INTERACTIONS OF HYDROLOGY AND WATER CHEMISTRY IN
TWO COASTAL PLAIN STREAMS IN A
FORESTED WATERSHED

by

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A THESIS

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ABSTRACT

The goal of this study was to compare and contrast the annual seasonal changes in hydrology and water chemistry of Mayfield Creek and Talladega Branch, two low-order streams located within the same forested watershed. Mayfield Creek and Talladega Branch, third-order and first-order streams, respectively, are Coastal Plain streams located in west central Alabama. Samples for water chemistry analysis, as well as instantaneous discharge measurements, were collected weekly from both streams from January – December 2009. Dataloggers also collected continuous stage measurements at both streams. These data were used to estimate annual flux of nutrients from the streams.

Mayfield Creek and Talladega Branch showed significant differences in discharge due to stream size; average annual values were 0.308 and 0.120 m$^3$/s, respectively. Mean annual concentrations of NH$_4$-N and NO$_3$-N were significantly higher in Mayfield Creek, while DON and DOC values were higher in Talladega Branch. NH$_4$-N levels for Mayfield Creek and Talladega Branch (43.11 and 36.07 µg/L, respectively) were consistently higher than nitrate levels (15.45 and 5.06 µg/L) in both streams.

Similar seasonal changes in hydrology and nutrient concentrations were observed in both streams. Annual flow patterns were typical of streams in the eastern U.S., having low flow conditions during the dry, summer months and high, winter baseflow during the wet, winter months. All nutrient concentrations peaked in the spring or summer months, likely due to the concentrating effect of low, summer baseflow. NO$_3$-N, SRP, DOC, and DON concentrations
showed a positive linear relationship with discharge during high flow conditions in both streams, while NH₄-N did not increase with increasing discharge, implying that the stream itself, rather than the terrestrial environment, is likely the source of NH₄-N to these streams.

Annual estimates of DOC flux for Mayfield Creek and Talladega Branch, 30,602.4 and 19,456.8 kg C/year, respectively, were higher than fluxes reported for other coastal plain streams of similar size. DIN flux was similar to values reported for other systems. However, the dominant form of DIN exported from these streams is NH₄-N rather than NO₃-N, which typically predominates.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ANC</td>
<td>acid neutralizing capacity</td>
</tr>
<tr>
<td>ANOVA</td>
<td>analysis of variance</td>
</tr>
<tr>
<td>CA</td>
<td>California</td>
</tr>
<tr>
<td>CO</td>
<td>Colorado</td>
</tr>
<tr>
<td>CPOM</td>
<td>coarse particulate organic matter</td>
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<tr>
<td>DIN</td>
<td>dissolved inorganic nitrogen</td>
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<td>DOC</td>
<td>dissolved organic carbon</td>
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<tr>
<td>DON</td>
<td>dissolved organic nitrogen</td>
</tr>
<tr>
<td>DNRA</td>
<td>dissimilatory reduction of nitrate to ammonium</td>
</tr>
<tr>
<td>e.g.</td>
<td><em>exempli gratia</em>; for example</td>
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<tr>
<td>ENSO</td>
<td>El Niño/Southern Oscillation</td>
</tr>
<tr>
<td>et al.</td>
<td><em>et alia</em>; and others</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>ferrous iron</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>ferric iron</td>
</tr>
<tr>
<td>F stat</td>
<td>critical value used in regression analysis to determine if variances between the means of two populations are equal</td>
</tr>
<tr>
<td>ha</td>
<td>hectares</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
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</tbody>
</table>
H$_2$SO$_4$  sulfuric acid

i.e.  *id est*; that is to say

ITCZ  intertropical convergence zone

kg C/ha/year  kilograms of carbon per hectare per year

kg C/year  kilograms of carbon per year

kg N/ha/year  kilograms of nitrogen per hectare per year

kg N/year  kilograms of nitrogen per year

L  liter

MCT  multiple comparisons test

meq/L  milli-equivalents per liter

mg/L  milligrams per liter

mL  milliliter

mm  millimeters

m/s  meters per second

m$^3$/s  cubic meters per second

N  normal

N  nitrogen

NEON  National Ecological Observatory Network

NH$_4$-N  ammonium nitrogen

NO$_2$-N  nitrite nitrogen

NO$_3$-N  nitrate nitrogen

OH  Ohio

P  phorphorus
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>PAR</td>
<td>photosynthetically active radiation</td>
</tr>
<tr>
<td>pH</td>
<td>numerical measure of the acidity or alkalinity of a solution</td>
</tr>
<tr>
<td>p-value</td>
<td>the probability of getting a test statistic as extreme or more extreme than the observed value, given that a null hypothesis is true</td>
</tr>
<tr>
<td>Q</td>
<td>discharge</td>
</tr>
<tr>
<td>r^2</td>
<td>coefficient of determination; in regression analysis, measures the amount of variation in a y-variable that is explained by the independent x-variable</td>
</tr>
<tr>
<td>SE</td>
<td>standard error</td>
</tr>
<tr>
<td>Sp Cond</td>
<td>specific conductance</td>
</tr>
<tr>
<td>SRP</td>
<td>soluble reactive phosphorus</td>
</tr>
<tr>
<td>T</td>
<td>value of test statistic for a t-test</td>
</tr>
<tr>
<td>Temp</td>
<td>temperature</td>
</tr>
<tr>
<td>Total N</td>
<td>total nitrogen</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>United States of America</td>
</tr>
<tr>
<td>U.S.</td>
<td>United States</td>
</tr>
<tr>
<td>USFS</td>
<td>United States Forest Service</td>
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<tr>
<td>USGS</td>
<td>United States Geological Survey</td>
</tr>
<tr>
<td>UT</td>
<td>Utah</td>
</tr>
<tr>
<td>vs.</td>
<td>versus</td>
</tr>
<tr>
<td>WA</td>
<td>Washington</td>
</tr>
<tr>
<td>WI</td>
<td>Wisconsin</td>
</tr>
<tr>
<td>α</td>
<td>alpha-level; level of significance</td>
</tr>
<tr>
<td>μg/L</td>
<td>micrograms per liter</td>
</tr>
</tbody>
</table>
µm  micrometers
µS/cm  micro-Siemens per centimeter
°C  degrees Celsius
>  greater than
≤  less than or equal to
+/−  plus or minus, as in a range
=  equal to
+  plus
−  minus or negative value
%  percent
~  estimated to be
#  number
≈  approximately equal to
ACKNOWLEDGMENTS

The completion of this thesis would not have been possible without the assistance and advice of others. I would first like to thank each of my graduate committee members: Drs. Amy Ward, Milt Ward, Ryan Sponseller, and Lisa Davis. Their guidance and input were paramount in the execution and completion of this project. I would like to extend a special thanks to my advisor, Dr. Amy Ward. Her patience, advice, and financial support have made my graduate experience here at the University of Alabama invaluable and unforgettable.

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I extend much gratitude to Debbie Cook and the staff of the Department of Biological Sciences for processing paperwork and handling other administrative affairs.

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# CONTENTS

ABSTRACT ................................................................................................ ii

LIST OF ABBREVIATIONS AND SYMBOLS .......................................... .iv

ACKNOWLEDGMENTS ........................................................................ viii

LIST OF TABLES .................................................................................. x

LIST OF FIGURES ................................................................................ xii

INTRODUCTION .....................................................................................1

SITE DESCRIPTION .................................................................................7

MATERIALS AND METHODS .............................................................10

RESULTS ...............................................................................................16

DISCUSSION ..........................................................................................40

LITERATURE CITED ..............................................................................57

APPENDIX .............................................................................................63
LIST OF TABLES

TABLE 1  
2009 Monthly Precipitation Totals and Average Monthly Discharge Values for Mayfield Creek and Talladega Branch, Alabama, U.S.A. .................................................................23

TABLE 2  
Mayfield Creek and Talladega Branch Means, Standard Error, and Independent t-test T and p values, 1/5/09 – 12/16/09. ...............26

TABLE 3  
Mean Seasonal Water Chemistry Parameters (+ 1 SE) at Mayfield Creek, Alabama, U.S.A. .................................................................28

TABLE 4  
Mean Seasonal Water Chemistry Parameters (+1 SE) at Talladega Branch, Alabama, U.S.A. .................................................................31

TABLE 5  
Results of Linear Regression Analysis Between Instantaneous Discharge and Nutrient Concentrations in Mayfield Creek and Talladega Branch. .................................................................34

TABLE 6  
Annual Flux Estimates for Mayfield Creek and Talladega Branch, January–December 2009. .................................................................39

TABLE 7  
The Relationships Between Nutrient Concentrations and Stream Discharge in Streams of Various Sizes and Locations (modified from Meyer et al. 1988). .................................................................56
LIST OF FIGURES

FIGURE 1  The study sites, Mayfield Creek and Talladega Branch, are located in the Oakmulgee District of the Talladega National Forest, Alabama, U.S.A. ................................................................. 9
FIGURE 2  Datalogger at Mayfield Creek, Alabama, U.S.A. ..................11
FIGURE 5  Ammonium and nitrate concentrations for Mayfield Creek and Talladega Branch, January – December 2009. .........................27
FIGURE 6  Seasonal changes in ammonium, nitrate, and dissolved organic carbon concentrations compared to seasonal changes in discharge at Mayfield Creek, January–December 2009. ............................................................. 30
FIGURE 7  Seasonal changes in ammonium, nitrate, and dissolved organic carbon concentrations compared to seasonal changes in discharge at Talladega, January–December 2009. ............................................................. 33
FIGURE 8  Changes in NH₄-N and NO₃-N concentrations in response to high flow related to rain events in Mayfield Creek (a) and Talladega Branch (b). ............................................................. 36
FIGURE 9  Changes in DON and DOC concentrations in response to high flow related to rain events in Mayfield Creek (a) and Talladega Branch (b). ............................................................. 38
INTRODUCTION

Because headwater streams form the basal link in river networks, studies of these low-order systems have provided important advances in biogeochemistry (Meyer et al. 1988; Tank et al. 2000; Martin et al. 2001; Wollheim et al. 2001), the ecosystem-level impacts of disturbances (Resh et al. 1988), and the importance of lateral and longitudinal linkages within a stream (Vannote et al. 1980; Junk et al. 1989), among other areas. Hynes (1975) proposed the idea that aquatic floral and faunal communities and most in-stream processes are strongly influenced by the surrounding watershed of the stream. These headwater streams form the primary link between the terrestrial and aquatic ecosystems and, therefore, tend to collect materials from the landscape, process them, and transport them downstream (Likens et al. 1977; Vannote et al. 1980; Newbold et al. 1983). Therefore, riparian zones are critical to these small stream ecosystems because they serve as the main source of organic matter to the stream, while regulating the input of nutrients from the landscape (Golladay and Webster 1988; Gregory et al. 1991; Fortino et al. 2004). Riparian zones also play an important role in controlling other abiotic factors, such as water temperature and sedimentation, in the stream channel (Naiman and Décamps 1997).

From a biogeochemical perspective, this strong lateral relationship that headwater streams have with their terrestrial landscape implies that a stream is comprised of not only the surface water in the stream channel, but also the environment through which it flows (Fisher et al. 2004). The water chemistry of surface water is influenced by numerous factors, including
land-use history of the catchment, geology, hydrology, and geomorphology of the watershed, and the composition of terrestrial vegetation in the catchment (Likens et al. 1977; Schlesinger 1997; Allan and Castillo 2008). Junk et al. (1989) described the importance of such lateral linkages within lotic systems in their flood pulse concept. Floodplains serve as an important source of nutrients to rivers and streams, especially those that frequently overflow their banks. For example, studies of the Amazon River have shown that the amount of organic material transported to the river by its tributaries is not sufficient to support the rates of respiration observed there; therefore, the Amazonian floodplain must be the river’s main source of organic carbon (Meyer et al. 1988).

Just as terrestrial systems can subsidize the channel, upstream processes influence downstream reaches. The theory of nutrient spiraling describes the cycling of a nutrient between organic and inorganic forms as it is assimilated and remineralized by biota while simultaneously moving downstream with the flow of water (Newbold et al. 1983). The tightness of a spiral determines the rate of transport of nutrients to downstream reaches; a tight spiral signifies a retentive stream with few nutrients traveling down-gradient, while a loose spiral implies decreased retention and increased export downstream. This longitudinal link between upstream and downstream reaches can have significant impacts on the nutrient dynamics and biological communities in a stream system. For example, a study of Sycamore Creek in Arizona showed that nitrogen uptake led to depletion of nitrate concentrations downstream over successional time, resulting in nitrogen-fixing blue-green algae prevailing over other filamentous algal groups in the downstream reaches (Fisher et al. 1982). Because nutrients are essential to the growth and development of organisms, changes in quantity, quality, and timing of nutrient availability can have important effects on stream communities.
Changes in nutrient availability have been observed on various temporal scales, from short-term pulse events to seasonal cycles to long-term changes in nutrient concentrations. Seasonal changes in climate and biological activity cause temporal changes in streamwater chemistry, and these annual cycles have been the topic of numerous ecological studies. Mulholland (2004) found that Walker Branch in eastern Tennessee undergoes predictable seasonal fluctuations in nitrogen, particularly nitrate, and phosphorus concentrations, and that these changes are largely driven by changes in biological activity through the growing and dormant seasons. Similarly, Chapman et al. (2001) found that the dominant form of dissolved nitrogen in upland streams of Scotland changed seasonally; nitrate concentrations were higher in the cool, winter months, while DON concentrations dominated summer months. This temporal shift in available nitrogen can have important impacts on in-stream activities. For example, Starry et al. (2005) reported that rates of nitrification in Hugh White Creek, North Carolina, were closely linked to changes in the supply and quality of organic matter in the stream throughout an annual period; therefore, nitrification rates were high during spring and summer when C:N ratios were low.

Long-term temporal changes have also been observed, particularly in forested watersheds. Vitousek and Reiners (1975) showed that the nutrient retention of the soil in forested catchments decreased over time with forest succession, indicating that streams draining old-growth forests may have higher concentrations of nitrogen and phosphorus than do streams flowing through young forests. However, subsequent studies have provided evidence that nitrogen losses in forests are related to nitrogen mineralization rates and nitrogen flux of leaf litter, which are factors independent of forest age or succession (Fisk et al. 2002). Contradictions
such as this are why long-term studies are necessary to further our understanding of aquatic ecosystems.

In addition to biological drivers, hydrology plays a significant role in the seasonal dynamics of lotic systems. Streams and rivers in the temperate eastern United States have predictable hydrographs that reflect a wet winter season and a dry summer season (Poff et al. 1997). This seasonal change in stream flow has important impacts on the nutrient concentrations in streams. Increases in stream discharge, such as during winter baseflow, can have a diluting effect on nutrient concentrations. In contrast, decreased summer baseflow can have a concentrating effect on streamwater. This combination of hydrology and biological activity results in the high summer nutrient concentrations and low winter concentrations commonly observed throughout the southeastern United States. Short-term changes in discharge, such as storm events, also cause apparent changes in stream nutrient availability. Materials flushed from the upper soil horizons of the terrestrial landscape are transported to the stream channel via run-off, causing transient pulses in concentrations. The importance of these pulse inputs to stream processes is largely dependent on the retentiveness of the stream and the biological demand for nutrients.

The important roles of small streams in nutrient retention, particularly with regard to nitrogen metabolism, have been well documented (e.g., Mulholland et al. 2008; Peterson et al. 2001). However, these studies have typically excluded coastal plain streams in south temperate regions (Peterson et al. 2001; Grimm et al. 2005; Hamilton et al. 2001; Tank et al. 2000). The increased flux of nitrogen transported down the Mississippi River to the Gulf of Mexico, creating the seasonally hypoxic “dead zone” in the shallow waters off the coast of Louisiana (Alexander et al. 2000), has increased attention on the sites and mechanisms of nutrient retention in riverine
ecosystems, including those in small streams. The current consensus is that the large surface area-to-volume ratio of the stream bed in headwater streams allows increased immobilization and assimilation of nitrogen, which reduces nitrogen export downstream (Peterson et al. 2001). Because ~85% of the length of river networks are composed of headwater streams (Peterson et al. 2001), surface water spends more time in these upper reaches resulting in less nitrogen transported to larger rivers (Alexander et al. 2000). On the other hand, a recent analysis of small stream systems by Brookshire et al. (2009) showed that nitrogen and phosphorus in headwaters may actually tend toward a steady-state (inputs equal outputs), indicating that small streams may not play such a significant role in the export of nutrients from the watershed. Because anthropogenically-induced nutrient loading continues to threaten freshwater systems, understanding the role of headwater streams in biogeochemical cycling is of increasing importance.

The Mobile River Basin is the largest watershed east of the Mississippi River that drains into the Gulf of Mexico, and it has the 4th largest river discharge into a coastal area in North America (Ward et al. 2005). It also has unusually high nitrogen retention capabilities, exporting only 5-7% of inputs compared to 20-25% in other watersheds (Carey et al. 2003). Therefore, further investigation of this river system may provide insight into the roles of lotic ecosystems in nutrient retention and transport and how they may contrast with those of the Mississippi River Basin. More detailed studies of headwater streams in this basin are needed, especially those in the Coastal Plain, which constitutes ~56% of the basin, and with a focus on nutrient concentrations and flux in relation to seasonal and hydrological changes.

This study examines the annual hydrological and nutrient dynamics of two headwater streams in the Coastal Plain physiographic region of Alabama. Mayfield Creek, a third-order
stream, and its tributary, Talladega Branch, eventually flow to the Black Warrior River, one of seven major rivers of the Mobile River Basin. Understanding variations in nutrient availability and export in these low-order streams may enable us to better understand the unusual behavior of the Mobile River Basin as a whole.

Specific objectives of this study were: 1) to compare and contrast the hydrological patterns of Mayfield Creek and Talladega Branch, 2) to compare and contrast seasonal changes in the water chemistry of the two streams, and 3) to determine what effect changes in stream discharge have on the nutrient dynamics of the streams. A further goal was to use the above information to calculate the flux of nitrate, ammonium, dissolved organic nitrogen, and dissolved organic carbon from these streams to down-gradient streams and rivers.
SITE DESCRIPTION

This study was conducted in Mayfield Creek, a third-order stream, and Talladega Branch, a first order tributary to Mayfield Creek, located in the Oakmulgee District of the Talladega National Forest in Bibb County, Alabama (Figure 1). Three sites for water chemistry sampling were chosen—two at Mayfield Creek and one at Talladega Branch. Mayfield Creek flows south to north, and Talladega Branch flows west to east. These small, low-order streams are tributaries to the Black Warrior River, located in west-central Alabama, and are part of the network of waterways that form the headwaters of the Mobile River Basin. These streams lie in the East Gulf Coastal Plain physiographic province of Alabama, and the substrata of the streams primarily consist of unconsolidated sediment, such as sand, clay, and silt, which are typical of coastal plain streams (Ward et al. 2005). The total watershed area is about 3200 ha, with the Mayfield Creek and Talladega Branch drainage areas measuring about 2450 ha and 750 ha, respectively.

The Talladega National Forest is managed by the United States Forest Service (USFS). The vegetation of the Mayfield Creek watershed is a mixed forest comprised primarily of pine (e.g., longleaf, shortleaf, yellow, and loblolly) with some hardwood (e.g., oak, hickory, sweetgum, dogwood). Areas of the forest are managed for timber harvest. The USFS also implements regular, low-intensity, prescribed burns in the forest to facilitate growth and reproduction of the longleaf pine (Pinus palustris) stands, which provide habitat for the endangered red-cockaded woodpecker (Picoides borealis). Beaver activity is also common
throughout the forest, resulting in the formation of wetland areas caused by beaver dam
construction.

The Talladega National Forest is a temperate forest, and the climate of the area follows
four distinct seasons. Summers are hot, humid, and dry, while winters tend to be mild and wet.
The average air temperature in the Talladega National Forest from January–December 2009 was
about 15.6°C. The total rainfall for the same period was about 1929 mm. This study was
conducted during an el Niño year, so rainfall amounts may exceed the normal averages for the
area (Ropelewski and Halpert 1986; Hepner and Davis 2004).
FIGURE 1. The study sites, Mayfield Creek and Talladega Branch, are located in the Oakmulgee District of the Talladega National Forest, Alabama, U.S.A. Circles indicate sampling sites for water chemistry analysis. Arrows indicate the direction of stream flow.
MATERIALS AND METHODS

Hydrology

Instantaneous discharge was measured weekly at Mayfield Creek and Talladega Branch via the velocity-area method using a Flow-Mate Model 2000 flow meter (Hach Company, Loveland, CO). These measurements typically coincided with days when samples for water chemistry analysis were collected. When water samples were collected on days when instantaneous discharge was not measured, stage was recorded for both streams in order to estimate flow. These instantaneous discharge measurements were used to create a stage-discharge rating curve for each stream.

Stream stage was continuously measured and stored at 15-minute intervals at Mayfield Creek and Talladega Branch using CR-10x dataloggers (Campbell Scientific, Inc., Logan, UT) equipped with pressure transducers (model PS9105E, Instrumentation Northwest Inc., Kirkland, WA) (Figure 2). Data were collected from each station once a week and transferred to a laboratory computer for further analysis. These stage data recorded by the pressure transducers, along with the rating curves created for the streams, were used to calculate discharge at each 15-minute interval. From these data, average daily discharge measurements were calculated by averaging all 15-minute intervals in a 24-hour period, and these daily values were used to create an annual hydrograph for both Mayfield Creek and Talladega Branch. The datalogger at Mayfield Creek measured precipitation with an electronic tipping bucket rain gauge (Weather
FIGURE 2. Datalogger at Mayfield Creek, Alabama, U.S.A. Datalogger recorded stage, water temperature, air temperature, PAR, and precipitation.
Measure Corp., Sacramento, CA) from June to December 2009. Monthly precipitation totals presented for January 2009 – June 2009 are values recorded by a rain gauge at Payne Creek, a nearby stream in the Talladega Wetland Ecosystem.

The datalogger station at Mayfield Creek was installed on 13 April 2009. Installation at Talladega Branch was completed 28 August 2009. Average daily discharge values for Mayfield Creek prior to installation of the datalogger station were estimated by regressing average daily discharge values for Mayfield Creek with values recorded by a USGS gauging station at Elliotts Creek (#02465493), a nearby stream of comparable size. Average daily discharge measurements for Talladega Branch prior to installation of the datalogger were estimated by regressing average daily discharge values for Talladega Branch with those for Mayfield Creek.

To gain a more accurate prediction of high discharges, we created high flow rating curves for Mayfield Creek and for Talladega Branch. Only instantaneous discharge measurements taken when stage was greater than 2 feet were used to create these high flow stage-discharge rating curves. These regression equations were used to calculate discharge for all stage > 2 feet.

During two storm events, stages at Talladega Branch, the first-order stream, were well beyond upper values of our high flow rating curve. In order to estimate flows at stages above the rating curve, we determined channel cross-sectional area at 1 meter elevation intervals at the location of the datalogger.

From these data, a stage-channel cross-sectional area relationship were calculated. To obtain a discharge for each measured stage during a storm, we used the estimated cross-sectional area multiplied by the maximum velocity that we measured at the site (0.5 m/s). From these post-flood observations, there were strong indications that above a stage of 9 feet velocities were low (or near zero) because the storm flow was ponded at our gauge site, backed up by the
confluence with Mayfield Creek. Using more than one rating curve with various regressions to estimate discharge values increases the error of our flow calculations. We do not currently know what that error is, but we believe the data presented in these annual hydrographs are reasonable for the streams examined in this study.

**Water Chemistry**

Surface water samples were collected weekly from 3 study sites—two at Mayfield Creek and one at Talladega Branch—from January 2009 until February 2010. Water samples were collected in 1 L acid-washed, amber, polyethylene bottles, immediately placed on ice, and returned to the laboratory. In the laboratory, samples were vacuum filtered using pre-combusted 0.7 µm Whatman GF/F filters. Twenty mL of filtered water from each sample were transferred to glass vials, preserved with 2 mL of 2N HCl, centrifuged, and refrigerated for dissolved organic carbon analysis using a Shimadzu T5000 Total Organic Carbon Analyzer (Shimadzu Corporation, Japan). Three 250 mL acid-washed amber polyethylene bottles were filled ¾ full with filtered water from each sample and frozen for analysis of nitrate, ammonium, nitrite, total nitrogen, and soluble reactive phosphorus (SRP). Inorganic nutrient levels were measured from thawed samples via flow injection analysis using a QuickChem 8500 Automated Ion Analyzer (Lachat Instruments, Milwaukee, WI). Dissolved organic nitrogen (DON) values were calculated by subtracting NH₄-N + NO₃-N+NO₂-N from total dissolved nitrogen concentrations. Alkalinity was measured in the laboratory by performing an alkalinity titration with 0.0202N H₂SO₄. Specific conductance (YSI model 33, Yellow Springs, OH) and pH (Orion model 710A pH/ISE) were also measured for each sample in the laboratory. Water temperature was measured in the field at each sampling site using a glass mercury thermometer.
Data analysis

A series of t-tests were conducted in order to compare the mean annual nutrient concentrations and physical water chemistry measurements of the two streams. Because samples were collected and analyzed from two study sites at Mayfield Creek and t-test analyses showed no significant differences between the means of the two sites, measurements from these sites were averaged. Tests with a p-value ≤ 0.05 were considered statistically significant.

Mean seasonal water chemistry parameters were compared using one-way analysis of variance (ANOVA) using season as the main effect. Significant ANOVAs (p ≤ 0.05; α = 0.05) were further analyzed using Tukey’s multiple comparison test (MCT). Water samples were categorized by season in the following manner: January, February, and December samples were considered winter, March-May samples were considered spring, June-August samples were considered summer, and September-November samples were considered autumn.

Linear regression analysis was used to determine the relationship between precipitation and discharge for Mayfield Creek and Talladega Branch. Monthly precipitation totals and average monthly discharge values were compared. Regressions with a p-value ≤ 0.05 (α = 0.05) were considered statistically significant.

Linear regression analysis was also used to compare the relationship between discharge and nutrient concentrations in the two streams. Instantaneous discharge values were categorized as “high flow” or “low flow” for both streams. On days when instantaneous discharge was not measured at the time of water collection, the time of water sampling was used to determine the discharge based on the stage recorded by the datalogger. For Mayfield Creek, discharge values of 0.25 m³/s or greater were considered high flow. For Talladega Branch, discharge values of 0.05 m³/s or greater were considered high flow. These values were chosen because winter
baseflow in Mayfield Creek and Talladega Branch was ≈ 0.25 m³/s and 0.05 m³/s, respectively. Regressions with a p-value ≤ 0.05 (α = 0.05) were considered statistically significant. Complete results of these linear regression analyses can be found in the Appendix.

These regressions were also used to estimate the annual flux of NH₄-N, NO₃-N, DON, and DOC in both streams. By using the linear regressions between discharge and nutrient concentration, we were able to estimate nutrient concentrations of the streamwater on days that water samples were not collected using average daily discharge. Discharge (L/s) and nutrient concentration (µg/L or mg/L) were multiplied to get daily flux values. Daily flux values were summed to get annual flux (kg/year). Estimates are also presented as yield (kg/ha/year) in order to compare our results with previous studies found in the literature.
RESULTS

Hydrology

Stream discharge was significantly correlated with the amount of rainfall in the watershed for both streams (p-value = 0.02, $r^2 = 0.43$ for Mayfield Creek; p-value = 0.01, $r^2 = 0.47$ for Talladega Branch) (Table 1). Total rainfall from January – December 2009 was 1,929 mm. September was the wettest month in the watershed. During the month of September, 371.8 mm of rain were recorded. June was the driest month with only 28.4 mm of rain. Both Mayfield Creek and Talladega Branch had the highest mean monthly discharges in March and December. In Mayfield Creek, average monthly discharge for March and December were 0.610 m$^3$/s and 0.621 m$^3$/s, respectively. Average monthly discharge at Talladega Branch for March and December were 0.417 m$^3$/s and 0.218 m$^3$/s, respectively. The lowest mean monthly discharge for both streams occurred in the month of June, the month with the least precipitation. The monthly average at Mayfield Creek for June was 0.067 m$^3$/s, and the monthly average at Talladega Branch for the same month was 0.009 m$^3$/s. Mean annual discharge for Mayfield Creek from January-December 2009 was 0.308 m$^3$/s. The mean annual discharge for Talladega Branch for 2009 was 0.120 m$^3$/s.

Discharge at Mayfield Creek and Talladega Branch during 2009 followed a seasonal pattern typical of temperate streams in the southeastern United States (Figure 3 and Figure 4). After a period of spring rainfall in March (Julian Days 60-90), discharge began to decrease in early April (Julian Days 91-120), reaching annual, low, summer baseflow conditions by June.
(Julian Days 152-181). These low flow conditions persisted until mid-September (Julian Days 244-273), when discharge began to increase and remained high throughout the months of November (Julian Days 305-334) and December (Julian Days 335-365).

_Storm Events_

Storm events at Mayfield Creek and Talladega Branch caused brief peaks in the hydrographs that lasted about 3-5 days (Figure 3 and Figure 4). There was a brief lag-time between the initial rainfall and the increase in stream discharge. This lag time consisted of minutes to hours depending on the magnitude of the storm. Substantial amounts of rainfall caused quick and very pronounced changes in stream flows. These increased stream flows were typically sustained for a variable period of time, depending on the time and magnitude of the storm event.

Three major storm events occurred in the Mayfield Creek watershed during 2009. These storms occurred during March, September, and November. Only the September and November events were recorded by the datalogger stations. On 20-21 September 2009 (Julian Day 263-264), the watershed received 248 mm of rain in less than 24 hours. Mayfield Creek reached peak flow conditions 5 hours after the rainfall began. The maximum stage and discharge recorded during this storm event at Mayfield Creek were 9.5 feet and 5.4 m$^3$/s, respectively. The maximum stage recorded at Talladega Branch was 12 feet. Because this stream is a tributary of Mayfield Creek, we believe that the increased flow of both streams resulted in the ponding of water at Talladega Branch because water could not flow into Mayfield Creek, resulting in zero flow at stage heights above 9 feet. Therefore, a maximum discharge of 4.3 m$^3$/s was recorded 3
hours after the rainfall began. During the peak flow conditions of this storm, we believe that the simultaneous flooding of these two streams caused them to be temporarily joined.

The November storm was less intense in magnitude than the September event. On 9-10 November 2009, 150 mm of rain fell in the watershed in less than 24 hours. Mayfield Creek reached peak flow conditions at 7.5 feet and 3.9 m$^3$/s about 23 hours after the first rainfall was recorded. Maximum measured stage and estimated discharge, 8.9 feet and 4.5 m$^3$/s, respectively, were recorded at Talladega Branch about 24 hours after the storm commenced.

**Water Chemistry**

Throughout the period of this study, mean nutrient concentrations in both Mayfield Creek and Talladega Branch were low compared to urban and anthropogenically impacted streams (Table 2). Mean ammonium (NH$_4$-N), nitrate (NO$_3$-N), and total N concentrations in Mayfield Creek were 49 µg/L, 14 µg/L, and 126 µg/L, respectively, compared to 29 µg/L, 5 µg/L, and 109 µg/L in Talladega Branch. All mean inorganic nutrient concentrations were higher in Mayfield Creek, except soluble reactive phosphorus (SRP), which was 1 µg/L for both streams. Mean dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) concentrations were higher in Talladega Branch. In Talladega Branch, mean DOC was 3.52 mg/L, compared to 2.86 mg/L at Mayfield Creek. Mean DON concentration at Talladega Branch was 76 µg/L, compared to 64 µg/L at Mayfield Creek. Mean NH$_4$-N, NO$_3$-N, and DOC concentrations were significantly different between the two streams ($p \leq 0.05$; Table 2).

NH$_4$-N was consistently higher than NO$_3$-N in both streams throughout the study period, with the exception of four sampling times at Mayfield Creek (Julian Days 85, 211, 258, and 314)
and one sampling time at Talladega Branch (Julian Day 314). All of these sampling days corresponded to rain events in the watershed (Figure 5).

Physical parameters of the streamwater, such as pH, alkalinity, and specific conductance were typical of other Coastal Plain streams in the region (Table 2). These measurements remained fairly constant throughout the annual period. Mean pH at Mayfield Creek and Talladega Branch was 5.9 and 5.7, respectively. Mean specific conductance at Mayfield Creek and Talladega Branch was 12.7 µS/cm and 15 µS/cm, respectively. The mean alkalinity for the two streams was the same at 0.09 meq/L. Mean specific conductance and pH values were statistically different between the streams. Water temperature varied seasonally with air temperature, with warmer temperatures in the summer and colder temperatures in the winter. Mean water temperature for Mayfield Creek and Talladega Branch was 16.7 °C and 16.2 °C, respectively.

Seasonal Changes in Water Chemistry

The water chemistry of Mayfield Creek and Talladega Branch also showed seasonal changes throughout the study period (Table 3 and Table 4). In Mayfield Creek, NH₄-N was significantly higher in the spring and summer than in autumn and winter (MCT, p < 0.05; Table 3; Figure 6). NO₃-N was higher in summer than any other season (25 µg/L), but concentrations in winter, spring, and autumn were not significantly different (MCT, p > 0.05; Table 3; Figure 6). DOC varied less over the annual period with concentrations higher in spring, summer, and autumn than in winter (MCT, p < 0.05; Table 3; Figure 6). Concentrations of DON were almost identical in the winter and spring (17 µg/L and 16 µg/L, respectively), but summer and autumn concentrations were significantly higher (126 µg/L and 93 µg/L, respectively) (MCT, p < 0.05;
Table 3). SRP was consistently low throughout the year (ANOVA; Table 3). Maximum water temperatures occurred in summer (23.1 °C), and minimum water temperatures were recorded in winter (8.2 °C); spring and autumn temperatures were not significantly different (MCT, p > 0.05; Table 3). Specific conductance and alkalinity varied little throughout the annual period (ANOVA; Table 3).

At Talladega Branch, NH₄-N was highest in spring and summer months (31 µg/L and 39 µg/L, respectively) and lowest in the winter (19 µg/L) (MCT, p < 0.05; Table 4; Figure 7). The highest concentrations of NO₃-N were observed in summer (9 µg/L), but winter, spring, and autumn concentrations were not significantly different (MCT, p < 0.05; Table 4; Figure 7). DOC was significantly lower in the winter than in the spring, summer, and autumn (MCT, p < 0.05; Table 4; Figure 7). DON concentrations were higher in the summer and autumn (124 µg/L and 134 µg/L, respectively) compared to winter and spring concentrations (33 µg/L and 34 µg/L, respectively) (MCT, p < 0.05; Table 4). Concentrations of SRP were consistently very low all year (ANOVA; Table 4). Water temperature was warmest in the summer (22.4 °C), and coolest in the winter (8.2 °C), while spring and autumn temperatures were not significantly different (15.9 °C and 16.4 °C, respectively). Alkalinity and specific conductance showed little variation throughout the year (ANOVA; Table 4).

**Nutrients and Stream Flow**

Various relationships between discharge and nutrient concentration in Mayfield Creek and Talladega Branch were detected (Table 5). During low flow conditions at Mayfield Creek, NH₄-N, NO₃-N, DON, and SRP concentrations decreased with increasing discharge, indicated by a negative linear relationship between nutrient concentration and discharge (Table 5). DOC
showed no change in concentration with changes in discharge. Only correlations between NH$_4$-N, NO$_3$-N, and SRP were statistically significant (p ≤ 0.05; Table 5). During high flow conditions, DOC, NO$_3$-N, SRP, and DON increased with increasing discharge (Table 5). Only NH$_4$-N concentrations showed a negative correlation with discharge during high flow conditions (Table 5). During high flow conditions, all relationships between nutrient concentration and discharge, except total N, were statistically significant (p ≤ 0.05; Table 5).

At Talladega Branch, DOC and DON increased with discharge during times of low flow (Table 5). NH$_4$-N, NO$_3$-N, and SRP concentrations decreased as discharge increased. Only correlations between NH$_4$-N and NO$_3$-N were statistically significant at low flow (p ≤ 0.05; Table 5). During high flow conditions, DOC, NO$_3$-N, SRP, and DON concentrations increased with increasing discharge (Table 5). NH$_4$-N was the only nutrient that decreased as discharge increased during high flow. DOC showed the only statistically significant relationship with discharge during high flow conditions at Talladega Branch (p ≤ 0.05; Table 5).

Water samples were collected during peak times in the hydrographs on ten occasions in 2009 (Figure 8 and Figure 9). Three of those samples were collected on the ascending limb of the hydrograph (Events C, G, and J; denoted by stars) (Figure 8 and Figure 9). NH$_4$-N and NO$_3$-N responded inversely to rain events in Mayfield Creek (Figure 8a). On all occasions except B, D, and G, NH$_4$-N concentrations decreased, and NO$_3$-N concentrations increased in response to increased discharge (Figure 8a). On event D, NH$_4$-N decreased, but NO$_3$-N showed no change. Changes in Talladega Branch were much more variable, and NH$_4$-N concentrations changed unpredictably, even during baseflow conditions (Figure 8b). During events E and I, NH$_4$-N concentrations decreased, and NO$_3$-N increased (Figure 8b). However, during events A, C, G, H, and J, NH$_4$-N increased, while NO$_3$-N either increased or did not change (Figure 8b). There
did not appear to be a difference between samples taken on ascending or descending limbs of the hydrograph in Mayfield Creek. However, all samples collected on the ascending limb of the hydrograph in Talladega Branch showed increased NH$_4$-N concentrations (Figure 8b).

In general, DOC and DON concentrations followed very similar patterns throughout the annual period, including rain events in the watershed (Figure 9). On almost all sampled rain events, DOC and DON increased with increases in discharge in Mayfield Creek and in Talladega Branch.

Flux

Annual fluxes of DIN, DOC, and DON were higher in Mayfield Creek than Talladega Branch in 2009 (Table 6). Mayfield Creek transported 376.4 kg N/year and 93 kg N/year of NH$_4$-N and NO$_3$-N, respectively. The flux of NH$_4$-N and NO$_3$-N in Talladega Branch was significantly less at 72.9 kg N/year and 19.5 kg N/year, respectively. Flux of DIN from Mayfield Creek and Talladega Branch was 469.4 kg N/year and 92.4 kg N/year, respectively. Transport of DOC and DON was higher than that of DIN in both streams. Mayfield Creek transported 30,602.4 kg C/year and 740.7 kg N/year of DOC and DON, respectively, compared to 19,455.8 kg C/year and 428 kg N/year in Talladega Branch. DON was the dominant form of nitrogen exported from both streams.
TABLE 1. 2009 Monthly Precipitation Totals and Average Monthly Discharge Values for Mayfield Creek and Talladega Branch, Alabama, U.S.A. Total precipitation values for the months of January – June were measurements from nearby Payne Creek, as the Mayfield rain gauge was not functional until June 2009.

<table>
<thead>
<tr>
<th>Month</th>
<th>Total Precipitation (mm)</th>
<th>Mayfield (m³/s)</th>
<th>Talladega (m³/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>120.3</td>
<td>0.273</td>
<td>0.091</td>
</tr>
<tr>
<td>February</td>
<td>117.4</td>
<td>0.185</td>
<td>0.030</td>
</tr>
<tr>
<td>March</td>
<td>259.1</td>
<td>0.610</td>
<td>0.417</td>
</tr>
<tr>
<td>April</td>
<td>102.6</td>
<td>0.309</td>
<td>0.110</td>
</tr>
<tr>
<td>May</td>
<td>132.6</td>
<td>0.192</td>
<td>0.039</td>
</tr>
<tr>
<td>June</td>
<td>28.5</td>
<td>0.067</td>
<td>0.009</td>
</tr>
<tr>
<td>July</td>
<td>121.4</td>
<td>0.073</td>
<td>0.011</td>
</tr>
<tr>
<td>August</td>
<td>150.9</td>
<td>0.083</td>
<td>0.011</td>
</tr>
<tr>
<td>September</td>
<td>371.9</td>
<td>0.376</td>
<td>0.207</td>
</tr>
<tr>
<td>October</td>
<td>164.8</td>
<td>0.385</td>
<td>0.087</td>
</tr>
<tr>
<td>November</td>
<td>173.7</td>
<td>0.520</td>
<td>0.209</td>
</tr>
<tr>
<td>December</td>
<td>185.7</td>
<td>0.621</td>
<td>0.218</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>160.7</strong></td>
<td><strong>0.308</strong></td>
<td><strong>0.120</strong></td>
</tr>
</tbody>
</table>
TABLE 2. Mayfield Creek and Talladega Branch Means, Standard Error, and Independent t-test T and p values, 1/5/09 – 12/16/09. *= Statistically significant (p = ≤ 0.05).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mayfield Mean (+/− SE)</th>
<th>Talladega Mean (+/− SE)</th>
<th>t-test T value</th>
<th>t-test p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄-N (µg/L)</td>
<td>49 ± 3.16 (19 - 129)</td>
<td>29 ± 1.78 (9 - 54)</td>
<td>5.6475</td>
<td>0.0000 *</td>
</tr>
<tr>
<td>NO₃-N (µg/L)</td>
<td>14 ± 1.79 (2 - 54)</td>
<td>5 ± 0.60 (0 - 27)</td>
<td>5.1321</td>
<td>0.0000 *</td>
</tr>
<tr>
<td>NO₂-N (µg/L)</td>
<td>0.36 ± 0.05 (0 - 2)</td>
<td>0.46 ± 0.07 (0 - 3)</td>
<td>-1.239</td>
<td>0.2181</td>
</tr>
<tr>
<td>Total N (µg/L)</td>
<td>126 ± 11.31 (6 - 307)</td>
<td>109 ± 9.45 (7 - 277)</td>
<td>1.1865</td>
<td>0.2382</td>
</tr>
<tr>
<td>DON (µg/L)</td>
<td>64 ± 8.38 (0 - 219)</td>
<td>76 ± 8.37 (0 - 227)</td>
<td>-1.3778</td>
<td>0.1712</td>
</tr>
<tr>
<td>SRP (µg/L)</td>
<td>1 ± 0.07 (0 - 2)</td>
<td>1 ± 0.09 (0 - 3)</td>
<td>-0.0267</td>
<td>0.7157</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>2.86 ± 0.15 (1.35 - 7.35)</td>
<td>3.52 ± 0.22 (1.68 - 9.16)</td>
<td>-2.4994</td>
<td>0.014 *</td>
</tr>
<tr>
<td>pH</td>
<td>5.9 ± 7.04 (5.44 - 6.70)</td>
<td>5.7 ± 6.74 (5.15 - 6.8)</td>
<td>-3.6201</td>
<td>0.0005 *</td>
</tr>
<tr>
<td>Water Temp (°C)</td>
<td>16.7 ± 0.88 (3.5 - 24)</td>
<td>16.2 ± 0.85 (3 - 24)</td>
<td>0.38</td>
<td>0.7048</td>
</tr>
<tr>
<td>Alkalinity (meq/L)</td>
<td>0.09 ± 0.003 (0.04 - 0.16)</td>
<td>0.09 ± 0.005 (0.04 - 0.16)</td>
<td>0.5756</td>
<td>0.5662</td>
</tr>
<tr>
<td>Sp Cond (µS/cm)</td>
<td>12.7 ± 0.26 (10.5 - 18.5)</td>
<td>15 ± 0.39 (11 - 20)</td>
<td>-4.8715</td>
<td>0.0000 *</td>
</tr>
</tbody>
</table>
FIGURE 5. Ammonium and nitrate concentrations for Mayfield Creek and Talladega Branch, January – December 2009. Points to the right of the 1:1 line indicate sampling events when NO$_3$-N concentrations were greater than NH$_4$-N concentrations.
TABLE 3. Mean Seasonal Water Chemistry Parameters (+ 1 SE) at Mayfield Creek, Alabama, U.S.A. Different superscripts denote significant differences between or among seasons.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄-N (µg/L)</td>
<td>31 ± 2.15&lt;sup&gt;c&lt;/sup&gt;</td>
<td>53 ± 7.85&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>68 ± 5.06&lt;sup&gt;a&lt;/sup&gt;</td>
<td>42 ± 3.24&lt;sup&gt;bc&lt;/sup&gt;</td>
</tr>
<tr>
<td>NO₃-N (µg/L)</td>
<td>7 ± 0.94&lt;sup&gt;b&lt;/sup&gt;</td>
<td>7 ± 1.42&lt;sup&gt;b&lt;/sup&gt;</td>
<td>25 ± 2.50&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17 ± 4.69&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td>Total N (µg/L)</td>
<td>51 ± 10.61&lt;sup&gt;c&lt;/sup&gt;</td>
<td>70 ± 13.08&lt;sup&gt;c&lt;/sup&gt;</td>
<td>220 ± 11.75&lt;sup&gt;a&lt;/sup&gt;</td>
<td>152 ± 14.35&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>DON (µg/L)</td>
<td>17 ± 8.31&lt;sup&gt;b&lt;/sup&gt;</td>
<td>16 ± 6.83&lt;sup&gt;b&lt;/sup&gt;</td>
<td>126 ± 12.73&lt;sup&gt;a&lt;/sup&gt;</td>
<td>93 ± 12.33&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>SRP (µg/L)</td>
<td>1 ± 0.13</td>
<td>1 ± 0.11</td>
<td>1 ± 0.11</td>
<td>1 ± 0.12</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>1.91 ± 0.13&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.73 ± 0.28&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>3.42 ± 0.11&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.21 ± 0.39&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Water Temp (°C)</td>
<td>8.2 ± 1.20&lt;sup&gt;c&lt;/sup&gt;</td>
<td>16.5 ± 1.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>23.1 ± 0.29&lt;sup&gt;a&lt;/sup&gt;</td>
<td>16.8 ± 1.22&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Alkalinity (meq/L)</td>
<td>0.07 ± 0.004&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.08 ± 0.009&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.11 ± 0.006&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.09 ± 0.004&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td>Sp. Cond. (µS/cm)</td>
<td>12.5 ± 0.64&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>13.2 ± 0.55&lt;sup&gt;a&lt;/sup&gt;</td>
<td>13.6 ± 0.53&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.6 ± 0.17&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
FIGURE 6. Seasonal changes in ammonium, nitrate, and dissolved organic carbon concentrations compared to seasonal changes in discharge at Mayfield Creek, January – December 2009.
Table 4. Mean Seasonal Water Chemistry Parameters (+ 1 SE) at Talladega Branch, Alabama, U.S.A. Different superscripts denote significant differences between or among seasons.

<table>
<thead>
<tr>
<th></th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄-N (µg/L)</td>
<td>19 ± 2.51c</td>
<td>31 ± 3.64ab</td>
<td>39 ± 2a</td>
<td>25 ± 3.28bc</td>
</tr>
<tr>
<td>NO₃-N (µg/L)</td>
<td>3 ± 0.41b</td>
<td>3 ± 0.40b</td>
<td>9 ± 1.58a</td>
<td>4 ± 1.03b</td>
</tr>
<tr>
<td>Total N (µg/L)</td>
<td>54 ± 15.86b</td>
<td>64 ± 14.28b</td>
<td>173 ± 13.96a</td>
<td>134 ± 9.75a</td>
</tr>
<tr>
<td>DON (µg/L)</td>
<td>33 ± 14.77b</td>
<td>34 ± 11.13b</td>
<td>124 ± 14.28a</td>
<td>106 ± 10.03a</td>
</tr>
<tr>
<td>SRP (µg/L)</td>
<td>0 ± 0.15</td>
<td>1 ± 0.15</td>
<td>1 ± 0.14</td>
<td>1 ± 0.20</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>2.38 ± 0.19b</td>
<td>3.68 ± 0.46ab</td>
<td>3.66 ± 0.39ab</td>
<td>4.13 ± 0.46a</td>
</tr>
<tr>
<td>Water Temp (°C)</td>
<td>8.2 ± 1.14c</td>
<td>15.9 ± 1.05b</td>
<td>22.4 ± 0.29a</td>
<td>16.4 ± 1.20b</td>
</tr>
<tr>
<td>Alkalinity (meq/L)</td>
<td>0.06 ± 0.006c</td>
<td>0.07 ± 0.007bc</td>
<td>0.13 ± 0.009a</td>
<td>0.09 ± 0.003b</td>
</tr>
<tr>
<td>Sp. Cond. (µS/cm)</td>
<td>15.4 ± 0.94a</td>
<td>15.5 ± 0.57a</td>
<td>17 ± 0.57a</td>
<td>12.3 ± 0.32b</td>
</tr>
</tbody>
</table>
FIGURE 7. Seasonal changes in ammonium, nitrate, and dissolved organic carbon concentrations compared to seasonal changes in discharge at Talladega Branch, January – December 2009.
TABLE 5. Results of Linear Regression Analysis Between Instantaneous Discharge and Nutrient Concentrations in Mayfield Creek and Talladega Branch. “+” indicates a positive relationship between concentration and discharge, “−” indicates a negative relationship between concentration and discharge, and “0” indicates no change in concentration with changing discharge. * = statistically significant (p ≤ 0.05).

<table>
<thead>
<tr>
<th>Location</th>
<th>Flow Condition</th>
<th>Parameter</th>
<th>r²</th>
<th>F Stat</th>
<th>p-value</th>
<th>Linear Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mayfield</td>
<td>Low Flow N=21</td>
<td>DOC</td>
<td>0.008</td>
<td>0.152</td>
<td>0.7011</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH₄-N</td>
<td>0.238</td>
<td>5.928</td>
<td>0.0249*</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO₃-N</td>
<td>0.250</td>
<td>6.348</td>
<td>0.0209*</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total N</td>
<td>0.216</td>
<td>5.235</td>
<td>0.0338*</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SRP</td>
<td>0.217</td>
<td>5.269</td>
<td>0.0333*</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DON</td>
<td>0.064</td>
<td>1.225</td>
<td>0.2829</td>
<td>−</td>
</tr>
<tr>
<td>Talladega</td>
<td>Low Flow N=19</td>
<td>DOC</td>
<td>0.383</td>
<td>9.913</td>
<td>0.0062*</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH₄-N</td>
<td>0.449</td>
<td>13.025</td>
<td>0.0024*</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO₃-N</td>
<td>0.617</td>
<td>25.723</td>
<td>0.0001*</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total N</td>
<td>0.129</td>
<td>2.360</td>
<td>0.1440</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SRP</td>
<td>0.234</td>
<td>4.891</td>
<td>0.0419*</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DON</td>
<td>0.286</td>
<td>5.603</td>
<td>0.0329*</td>
<td>+</td>
</tr>
<tr>
<td>Talladega</td>
<td>High Flow N=18</td>
<td>DOC</td>
<td>0.200</td>
<td>4.240</td>
<td>0.0551</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH₄-N</td>
<td>0.278</td>
<td>6.537</td>
<td>0.0204*</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO₃-N</td>
<td>0.222</td>
<td>4.862</td>
<td>0.0415*</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total N</td>
<td>0.003</td>
<td>0.046</td>
<td>0.8329</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SRP</td>
<td>0.035</td>
<td>0.623</td>
<td>0.4407</td>
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<td></td>
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<td>0.005</td>
<td>0.076</td>
<td>0.7857</td>
<td>+</td>
</tr>
<tr>
<td>Talladega</td>
<td>High Flow N=18</td>
<td>DOC</td>
<td>0.290</td>
<td>6.534</td>
<td>0.0211*</td>
<td>+</td>
</tr>
<tr>
<td></td>
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<td>NH₄-N</td>
<td>0.042</td>
<td>0.700</td>
<td>0.4153</td>
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<tr>
<td></td>
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<td>NO₃-N</td>
<td>0.177</td>
<td>3.450</td>
<td>0.0817</td>
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<td></td>
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<td>Total N</td>
<td>0.067</td>
<td>1.156</td>
<td>0.2982</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SRP</td>
<td>0.140</td>
<td>2.611</td>
<td>0.1257</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DON</td>
<td>0.123</td>
<td>2.107</td>
<td>0.1672</td>
<td>+</td>
</tr>
</tbody>
</table>
FIGURE 8. Changes in NH$_4$-N and NO$_3$-N concentrations in response to high flow related to rain events in Mayfield Creek (a) and Talladega Branch (b). Letters indicate water samples collected during peaks in the hydrographs. * denotes samples collected during the ascending limb of the peak.
FIGURE 9. Changes in DON and DOC concentrations in response to high flow related to rain events in Mayfield Creek (a) and Talladega Branch (b). Letters indicate water samples collected during peaks in the hydrographs. * denotes samples collected during the ascending limb of the peak.
TABLE 6. Flux Estimates for Mayfield Creek and Talladega Branch, January–December 2009. Values are presented as annual nutrient flux (kg/year) and annual nutrient yield (kg/ha/year).

<table>
<thead>
<tr>
<th></th>
<th>Mayfield</th>
<th>Talladega</th>
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<tr>
<td>NH₄-N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(kg N/year)</td>
<td>376.4</td>
<td>72.9</td>
</tr>
<tr>
<td>(kg N/ha/year)</td>
<td>0.15</td>
<td>0.10</td>
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<tr>
<td>NO₃-N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(kg N/year)</td>
<td>93</td>
<td>19.5</td>
</tr>
<tr>
<td>(kg N/ha/year)</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>DON</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(kg N/year)</td>
<td>740.7</td>
<td>428</td>
</tr>
<tr>
<td>(kg N/ha/year)</td>
<td>0.30</td>
<td>0.56</td>
</tr>
<tr>
<td>DOC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(kg C/year)</td>
<td>30,602.4</td>
<td>19,455.8</td>
</tr>
<tr>
<td>(kg C/ha/year)</td>
<td>12.54</td>
<td>26.26</td>
</tr>
</tbody>
</table>
DISCUSSION

Hydrology

Seasonal patterns in discharge in forested streams in the southeastern United States are the result of regional climate patterns, geomorphology, and interactions with the terrestrial landscape (Poff et al. 1997). Streams in this region tend to have higher flows in the winter and spring and lower flows in the summer, and the hydrological patterns observed in Mayfield Creek and Talladega Branch were typical for the region (Mulholland et al. 2004). Winter and early spring months received the most precipitation, and this increased precipitation resulted in higher discharges in the streams. Additionally, cooler temperatures and leaf abscission in mid-September likely decreased primary production of the riparian vegetation, thus decreasing rates of evapotranspiration and, therefore, the volume of water removed from the streams by trees and plants. As a result, the amount of surface water that remained in the stream channels increased.

As air temperature increased and the photoperiod lengthened in spring and summer, primary production in the terrestrial environment increased, evapotranspiration increased, and the stream flow decreased. The summer months, June through August, received little rainfall (300 mm), further confounding the low flow conditions of the streams.

The annual hydrographs for Mayfield Creek and Talladega Branch were very similar. Because these two streams are located in the same watershed, it is reasonable to assume that they experienced the same meteorological conditions and, thus, responded similarly to changes in those conditions over time. Therefore, the annual hydrographs show that seasonal changes in
flow occurred at the same time in both streams. Summer and winter baseflow discharge was much less in Talladega Branch, the first-order stream. However, discharge was similar for the two streams during storm flows, indicating that storm events may have a more pronounced effect on the smaller stream.

In areas with a hilly landscape, such as the Talladega National Forest, run-off moves down-gradient to the stream channel quickly, resulting in flashy hydrographs (Allan and Castillo 2008). Poff et al. (1997) define “flashy” streams as having a rapid rate of change in flow. During the September storm, the event of greatest magnitude experienced by the watershed in 2009, both Mayfield Creek and Talladega Branch reached maximum flow conditions five hours after the first rainfall was recorded. The flashiness of these streams is due to the geomorphological characteristics of the watershed. These are low-gradient streams, but the steep, hilly landscape of the watershed decreases the time required for run-off to reach the stream channel, increasing the flashiness of the streams.

This study was conducted during a year of the El Niño/Southern Oscillation (ENSO). A shifting of the Intertropical Convergence Zone (ITCZ) results in increased strength of the Equatorial Countercurrent, which brings warmer than usual waters to the eastern Pacific Ocean (Hepner and Davis 2004). ENSO years are known to cause cool temperatures and increased rainfall in the coastal plain of the southeastern U.S. (Hansen et al. 1998). Increased precipitation in the autumn months tends to cause a lagged increase in winter streamflow of southeastern streams (Zorn and Waylen 1997). Therefore, the total precipitation recorded from January – December 2009 (1926.926 mm) is higher than the average annual precipitation for the area, which is about 1250 mm (M. Ward, unpublished data). As a result, the hydrographs presented
for Mayfield Creek and Talladega Branch for 2009 may reflect higher-than-average annual discharges typical for these streams.

Water Chemistry

It is well-documented that forested headwater streams are closely linked to their surrounding terrestrial landscape (Hynes 1975; Likens et al. 1977; Vannote et al. 1980; Junk et al. 1989). The geology, geomorphology, hydrology, and biology of a watershed largely determine the water chemistry of a stream (Schlesinger 1997). Terrestrial inputs of N and P in forested catchments are typically low because nutrients are retained in the upper soil horizons, decreasing transport of nutrients by run-off (Mulholland 1992). Nutrient retention, particularly of nitrogen, has been shown to decrease over time in old-growth forests (Vitousek and Reiners 1975) and in clear-cut forest stands (Bormann et al. 1968; Likens et al. 1970). Mayfield Creek and Talladega Branch are undisturbed, pristine headwater streams. Because these streams are located in a federally protected national forest, agriculture, livestock, and urbanization, all factors known to increase nutrient input to freshwater systems, were not issues of concern. As a result, all nutrient concentrations in these streams were lower than those reported for urban and agricultural streams of similar size. The pH of the streamwater in Mayfield Creek and Talladega Branch was circumneutral and typical of coastal plain streams (Ward et al. 2005). The alkalinity of the streams was very low as well. This can be attributed to the lack of underlying carbonate and bicarbonate rock in this coastal plain landscape. Streambeds are composed mostly of unconsolidated sand. As a result, the acid neutralizing capacity (ANC) of these streams was low, making them highly susceptible to inputs that might change streamwater pH (Wetzel 2001). Because there was no underlying bedrock in these streams to cause leaching of ions and nutrients
into the streamwater, atmospheric deposition, along with groundwater and terrestrial inputs, such as subsoil leaching transported by run-off, were likely the primary sources of nutrients to these streams.

Mayfield Creek, the larger of the two streams, had mean inorganic nutrient concentrations that were higher than Talladega Branch. Because the area of land that a stream drains is relative to its size, a larger stream, like Mayfield Creek, has more run-off and so higher inputs of nutrients from the terrestrial landscape (Allan and Castillo 2008). DOC and DON concentrations were higher in Talladega Branch, the smaller of the two streams. This is likely due, in part, to the fact that the channel width of the first-order stream was smaller, so the riparian canopy covered more of the stream’s surface. Therefore, it is likely that more allochthonous inputs of organic matter were deposited into the stream. These allochthonous inputs were decomposed by mechanical and microbial processes in the stream, and, in the process, organic compounds were leached into the streamwater, increasing DOC and DON. A litter exclusion study conducted by Meyer et al. (1998) in a first-order, headwater stream at the Coweeta Hydrologic Laboratory showed that ~30% of DOC exported from the stream daily was the result of in-stream leaf litter leaching. The lower water velocity and the presence of debris jams throughout the Talladega Branch stream channel likely increased the retention capacity of coarse particulate organic matter (CPOM) inputs from the riparia and, therefore, increased DOC and DON concentrations as well (Mulholland 1981). Debris jams were also present in Mayfield Creek, but the faster flowing water and wider stream channel likely reduced the retention of organic matter that could produce DOC and DON in the stream reach, compared to Talladega Branch.
Elevated Ammonium Concentrations Compared to Nitrate

In both Mayfield Creek and Talladega Branch, NH₄-N concentrations were consistently higher than NO₃-N concentrations. This is an unusual phenomenon, as NH₄-N is the most reduced form of nitrogen and, thus, the form most readily assimilated by primary producers and microbes in a stream. Also, under aerobic conditions, NH₄-N is readily oxidized to NO₃-N by nitrifying bacteria via the process of nitrification. Therefore, studies of nutrient dynamics in stream ecosystems have typically shown results in contrast to those found in this study, i.e. NO₃-N was the dominant form of inorganic nitrogen in streams (Mulholland 2004). Furthermore, NH₄-N concentrations did not increase during high flow events in either stream, indicating that the elevated NH₄-N concentrations consistently recorded in these two streams did not originate in the terrestrial environment but, instead, were the result of in-stream or near-stream processes.

The experimental design of this study does not allow for a conclusive explanation as to why Mayfield Creek and Talladega Branch exhibited this unusual pattern of inorganic nitrogen composition. However, possible explanations for the increased NH₄-N in the streamwater may be due to biotic processes taking place in the stream sediment and/or hyporheic zone, such as dissimilatory reduction of nitrate to ammonium (DNRA) or nitrate-dependent iron oxidation (Weber et al. 2001; Burgin and Hamilton 2007).

Unlike denitrification, which serves as a nitrogen sink in most ecosystems, DNRA is a microbially-mediated process by which NO₃-N is reduced to NH₄-N, which can then be biologically assimilated by microbes and plants and retained in the system rather than permanently removed as N₂ gas (An and Gardner 2002; Burgin and Hamilton 2007). Little is known about the ecological and environmental conditions conducive to DNRA, especially in freshwater systems, but the conditions necessary for DNRA to occur may be similar to those
necessary for denitrification—an anoxic environment, an abundant supply of NO₃-N, and an organic substrate to serve as an electron donor (Burgin and Hamilton 2007). Work by Kelso et al. (1997) demonstrated that the DNRA pathway of nitrate reduction may be favored over denitrification when NO₃-N is limiting and the supply of organic carbon is abundant, both of which are characteristics of Mayfield Creek and Talladega Branch. There are two possible pathways to facilitate the process of DNRA. One is a series of microbial fermentation reactions that uses organic matter as an electron donor for nitrate reduction (Tiedje 1988). The other is a coupling of nitrate reduction with sulfur oxidation. Free sulfide has been shown to inhibit steps of the denitrification process (Burgin and Hamilton 2007), so under such conditions, any NO₃-N present is available for DNRA rather than denitrification (An and Gardner 2002). This study did not involve an analysis of the microbial community inhabiting the sediment of Mayfield Creek and Talladega Branch to determine whether or not there are taxa present that may facilitate DNRA reactions. However, this biological process would explain the unusually high levels of NH₄-N compared to NO₃-N in these streams.

Biological nitrate dependent iron oxidation is another hypothesis for the observed composition of inorganic nitrogen in these two streams. Numerous studies have supported the possibility that microbes capable of reducing Fe(II) with reduction of NO₃-N inhabit freshwater environments (Straub et al. 1996; Weber et al. 2001; Emerson and Weiss 2004). When the supply of organic material is low, these lithotrophic microbes use Fe(II) as an alternative electron donor to reduce available NO₃-N while oxidizing Fe(II) to Fe(III). A laboratory experiment conducted by Weber et al. (2006) on a sediment core from the Talladega Wetland Ecosystem, also located in the Talladega National Forest, confirmed that biological nitrate dependent iron oxidation was occurring in this system and that the reduced form of nitrogen that resulted from
this coupled process was NH$_4$-N. However, little is known about this microbial pathway and the microorganisms responsible for its occurrence, especially in streams and rivers, and other studies have not shown NH$_4$-N to be the result of NO$_3$-N reduction. Whether this microbial process is restricted to the anaerobic sediments of wetland ecosystems or if it could potentially occur in the benthic sediment or hyporheic zones of streams has not been established. Because the supply of iron is abundant throughout this system, this process could be contribute to the elevated ammonium concentrations compared to nitrate in Mayfield Creek and Talladega Branch.

Seasonal Changes in Nutrient Concentrations

Ecologists have known for decades that stream nutrient concentrations vary seasonally due to the biological effects of the growing season and changes in hydrology (Meyer et al. 1988; Chetelat and Pick 2001). Seasonal changes in nutrient concentrations in Mayfield Creek and Talladega Branch were observed during the study. All forms of N peaked during the summer months and were lowest during the winter and early spring months. A long-term analysis conducted by Mulholland (2004) in the Walker Branch watershed showed similar results with regards to NO$_3$-N and SRP. He found that concentrations were lowest in the fall due to increased heterotrophic activity and in early spring due to increased autotrophic activity. In general, increased microbial and invertebrate activity increases the demand for N and P in the fall after leaf abscission. Primary production is stimulated in the spring by increased sunlight and warmer temperatures, thus, increasing nutrient uptake. Both of these in-stream processes increase the demand of nutrients in the stream, while decreasing the concentrations of available N and P in the streamwater (Mulholland 2004). Furthermore, in the summer months after leaf-out, increased evapotranspiration reduces stream flow and has a concentrating effect on stream
nutrients. During winter baseflow conditions, the increased winter baseflow has a diluting effect on nutrient concentrations. All of these factors combined result in an expected annual pattern of high nutrient concentrations in the summer and low nutrient concentrations in the winter, like that observed in the Mayfield Creek watershed. This pattern has been documented in other areas of the southeastern U.S., such as the Walker Branch Watershed in Tennessee and streams near the Coweeta Hydrologic Laboratory in North Carolina (Mullholland 1992: Swank and Vose 1997). Similar studies conducted in the northeastern United States, Canada, and Scotland have shown the opposite trend—higher nutrient concentrations, particularly NO₃-N, in the winter and spring compared to those in the summer (Murdoch and Stoddard 1993; Chapman et al. 2001; Goodale et al. 2003). It is believed that these variations in seasonal patterns are the result of differences in latitude, particularly temperature, which affect the biological processes in the soil and in the streams (Mulholland 1992; Mulholland 2004). At latitudes where upper soil horizons do not freeze and water temperatures remain above 0 °C, microbial activity persists through the dormant period due to the decomposition of leaves after autumn leaf-off, resulting in continued immobilization of N and P in the terrestrial soil (Mulholland 1994; Mulholland 2004), which results in fewer inputs to streams.

DOC levels in Mayfield Creek and Talladega Branch also showed noticeable temporal changes. Concentrations were significantly higher in the spring, summer, and fall than in the winter in both streams. Because these are forested, headwater streams with little primary production, seasonal changes in DOC were likely driven by seasonal patterns of terrestrial primary production and in-stream microbial activity. Leaf-out occurred in the spring, and this increased growth of riparian vegetation increased the potential for inputs of allochthonous carbon from the landscape to the stream. Leaching of this CPOM and decomposition by microbial
communities resulted in an increase in stream DOC levels, which remained elevated throughout the growing season. In mid-September when leaf-off occurred, a pulse of carbon entered the stream in the form of abscised leaves. Again, as organic compounds were leached from the decomposing leaves and microbial decomposition increased, a second peak in the concentration of DOC was observed in the streams. This second peak was more noticeable in Talladega Branch. As cooler temperatures decreased microbial activity and in-stream leaching attenuated, winter concentrations of DOC decreased and remained low into the dormant season.

Another interesting seasonal trend observed in these streams was the delayed increase in NO$_3$-N compared to NH$_4$-N in spring and summer months. This occurrence is likely the result of either in-stream or riparian biological processes. The primary biological sinks for NO$_3$-N in streams and riparian zones are denitrification and uptake by primary producers (Duff et al. 2007). Primary production in these heavily shaded, headwater streams is believed to be low, so increased uptake of nitrate by algae in late summer, or any other time of the year, is not likely. Decreased rates of denitrification in the channel could result in higher concentrations of nitrate in the stream, but areas of anoxic sediment on the streambed or in the hyporheic zone where denitrification is favored should increase as summer progresses, resulting in lower concentrations of NO$_3$-N over time, not higher concentrations as we observed in these streams. However, it is possible that a rapid increase in the mineralization of organic N to form of NH$_4$-N relative to NO$_3$-N further confounded the concentrating effect of decreased stream flow in spring months and resulted in higher NH$_4$-N concentrations compared to NO$_3$-N early in the growing season.

Terrestrial soil activity could also play a significant role in these patterns of NH$_4$-N and NO$_3$-N observed in the surface water. The rate of removal of NO$_3$-N from the soil is strongly influenced by interactions between groundwater flow paths through shallow root zones and the
characteristics of terrestrial soils (Duff et al. 2007). Available nitrogen that is not immobilized by riparian vegetation is available for transformation by biological processes in the soil. Soil temperature, pH, moisture, microbial community composition determine nitrification and denitrification rates in riparian soils (Shammas 1986; Naiman and Décams 1997). Changes in any of these conditions could cause a shift in the form of inorganic nitrogen exported to the stream (i.e., increased nitrification results in more NO$_3$-N and less NH$_4$-N available for export), which may explain the delayed increase in NO$_3$-N in the stream channel. While the role of the riparian zones in seasonal nutrient export at Mayfield Creek and Talladega Branch is not well understood, it is likely that terrestrial processes are in some way responsible for the delayed peak in NO$_3$-N observed in both streams.

Effects of Discharge on Nutrient Concentrations

Pulses in ambient stream nutrient concentrations due to short-term increases in discharge, such as storm events, are not as well understood (Meyer et al. 1988). There is some speculation that the short-term increases in nutrient concentrations caused by remobilization of particles when sediment is shifted during storm flows may be just as important as less dramatic, seasonal changes in a stream (Meyer et al. 1988). Studies have shown varying patterns in the relationship between discharge and elemental nutrients, and this variation occurs between streams of differing latitudes, between streams in the same basin, and even between storms for the same stream (Meyer et al. 1988). This high variation is due to the extreme differences between topography, geology, land use, geomorphology, and various other factors that control the flow of nutrients and water from the terrestrial landscape to the stream and to biological transformations of nutrients within the stream itself (Meyer et al. 1988; Chetelat and Pick 2001). Concentrations
depend on the discharge of a stream at the time a water sample is collected, but they also vary depending on whether discharge was increasing, decreasing, or at baseflow at the time of sampling (Meyer 1990). Within a single stream, nutrient concentrations may vary between storm events depending on the intensity of the storm, the scouring activity caused by a storm, and the time that has elapsed since the previous storm event (Poff and Ward 1989; Meyer 1990).

The results of this study indicated that changes in discharge during storm events caused changes in nutrient concentrations in Mayfield Creek and Talladega Branch. When water samples were collected during, or shortly after, a rain event (i.e., the rising limb of the hydrograph), elevated levels of NO$_3$-N, SRP, DON, and DOC were observed in both streams. These elevated nutrient concentrations were likely due to the mobilization of nutrients from the terrestrial soil that were transported to the stream via run-off. However, as previously noted, NH$_4$-N concentrations did not increase during these high flow events, indicating that changes in NH$_4$-N in the stream were likely the result of in-stream processes. Therefore, with the possible exception of NH$_4$-N, it is believed that the nearby terrestrial landscape acts as a source of nutrients to these streams, particularly during storms.

While this study was not designed to observe the effects of storm events on in-stream nutrient concentrations, interesting changes were observed in samples collected during high flows. Nutrient increases were less pronounced at Talladega Branch, but for both streams, the elevated nutrient levels were short-lived. On all occasions when these increases were observed, concentrations returned to pre-storm levels by the next sampling time, which on one occasion was the next day. Depending on the time of year and the intensity of the stream velocity, these nutrients may have been immobilized and assimilated by biota in the stream channel or transported downstream with the flow of water (Chetelat and Pick 2001). With frequent,
continuous sampling during storms, we could determine how storms of varying magnitude influence nutrient concentrations, at what point dilution by storm water overcomes increased input of nutrients, and how long these pulse concentrations are sustained in the stream channel. With this type of sampling technique, we would have a much better understanding of the behavior of water chemistry in Mayfield Creek and Talladega Branch during storm events.

Not all of the relationships between concentration and discharge were statistically significant for these streams, and in many cases, discharge explained little of the variation in nutrient concentrations. However, our findings were consistent with those reported in other streams. When the nutrient concentration-discharge relationships observed in Mayfield Creek and Talladega Branch are compared to those reported in other streams and rivers, the high variability of this relationship becomes apparent (Table 7). There appears to be no predictable patterns associated with NH₄-N, NO₃-N, or SRP across stream orders or region. However, DOC concentrations do increase with discharge in all eight streams. This is usually explained, especially in headwater streams, by the transport of organic material to the stream channel during storms because overland flow comprises a larger proportion of stream water in the channel during rain events (Schlesinger 1997). This unpredictability is somewhat expected due to the number of biotic and abiotic factors that impact elemental dynamics in a stream. Not all streams have the same environmental and biological forces acting upon them, so we do not expect all streams to have the same water chemistry. Therefore, we should not expect all streams to behave the same during storm flow conditions.
**Nutrient Flux**

DOC flux estimates for Mayfield Creek and Talladega Branch were higher than flux estimates reported for other streams of similar size. Reardon (1998) reported annual flux of DOC in Payne Creek, a second-order stream in the Talladega National Forest, as 1,765 kg C/year. This is much lower than our DOC flux estimates for Mayfield Creek and Talladega Branch, which were 30,602 kg C/year and 19,455 kg C/year, respectively. Values of DOC transport for these two streams were comparable to those reported for low-gradient, coastal plain streams in the southeastern U.S. that drain wetlands or swamplands. For example, Buzzard’s Branch, a first-order stream in Virginia, transports about 38,248 kg C/year (Mulholland 1997). However, mean annual DOM in the stream was 20.2 mg/L, much higher than the mean annual values for these two streams (2.86 mg/L and 3.52 mg/L). Similarly, Fourmile Branch, a second-order, blackwater, coastal plain stream in South Carolina transports about 28,900 kg C/year (Dosskey and Bertsch 1994). Because Mayfield Creek and Talladega Branch do not drain areas dominated by wetlands and swamplands, nor do they have regular interaction with the surrounding floodplain, we expect DOC flux from these streams to be higher than, but close to that of nearby Payne Creek. One possible explanation for our high flux values for these streams is the higher average discharge reported for these streams in 2009. Nutrient flux is strongly influenced by the discharge of the stream. Because these calculations are based on streamflow during an El Niño year, transport may be higher than average.

Nitrate flux in Mayfield Creek and Talladega Branch was less than values reported for other streams of similar size because NO$_3$-N concentrations, in general, were lower than in other systems. According to Swank and Vose (1997), mean NO$_3$-N export at a reference watershed at Coweeta was less than 0.25 kg N/ha/year between 1972 and 1994. Annual nitrate yield at Pond
Branch, a small forested watershed in Baltimore, Maryland was 0.12 kg N/ha/year, 0.14 kg N/ha/year, and 0.11 kg N/ha/year in 1999, 2000, and 2001, respectively (Groffman et al. 2004). The nitrate yield of Mayfield Creek and Talladega Branch, 0.04 kg N/ha/year and 0.03 kg N/ha/year, respectively. Because NH$_4$-N is the dominant form of inorganic nitrogen in this system, values of DIN flux provide a better context for nitrogen export in these streams. DIN flux in Mayfield Creek and Talladega Branch was 0.19 kg N/ha/year and 0.13 kg N/ha/year, respectively. The amount of nitrogen export from these streams may be similar to other systems, but NH$_4$-N, rather than NO$_3$-N, is the dominant form of inorganic nitrogen exported.

Conclusion

Water chemistry and stream discharge were observed in Mayfield Creek and Talladega Branch from January–December 2009, an El Niño year of higher-than-average stream flow. The collection of weekly water samples resulted in a fine-scale temporal dataset that allowed for the observation of annual changes in water chemistry that could not be detected with less frequent, monthly sampling.

The hydrological patterns observed in Mayfield Creek and Talladega Branch were typical of streams in the eastern United States (Poff et al. 1997). Flows were low during the dry, summer months and high during the wet, winter months, resulting in typical low summer baseflow and high winter baseflow conditions.

Mean annual concentrations of NH$_4$-N and NO$_3$-N were significantly higher in Mayfield Creek, the larger of the two streams. DON and DOC were higher in Talladega Branch. Throughout the year, NH$_4$-N was consistently higher than NO$_3$-N in both streams, an
observation contrary to previous studies of inorganic nitrogen composition in streams
(Mulholland 2004).

Seasonal changes in nutrient concentrations were also observed in both streams. NH$_4$-N, NO$_3$-N, DON, and DOC showed peaks in the spring and summer months during low, summer baseflow, and the seasonal peak in NO$_3$-N occurred later in the growing season than the NH$_4$-N peak in both streams.

Interesting relationships between discharge and nutrient concentrations were also observed in the two streams. During high flow conditions, DOC, NO$_3$-N, DON, and SRP concentrations increased as discharge increased in both Mayfield Creek and Talladega Branch. In contrast, NH$_4$-N showed a negative relationship with stream flow, implying that NH$_4$-N is not being transported into the stream channel by overland flow during storm events. However, many of these concentration-discharge relationships were not statistically significant, especially in Talladega Branch, and of those that were significant, discharge explained little of the variation in nutrient concentration (i.e., had low r$^2$ values).

Many of the hydrology and water chemistry patterns observed in Mayfield Creek and Talladega Branch were similar over the annual period. However, variations in mean annual nutrient concentrations and seasonal fluctuations were observed between the two streams. Because these streams are located in the same watershed, it is reasonable to assume that they experienced the same environmental factors throughout the annual period. Therefore, we attribute the observed differences in water chemistry between these streams to variations in flow and channel morphology related to differences in stream size and drainage area.

The detailed water chemistry data provided by the weekly sampling of these two streams are important in increasing our understanding of the seasonal nutrient dynamics of headwater
streams, specifically those in the coastal plain. However, while an annual cycle is interesting to observe and analyze, one year of data provides little insight into the long-term behavior of a lotic system. Long-term datasets enhance our ability to recognize and predict changes in stream water chemistry over various hydrological and climatological conditions. Therefore, these data are important in establishing a baseline for long-term studies, such as those designed by the National Ecological Observatory Network (NEON).
TABLE 7. The Relationships Between Nutrient Concentrations and Stream Discharge in Streams of Various Sizes and Locations. “+” indicates a positive relationship between concentration and discharge, “−” indicates a negative relationship between concentration and discharge, and “0” indicates no change in concentration with changing discharge. Multiple symbols indicate varying reports for the same location. (modified from Meyer et al. 1988)

<table>
<thead>
<tr>
<th></th>
<th>Kuparuk River, Alaska</th>
<th>Bear Brook, New Hampshire</th>
<th>Rhode River Watershed, Maryland</th>
<th>Walker Branch, Tennessee</th>
<th>Hugh White Creek, North Carolina</th>
<th>Quebrada Sonadora, Puerto Rico</th>
<th>Mayfield Creek, Alabama</th>
<th>Talladega Branch, Alabama</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream Order</td>
<td>4</td>
<td>1</td>
<td>1-2</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Nitrate</td>
<td>−</td>
<td>+</td>
<td>0, −</td>
<td>n.d.</td>
<td>0, +</td>
<td>0</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0</td>
<td>n.d.</td>
<td>+</td>
<td>n.d.</td>
<td>0</td>
<td>0</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>SRP</td>
<td>0</td>
<td>n.d.</td>
<td>+</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>DOC</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>
LITERATURE CITED


57


APPENDIX

Discharge-Nutrient Concentrations Regressions

Mayfield Creek:

**Mayfield**

**Low Flow vs DOC**

\[ y = 0.0174x + 0.5436 \]

\[ R^2 = 0.0079 \]

**Mayfield**

**Low Flow vs NH\(_4\)-N**

\[ y = -0.1869x + 1.5766 \]

\[ R^2 = 0.2378 \]
Mayfield
Low Flow vs NO$_3$-N

$y = -0.5209x + 0.6956$
$R^2 = 0.2504$

Mayfield
Low Flow vs Total N

$y = -0.2678x + 1.9474$
$R^2 = 0.216$

Mayfield
Low Flow vs SRP

$y = -0.2703x - 0.2746$
$R^2 = 0.2171$
Mayfield
Low Flow vs DON

$y = -0.3171x + 1.5451$
$R^2 = 0.063$

Mayfield
High Flow vs DOC

$y = 0.3092x + 0.5173$
$R^2 = 0.3825$

Mayfield
High Flow vs NH$_4$-N

$y = -0.2843x + 1.5339$
$R^2 = 0.4487$
Mayfield
High Flow vs NO₃-N

\[ y = 0.9363x + 1.0821 \]
\[ R^2 = 0.6165 \]

Mayfield
High Flow vs Total N

\[ y = 0.2974x + 2.1228 \]
\[ R^2 = 0.1285 \]

Mayfield
High Flow vs SRP

\[ y = 0.324x + 0.0277 \]
\[ R^2 = 0.2341 \]
Mayfield
High Flow vs DON

\[ y = 0.4228x + 1.9539 \]
\[ R^2 = 0.2858 \]

Talladega Branch:

Talladega
Low Flow vs DOC

\[ y = 0.174x + 0.9055 \]
\[ R^2 = 0.2083 \]

Talladega
Low Flow vs NH\textsubscript{4}-N

\[ y = -0.2229x + 1.0925 \]
\[ R^2 = 0.2749 \]
**Talladega**

**Low Flow vs NO$_3$-N**

\[ y = -0.3407x + 0.1077 \]

\[ R^2 = 0.2194 \]

**Talladega**

**Low Flow vs Total N**

\[ y = -0.0145x + 2.1267 \]

\[ R^2 = 0.0014 \]

**Talladega**

**Low Flow vs SRP**

\[ y = -0.1711x - 0.3266 \]

\[ R^2 = 0.0388 \]
Talladega
Low Flow vs DON

\[ y = 0.0495x + 2.0675 \]
\[ R^2 = 0.0048 \]

High Flow vs DOC

\[ y = 0.1931x + 0.7419 \]
\[ R^2 = 0.29 \]

High Flow vs NH\(_4\)-N

\[ y = -0.0968x + 1.3265 \]
\[ R^2 = 0.0419 \]
Talladega
High Flow vs NO$_3$-N

\[ y = 0.2982x + 0.7022 \]

\[ R^2 = 0.1774 \]

Talladega
High Flow vs Total N

\[ y = 0.1322x + 2.1651 \]

\[ R^2 = 0.0674 \]

Talladega
High Flow vs SRP

\[ y = 0.1991x + 0.1132 \]

\[ R^2 = 0.1403 \]
Talladega
High Flow vs DON

\[ y = 0.1881x + 2.1015 \]

\[ R^2 = 0.1232 \]