled off 35 days after restoration (Arango et al. 2015). An 8-year chronosequence of 5 restored urban streams in North Carolina, USA found that P uptake was greater in newly restored sites, a finding attributed to assimilation by algal biofilms (McMillan et al. 2014). Coarser substrates (e.g., cobbles, rocks, and boulders) can serve as a more stable surface for biofilms because they are less likely to be disturbed by turbulence during high flow

events than finer substrates like sand and silt (Smith and Lake 1993). Likewise, larger substrates enhance stream–subsurface water exchange and the transfer of dissolved solutes from the stream to the streambed (Kasahara and Hill 2006, Hoellein et al. 2012).

Elevated uptake rates due to increased sunlight availability are likely to be temporary as the canopy regrows. Elevated uptake rates due to coarser sediment composition may be temporary if interstitial spaces are clogged with finer sediments from upstream erosion. However, a watershed management plan that integrates stormwater management, wetlands, and conservation practices that reduce effective imperviousness and retain runoff may be able to reduce erosion rates. These studies demonstrate that stream restoration projects evolve over time so it is important to continue monitoring efforts past when the canopy regrows to determine the duration for increased nutrient retention as well as potential maintenance needs.

#### Low nutrient uptake rates in AMD remediated streams

Some of the lowest uptake velocity rates in restored streams were in watersheds with AMD from coal (Northington et al. 2011, Bott et al. 2012). In the United States, coal companies are mandated to complete compensatory mitigation for mining related watershed disturbances and many choose to restore sections of stream in older coal mining areas (Northington et al. 2011). One study of AMD stream remediation showed restored  $\text{NH}_4^+$  uptake, reduced  $\text{NO}_3^-$  uptake to undetectable level, and restored SRP uptake to near normal rates (Bott et al. 2012). In contrast, another study of AMD remediated streams found no site differences for any measured physicochemical or functional variables (Northington et al. 2011). Likewise, a seasonal analysis

showed no differences between restored and unrestored streams during the winter (Sudduth et al. 2011).

### Size matters: optimizing reactive sediment volume and transient storage

As previously discussed, restored urban and agricultural streams can have high uptake rates; however, mass removal rates can be limited in tile drains and buried or straightened concrete channels due to limited surface area, hyporheic exchange, and transient storage (Beaulieu et al. 2014, Pennino et al. 2014). My analysis of watershed and reach scale controlling factors demonstrated that size matters. It takes longer for a molecule to be removed from the water column in a larger river than a small headwater stream as demonstrated by the positive relationships seen between uptake length and the variables that demonstrate size: watershed area, discharge, and velocity (Klockner et al. 2009). This size dependency has been attributed to larger surface-to-volume ratios in smaller headwater streams favoring rapid N uptake and processing.

Through restoration, managers can increase mass removal rates by optimizing the surface area and depth of reactive sediments and lengthening transient storage times (Newcomer Johnson et al. 2014). For example, two narrow, incised rivers were restored to structurally diverse, meandering channels with step-pool sequences and considerable accumulation of woody debris (Weigelhofer et al. 2013). Weigelhofer et al. (2013) found 4-5x higher transient storage in both morphologically pristine and restored reaches than in channelized sections, resulting in significantly shorter uptake lengths and higher mass transfer coefficients. Hyporheic exchange in this study was restricted by fine sediments clogging interstitial spaces so the increased transient

storage is attributed to surface retention in debris dams and pools, similar to findings by (Ensign and Doyle 2005, Roberts et al. 2007, Bukaveckas 2007).

I found that relationships linking transient storage with nutrient uptake are not always consistent because diverse stream compartments such as algal mats, hyporheic zones, and backwater areas can all contribute to transient storage and these compartments can have distinct biological communities with different uptake rates and processes (Argerich et al. 2011). Some studies showed significant relationships between transient storage and nutrient uptake (Valett et al. 1996, Thomas et al. 2003, Ensign and Doyle 2005, Jordan et al. 2007), while others show weaker relationships (Lautz and Siegel 2007, Bukaveckas 2007), or contrasting findings for phosphate (e.g., (Hall Jr et al. 2002)), and some studies found no trends (e.g., (Webster et al. 2003, Ensign and Doyle 2006)). Hence, there is a need to better understand the structure and function of different types of transient storage zones (Argerich et al. 2011).

#### Restored riffles, substrate, and coarse woody debris

When restoring streams, projects can be designed to improve nutrient uptake by raising water levels, lowering velocity, increasing transient storage, and increasing organic matter accumulation. Installing rocky riffles and raising channel bed elevation in the restored reach of the Truckee River increased transient storage zone cross-sectional area ( $A_S$ ) leading to increased hyporheic residence time and hydrologic retention in the vicinity of channel reconstructions and model simulations predicted greater N retention (Knust and Warwick 2009). Likewise, a study that examined constructed riffles and a step in restored reaches of several N-rich agricultural and urban streams in southern Ontario found a range of 50% to 99% N removal in hyporheic zones

composed of less than 25% stream water (Kasahara and Hill 2006). Though the natural riffle had greater %  $\text{NO}_3^-$  removal than the constructed riffle, the constructed riffle removed 3x more N mass because of larger hyporheic exchange flux (Kasahara and Hill 2006). These small constructed features removed 0.003% - 0.06% of daily stream load.

In studies that raised the stream bottom with experimental flow deflectors, transient storage increased and stream velocity decreased thus increasing the residence time of water within benthic communities (Ensign and Doyle 2005, Roberts et al. 2007, Argerich et al. 2011). The addition of baffles, structures added to the stream to obstruct flow, significantly increased both phosphate and ammonium uptake velocity (Ensign and Doyle 2005). Ammonium uptake significantly increased when enough coarse woody debris was added to double transient storage (Roberts et al. 2007). In contrast, substrate packs (containing cobbles, sand, or mud) added to an irrigation canal near Barcelona, Spain doubled transient storage but did not significantly influence whole-stream phosphate and ammonium uptake which is attributed to the short 20 m study reaches and relatively low levels of transient storage even after addition of the substrate packs (Argerich et al. 2011). When the substrate packs were compared, mud packs had the highest uptake coefficients attributed to greater organic matter content, greater water residence time, and lower dissolved oxygen concentrations (Argerich et al. 2011). However, the authors of this study did not advocate adding mud to streams because excess soil inputs from the watershed can clog sediments and inhibit the exchange between interstices and stream water.

Coarse woody debris (CWD) treatments increased ammonium uptake velocity ( $V_f$ ) by 23-154% and uptake rate (U) by 61-235% when compared to the control reaches (Roberts et al. 2007). As wood is characterized by higher C:N ratios than biofilms or microorganisms (Dodds et al. 2004), its decomposition requires additional nitrogen sources, thereby increasing the nutrient

demand of microbial decomposers (Newcomer et al. 2012). Carbon limitation of N uptake typically occurs below DOC levels of 2 mg/L (Goodale et al. 2005). Flashy hydrology in degraded channelized streams can prevent formation of organic debris dams (Groffman et al. 2005) which have been shown, along with pools, to have higher denitrification potential than other in-stream features (Harrison et al. 2012).

### *Conclusions and management implications*

Many restoration strategies can foster nutrient retention within hydrologically disconnected streams and floodplains. The commonality between all of these restoration practices is that they reconnect surface and groundwater and increase retention time in order to promote N retention. From my database of hydrologic stream restoration studies, I learned that the effect of all of the typologies was an overall retention of nutrients. Most of the restoration projects implemented only 1 or 2 typologies. However, combining multiple typologies increased the likelihood of a positive performance (Fig. 4.10). Therefore, if a watershed is impaired by nutrient pollution, restoration practitioners may be able to “hedge their bets” and increase the odds that their project will successfully reduce nutrient loads by implementing multiple hydrologic restoration strategies.

In order to optimize watershed nutrient retention it is important to increase residence time and the volume of water interacting with reactive biofilms and sediments. It is essential to consider all 4 dimensions of a stream network: lateral, longitudinal, vertical, and temporal (Venkatesh Merwade 2010, Kaushal and Belt 2012). Laterally, channels can be widened, connected to their floodplains, and oxbow wetlands or side-channels can be integrated.

Longitudinally, sinuosity can be increased to attenuate excess energy and increase residence time. Vertically, step pool sequences can foster turbulence and mixing between surface water and groundwater. Urban and agricultural land use can clog channels with fine sediments that limit hyporheic exchange. Thus it is important to incorporate stormwater management and other structures that can limit the flux of fine sediments from clogging newly restored reaches. When considering time, it is important to provide sufficient hydrologic residence time for high flow events and to consider maintenance needs for the future. An efficient time to conduct stream restoration is during already planned sewer and drinking water infrastructure upgrades.

#### Gaps and future directions

Now that I have reviewed the current state of the literature it has become apparent that the majority of studies are sampling during baseflow while the majority of the annual load is often delivered during high flow events. This sampling gap may have led to my study finding a more positive conclusion than what is occurring in reality. Reducing peak flows is vital to providing streams enough time to act as transformers instead of just transporters. Such watershed adaptation is especially important in areas where climate change is changing precipitation patterns and causing increased storminess. More studies that examine retention across a range of flow conditions including extreme events are necessary to better elucidate the role of restoration in nutrient management. Additionally, I found that for examining the impact of restoration on nutrient retention a degraded reference is more useful than a “pristine” reference. Stream restoration for nutrient retention is not going to get you back to a pristine state if you are not also changing watershed inputs. Thus, stream restoration for water quality is really more of a way to

re-engineer the system for better performance. Another suggestion for future studies is to seek out failed restoration projects to determine what went wrong and how such failures can be prevented in the future. There is also a need to expand geographically to areas beyond North America, Europe, and the few studies found in Asia. Likewise modeling studies are an essential complement to field studies for demonstrating how restoration may be applied at a watershed scale and what effect restoration may have in reducing loads to coastal zones and estuaries (Abdelnour et al. 2011, 2013, McKane 2014a, 2014b). Also, there is a need to connect to social science to understand the social, political, and economic forces driving stream restoration practices (Doyle et al. 2015).

#### *Acknowledgements*

This research was supported by MD Sea Grant Awards SA7528085-U, R/WS-2 and NA05OAR4171042, EPA NNEMS Award 2010-308, the U.S. EPA Office of Research and Development, and Baltimore Ecosystem Study LTER project (NSF DEB-0423476). I thank Michael Pennino, Walter Boynton, Peter Groffman, and Jeff Cornwell for improving earlier drafts. I thank Shuiwang Duan for help with translation from Chinese to English. The information in this document has been subjected to Agency peer and administrative review, and it has been approved for publication as an Agency document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 4.1. The 79 empirical nutrient studies were divided into 4 strategies used to increase hydrologic connectivity. We recorded the number of results for each strategy as well as percentage of nutrient results that were positive, neutral, and negative. Note the total number of results is higher than the total number of studies because many studies used multiple strategies and many studies had multiple results based upon seasonality and nutrient species.

| Strategies used to Increase Hydrologic Connectivity | Number of Results from 79 Studies | Positive Results (%) | Neutral Results (%) | Negative Results (%) |
|---|-----------------------------------|----------------------|---------------------|----------------------|
| Floodplain Reconnection                             | 62                                | 60%                  | 28%                 | 12%                  |
| Streambed Reconnection                              | 9                                 | 70%                  | 20%                 | 10%                  |
| Increased Stream Surface Area                       | 19                                | 65%                  | 22%                 | 13%                  |
| Increased Wetland Surface Area                      | 24                                | 75%                  | 14%                 | 11%                  |
| <b>Total</b>  | <b>114</b>                        | <b>62%</b>           | <b>26%</b>          | <b>12%</b>           |

Table 4.2. We recorded the nutrient spiraling tracers ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and/or SRP) and uptake metrics [ $k$  (uptake rate coefficient;  $\text{sec}^{-1}$ ),  $S_w$  (uptake length; m),  $U$  (areal uptake;  $\mu\text{g}/\text{m}^2/\text{sec}$ ), and  $V_f$  (uptake velocity; mm/min)] that were recorded as well as a summary for each study.

| Citation                     | Tracer Used     |                 |     | Uptake Metrics* Recorded |       |     |       |   |                   | Description of Study Streams                       | N  | Summary  |
|------------------------------|-----------------|-----------------|-----|--------------------------|-------|-----|-------|---|-------------------|--|----|--|
|                              | $\text{NH}_4^+$ | $\text{NO}_3^-$ | SRP | $k$                      | $S_w$ | $U$ | $V_f$ | % | Other             |  |    |  |
| Weigelhofer et al. 2013      |                 |                 |     |                          |       |     |       |   |                   | Pristine, restored, broadened, and incised streams | 31 | Restored/pristine reaches had significantly shorter $S_w$ & larger $V_f$ than channelized reaches, and $\text{NH}_4^+$ uptake was positively correlated with transient storage.  |
| Roberts et al. 2007          |                 |                 |     |                          |       |     |       |   |                   | Coarse woody debris treatment and control          | 16 | Coarse woody debris (CWD) treatments had significantly higher uptake than the control ( $V_f$ increased by 23-154% and $U$ by 61-235%).  |
| Northington et al. 2011      |                 |                 |     |                          |       |     |       |   |                   | Acid mine drainage (AMD)                           | 9  | All streams were net heterotrophic with varying levels of $\text{NH}_4^+$ uptake. No site differences were found.  |
| Hines and Hershey 2011       |                 |                 |     |                          |       |     |       |   |                   | Restored and unrestored reference streams          | 12 | Significantly shorter $\text{NH}_4^+$ uptake length ( $S_w$ ) was observed in restored compared to unrestored sites 2 years post-restoration. They attributed this to greater biofilm development on larger substrate with less canopy cover. There was not a significant change to $U$ or $V_f$ . |
| Argerich et al. 2011         |                 |                 |     |                          |       |     |       |   | $\lambda_s$       | Control stream plus 4 treatments                   | 24 | Substrate treatment increased transient storage zone and decreased velocity in 20 m reaches but did not significantly affect larger reach.   |
| Arango et al. 2015           |                 |                 |     |                          |       |     |       |   |                   | Pre-restoration, restored, and reference           | 14 | After restoration, nutrient demand spiked to levels that have rarely been reported, but demand recovered within 35 days.   |
| Kasahara and Hill 2006       |                 |                 |     |                          |       |     |       |   | $\text{day}^{-1}$ | Man-made riffles/step vs. natural riffle           | 4  | Natural riffle had greater $\text{NO}_3^-$ % removal than constructed riffle, but constructed riffle removed 3x more due to larger hyporheic exchange flux. Constructed features removed 0.003%-0.06% of daily load.   |
| Filoso and Palmer 2011       |                 |                 |     |                          |       |     |       |   |                   | 3 restored streams                                 | 6  | Doubling tracer N concentration increased $S_w$ and decreased $U$ & $V_f$ .  |
| Klocker et al. 2009          |                 |                 |     |                          |       |     |       |   |                   | 2 degraded & 2 restored streams                    | 5  | $S_w$ increased with velocity  |
| Newcomer Johnson et al. 2014 |                 |                 |     |                          |       |     |       |   |                   | Restored, urban, and forest streams                | 6  | $V_f$ and $U$ were greater in stream reaches than adjacent stormwater control measures   |

| Citation              | Tracer Used                  |                              |     | Uptake Metrics* Recorded |                |   |                |   |       | Description of Study Streams                               | N  | Summary  |
|-----------------------|------------------------------|------------------------------|-----|--------------------------|----------------|---|----------------|---|-------|--|----|--|
|                       | NH <sub>4</sub> <sup>+</sup> | NO <sub>3</sub> <sup>-</sup> | SRP | k                        | S <sub>w</sub> | U | V <sub>r</sub> | % | Other |  |    |  |
| Sudduth et al. 2011   |                              |                              |     |                          |                |   |                |   |       | 3 restored, 3 urban degraded, & 3 forest streams           | 24 | In summer, restored reaches had higher uptake rates than unrestored/forested reaches; Temperature & % canopy cover explained 80% of the variation in uptake.   |
| Bukaveckas 2007       |                              |                              |     |                          |                |   |                |   |       | Channelized, restored, and reference reach                 | 44 | Lowering velocity and raising transient storage in restored stream increased uptake but difference was not statistically significant.  |
| Mc Millan et al. 2014 |                              |                              |     |                          |                |   |                |   |       | 5 streams restored from 2002-2010                          | 15 | P uptake was greater in newly restored sites (attributed to assimilation by algal biofilms), whereas NO <sub>3</sub> <sup>-</sup> uptake was highest in older sites potentially due to greater channel stability and establishment of microbial communities. |
| Hoellein et al. 2012  |                              |                              |     |                          |                |   |                |   |       | Restored and reference                                     | 24 | Increases in gravel, cobble and boulder habitat in the restoration reaches were correlated with higher rates of nutrient uptake and metabolism.  |
| Bott et al. 2012      |                              |                              |     |                          |                |   |                |   |       | Acid mine drainage (AMD) degraded, restored, and reference | 6  | Acid Mine Drainage (AMD) remediation restored NH <sub>4</sub> <sup>+</sup> uptake, reduced NO <sub>3</sub> <sup>-</sup> uptake to undetectable level, and restored SRP uptake to near normal rates.  |

Table 4.3. The 15 nutrient spiraling studies measured 45 diverse potential controlling variables. We divided these variables into 5 categories: watershed, reach, water chemistry, transient storage, and metabolism characteristics. Shaded boxes indicate that a variable was measured in the specific study. The two columns on the right show the total number and percent of studies that recorded each variable.

| Categories                      | Variables                                 | Weigelhofer et al. 2013 | Roberts et al. 2007 | Northington et al. 2011 | Hines and Hershey 2011 | Argerich et al. 2011 | Arango et al. 2015 | Kasahara and Hill 2006 | Filoso and Palmer 2011 | Klocker et al. 2009 | Newcomer Johnson et al. 2014 | Sudduth et al. 2011 | Bukaveckas 2007 | McMillan et al. 2014 | Hoellein et al. 2012 | Bott et al. 2012 | N | % of Studies |     |
|---------------------------------|---|-------------------------|---------------------|-------------------------|------------------------|----------------------|--------------------|------------------------|------------------------|---------------------|------------------------------|---------------------|-----------------|----------------------|----------------------|------------------|---|--------------|-----|
| Watershed Characteristics       | Watershed Area                            |                         | ■                   |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 7 | 47           |     |
|                                 | % Impervious                              |                         |                     |                         |                        |                      |                    |                        | ■                      |                     | ■                            |                     |                 | ■                    |                      |                  |   | 4            | 27  |
|                                 | % Disturbance                             |                         | ■                   |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  |   | 1            | 7   |
|                                 | % Developed                               |                         |                     |                         |                        |                      |                    |                        |                        |                     |                              | ■                   |                 |                      |                      |                  |   | 1            | 7   |
| Reach Characteristics           | Study Reach Length                        | ■                       | ■                   | ■                       | ■                      | ■                    | ■                  | ■                      | ■                      | ■                   | ■                            | ■                   | ■               | ■                    | ■                    | ■                | ■ | 15           | 100 |
|                                 | Width                                     | ■                       | ■                   |                         | ■                      | ■                    | ■                  | ■                      | ■                      | ■                   | ■                            | ■                   | ■               | ■                    | ■                    | ■                | ■ | 10           | 67  |
|                                 | Depth                                     |                         |                     |                         |                        | ■                    | ■                  | ■                      | ■                      | ■                   | ■                            | ■                   | ■               | ■                    | ■                    | ■                | ■ | 5            | 33  |
|                                 | Discharge (Q)                             | ■                       | ■                   | ■                       | ■                      | ■                    | ■                  | ■                      | ■                      | ■                   | ■                            | ■                   | ■               | ■                    | ■                    | ■                | ■ | 15           | 100 |
|                                 | Velocity                                  |                         | ■                   |                         |                        | ■                    | ■                  |                        |                        | ■                   |                              |                     |                 |                      |                      | ■                | ■ | 6            | 40  |
|                                 | Flashiness                                |                         |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     | ■               |                      |                      |                  |   | 1            | 7   |
|                                 | Slope                                     |                         |                     |                         |                        |                      |                    | ■                      |                        |                     |                              |                     |                 |                      |                      |                  |   | 1            | 7   |
|                                 | % Canopy Cover                            |                         |                     |                         | ■                      | ■                    |                    |                        |                        |                     |                              |                     | ■               |                      | ■                    |                  | ■ | 4            | 27  |
|                                 | % Woody Debris                            |                         | ■                   |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  |   | 1            | 7   |
|                                 | Radiation (PAR)                           |                         |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | ■ | 1            | 7   |
|                                 | % Substrate                               |                         |                     |                         | ■                      | ■                    |                    |                        |                        |                     |                              |                     |                 |                      |                      | ■                | ■ | 2            | 13  |
| Water Chemistry Characteristics | Ammonium (NH <sub>4</sub> <sup>+</sup> )  | ■                       | ■                   | ■                       | ■                      | ■                    | ■                  | ■                      | ■                      | ■                   | ■                            | ■                   | ■               | ■                    | ■                    | ■                | ■ | 11           | 65  |
|                                 | Nitrate (NO <sub>3</sub> <sup>-</sup> )   |                         |                     | ■                       | ■                      | ■                    | ■                  | ■                      | ■                      | ■                   | ■                            | ■                   | ■               | ■                    | ■                    | ■                | ■ | 11           | 65  |
|                                 | Nitrite (NO <sub>2</sub> <sup>-</sup> )   | ■                       |                     |                         |                        |                      |                    |                        |                        |                     | ■                            |                     |                 |                      |                      |                  |   | 2            | 12  |
|                                 | Total N (TN)                              |                         |                     |                         |                        |                      |                    |                        | ■                      |                     |                              |                     |                 |                      |                      |                  | ■ | 2            | 12  |
|                                 | Dissolved Organic N                       |                         |                     |                         |                        |                      |                    |                        | ■                      |                     |                              | ■                   |                 |                      |                      |                  |   | 2            | 12  |
|                                 | SRP                                       |                         |                     |                         |                        |                      | ■                  |                        |                        |                     |                              |                     | ■               |                      | ■                    | ■                | ■ | 4            | 24  |
|                                 | Dissolved Organic C                       |                         |                     |                         |                        |                      |                    | ■                      | ■                      |                     |                              | ■                   |                 | ■                    |                      |                  |   | 4            | 24  |
|                                 | Phosphate (PO <sub>4</sub> <sup>-</sup> ) |                         |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      | ■                    |                  |   | 1            | 6   |
|                                 | Total P                                   |                         |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | ■ | 1            | 6   |

| Categories                                  | Weigelhofer et al. 2013           | Roberts et al. 2007 | Northington et al. 2011 | Hines and Hershey 2011 | Argerich et al. 2011 | Arango et al. 2015 | Kasahara and Hill 2006 | Filoso and Palmer 2011 | Klocker et al. 2009 | Newcomer Johnson et al. 2014 | Sudduth et al. 2011 | Bukaveckas 2007 | McMillan et al. 2014 | Hoellein et al. 2012 | Bott et al. 2012 | N | % of Studies |
|---|-----------------------------------|---------------------|-------------------------|------------------------|----------------------|--------------------|------------------------|------------------------|---------------------|------------------------------|---------------------|-----------------|----------------------|----------------------|------------------|---|--------------|
| Water Chemistry Characteristics (Continued) | Total Dissolved P                 |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 1 | 6            |
|   | Benthic Organic Matter (BOM)      |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 1 | 6            |
|   | Total Dissolved Solids (TDS)      |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 1 | 6            |
|   | Temperature                       |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 5 | 33           |
|   | Dissolved O <sub>2</sub>          |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 3 | 20           |
|   | % Dissolved O <sub>2</sub>        |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 2 | 13           |
|   | Specific Conductance              |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 2 | 13           |
| pH  |                                   |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      | 1                | 7 |              |
| Transient Storage Characteristics           | $F_{med}^{200}$                   |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 5 | 33           |
|   | Stream Area (A)                   |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 1 | 7            |
|   | Storage Area (A <sub>S</sub> )    |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 2 | 13           |
|   | Storage Ratio (A <sub>S</sub> /A) |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 4 | 27           |
|   | Dispersion Coefficient            |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 3 | 20           |
|   | $\alpha$ Exchange Coefficient     |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 2 | 13           |
|   | Rh Factor (A <sub>S</sub> /Q)     |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 1 | 7            |
| Metabolism Characteristics                  | Production (GPP)                  |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 5 | 33           |
|   | Respiration (ER)                  |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 5 | 33           |
|   | Net Metabolism                    |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 3 | 20           |
|   | P:R                               |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 1 | 7            |
|   | Chl- <i>a</i>                     |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 4 | 27           |
|   | U/Chl- <i>a</i>                   |                     |                         |                        |                      |                    |                        |                        |                     |                              |                     |                 |                      |                      |                  | 1 | 7            |

Table 4.4. Mean, median, range, and number of studies reporting each nutrient spiraling metric by stream type (restored, degraded, and reference). Uptake metrics included:  $S_w$  (uptake length in m),  $U$  (areal uptake in  $\mu\text{g}/\text{m}^2/\text{sec}$ ), and  $V_f$  (uptake velocity in mm/min).  $P$  values are listed for ANOVA comparisons between stream types that are significant or marginally significant.

| Stream Type                   |        | $\text{NO}_3^-$              |  |                   | $\text{NH}_4^+$              |  |                              | SRP          |  |                   |
|-------------------------------|--------|------------------------------|--|-------------------|------------------------------|--|------------------------------|--------------|--|-------------------|
|                               |        | $S_w$<br>(m)                 | $U$<br>( $\mu\text{g}/\text{m}^2/\text{s}$ ) | $V_f$<br>(mm/min) | $S_w$<br>(m)                 | $U$<br>( $\mu\text{g}/\text{m}^2/\text{s}$ ) | $V_f$<br>(mm/min)            | $S_w$<br>(m) | $U$<br>( $\mu\text{g}/\text{m}^2/\text{s}$ ) | $V_f$<br>(mm/min) |
| Restored                      | Mean   | 316                          | 5.2  | 2.2               | 245.6                        | 0.6  | 9.4                          | 153.2        | 13.8   | 5.7               |
|                               | Median | 136                          | 1.8  | 1.1               |                              | 0.5  | 4.1                          | 77.8         | 3.4  | 1.9               |
|                               | Range  | 34-2,668                     | 0.15-32                                      | 0.0-8.9           | 70-421                       | 0.0-1.4                                      | 0.2-49                       | 12-572       | 0.3-117                                      | 0.1-33            |
|                               | Number | 25                           | 32   | 36                | 2                            | 9  | 18                           | 18           | 17   | 28                |
| <b>Restored vs. Degraded</b>  |        | <b><math>P = 0.03</math></b> |  |                   | <b><math>P = 0.07</math></b> |  | <b><math>P = 0.11</math></b> |              | <b><math>P = 0.03</math></b>                 |                   |
| Degraded                      | Mean   | 3,107                        | 5.3  | 3.0               | 609.5                        | 0.7  | 3.5                          |              |  | 19.9              |
|                               | Median | 1,341                        | 0.42   | 1.0               | 789.5                        | 0.6  | 1.0                          | 1,403        |  | 11.8              |
|                               | Range  | 108-18,632                   | 0.01-33.6                                    | 0.02-38.2         | 197-                         | 0.0-2.2                                      | 0.0-22.8                     |              |  | 1.4-87.4          |
|                               | Number | 13                           | 12   | 24                | 842                          | 17   | 23                           | 1            | 0  | 8                 |
| <b>Degraded vs. Reference</b> |        |                              |  |                   |                              |  |                              |              | <b><math>P = 0.05</math></b>                 |                   |
| Reference                     | Mean   | 2,714                        | 0.19   | 3.3               |                              |  | 3.9                          |              |  | 4.2               |
|                               | Median | 345                          | 0.03   | 0.4               | 210.5                        | 1.6  | 0.4                          | 413          |  | 4.9               |
|                               | Range  | 238-7,558                    | 0.00-1.43                                    | 0.03-35           |                              |  | 0.03-35                      |              |  | 2.2-5.9           |
|                               | Number | 3                            | 10   | 13                | 1                            | 1  | 11                           | 1            | 0  | 9                 |
| <b>Reference vs. Restored</b> |        | <b><math>P</math> value</b>  |  |                   |                              |  |                              |              |  |                   |

Table 4.5. The 15 nutrient spiraling studies measured 45 diverse potential controlling variables. We found 12 significant relationships between each controlling variable and nutrient spiraling metrics ( $p \leq 0.05$ ). Yellow boxes with a plus sign (+) indicate a significant positive relationship and the blue box with the minus sign (-) indicates a significant negative relationship. Relationships that were marginally significant ( $P > 0.05$ ) are lighter colored. \*Nitrate  $S_w$  relationships were only significant after a high winter value of 2,668 m from McMillan et al. (2014) was excluded.

| Tracer Used                  | Uptake Metrics Recorded | Watershed      |              |               | Reach      |             |           | Concentration                |           | Transient Storage |                                     | Metabolism    |
|------------------------------|-------------------------|----------------|--------------|---------------|------------|-------------|-----------|------------------------------|-----------|-------------------|-------------------------------------|---------------|
|                              |                         | Watershed Area | % Impervious | % Disturbance | Width      | Discharge   | Velocity  | NH <sub>4</sub> <sup>+</sup> | SRP       | A <sub>s</sub> /A | F <sub>med</sub> <sup>200</sup> (%) | Chl- <i>a</i> |
| NO <sub>3</sub> <sup>-</sup> | S <sub>w</sub>          | < 0.001* (+)   |              |               | 0.002* (+) |             |           |                              |           |                   |                                     |               |
|                              | U                       |                | 0.04 (+)     |               |            |             |           |                              |           |                   |                                     |               |
|                              | V <sub>f</sub>          |                |              |               |            |             |           |                              |           |                   |                                     |               |
| NH <sub>4</sub> <sup>+</sup> | S <sub>w</sub>          |                |              |               |            |             |           |                              |           |                   |                                     |               |
|                              | U                       |                |              | 0.03 (-)      |            |             |           | 0.07 (-)                     |           |                   |                                     |               |
|                              | V <sub>f</sub>          |                |              | 0.11 (-)      |            | 0.002 (+)   | 0.002 (+) | < 0.001 (-)                  |           | 0.07 (+)          | 0.20 (-)                            |               |
| SRP                          | S <sub>w</sub>          | 0.01 (+)       |              |               |            | 0.02 (+)    |           |                              |           |                   |                                     |               |
|                              | V <sub>f</sub>          |                |              |               |            | < 0.001 (+) |           | 0.11 (-)                     | 0.002 (+) |                   |                                     | 0.04 (+)      |
| No. of Correlations:         |                         | 2              | 1            | 2             | 1          | 3           | 1         | 3                            | 1         | 1                 | 1                                   | 1             |

## Figure Captions

Figure 4.1. (a) Based on our search criteria, we found 550 publications about stream restoration since 1978 and (b) 79 empirical nutrient studies about stream restoration since 1997. (c) The 79 empirical nutrient studies were located in the United States (45 studies), Austria (6), Denmark (6), Germany (4), England (3), Spain (3), China (3), France (2) and the following countries each had 1 study: Canada, Iraq/Iran, Japan, Korea, Poland, Taiwan, and Mexico/USA. American states with studies were Maryland (11), North Carolina (7), Indiana (2), Michigan (2), Mississippi (2), Nevada (2), New York (2), Ohio (2), Virginia (2), Wisconsin (2), and the following states each had 1 study: Arkansas, California, Florida, Georgia, Illinois, Kentucky, Tennessee, Wyoming, Washington, Texas and there was a study comparing sites in Maryland, Illinois, and Iowa.

Figure 4.2. Pie chart representing methods used for evaluating stream and floodplain restoration. The primary methods used were changes in water chemistry, mass balances, denitrification, and nutrient spiraling. Alternative methods were sediment dynamics, plant dynamics, nitrification, stable isotope ratios, dissimilatory nitrate reduction to ammonium (DNRA), anammox, microbial biomass nitrogen (MBN) and potentially mineralizable nitrogen (PMN). The percentage of the 79 studies using each method is listed along with the total number of studies. The total percentages do not add up to 100% because many studies used multiple methods.

Figure 4.3. Restoration projects were divided into 9 typologies: (A) raise stream bottom, (B) lower floodplain, (C) raise water levels with drainage control structures, (D) reconnect wetlands, (E) remove concrete liner, and (F) daylighting urban streams buried in pipes, (G) increase sinuosity, (H) add in-stream wetlands, and (I) reconnect oxbow wetlands.

Figure 4.4. Meta-analysis of nutrient spiraling showed that nitrate uptake length (m) had a positive correlation with (a) watershed area (ha) and (b) discharge (L/s). Nitrate uptake length relationships were only significant after a high winter value of 2,668 m from McMillan et al. (2014) was excluded (this high value has been circled).

Figure 4.5. Meta-analysis of nutrient spiraling showed that in restored streams, nitrate areal uptake rate ( $U$ ;  $\mu\text{g}/\text{m}^2/\text{s}$ ) had a positive relationship with impervious surface coverage (%).

Figure 4.6. In restored streams, ammonium areal uptake rate ( $U$ ;  $\mu\text{g}/\text{m}^2/\text{s}$ ) was negatively correlated with (a) disturbance intensity (%) and (b) ammonium concentration ( $\mu\text{g}/\text{L}$ ).

Figure 4.7. In restored streams, ammonium uptake velocity ( $V_f$ ; mm/min) has a significant negative relationship with (a) disturbance intensity (%) and (b) ammonium concentration ( $\mu\text{g}/\text{L}$ ) and a significant positive relationship with (c) discharge and (d) velocity. There was also a marginally significant positive correlation with (e) the relative extent of transient storage ( $A_s/A$ ) and (f) the median travel time due to transient storage over a standardized 200 m reach (%).

Figure 4.8. Meta-analysis of nutrient spiraling showed that SRP uptake length (m) had a positive correlation with (a) watershed area (ha) and (b) discharge (L/s).

Figure 4.9. Meta-analysis of nutrient spiraling showed that SRP uptake velocity (mm/min) had a positive correlation with (a) discharge (L/s), (b) Chl-*a* (mg/m<sup>2</sup>) and (c) SRP concentration (µg/L), and a negative correlation with (d) ammonium concentration (µg/L).

Figure 4.10. Top panel: As the number of typologies per study increased from 1 to 5, the number of studies declined exponentially from 45 to 1. Bottom panel: In contrast, as the number of typologies per study increased from 1 to 5, the % of positive results increased from 59% to 100%.

Figure 4.1. (a) Based on our search criteria, we found 550 publications about stream restoration since 1978 and (b) 79 empirical nutrient studies about stream restoration since 1997. (c) The 79 empirical nutrient studies were located in the United States (45 studies), Austria (6), Denmark (6), Germany (4), England (3), Spain (3), China (3), France (2) and the following countries each had 1 study: Canada, Iraq/Iran, Japan, Korea, Poland, Taiwan, and Mexico/USA. American states with studies were Maryland (11), North Carolina (7), Indiana (2), Michigan (2), Mississippi (2), Nevada (2), New York (2), Ohio (2), Virginia (2), Wisconsin (2), and the following states each had 1 study: Arkansas, California, Florida, Georgia, Illinois, Kentucky, Tennessee, Wyoming, Washington, Texas and there was a study comparing sites in Maryland, Illinois, and Iowa.

Figure 4.2.

# A Young Growing Field of Study

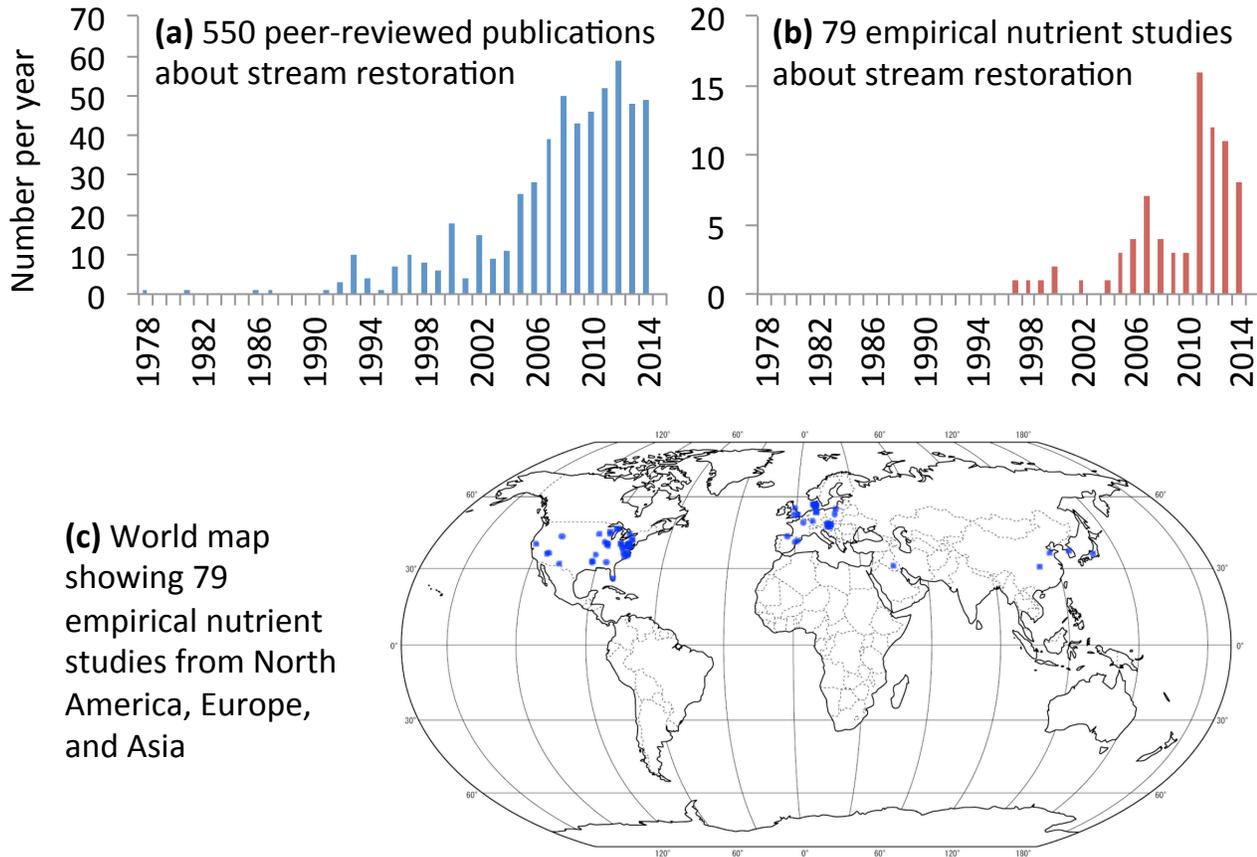


Figure 4.2.

### Methods Used to Evaluation Empirical Nutrient Studies

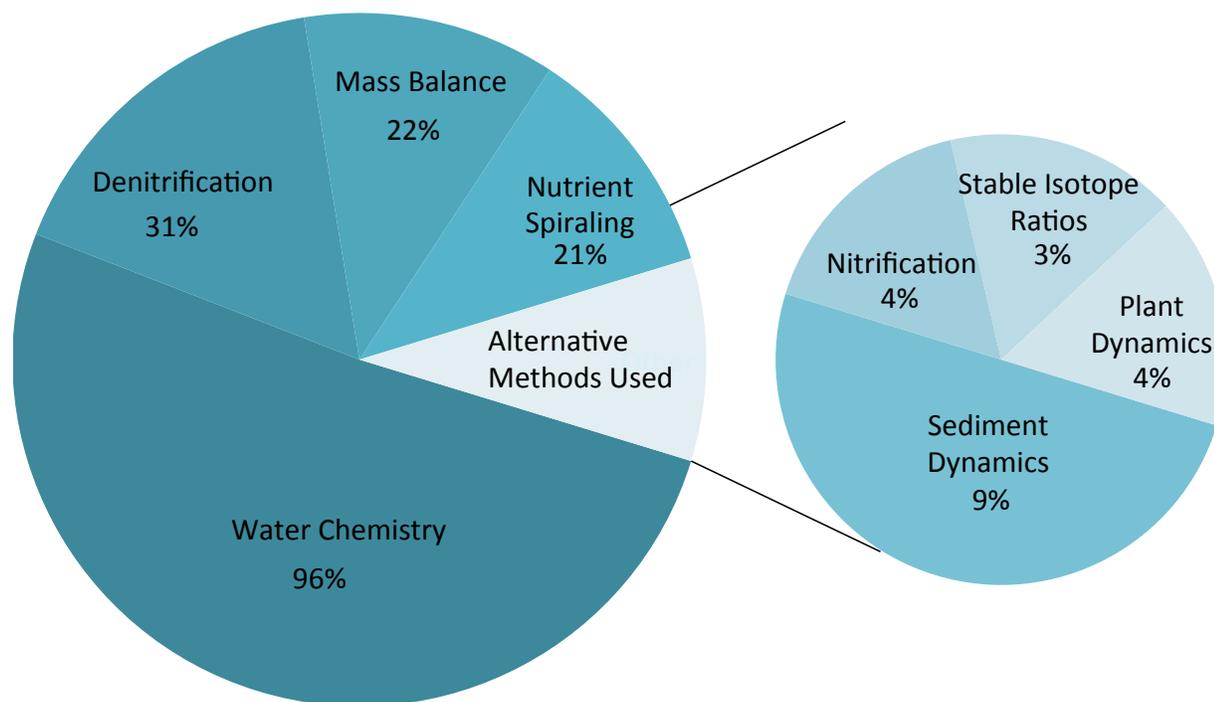


Figure 4.3.

### Restoration Typologies that Increase Hydrologic Connectivity

■ Positive Results    
 ■ Neutral Results    
 ■ Negative Results

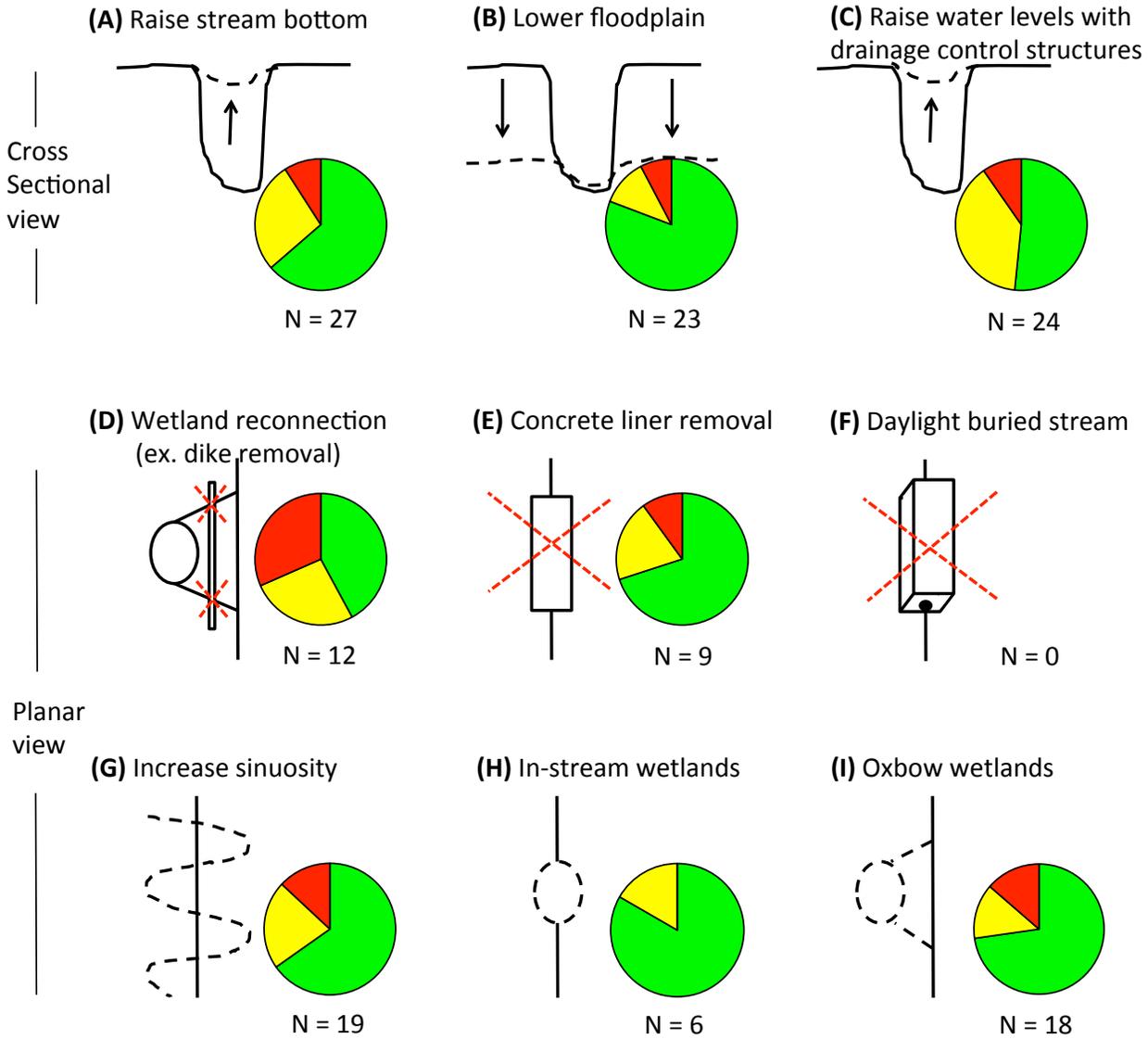


Figure 4.4.

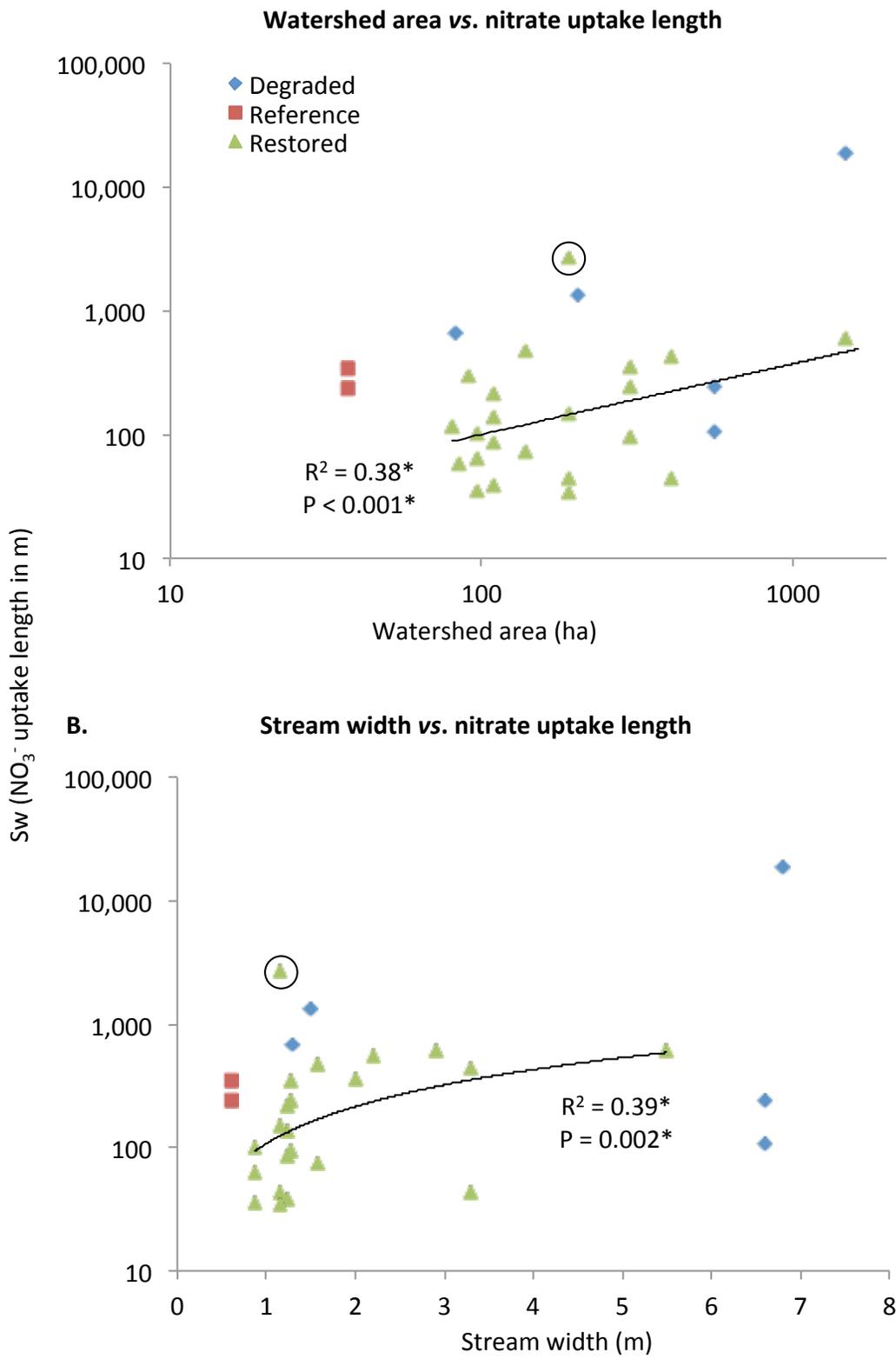


Figure 4.5.

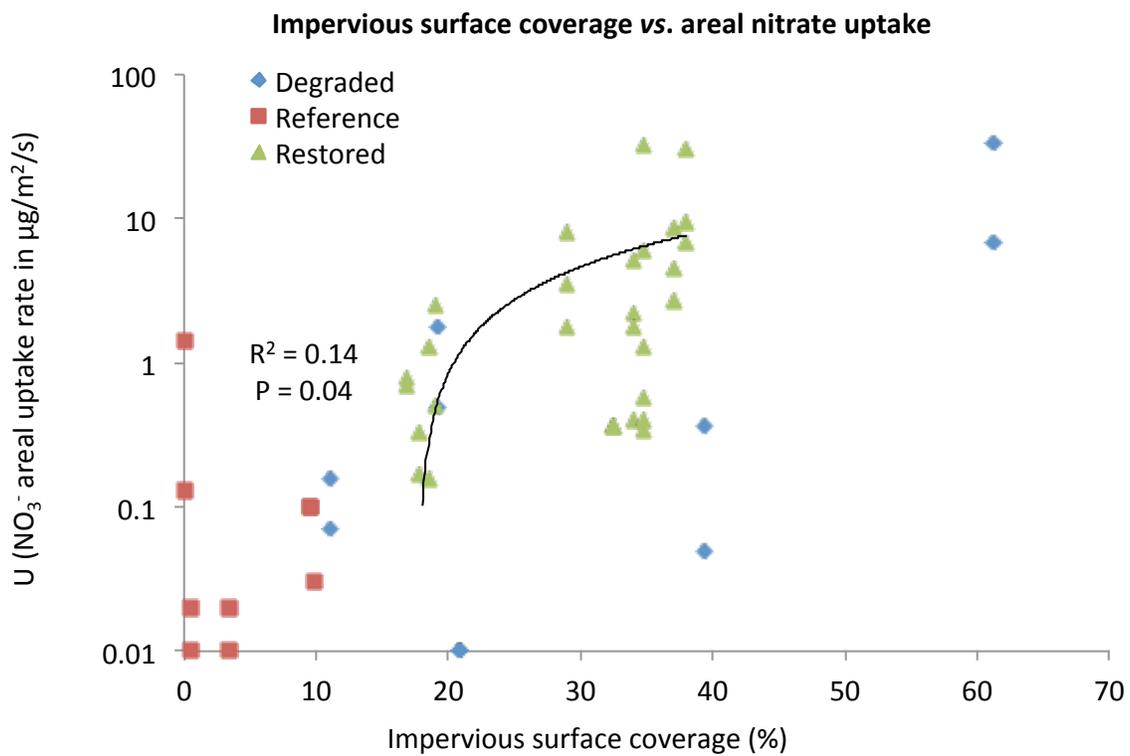


Figure 4.6.

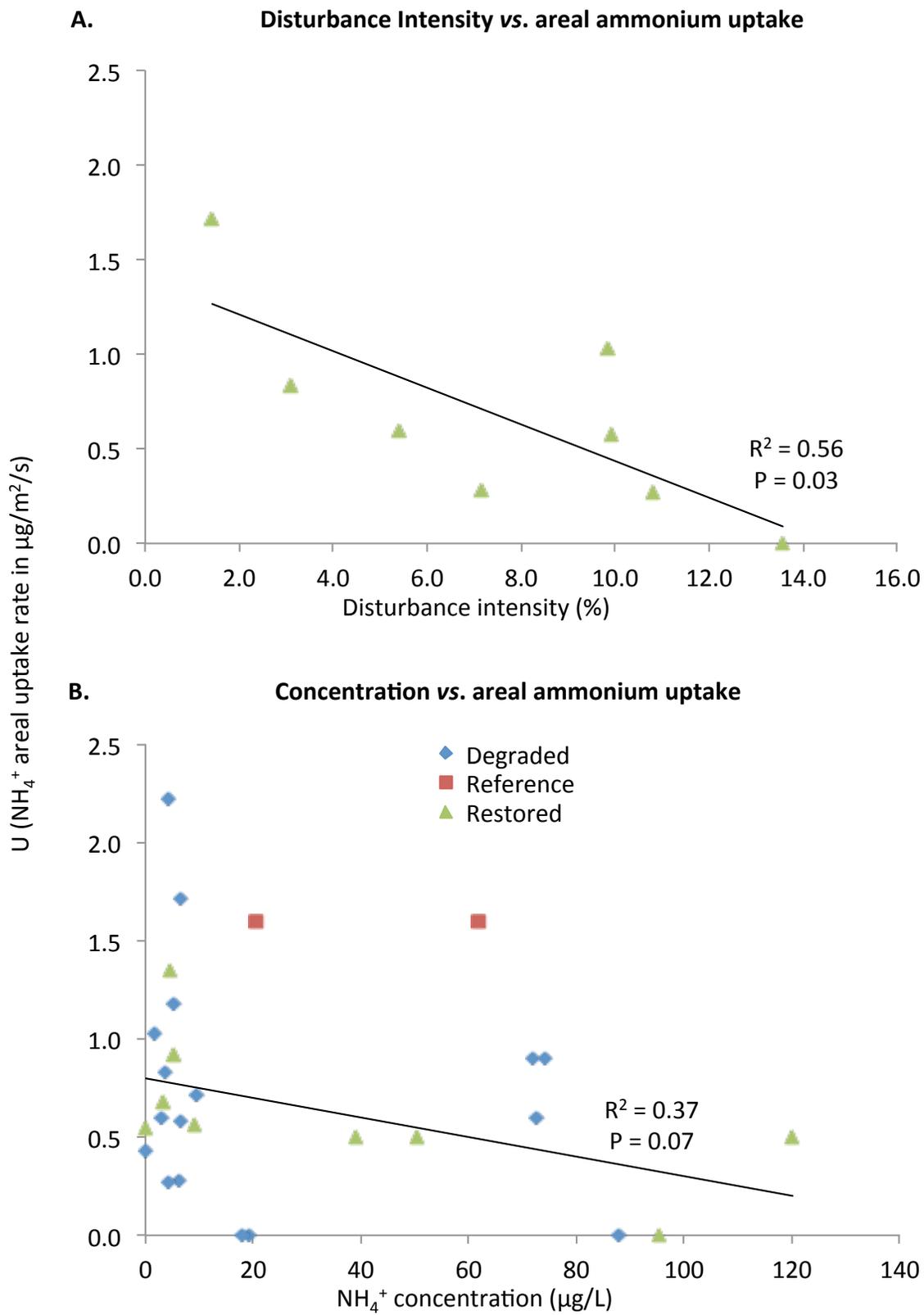


Figure 4.7.

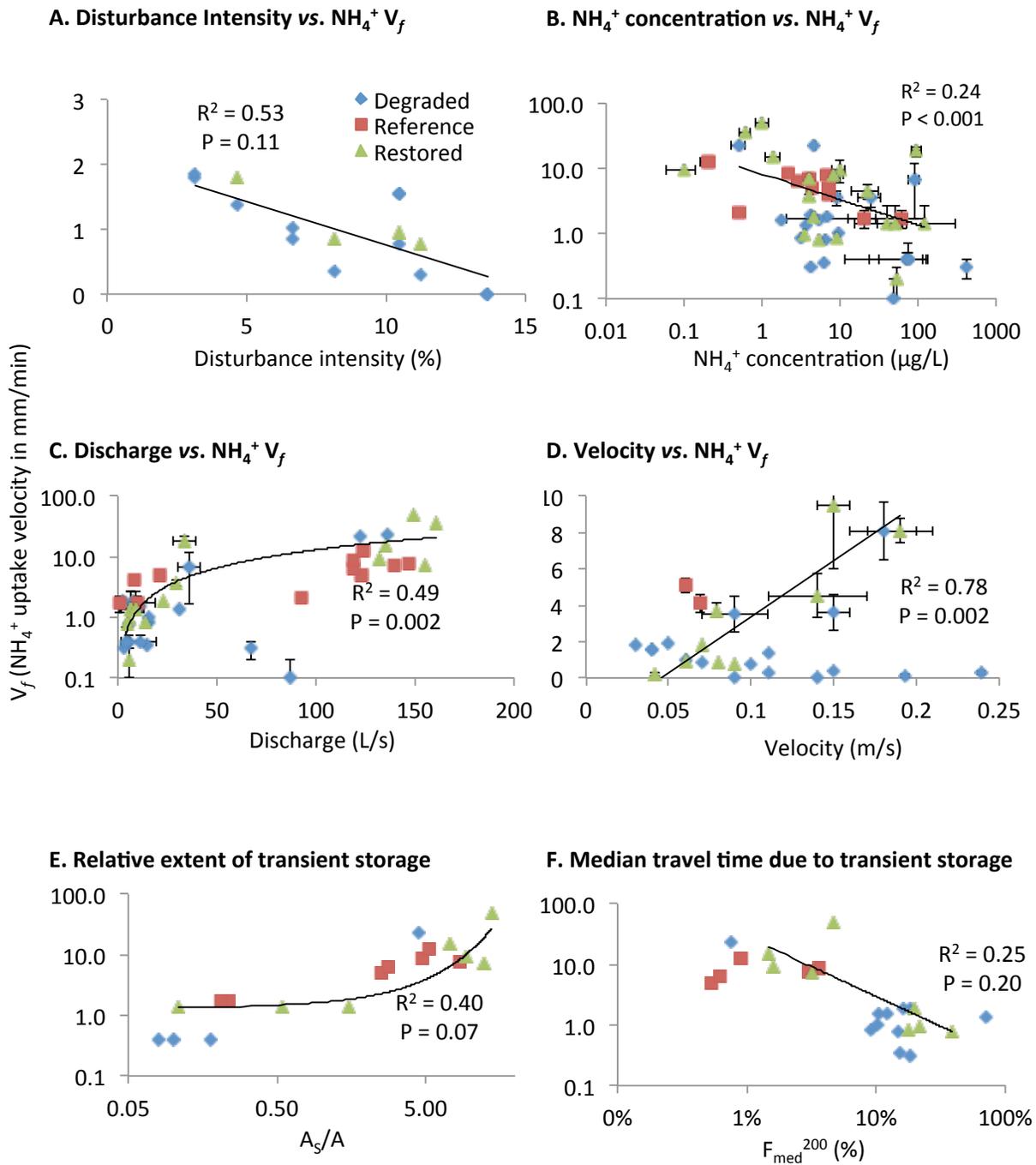


Figure 4.8.

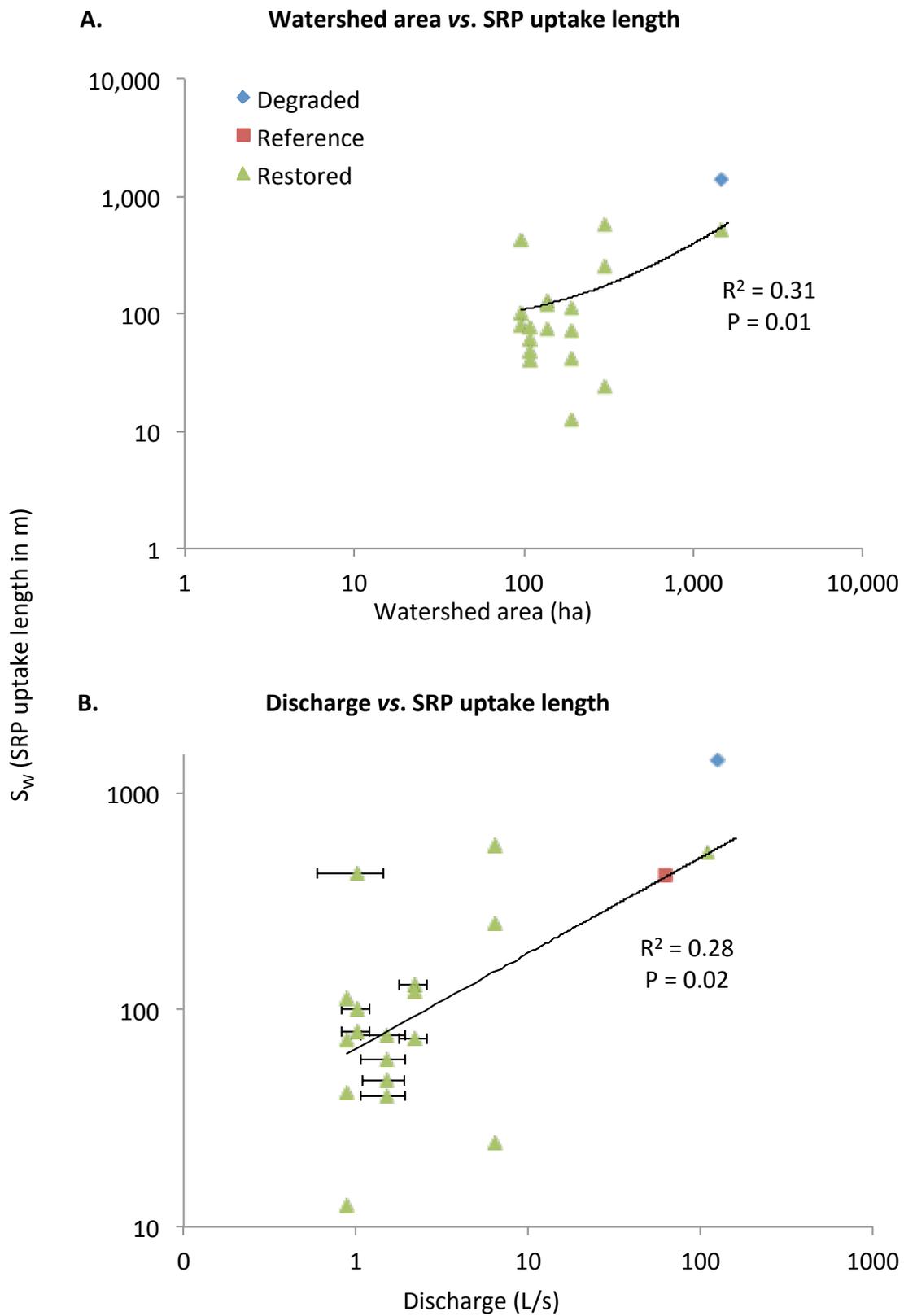


Figure 4.9.

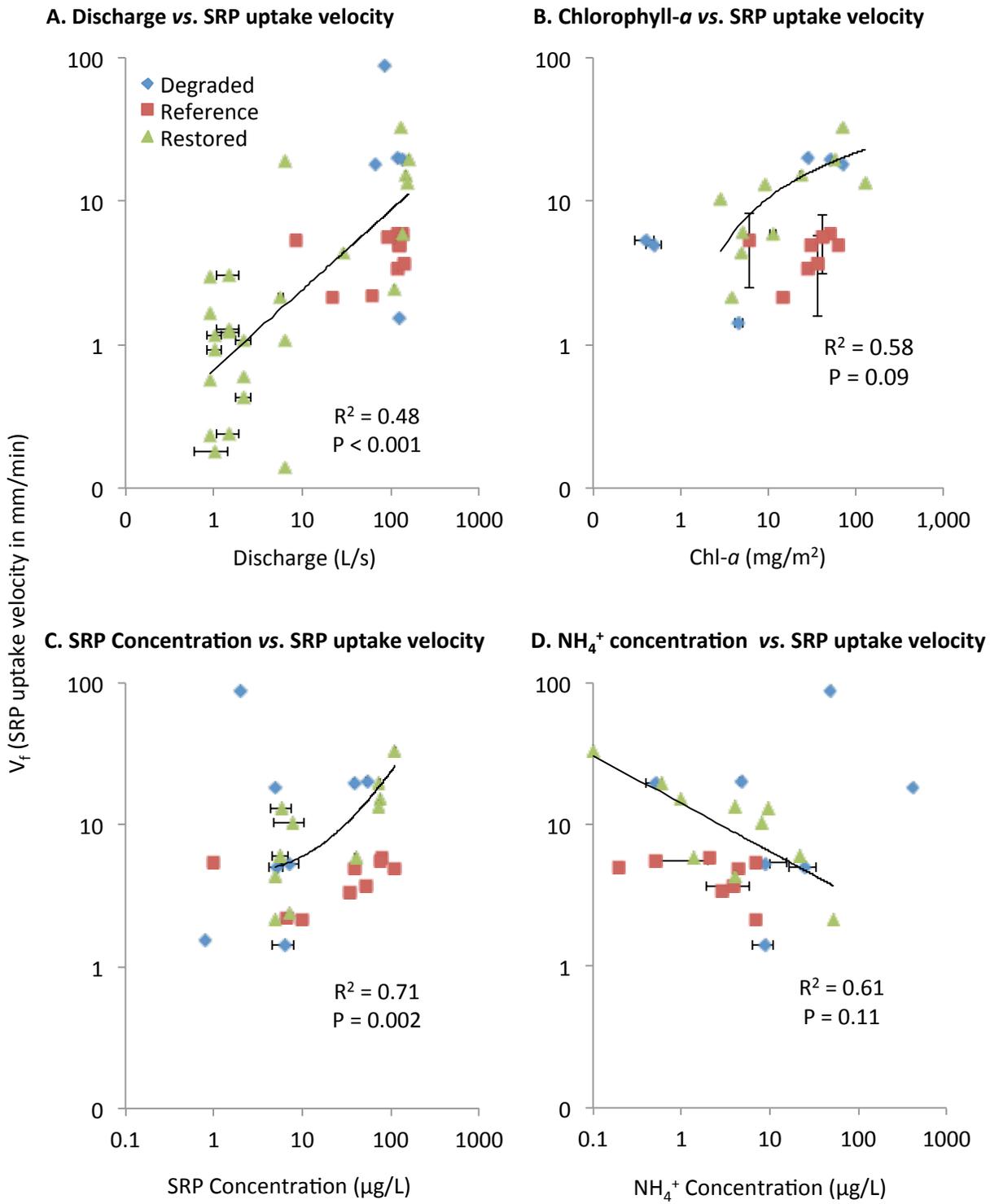
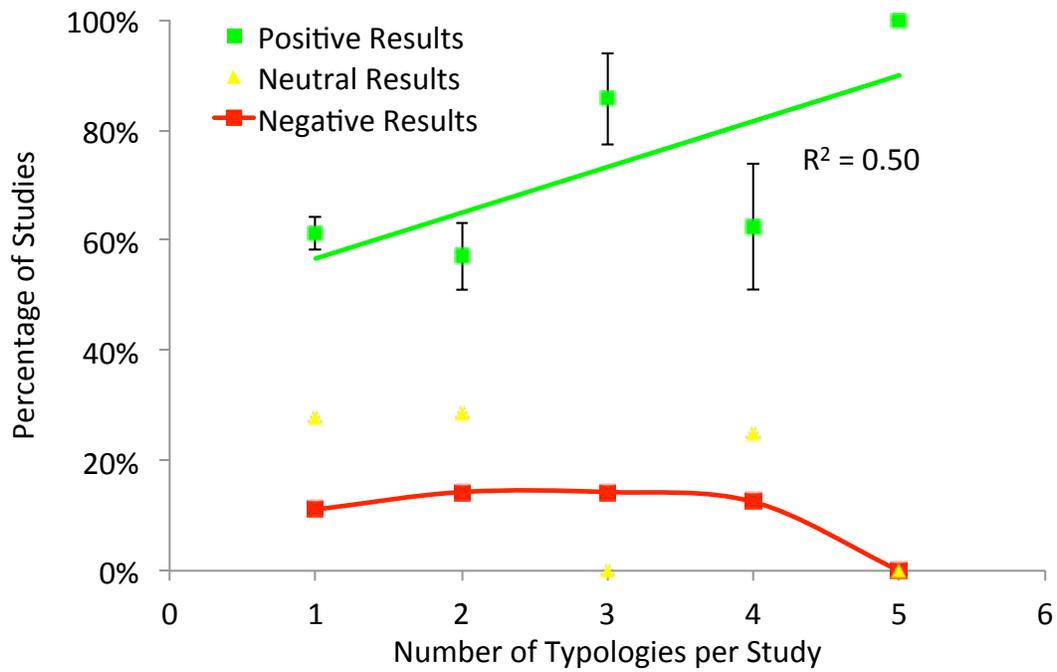
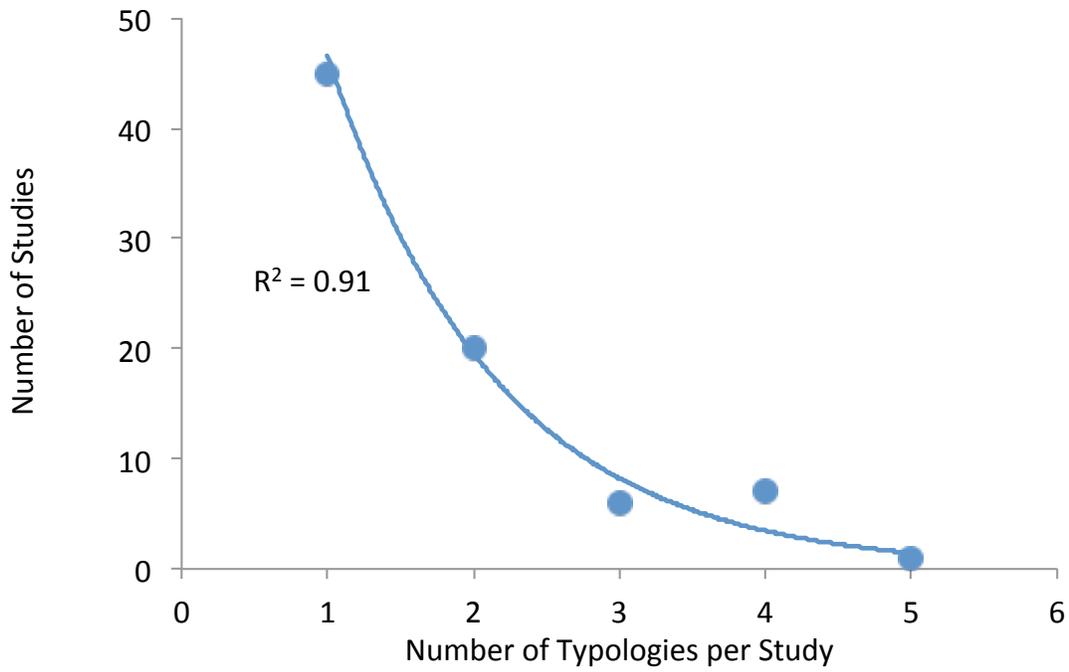


Figure 4.10.



Appendix D. Method, land use, management action, nutrient retention effectiveness, location, and source for 79 empirical nutrient case studies.

Denit. Indicates denitrification was measured and other indicates an alternative method was used.

Land use abbreviations are: ag (agriculture), urb (urban), for (forest), log (logging), mine (mining), base (military base), and unk (unkown).

Type refers to the typologies developed in Figure 4: A) raise stream bottom, B) lower floodplain, C) raise water levels with drainage control structures, D) increase sinuosity, E) add in-stream wetlands, F) reconnect oxbow wetlands, G) reconnect wetlands, H) remove concrete liner, and I) daylighting urban streams buried in pipes.

| Method                                   | LU       | Type | Management Action   | Summary of Results   | Location and Citation  |
|--|----------|------|---|--|--|
| Nutrient Spiraling, Mass balance, Denit. | Urb.     | ABEH | Stream restoration & stormwater management  | Inline stormwater management decreased total dissolved N concentrations & there were high rates of denitrification in both restored floodplains & stormwater management.   | Baltimore LTER, Maryland, USA [58]                           |
| Nutrient Spiraling                       | Ag       | A    | Experimental channel manipulations: removal of vegetation and CWD followed by addition of flow baffles                                  | NH <sub>4</sub> <sup>+</sup> and PO <sub>4</sub> uptake velocity (V <sub>u</sub> ) decreased after CWD removal by 88% and 38%, respectively. After baffles were installed, NH <sub>4</sub> <sup>+</sup> and PO <sub>4</sub> V <sub>u</sub> increased dramatically.   | North Carolina coastal plain, USA [59]                       |
| Nutrient Spiraling                       | Ag       | A    | Addition of experimental substrate deflector packs (control, mud, sand, & cobble)   | Adding substrate deflector packs doubled the size of the transient storage zone but did not significantly influence total NH <sub>4</sub> <sup>+</sup> and PO <sub>4</sub> uptake. This may be because of the small reach size (20 m long by 60 cm wide) and relatively small initial transient storage. Also, NH <sub>4</sub> <sup>+</sup> uptake coefficient was 1.6x higher than PO <sub>4</sub> in mud packs. In contrast, PO <sub>4</sub> uptake coefficients were 50x higher than NH <sub>4</sub> <sup>+</sup> in sand and cobble packs. | Irrigation canal 60 km north of Barcelona, Spain [60]        |
| Nutrient Spiraling                       | Ag       | AGI  | Channel relocated using natural channel design & the former channel was left in place as a remnant oxbow                                | Stream restoration decreased flow velocity and reduced downstream transport of nutrients. N and P uptake rate coefficients were 30- & 3-fold higher, respectively, within restored relative to pre-restoration.  | Wilson Creek stream restoration in Kentucky, USA [26]        |
| Nutrient Spiraling                       | Ag, Urb. | A    | Constructed riffles & a step  | Constructed riffles & step increased hyporheic exchange & N removal in hyporheic zone. A 40 meter constructed riffle removed 50-99% of streamwater NO <sub>3</sub> <sup>-</sup> that entered the hyporheic zone which was similar to the natural reach.  | Toronto, Southern Ontario, Canada [61]                       |
| Nutrient Spiraling                       | Log      | A    | Headwater stream restored by building a 10 m sediment trap & lining banks with boulders & logs parallel to direction of flow            | Restored reaches had higher gas exchange rate & increased transient storage. There was a significant positive relationship between perfect rock (gravel + cobble + boulder) coverage and nutrient uptake. However, nutrient uptake & community respiration rates were different between reaches at only one site.  | Ontonagon River basin of Lake Superior in Michigan, USA [62] |
| Nutrient Spiraling                       | Base     | A    | Coarse woody debris was added to increase structural complexity. In 100 m stream sections, 10 logjams were arranged in a zigzag pattern | Within a month of adding coarse woody debris, transient storage doubled (measured as A <sub>u</sub> , A <sub>s</sub> /A, R <sub>h</sub> , and F <sub>res</sub> <sup>200</sup> ) and NH <sub>4</sub> <sup>+</sup> uptake rates (V <sub>u</sub> and U) increased significantly. V <sub>u</sub> increased by 23-154% and U increased 61-235% in streams with coarse woody debris additions.   | Fort Benning, Military Installation, Georgia, USA [56]       |
| Nutrient Spiraling                       | Mine     | AC   | Natural channel design with cross-vanes and j-hooks.  | Restoration did not change NH <sub>4</sub> <sup>+</sup> uptake in a highly disturbed, acid mine drainage impacted stream.  | Appalachian coalfield, Virginia, USA [63]                    |
| Nutrient Spiraling                       | Urb.     | AB   | Stream restoration as mitigation projects for highway construction  | NH <sub>4</sub> <sup>+</sup> uptake lengths were significantly (2.5-3x) shorter in restored stream due to greater biofilm development on large substrates (boulder, cobble, & gravel) and less canopy cover. Denitrification was high, representing approximately 45% of N loading in North Buffalo Creek.   | Greensboro, North Carolina, USA [64]                         |

| Method                        | LU           | Type         | Management Action  | Summary of Results   | Location and Citation   |
|-------------------------------|--------------|--------------|--|--|---|
| Nutrient Spiraling            | Urb.         | A            | Installation of rocky riffles & raised channel bed elevations  | Otis model simulation predicted higher denitrification & in-stream NO <sub>3</sub> retention in restored stream based on increased subsurface residence time. Should this be eliminated? The hydrology was empirically measured but the nitrate changes were modeled...  | Truckee River, Nevada, USA [65]   |
| Nutrient Spiraling            | Urb.         | C<br>G       | 5 stream restoration projects ranging from 200 to 1,800 m that included designs like riffle/step/pool sequences using large wood J-hooks, boulder cross-vanes, and floodplain reconnection               | V <sub>s</sub> of nitrate (0.02-3.56 mm/min) and phosphate (0.14-19.1 mm/min) was similar to other urban restored streams and higher than forest reference streams. Variability influenced by restoration age and geomorphology. Nitrate uptake was highest in older sites possibly due to greater channel stability and establishment of microbial communities. Phosphate uptake was greater in newly restored sites, which was attributed to algal assimilation. | 5 restored streams in Charlotte and Raleigh, North Carolina, USA [66]   |
| Nutrient Spiraling            | Urb.         | A            | Natural channel design stream restoration project  | In summer, restored stream reaches had substantially higher NO <sub>3</sub> uptake than unrestored or forested reaches. In winter, uptake rates did not vary by stream type. Stream temperature & canopy cover explained 80% of NO <sub>3</sub> uptake variation.  | Piedmont area of North Carolina, USA [67]   |
| Nutrient Spiraling            | Urb.<br>Eoc. | G<br>I       | New, longer meandering channel was excavated and it included 2 backwater oxbows, 2 deep pools & 3 short riffles, fixed large woody debris with root wads, large boulders, and native riparian vegetation | After restoration, nutrient demand for NH <sub>4</sub> <sup>+</sup> and SRP temporarily increased to levels that have rarely been reported. Rapid periphyton accrual dramatically increased NH <sub>4</sub> <sup>+</sup> V <sub>s</sub> . Within 35 days periphyton biomass began to senesce and nutrient demand for both N and P recovered to background levels. Peak P demand occurred 2 weeks after peak N demand due to different controlling factors.         | Wilson Creek, a 3rd-order stream, forest headwaters in Okanogan-Wenatchee National Forest of Central Washington, USA [68] |
| Nutrient Spiraling and Denit. | Ag           | AB<br>G      | Excavation of stream banks & restructuring with a 2-stage ditch design, increased sinuosity, plus logs were used for stabilization of channel & stream bed   | Restored & forest reaches had shorter NH <sub>4</sub> <sup>+</sup> uptake lengths & larger mass transfer coefficients than channelized reaches. NH <sub>4</sub> <sup>+</sup> uptake positively correlated with transient storage in restored & forest reference. Potential denitrification lowest in restored reaches  | Weinviertel in north east Austria [69]  |
| Nutrient Spiraling, Denit.    | Urb.         | AB<br>E<br>G | Stream restoration raised stream bottom, lowering stream banks   | ~40% of daily NO <sub>3</sub> load removed via denitrification over 220.5 m in restored reach that was reconnected to its floodplain   | Minebank Run & Spring Branch, MD, USA [27]  |
| Denit.                        | Ag           | D            | Stream restoration through bank stabilization & riparian buffer plantings  | Denitrification removal in sediments with macrophytes was equivalent to 43% of the nitrate stream load (463.7 kg N day <sup>-1</sup> ) during spring and nitrification in sediments with macrophytes was equivalent to 247% of summer ammonium load (3.5 kg N day <sup>-1</sup> ).   | Black Earth Creek, Wisconsin, USA [39]  |

| Method           | LU         | Type   | Management Action  | Summary of Results   | Location and Citation   |
|------------------|------------|--------|--|--|---|
| Denit.           | Ag         | CD     | Reflooding a leveed Midwestern floodplain to create open water floodplain pond and wet meadows       | A drained floodplain used for row crop agriculture for >50 years was sampled 1-year pre and 2-years post restoration. The floodplain soils had the potential to support denitrification (from 0.00 to 15.0 $\mu\text{g N}_2\text{O-N [kg soil]}^{-1} \text{h}^{-1}$ , mean: $1.41 \pm 1.98$ ), but restoration did not immediately increase denitrification rates.   | Baraboo River floodplain in Wisconsin, USA [70]   |
| Denit.           | Ag         | B      | Two-stage ditch floodplain connection  | 1-year pre and 2-years post restoration, denitrification measurements along the floodplain showed the restoration contributed significantly to $\text{NO}_3^-$ retention during storm events. However, during storms <10% of load was removed due to high $\text{NO}_3^-$ concentrations.  | Shatto Ditch, tributary of Tippecanoe River, Indiana, USA [53]                          |
| Denit.           | Ag         | B      | Two-stage ditch floodplain connection  | On vegetated floodplains, denitrification rates were enhanced during inundation. The floodplain was inundated 12 times per year. Scaling up rates showed that the restoration tripled retention during storms.   | Shatto Ditch, tributary of Tippecanoe River, Indiana, USA [40]                          |
| Denit.           | Ag         | D      | Levee breached to restore connection between main channel & historic floodplain                      | Floodplain restoration increased N retention through denitrification. Scaling up showed the restored floodplain could remove 118 kg-N/yr. (~24% of annual river load) in the dry year when it was flooded 24% of the time and 850-6,150 kg-N/yr. (0.6-4.4% of annual load) during the wet year when it was flooded 43% of the time   | Lower Cosumnes River, California, USA [71]  |
| Denit.           | Ag         | D      | Wetland reconnection through experimental levee breach   | 2 years after restoration, the restored site had significantly higher bulk density and lower total C, total N, microbial biomass, PMN and ~50% lower potential denitrification than the natural reference site. Differences were linked to organic matter loss during 50 years of isolation.   | Redman point bar, Mississippi River, Arkansas, USA [57]                                 |
| Denit.           | For        | I      | 13-yr-old restored forested wetland amended with cotton gin trash as C source to enhance N retention | Denitrification in the restored forested wetland was limited by organic carbon availability. Cotton gin trash amendment increased denitrification rates in the restored forest soils to the level of the natural forest soils.   | Panther Swamp National Wildlife Refuge, Northwestern Mississippi, USA [72]              |
| Denit.<br>P min. | Eor.<br>Ag | BC     | Creation of 12.9-ha floodplain wetland & upland buffer complex                                       | Reconnecting the floodplain to the stream channel increased terrestrial inputs and stimulated soil N & P cycling that likely led to greater retention of sediment and nutrients in created & natural wetlands. P mineralization increased with sedimentation and sediment-N loading rate.  | Piedmont physiographic province of Virginia, USA [73]                                   |
| Denit.           | Mix        | B      | Floodplain reconnection  | Increasing floodplain's hydrological connection to main river channel increased N retention. Denitrification was out-competed by assimilation (estimated to use $\leq 70\%$ of available $\text{NO}_3^-$ ). Denitrification was higher in the restored site ( $5.7 \pm 2.8 \text{ mmol N m}^{-2} \text{ h}^{-1}$ ) compared to the disconnected site ( $0.6 \pm 0.5 \text{ mmol N m}^{-2} \text{ h}^{-1}$ ). | Lower Lobau & Orth floodplains, Alluvial Zone National Park, Danube River, Austria [74] |
| Denit.           | Mix        | D<br>I | Floodplain and side arm channel reconnection through partial levee breach                            | Denitrification potential was lower in the reconnected floodplain than the isolated floodplain. However, the authors suggest floodplain reconnection changes conditions like temperature, dissolved oxygen, and macrophyte distribution, which should increase N and C cycling efficiency.   | Lower Lobau & Orth floodplains, Danube River, Austria [75]                              |

| Method       | LU        | Type              | Management Action  | Summary of Results  | Location and Citation  |
|--------------|-----------|-------------------|--|---|--|
| Denit.       | Ag<br>Mix | A<br>G            | Floodplain reconnection  | The reconnected floodplain supported both denitrification and DNRA. Both processes were limited by organic carbon availability. Denitrification rates ( $0.4\text{--}4.2 \text{ mmol N g}^{-1} \text{ dry soil d}^{-1}$ ) were ~10x greater than DNRA.  | 2 km stretch of River Cole floodplain, Coleshill, Oxfordshire, United Kingdom [76] |
| Denit.       | Urb.      | AB<br>E<br>G      | Stream restoration through natural channel design  | In the riparian zone, restored sites had highest denitrification potentials but the difference was not statistically significant. The highest rates were in the top 10 cm of soil, which was linked to high levels of soil organic matter and root biomass. Increasing riparian water tables fosters interaction of groundwater $\text{NO}_3^-$ with near-surface soils with higher denitrification potential.  | Baltimore LTER, Maryland, USA [77]   |
| Denit.       | Urb.      | AB<br>E<br>G<br>I | Constructed & relict oxbow wetlands  | High rates of denitrification found in urban wetlands in both summer and winter. Sediment denitrification rates could remove between 23-28% of the $\text{NO}_3^-$ standing stock in the overlying water column (8-11% of daily stream load). A residence time of ~4 days would result in complete removal of any $\text{NO}_3^-$ that enters these wetlands.   | Baltimore LTER, Maryland, USA [78]   |
| Denit.       | Urb.      | AB<br>E<br>G      | Stream restoration raised stream bottom, lowered stream banks, and added cross vanes and riffles | Restoration did not dramatically change the distribution of geomorphic features (pools, riffles, debris dams) so degraded sites and restored sites had similar laboratory rates. Reach scale denitrification rates were lower than net nitrification rates suggesting that these stream features are both a sink for N and a net nitrate source. Denitrification potential rates were positively related to microbial biomass N and % sediment organic matter.                                  | Baltimore LTER, Maryland, USA [79]   |
| Denit.       | Urb.      | AB<br>E<br>G      | Stream restoration raised stream bottom, lowered stream banks, and added cross vanes and riffles | Mean rates of denitrification were significantly greater in the restored reach of the stream than the unrestored reach ( $77.4 \pm 12.6$ vs. $34.8 \pm 8.0 \mu\text{g N kg}^{-1} \text{d}^{-1}$ , respectively). N retention increased with hydrologic retention time. Not all areas of the restoration performed equally; reaches with low connected stream banks had higher denitrification rates than high banks.  | Minebank Run, Baltimore, Maryland, USA [37]  |
| Denit.       | Urb.      | AB<br>E<br>G      | Stream restoration   | Denitrification potential rates in hyporheic sediment were significantly higher in unrestored than restored streams when grass clippings were used as a carbon source. In contrast, when other materials (such as periphyton, leaves, and stormwater runoff) were used as the carbon source restored and unrestored streams were not significantly different but they were both significantly higher than forest reference streams. Denitrification in the restored streams was carbon limited. | Baltimore LTER, Maryland, USA [80]   |
| Mass balance | Urb.      | E<br>G            | Stream restoration   | The restoration reduced $\text{NH}_4^+$ and $\text{NO}_3^-$ , which was linked to higher amounts of hydrophytes.  | Zhuangba River, Beijing, China [81]  |
| Mass balance | Ag        | G                 | River & floodplain restoration   | Enhanced $\text{NO}_3^-$ retention in restored reach compared to upstream reference during 3 months of flooding post completion of restoration.   | River Brede, Denmark [82]  |

| Method       | LU   | Type    | Management Action   | Summary of Results  | Location and Citation  |
|--------------|------|---------|---|---|--|
| Mass balance | Ag   | G       | 4 river restorations that included restoration of riparian wetlands                 | Among 4 river restoration projects, restored riparian wetlands retained 0.13-10 kg ha <sup>-1</sup> year <sup>-1</sup> of P and 52-337 kg P ha <sup>-1</sup> year <sup>-1</sup> of N.                         | Denmark [83]   |
| Mass balance | Ag   | CD      | Riparian wetland restoration  | There were high rates of N removal & low rates of P release within wetlands   | Island of Eunen, Denmark [84]  |
| Mass balance | Ag   | I       | 0.07 ha diversion oxbow wetland   | Diversion wetland reduced NO <sub>3</sub> <sup>-</sup> during storm pulses  | Olentangy River Wetland Park, Ohio, USA [85]   |
| Mass balance | Ag   | BC<br>I | Wetland creation  | Wetlands continued to retain NO <sub>3</sub> <sup>-</sup> 10 years after creation   | Olentangy River Wetland Park, Ohio, USA [86]   |
| Mass balance | Ag   | B       | Constructed pond between agricultural field & creek                                 | Model predicted that restoration of ponds at a density of 5% of agricultural area would reduce riverine N export by up to 25% in regions with impermeable lithology.  | Seine River Basin, France [87]   |
| Mass balance | Ag   | CD<br>G | Replaced drainage canals with floodplain meadows & wetlands and increased sinuosity | Restored area retained 10% of total N load.   | Skjern River, Denmark [88]   |
| Mass balance | Ag   | CD      | Ditch blocking and displacement of drainage pipes to restore stream wetland complex | Despite re-wetting measures, during the growing season the restored wetland exported all N and P species except for NH <sub>4</sub> <sup>+</sup> . Nitrate retention occurred during summer flood & low flow. | Northeast of Hamburg in Schleswig-Holstein, Northern Germany [89]                    |
| Mass balance | Ag   | BC      | 2.8-ha multi-function constructed wetland   | More than 77% of total coliforms (TC), 78% of biochemical oxygen demand (BOD), 88% of total nitrogen (TN), and 96% of ammonia nitrogen were removed via the constructed wetland system                        | Linlo Constructed Wetland, Pingtung County, Taiwan [90]                              |
| Mass balance | For  | B       | Substratum excavation to wash away fine materials                                   | 100 days after restoration there was a significant decline in hyporheic NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , and NH <sub>4</sub> <sup>+</sup>  | River Moosach, a highly regulated subalpine calcareous stream, Bavaria, Germany [91] |
| Mass balance | Ag   | CD      | Wetland restoration & reconnection  | Within wetlands there was typically NO <sub>3</sub> <sup>-</sup> & NH <sub>4</sub> <sup>+</sup> retention & organic N release. TN budgets were variable.  | Robnsdorfer Stauung, Northern Germany [92]   |
| Mass balance | Urb. | AB<br>H | Floodplain lowered, streambed elevated, & in-stream wetland creation                | Average of 18% total N mass removal within created wetlands   | Liza's Bottom, Chowan County, North Carolina, USA [93]                               |
| Mass balance | Urb. | AC      | Natural channel design & stream-wetland complexes                                   | 2 of 6 restored reaches were clearly effective at reducing TN export & only 1 was effective during stormflow conditions   | Wilhelinox project, Coastal Plain of Maryland, USA [94]                              |

| Method               | LU   | Type         | Management Action  | Summary of Results   | Location and Citation   |
|----------------------|------|--------------|--|--|---|
| Mass balance         | Urb. | I            | Relict oxbow wetlands  | 2 oxbows received 1.6-7.4% of cumulative stream flow during storm events, and retained runoff from 0.2 to 6.7 days, during which 23-87% on N was retained (0.25-2.7 g N/m <sup>2</sup> /day) and during the storms a small amount of dissolved P was released (0.23-24.8 mg P/m <sup>2</sup> /day).  | Baltimore LTER, Maryland, USA [95]  |
| Mass balance         | Urb. | I            | <i>In-situ</i> remediation engineering, ex-situ remediation engineering and constructed wetland engineering based on the different environmental characteristics of the river was applied to treat low concentration sewage                            | The average values of chemical oxygen demand, biochemical oxygen demand, ammonia nitrogen, total phosphorus and total nitrogen in the same monitoring point of the river were all decreased from 244.45, 84.95, 28.75, 2.28 and 36.05 mg/L in 2009 to 28.67, 8.58, 6.92, 0.38 and 13.40 mg/L in 2012, respectively.  | Xinyunliang River in Kunming City, Yunnan Province, China [96]                |
| Mass balance         | Urb. | A            | stream channel is transformed into a stormwater management structure designed to reduce peak flows and enhance hydraulic retention of stream flow with the goals of reducing bank erosion and promoting retention of nutrients and suspended sediments | Net annual removal of N was insignificant in the Wilelinor project despite a long restored reach and an extensive floodplain. The "best-case scenario" for reducing N was found in the Howard's Branch sand-seepage project, which also has an extensive flood-plain. Because stormflow accounts for up to 70% of the annual discharge in these small urbanized streams, load reduction during stormflow conditions is essential to the effectiveness of the system. | Wilelinor project, Coastal Plain of Maryland, USA                             |
| Mass balance         | Urb. | BC<br>H      | 3-phase floodplain restoration, storm water wetland complex & surface treatment wetland to increase stream wetland connection  | There was a 64% reduction in load due to effects of all three-restoration phases.  | Sandy Creek, a headwater stream for Cape Fear River, North Carolina, USA [97] |
| Mass balance         | Urb. | AB<br>E<br>G | Stream restoration: raising stream bottom, lowering stream banks   | In restored streams, mass balances showed net TDN retention and net DOC release across reaches. In contrast there was net TDN release and DOC retention in unrestored streams suggesting an influence of the restoration.  | Baltimore LTER, Maryland, USA [98]  |
| Mass balance, Denit. | Ag   | D<br>H       | Wetland restoration  | N retention efficiency close to 100% except for DON: denitrification rates at 0-12% of incoming DIN.   | Ebro River Delta, northeast Spain [99]  |
| Other                | Ag   | C<br>H       | Runoff attenuation features  | Removal of NO <sub>3</sub> <sup>-</sup> was negligible, probably due to short residence time in feature.   | Belford Burn catchment, England [100]   |
| Other                | Ag   | B            | Removal of river embankments   | Embankment removal increased how frequently surface water reached the floodplain thus enabling the possibility of greater processing of high nitrate river water (6.2 mg/L) by floodplain sediments containing low nitrate groundwater (0.5 mg/L).   | River Glaven, England [101]   |

| Method | LU        | Type   | Management Action   | Summary of Results  | Location and Citation  |
|--------|-----------|--------|---|---|--|
| Other  | Ag        | A<br>G | Stream restoration with cross vanes   | Cross vanes had strong downwelling zones, high DO levels, streambed chemistry similar to surface water, & sulfate & NO <sub>3</sub> <sup>-</sup> reduction occurring in streambed (but not in reference reach); at restored sites, hyporheic NO <sub>3</sub> <sup>-</sup> concentrations always equal to or less than overlying stream water NO <sub>3</sub> <sup>-</sup> concentrations & strongly correlated with concentrations of DO. | Restored streams Owego Creek & Ninemile Creek, Catskills region of Central New York, USA [102] |
| Other  | Ag        | C      | Stream restoration with cross vane structures   | Restoration structures do promote low magnitude hyporheic exchange around steps in water surface profile & secondary pool & riffle bed forms. Cross-vanes in studied systems do not process significant amounts of nutrients or pollutants for whole-stream system.   | Central New York, USA [103]  |
| Other  | Ag        | I      | River restoration   | During storms N rich water flowed from Danube River into oxbow side channel & concentrations significantly declined after storms  | Danube-Auen National Park, Danube River, Vienna, Austria [104]                                 |
| Other  | Ag        | C      | Small log dam restoration structures  | Log dams can create hot spots of biogeochemical activity.   | Red Canyon Creek, Wyoming, USA [105]   |
| Other  | Ag        | A<br>G | Stream restoration  | Total N & NO <sub>3</sub> <sup>-</sup> concentrations not significantly different between restored, reference, & channelized stream reaches.  | Jutland, Denmark [106]   |
| Other  | Ag        | C<br>H | Wetlands constructed by building low earthen berm with outflow passing through control device                       | Wetlands removed up to 68% of NO <sub>3</sub> <sup>-</sup> & 43% of P from drainage water. % varied considerably with highest removal in wetlands with 1-2 week retention times & large surface area to drainage area ratio   | Case studies in Maryland, Illinois, & Iowa, USA [107]  |
| Other  | Ag<br>Eoc | C<br>I | Backwater oxbow rehabilitated by constructing two weirs in its lower limb (one of which was used to create wetland) | The diversion of polluted runoff and the use of water control structures to maintain greater water depth were observed to be effective management tools, but the former reduces the water supply to habitats that tend to dry up and the latter reduces connectivity.   | Yazoo River Basin Northwestern Mississippi, USA [108]  |
| Other  | Ag<br>Urb | G      | Floodplain restoration  | Low N release from sediments deposited on restored floodplain   | Odense River, Denmark [109]  |
| Other  | For       | D      | Wetland tree island restoration through levee removal   | Tree islands distinct in structure & biogeochemical properties from surrounding marsh: higher organically bound P & N, but lower inorganic N. NH <sub>4</sub> <sup>+</sup> dominant N constituent & it was low at both island types (3.97 mM).  | Florida Coastal Everglades LTER, southern Florida, USA [110]                                   |
| Other  | For       | A      | Added 25 aspen logs (each 2.5 m length x 0.5 m diameter) to 100-m reaches in 3 streams                              | In a low nutrient, wood-poor stream, restoration through wood addition increased nitrate concentrations (associated with faster leaf decomposition rates)   | Upper peninsula of Michigan, USA [111]   |
| Other  | Mix       | I      | Floodplain reconnection "partly restored hydrological exchange patterns"  | A dynamic exchange allows river to benefit from floodplain production under connected conditions  | Regelsbrunn floodplain, Danube River, Austria [112]  |

| Method | LU      | Type | Management Action  | Summary of Results   | Location and Citation  |
|--------|---------|------|--|--|--|
| Other  | Mix     | I    | River restoration reconnection to side channels                              | Nutrient concentrations in restored side channels vs. reference side channels were not significantly different.  | Rhine River floodplain, France & Germany [113]   |
| Other  | Unk     | I    | Side arm oxbow channel reconnection  | Side channel was connected for 44% of study period & timing & duration of connection varied between years. N & P concentrations highest during flood pulses but decreased during connectivity phases when water age increased. During isolation phases, concentrations rose again, but declined after isolation periods exceeding 37 days. | Danube River in National Park <u>Donauauen</u> , <u>Regelsbrunn</u> , Austria [114]      |
| Other  | Urb.    | B    | Removal of sediments to reconnect floodplain                                 | Stable isotope $d^{15}N$ value of riparian plants increased, suggesting enhanced uptake of river water N by floodplain plants  | <u>Chikuma</u> River, Japan [115]  |
| Other  | Urb.    | I    | Engineered wetlands  | The flow diverter bed (FDB) system transported stream water to an aerobic wetland & then an anaerobic wetland significantly decreased N concentrations   | <u>Kyungan</u> Stream at central western part of Korea [116]                             |
| Other  | Urb.    | C    | Erosion control structures   | Structures retained organic matter & there was lower $NO_3^-$ (50.3 vs. 56.9 mg/L) & ammonia concentrations but difference was not significant   | Wastewater dominated drainage (Wash) in Las Vegas, Nevada, USA [117]                     |
| Other  | Urb.    | I    | Created Rio Bosque Wetlands  | Wetlands reduced $NO_3^-$ concentrations however agricultural water diversions left wetland dry & without macrophytes in summer limiting ability to retain N   | El Paso–Ciudad Juárez <u>metroplex</u> , Rio Grande River, United States & Mexico [118]  |
| Other  | Urb.    | C    | River restoration: water aerated 3 dams constructed 5 km apart               | Engineering & biological techniques dramatically improved water quality; $NH_4^+$ decreased from 27 to 4 mg/L, total suspended solids decreased from 270 to 40 mg/L, among other parameters.   | <u>Dihe</u> River is located in <u>Changyi</u> , Shandong Province, northern China [119] |
| Other  | Urb. Ag | C    | River diversion & wetland drainage followed by wetland restoration           | River diversion & wetland drainage increased turbidity & $NO_3^-$ levels. Wetland restoration decreased turbidity (N wasn't measured after restoration).   | Northwestern Arabian Gulf, Asia [120]  |
| Other  | Urb. Ag | C    | Wetlands restored by closing main drainage ditches                           | Wetland effectively reduces $NO_3^-$ concentration entering <u>Alegria</u> River from storms   | Vitoria-Gasteiz, North Spain [121]   |
| Other  | Unk     | AB   | Natural channel design to increase stream floodplain hydrologic connectivity | N concentrations and transport were reduced by 20-70% with in-stream and constructed storm water wetlands.   | Chowan Golf Course, North Carolina, USA [122]  |
| Other  | Unk     | I    | Oxbow lakes left after river channelization                                  | Oxbow lakes had significantly lower $NO_3^-$ concentrations than adjacent river channel  | <u>Lyna</u> & <u>Drweca</u> Rivers, N Poland [123]                                       |

| Method | LU                   | Type   | Management Action  | Summary of Results  | Location and Citation   |
|--------|----------------------|--------|--|---|---|
| Other  | <a href="#">Link</a> | C<br>I | Two-stage baffled surface-flow constructed wetland 7400 m <sup>2</sup> demonstration project | Mean removal rates of total N, total phosphorus (TP), NH <sub>4</sub> <sup>+</sup> , chemical oxygen demand (COD <sub>Cr</sub> ), suspended solid (SS) were about 75%, 78%, 85%, 40%, 80% respectively in summer & autumn. While it decreased in winter, average removal rates were respectively about 30%, 73%, 45%, 25%, 78%. | Jialu River, Hinterland of central China [124]                          |
| Other  | <a href="#">Link</a> | C      | Controlled drainage in canal to restore water levels   | Monthly monitoring showed higher N concentrations in reach with controlled drainage than uncontrolled canal   | Tull Creek, North Carolina, USA [122]                                   |
| Other  | Ag                   | D      | Wetland reconnection   | Total C, total N, and P was lower at all sites compared to the natural reference site. Although hydrology has been restored to the wetlands, functionality may take a considerable amount of time to be detectable.   | Redman Point–Loosahatchie Bar Restoration Project, Tennessee, USA [125] |
| Other  | Ag                   | C      | Floodplain restoration   | Both sites shifted from reducing to more oxidizing environments, based on changes in soil redox potential.  | St. Joseph Wetland, Illinois, USA [126]                                 |

## Citations

1. Newcomer Johnson, T. A.; Kaushal, S. S.; Mayer, P. M.; Grese, M. M. Effects of stormwater management and stream restoration on watershed nitrogen retention. *Biogeochemistry* **2014**, *121*, 81–106.
2. Ensign, S. H.; Doyle, M. W. In-channel transient storage and associated nutrient retention: Evidence from experimental manipulations. *Limnol. Oceanogr.* **2005**, *50*, 1740–1751.
3. Argerich, A.; Martí, E.; Sabater, F.; Haggerty, R.; Ribot, M. Influence of transient storage on stream nutrient uptake based on substrata manipulation. *Aquat. Sci.* **2011**, *73*, 365–376.
4. Bukaveckas, P. A. Effects of channel restoration on water velocity, transient storage, and nutrient uptake in a channelized stream. *Environ. Sci. Technol.* **2007**, *41*, 1570–1576.
5. Kasahara, T.; Hill, A. R. Effects of riffle–step restoration on hyporheic zone chemistry in N-rich lowland streams. *Can. J. Fish. Aquat. Sci.* **2006**, *63*, 120–133.
6. Hoellein, T. J.; Tank, J. L.; Entekin, S. A.; Rosi-Marshall, E. J.; Stephen, M. L.; Lamberti, G. A. Effects of benthic habitat restoration on nutrient uptake and ecosystem metabolism in three headwater streams: stream restoration and ecosystem function. *River Res. Appl.* **2012**, *28*, 1451–1461.
7. Roberts, B. J.; Mulholland, P. J.; Houser, J. N. Effects of upland disturbance and instream restoration on hydrodynamics and ammonium uptake in headwater streams. *J. North Am. Benthol. Soc.* **2007**, *26*, 38–53.
8. Northington, R. M.; Benfield, E. F.; Schoenholtz, S. H.; Timpano, A. J.; Webster, J. R.; Zippe, C. An assessment of structural attributes and ecosystem function in restored Virginia coalfield streams. *Hydrobiologia* **2011**, *671*, 51–63.

9. Hines, S. L.; Hershey, A. E. Do channel restoration structures promote ammonium uptake and improve macroinvertebrate-based water quality classification in urban streams? *Inland Waters* **2011**, *1*, 133–145.
10. Knust, A. E.; Warwick, J. J. Using a fluctuating tracer to estimate hyporheic exchange in restored and unrestored reaches of the Truckee River, Nevada, USA. *Hydrol. Process.* **2009**, *23*, 1119–1130.
11. McMillan, S. K.; Tuttle, A. K.; Jennings, G. D.; Gardner, A. Influence of Restoration Age and Riparian Vegetation on Reach-Scale Nutrient Retention in Restored Urban Streams. *JAWRA J. Am. Water Resour. Assoc.* **2014**, *50*, 626–638.
12. Sudduth, E. B.; Hassett, B. A.; Cada, P.; Bernhardt, E. S. Testing the field of dreams hypothesis: functional responses to urbanization and restoration in stream ecosystems. *Ecol. Appl.* **2011**, *21*, 1972–1988.
13. Arango, C. P.; James, P. W.; Hatch, K. B. Rapid ecosystem response to restoration in an urban stream. *Hydrobiologia* **2015**, *749*, 197–211.
14. Weigelhofer, G.; Welti, N.; Hein, T. Limitations of stream restoration for nitrogen retention in agricultural headwater streams. *Ecol. Eng.* **2013**, *60*, 224–234.
15. Klocker, C. A.; Kaushal, S. S.; Groffman, P. M.; Mayer, P. M.; Morgan, R. P. Nitrogen uptake and denitrification in restored and unrestored streams in urban Maryland, USA. *Aquat. Sci.* **2009**, *71*, 411–424.
16. Forshay, K. J.; Dodson, S. I. Macrophyte presence is an indicator of enhanced denitrification and nitrification in sediments of a temperate restored agricultural stream. *Hydrobiologia* **2011**, *668*, 21–34.

17. Orr, C. H.; Stanley, E. H.; Wilson, K. A.; Finlay, J. C. Effects of restoration and reflooding on soil denitrification in a leveed Midwestern floodplain. *Ecol. Appl.* **2007**, *17*, 2365–2376.
18. Roley, S. S.; Tank, J. L.; Stephen, M. L.; Johnson, L. T.; Beaulieu, J. J.; Witter, J. D. Floodplain restoration enhances denitrification and reach-scale nitrogen removal in an agricultural stream. *Ecol. Appl.* **2012**, *22*, 281–297.
19. Roley, S. S.; Tank, J. L.; Williams, M. A. Hydrologic connectivity increases denitrification in the hyporheic zone and restored floodplains of an agricultural stream. *J. Geophys. Res.* **2012**, *117*.
20. Sheibley, R. W.; Ahearn, D. S.; Dahlgren, R. A. Nitrate loss from a restored floodplain in the lower Cosumnes River, California. *Hydrobiologia* **2006**, *571*, 261–272.
21. Theriot, J. M.; Conkle, J. L.; Reza Pezeshki, S.; DeLaune, R. D.; White, J. R. Will hydrologic restoration of Mississippi River riparian wetlands improve their critical biogeochemical functions? *Ecol. Eng.* **2013**, *60*, 192–198.
22. Ullah, S.; Faulkner, S. P. Use of cotton gin trash to enhance denitrification in restored forested wetlands. *For. Ecol. Manag.* **2006**, *237*, 557–563.
23. Wolf, K. L.; Noe, G. B.; Ahn, C. Hydrologic Connectivity to Streams Increases Nitrogen and Phosphorus Inputs and Cycling in Soils of Created and Natural Floodplain Wetlands. *J. Environ. Qual.* **2013**, *42*, 1245–1255.
24. Welti, N.; Bondar-Kunze, E.; Mair, M.; Bonin, P.; Wanek, W.; Pinay, G.; Hein, T. Mimicking floodplain reconnection and disconnection using N-15 mesocosm incubations. *Biogeosciences* **2012**, *9*, 4263–4278.

25. Welti, N.; Bondar-Kunze, E.; Singer, G.; Tritthart, M.; Zechmeister-Boltenstern, S.; Hein, T.; Pinay, G. Large-scale controls on potential respiration and denitrification in riverine floodplains. *Ecol. Eng.* **2012**, *42*, 73–84.
26. Sgouridis, F.; Heppell, C. M.; Wharton, G.; Lansdown, K.; Trimmer, M. Denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in a temperate re-connected floodplain. *Water Res.* **2011**, *45*, 4909–4922.
27. Gift, D. M.; Groffman, P. M.; Kaushal, S. S.; Mayer, P. M. Denitrification Potential, Root Biomass, and Organic Matter in Degraded and Restored Urban Riparian Zones. *Restor. Ecol.* **2010**, *18*, 113–120.
28. Harrison, M. D.; Groffman, P. M.; Mayer, P. M.; Kaushal, S. S.; Newcomer, T. A. Denitrification in alluvial wetlands in an urban landscape. *J. Environ. Qual.* **2011**, *40*, 634–646.
29. Harrison, M. D.; Groffman, P. M.; Mayer, P. M.; Kaushal, S. S. Microbial biomass and activity in geomorphic features in forested and urban restored and degraded streams. *Ecol. Eng.* **2012**, *38*, 1–10.
30. Kaushal, S. S.; Groffman, P. M.; Mayer, P. M.; Striz, E.; Gold, A. J. Effects of stream restoration on denitrification in an urbanizing watershed. *Ecol. Appl.* **2008**, *18*, 789–804.
31. Newcomer, T. A.; Kaushal, S. S.; Mayer, P. M.; Shields, A. R.; Canuel, E. A.; Groffman, P. M.; Gold, A. J. Influence of natural and novel organic carbon sources on denitrification in forest, degraded urban, and restored streams. *Ecol. Monogr.* **2012**, *82*, 449–466.
32. Li, W.; Zhang, N.; Wu, F.-F. [Influence of ecological restoration of riparian zone on water quality of Zhuanhe River in Beijing]. *Huan Jing Ke Xue Huanjing Kexue Bian Ji*

*Zhongguo Ke Xue Yuan Huan Jing Ke Xue Wei Yuan Hui Huan Jing Ke Xue Bian Ji Wei Yuan Hui* **2011**, *32*, 80–87.

33. Hoffmann, C. C.; Pedersen, M. L.; Kronvang, B.; Ovig, L. Restoration of the rivers Brede, Cole and Skerne: a joint Danish and British EU-LIFE demonstration project, IV - Implications for nitrate and iron transformation. *Aquat. Conserv.-Mar. Freshw. Ecosyst.* **1998**, *8*, 223–240.
34. Hoffmann, C. C.; Kronvang, B.; Audet, J. Evaluation of nutrient retention in four restored Danish riparian wetlands. *Hydrobiologia* **2011**, *674*, 5–24.
35. Hoffmann, C. C.; Heiberg, L.; Audet, J.; Schønfeldt, B.; Fuglsang, A.; Kronvang, B.; Ovesen, N. B.; Kjaergaard, C.; Hansen, H. C. B.; Jensen, H. S. Low phosphorus release but high nitrogen removal in two restored riparian wetlands inundated with agricultural drainage water. *Ecol. Eng.* **2012**, *46*, 75–87.
36. Huang, J.-C.; Mitsch, W. J.; Johnson, D. L. Estimating biogeochemical and biotic interactions between a stream channel and a created riparian wetland: A medium-scale physical model. *Ecol. Eng.* **2011**, *37*, 1035–1049.
37. Mitsch, W. J.; Day, J. W.; Zhang, L.; Lane, R. R. Nitrate-nitrogen retention in wetlands in the Mississippi River Basin. *Ecol. Eng.* **2005**, *24*, 267–278.
38. Passy, P.; Garnier, J.; Billen, G.; Fesneau, C.; Tournebize, J. Restoration of ponds in rural landscapes: Modelling the effect on nitrate contamination of surface water (the Seine River Basin, France). *Sci. Total Environ.* **2012**, *430*, 280–290.
39. Pedersen, M.; Friberg, N.; Skriver, J.; Baattrup-Pedersen, A.; Larsen, S. Restoration of Skjern River and its valley - Short-term effects on river habitats, macrophytes and macroinvertebrates. *Ecol. Eng.* **2007**, *30*, 145–156.

40. Rücker, K.; Schrautzer, J. Nutrient retention function of a stream wetland complex—A high-frequency monitoring approach. *Ecol. Eng.* **2010**, *36*, 612–622.
41. Wu, C. Y.; Fu, Y. T.; Yang, Z. H.; Kao, C. M.; Tu, Y. T. Using Multi-Function Constructed Wetland for Urban Stream Restoration. *Appl. Mech. Mater.* **2011**, *121-126*, 3072–3076.
42. Sternecker, K.; Wild, R.; Geist, J. Effects of substratum restoration on salmonid habitat quality in a subalpine stream. *Environ. Biol. Fishes* **2013**, *96*, 1341–1351.
43. Kieckbusch, J. J.; Schrautzer, J. Nitrogen and phosphorus dynamics of a re-wetted shallow-flooded peatland. *Sci. Total Environ.* **2007**, *380*, 3–12.
44. Bass, K. L.; Evans, R. O. Water Quality Improvement by a Small In-Stream Constructed Wetland in North Carolina's Coastal Plain. In *Watershed Management and Operations Management 2000*; ASCE, 2000; pp. 1–10.
45. Filoso, S.; Palmer, M. A. Assessing stream restoration effectiveness at reducing nitrogen export to downstream waters. *Ecol. Appl.* **2011**, *21*, 1989–2006.
46. Harrison, M. D.; Miller, A. J.; Groffman, P. M.; Mayer, P. M.; Kaushal, S. S. Hydrologic Controls on Nitrogen and Phosphorous Dynamics in Relict Oxbow Wetlands Adjacent to an Urban Restored Stream. *JAWRA J. Am. Water Resour. Assoc.* **2014**, *50*, 1365–1382.
47. Huang, K.; Jin, Z.; Li, J.; Yang, F.; Zhou, B. Technologies and engineering practices of water pollution control for a typical urban river in Dianchi watershed. *Fresenius Environ. Bull.* **2014**, *23*, 3469–3475.
48. Richardson, C.; Flanagan, N.; Ho, M.; Pahl, J. Integrated stream and wetland restoration: A watershed approach to improved water quality on the landscape. *Ecol. Eng.* **2011**, *37*, 25–39.

49. Sivorichi, G. M.; Kaushal, S. S.; Mayer, P. M.; Welty, C.; Belt, K. T.; Newcomer, T. A.; Newcomb, K. D.; Grese, M. M. Longitudinal variability in streamwater chemistry and carbon and nitrogen fluxes in restored and degraded urban stream networks. *J. Environ. Monit.* **2011**, *13*, 288–303.
50. Comin, F. A.; Romero, J. A.; Astorga, V.; Garcia, C. Nitrogen removal and cycling in restored wetlands used as filters of nutrients for agricultural runoff. *Water Sci. Technol.* **1997**, *35*, 255–261.
51. Barber, N. J.; Quinn, P. F. Mitigating diffuse water pollution from agriculture using soft-engineered runoff attenuation features. *Area* **2012**, *44*, 454–462.
52. Clilverd, H. M.; Thompson, J. R.; Heppell, C. M.; Sayer, C. D.; Axmacher, J. C. River–floodplain hydrology of an embanked lowland Chalk river and initial response to embankment removal. *Hydrol. Sci. J.* **2013**, *58*, 627–650.
53. Daniluk, T. L.; Lautz, L. K.; Gordon, R. P.; Endreny, T. A. Surface water–groundwater interaction at restored streams and associated reference reaches. *Hydrol. Process.* **2013**, *27*, 3730–3746.
54. Gordon, R. P.; Lautz, L. K.; Daniluk, T. L. Spatial patterns of hyporheic exchange and biogeochemical cycling around cross-vane restoration structures: implications for stream restoration design: hyporheic exchange around cross-vanes. *Water Resour. Res.* **2013**, *49*, 2040–2055.
55. Hein, T.; Heiler, G.; Pennetzdorfer, D.; Riedler, P.; Schagerl, M.; Schiemer, F.; Layzer, J. B. The Danube restoration project: functional aspects and planktonic productivity in the floodplain system. *Regul. Rivers Res. Manag.* **1999**, *15*, 259–270.

56. Lautz, L. K.; Fanelli, R. M. Seasonal biogeochemical hotspots in the streambed around restoration structures. *Biogeochemistry* **2008**, *91*, 85–104.
57. Pedersen, T. C. M.; Baattrup-Pedersen, A.; Madsen, T. V. Effects of stream restoration and management on plant communities in lowland streams. *Freshw. Biol.* **2006**, *51*, 161–179.
58. Woltemade, C. J. Ability of restored wetlands to reduce nitrogen and phosphorus concentrations in agricultural drainage water. *J. Soil Water Conserv.* **2000**, *55*, 303–309.
59. Shields, F. D.; Lizotte, R. E.; Knight, S. S. Spatial and Temporal Water Quality Variability in Aquatic Habitats of a Cultivated Floodplain. *River Res. Appl.* **2013**, *29*, 313–329.
60. Audet, J.; Hoffmann, C. C.; Jensen, H. S. Low nitrogen and phosphorus release from sediment deposited on a Danish restored floodplain. *Ann. Limnol.-Int. J. Limnol.* **2011**, *47*, 231–238.
61. Troxler Gann, T. G.; Childers, D. L.; Rondeau, D. N. Ecosystem structure, nutrient dynamics, and hydrologic relationships in tree islands of the southern Everglades, Florida, USA. *For. Ecol. Manag.* **2005**, *214*, 11–27.
62. Entrekin, S. A.; Tank, J. L.; Rosi-Marshall, E. J.; Hoellein, T. J.; Lamberti, G. A. Responses in organic matter accumulation and processing to an experimental wood addition in three headwater streams. *Freshw. Biol.* **2008**, *53*, 1642–1657.
63. Aspetsberger, F.; Huber, F.; Kargl, S.; Scharinger, B.; Peduzzi, P.; Hein, T. Particulate organic matter dynamics in a river floodplain system: impact of hydrological connectivity. *Arch. Hydrobiol.* **2002**, *156*, 23–42.
64. Meyer, A.; Combroux, I.; Tremolieres, M. Dynamics of Nutrient Contents (Phosphorus, Nitrogen) in Water, Sediment and Plants After Restoration of Connectivity in Side-Channels of the River Rhine. *Restor. Ecol.* **2013**, *21*, 232–241.

65. Schagerl, M.; Drozdowski, I.; Angeler, D. G.; Hein, T.; Preiner, S. Water age - a major factor controlling phytoplankton community structure in a reconnected dynamic floodplain (Danube, Regelsbrunn, Austria). *J. Limnol.* **2009**, *68*, 274–287.
66. Akamatsu, F.; Shimano, K.; Denda, M.; Ide, K.; Ishihara, M.; Toda, H. Effects of sediment removal on nitrogen uptake by riparian plants in the higher floodplain of the Chikuma River, Japan. *Landsc. Ecol. Eng.* **2008**, *4*, 91–96.
67. Kim, S.; Hong, S.; Choi, Y.; Bae, W.; Lee, S. Performance evaluation of a newly developed flow diverted bed system for stream restoration. *Process Biochem.* **2007**, *42*, 199–209.
68. Nelson, S. M. Response of stream macroinvertebrate assemblages to erosion control structures in a wastewater dominated urban stream in the southwestern US. *Hydrobiologia* **2011**, *663*, 51–69.
69. Rodriguez, R.; Lougheed, V. L. The potential to improve water quality in the middle Rio Grande through effective wetland restoration. *Water Sci. Technol.* **2010**, *62*, 501–509.
70. Sheng, Y.; Qu, Y.; Ding, C.; Sun, Q.; Mortimer, R. J. G. A combined application of different engineering and biological techniques to remediate a heavily polluted river. *Ecol. Eng.* **2013**, *57*, 1–7.
71. Al-Yamani, F. Y.; Bishop, J. M.; Al-Rifaie, K.; Ismail, W. The effects of the river diversion, Mesopotamian Marsh drainage and restoration, and river damming on the marine environment of the northwestern Arabian Gulf. *Aquat. Ecosyst. Health Manag.* **2007**, *10*, 277–289.
72. Garcia-Linares, C.; Martinez-Santos, M.; Martinez-Bilbao, V.; Sanchez-Perez, J. M.; Antiguada, I. Wetland restoration and nitrate reduction: the example of the peri-urban

wetland of Vitoria-Gasteiz (Basque Country, North Spain). *Hydrol. Earth Syst. Sci.* **2003**, *7*, 109–121.

73. Evans, R. O.; Bass, K. L.; Burchelt, M. R.; Hinson, R. D.; Johnson, R.; Doxey, M. Management alternatives to enhance water quality and ecological function of channelized streams and drainage canals. *J. Soil Water Conserv.* **2007**, *62*, 308–320.
74. Glinska-Lewczuk, K.; Burandt, P. Effect of river straightening on the hydrochemical properties of floodplain lakes: Observations from the Lyna and Drweca Rivers, N Poland. *Ecol. Eng.* **2011**, *37*, 786–795.
75. Wang, W.; Gao, J.; Guo, X.; Li, W.; Tian, X.; Zhang, R. Long-term effects and performance of two-stage baffled surface flow constructed wetland treating polluted river. *Ecol. Eng.* **2012**, *49*, 93–103.
76. Koontz, M. B.; Pezeshki, S. R.; DeLaune, R. D. Nutrient Dynamics in a Restored Wetland. *Commun. Soil Sci. Plant Anal.* **2014**, *45*, 609–623.
77. Peralta, A. L.; Ludmer, S.; Matthews, J. W.; Kent, A. D. Bacterial community response to changes in soil redox potential along a moisture gradient in restored wetlands. *Ecol. Eng.* **2014**, *73*, 246–253.

## Chapter 5: Conclusions

The aim of my dissertation research was to expand knowledge of how restored streams and integrated stormwater management networks transport and transform nitrogen, and how such transformation can be coupled with the carbon cycle. The second chapter examined how different natural organic carbon sources can affect denitrification rates in forest, restored, and degraded-urban streams. The third chapter evaluated factors influencing N and C fluxes, N and C retention, and denitrification in streams with integrated stormwater management practices. The fourth chapter reviewed nitrogen retention within hydrologically restored streams & floodplains.

In the second chapter, I concluded that concentrations and loads of nitrate and DOC varied with runoff and there was flashy delivery at urban sites. Stable isotope and lipid biomarker data suggest that urbanization alters the amount and source of organic carbon delivered to streams. Management of riparian vegetation may influence denitrification rates at the riparian-stream interface. Managing amounts, sources, and quality of organic carbon may be critical for managing nitrogen flux in stormwater management systems and urban restoration stream projects. Because DOC, nitrate, and other contaminants can be delivered in pulses, future work should investigate how specific restoration and stormwater management features like hydrologically connected pond and wetland systems may affect organic carbon sources and hydrologic residence times, which are both important to denitrification.

In the third chapter, I concluded there is considerable interest in managing the amount of N leaving watersheds and entering coastal zones (Boesch et al. 2001; Rabalais 2002). Urban

stormwater is one of the fastest growing forms of nitrogen pollution in many coastal zones globally (NRC 2008). My results show that hydrologic flux must be integrated with process level measurements when considering management activities at the watershed scale. It also suggests that understanding the hydrology of a region may be important in terms of understanding fluxes, flowpaths, and sources of nitrogen that are influencing watersheds. I found that only a small portion of the water budget was moving through the BMPs and that the majority of water fluxes occurred along the stream network and groundwater can be an important source. Future research needs to be done to evaluate hydrologic variability on biogeochemical processes and quantify how stormwater management affects the quantity and quality of carbon in streams.

In the fourth chapter, I concluded there is growing interest in monitoring case studies of how stream and floodplain restoration influence N retention. There is a need for studies in N contaminated areas beyond North America, Europe, and the few studies found in Asia. There are many different restoration strategies that can be used to foster N retention within hydrologically disconnected streams and floodplains. The commonality between all of these restoration practices is that they reconnect surface and groundwater and increase retention time in order to promote N retention.

### *Future Horizons*

#### Influence of organic matter

There are many further questions regarding how to manage organic carbon in urban riparian zones. Restoration practitioners are interested in planting species that best improve water

quality. It would be useful to explore how different herbaceous and woody plant species affect the delivery of dissolved and particulate organic matter in terms of the production of organic carbon debris (flowers, leaves, etc) and interactions with root networks to explore how this source specific organic carbon is linked to nitrogen transport and denitrification. I would like to examine how different tree species used in restoration influence denitrification potential rates. I hypothesize that species that produce leaves with lots of labile carbon like maples will stimulate the highest rates in the fall and that species with more recalcitrant leaves will have lower rates but continue to stimulate denitrification in later seasons.

Additionally my finding that the hyporheic zone can be carbon limited leads to the question of whether it would be worthwhile to increase the carbon content of hyporheic sediments during stream engineering. Some stream restoration projects have tried to increase sediment carbon content by adding large woody debris. In agricultural ecosystems, “denitrification walls” have been created by adding carbon to a “wall” of sediment draining high-intensity agriculture (Long et al. 2011; Schmidt and Clark 2012a; Schmidt and Clark 2012b; Passeport et al. 2013). It is important that the carbon source added is something recalcitrant like wood chips so that it can support sustained denitrification rather than something labile like acetate that can stimulate microbial production. It would be interesting to conduct experiments in which different amounts and types of carbon are mixed with sediment to determine the response over time.

#### Factors influencing n retention and denitrification

To improve upon the findings of Chapter 3, it would be useful to have more detailed mapping of the groundwater concentrations, movement, stable isotope ratios, and groundwater

age dating to better quantify the role of groundwater in N loading. Such information could help determine if groundwater contamination is from an older legacy source like agriculture or if it is from a newer source like septic systems and/or leaking sanitary lines. Knowing this could help managers determine if there will be a lag-time before nitrogen concentrations in the stream decrease or if management actions like fixing infrastructure or changing requirements for septic system maintenance could improve water quality. Additionally this information would allow for more comprehensive and accurate mass balances.

Likewise, it important to consider how management actions like integrating stormwater management and restored floodplains influences biogeochemical cycles other than nitrogen. For example, some of the same conditions that promote denitrification also can promote phosphorus release and methylation of mercury (Vidon et al. 2010). There is currently at total maximum daily load (TMDL) set for phosphorus for the Loch Raven drinking water reservoir so it would be very useful to analyze my samples for phosphorus species to determine how the stormwater BMPs and stream networks process phosphorus. Additionally, it would be useful to examine the flux and transformation of anions and metals.

Another future direction would be to examine a chronosequence of stormwater management BMPs that were constructed under evolving regulations. Older designs like wet and dry ponds were designed for the purpose of decreasing runoff but new stormwater BMPs are designed to also improve water quality. It would be useful compare a spectrum older and newer designs to determine if they increase rates of ecosystem functions like denitrification (Kaushal and Belt 2012). It would likewise be useful to use the same type of approach to examine of chronosequence of stream restoration projects as stream restoration designs have also evolved considerably over the past couple decades.

## Comparisons of *in situ* denitrification in other ecosystems

I found that across features, *in situ* denitrification rates were negative related to DO concentrations and positively related to temperature and nitrate concentrations. These trends make sense given that other laboratory studies have found these to be controlling factors. Laboratory assays from Chapter 2 showed that DOC was also controlling factor to denitrification in the hyporheic zones of Baltimore LTER streams. In contrast, Chapter 3 did not find a significant relationship between DOC concentrations and *in situ* denitrification and this may likely be due to the fact that DOC samples were collected seasonally instead of at the time of the denitrification measurements and the Pond Branch forested sites had high DOC and low nitrate and low denitrification rates.

As an exercise out of curiosity, I now present an analysis of all of the  $^{15}\text{N}$  *in situ* denitrification measures that I could find, in order to provide a sense of the range of values that occur in nature (negligible to  $110,000 \pm 6,700 \mu\text{g N/kg soil/day}$ ; Table 5; Fig. 5; Warneke et al. 2011). The highest rates were in denitrifying woodchip bioreactors (denitrification beds) draining hydroponic greenhouses in New Zealand (Warneke et al. 2011), a seepage wetland draining a New Zealand dairy farm (Zaman et al. 2008), and an N contaminated aquifer in Korea (Kim et al. 2005). These studies with extremely high denitrification rates also have extremely high N and C levels (though Zaman et al. 2008 lacked high nitrate – it did have high ammonium levels ( $50.3 \pm 3.5 \text{ mg/L NH}_4^+ \text{-N mg/kg soil}$ )). I do not fully understand why the study of braided islands in an Alaskan River with low nitrate had the next highest rates – perhaps there is something else going on in this ecosystem (Clilverd et al. 2008).

Table 5. Comparison of 10 studies that measure denitrification ( $\mu\text{g N/kg soil/day}$ ) using the  $^{15}\text{N}$  *in situ* push-pull method.

| Land Use | Location | Feature Type | Denitrification ( $\mu\text{g N/ kg dry soil/day}$ ) | DO (mg/L)     | Temp ( $^{\circ}\text{C}$ ) | Nitrate (mg/L)  | DOC (mg/L)    | Study                |
|----------|----------|--------------|--|---------------|-----------------------------|-----------------|---------------|----------------------|
| Urban    | MD, USA  | BMP          | $24.3 \pm 0.9$                                       | 0.6           | 21.5                        | 0.15            | 10            | Harrison et al. 2011 |
| Urban    | MD, USA  | BMP          | $55.1 \pm 6.1$                                       | 0.71          | 22.1                        | 0.05            | 3.7           | Harrison et al. 2011 |
| Urban    | MD, USA  | BMP          | $80.9 \pm 23.8$                                      | 0.72          | 21                          | 7.95            | 2.5           | Harrison et al. 2011 |
| Urban    | MD, USA  | BMP          | $160.4 \pm 74.1$                                     | $2.4 \pm 0.5$ | $16.4 \pm 2.1$              | $2.44 \pm 0.68$ | $1.0 \pm 0.1$ | Present Study        |
| Urban    | MD, USA  | BMP          | $300.9 \pm 93.8$                                     | $2.0 \pm 0.4$ | $19.4 \pm 2.5$              | $0.42 \pm 0.17$ | $6.8 \pm 1.4$ | Present Study        |
| Urban    | MD, USA  | Floodplain   | $4.2 \pm 0.2$  | $4.9 \pm 0.8$ | $16.2 \pm 1.5$              | $1.47 \pm 0.05$ | <1            | Kaushal et al. 2008  |
| Urban    | MD, USA  | Floodplain   | $48.8 \pm 22.7$                                      | $4.5 \pm 0.5$ | $15.9 \pm 1.1$              | $1.47 \pm 0.05$ | <1            | Kaushal et al. 2008  |
| Urban    | MD, USA  | Floodplain   | $60.7 \pm 31.5$                                      | $5.3 \pm 1.2$ | $15.6 \pm 1.7$              | $1.47 \pm 0.05$ | <1            | Kaushal et al. 2008  |
| Urban    | MD, USA  | Floodplain   | $186.6 \pm 88.3$                                     | $1.1 \pm 0.3$ | $18.0 \pm 2.3$              | $0.59 \pm 0.24$ | $4.5 \pm 0.4$ | Present Study        |
| Urban    | MD, USA  | High Bank    | $19.5 \pm 16.9$                                      | $4.1 \pm 0.9$ | $15.2 \pm 0.6$              | $1.47 \pm 0.05$ | <1            | Kaushal et al. 2008  |
| Urban    | MD, USA  | High Bank    | $40.2 \pm 15.9$                                      | $3.7 \pm 0.7$ | $15.5 \pm 0.5$              | $1.47 \pm 0.05$ | <1            | Kaushal et al. 2008  |
| Urban    | MD, USA  | Relict Oxbow | $31.4 \pm 7.0$                                       | 0.92          | 18.6                        | 1.3             | 0.62          | Harrison et al. 2011 |
| Urban    | MD, USA  | Relict Oxbow | $47.9 \pm 23.8$                                      | 1.8           | 20.83                       | 1               | 1.2           | Harrison et al. 2011 |

| Land Use    | Location    | Feature Type                    | Denitrification ( $\mu\text{g N/ kg dry soil/day}$ ) | DO (mg/L)      | Temp ( $^{\circ}\text{C}$ ) | Nitrate (mg/L)      | DOC (mg/L)    | Study                |
|-------------|-------------|---------------------------------|--|----------------|-----------------------------|---------------------|---------------|----------------------|
| Urban       | MD, USA     | Restored Floodplain             | $108.6 \pm 40$                                       | $3.6 \pm 0.8$  | $14.5 \pm 2.1$              | $1.15 \pm 0.04$     | <1            | Kaushal et al. 2008  |
| Urban       | MD, USA     | Restored Floodplain             | $156.2 \pm 21.3$                                     | $3.1 \pm 1.7$  | $15.8 \pm 1.7$              | $1.15 \pm 0.04$     | <1            | Kaushal et al. 2008  |
| Urban       | MD, USA     | Restored Floodplain             | $258.3 \pm 109.6$                                    | $3.0 \pm 0.4$  | $15.7 \pm 1.7$              | $2.15 \pm 0.29$     | $1.6 \pm 0.4$ | Present Study        |
| Urban       | MD, USA     | Restored High Bank              | $26.1 \pm 6.1$                                       | $3.6 \pm 1.3$  | $15.9 \pm 1.9$              | $1.15 \pm 0.04$     | <1            | Kaushal et al. 2008  |
| Urban       | MD, USA     | Restored High Bank              | $41.1 \pm 18.4$                                      | $4.5 \pm 1.3$  | $17.6 \pm 3.4$              | $1.15 \pm 0.04$     | <1            | Kaushal et al. 2008  |
| Urban       | RI, USA     | -                               | $23.9 \pm 12.7$                                      | $1.6 \pm 0.2$  | -                           | $3.2 \pm 0.9$       | $1.4 \pm 0.3$ | Watson et al. 2010   |
| Agriculture | New Zealand | Seepage Wetland Denitrification | $101,000 \pm 43,000$                                 | $0.4 \pm 0.02$ | $17.5 \pm 0.03$             | $0.012 \pm 0.002$   | -             | Zaman et al. 2008    |
| Agriculture | New Zealand | Bed Denitrification             | $38,200 \pm 7,800$                                   | -              | 19                          | $123 \pm 13$        | -             | Warneke et al. 2011  |
| Agriculture | New Zealand | Bed Denitrification             | $110,000 \pm 6,700$                                  | -              | 19                          | $154 \pm 13$        | -             | Warneke et al. 2011  |
| Agriculture | RI, USA     | -                               | $17.2 \pm 6.0$                                       | $3.6 \pm 0.4$  | -                           | $3.3 \pm 1.1$       | $1.0 \pm 0.2$ | Watson et al. 2010   |
| Forest      | AK, USA     | River Island                    | $7,800 \pm 2,400$                                    | $2.3 \pm 0.2$  | -                           | $0.029 \pm 0.002$   | $3.8 \pm 0.7$ | Clilverd et al. 2008 |
| Forest      | AK, USA     | River Island                    | $10,400 \pm 3,900$                                   | $1.5 \pm 0.2$  | -                           | $0.0243 \pm 0.0020$ | $2.7 \pm 0.1$ | Clilverd et al. 2008 |
| Forest      | MD, USA     | Floodplain                      | $166.7 \pm 40.4$                                     | $2.2 \pm 0.5$  | $16.5 \pm 1.2$              | $0.70 \pm 0.38$     | $1.4 \pm 0.1$ | Present Study        |
| Forest      | MD, USA     | Pond                            | $31.1 \pm 10.1$                                      | $2.3 \pm 0.4$  | $15.9 \pm 1.3$              | $0.12 \pm 0.09$     | $2.5 \pm 0.6$ | Present Study        |
| Forest      | MD, USA     | Wetland                         | $51.5 \pm 20.3$                                      | 1.79           | 20.7                        | 0.14                | 5.7           | Harrison et al. 2011 |

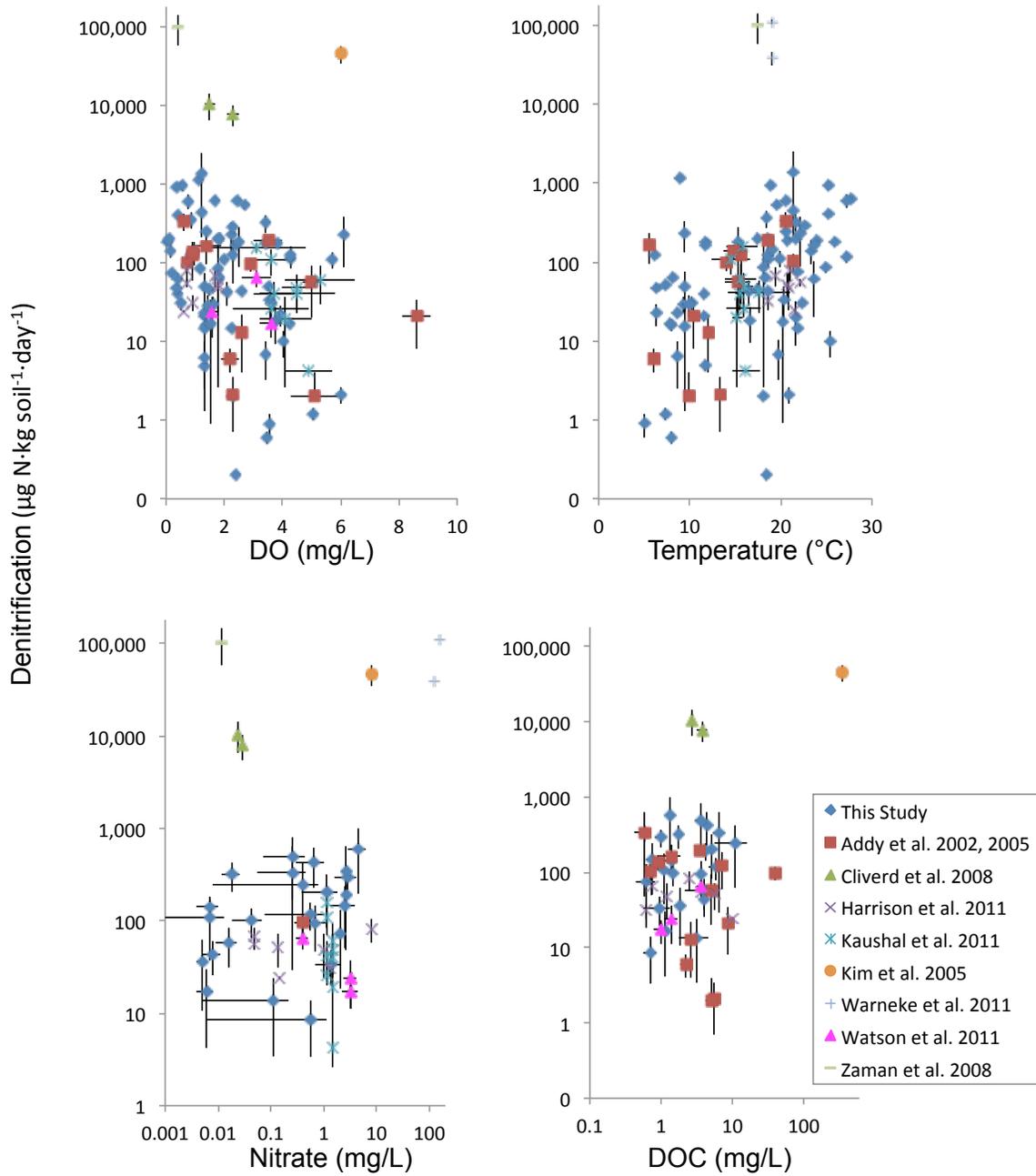
| Land Use | Location | Feature Type    | Denitrification<br>( $\mu\text{g N/ kg dry soil/day}$ ) | DO<br>(mg/L)  | Temp<br>( $^{\circ}\text{C}$ ) | Nitrate<br>(mg/L) | DOC<br>(mg/L) | Study                |
|----------|----------|-----------------|---|---------------|--------------------------------|-------------------|---------------|----------------------|
| Forest   | MD, USA  | Wetland         | $66.7 \pm 17.9$   | 1.68          | 19.4                           | 0.05              | 0.73          | Harrison et al. 2011 |
| Forest   | RI, USA  | -               | $64.3 \pm 15.3$   | $3.1 \pm 0.5$ | -                              | $0.4 \pm 0.1$     | $3.6 \pm 0.5$ | Watson et al. 2010   |
| -        | RI, USA  | Floodplain      | $96.7 \pm 19.7$   | 2.9           | 14.1                           | 0.4               | 39.6          | Addy et al. 2002     |
| -        | RI, USA  | High Marsh      | $6 \pm 2$   | $2.2 \pm 0.3$ | $6.1 \pm 0.3$                  | -                 | $2.2 \pm 0.3$ | Addy et al. 2005     |
| -        | RI, USA  | High Marsh      | $102 \pm 28$  | $0.7 \pm 0.1$ | $21.4 \pm 0.5$                 | -                 | $0.7 \pm 0.1$ | Addy et al. 2005     |
| -        | RI, USA  | High Marsh      | $137 \pm 31$  | $0.9 \pm 0.2$ | $14.8 \pm 1.1$                 | -                 | $0.9 \pm 0.2$ | Addy et al. 2005     |
| -        | RI, USA  | Marsh           | $123.2 \pm 63.8$  | 0.9           | 15.7                           | 0.0               | 7.2           | Addy et al. 2002     |
| -        | RI, USA  | Marsh           | $165 \pm 70$  | $1.4 \pm 0.5$ | $5.6 \pm 0.1$                  | -                 | $1.4 \pm 0.5$ | Addy et al. 2005     |
| -        | RI, USA  | Marsh           | $337 \pm 82$  | $0.6 \pm 0.1$ | $20.5 \pm 0.6$                 | -                 | $0.6 \pm 0.1$ | Addy et al. 2005     |
| -        | RI, USA  | Marsh Fringe    | $2.1 \pm 1.4$   | 2.3           | 13.3                           | 0.0               | 5.5           | Addy et al. 2002     |
| -        | RI, USA  | Transition Zone | $2 \pm 2$   | $5.1 \pm 0.8$ | $9.9 \pm 0.3$                  | -                 | $5.1 \pm 0.8$ | Addy et al. 2005     |
| -        | RI, USA  | Transition Zone | $13 \pm 9$  | $2.6 \pm 0.1$ | $12 \pm 0.2$                   | -                 | $2.6 \pm 0.1$ | Addy et al. 2005     |
| -        | RI, USA  | Transition Zone | $21 \pm 13$   | $8.6 \pm 0.5$ | $10.4 \pm 0.1$                 | -                 | $8.6 \pm 0.5$ | Addy et al. 2005     |
| -        | RI, USA  | Transition Zone | $56 \pm 36$   | $5 \pm 0.3$   | $15.3 \pm 1.4$                 | -                 | $5 \pm 0.3$   | Addy et al. 2005     |
| -        | RI, USA  | Transition Zone | $191 \pm 24$  | $3.5 \pm 0.5$ | $18.6 \pm 0.3$                 | -                 | $3.5 \pm 0.5$ | Addy et al. 2005     |

| Land Use | Location | Feature Type         | Denitrification<br>( $\mu\text{g N/ kg dry soil/day}$ ) | DO<br>(mg/L) | Temp<br>( $^{\circ}\text{C}$ ) | Nitrate<br>(mg/L) | DOC<br>(mg/L) | Study              |
|----------|----------|----------------------|---|--------------|--------------------------------|-------------------|---------------|--------------------|
| -        | Korea    | Contaminated Aquifer | 45,800 $\pm$<br>11,600                                  | 6            | -                              | 8                 | >350          | Kim et al.<br>2005 |

## Figure Captions

Figure 5. A comparison of denitrification rates ( $\mu\text{g N}\cdot\text{kg soil}^{-1}\cdot\text{day}^{-1}$ ) versus dissolved oxygen (mg/L), temperature ( $^{\circ}\text{C}$ ), nitrate (mg/L), and DOC (mg/L) from mean values for the present study and the available literature.

Figure 5.



## Bibliography

- Addy, K., D. Q. Kellogg, A. J. Gold, P. M. Groffman, G. Ferendo, and C. Sawyer. 2002. In situ push-pull method to determine ground water denitrification in riparian zones. *J. Environ. Qual* 31:1017–1024.
- Alexander, R. B., R. A. Smith, and G. E. Schwarz. 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* 403:758–761.
- Baltimore City, D. of P. W. 2005. Gwynns Run Pollution Control Facility fact sheet.
- Bates, D., M. Maechler, B. Bolker, and S. Walker. 2013. lme4: Linear mixed-effects models using Eigen and S4. R package version 1.0-5.
- Beaulieu, J. J., P. M. Mayer, S. S. Kaushal, M. P. Pennino, C. P. Arango, D. A. Balz, K. M. Fritz, B. H. Hill, C. M. Elonen, J. W. Santo Domingo, H. Ryu, and T. J. Canfield. 2014. Effects of urban stream burial on organic matter dynamics and reach scale nitrate retention. *Biogeochemistry* 121:107–126.
- Belt, K. T., C. Hohn, A. Gbakima, and J. A. Higgins. 2007. Identification of culturable stream water bacteria from urban, agricultural, and forested watersheds using 16S rRNA gene sequencing. *Journal of Water and Health* 5:395.
- Bernhardt, E. S., L. E. Band, C. J. Walsh, and P. E. Berke. 2008. Understanding, managing, and minimizing urban impacts on surface water nitrogen loading. *Year in Ecology and Conservation Biology* 2008 1134:61–96.
- Bernhardt, E. S., and G. E. Likens. 2002. Dissolved organic carbon enrichment alters nitrogen dynamics in a forest stream. *Ecology* 83:1689–1700.

- Bernhardt, E. S., M. Palmer, J. Allan, G. Alexander, K. Barnas, S. Brooks, J. Carr, S. Clayton, C. Dahm, J. Follstad-Shah, and others. 2005. Synthesizing US river restoration efforts. *Science* 308:636.
- Bettez, N. D., and P. M. Groffman. 2012. Denitrification potential in stormwater control structures and natural riparian zones in an urban landscape. *Environmental Science & Technology* 46:10909–10917.
- Bhaskar, A. S., and C. Welty. 2012. Water balances along an urban-to-rural gradient of metropolitan Baltimore, 2001–2009. *Environmental & Engineering Geoscience* 18:37–50.
- Boesch, D. F., R. B. Brinsfield, and R. E. Magnien. 2001. Chesapeake Bay eutrophication: scientific understanding, ecosystem restoration, and challenges for agriculture. *Journal of Environment Quality* 30:303–320.
- Boone, C. G. 2003. Obstacles to infrastructure provision: the struggle to build comprehensive sewer works in Baltimore. *Historical Geography* 31:151–168.
- Boyer, E. W., R. B. Alexander, W. J. Parton, C. Li, K. Butterbach-Bahl, S. D. Donner, R. W. Skaggs, and S. J. D. Grosso. 2006. Modeling denitrification in terrestrial and aquatic ecosystems at regional scales. *Ecological Applications* 16:2123–2142.
- Brunke, M., and T. O. M. Gonser. 1997. The ecological significance of exchange processes between rivers and groundwater. *Freshwater Biology* 37:1–33.
- Bukaveckas, P. A. 2007. Effects of channel restoration on water velocity, transient storage, and nutrient uptake in a channelized stream. *Environmental Science & Technology* 41:1570–1576.
- Burns, D. A. 1998. Retention of NO<sub>3</sub><sup>-</sup> in an upland stream environment: A mass balance approach. *Biogeochemistry* 40:73–96.

- Cadenasso, M. L., S. T. A. Pickett, P. M. Groffman, L. E. Band, G. S. Brush, M. F. Galvin, J. M. Grove, G. Hagar, V. Marshall, B. P. McGrath, J. P. M. O'Neil-Dunne, W. P. Stack, and A. R. Troy. 2008. Exchanges across Land-Water-Scape Boundaries in Urban Systems. *Annals of the New York Academy of Sciences* 1134:213–232.
- Canuel, E. A., J. E. Cloern, D. B. Ringelberg, J. B. Guckert, and G. H. Rau. 1995. Molecular and isotopic tracers used to examine sources of organic matter and its incorporation into the food webs of San Francisco Bay. *Limnology and Oceanography* 40:67–81.
- Canuel, E. A., and C. S. Martens. 1993. Seasonal variations in the sources and alteration of organic matter associated with recently-deposited sediments. *Organic Geochemistry* 20:563–577.
- Carpenter, S. R., N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications* 8:559–568.
- Carstensen, J., D. J. Conley, J. H. Andersen, and G. Ertebjerg. 2006. Coastal Eutrophication and Trend Reversal: A Danish Case Study. *Limnology and Oceanography* 51:398–408.
- CBT, C. B. P. 2009. Bay Barometer: A Health and Restoration Assessment of the Chesapeake Bay and Watershed in 2008. Pages 1–40.
- Chen, X., E. Peltier, B. S. M. Sturm, and C. B. Young. 2013. Nitrogen removal and nitrifying and denitrifying bacteria quantification in a stormwater bioretention system. *Water Research* 47:1691–1700.
- Clausen, J. C., K. Guillard, C. M. Sigmund, and K. M. Dors. 2000. Water quality changes from riparian buffer restoration in Connecticut. *Journal of Environmental Quality* 29:1751–1761.

- Collins, K. A., T. J. Lawrence, E. K. Stander, R. J. Jontos, S. S. Kaushal, T. A. Newcomer, N. B. Grimm, and M. L. Cole Ekberg. 2010. Opportunities and challenges for managing nitrogen in urban stormwater: A review and synthesis. *Ecological Engineering* 36:1507–1519.
- Davidson, E. A., K. E. Savage, N. D. Bettez, R. Marino, and R. W. Howarth. 2009. Nitrogen in runoff from residential roads in a coastal area. *Water, Air, & Soil Pollution* 210:3–13.
- Davidson, E. A., and J. P. Schimel. 1995. Microbial processes of production and consumption of nitric oxide, nitrous oxide and methane. Pages 327–357 Matson, P.A., and R. C. Harriss, editors. *Biogenic trace gases: measuring emissions from sediment and water*. Blackwell Science, Cambridge, MA, USA.
- DEPRM. 2008a. Spring Branch subwatershed - small watershed action plan; addendum to the water quality management plan for loch raven watershed; Volume 1. Pages 1–115.
- DEPRM. 2008b. Spring Branch subwatershed - small watershed action plan; addendum to the water quality management plan for loch raven watershed; Volume 2: Appendices D Through G. Pages 1–369.
- Dodds, W. K., E. Martí, J. L. Tank, J. Pontius, S. K. Hamilton, N. B. Grimm, W. B. Bowden, W. H. McDowell, B. J. Peterson, H. M. Valett, J. R. Webster, and S. Gregory. 2004. Carbon and nitrogen stoichiometry and nitrogen cycling rates in streams. *Oecologia* 140.
- Doheny, E. J., R. J. Staroneck, E. A. Striz, and P. M. Mayer. 2006. Watershed characteristics and pre-restoration surface-water hydrology of Minebank Run, Baltimore County, Maryland, water years 2002-04. Page 42.

- Dosskey, M. G., P. Vidon, N. P. Gurwick, C. J. Allan, T. P. Duval, and R. Lowrance. 2010. The role of riparian vegetation in protecting and improving chemical water quality in streams. *Journal of the American Water Resources Association* 46:261–277.
- Duncan, J. M., P. M. Groffman, and L. E. Band. 2013. Towards closing the watershed nitrogen budget: Spatial and temporal scaling of denitrification. *Journal of Geophysical Research: Biogeosciences* 118:1105–1119.
- Edwards, R. T., and J. L. Meyer. 1987. Metabolism of a sub-tropical low gradient blackwater river. *Freshwater Biology* 17:251–263.
- Elliott, E. M., C. Kendall, S. D. Wankel, D. A. Burns, E. W. Boyer, K. Harlin, D. J. Bain, and T. J. Butler. 2007. Nitrogen Isotopes as Indicators of  $\text{NO}_x$  Source Contributions to Atmospheric Nitrate Deposition Across the Midwestern and Northeastern United States. *Environmental Science & Technology* 41:7661–7667.
- Elmore, A. J., and S. S. Kaushal. 2008. Disappearing headwaters: patterns of stream burial due to urbanization. *Frontiers in Ecology and the Environment* 6:308–312.
- EPA. 1993. Process Design Manual for Nitrogen Removal. EPA 625/R-93-010. U.S. Environmental Protection Agency, Cincinnati, OH.
- EPA. 2006. Baltimore County stream restoration improves quality of life. EPA/903/F-06/008. U.S. Environmental Protection Agency, Mid-Atlantic Integrated Assessment. Fort Meade, MD.
- EPA. 2011. Section 319 nonpoint program success story; restoring stream improves water quality and fish community health. EPA 841-F-11-001G. US Environmental Protection Agency, Washington, DC.

- Fan, Y., H. Li, and G. Miguez-Macho. 2013. Global patterns of groundwater table depth. *Science* 339:940–943.
- Filoso, S., and M. A. Palmer. 2011. Assessing stream restoration effectiveness at reducing nitrogen export to downstream waters. *Ecological Applications* 21:1989–2006.
- Findlay, S., J. M. Quinn, C. W. Hickey, G. Burrell, and M. Downes. 2001. Effects of land use and riparian flowpath on delivery of dissolved organic carbon to streams. *Limnology and Oceanography* 46:345–355.
- Findlay, S., and R. L. Sinsabaugh. 1999. Unravelling the sources and bioavailability of dissolved organic matter in lotic aquatic ecosystems. *Marine and Freshwater Research* 50:781–790.
- Fisher, G. T. 2001. Evaluation of contributions of leaking water and sewer infrastructure in Gwynns Run and Maidens Choice Run to streamflow in the lower Gwynns Falls watershed, Baltimore, Maryland.
- Fisher, S. G., and G. E. Likens. 1973. Energy flow in Bear Brook, New Hampshire: an integrative approach to stream ecosystem metabolism. *Ecological Monographs* 43:421–439.
- Fissore, C., S. E. Hobbie, J. Y. King, J. P. McFadden, K. C. Nelson, and L. A. Baker. 2012. The residential landscape: fluxes of elements and the role of household decisions. *Urban Ecosystems* 15:1–18.
- Frost, P. C., J. H. Larson, L. E. Kinsman, G. A. Lamberti, and S. D. Bridgham. 2005. Attenuation of ultraviolet radiation in streams of northern Michigan. *Journal of the North American Benthological Society* 24:246–255.
- Galloway, J. N., J. D. Aber, J. W. Erisman, S. P. Seitzinger, R. W. Howarth, E. B. Cowling, and B. J. Cosby. 2003. The nitrogen cascade. *BioScience* 53:341–356.

- Gift, D. M., P. M. Groffman, S. S. Kaushal, and P. M. Mayer. 2010. Denitrification potential, root biomass, and organic matter in degraded and restored urban riparian zones. *Restoration Ecology* 18:113–120.
- Golubiewski, N. E. 2006. Urbanization increases grassland carbon pools: effects of landscaping in Colorado's front range. *Ecological Applications* 16:555–571.
- Griffiths, N. A., J. L. Tank, T. V. Royer, E. J. Rosi-Marshall, M. R. Whiles, C. P. Chambers, T. C. Frauendorf, and M. A. Evans-White. 2009. Rapid decomposition of maize detritus in agricultural headwater streams. *Ecological Applications* 19:133–142.
- Grimm, N. B., D. Foster, P. Groffman, J. M. Grove, C. S. Hopkinson, K. J. Nadelhoffer, D. E. Pataki, and D. P. Peters. 2008. The changing landscape: ecosystem responses to urbanization and pollution across climatic and societal gradients. *Frontiers in Ecology and the Environment* 6:264–272.
- Grimm, N. B., R. W. Sheibley, C. L. Crenshaw, C. N. Dahm, W. J. Roach, and L. H. Zeglin. 2005. N retention and transformation in urban streams. *Journal of the North American Benthological Society* 24:626–642.
- Groffman, P. M., M. A. Altabet, J. K. Bohlke, K. Butterbach-Bahl, M. B. David, M. K. Firestone, A. E. Giblin, T. M. Kana, L. P. Nielsen, and M. A. Voytek. 2006. Methods for measuring denitrification: diverse approaches to a difficult problem. *Ecological Applications* 16:2091–2122.
- Groffman, P. M., A. M. Dorsey, and P. M. Mayer. 2005. N processing within geomorphic structures in urban streams. *Journal of the North American Benthological Society* 24:613–625.

- Groffman, P. M., E. Holland, D. D. Myrold, G. P. Robertson, and X. Zou. 1999. Denitrification. Pages 272–288 *Standard soil methods for long-term ecological research*. Oxford University Press, New York, New York, USA.
- Groffman, P. M., N. L. Law, K. T. Belt, L. E. Band, and G. T. Fisher. 2004. Nitrogen fluxes and retention in urban watershed ecosystems. *Ecosystems* 7:393–403.
- Groffman, P. M., and R. V. Pouyat. 2009. Methane uptake in urban forests and lawns. *Environmental Science & Technology* 43:5229–5235.
- Halden, R. U., and D. H. Paull. 2005. Co-occurrence of triclocarban and triclosan in U.S. water resources. *Environmental Science & Technology* 39:1420–1426.
- Harrison, M. D., P. M. Groffman, P. M. Mayer, S. S. Kaushal, and T. A. Newcomer. 2011. Denitrification in alluvial wetlands in an urban landscape. *Journal of Environmental Quality* 40:634–646.
- Hassett, B., M. Palmer, E. Bernhardt, S. Smith, J. Carr, and D. Hart. 2005. Restoring watersheds project by project: trends in Chesapeake Bay tributary restoration. *Frontiers in Ecology and the Environment* 3:259–267.
- Hedin, L. O., J. C. von Fischer, N. E. Ostrom, B. P. Kennedy, M. G. Brown, and G. P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. *Ecology* 79:684–703.
- Hefting, M., J. C. Clement, D. Dowrick, A. C. Cosandey, S. Bernal, C. Cimpian, A. Tatur, T. P. Burt, and G. Pinay. 2004. Water table elevation controls on soil nitrogen cycling in riparian wetlands along a European climatic gradient. *Biogeochemistry* 67:113–134.
- Hook, A. M., and J. A. Yeakley. 2005. Stormflow dynamics of dissolved organic carbon and total dissolved nitrogen in a small urban watershed. *Biogeochemistry* 75:409–431.

- Howarth, R. W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J. A. Downing, R. Elmgren, N. Caraco, and T. Jordan. 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Pages 75–139 *Nitrogen cycling in the North Atlantic Ocean and its watersheds*. Springer.
- Howarth, R. W., A. Sharpley, and D. Walker. 2002. Nutrient Pollution to Coastal Waters in the United States: Implications for Achieving Coastal Water Quality Goals. *Estuaries* 25:656–676.
- Howarth, R. W., D. P. Swaney, E. W. Boyer, R. Marino, N. Jaworski, and C. Goodale. 2006. The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. *Biogeochemistry* 79:163–186.
- Janke, B. D., J. C. Finlay, S. E. Hobbie, L. A. Baker, R. W. Sterner, D. Nidzgorski, and B. N. Wilson. 2013. Contrasting influences of stormflow and baseflow pathways on nitrogen and phosphorus export from an urban watershed. *Biogeochemistry*:1–20.
- Jantz, P., S. Goetz, and C. Jantz. 2005. Urbanization and the Loss of Resource Lands in the Chesapeake Bay Watershed. *Environmental Management* 36:808–825.
- Johnson, L. T., J. L. Tank, and C. P. Arango. 2009. The effect of land use on dissolved organic carbon and nitrogen uptake in streams. *Freshwater Biology* 54:2335–2350.
- Kaushal, S. S., and K. T. Belt. 2012. The urban watershed continuum: evolving spatial and temporal dimensions. *Urban Ecosystems* 15:409–435.
- Kaushal, S. S., and M. W. Binford. 1999. Relationship between C:N ratios of lake sediments, organic matter sources, and historical deforestation in Lake Pleasant, Massachusetts, USA. *Journal of Paleolimnology* 22:439–442.

- Kaushal, S. S., K. Delaney-Newcomb, S. E. G. Findlay, T. A. Newcomer, S. Duan, M. J. Pennino, G. M. Svirich, A. M. Sides-Raley, M. R. Walbridge, and K. T. Belt. 2014. Longitudinal patterns in carbon and nitrogen fluxes and stream metabolism along an urban watershed continuum. *Biogeochemistry* 121:23–44.
- Kaushal, S. S., P. M. Groffman, L. E. Band, E. M. Elliott, C. A. Shields, and C. Kendall. 2011. Tracking nonpoint source nitrogen pollution in human-impacted watersheds. *Environmental Science & Technology* 45:8225–8232.
- Kaushal, S. S., P. M. Groffman, L. E. Band, C. A. Shields, R. P. Morgan, M. A. Palmer, K. T. Belt, C. M. Swan, S. E. G. Findlay, and G. T. Fisher. 2008a. Interaction between Urbanization and Climate Variability Amplifies Watershed Nitrate Export in Maryland. *Environmental Science & Technology* 42:5872–5878.
- Kaushal, S. S., P. M. Groffman, P. M. Mayer, E. Striz, and A. J. Gold. 2008b. Effects of stream restoration on denitrification in an urbanizing watershed. *Ecological Applications* 18:789–804.
- Kaushal, S. S., and W. M. Lewis, Jr. 2003. Patterns in the chemical fractionation of organic nitrogen in Rocky Mountain streams. *Ecosystems* 6:483–492.
- Kaushal, S. S., and W. M. Lewis, Jr. 2005. Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA. *Biogeochemistry* 74:303–321.
- Kaushal, S. S., W. M. Lewis, Jr., and J. H. McCutchan Jr. 2006. Land use change and nitrogen enrichment of a rocky mountain watershed. *Ecological Applications* 16:299–312.
- Kaushal, S. S., M. L. Pace, P. M. Groffman, L. E. Band, K. T. Belt, P. M. Mayer, and C. Welty. 2010. Land use and climate variability amplify contaminant pulses. *Eos, Transactions, American Geophysical Union* 91:221–222.

- Kaye, J. P., R. L. McCulley, and I. C. Burke. 2005. Carbon fluxes, nitrogen cycling, and soil microbial communities in adjacent urban, native and agricultural ecosystems. *Global Change Biology* 11:575–587.
- Kemp, W. M., W. R. Boynton, J. E. Adoli, D. F. Boesch, W. C. Boicourt, G. S. Brush, J. C. Cornwell, T. R. Fisher, P. M. Glibert, J. D. Hagy, L. W. Harding, E. D. Houde, D. G. Kimmel, W. D. Miller, R. I. E. Newell, M. R. Roman, E. M. Smith, and J. C. Stevenson. 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. *Marine Ecology Progress Series* 303:1–29.
- Klocker, C. A., S. S. Kaushal, P. M. Groffman, P. M. Mayer, and R. P. Morgan. 2009. Nitrogen uptake and denitrification in restored and unrestored streams in urban Maryland, USA. *Aquatic Sciences* 71:411–424.
- Krasner, S. W., M. J. McGuire, J. G. Jacangelo, N. L. Patania, K. M. Reagan, and E. M. Aieta. 1989. The occurrence of disinfection by-products in US drinking water. *Journal of the American Water Works Association* 81:41–53.
- Kraus, T. E. C., B. A. Bergamaschi, P. J. Dillon, R. G. M. Spencer, R. Stepanauskas, C. Kendall, R. F. Losee, and R. Fujii. 2008. Assessing the contribution of wetlands and subsided islands to dissolved organic matter and disinfection byproduct precursors in the Sacramento–San Joaquin River Delta: A geochemical approach. *Organic Geochemistry* 39:1302–1318.
- Larson, K. L., D. Casagrande, S. L. Harlan, and S. T. Yabiku. 2009. Residents’ yard choices and rationales in a desert city: social priorities, ecological impacts, and decision tradeoffs. *Environmental Management* 44:921–937.

- Laub, B. G., D. W. Baker, B. P. Bledsoe, and M. A. Palmer. 2012. Range of variability of channel complexity in urban, restored and forested reference streams. *Freshwater Biology* 57:1076–1095.
- Lofton, D. D., A. E. Hershey, and S. C. Whalen. 2007. Evaluation of denitrification in an urban stream receiving wastewater effluent. *Biogeochemistry* 86:77–90.
- Lowrance, R., R. Hubbard, and G. Vellidis. 1995. Riparian forest restoration to control agricultural water pollution.
- Mallin, M. A., S. H. Ensign, T. L. Wheeler, and D. B. Mayes. 2002. Pollutant removal efficacy of three wet detention ponds. *Journal of Environmental Quality* 31:654–660.
- Mallin, M. A., M. R. McIver, S. H. Ensign, and L. B. Cahoon. 2004. Photosynthetic and heterotrophic impacts of nutrient loading to blackwater streams. *Ecological Applications* 14:823–838.
- Mann, C. J., and R. G. Wetzel. 1995. Dissolved organic carbon and its utilization in a riverine wetland ecosystem. *Biogeochemistry* 31:99–120.
- Mayer, P. M., P. M. Groffman, E. A. Striz, and S. S. Kaushal. 2010. Nitrogen dynamics at the groundwater-surface water interface of a degraded urban stream. *Journal of Environmental Quality* 39:810–823.
- Mayer, P. M., S. P. Schechter, S. S. Kaushal, and P. M. Groffman. 2013. Effects of stream restoration on nitrogen removal and transformation in urban watersheds: lessons from Minebank Run, Baltimore, Maryland. *Watershed Science Bulletin* 4.
- McDowell, W. H., and G. E. Likens. 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. *Ecological Monographs* 58:177–195.

- Menninger, H. L., and M. A. Palmer. 2007. Herbs and grasses as an allochthonous resource in open-canopy headwater streams. *Freshwater Biology* 52:1689–1699.
- Meyer, J. L., M. J. Paul, and W. K. Taulbee. 2005. Stream ecosystem function in urbanizing landscapes. *Journal of the North American Benthological Society* 24:602–612.
- Milesi, C., S. W. Running, C. D. Elvidge, J. B. Dietz, B. T. Tuttle, and R. R. Nemani. 2005. Mapping and modeling the biogeochemical cycling of turf grasses in the United States. *Environmental Management* 36:426–438.
- Mulholland, P. J., R. O. Hall, Jr., D. J. Sobota, W. K. Dodds, S. E. G. Findlay, N. B. Grimm, S. K. Hamilton, W. H. McDowell, J. M. O'Brien, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, S. V. Gregory, S. L. Johnson, J. L. Meyer, B. J. Peterson, G. C. Poole, H. M. Valett, J. R. Webster, C. P. Arango, J. J. Beaulieu, M. J. Bernot, A. J. Burgin, C. L. Crenshaw, A. M. Helton, L. T. Johnson, B. R. Niederlehner, J. D. Potter, R. W. Sheibley, and S. M. Thomas. 2009. Nitrate removal in stream ecosystems measured by  $^{15}\text{N}$  addition experiments: Denitrification. *Limnology and Oceanography* 54:666–680.
- Newcomer, T. A., S. S. Kaushal, P. M. Mayer, A. R. Shields, E. A. Canuel, P. M. Groffman, and A. J. Gold. 2012. Influence of natural and novel organic carbon sources on denitrification in forest, degraded urban, and restored streams. *Ecological Monographs* 82:449–466.
- NRC, N. R. C. Committee on Reducing Stormwater Contributions to Water Pollution. 2008. *Urban Stormwater Management in the United States*. Page 529. National Academy Press, Washington, DC, USA.
- Park, J. B. K., R. J. Craggs, and J. P. S. Sukias. 2008. Treatment of hydroponic wastewater by denitrification filters using plant prunings as the organic carbon source. *Bioresource Technology* 99:2711–2716.

- Paul, M. J., and J. L. Meyer. 2001. Streams in the urban landscape. *Annual Review of Ecology and Systematics* 32:333–365.
- Paul, M. J., J. L. Meyer, and C. A. Couch. 2006. Leaf breakdown in streams differing in catchment land use. *Freshwater Biology* 51:1684–1695.
- Pennino, M. P., S. S. Kaushal, J. J. Beaulieu, P. M. Mayer, and C. P. Arango. 2014. Effects of urban stream burial on nitrogen uptake and ecosystem metabolism: implications for watershed nitrogen and carbon fluxes. *Biogeochemistry* 121:247–269.
- Perdue, E. M., K. C. Beck, and J. H. Reuter. 1976. Organic complexes of iron and aluminum in natural waters. *Nature* 260:418–420.
- Pernet-Coudrier, B., G. Varrault, M. Saad, J. P. Croue, M.-F. Dignac, and J.-M. Mouchel. 2010. Characterisation of dissolved organic matter in Parisian urban aquatic systems: predominance of hydrophilic and proteinaceous structures. *Biogeochemistry* 106:89–106.
- Peterson, B. J., W. M. Wollheim, P. J. Mulholland, J. R. Webster, J. L. Meyer, J. L. Tank, E. Martí, W. B. Bowden, H. M. Valett, A. E. Hershey, W. H. McDowell, W. K. Dodds, S. K. Hamilton, S. V. Gregory, and Morrall. 2001. Control of nitrogen export from watersheds by headwater streams. *Science* 292:86–90.
- Petrone, K. C. 2010. Catchment export of carbon, nitrogen, and phosphorus across an agro-urban land use gradient, Swan-Canning River system, southwestern Australia. *Journal of Geophysical Research* 115:G01016.
- Petrone, K. C., J. S. Richards, and P. F. Grierson. 2009. Bioavailability and composition of dissolved organic carbon and nitrogen in a near coastal catchment of south-western Australia. *Biogeochemistry* 92:27–40.

- Pickett, S. T. A., M. L. Cadenasso, J. M. Grove, C. G. Boone, P. M. Groffman, E. Irwin, S. S. Kaushal, V. Marshall, B. P. McGrath, and C. H. Nilon. 2011. Urban ecological systems: Scientific foundations and a decade of progress. *Journal of Environmental Management* 92:331–362.
- Pouyat, R. V., D. E. Pataki, K. T. Belt, P. M. Groffman, J. Hom, and L. E. Band. 2007. Effects of urban land-use change on biogeochemical cycles. Pages 45–58 In: Canadell, J.G.; Pataki, D.E.; Pitelka, L.F., eds. *Terrestrial ecosystems in a changing world*. Berlin. Springer-Verlag.
- Pouyat, R. V., I. D. Yesilonis, and N. E. Golubiewski. 2009. A comparison of soil organic carbon stocks between residential turf grass and native soil. *Urban Ecosystems* 12:45–62.
- Rabalais, N. N. 2002. Nitrogen in aquatic ecosystems. *AMBIO: A Journal of the Human Environment* 31:102–112.
- R Core Team. 2013. *R: A language and environment for statistical computing*. R Foundation for Statistical Computing, Vienna, Austria.
- Roach, W. J., and N. B. Grimm. 2011. Denitrification mitigates N flux through the stream-floodplain complex of a desert city. *Ecological Applications* 21:2618–2636.
- Roley, S. S., J. L. Tank, M. L. Stephen, L. T. Johnson, J. J. Beaulieu, and J. D. Witter. 2012a. Floodplain restoration enhances denitrification and reach-scale nitrogen removal in an agricultural stream. *Ecological Applications* 22:281–297.
- Roley, S. S., J. L. Tank, and M. A. Williams. 2012b. Hydrologic connectivity increases denitrification in the hyporheic zone and restored floodplains of an agricultural stream. *Journal of Geophysical Research* 117.

- Rosenzweig, B. R., J. A. Smith, M. L. Baeck, and P. R. Jaffé. 2011. Monitoring nitrogen loading and retention in an urban stormwater detention pond. *Journal of Environment Quality* 40:598.
- Rosgen, D. L. 1994. A classification of natural rivers. *Catena* 22:169–199.
- Royer, T. V., and M. B. David. 2005. Export of dissolved organic carbon from agricultural streams in Illinois, USA. *Aquatic Sciences* 67:465–471.
- Rücker, K., and J. Schrautzer. 2010. Nutrient retention function of a stream wetland complex—A high-frequency monitoring approach. *Ecological Engineering* 36:612–622.
- Ryan, R. J., C. Welty, and P. C. Larson. 2010. Variation in surface water-groundwater exchange with land use in an urban stream. *Journal of Hydrology* 392:1–11.
- Schaller, J. L., T. V. Royer, M. B. David, and J. L. Tank. 2004. Denitrification associated with plants and sediments in an agricultural stream. *Journal of the North American Benthological Society* 23:667–676.
- Seitzinger, S. P., R. W. Sanders, and R. Styles. 2002a. Bioavailability of DON from natural and anthropogenic sources to estuarine plankton. *Limnology and Oceanography* 47:353–366.
- Seitzinger, S. P., R. V. Styles, E. W. Boyer, R. B. Alexander, G. Billen, R. W. Howarth, B. Mayer, and N. Van Breemen. 2002b. Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. *Biogeochemistry* 57:199–237.
- Sickman, J. O., M. J. Zanolli, and H. L. Mann. 2007. Effects of urbanization on organic carbon loads in the Sacramento River, California. *Water Resources Research* 43:W11422.
- Sivirichi, G. M., S. S. Kaushal, P. M. Mayer, C. Welty, K. T. Belt, T. A. Newcomer, K. D. Newcomb, and M. M. Grese. 2011. Longitudinal variability in streamwater chemistry and

- carbon and nitrogen fluxes in restored and degraded urban stream networks. *Journal of Environmental Monitoring* 13:288–303.
- Smith, M. S., and J. M. Tiedje. 1979. Phases of denitrification following oxygen depletion in soil. *Soil Biology and Biochemistry* 11:261–267.
- Sobczak, W. V., S. Findlay, and S. Dye. 2003. Relationships between DOC bioavailability and nitrate removal in an upland stream: An experimental approach. *Biogeochemistry* 62:309–327.
- Striz, E. A., and P. M. Mayer. 2008. Assessment of near-stream ground water-surface water interaction (GSI) of a degraded stream before restoration. US Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory.
- Sudduth, E. B., and J. L. Meyer. 2006. Effects of bioengineered streambank stabilization on bank habitat and macroinvertebrates in urban streams. *Environmental Management* 38:218–226.
- Taylor, G., T. Fletcher, T. Wong, P. Breen, and H. Duncan. 2005. Nitrogen composition in urban runoff—implications for stormwater management. *Water Research* 39:1982–1989.
- Taylor, P. G., and A. R. Townsend. 2010. Stoichiometric control of organic carbon–nitrate relationships from soils to the sea. *Nature* 464:1178–1181.
- Urban, D. L. 2005. Modeling ecological processes across scales. *Ecology* 86:1996–2006.
- Vannote, R. L., G. W. Minshall, K. W. Cummins, J. R. Sedell, and C. E. Cushing. 1980. The river continuum concept. *Canadian Journal of Fisheries and Aquatic Sciences* 37:130–137.
- VerHoef, J. R., C. Welty, J. Miller, M. McGuire, M. Grese, S. Kaushal, A. J. Miller, J. M. Duncan, P. M. Groffman, L. E. Band, and R. M. Maxwell. 2011. Analysis of high

frequency water quality data in the Baltimore Ecosystem Study LTER. Page Abstract #H53J-1546. San Francisco, CA, USA.

- Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, W. H. Schlesinger, and D. G. Tilman. 1997. Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications* 7:737–750.
- Walsh, C. J., A. H. Roy, J. W. Feminella, P. D. Cottingham, P. M. Groffman, and R. P. Morgan II. 2005. The urban stream syndrome: current knowledge and the search for a cure. *Journal of the North American Benthological Society* 24:706–723.
- Warner, T. J., T. V. Royer, J. L. Tank, N. A. Griffiths, E. J. Rosi-Marshall, and M. R. Whiles. 2009. Dissolved organic carbon in streams from artificially drained and intensively farmed watersheds in Indiana, USA. *Biogeochemistry* 95:295–307.
- Wazniak, C. E., and P. M. Glibert. 2004. Potential impacts of brown tide, *Aureococcus anophagefferens*, on juvenile hard clams, *Mercenaria mercenaria*, in the coastal bays of Maryland, USA. *Harmful Algae* 3:321–329.
- Webster, J. R., and H. M. Valett. 2006. Solute dynamics. Pages 169–187 in Hauer, F. R. and G. A. Lamberti, editors. *Methods in stream ecology*. 2nd ed. Academic Press/Elsevier, Boston, MA, USA.
- Weller, D. E., T. E. Jordan, D. L. Correll, and Z. J. Liu. 2003. Effects of land-use change on nutrient discharges from the Patuxent River watershed. *Estuaries and Coasts* 26:244–266.
- Wiegner, T. N., and S. P. Seitzinger. 2001. Photochemical and microbial degradation of external dissolved organic matter inputs to rivers. *Aquatic Microbial Ecology* 24:27–40.
- Winter, B. 2013. Linear models and linear mixed effects models in R with linguistic applications. arXiv:1308.5499.

- Wriedt, G., J. Spindler, T. Neef, R. Meißner, and M. Rode. 2007. Groundwater dynamics and channel activity as major controls of in-stream nitrate concentrations in a lowland catchment system? *Journal of Hydrology* 343:154–168.
- Yesilonis, I. D., R. V. Pouyat, and N. K. Neerchal. 2008. Spatial distribution of metals in soils in Baltimore, Maryland: role of native parent material, proximity to major roads, housing age and screening guidelines. *Environmental Pollution* 156:723–731.
- Zhu, W. X., N. D. Dillard, and N. B. Grimm. 2004. Urban nitrogen biogeochemistry: status and processes in green retention basins. *Biogeochemistry* 71:177–196.
- Zinger, Y., G.-T. Blecken, T. D. Fletcher, M. Viklander, and A. Deletić. 2013. Optimising nitrogen removal in existing stormwater biofilters: Benefits and tradeoffs of a retrofitted saturated zone. *Ecological Engineering* 51:75–82.

## Tammy Newcomer Johnson

<http://tinyurl.com/LinkedIn-TammyNewcomerJohnson>

109 New Ave, Reisterstown, MD 21136

[Tammy.A.Newcomer@gmail.com](mailto:Tammy.A.Newcomer@gmail.com)

Cell: [\(410\) 227-6982](tel:(410)227-6982)

### Experience

---

#### **Knauss Marine Policy Fellow**, Natural Resource Specialist, National Sea Grant Office, 2014

Coordinated and supported natural resources activities for the Sea Grant Network. Topics included pharmaceuticals and personal care products, habitat restoration, harmful algal blooms, aquatic invasive species, commercial and recreational fisheries, aquaculture development, seafood safety certification and ocean acidification. Shared leadership in initiating, sustaining and evaluating activities with network leaders and national office staff.

#### **National Network for Environmental Management Studies Fellow**, EPA, 2010-2013

Led project, "Stream restoration as an approach for managing nitrogen pollution in urban watersheds (#2010-308)." Synthesized data from published literature to aid watershed managers in decisions to implement restoration best management practices (BMPs). Worked with a team from EPA on a meta-analysis of stream restoration methods as a BMP for nitrogen control.

#### **National Science Foundation G6-12 Fellow**, Cary Institute of Ecosystem Studies, 2010-2012

Pathways to Environmental Science Literacy Project, funded by the National Science Foundation, at four Long Term Ecological Research (LTER) sites around the nation. Contributed to developing environmental science literacy frameworks and teaching resources for Baltimore area teachers and students in grades 6-12 on the topics of water, biodiversity and carbon cycling. Worked in twenty classrooms to help teachers implement new teaching approaches in their classrooms and schoolyards. Worked with a team to organize and run ten professional development workshops and two 9-day summer sessions for teachers.

#### **Sea Grant Fellow**, Maryland Sea Grant, 2007-2009

Led grant funded project, "Investigation of stream restoration as a means of reducing nitrogen pollution from rapidly urbanizing coastal watersheds of the Chesapeake Bay." Assessed efficacy of stream restoration as a best management practice (BMP) for nitrogen control in urban watersheds using a field-based research approach.

#### **Teaching Assistant for Principles and Practices of Ecological Restoration**, UMCP, 2009

### Education

---

- |      |   |
|------|---|
| 2015 | Ph.D. University of Maryland<br>Marine Estuarine Environmental Science<br><i>Adviser: Professor Sujay Kaushal</i> |
| 2008 | Fundamentals of Ecosystem Ecology at Cary Institute in New York   |
| 2007 | B.S. UMBC (Environmental Science)<br><i>Adviser: Professor Andy Miller</i>  |
| 2006 | Study Abroad Program at the School for Field Studies in Costa Rica  |

---

## Publications

---

### 2014

**Newcomer Johnson, TA**, SS Kaushal, PM Mayer and M Grese. 2014. Effects of stormwater management and stream restoration on watershed nitrogen retention. *Biogeochemistry* doi: 10.1007/s10533-014-9999-5

Kaushal SS, Delaney-Newcomb, KA, SEG Findlay, PM Groffman, AM Sides, **TA Newcomer Johnson**, G Svirichchi and MR Walbridge. 2014. Longitudinal patterns in carbon and nitrogen fluxes and stream metabolism along an urban watershed continuum. *Biogeochemistry* doi:10.1007/s10533-014-9979-9

Kaushal, SS, PM Mayer, PG Vidon, RM Smith, MJ Pennino, SW Duan, **TA Newcomer**, C Welty and KT Belt. 2014. Land use and climate variability amplify carbon, nutrient, and contaminant pulses: a review with management implications. *Journal of the American Water Resources Association* doi:10.1111/jawr.12204

### 2012

**Newcomer, TA**, SS Kaushal, PM Mayer, AR Shields, EA Canuel, PM Groffman and AJ Gold. 2012. Influence of natural & novel organic carbon sources on denitrification in forested, degraded-urban, & restored streams. *Ecological Monographs* 82:449-466.

**Newcomer, TA**, SS Kaushal, PM Mayer, AR Shields, EA Canuel, PM Groffman and AJ Gold. 2012. Data from: Influence of natural and novel organic carbon sources on denitrification in forest, degraded urban, and restored streams. Dryad Digital Repository. [doi:10.5061/dryad.4gk00](https://doi.org/10.5061/dryad.4gk00)

### 2011

Harrison, MD, PM Groffman, PM Mayer, SS Kaushal and **TA Newcomer**. 2011. Denitrification in alluvial wetlands in an urban landscape. *Journal of Environment Quality* 40:634–646.

Svirichchi, GM, SS Kaushal, PM Mayer, C Welty, KT Belt, **TA Newcomer**, KD Newcomb and MM Grese. 2011. Longitudinal variability in streamwater chemistry and carbon and nitrogen fluxes in restored and degraded urban stream networks. *Journal of Environmental Monitoring* 13:288-303.

### 2010

Collins, KA, TJ Lawrence, EK Stander, RJ Jontos, SS Kaushal, **TA Newcomer**, NB Grimm and ML Cole Ekberg. 2010. Opportunities and challenges for managing nitrogen in urban stormwater: A review and synthesis. *Ecological Engineering* 36:1507-1519.

---

## Grades 6-12 Curricula

---

**Newcomer, T**, A Berkowitz, B Blank, A Cano, B Caplan, B Covitt, K Emery, K Gunckel, L Hammond, B Hoyt, N LaDue, J Moore, T Noel, L Pitot, J Schuttlefield, S Syswerda, D Swartz, R Tschillard, A Warnock and A Whitmer. "Substances In Water." Pathways to Environmental Science Literacy LTER Math Science Partnership Project Funded by The National Science Foundation, 2012. Online: <http://www.cns-eoccolostate.edu/msp-nrel.html>

Warnock, A, A Berkowitz, B Blank, A Cano, B Caplan, B Covitt, K Emery, K Gunckel, L Hammond, B Hoyt, N LaDue, J Moore, **T Newcomer**, T Noel, L Pitot, J Schuttlefield, S Syswerda, D Swartz, R Tschillard and A Whitmer. "Schoolyard Water Pathways." Pathways to Environmental Science Literacy LTER Math Science Partnership Project Funded by The National Science Foundation, 2012. Online: <http://www.cns-eoccolostate.edu/msp-nrel.html>

---

## Honors and Awards

---

|           |   |
|-----------|---|
| 2013      | University of Maryland Ann G. Wylie Dissertation Fellowship (\$10,800)  |
| 2012      | University of Maryland Bioscience Day<br>Best Student Poster for "Water Quality and Management"   |
| 2012      | University of Maryland College of Computers, Math & Natural Sciences<br>Dean's Award (\$5,000)  |
| 2009      | Coastal Estuarine Research Federation (CERF) Conference in Portland, Oregon<br>Travel Awards from CERF (\$325), Atlantic Estuarine Research Federation (\$600) and<br>Chesapeake Biological Laboratory Graduate Education Committee (\$500) |
| 2009      | National Science Foundation Denitrification Research Coordination Network<br>Selected Participant (\$2,000)   |
| 2006      | National Science Foundation's Research Experience for Undergraduates (REU)  |
| 2006      | BlogAbroad Scholarship to Costa Rica, School for Field Studies (\$2,000)  |
| 2003-2007 | UMBC University Scholar, merit-based academic full-ride (\$54,000)  |

---

## Service

- 
- 2015 Reviewed ~400 Maryland Sea Grant Research Experiences for Undergraduate applications.
- 2014 Led special session: “Using Social Science and Education to Prevent and Reduce Pharmaceuticals and Personal Care Product Contaminants in Watersheds.” Co-convened by Jennifer Lam, Sam Chan, Laura Kammin and Marti Martz. American Water Resources Association (AWRA) Annual Meeting. Tysons Corner, VA. November 3-6
- 2014 Reviewer for NOAA’s Coastal Management Fellowships
- 2013 American Inst. of Biological Sciences Congressional Visit Day
- 2013 Reviewer for American Geophysical Union Student Travel Grants
- 2013 Co-convenor of Session: “SCI-007 Translational Science: The Complexities of Watershed and Estuarine Restoration Efforts.” Convened by: Mike Allen, Amanda Rockler, Fredrika Moser and Tamara Newcomer. Coastal Estuarine Research Federation (CERF) Biennial Conference. San Diego, CA. November 3-7
- 2013 Co-led tour of Gwynns Falls Watershed for ~15 teachers
- 2013-2014 Member of Chestnut Ridge Volunteer Fire Station
- 2011-present *Ad hoc* reviewer for Ecological Engineering and Biogeochemistry
- 2010-2011 Elected Graduate Student Representative for the Baltimore Ecosystem Study and National Science Foundation Long-Term Ecological Research Site
- 2009 3-week Boynton Lab Chesapeake Bay Research Cruise
- 2008-2009 Elected Graduate Student Representative for University of Maryland’s Marine Estuarine Environmental Science Department

## **Selected Presentations**

---

### **2014**

**Newcomer Johnson, TA.** 2014. Nitrogen cycling in local watersheds. Presentation to 300 biology students in 13 Howard County High Schools working with Howard County Conservancy on a Subwatershed Report Card. [Invited Webinar]

**Newcomer Johnson, TA** and KR MacDonald. 2014. Citizen science in the Sea Grant Network. Restore America's Estuaries; 7<sup>th</sup> National Summit on Coastal and Estuarine Restoration. Washington, DC. [Poster]

**Newcomer Johnson, TA**, EM Bevan and JE Brown. 2014. Position #345: Natural Resource Specialist and position #289: Coastal Communities Specialist, Selection Week Host Presentations for 2015 Knauss Finalists. Washington, DC. [Oral]

**Newcomer Johnson, TA** and B Bisson. 2014. Citizen Science in the Sea Grant Network. Sea Grant Week Extension Assembly Meeting. Clearwater Beach, Florida. [Oral]

Moser, FC, JS Diana, AM Lazur, RE Malouf, **TA Newcomer Johnson** and EM Bevan. 2014. Linking research and extension. Sea Grant Week Workshop. Clearwater Beach, Florida. [Oral]

**Newcomer Johnson, TA** and EM Bevan. 2014. Focus area updates. Sea Grant Week Presentation for the Sea Grant Advisory Board. Clearwater Beach, Florida. [Oral]

**Newcomer Johnson, TA**, SS Kaushal, PM Mayer and M Grese. 2014. Effects of stormwater management and stream restoration on watershed nitrogen retention. Conference on Ecological and Ecosystem Restoration (CEER). New Orleans, Louisiana. [Poster]

**Newcomer Johnson, TA**, SS Kaushal, PM Mayer and M Grese. 2014. Effects of stormwater management and stream restoration on watershed nitrogen retention. NOAA Brownbag Seminar Series. Silver Spring, Maryland. [Oral/Webinar]

Ban, E, **TA Newcomer Johnson** and EM Bevan. 2014. Importance of planning, implementation, evaluation, and resources (PIER) reporting. Great Lakes Sea Grant Network Meeting. Erie, Pennsylvania. [Oral]

**Newcomer Johnson, TA**, SS Kaushal, PM Mayer and M Grese. 2014. Effects of stormwater management and stream restoration on watershed nitrogen retention. Association for the Sciences of Limnology and Oceanography (ASLO) Joint Aquatic Sciences Meeting. Portland, Oregon. [Oral]

Kaushal, SS, PM Mayer, PG Vidon, RM Smith, MJ Pennino, **TA Newcomer Johnson**, SW Duan, C Welty, KT Belt and M Yepsen. 2014. Land use and climate variability amplify carbon, nutrient, and contaminant pulses. Association for the Sciences of Limnology and Oceanography (ASLO) Joint Aquatic Sciences Meeting. Portland, Oregon. [Oral]

Mayer, PM, JJ Beaulieu, C Cooper, KJ Forshay, M Harrison, SS Kaushal, DJ Merritts, **T Newcomer**, MJ Pennino and RC Walter. 2014. The legacy of land-use is revealed in the biogeochemistry of urban streams. Association for the Sciences of Limnology and Oceanography (ASLO) Joint Aquatic Sciences Meeting. Portland, Oregon. [Oral]

**Newcomer Johnson, TA** and EM Bevan. 2014. National Sea Grant Office (NSGO) Communications Update. Mid-Atlantic Sea Grant Regional Meeting. Corolla, North Carolina. [Oral]

Lazur, AM, **TA Newcomer Johnson and** EM Bevan. 2014. Integrating research and extension. Mid-Atlantic Sea Grant Regional Meeting. Corolla, North Carolina. [Oral]

**TA Newcomer Johnson and** EM Bevan. 2014. Focus area updates. Mid-Atlantic Sea Grant Regional Meeting. Washington, DC. [Oral]

**TA Newcomer Johnson and** EM Bevan. 2014. Focus area updates. Sea Grant Advisory Board Meeting. Silver Spring, Maryland. [Webinar]

### **2013**

**Newcomer, TA**, SS Kaushal, PM Mayer, PM Groffman and M Grese. 2013. Effects of stormwater management and stream engineering on nitrogen uptake and denitrification in streams. University of Maryland Geology Department Grad Talks. College Park, Maryland. [Oral]

**Newcomer, TA**, SS Kaushal, PM Mayer, PM Groffman and M Grese. 2013. Nitrogen processing in engineered stream networks with integrated stormwater management. Maryland Institute for Applied Environmental Health (MIAEH) Weekly Seminar. College Park, Maryland. [Oral]

**Newcomer, TA**, SS Kaushal, PM Mayer, PM Groffman and M Grese. 2013. Effects of integrated stormwater management and stream engineering on nitrogen uptake and denitrification in streams. Society for Ecological Restoration (SER)'s Mid-Atlantic Chapter Annual Conference. College Park, Maryland. [Oral]

**Newcomer, TA**, SS Kaushal, PM Mayer, PM Groffman and M Grese. 2013. Effects of integrated stormwater management and stream engineering on nitrogen uptake and denitrification in streams. Environmental Protection Agency (EPA) National Center for Environmental Assessment. Washington, DC. [Oral]

**Newcomer, TA**, SS Kaushal, PM Mayer, AR Shields, EA Canuel, PM Groffman and AJ Gold. 2013. Effects of carbon sources and stream restoration on denitrification. Center for Watershed Protection. Ellicott City, Maryland. [Oral/Webinar]

**Newcomer, TA**, SS Kaushal, PM Mayer and M Grese. 2013. Effects of stormwater management and stream engineering on watershed nitrogen retention. Marine Estuarine Environmental Science (MEES)'s Colloquium. Cambridge, Maryland. [Oral]

**Newcomer, TA**, SS Kaushal, PM Mayer and M Grese. 2013. Effects of stormwater management and stream engineering on watershed nitrogen retention. Coastal Estuarine Research Federation (CERF) Biennial Conference. San Diego, California. [Poster]

## 2012

**Newcomer, TA**, SS Kaushal, PM Mayer, PM Groffman and M Grese. 2012. Effects of integrated stormwater management and stream engineering on nitrogen uptake and denitrification in streams. Fall Meeting, American Geophysical Union (AGU). San Francisco, California. [Oral]

Kaushal, SS, C Smith, **TA Newcomer**, RM Smith, SW Duan, KT Belt, KD Newcomb, SEG Findlay, PM Groffman and PM Mayer. 2012. The Urban Watershed Continuum: Biogeochemistry of Carbon. American Geophysical Union Meeting. San Francisco, California. [Oral]

**Newcomer, TA** and B Caplan. 2012. Investigating local water conductivity. Century High School's Annual Career and Applications Fair. Sykesville, Maryland. [Oral]

Rajendran, S and **TA Newcomer**. 2012. Investigating local water conductivity. Maryland Association for Environmental and Outdoor Education (MAEOE) Annual Meeting. Ocean City, Maryland. [Oral]

**Newcomer, TA** and SS Kaushal. 2012. Effects of stormwater management and stream engineering on nitrogen uptake and denitrification in streams. Geology Department Graduate Seminar Day. College Park, Maryland. [Oral]

## 2011

**Newcomer, TA**, SS Kaushal, PM Mayer, PM Groffman and MM Grese. 2011. Effects of stormwater management and stream engineering on nitrogen uptake and denitrification in streams. Fall Meeting, American Geophysical Union (AGU). San Francisco, California. [Oral]

**Newcomer, TA**, SS Kaushal and PM Mayer. 2011. Managing N sinks in watersheds and streams. EPA Water Protection Division Knowledge Transfer Session. Philadelphia, Pennsylvania. [Oral]

Kaushal SS, **TA Newcomer** and MJ Pennino. 2011. Nutrient processing in streams and stormwater control systems. BREG 667: Watershed Hydrochemistry, University of Delaware. Newark, Delaware. [Invited Oral].

**Newcomer, TA**, N Mollet, B Caplan and S Rajendran. 2011. Carbon in an urban setting: innovative and tested techniques for providing a hands-on schoolyard based way of teaching photosynthesis and cellular respiration. Baltimore City Schools' Sustainability Day. Baltimore, Maryland. [Oral]

**Newcomer, TA**, SS Kaushal and PM Mayer. 2011. Nitrogen uptake and denitrification in restored and degraded-urban streams. Marine Estuarine Environmental Science (MEES) Colloquium. Frostburg, Maryland. [Poster]

**Newcomer, TA**, SS Kaushal, PM Mayer, PM Groffman and MM Grese. 2011. Effects of stormwater management and stream engineering on nitrogen uptake and denitrification in streams. Baltimore Ecosystem Study Annual Meeting. Baltimore, Maryland. [Oral]

Caplan B and **TA Newcomer**. 2011. Developing learning progressions for student understanding of water systems in Baltimore. Baltimore Ecosystem Study Annual Meeting. Baltimore, Maryland. [Oral]

KA Collins, TJ Lawrence, EK Stander, RJ Jontos, SS Kaushal, **TA Newcomer**, NB Grimm and MC Ekberg. 2011. Opportunities and challenges for managing nitrogen in urban storm water: a review and synthesis. Land Grant/Sea Grant National Water Conference. Washington, DC. [Invited Oral]

Kaushal, SS, PM Groffman, LE Band, EM Elliott, CA Shields, C Kendall, PM Mayer and **TA Newcomer**. 2011. Tracking stream nitrogen sources using isotopes: implications for managing coastal eutrophication and urban sustainability. Maryland Department of Natural Resources Stream Symposium. Westminster, Maryland. [Invited Oral]

**Newcomer, TA**, N Mollet, J Baynard, B Caplan, AR Berkowitz, S Haines, C Harris and EG Keeling. 2011. Baltimore Partnership for Environmental Science Literacy. Baltimore Ecosystem Study Annual Meeting. Baltimore, Maryland. [Poster]

**Newcomer, TA**, SS Kaushal and PM Mayer. 2011. Nitrogen uptake and denitrification in restored and degraded-urban streams. Geology Fest: The Mike Brown Decades. College Park, Maryland. [Poster]

Caplan, B and **TA Newcomer**. 2011. Using online simulations to study water. The Baltimore Partnership for Environmental Science Literacy: Investigating Urban Ecosystems Workshop. Baltimore, Maryland. [Oral]

## **2010**

Caplan, B and **TA Newcomer**. 2010. Schoolyard greening and ecological restoration. The Baltimore Partnership for Environmental Science Literacy: Investigating Urban Ecosystems Workshop. Baltimore, Maryland. [Oral]

**Newcomer, TA**, SS Kaushal, PM Mayer, AR Shields, EA Canuel, PM Groffman and AJ Gold. 2010. Relative importance of organic C sources for denitrification in hyporheic zones of forested, unrestored, and restored streams. Baltimore Ecosystem Study Annual Meeting. Baltimore, Maryland. [Oral]

Caplan, B, AR Berkowitz, S Haines, C Harris, EG Keeling, T Grant, R Foot, **T A Newcomer** and P Bond. 2010. Baltimore Partnership for Environmental Science Literacy. Baltimore Ecosystem Study Annual Meeting. Baltimore, Maryland. [Poster]

**Newcomer, TA**, SS Kaushal, PM Mayer and PM Groffman. 2010. COS 98-8: Effects of organic carbon sources on denitrification in forested, restored, and urbanized streams. Ecological Society of America (ESA) Global Warming: The legacy of our past, the challenge for our future. Pittsburgh, Pennsylvania. [Oral]

Duan, SW, SS Kaushal, PM Groffman, SEG Findlay, MM Grese, **TA Newcomer**, MJ Pennino and C Sperling. 2010. COS 98: Effects of temperature and source on organic matter leaching and decomposition in Baltimore urban area. Ecological Society of America (ESA) Global Warming: The legacy of our past, the challenge for our future. Pittsburgh, Pennsylvania. [Oral]

SS Kaushal, PM Groffman, LE Band, EM Elliott, CA Shields, C Kendall, PM Mayer and **TA Newcomer**. 2010. COS 26-4: Tracking stream nitrogen sources using isotopes: implications for managing coastal eutrophication and urban sustainability. Ecological Society of America (ESA) Global Warming: The legacy of our past, the challenge for our future. Pittsburgh, Pennsylvania. [Oral]

Grese, MM, SS Kaushal, **TA Newcomer**, SEG Findlay and PM Groffman. 2010. PS 26-16: Effects of urbanization on variability in temperature and diurnal oxygen patterns in streams. Ecological Society of America (ESA) Global Warming: The legacy of our past, the challenge for our future. Pittsburgh, Pennsylvania. [Poster]

**Newcomer, TA** and P Bond. 2010. Evolution; Student misconceptions, political controversy, & teaching strategies. The Baltimore Partnership for Environmental Science Literacy: Research Experience for Teachers Course. Baltimore, Maryland. [Oral]

**Newcomer, TA**, SS Kaushal. 2010. Denitrification in BES streams; investigation of effect of land use, feature type and available carbon. Baltimore Ecosystem Study Quarterly Meeting. Baltimore, Maryland. [Oral]

Manrique, H, SS Kaushal, KM Delaney, **TA Newcomer** and AM Sides. 2010. Effects of temperature on biochemical oxygen demand in urbanizing streams. American Society for Limnology and Oceanography (ASLO) Aquatic Sciences: Global Changes from the Center to the Edge. Sante Fe, New Mexico. [Poster]

**Newcomer, TA**. 2010. How campus landscapes impact the Chesapeake Bay's ecosystem. Association of Physical Plant Administrators (APPA) Annual Meeting. St. Mary's City, Maryland. [Oral]

## **2009**

**Newcomer, TA**, SS Kaushal, PM Mayer, AR Shields and PM Groffman. 2009. Effects of Watershed Organic Carbon Sources on Denitrification in Forested, Restored and Urbanized Streams. Coastal Estuarine Research Federation (CERF) Estuaries and Coasts in a Changing World. Portland, Oregon. [Oral]

Harrison, MD and **TA Newcomer**. 2009. Restoration Ecology and Ecological Restoration: What does it mean across LTER's? National Science Foundation Long Term Ecological Research (LTER) All Scientists Meeting: Integrating Science and Society in a World of Constant Change. Estes Park, Colorado. [Oral]

**Newcomer, TA**, SS Kaushal, PM Mayer, AR Shields and PM Groffman. 2009. Effects of watershed organic carbon sources on denitrification in forested, restored, and urbanized streams. NSF Research Coordination Network on Denitrification; Denitrification in Managed Ecosystems. Narragansett, Rhode Island. [Poster]

**Newcomer, TA**, SS Kaushal, PM Mayer, AR Shields and PM Groffman. 2009. Restored streams may process nitrogen more similarly to forested reference streams than to unrestored streams. Chesapeake Bay Research Consortium Ecosystem Based Management Conference. Baltimore, Maryland. [Poster]

## **2008**

Roman, L, DN Schwarzmann, A Burton, MV Wright, **TA Newcomer**, J Ambrosio, D Lipinski, VD McConnell and RJ Neff. 2008. Social feasibility of energy-efficiency retrofits and educational campaigns for sustainable energy use in pre-existing college residence halls. EPA People Prosperity and the Planet (P3) Student Design Competition for Sustainability. Washington, DC. [Poster]

## **2007**

**Newcomer, TA** and SS Kaushal. 2007. Relative importance of carbon sources for denitrification in hyporheic zones as a potential indicator of stream restoration success in piedmont streams of the Baltimore LTER. Baltimore Ecosystem Study (BES) Annual Meeting. Baltimore, Maryland. [Poster]

Rivkin, MS and **TA Newcomer**. 2007. IPM in P-16: A case study at UMBC on environmental literacy: educating for environmental well-being. American Association for Advancement of Science (AAAS). San Francisco, California. [Oral]

## **2005**

**Newcomer, TA**, MK Preston and AJ Miller, 2005. Assessment of flood hazard risk in urban watersheds with computer models. Council of University Systems Faculty (CUSF) University System of Maryland (USM) Undergraduate Research Days in Annapolis. Annapolis, Maryland. [Poster]

## **Society Memberships**

---

Association for the Sciences of Limnology and Oceanography (ASLO)  
American Water Resources Association (AWRA)

Society for Ecological Restoration (SER)  
American Geophysical Union (AGU)  
Coastal Estuarine Research Federation (CERF)

## **Coursework**

---

### **University of Maryland, College Park, Maryland**

Principles and Practices of Ecosystem Restoration (MEES698E)  
Advanced Stream Restoration (MEES708R)  
Hydrologic Effects of Land Use (MEES698O)  
Foundations of Stream Restoration (MEES698Y)  
Land Margin Interactions (MEES610)  
Introduction to Ecotoxicology (MEES643)  
Applications of State-of-the-Art Analytical Techniques in Environ. Sci. (MEES 608T)  
Biostatistics I (BIOM601)  
Quantitative Methods in Environmental Science (MEES607)  
Uncertainty in Environmental Science (MEES608V)  
Scientific Writing & Communication (MEES608D)

### **University of Maryland, Baltimore County (UMBC) Baltimore, Maryland**

Natural Environment of the Chesapeake Bay (GES 318)  
Aquatic Ecology (GES 406)  
Organic Chemistry (CHEM 351)  
Calculus II (MATH 152)  
Hydrology (GEOG 416)  
Geomorphology (GEOG 310)  
Geography of Soils (GEOG 314)