ABSTRACT

SINGH, NITIN KUMAR. Hydrological and Biogeochemical Processes in Forested Headwater Catchments of the Southern Appalachians. (Under the direction of Dr. Ryan E. Emanuel)

This dissertation provides a holistic understanding of how climate, topography and vegetation mediate hydrologic processes that influence runoff generation and biogeochemical processes in the Southern Appalachians. These mountains are characterized by a temperate and humid climate, and their headwater basins generally contain steep slopes and deep soils. The topics we investigate are: i) the spatiotemporal patterns of baseflow and its relationship to catchment structure, ii) hillslope-scale controls on soil moisture and shallow groundwater responses to storms, and iii) controls on long-term patterns of dissolved organic carbon in runoff. To addresses these objectives the dissertation makes use of a wealth of datasets that includes hydrometric, isotopic, and water quality data, collected by others and me at Coweeta over time span of past few years to more than two decades. This dissertation builds on findings of prior studies at Coweeta, and it contributes to the legacy of catchment hydrology research at Coweeta.

We characterize the influence of internal watershed structure on spatial patterns of baseflow in two headwater streams of Coweeta, and we demonstrate that the strength of these relationships vary with hydrologic conditions. We detect large spatiotemporal variability in soil moisture and groundwater responses to storms across study hillslopes. The spatiotemporal patterns of soil moisture and groundwater responses (timing) to storms are largely correlated with storm properties and topography. However, the magnitude of responses for both soil moisture and groundwater are weakly correlated or uncorrelated with
topography for most of the storms. Together, topography and storm depth mediate the strength of groundwater-runoff relationships, including the patterns of source area that contributes to peak runoff at catchment outlet during storms. We analyze the temporal patterns of stream DOC concentration and flux over 25-years for a Coweeta stream. We also investigated the potential drivers of these patterns including, rising air temperatures, hydrological changes, recovery from acidification and nitrogen enrichment in atmospheric deposition. The temporal patterns of stream DOC show bi-directional trends (a decline followed by an increase), which could be attributed to hydroclimatological changes. This work highlights the critical role of long-term data in understanding the impact of climate change on water quality and water quantity of these forested catchments. Overall, this dissertation advances our understanding of water and carbon cycles in these steep catchments of the Southern Appalachians and similar landscapes elsewhere.
Hydrological and Biogeochemical Processes in Forested Headwater Catchments of the Southern Appalachians

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Forestry and Environmental Resources

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DEDICATION

This dissertation is dedicated to my wife Dr. Ruchi Bhattacharya, who compromised her academic ambitions and decided to stay with me to support my work. Her selfless help in the fieldwork was above and beyond the call of duty. This dissertation would not have been possible without her.
BIOGRAPHY

Nitin grew up in India and came to the United States in the year of 2005 to pursue his MS in Biological and Agricultural Engineering at the University of Arkansas. After graduating in 2007, he worked as a surface-water hydrologist with World Wildlife Fund (WWF-US) in the Everglades Agricultural Area near Lake Okeechobee, Florida. In the summer of 2011, Nitin began his doctoral program with Dr. Ryan Emanuel at the NC State University.
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TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................... viii

LIST OF FIGURES ......................................................................................................... ix

Chapter 1. Introduction .............................................................................................. 1
1.1 Introduction .......................................................................................................... 1
1.2 Dissertation Outline ......................................................................................... 5
1.3 References ......................................................................................................... 8

Chapter 2. Space time Variability of Baseflow in Headwater Streams of the Southern Appalachians ................................................................. 11
Abstract .................................................................................................................. 11
2.1 Introduction ....................................................................................................... 12
2.2 Study Site ......................................................................................................... 16
2.3 Methods. ........................................................................................................... 18
  2.3.1 Geospatial Analysis ......................................................................................... 18
  2.3.2 Isotopic Measurements ................................................................................. 19
  2.3.3 Lateral Inflows of δ18O ................................................................................ 21
  2.3.4 Assessing the Influence of Hillslope Arrangement ................................... 23
2.4 Results. ............................................................................................................... 25
  2.4.1 Spatial Characteristics of Catchments and Hillslopes .............................. 25
  2.4.2 Catchment Water Balance and Isotopic Compositions ......................... 25
  2.3.3 Spatiotemporal Patterns of Baseflow δ18O ............................................... 28
  2.3.4 Landscape Controls on Baseflow δ18O and Lateral Inflow δ18O ........... 29
2.5 Discussion .......................................................................................................... 31
  2.5.1 How do Hydrologic Conditions Affect the Spatiotemporal Variability of Baseflow δ18O? ................................................................. 31
  2.5.2 How do the Structure and Arrangement of Hillslopes within Catchments Affect Baseflow δ18O? ................................................................. 33
  2.5.3 Implications ................................................................................................. 34
2.6 Conclusions ...................................................................................................... 37
2.7 References ....................................................................................................... 38

Chapter 3. Spatiotemporal Patterns of Soil Moisture Responses to Storms in a Forested Headwater Catchment ............................................. 58
Abstract .................................................................................................................. 58
3.1 Introduction ...................................................................................................... 60
3.2 Study Site ......................................................................................................... 63
3.3 Methods. ........................................................................................................... 64
  3.3.1 Geospatial Analysis ....................................................................................... 64
  3.3.2 Data Collection ............................................................................................ 64
  3.3.3 Data Analysis ............................................................................................... 66
3.4 Results .............................................................................................................. 68
### Chapter 4. Shallow Groundwater Responses to Storms and Implications for Runoff in the Southern Appalachian Mountains

**Abstract**

4.1 Introduction .........................................................................................................................109

4.2 Study Site ...........................................................................................................................110

4.3 Methods ..............................................................................................................................115

4.3.1 Geospatial Analysis ........................................................................................................115

4.3.2 Data Collection ..............................................................................................................115

4.3.3 Data Analysis ................................................................................................................116

4.4 Results ...............................................................................................................................118

4.4.1 Annual Dynamics of Rainfall, Runoff and Groundwater and Storm Characteristics ..........118

4.4.2 Shallow Groundwater Response Metrics across Catchments .......................................119

4.4.3 Spatiotemporal Controls on the Groundwater Response ..............................................121

4.4.4 Relationship between Shallow Groundwater and Runoff across Catchments .........................122

4.5 Discussion ........................................................................................................................124

4.5.1 Spatiotemporal Controls on Groundwater Responses (magnitude and timing) ......................124

4.5.1.1 Rainfall Requirements for Groundwater Responses ...................................................124

4.5.1.2 Absolute Rise of Groundwater ...............................................................................125

4.5.1.3 Timing of Groundwater Response .........................................................................126

4.5.2 Relationship between Runoff and Groundwater .............................................................128

4.6 Conclusions ....................................................................................................................130

4.7 References .......................................................................................................................131
Chapter 5  Hydro-Climatological Influences on Long-Term Dissolved Organic Carbon in a Mountain Stream of the Southeastern United States Mountains ........................................154

Abstract ..................................................................................................................................................154
5.1 Introduction ......................................................................................................................................155
5.2 Study Site and Methods ..................................................................................................................157
  5.2.1 Study Site ..................................................................................................................................157
  5.2.2 Methods ...................................................................................................................................158
5.3 Results ..............................................................................................................................................162
  5.3.1 Temporal Trends in Stream DOC Concentrations and Fluxes ..............................................162
  5.3.2 Hydro-Climatological Trends ...................................................................................................163
  5.3.3 Stream DOC and Discharge .....................................................................................................164
5.4 Discussion ........................................................................................................................................166
  5.4.1 Rising Air Temperature ............................................................................................................166
  5.4.2 Hydrological Changes ..............................................................................................................166
  5.4.3 Other Potential Drivers ............................................................................................................169
  5.4.4 Implications and Limitations ...................................................................................................171
5.5 References .......................................................................................................................................173

Chapter 6 Conclusions ..............................................................................................................................194

Appendices ..............................................................................................................................................197
  Appendix A Correlation matrix of topographic variables and Phase Diagrams for Chapter 1 .................198
  Appendix B An example of soil moisture data used in the analysis of chapter 2 ........................................201
  Appendix C Groundwater elevations recorded across 12 instrumented hillslopes ................................203
  Appendix D Study Site, Air Temperature and NADP Data .................................................................208
LIST OF TABLES

Table 2.1  Summary of landscape characteristics for the study catchments ..........................48
Table 2.2  Relationship between baseflow $\delta^{18}$O and the distance from channel head to the catchment outlet .................................................................49
Table 3.1  Bulk density of soil moisture monitoring locations in WS02 .................................91
Table 3.2  Summary (means) of topographic variables for instrumented hillslopes in WS02 .............................................................................................................92
Table 3.3  Mean soil moisture (coefficient of variation) during the study period ............................................................93
Table 3.4  Select characteristics of 39 storm events ................................................................94
Table 3.5  Response percentage for monitored locations .........................................................96
Table 3.6  Lag times between soil moisture, groundwater, and runoff in WS02 ..........................................................97
Table 3.7  Relationship (Spearman’s $\rho$) between topographic variables and median soil moisture lag time ($\Delta t$) .................................................................99
Table 4.1  Summary of landscape variables for study catchments ........................................138
Table 4.2  Spatial characteristics for the study hillslopes ......................................................139
Table 4.3  Summary of physical measurements and distribution of shallow groundwater stages for the study wells ....................................................140
Table 4.4  Storm characteristics for rain gauges (RG20, RG96) located in South and North Facing catchments ....................................................141
Table 4.5  Groundwater response percentages for study wells .............................................143
Table 4.6  Correlation matrix (Spearman’s $\rho$) among groundwater response variables for south facing catchments ....................................................144
Table 4.7  Correlation between topographic variables and groundwater response ..........................................................145
Table 5.1  List of recent studies reporting long-term changes in surface water DOC ..........................................................185
LIST OF FIGURES

Figure 2.1 Catchments WS01 and WS02 showing streams drainage area, and sampling points together with instrumentation. Inset shows the location of Coweeta Hydrologic Lab (Otto, North Carolina) .......................................................... 50

Figure 2.2 Boxplots showing distribution of flow path lengths for WS01 (a), and WS02 (b). For each box plot, Upper and lower whiskers represent interquartile range and red line represents the median of the distribution .............................................. 51

Figure 2.3 Boxplots and time series of precipitation δ18O (a, b), baseflow and shallow groundwater δ18O for WS01 (c, d); and baseflow and shallow groundwater δ18O for WS02 (e, f). Boxplots show median (red), interquartile range (blue). Time series show low elevation (filled circle) and high elevation (open circle) for precipitation, or baseflow (filled circle) and shallow groundwater (open circle) for WS01 and WS02. Error bars represent uncertainty in the isotopic concentrations of the water pools ........................................ 52

Figure 2.4 Interpolated contour plot of baseflow δ18O for 605 samples collected in WS01. Black dots represent discrete samples in space and time. Boxplots (above) show the temporal distribution of baseflow δ18O at each sampling point. Boxplot range is 5th to 95th percentile. Hydrograph (R) and hyetograph (P) for WS01 (right) show sampling events in red ................................................................................. 53

Figure 2.5 Interpolated contour plot of baseflow δ18O for 378 samples collected in WS02. Black dots represent discrete samples in space and time. Boxplots (above) show the temporal distribution of baseflow δ18O at each sampling point. Boxplot range is 5th to 95th percentile. Hydrograph (R) and hyetograph (P) for WS02 (right) show sampling events in red ................................................................................. 54

Figure 2.6 Scatter plot showing the relationship between spatiotemporal variability of baseflow δ18O and incremental contributing area (ICA) for both catchments. The relationships were significant at p<0.05. Range is the mid-90th (5th to 95th) percentile of baseflow δ18O measured adjacent to each hillslope as shown in figures 2.4 and 2.5 ................................................................. 55

Figure 2.7 Median of lateral inflow δ18O organized by each hillslope’s corresponding flow path lengths for WS01 and WS02. Error bar represents uncertainty in lateral inflow δ18O .................................................. 56

Figure 2.8 Test statistics (r², slope) for observed values (red filled circle) and simulated values for 10,000 random arrangements of hillslopes (black dots) for WS01 (a) and WS02 (b) .................................................. 57
Figure 3.1  Showing delineated hillslopes with landscape positions of soil moisture probes and groundwater wells in WS02 ................................................................. 100

Figure 3.2  Precipitation and runoff measured at 30 min intervals for WS02. Rainfall data were recorded at the rain gauge (RG20). Red filled circle represents flow condition prior of storm arrivals ......................................................................................... 101

Figure 3.3  Magnitude (a, b) and lag time (c, d) of soil moisture responses to selected storm events for H1. Circle diameter shows relative magnitude of response. Color shows antecedent moisture conditions (AMC) prior to the event. Light gray rectangular box represents missing data .............................................................. 102

Figure 3.4  Magnitude (a, b) and lag time (c, d) of soil moisture responses to selected storm events for H2. Circle diameter shows relative magnitude of response. Color shows antecedent moisture conditions (AMC) prior to the event. Light gray rectangular box represents missing data .............................................................. 103

Figure 3.5  Magnitude (a, b) and lag time (c, d) of soil moisture responses to selected storm events for H3. Circle diameter shows relative magnitude of response. Color shows antecedent moisture conditions (AMC) prior to the event. Light gray rectangular box represents missing data .............................................................. 104

Figure 3.6  Correlation between topographic variables and groundwater response ................................................................................................................................. 105

Figure 3.7  Hysteresis between soil moisture and runoff during two events; storm 12 (a, b), and storm 29 (c, d), for H1 and H2 ........................................................................ 106

Figure 3.8  Relationship between $\Delta s$ and storm characteristics (a), and $\Delta t$ and storm characteristics (b) for all study hillslopes. Significant Spearman’s $\rho$ correlations (P<0.05) shown in color. Storm properties include storm depth (SD), storm period (SP), mean intensity (MI), and peak intensity (PI) ......................................................................................... 107

Figure 3.9  Hysteresis between soil moisture and runoff (a, c) and soil moisture and groundwater stage (b, d) during an event (storm 12) for hillslopes H1 and H2. Runoff peaks first, followed by soil moisture and groundwater on H1 (a-b), and groundwater peaks first, followed by runoff and soil moisture on H2 (c-d). These patterns can be inferred from Table 6 using the sequences of lags ........................................................................................................ 108

Figure 4.1  Showing the map of WS02 (a), WS01 (b), WS18(c), and WS17 (d) with delineated hillslopes and landscape positions of groundwater wells ........................................................................................................ 146

Figure 4.2  Distribution of groundwater response metrics, $P_t$ (a), AR (c), $T_p$ (d), $T_{p2p}$ (e), and $S_r$ (f), to the selected storms for near stream (NS, left side of the panels) and hillslope (HS, right side of the panels) wells for south facing
catchments. Filled boxes represent WS01, and open boxes represent WS02. The NS wells (left column) and HS wells (right column) are arranged by increasing drainage area within each group.

**Figure 4.3** Distribution of groundwater response metrics, Pᵢ (a), Tᵢ (b), AR (c), Tᵢ (d), Tᵢ (e), and Sᵢ (f), to the selected storms for near stream (NS, left side of the panels) and hillslope (HS, right side of the panels) wells for north facing catchments. Filled boxes represent WS17, and open boxes represent WS18. The NS wells (left column) and HS wells (right column) are arranged by increasing drainage area within each group.

**Figure 4.4** Median groundwater response metrics, Pᵢ (a), Tᵢ (b),  AR (c), Tᵢ (d), Tᵢ (e), and Sᵢ (f) for all wells with the corresponding drainage area for south facing (black filled circle) and north facing (red filled circle) catchments.

**Figure 4.5** Spatiotemporal patterns for response metrics, Pᵢ (a) and Tᵢ (b), AR and Tᵢ (b), for the near stream (NS, top panel of each subplot) and hillslope (HS, bottom panel of each subplot) wells in the south facing catchments. The size of circle represents time (hour) for Tᵢ and Tᵢ. The NS and HS wells are arranged by increasing drainage area within each group. Gray cross represents no response during the storms. Gap represents missing data.

**Figure 4.6** Spatiotemporal patterns for response metrics, Pᵢ (a) and Tᵢ (b), AR and Tᵢ (b), for the near stream (NS, top panel of each subplot) and hillslope (HS, bottom panel of each subplot) wells in the north facing catchments. The size of circle represents amount for Pᵢ (mm) and AR (mm), and color represents time (hour) for Tᵢ and Tᵢ. The NS and HS wells are arranged by increasing drainage area within each group. Gray cross represents no response during the storms. Gap represents missing data.

**Figure 4.7** Spearman correlations (ρ) between response metrics, storm characteristics and antecedent wetness conditions for near stream (NS) and hillslope (HS) wells. Color represents significant correlations (p<0.05).

**Figure 4.8** Variation of ρmax and lmax with storm depth for near stream and hillslope wells along select hillslopes in WS01 (a, b), WS02 (c, d), WS17 (e, f) and WS18 (g, h). Color represents lmax from zero (dark blue) to 10 (light yellow).

**Figure 5.1** Trends for annual mean volume-weighted dissolved organic carbon (DOCvw) for a 25-year period (1988-2012) in WS27 at Coweeta Hydrologic Laboratory, NC. Solid red lines
show linear trends, dashed line shows the breakpoint interval (BI)(1997-2001), black error bars in the DOC_{vw} represent standard error based on the number of samples collected during the study period

**Figure 5.2** Monthly trends of volume-weighted dissolved organic carbon concentration (DOC_{vw}) for the months of April (a), June (b), September (c), and October (d) during a 25-year period (1988-2012). Dashed lines and double arrows show the duration of lengths for which trends were significant (p<0.05)

**Figure 5.3** Trends for annual dissolved organic carbon flux for a 25-year period (1988-2012) in WS27 at Coweeta Hydrologic Laboratory, NC

**Figure 5.4** Trends in annual precipitation (a), annual runoff (b), and annual runoff ratio (c), for WS27 from 1988 to 2012. Solid red lines show the SS estimates, and red dashed lines represent 95% confidence interval for the SS estimates

**Figure 5.5** Trends for monthly precipitation and monthly runoff for the months of April (a, b), June (c, d), September (e, f), and October (g, h) during a year period. Symbols represent type of data, precipitation (open circle) and runoff (filled circle). Dashed lines and double arrows show the duration of lengths for which trends were significant (p<0.05) SS estimates

**Figure 5.6** Total number of storms observed in the month of September (a), and percentage (%) of storms exceeding 75th percentile (17 mm) (b), during 1988-2008. Data provided by Laseter et al., (2012), and gap represents no storms exceeding 75th percentile for that particular year

**Figure 5.7** Raw (non-volume weighted) dissolved organic carbon (DOC) concentration from weekly and biweekly samples (n~1000) shown with instantaneous discharge at the time of sampling for all months (a), and for the individual months of April (b), June (c), September (d), and October (e). Black open circle and grey markers show study intervals 1988-2001 and 1997-2012, respectively SS estimates

**Figure A1** Correlation matrix (Pearson’s r) between five landscape variables in WS01 (a), and WS02 (b). Correlations were calculated between hillslope scale median values of landscape variables. White color represents non-significant relationships (p>0.05). Diagonal values (left to right) are correlation of landscape variable with itself. Hillslope Size
Figure A2 Isotopic composition (δ¹⁸O and δ²H) of baseflow, groundwater, soil water, and precipitation samples for both study catchments. Local meteoric water line (LMWL) and global water lines (GMWL) shown for reference. Inset shows groundwater and baseflow samples relative to LMWL. Baseflow was sampled from 33 locations along streams, groundwater was sampled from 12 shallow wells, soil water was sampled from 5 lysimeters (WS02 only) and precipitation was sampled from high and low elevation rain gauges.

Figure B1 Time series of volumetric water content for an upslope position along H1 (a), H2 (b), and H3 (c), at four depths (10, 30, 60, 100 cm) in WS02. Gaps show missing data. Color represents depths from lighter (greater) to darker (shallower).

Figure C1 Time series of runoff and rainfall (a), with groundwater stage for wells in WS02 (b-d). Gaps show missing data for a particular well.

Figure C2 Time series of runoff and rainfall (a), with groundwater stage for wells in WS01 (b-d). Gaps show missing data for a particular well and runoff.

Figure C3 Time series of runoff and rainfall (a), with groundwater stage for wells in WS17 (b-d). Gaps show missing data for a particular well.

Figure C4 Time series of runoff and rainfall (a), with groundwater stage for wells in WS18 (b-d). Gaps show missing data for a particular well.

Figure D1 Watershed 27 at Coweeta Hydrologic Laboratory in Otto, NC, USA showing 25 m contours, tree height, streams, outlet, and the climate station.

Figure D2 Trends for the annual maximum daily air temperature observed during study period (1988-2012) at CS01. Solid red line represents SS and dashed lines represents 95% confidence interval for the SS estimate.

Figure D3 Trends for annual mean concentration of [SO₄²⁻] (a), [NO₃⁻] (b), [NH₄⁺] (c), for atmospheric wet deposition collected from CS01 available via National Atmospheric Deposition Program (NADP; http://nadp.sws.uiuc.edu; NC25) for the 25 year study period (1998-2012). Solid red line represents SS and dashed lines represents 95% confidence interval for the SS estimates estimate.
CHAPTER 1

Introduction

1.1 Introduction

Forested catchments contribute significantly to water quantity and water quality worldwide [Hamilton, 2008]. Almost one-third of the world’s megacities depend on these forested catchments for their clean drinking water [Dudley and Stolton, 2003]. In the United States, 80% of streams originate from forested catchments, and these streams contribute nearly 53% of the nation’s water supply [Sedell et al., 2000]. For the southeastern US, 55% of the land is forested [Flather et al., 1989] and serves as a major source of freshwater for millions of people [Caldwell et al., 2014]. These forested catchments also provide a range of ecosystem services. Thus, forested catchments are intimately linked with our society and play a pivotal role in maintaining a sustainable habitat for the living beings.

The importance of forests on water quantity was realized as early as ca. 27-17 BC, when Vitruvius proposed that canopy cover in mountainous catchments can reduce evaporation, leading to a rise in discharge [Biswas, 1970]. However, it was not until 1909, when one of the first experiments of the catchment hydrology began to investigate the role of forests on the magnitude and timing of runoff (i.e., stream discharge per unit watershed area) for a paired catchment study in the Rio Grande National Forest near Wagon Wheel Gap, Colorado. The results from this experiment inspired several studies on the same topic and led to the development of other experimental forests such as Coweeta Hydrologic Laboratory (hereafter, Coweeta) in 1934, located in the southern Appalachian Mountains. Coweeta is
representative of many mountainous areas worldwide that are characterized by humid-temperate climates and steep landscapes overlain by deep soil mantles.

Researchers at Coweeta historically explored fundamental processes and factors that influence runoff generation in forested catchments [Hursh and Brater, 1941; Hoover and Hursh, 1941; Hursh and Fletcher, 1942]. In the early 1960s, studies at Coweeta suggested that deep soil reservoirs acted as a major contributor to runoff in the form of baseflow. This baseflow can sustain flow in forested streams between storms or during prolonged dry periods [Hewlett 1961; Hewlett and Hibbert 1963]. Around the same time, Hewlett and Hibbert [1967] suggested the variable source area concept, which proposes that active contributing areas expand and contract during storms. The study also suggested that runoff during storms is nominal in these forested catchments, and sources contributing to peak runoff are limited to relatively wet, near-stream areas. This concept was verified later by other intensive field experiments [cf., Dunne, 1978]. These studies underline the significant contribution of baseflow to runoff generation, and they also highlight the critical importance of subsurface processes related to soil moisture and shallow groundwater in mediating runoff in catchments with deep soils. Despite several decades of work at Coweeta and elsewhere, many questions about these and other hydrological processes remain unaddressed. This dissertation attempts to investigate a few of these questions that have implications for water quantity and water quality in forested catchments such as these.

Historically, studies in catchment hydrology have focused on investigating runoff generation processes during storm flow conditions, especially for small, forested headwaters, and by comparison little attention has been given to baseflow generation. Until the early
1980s, studies concentrated on understanding rainfall-runoff processes at either hillslope-scales or at the catchment outlet. How runoff varies between hillslopes and the catchment outlet was mostly ignored. Since the inception of the representative elementary area (REA) concept, studies have explored the spatial variability of runoff along streams and suggested that most of the observed variability could be attributed to topography [Woods et al., 1988; Shaman et al., 2004]. However, most of these studies analyzed discharge or stream chemistry at the catchment outlet, sub-catchment scale, or at relatively large spatial scales. Due to the focus of these studies on larger spatial scales, spatial patterns of runoff for small headwater streams were largely overlooked. However, some of these studies reported discharge measurements [Genereux et al., 1993] or solute chemistry [Likens and Buso, 2006] for few headwater streams at relatively high spatial resolution, but studies remained limited to a few sampling campaigns. Relatively few of these studies came from humid catchments that received rain throughout year with little or no snow. Thus, spatiotemporal patterns of runoff for small headwater catchments in humid climate remain understudied. Chapter 2 of this dissertation aims to investigate the patterns of runoff for paired catchments that are characterized by similar aspect, bedrock, soil type, but different topographic characteristics and different vegetation.

Studies at Coweeta and elsewhere have shown the crucial importance of forested soils. These soils are characterized with high infiltration rates and large storage capacities and play a key role in mediating runoff processes for these landscapes. Due to some of these soil characteristics, runoff generation is minimal during most of the storms as suggested by Hewlett and Hibbert [1967]. Given the important role of deeps soils for storing water in these
forested catchments, a few studies have analyzed the spatial patterns of soil moisture response to storms along hillslope. Most of these studies came from catchments where hydrographs were snow-dominated, or from catchments where the terrain was flatter and contained shallower soils than Coweeta. Furthermore, the previous studies were limited to only a few landscape positions or soil depths. A need exists to evaluate spatial patterns of responses to storms (both magnitude and timing) at multiple landscape positions and soil depths along hillslopes in these environments. How do these response patterns vary among hillslopes within a catchment for the same storm? Chapter 3 of this dissertation attempts to address some of these issues.

Studies show that spatiotemporal patterns of shallow groundwater exert strong control on runoff generation [McGlynn et al., 2004]. For small headwater catchments such as Coweeta, intimate linkages exist between shallow groundwater and runoff. Thus, in order to truly understand how catchments function and generate runoff, we need to investigate shallow groundwater dynamics in these catchments. There is a large body of literature that has investigated the spatiotemporal patterns of shallow groundwater and their associated controls [cf., Bachmair and Weiler, 2011]. However, relatively few studies have investigated the shallow groundwater response to storms (both magnitude and timing) along steep forested hillslopes in humid environments. Most of the studies that reported shallow groundwater responses to storms were conducted in catchments with shallow soils (<2 m), where runoff was snow dominated, or where the landscape was relatively flat. Thus, groundwater response patterns remain partially understood for landscapes and climates represented by Coweeta. We still need to understand how these patterns relate to topography
and storm properties for these steep catchments. How do these patterns relate to runoff during storms in space and time? Along with this major question, we also seek to answer some additional questions, such as how much rain is needed to initiate a groundwater response, and how does the requirement of rain vary with topography? Chapter 4 of this dissertation addresses some of these questions using data from four catchments at Coweeta.

Most of this dissertation revolves around hydrologic processes that influence runoff generation, but one chapter explores the temporal patterns of dissolved organic carbon (DOC) over 25 years in a deciduous catchment at Coweeta. In the past decade, there has been a flurry of studies demonstrating patterns of increasing DOC for aquatic ecosystems across the Northern Hemisphere. Most of these studies come from large water-bodies (major rivers or lakes). Long-term datasets for smaller streams are limited, and the directions of temporal trends (positive, negative or none at all) remain unclear. Long-term datasets collected at Coweeta provide an opportunity to examine DOC in such a smaller stream while evaluating the role of climate change. Chapter 5 of this dissertation makes use of long-term data to identify the temporal patterns of stream DOC and their potential drivers for a headwater stream of Coweeta.

1.2 Dissertation Outline

This dissertation is organized around four chapters, each representing a separate research investigation. Chapter 2 examines the spatiotemporal patterns of baseflow for two headwater streams of Coweeta during a two-year period. The study quantifies the role of catchment structure in mediating these patterns in space and time. The study combines
spatially intensive stream samples of stable isotope ($^{18}\text{O}$, $^2\text{H}$) with dilution gauging and geospatial analysis. The questions we seek to answer are:

(i) How does the isotopic composition of baseflow vary in space and time along these two first-order streams?

(ii) How do the internal structure and arrangement of hillslopes within these catchments relate to observed isotopic patterns in baseflow?

(iii) To what extent are the observed isotopic patterns unique to the arrangement of hillslopes within each catchment?

Chapter 3 investigates patterns of soil moisture responses to storms (magnitude and timing) for multiple landscape positions and depths along three instrumented hillslopes within one deciduous Coweeta catchment. The study determines spatiotemporal controls on these response patterns and examines how the patterns of response timing relate to groundwater and runoff responses to storms. The study uses soil moisture observations from 45 combinations of landscape position and depth distributed among three hillslopes. The questions we address here are:

(i) How do soil moisture responses to storm vary with depth, landscape position and storm characteristics?

(ii) How does topography influence the soil moisture response to storms, and how does this response vary among seasons and hillslopes?

(iii) How can relationships between soil moisture responses, shallow groundwater responses and runoff responses help characterize the hydrologic behavior of hillslopes?
Chapter 4 focuses on spatiotemporal patterns of shallow groundwater responses to storms and their controls using data from 12 instrumented hillslopes in four catchments. This study also explores the groundwater-runoff relationships during storms, and it identifies the influence of storm properties and topography on these relationships. Our specific questions are:

(i) How do shallow groundwater responses to storms vary across a range of landscape conditions in steep, forested headwaters characterized by humid and temperate climatic conditions?

(ii) How do these shallow groundwater responses relate to runoff responses?

Chapter 5 explores long-term (>20 years) temporal patterns of stream DOC concentration and flux and associated drivers for a high elevation catchment at Coweeta. The study also identifies patterns of environmental drivers such as air temperature, hydrological changes, recovery from acid rain, and nitrogen deposition, and it relates these drives to the temporal patterns of stream DOC.

The question we ask here are:

(i) What are the trends for long-term trends of DOC concentration and export in runoff over the 25-year period (1988 – 2012)?

(ii) What are the potential drivers responsible for the observed DOC trends?
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CHAPTER 2

Space-time Variability of Baseflow in two Headwater Streams of the Southern Appalachians

Abstract

Understanding the influence of catchment structure on the spatiotemporal patterns of streamflow is an area of great interest in hydrology. We investigated the combined role of spatial structure and arrangement of hillslopes in mediating the streamflow variability under baseflow conditions in first-order, forested headwater streams. The study focused on two forested catchments at the Coweeta Hydrologic Laboratory in the southern Appalachian Mountains. We used stable isotopes (\(^{18}\)O and \(^{2}\)H) of water together with stream gauging and geospatial analysis to evaluate the relationship between catchment structure and the spatial and temporal patterns of baseflow. Baseflow \(\delta^{18}\)O was variable in space and time along streams in both study catchments. In general, \(\delta^{18}\)O increased along streams from channel heads to catchment outlets in drier conditions but not during wetter conditions. Temporal variability in baseflow \(\delta^{18}\)O was associated with variability in flow path lengths along hillslopes as well as the relative arrangement of hillslopes within catchments. The strength of the landscape influence on baseflow \(\delta^{18}\)O varied through time, suggesting interactions between catchment wetness on landscape influences on baseflow. The observed relationship between internal catchment structure and spatial patterns of baseflow \(\delta^{18}\)O elucidates the role of topography in mediating runoff generation in the headwater streams of the Southern Appalachians and similar regions worldwide.
2.1 Introduction

Understanding the spatiotemporal patterns of streamflow generation and their relationship with catchment structure remain one of the key challenges in catchment hydrology [e.g., Beven 2006a; 2012; Payn et al., 2012]. Much research has focused on hydrological processes associated with streamflow generation during storms, whereas streamflow generation during baseflow conditions remains understudied by comparison [e.g., Tetzlaff and Soulsby, 2008]. In general, baseflow is the portion of rainfall that infiltrates the soil and becomes part of groundwater, gradually contributing to streamflow over relatively long durations [e.g., Freeze, 1974]. Baseflow sustains perennial streams between precipitation events and during dry conditions. Baseflow magnitude and composition directly influences stream habitat [e.g., Boulton, 2003], nutrient cycling [e.g., Meyer and Wallace, 2001], and overall functioning of the stream ecosystem [e.g., Montgomery, 1999; see review by Price, 2011].

Headwater streams constitute 70% of streams in the United States by length [Leopold et al., 1964], and they exert strong control on hydrological and biogeochemical processes of downstream aquatic ecosystems. Headwater streams can be a major source of nutrients, organic matter, and sediments to higher order streams [Gomi et al., 2002; Alexander et al., 2007]. Baseflow from these headwater streams serves as a significant source for drinking water, irrigation, and recreation for communities living downstream [Freeman et al., 2007].

Many studies have reported on spatiotemporal patterns of baseflow, magnitude [Huff et al., 1982; Woods et al., 1988; Wolock, 1995; Genereux et al., 1993; Shaman et al., 2004; Kuras et al., 2008; Payn et al., 2012], isotopic compositions [Bishop, 1991; Rodgers et al.,
2005; Tetzlaff and Soulsby, 2008; Laudon et al., 2007; Broxton et al., 2008; Brooks et al., 2012] and stream chemistry [Wolock et al., 1997; Zimmer et al., 2013; Blumstock et al., 2015] across spatial scales. In general, these studies focused on measurements of streamflow and synoptic observation of tracers (e.g., $^{18}$O, $^2$H, Cl$^-$) to provide insights into the longitudinal variability of sources, flow paths, and hydrologic processes that influence the formation of baseflow within and among catchments. Together, these studies provided important knowledge about baseflow generation in headwater catchments, particularly catchments ranging from one to $10^3$ km$^2$ in size with many focused on catchments dominated by snow. In temperate, humid mountain regions, such as those of the southern Appalachian Mountains, first-order headwater catchments can be as small as 10 ha (0.1 km$^2$) in size. These mountain headwaters are often forested, and snow is normally of minor importance in the annual water balance. In these relatively small, rain dominated headwaters and in similar catchments worldwide, our understanding of baseflow dynamics is incomplete.

Topography and geology can be important controls on baseflow variability at spatial scales ranging from 1 to $10^3$ km$^2$ [Genereux et al., 1993; Kuras et al., 2008; Payn et al., 2012]. For headwater catchments in general, strong relationships exist between catchment structure and streamflow generation [Dunne and Black, 1970; Anderson and Burt, 1978; Beven, 1978; Beven and Kirkby, 1979; Tetzlaff et al., 2009; Jencso et al., 2009; Nippgen et al., 2011]. Most of these studies focused on large spatial scales, and a few of them [Jencso et al., 2009; Jencso and McGlynn and 2011] considered the role of hillslope characteristics (e.g., contributing area, flow path length, gradient, vegetation height) in mediating streamflow. Most of these studies focused on snow-dominated systems, and additional work
is needed to understand how catchment structure influences streamflow variability in systems where snow is less important.

Stable isotopes are well-established tools for understanding sources, flow paths and residence times of natural waters at various spatial and temporal scales [Sklash and Farvolden, 1979; McDonnell et al., 1991; Rose, 1996; Kirchner et al., 2001; Uhlenbrook et al., 2002; Weiler et al., 2003; Laudon et al., 2004; see review by Tetzlaff et al., 2015]. Isotopic studies have also helped to reveal relationships between hydrologic responses and catchment structure [McGlynn et al., 2003; McGuire et al., 2005; Laudon et al., 2007]. Other field studies [e.g., McGlynn et al., 2004] suggest that as catchment area increases, hydrologic response at the outlet might be an inaccurate depiction of hydrologic processes upstream, and equifinality may further confound the ability to draw valid conclusions based on observations made at the catchment outlet [Beven, 2006b]. To address such issues and to gain insight into spatiotemporal patterns of baseflow generation and relationships to spatial characteristics of catchments, we evaluated the isotopic composition of baseflow by sampling streams from their channel heads to their outlets. Our general goal was to investigate the role of hillslope structure and arrangement in mediating baseflow patterns within a catchment.

The specific objectives of this study were to assess the spatiotemporal variability of baseflow in two small (approximately 10 ha), forested headwater catchments and to quantify the role of internal catchment structure in mediating patterns of baseflow. We combined spatially intensive sampling of stable isotopes ($^{18}O$, $^2$H) in catchment waters with dilution stream gauging and geospatial analysis, using a two-component mixing model to estimate the isotopic composition of lateral hillslope inflows along stream reaches, and exploring links
between hillslope spatial characteristics and observed patterns of stream water isotopes in forested headwaters. We address the following questions: (i) How does the isotopic composition of baseflow vary in space and time along two first-order streams in the southern Appalachian Mountains? (ii) How do the internal structure and arrangement of hillslopes within these catchments relate to observed isotopic patterns, and are these patterns unique to each catchment?
2.2 Study Site

Fieldwork was conducted at the Coweeta Hydrologic Laboratory (hereafter, Coweeta), located in the southern Appalachian Mountains of western North Carolina, US (35°03’N, 83°25’W; Figure 2.1). Coweeta contains 26 gauged catchments covering a total of 21.85 km² and ranging in elevation from approximately 680 m to 1500 m above mean sea level. Coweeta Creek, to which these catchments eventually drain, lies within the headwaters of the Tennessee River.

Coweeta’s climate is classified as Marine and Humid Temperate under Koppen’s climate system with frequent short duration rainfall events distributed year-round [Swift et al., 1988]. Mean annual precipitation at a low elevation climate station (CS01) averages 1791 mm for the 75-year period 1937-2011. Mean annual air temperature at CS01 is 12.6 °C. Soils in our study catchments are predominantly ultisols and inceptisols underlain by deeply weathered saprolite. The Coweeta basin has two major bedrock formations, both metamorphic - Tallulah Falls and the Coweeta Group [Hatcher, 1971]. Tallulah Falls consists mostly of pelitic, schists and metavolcanic rocks. The Coweeta Group consists mainly of quartzites, gneisses, biotite, schists and metasandstones [Hatcher, 1974; 1979].

This study focused on two adjacent, south-facing catchments that include a broadleaf deciduous forest (WS02) and an evergreen coniferous forest (WS01) (Figure 2.1). The catchments are part of a long-term experiment evaluating effects of forest conversion on catchment water balances [Swank and Douglass, 1974]. WS02 was abandoned to secondary ecosystem succession around 1920 and serves as a reference for multiple paired catchment studies at Coweeta. WS01 was completely cleared in 1950 and replanted with white pine.
Landscape characteristics for each catchment are summarized in Table 1. Both catchments share similar drainage areas (DA), elevations, soils and bedrock geology.

The US Forest Service (USFS) has measured discharge continuously since 1934 at the outlet of each catchment using V-notch weirs. The month of February 2013 was marked by extremely wet conditions and high discharge. Unrealistically high discharge measurements in WS02 during this month led to the exclusion of February 2013 discharge data from this analysis. Climatological records for precipitation, air temperature and relative humidity have been measured by the USFS at climate stations near these catchments (CS01, CS21). Station CS21 is located at an elevation of 817 m on a lateral ridge between the two study catchments, and CS01 is situated in a valley approximately 400 m away from the outlet of WS01 at an elevation of 685 m.
2.3 Methods

2.3.1 Geospatial Analysis

Light detection and ranging (LIDAR) data were collected in 2010 by the National Center for Airborne Laser Mapping (NCALM). Datasets provided by NCALM included 1 m x 1 m digital elevation models (DEMs) of the bare earth surface and the top of the vegetation canopy. We resampled the 1 m x 1 m bare earth DEM to 10 m resolution to avoid the confounding effects of microtopography on geospatial algorithms used to estimate subsurface drainage patterns from surface topography [Seibert and McGlynn, 2007]. To delineate the stream network, we used a drainage area threshold of 2.8 ha, which closely matched our field measurements of channel head locations for each catchment. We used the multidirectional flow accumulation algorithm of Seibert and McGlynn [2007] to estimate the drainage area (DA) contributing to each 10 m pixel. Using the algorithms of Grabs et al. [2010] in SAGA GIS [Bohner et al., 2008], we delineated hillslopes within each catchment, which were defined as the topographically delineated areas contributing to stream reaches between discrete sampling points. In the case of the channel head sampling point, the contributing area was defined as the entire catchment area upstream of that point. Landscape variables computed at 10 m resolution included: elevation, slope, DA, flow path length to the stream, and gradient to creek (GTC). Later, we aggregated pixel-based landscape variables to obtain hillslope-scale median values contributing to the sampling reaches along the streams.

For each hillslope, defined as the local area contributing to the stream between sampling points, we used DA to compute hillslope size and incremental contributing area (ICA) with hillslope size (ΔDA) defined for each sampling point as
\[ \Delta DA_x = DA_x - DA_{x+1} \]  

where \( x \) represents a sampling point on the stream, \( x+1 \) is the next sampling point upstream, \( DA_x \) is the catchment drainage area for sampling point \( x \), and \( DA_{x+1} \) is the catchment drainage area for sampling point \( x+1 \). We then computed ICA for each sampling point along stream as

\[ ICA_x = \frac{\Delta DA_x}{DA_{x+1}} \]  

where \( x \) and \( DA \) are defined following Equation (1). Variables \( DA \) and ICA depend upon the position and spacing of sampling locations along the stream. We confirmed that \( DA \) and ICA were not sensitive to the spatial resolution of the DEM by comparing results from analyses performed on 1 m, 5 m, and 10 m DEMs (Kruskal-Wallis, \( p>0.05 \)). Hereafter, references to catchment structure pertain to both hillslope-scale landscape characteristics (e.g., flow path lengths) and the arrangement (ICA) of hillslopes along the stream within a catchment.

2.3.2 Isotopic Measurements

We sampled water from three pools: precipitation, baseflow (i.e., stream water during baseflow conditions), and shallow groundwater each month from June 2011 to June 2013 and analyzed samples for stable isotopes of water (\(^{18}\)O, \(^{2}\)H). Baseflow samples were collected at points located approximately 25 m apart along each of the two streams between each outlet and its channel head. This sampling design was intended to capture a wide range of local stream and hillslope conditions within each catchment. During each monthly sampling visit, baseflow samples for each catchment were collected during a two-hour period on the same day. No detectable changes in runoff were noted at the catchment outlet during the two-hour periods.
Precipitation samples were collected in composite rainfall collectors located at the WS01 weir and at CS21 (Figure 2.1). Collectors were constructed from 10 cm diameter polycarbonate rain gauges protected against evaporation by foil-faced insulation on the outside and a thin (5-10 mm) layer of mineral oil inside. After sampling, precipitation collectors were cleaned and dried, and new mineral oil was added. Precipitation samples were collected every 1-4 weeks depending on rainfall amount, and total water depth in the collector at the time of sampling was used to compute depth-weighted averages of precipitation $^{18}$O and $^2$H for each month. Frozen precipitation samples were rare and not included in the analysis.

Shallow groundwater was sampled monthly from 12 wells located across both catchments. In each catchment, three hillslopes of different sizes were instrumented with two wells each, a near-stream well and a hillslope well. Wells were made of 3.8 cm inner-diameter Poly vinyl chloride (PVC) conduit screened from approximately 10 cm below ground to the completion depth. Completion depths for all wells ranged from 0.9-3.5 m below the surface. Well screens were installed using a solid steel rod inserted into the screen and driven with a sledgehammer through soil and saprolite until refusal at the bedrock surface. A gas-powered auger whose bit matched the outer diameter of the PVC screening was used in some cases to probe for suitable locations. Bentonite clay was packed around each well at the soil surface to prevent surface runoff or direct precipitation from entering wells. Wells were purged prior to sampling and allowed to recharge. Samples were collected from the recharge water using a peristaltic pump (Geotech Environmental Equipment Inc., Denver, CO) with dedicated PVC sampling tubes installed in each well.
All water samples for isotopic analysis were collected in 20 mL high-density polyethylene (HDPE) vials sealed with a cone top cap to eliminate headspace and avoid isotopic fractionation. Samples were stored in a cool place until analyzed in the lab at the NC State University. At the time of analysis, samples were transferred to 2 mL glass vials and analyzed using a cavity ring down laser spectrometer (Model L2120i, Picarro Inc., Santa Clara, CA, ±0.05 ‰). Isotopic compositions ($\delta^{18}$O) were reported in per mille (‰) relative to a standard as $\delta^{18}$O = ($R_{\text{sample}}/R_{\text{std}} - 1$)*1000, where $R_{\text{sample}}$ and $R_{\text{std}}$ are $^{18}$O / $^{16}$O ratios for the sample and lab standards, respectively. Internal lab standards were calibrated against International Atomic Energy Agency standards, VSMOW2 (0 ‰ $\delta^{18}$O, 0 ‰ $\delta^2$H), GISP (-24.76 ‰ $\delta^{18}$O, -189.5 ‰ $\delta^2$H) and SLAP2 (-55.50 ‰ $\delta^{18}$O, -427.5 ‰ $\delta^2$H). We assessed overall uncertainty in the isotopic analysis as the sum of accuracy (mean absolute difference between the measured and calibrated values of the duplicated blind unknown standards) and precision (mean standard deviation of the measured values of duplicated blind unknown standards). Total uncertainty was ±0.14 ‰ for $\delta^{18}$O and ±1.76 ‰ for $\delta^2$H. Given the relatively large uncertainty in $\delta^2$H compared to the range of values observed at Coweeta, $\delta^2$H data were only used to develop a local meteoric water line and to assess the potential for evaporative enrichment of catchment waters.

2.3.3 Lateral Inflows of $\delta^{18}$O

We employed a simple mass balance approach to estimate $\delta^{18}$O of net lateral inflows. The approach involved dilution gauging [Day, 1977] to develop an empirical relationship between drainage area and discharge combined with a linear mixing model of $\delta^{18}$O. On three separate dates (June 2012, June 2013 and October 2013), we used dilution gauging to
estimate discharge at 50-100 m intervals along streams in both study catchments. Temperature and conductivity were measured using a conductivity probe (Model Professional Plus, YSI Inc., Ohio, US) positioned in the thalweg of the stream and recording at 2 sec intervals. Discharge at a given location along a stream \( Q_i \) was calculated as

\[
Q_x = \frac{M_t}{\int_0^t C(\tau)d\tau} \tag{3}
\]

where \( C(\tau) \) is the concentration [Cl\(^-\)] at location \( x \) for time variable \( \tau \) starting at time 0 (time of tracer injection) and ending at \( t \) (time at which conductivity returns to the initial base value) and \( M_t \) is the mass of [Cl\(^-\)] injected into the stream. Each set of dilution gauging measurements lasted 10-14 hours per catchment, and we used the continuous record of discharge at the outlet of each catchment to confirm that flow remained steady during each set of measurements.

The dilution gauging measurements were used to develop empirical power functions for each of the three sampling dates, relating drainage area at a point along the stream to the fraction of total discharge measured by the weir at the catchment outlet. We combined the empirical power functions, whose \( r^2 \) values ranged from 0.70 to 0.97, with daily discharge measured at the outlet weir to estimate daily discharge at each stream sampling point. An empirical function was assigned to each catchment on each sampling date based on the dilution gauging event whose discharge most closely matched discharge on the sampling date. For each stream reach, net lateral inflow was calculated as the difference between estimated discharge at the upstream and downstream end of each stream reach (Equation 1).

We combined estimated discharge and \( \delta^{18}O \) for each stream sampling point with estimated lateral inflow to compute the isotopic composition of net lateral inflow \( C_i \) from
each hillslope to an individual sample reach as

$$C_i = \frac{Q_{x+1}C_{x+1} - Q_xC_x}{Q_{x+1} - Q_x}$$  \[4\]

where C and Q represent $\delta^{18}\text{O}$ (‰) and discharge (L sec$^{-1}$), respectively, for a sample reach, and indices $x$ and $x+1$ represent upstream and downstream sampling points of a reach. Subscript $i$ denotes lateral inflow. We used the standard method [e.g., Taylor, 1982; Genereux, 1998] to estimate the uncertainty of lateral inflows $\delta^{18}\text{O}$ (hereafter, lateral $\delta^{18}\text{O}$) for each hillslope contributing to the sample reach for each set of monthly samples. Uncertainty of lateral $\delta^{18}\text{O}$ was computed for each hillslope for the entire study period. We acknowledge the potential for hillslope area to confound our comparison of lateral $\delta^{18}\text{O}$ and hillslope spatial characteristics, since hillslope area factors into the computation of lateral $\delta^{18}\text{O}$ and has the potential to influence landscape variables. However, we verified that hillslope area was only weakly correlated with flow path length for WS02 ($r = 0.52$, $p = 0.06$) and WS01 ($r = 0.48$, $p = 0.04$). With this in mind, a comparison of lateral $\delta^{18}\text{O}$ and hillslope-scale landscape variables still serves to elucidate the influence of landscape characteristics on baseflow dynamics. To assess landscape influence on the temporal variability of baseflow $\delta^{18}\text{O}$ within sample reaches, we computed the mid-90th percentile range (difference between 5th and 95th percentile) of baseflow $\delta^{18}\text{O}$ for sample reaches and compared the range to ICA of the contributing hillslope.

2.3.4 Assessing the Influence of Hillslope Arrangement

We used a model-data fusion approach [See, 2008] and Monte-Carlo simulation to test the influence of hillslope arrangement within each catchment on spatial patterns of baseflow $\delta^{18}\text{O}$. Specifically, to test whether the relative arrangement of hillslopes within a
catchment affected the pattern of isotopic enrichment observed during some months, we randomized the relative arrangement of actual hillslopes within each of the catchments and simulated baseflow $\delta^{18}$O at each sampling point using Equation 4. For each catchment, we selected one month with a strong pattern of downstream enrichment of baseflow $\delta^{18}$O: March 2012 for WS01 and April 2012 for WS02. For each catchment, we randomly permuted the position of hillslopes along the streams. For each of 10,000 random permutations, we compared baseflow $\delta^{18}$O to distance upstream of the weir using linear least squares regression and computed the slope (i.e., isotopic enrichment per unit distance) and goodness of fit (i.e., $r^2$) of the relationship. Both of these test statistics were used as a means to assess the enrichment patterns of baseflow $\delta^{18}$O along the stream for each of the 10,000 realizations. Using a convex hull approach in MATLAB 13a (Mathworks Inc., Boston, MA), we estimated whether or not the slope and $r^2$ of the actual enrichment pattern fell within the 95% confidence interval of the bivariate distribution of 10,000 pairs of test statistics.
2.4 Results

2.4.1 Spatial Characteristics of Catchments and Hillslopes

Study catchments shared some similar spatial characteristics (Table 2.1) but their internal structure and the arrangement of their hillslopes differed substantially (Figures 2.2, A1). In general, WS01 was more dissected than WS02. In WS01, most hillslopes were relatively small (<1 ha) and were similarly sized (hillslope area $\sigma^2 = 0.20$ ha). In contrast, hillslopes in WS02 were more variable in size (hillslope area $\sigma^2 = 0.59$ ha) with more larger hillslopes (>1 ha) than WS01. Hillslopes in WS01 were steeper than those in WS02 (Wilcoxon p=0.02; Figure A1). In both catchments, several of the hillslope-scale landscape variables were correlated with one another (Figure A1).

Distributions of flow path lengths along streams were significantly different between catchments (Figure 2.2). In general, hillslopes in the upper reaches of the catchment were dominated by long flow paths, and hillslopes in the lower reaches of the catchments were dominated by short flow paths (Figure 2.2). Most notably, we found large spatial variability in the distribution of flow paths lengths along the hillslopes in the upper reaches of the catchment compared to lower reaches of the catchment. The transition from long flow path-dominated hillslopes to short flow path-dominated hillslopes was more gradual in WS02 than WS01. Overall, flow paths in WS01 were shorter than those in WS02.

2.4.2 Catchment Water Balance and Isotopic Compositions

The long-term climate station at Coweeta received a total of 3894 mm of precipitation from June 2011 to June 2013, or an average of 1869 mm yr$^{-1}$. Notably, January 2013 experienced 425 mm of precipitation, which was a single-month record for 81-years of data.
at CS01. Mean monthly precipitation at CS01 was 156 mm. For WS01 1170 mm of runoff occurred from June 2011 to June 2013, or an average of 511 mm yr\(^{-1}\) (1.40 mm day\(^{-1}\)). For WS02 1479 mm of runoff occurred during the study period, or an average of 715 mm yr\(^{-1}\) (1.96 mm day\(^{-1}\)). The difference in runoff between pine (WS01) and deciduous (WS02) catchments has been attributed to the phenological and eco-physiological differences between forest types in the two catchments [Swank and Douglass, 1974].

Precipitation \(^{\delta^{18}}\)O samples (n=46) showed high temporal variation at both low and high elevation sampling locations (Figure 2.3). Average monthly depth-weighted isotopic compositions were -5.02 ‰ and -5.16 ‰, for low and high elevations respectively. Neither the distributions of monthly precipitation \(^{\delta^{18}}\)O at high and low elevations nor their medians were significantly different (2-sample Kolmogorov–Smirnov test p>0.05, Wilcoxon p > 0.05, Figure 2.3a). Similarly, no significant difference was noted in the median of monthly precipitation recorded between high-elevation and low-elevation rain gauges (Wilcoxon p>0.05). In addition to monthly depth-weighted samples, weekly precipitation \(^{\delta^{18}}\)O samples collected from June to August 2012 did not exhibit any significant elevation effect. Thus, we conclude that no significant elevation effects on the amount or isotopic composition of monthly precipitation existed during the course of this study.

In general, winter precipitation was depleted in \(^{18}\)O relative to summer precipitation (Figure 2.3b). We used depth-weighted precipitation \(^{\delta^{18}}\)O and \(^{\delta^{2}}\)H to generate a local meteoric water line (LMWL) for the study period, which took the form 8.03*\(^{\delta^{18}}\)O+14 (r\(^{2}\) =0.95, Figure A2). The slope of the LMWL was similar to that of the global meteoric water line (GMWL) and representative of water vapor originating in humid environments [Clark
and Fritz, 1997]. However, the intercept of the LWML was greater than the intercept of the GWML, suggesting that moisture sources of events were altered during transport from their origins [Clark and Fritz, 1997]. Catchment waters generally fell along or to the left of the LMWL and did not show evidence of evaporative enrichment (Figure A2). During 2012 and 2013, 30 shallow (<60 cm) soil pore water samples collected periodically from five porous-cup lysimeters installed in WS02 did not show any evaporative enrichment relative to the LMWL (Figure A2).

In general, the isotopic composition of catchment waters differed significantly from that of precipitation. More specifically, precipitation $\delta^{18}O$ was greater than baseflow and shallow groundwater $\delta^{18}O$. For the study period as a whole, median baseflow $\delta^{18}O$ was significantly different from precipitation $\delta^{18}O$ (Wilcoxon $p=0.007$) for both catchments (Figure 2.3). As with precipitation, baseflow was isotopically lighter during the winter than during the summer (Figure 2.3). Streams in both catchments originated from perennial seeps that were relatively depleted in $^{18}O$.

More than 300 samples of shallow groundwater collected in WS01 and WS02 during the study period exhibited similar seasonal patterns of winter depletion and summer enrichment of $^{18}O$ (Figure 2.3). For both catchments, the medians of groundwater $\delta^{18}O$ were not significantly different from one another (Wilcoxon $p>0.05$). Groundwater $\delta^{18}O$ was more variable than stream $\delta^{18}O$ in both catchments during the study period (Figure 2.3). At the catchment scale, the relationship between stream $\delta^{18}O$ and groundwater $\delta^{18}O$ were unique to each catchment (Figure 2.3). Estimated lateral inflow $\delta^{18}O$ from hillslopes had a median value of -5.89 ‰ for WS01 and a median value of -6.0 ‰ for WS02. Lateral inflow $\delta^{18}O$
was significantly lighter than precipitation $\delta^{18}O$ (Wilcoxon $p < 0.05$), but it was not significantly different from baseflow or shallow groundwater $\delta^{18}O$.

2.4.3 Spatiotemporal Patterns of Baseflow $\delta^{18}O$

More than 1000 baseflow samples collected along streams in WS01 and WS02 revealed unique patterns of $\delta^{18}O$, which were highly variable in space and time for the study period (Figures 2.4, 2.5). In WS01, the temporal variability of baseflow $\delta^{18}O$ declined significantly moving from the channel head to the outlet ($r=0.79$, $P<0.001$; Figure 2.4). In WS02, we observed greater temporal variability in baseflow $\delta^{18}O$ than in WS01, but the strength of declining pattern from the channel head to the outlet was weaker than WS01 ($r=0.59$, $P=0.02$; Figure 2.5). In both catchments, especially in the upstream-most reaches, we observed large temporal variability in baseflow $\delta^{18}O$, with the 5th to 95th percentile range of $\delta^{18}O$ for those reaches varying from 0.86 ‰ (WS01) to 0.93 ‰ (WS02).

The spatiotemporal patterns of baseflow $\delta^{18}O$ along both streams depended on the hydrologic conditions (i.e., the wetness state) of the catchment, which we evaluated for both catchments by relative baseflow throughout the year. During the driest months of the year (July to September) baseflow $\delta^{18}O$ was indistinguishable from groundwater $\delta^{18}O$ in each catchment (Figures 2.3, 2.4, 2.5). As the catchments became wetter in the fall and winter (October to December), we observed increasing spatial variability in baseflow $\delta^{18}O$ along the streams, and this pattern was more pronounced in WS01 than WS02 (Figures 2.4, 2.5). After multiple consecutive wet months, baseflow samples in reaches near the catchment outlet were more enriched in $^{18}O$ than baseflow samples from reaches near the channel head, especially in WS01. In contrast, highly depleted rainfall in February 2012 produced relatively
depleted baseflow along the stream, with the effect being more pronounced in WS01 than WS02 (Figures 2.4, 2.5). Furthermore, during wet periods (e.g., December 2012 – March 2013), baseflow was highly enriched in $^{18}$O for multiple months along streams in both catchments, and it was almost indistinguishable from groundwater $\delta^{18}$O during this period (Figures 2.3, 2.4, 2.5).

Baseflow $\delta^{18}$O generally increased along streams from the channel head to the outlet of both catchments. However, the strength of this downstream enrichment, measured by slope and $r^2$, varied considerably (Table 2.2). Both catchments exhibited strong downstream enrichment during some months, but significant correlations occurred more frequently in WS01 than in WS02.

2.4.4 Landscape Controls on Baseflow $\delta^{18}$O and Lateral Inflow $\delta^{18}$O

We identified relationships in each watershed between the temporal variability in baseflow $\delta^{18}$O for a sampling reach and ICA of the reach (Figure 2.6). We also found that the sample reaches with the greater temporal variability in baseflow $\delta^{18}$O were flanked by hillslopes (approximately 1 ha) with high ICA values and more internal variability in flow path lengths (Figures 2.2, 2.4, 2.5, 2.6). Some of the samples reaches (e.g., 425 m in WS01, 325 m in WS02; Figures 2.2, 2.4, 2.5) that exhibited more temporal variability in baseflow $\delta^{18}$O were adjoined by large but steep hillslopes (i.e., small ratio of flow path length to GTC).

The estimated $\delta^{18}$O values of lateral inflows were indistinguishable from precipitation for all but the largest hillslopes. In particular, hillslopes larger than 1 ha with median flow paths longer than 150 m had estimated values of lateral $\delta^{18}$O that were significantly lighter than precipitation (Figure 2.7). Lateral $\delta^{18}$O estimates for individual months and hillslopes
exhibited large uncertainties (>2 ‰) that were inversely proportional to hillslope size and related to our method for estimating lateral δ^{18}O (Equation 4). These large uncertainties prevented us from assessing the significance of topographic influences on monthly estimates lateral δ^{18}O.
2.5 Discussion

2.5.1 How do Hydrologic Conditions Affect the Spatiotemporal Variability of Baseflow $\delta^{18}O$?

Study catchments exhibited spatiotemporal variability in baseflow $\delta^{18}O$ along streams during the 2-year period. Our results suggest that the observed spatiotemporal variability in baseflow $\delta^{18}O$ is due in part to hydrologic conditions, which is to say the relative wetness of the catchments at different times of the year. During drier months (July-September), we observed relatively homogenous and depleted baseflow $\delta^{18}O$ with a mean value of -6.01 ‰ ($\sigma=0.12$) for WS02, which was close to the mean value of -6.22 ‰ for groundwater $\delta^{18}O$ in that catchment. During drier months, baseflow rates were low, often falling below 1 mm day$^{-1}$, suggesting that hillslopes were most likely hydrologically disconnected and only a small fraction of the catchment was contributing actively to baseflow in the stream [Jencso and McGlynn, 2011]. Given what our dilution gauging results revealed about the strong relationship between incremental increases in baseflow and contributing area, it is possible that baseflow was predominantly supplied by a few large hillslopes acting as reservoirs and releasing stored water into the stream during dry periods [Hewlett, 1961; Jencso et al., 2009].

As the catchments transitioned from dry to wet, baseflow $\delta^{18}O$ became more variable along each of the streams. This increasing variability during the dry-to-wet transition may reflect non-uniform expansion of the connected catchment area contributing actively to baseflow in the stream [Nippgen et al., 2015]. It is likely that hillslopes with different isotopic signatures (Figure 2.7) activate at different times during the wet-up period and may contribute to an increase in observed spatial variability of baseflow $\delta^{18}O$. During the wettest times of the year, $\delta^{18}O$ of baseflow and shallow groundwater increased in both catchments.
(Figures 2.3, 2.4, 2.5). This simultaneous enrichment of baseflow and groundwater $^{18}$O suggests replacement of depleted groundwater by precipitation that was relatively enriched in $^{18}$O during the wettest part of the study period. This replacement of older water with relatively enriched $^{18}$O suggests the role of translatory flow in these catchments as suggested by Hewlett and Hibbert’s [1967]. The temporal variability of baseflow $\delta^{18}$O along the stream declined as drainage area increased, a dampening phenomenon that has been reported in other studies and linked to longer residence times [Rodgers et al., 2005].

Few studies have documented patterns of baseflow $\delta^{18}$O at the spatial and temporal scales presented here. In a larger (187 km$^2$) forested catchment in Georgia (USA), Rose [1996] found a range of 2.3 ‰ (n=27) for baseflow $\delta^{18}$O between the weir and channel head over a two-year period. Rodgers et al. [2005] sampled baseflow $\delta^{18}$O on a weekly basis at the weirs of six catchments that varied in size from 1.3 km$^2$ to 233 km$^2$ and represented different type of land use, soil, and geology in northeastern Scotland. They found baseflow $\delta^{18}$O ranges of 0.74 ‰ to 1.68 ‰ (n, not given), and similar ranges were observed by Tetzlaff and Soulsby [2008] in the same region. Broxton et al. [2009] found baseflow $\delta^{18}$O ranges of about 2 ‰ (n = 134) for 15 catchments in New Mexico varying in size from 0.1 to 14 km$^2$. The spatiotemporal variability observed by other studies is relatively high compared to the overall range of 1.4 ‰ (n=983) that we observed in baseflow at Coweeta. Although multiple hydroclimatic and landscape structure, and experimental design factors influence baseflow $\delta^{18}$O among sites, these results suggest that opportunities exist to incorporate isotopic data into cross-site syntheses to better understand general controls on baseflow dynamics across multiple sites.
2.5.2 How do the Structure and Arrangement of Hillslopes within Catchments Affect Baseflow $\delta^{18}O$?

We observed significant relationships between spatial and temporal measures of baseflow $\delta^{18}O$ variability and internal catchment structures (Figures 2.6, 2.8). Other studies have indicated that the temporal variability of stream $\delta^{18}O$ can be related to the age or residence time of water [Rodhe et al., 1996; Tetzlaff et al., 2009]. Studies show that the ratio of flow path length to GTC is an approximation to hydraulic gradient that influences the rate of movement of subsurface flow [Jencso and McGlynn, 2011], and is positively correlated with the residence time of water [McGuire et al., 2005]. In other words, smaller the ratio of flow path length to GTC, shorter the residence time. In our study catchments, the ratio of flow path lengths to GTC and flow path length are highly correlated (Figure A1). Thus, the greater temporal variability observed in baseflow $\delta^{18}O$ for some sample reaches adjoined by hillslopes with short median flowpaths (Figure 2.2; e.g., 425 m WS01, 250 m WS02) could be attributed to short residence times of water along these hillslopes.

The relationships between spatiotemporal variability of baseflow $\delta^{18}O$ along sample reaches and ICA of adjacent hillslopes suggests that the position of a given hillslope within a catchment influences the patterns of baseflow $\delta^{18}O$ along the stream (Figure 2.6). Given the functional relationship between drainage area and discharge for streams at Coweeta and the definition of ICA as the ratio of local contributing area of a reach to total upstream catchment area, ICA can be thought of as the potential for an individual hillslope to alter stream $\delta^{18}O$, given a sufficiently distinct lateral inflow $\delta^{18}O$ signal. To alter the stream’s isotopic composition, the adjacent hillslope must be large enough to produce sufficient amount of
lateral flow, and the isotopic composition of that water must differ substantially from water already in the stream. The relative position of the hillslope along the stream (i.e., closer to the channel head or closer to the weir) also affects the ability of a hillslope to alter the isotopic composition of stream water. Due to relatively low flow in upstream reaches near the channel head, it is easier for hillslopes along these reaches to alter stream isotopic composition than for hillslopes adjacent to downstream reaches where flows are typically greater. This effect, which is also described by rearranging Equation (4) to solve for $C_{x+1}$, may explain large spatiotemporal variability observed in the upstream reaches compared to downstream reaches.

Lateral inflow $\delta^{18}O$ was less variable for hillslopes with long flow paths (median flow path $>150$ m) and fell within the range of observed baseflow $\delta^{18}O$ (Figures 2.4, 2.5, 2.7). The only exception to this condition included large and steep hillslopes that contained relatively short flow paths. The reduced variability in lateral $\delta^{18}O$ may be attributed to greater storage on these large hillslopes [Tetzlaff et al., 2014]. Conversely, smaller hillslopes with relatively short flow paths would have less capacity to store water and dampen the precipitation $\delta^{18}O$ signal through mixing. Although smaller hillslopes may transmit precipitation $\delta^{18}O$ signals more readily than larger hillslopes, it may be more difficult for them to influence baseflow in the stream, since the magnitudes of their lateral inflows tends to be small relative to streamflow.

Our observations from Coweeta suggest that observed patterns of baseflow $\delta^{18}O$ are unique to the arrangement of hillslopes within catchments (Figure 2.8). We tested this claim for Coweeta using a Monte Carlo simulation to test the effects of randomly permuting the
position of hillslopes along streams in each study catchment. In each catchment, the 10,000 random permutations yielded a bivariate distribution of test statistics (slope and $r^2$) that differed from the slope and $r^2$ observed in the field (Figure 2.8). For WS01, we found that the observed $r^2$ (0.73) and slope (-0.05 ‰ 100 m$^{-1}$) in longitudinal baseflow $\delta^{18}$O enrichment fell outside of the 95% confidence interval of the bivariate distribution of $r^2$ (median $r^2 = 0.11$) and slope (median slope -0.04 ‰ 100 m$^{-1}$) for randomly arranged hillslopes. For WS02, the observed $r^2$ (0.84) and slope (-0.08 ‰ 100 m$^{-1}$) in longitudinal baseflow $\delta^{18}$O enrichment fell at about the 88th percentile of the bivariate distribution of $r^2$ (median $r^2 = 0.30$) and slope (median slope = -0.06 ‰ 100 m$^{-1}$) for randomly arranged hillslopes. For both catchments, the observed pattern of $^{18}$O enrichment was stronger (i.e., greater slope and $r^2$) than the average pattern generated by randomly arranged hillslopes. The simulation results demonstrate that observed patterns in baseflow $\delta^{18}$O enrichment are intimately linked to the unique arrangement of hillslopes in the study catchments. Each hillslope possesses a unique combination of several landscape characteristics (e.g., length of flow paths, flow path gradient), and has a unique ability to alter the isotope composition of baseflow in its adjoining reach, depending upon internal characteristics of the hillslope and its relative position within the catchment. Overall, these results indicate that the internal catchment structure, including the arrangement of hillslopes within a headwater catchment can influence patterns of baseflow $\delta^{18}$O. These results support a growing body of work suggesting that hydrologic response is inextricably linked to catchment structure [McGuire et al., 2005; Laudon et al., 2007].
2.5.3 Implications

Using stable isotopes of water ($^{18}$O), this study advances our understanding of how streamflow varies in space and time by extending observations from the catchment outlet into the catchment itself (Figures 2.4, 2.5). Our results corroborate previous findings that streamflow responses measured at a catchment outlet may not accurately represent the complexity of upstream processes [McGlynn et al., 2004]. Moreover, our results have implications for isotope-based hydrograph separation techniques, which generally assume that baseflow is homogenous in space within a catchment [cf., Buttle, 1994]. Minor differences in baseflow $\delta^{18}$O can drastically alter the hydrograph separation results [McDonnell et al., 1991; Genereux, 1998]. These results further suggest exercising caution while using isotope hydrograph separation methods for small headwater catchments such as here.

These results also help elucidate the role of hillslopes in mediating spatial patterns of baseflow through time within a catchment. Our work shows that both hillslope characteristics and their arrangement within a catchment can influence streamflow generation during baseflow conditions. It complements other work linking landscape controls to hillslope-stream connectivity [Jencso et al., 2009] and linking connectivity to water quality [McGlynn and McDonnell, 2003; Jencso et al., 2010; Pacific et al., 2010]. Recognizing the structural controls on streamflow patterns also has the potential to advance our understanding of spatiotemporal patterns in solute concentrations and their export from headwater catchments, possibly aiding identification of hotspots and sources of pollutants [Kimball et al., 2010].
2.6 Conclusions

We reported on δ\textsuperscript{18}O for precipitation, baseflow and shallow groundwater in two small headwater catchments of the southern Appalachian Mountains over a two-year period. Our analysis of almost 1000 baseflow samples revealed significant spatiotemporal variability in baseflow for relatively small (approximately 10 ha), forested headwater catchments. These results suggested heterogeneity in baseflow generation processes along streams during the study period. The relationship between ICA and the temporal range of baseflow δ\textsuperscript{18}O indicate that catchment structure influences patterns of baseflow for these first-order mountain streams. Relatively weak or non-existent enrichment patterns of baseflow in dry or extremely wet periods indicates that structural controls on baseflow δ\textsuperscript{18}O are likely sensitive to hydrologic conditions. Analysis of lateral inflow δ\textsuperscript{18}O highlighted the important role of large hillslopes in dampening precipitation δ\textsuperscript{18}O before releasing it to stream. Overall, these results further confirm and add to our fundamental understanding of intimate linkages between catchment structure and baseflow for small headwater catchments. Furthermore, the study emphasizes the utility of stable isotopes for understanding spatial and temporal patterns of baseflow at high spatial resolution.
2.7 References


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Table 2.1 Summary of landscape characteristics for the study catchments.

<table>
<thead>
<tr>
<th>Landscape Variables</th>
<th>WS01</th>
<th>WS02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median Elevation (m)</td>
<td>822</td>
<td>846</td>
</tr>
<tr>
<td>Median Slope (Degree)</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td>Median GTC</td>
<td>0.43</td>
<td>0.40</td>
</tr>
<tr>
<td>Median Length of Flow path (m)</td>
<td>86</td>
<td>127</td>
</tr>
<tr>
<td>Median Length of Flow path /GTC (m)</td>
<td>213</td>
<td>347</td>
</tr>
<tr>
<td>Median Vegetation Density (%)</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>Median Vegetation Height (m)</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>Aspect</td>
<td>South</td>
<td>South</td>
</tr>
<tr>
<td>Perennial Stream Length (m)</td>
<td>700</td>
<td>411</td>
</tr>
<tr>
<td>Drainage Area (DA) (ha)</td>
<td>15</td>
<td>13</td>
</tr>
</tbody>
</table>

GTC (Gradient to Creek)
Table 2.2 Relationship between baseflow δ¹⁸O and the distance from channel head to the catchment outlet.

<table>
<thead>
<tr>
<th>Date</th>
<th>( r^2 ) (Slope, ‰ 100 m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WS01</td>
</tr>
<tr>
<td>Jun-11</td>
<td>0.77(-0.07)</td>
</tr>
<tr>
<td>Jul-11</td>
<td>0.40(-0.06)</td>
</tr>
<tr>
<td>Aug-11</td>
<td>*</td>
</tr>
<tr>
<td>Sep-11</td>
<td>0.47(-0.03)</td>
</tr>
<tr>
<td>Oct-11</td>
<td>0.55(-0.06)</td>
</tr>
<tr>
<td>Nov-11</td>
<td>0.67(-0.07)</td>
</tr>
<tr>
<td>Dec-11</td>
<td>0.74(-0.05)</td>
</tr>
<tr>
<td>Jan-12</td>
<td>*</td>
</tr>
<tr>
<td>Feb-12</td>
<td>0.68(-0.06)</td>
</tr>
<tr>
<td>Mar-12</td>
<td>0.73(-0.05)</td>
</tr>
<tr>
<td>Apr-12</td>
<td>0.52(-0.05)</td>
</tr>
<tr>
<td>May-12</td>
<td>0.46(-0.03)</td>
</tr>
<tr>
<td>Jun-12</td>
<td>0.75(-0.06)</td>
</tr>
<tr>
<td>Jul-12</td>
<td>0.52(-0.04)</td>
</tr>
<tr>
<td>Aug-12</td>
<td>0.53(-0.04)</td>
</tr>
<tr>
<td>Sep-12</td>
<td>0.69(-0.04)</td>
</tr>
<tr>
<td>Oct-12</td>
<td>0.61(-0.05)</td>
</tr>
<tr>
<td>Dec-12</td>
<td>*</td>
</tr>
<tr>
<td>Feb-13</td>
<td>*</td>
</tr>
<tr>
<td>Mar-13</td>
<td>0.51(-0.04)</td>
</tr>
<tr>
<td>Jun-13</td>
<td>0.55(-0.04)</td>
</tr>
</tbody>
</table>

* represents months with no significant (p>0.05) relationship
Figure 2.1 Catchments WS01 and WS02 showing streams, drainage area, and sampling points together with instrumentation. Inset shows the location of Coweeta Hydrologic Lab (Otto, North Carolina).
Figure 2.2 Boxplots showing distribution of flow path lengths for WS01 (a), and WS02 (b). For each boxplot, upper and lower whiskers represent interquartile range and red line represents the median of the distribution.
Figure 2.3 Boxplots and time series of precipitation \( \delta^{18}O \) (a, b), baseflow and shallow groundwater \( \delta^{18}O \) for WS01 (c, d); and baseflow and shallow groundwater \( \delta^{18}O \) for WS02 (e, f). Boxplots show median (red), interquartile range (blue). Time series show low elevation (filled circle) and high elevation (open circle) for precipitation, or baseflow (filled circle) and shallow groundwater (open circle) for WS01 and WS02. Error bars represent uncertainty in the isotopic concentrations of the water pools.
Figure 2.4 Interpolated contour plot of baseflow $\delta^{18}$O for 605 samples collected in WS01. Black dots represent discrete samples in space and time. Boxplots (above) show the temporal distribution of baseflow $\delta^{18}$O at each sampling point. Boxplot range is 5th to 95th percentile. Hydrograph (R) and hyetograph (P) for WS01 (right) show sampling events in red.
Figure 2.5 Interpolated contour plot of baseflow $\delta^{18}O$ for 378 samples collected in WS02. Black dots represent discrete samples in space and time. Boxplots (above) show the temporal distribution of baseflow $\delta^{18}O$ at each sampling point. Boxplot range is 5th to 95th percentile. Hydrograph (R) and hyetograph (P) for WS02 (right) show sampling events in red.
Figure 2.6 Scatter plot showing the relationship between spatiotemporal variability of baseflow $\delta^{18}$O and incremental contributing area (ICA) for both catchments. The relationships were significant at $p<0.05$. Range is the mid-90th (5th to 95th) percentile of baseflow $\delta^{18}$O measured adjacent to each hillslope as shown in figures 4 and 5. Error bars represent uncertainty in the isotopic concentrations of baseflow.
Figure 2.7 Median of lateral inflow $\delta^{18}O$ organized by each hillslope’s corresponding flow path lengths for WS01 and WS02. Error bar represents uncertainty in lateral inflow $\delta^{18}O$. 
Figure 2.8 Test statistics ($r^2$, slope) for observed values (red filled circle) and simulated values for 10,000 random arrangements of hillslopes (black dots) for WS01 (a) and WS02 (b). The observed values were obtained in March 2012 (WS01) and April 2012 (WS02).
CHAPTER 3

Spatiotemporal Patterns of Soil Moisture Responses to Storms in a Forested Headwater Catchment

Abstract

Soil moisture exhibits complex spatiotemporal patterns, both laterally across the landscape and vertically within the soil profile. These patterns of soil moisture can have strong influences on runoff generation, especially in catchments having large capacities for soil water storage and transmission. We investigated soil moisture responses to storm events for several landscape positions in a forested headwater catchment of the southern Appalachian Mountains. We measured volumetric soil moisture continuously for more than 2 years at 45 points representing different combinations of landscape positions and depths within a 12 ha catchment at Coweeta Hydrologic Laboratory in the Southern Appalachian Mountains. We also monitored shallow groundwater levels at six locations within the catchment along with runoff at the catchment outlet. To investigate soil moisture response during events, we assessed absolute change in soil moisture ($\Delta s$) and lag time between peak precipitation and peak soil moisture ($\Delta t$) for 39 events. Our results reveal large spatiotemporal variability in $\Delta s$ and $\Delta t$ along three instrumented hillslopes during the study period. Storm properties and antecedent moisture conditions explained some of the spatiotemporal patterns of $\Delta s$ and $\Delta t$; however, the explanatory power varied among hillslopes and seasons. We found significant topographic influence on $\Delta t$ but not for $\Delta s$ for most of the locations monitored. By evaluating the sequence of response timings of soil moisture, groundwater, and runoff for each storm, we categorized the hydrologic behavior of
the study hillslopes for 39 storm events. The characterization of hydrologic behavior reveals interrelationships between soil moisture and shallow groundwater in relation to runoff at catchment outlet. This work provides new insights on links between the spatiotemporal variability of soil moisture and runoff responses in headwater catchments.
3.1 Introduction

Soil moisture is a key link between the water, carbon and energy balances of terrestrial ecosystems. Soil moisture has a critical role in influencing hydrological processes [Western et al., 2004; Blume et al., 2009], ecological processes [Rodríguez-Iturbe and Porporato, 2004; Emanuel et al., 2007] and land atmosphere interaction [Entekhabi et al., 1996; Eltahir, 1998]. Soil moisture also serves as a fundamental variable in regional and continental scale land atmosphere interaction [Alfieri et al., 2008; cf. Seneviratne et al., 2010]. At hillslope and catchment scales, the spatiotemporal patterns of soil moisture influence runoff generation [e.g., Dunne, 1978; Mosley, 1979; Grayson et al., 1997; Zehe et al., 2010], hydrological connectivity [Detty and McGuire, 2010; McGuire and McDonnell, 2010], plant-water dynamics [e.g., Eagleson, P. S., 1978; Porporato et al., 2004; van Meerveld and McDonnell 2006; Emanuel et al., 2010], and flooding [Borga et al. 2007]. Soil moisture patterns are especially important for forested catchments with relatively deep soils. These deep soils act as storage reservoirs to sustain low-order headwater streams between storms and during dry parts of the year [Hewlett, 1961].

Spatiotemporal patterns of soil moisture have been studied in many small catchments [Moore et al., 1988; Nyberg, 1996; Grayson et al., 1997; Famiglietti et al., 1998; Yeakely et al., 1998; Wilson et al., 2004; Brocca et al., 2007; Penna et al., 2009]. Using a wide range of methods, these studies have provided insight on the distribution of soil moisture and its various controls. Some of these controls include topography [Moore et al., 1988; Nyberg, 1996], soil heterogeneity [Crave and Gascuel-Odoux, 1997; Famiglietti et al., 1998], solar radiation [Moore et al., 1993; Western et al., 1999], and vegetation [Lull and Reinhart, 1955;
Qui et al., 2001]. However, we know little about the role of storm properties on spatiotemporal patterns of soil moisture during storms along hillslope. We still do not understand how soil moisture response to storms varies with multiple landscape positions along hillslopes. Many studies have explored the soil moisture response to storms, but they were limited to few landscape positions laterally or vertically along a hillslope [Dunne, 1978; Haga et al., 2005; Kim, 2009]. A need remains to investigate and understand how soil moisture responses to storms vary along hillslopes according to storm characteristics, topography and soil depth.

Studies investigating soil moisture responses to storms generally consider the absolute change in water content and the lag time between peak rainfall and peak soil moisture during each storm [Onda et al., 2001; Haga et al., 2005; Blume et al., 2009; Kim, 2009]. The spatial patterns of both response magnitude and lag have the potential to reveal variations in flow paths, water sources, and patterns of storage within catchments. As such, these patterns may also illuminate rainfall-runoff processes within a catchment. Evaluating the sequence of such response metrics (e.g., lag) for soil moisture, groundwater and runoff to storms, we can identify the similarity in hydrologic responses among hillslopes within a catchment. Furthermore, this approach can reveal more than we currently know about the hydrologic behavior of hillslopes and how they vary through time for variable storm conditions.

The specific objectives of this study were to investigate the spatiotemporal patterns of soil moisture responses to storms at multiple landscape positions and soil depths along three hillslopes in a small (12 ha), forested headwater catchment, and to combine these responses
with groundwater and runoff data to characterize the hydrologic behavior of these hillslopes. We used soil moisture observations from multiple landscape positions distributed among shallow and greater depths and along three hillslopes. These observations were combined with other hydroclimatic and geospatial datasets to determine the role of topography on soil moisture responses to storms. Our study focused on the following questions: i) How do soil moisture responses to storms vary with depth, landscape positions and storm characteristics? ii) How does topography influence the soil moisture response to storms and how does this response vary among seasons and hillslopes? iii) How can relationships between soil moisture responses, shallow groundwater responses and runoff responses help characterize the hydrologic behavior of hillslopes?
3.2 Study Site

This work was conducted primarily at the Coweeta Hydrologic Laboratory (hereafter, Coweeta) located in the Nantahala National Forest of western North Carolina, US (35°03’N, 83°25’W). The Coweeta basin contains 26 experimental watersheds covering a total of 21.85 km² and ranging in elevation from approximately 680 m to 1500 m above mean sea level (Figure 3.1). Coweeta Creek, to which the experimental watersheds eventually drain, lies within the headwaters of the Little Tennessee River, which is a tributary of the Tennessee River. The climate is classified as maritime and humid temperate with cool summers and mild winters, and with frequent short duration rainfall events distributed year-round. The mean annual rainfall varies between about 1700 mm at low elevations and 2500 mm at high elevations, and the mean annual temperature is about 12° C. A standard estimate of the growing season for this region is April 15 through October 14.

The study focuses on a small (12 ha) headwater catchment (hereafter, WS02), containing a broadleaf deciduous forest. The catchment is predominantly south facing with a mean slope of 28°. The Coweeta basin has two major bedrock formations, the Tallulah Falls Formation and the Coweeta Group [Hatcher, 1971]. Both formations are predominantly metamorphic and crystalline [Hatcher 1974; 1979].

Our study was focused on three instrumented hillslopes (H1-H3) representing ranges of slope, aspect and curvature (Figure 3.1). Two major soil identified for WS02 were Fannin (fine loamy, mica dominated) near the ridges and Cullasaja-Tuckasegee (Fine loamy, oxidic) close to the stream channels [Thomas, 1996]. The studies have identified upper horizons (O, A, BA) at depths up to 30 cm and deeper horizons (B, BC) at depths of 30 to 100 cm, which
was also representative of root zone [Gaskin et al., 1996; Yeakely et al., 1998]. Table 3.1 summarizes the bulk densities measured along the hillslopes, which were in agreement with other studies [e.g., Yeakely et al., 1998]. Yeakely et al. [1998] also reported physical properties for several soil samples collected in WS02, including clay fractions ranging from 20 to 35 % and sand fractions ranging from 45 to 60 %. We observed soil depths ranging from 1 m to 2.3 m during installation of shallow groundwater monitoring wells at several locations in WS02.

3.3 Methods

3.3.1 Geospatial Analysis

The National Center for Airborne Laser Mapping (NCALM) collected Light detection and ranging (LIDAR) data in 2010 that provided 1 m x 1 m digital elevation models (DEMs) of the bare earth surface and the top of the vegetation canopy. We resampled the 1 m x 1 m bare earth DEM to 5 m x 5 m resolution to avoid the confounding effects of microtopography on geospatial algorithms for computing subsurface drainage patterns from surface topography [e.g., Seibert and McGlynn, 2007]. We used the multidirectional flow accumulation algorithm of Seibert and McGlynn [2007] to estimate the drainage area for each 5 m pixel for the instrumented hillslopes. Topographic variables were computed from the 5 m x 5 m DEM and included slope, drainage area, topographic wetness index (TWI), plan curvature, profile curvature, flow path length to the stream, and gradient to creek (GTC). Table 3.2 summarizes the spatial characteristics of each hillslope.

3.3.2 Data Collection
We collected soil moisture observations from 15 landscape positions and multiple depths at 30 min intervals from October 2011 to December 2013. Observations were distributed among three hillslopes (H1-H3) with soil moisture probes located at four landscape positions (upslope, US; midslope, MS; lowerslope, LS; and near stream, NS), and up to five depths (10, 20, 30, 60, and 100 cm) on each hillslope. We referred to probes with the combination of landscape position and depth –XXYY, where XX is a landscape position (e.g., US, MS) and YY is depth (e.g., 10, 20 cm), US30 would mean probe installed at up-slope landscape position and 30 cm depth. Up-slope and mid-slope landscape positions had five probes at depths of 10 cm, 20 cm, 30 cm, 60 cm and 100 cm below the surface. The lower slope landscape position had three probes at depths of 20 cm, 60 cm, and 100 cm below the surface. The near-stream landscape position had two probes at depths of 60 cm and 100 cm below the surface. We used time domain reflectometry (TDR) probes (Model CS-650, Campbell Scientific, Logan, UT) at 10 cm, 20 cm and 30 cm depths, and coaxial impedance dielectric reflectometry (CIDR) probes (Model Hydra Probe II, Stevens Water Monitoring System Inc., Portland, OR) for 60 and 100 cm depths. We used the factory default calibrations for these probes. Site-specific calibrations were unnecessary given that analyses did not rely on absolute values of volumetric soil moisture. Occasional probe malfunctions and battery charging issues resulted in some data loss, but efforts were made to analyze data from storms where high quality data were available.

We also monitored shallow groundwater stage at two locations on each hillslope. Each groundwater well was equipped with a capacitance rod (TruTrack, Inc., Christchurch, NZ) to record stage and water temperature at 30 min intervals. Well screens were constructed
from 3.8 cm (1-1/4 inch) inner-diameter polyvinyl chloride (PVC) conduit slotted from
approximately 10 cm below ground to the completion depth. Completion depths ranged from
1 m to 3.5 m below the surface. Well screens were installed using a solid steel rod inserted
into the screen and driven with a sledgehammer through soil and saprolite until refusal at the
bedrock surface. A gas-powered auger whose bit matched the outer diameter of the PVC
screening was used in some cases to probe for suitable locations. Bentonite clay was packed
around each well at the soil surface to prevent surface runoff or direct precipitation from
entering wells.
Stream discharge was measured using a V-notch weir at the outlet of WS02. The US Forest
Service (USFS) maintained the weir and recorded stage continuously. Similarly, rainfall was
measured by the USFS at a climate station (CS21) located near the study hillslopes.

3.3.3 Data Analysis

Storm events were identified manually by inspecting rainfall data from CS21. The
following criteria were applied for event selection: i) 30-minute rainfall equaled or exceeded
0.5 mm, ii) total rainfall for the event exceeded 20 mm, and iii) a minimum of 3 hours
separated events. We identified 72 distinct storms that met the above criteria during the study
period, and out of those we selected 39 storms for which complete hydrologic datasets were
available immediately before, during and for 3 days after each storm. We calculated three
storm response metrics for each soil moisture probe for the selected storm events. The
absolute magnitude ($\Delta s$) of the soil moisture response was defined for each storm as the
difference between minimum and maximum soil moisture during a storm, where the
difference was greater than 0.01 m$^3$/m$^3$. The lag time ($\Delta t$) was defined for each storm as the
time difference between the time of peak rainfall and time of peak soil moisture response.
The response percentage was defined for all storms as the percentage of total storms that
generated a response from each soil moisture probe. Antecedent moisture conditions were
defined for each probe as the soil moisture value one hour prior to the arrival of a storm. We
also calculated lag times for runoff and shallow groundwater wells during each storm. Runoff
coefficients were calculated as the ratio of total quick flow, calculated using the local
minimum method [Sloto and Crouse, 1996], to total rainfall during each storm. We estimated
change in runoff percentage as the ratio of difference between minimum and maximum
runoff during storm to runoff prior to storm. We used the Wilcoxon Rank Sum Test
(Wilcoxon) and Kruskal-Wallis Test (Kruskal-Wallis) to compare medians of response
metrics, and we used Spearman’s Rank Correlation Coefficient (ρ) to relate soil moisture
responses to storm characteristics, antecedent moisture conditions and topographic variables.
3.4 Results

3.4.1 Annual Dynamics of Soil Moisture and Groundwater and Storm Characteristics

The study catchment received 2387 mm yr\(^{-1}\) of rainfall during the study period, which coincided with one of the wettest years (2013) on record at Coweeta (Figure 3.2). For the same period, annual runoff measured at the catchment outlet was about 945 mm yr\(^{-1}\).

Figure B1 shows soil moisture time series at an up-slope position for selected shallow and greater depths along study hillslopes. Table 3.3 summarizes the mean and coefficient of variation (CV) of soil moisture for all probes along the three-instrumented hillslopes. We found higher temporal variability in soil moisture for shallower soils compared to deeper soils, especially for US and MS landscape positions (Table 3.3). We observed high spatiotemporal variability in shallow groundwater stages (Figure C1). Some wells exhibited highest water table during wet dormant seasons and a gradual recession during growing seasons. In contrast, some wells remained wet throughout the study period. Shallow groundwater wells for H3 exhibited the largest temporal variability in groundwater stages with the water table of the HS well rising above the ground several times during large storm events during wet antecedent conditions.

We identified 39 storm events representing a range of rainfall characteristics and flow conditions (Table 3.4; Figure 3.2). These events occurred over the course of two dormant seasons (25 events) and two growing seasons (14 events). Runoff coefficients for the selected events were relatively small in magnitude (averaging 4\%) and did not show much temporal variability for the selected storms suggesting the minimal runoff generation during storm flow condition (Table 3.4). We noted a strong correlation between storm depth and storm period (Spearman’s \(\rho=0.66, P<0.001\) and storm depth and peak intensity (Spearman’s \(\rho\)
=0.44, P=0.004), but no significant correlation was observed between storm depth and mean intensity (Spearman’s ρ=0.25, P>0.1). For the selected events, antecedent runoff (i.e., runoff prior to storm) and peak runoff were correlated (Spearman’s ρ=0.54, P<0.001) suggesting the direct influence of antecedent wetness condition on the peak runoff during events.

3.4.2 Soil Moisture Response to Storms

3.4.2.1 Absolute Magnitude (Δs)

Boxplots of Δs revealed large spatiotemporal variability among landscape positions along instrumented hillslopes (Figures 3.3a, 3.4a, 3.5a). Table 3.5 summarizes the response percentage for all landscape positions to the selected storm events during the study period. For H1, median Δs declined with depth for each landscape position, with few exceptions, and was significantly different among all landscape positions (Kruskal-Wallis P<0.05; Figure 3.3a). However, for H2, we observed abrupt variations in median Δs with depths, where large number of landscape positions exhibited increase in median Δs with depth (e.g., US30, MS20, MS30, LS100; Figure 3.4a). Furthermore, median Δs was significantly different among most of the landscape positions. For H3, no significant difference was detected in median Δs among landscape positions along the hillslope (Figure 3.5a). Similar to H2, H3 also exhibited large variation in median Δs with depths, but for fewer landscape positions (Figure 3.5a). The median Δs was significantly higher for H3 compared to rest of the hillslopes (Wilcoxon P<0.001).

We found distinct spatial patterns of Δs that varied with AMC and storm properties across landscape positions and depths (Figures 3.3b, 3.4b, 3.5b). In general, we noted large values of Δs for landscape positions and depths that exhibited drier antecedent conditions.
Spatial variability in $\Delta s$ along hillslopes was higher during storms that occurred during dry dormant seasons and most of them were large storms (>100 mm). For H1, during most of the storm events, $\Delta s$ declined with depths as observed in Figure 3.3a. But, we detected abrupt increases in $\Delta s$ with depth at certain landscape position (e.g., MS $30^\circ$) along H1 during large storms (>100 mm) that occurred during the dormant period (Figure 3.3b). For H2 and H3, during most of the storms, we observed increases in $\Delta s$ with depth at multiple landscape positions, and such patterns were independent of storm characteristics (Figures 3.4b, 3.5b).

3.4.2.2 Lag Time ($\Delta t$)

We detected large spatiotemporal variability in lag time ($\Delta t$) at multiple landscape positions along hillslopes (Figures 3.3c, 3.4c, 3.5c). For H1, most of the landscape positions showed an increase in median $\Delta t$ with depth, and median $\Delta t$ was significantly different between US and LS (Wilcoxon $P=0.03$), US and NS (Wilcoxon $P=0.002$), MS and NS ($P=0.005$) landscape positions (Figure 3.3c). For H2, a few landscape positions exhibited abrupt decrease in $\Delta t$ with depths (e.g., US and MS), and median $\Delta t$ was significantly different among all landscape positions (Wilcoxon $P<0.001$; Figure 3.4c). For H3, median $\Delta t$ was significantly different among all landscape positions (Wilcoxon $P<0.05$), except MS and US (Wilcoxon $P>0.05$; Figure 3.5c). Overall, the largest temporal variability in $\Delta t$ was observed for H3 (CV=1.35), followed by H2 (CV=1.10) and H1 (CV=1.04). Also, the shortest $\Delta t$ were also observed for H3 (median $\Delta t = 2$ hr), and for few dormant season storms, shallow soils at H3 (US and MS) reached saturation earlier than the peak rainfall.

Figures 3.3d, 3.4d and 3.5d revealed influence of AMC on spatial patterns of $\Delta t$, where $\Delta t$ was shorter during wet dormant and early growing seasons (e.g., 1/12-4/12, 1/13-
than during dry dormant and late growing seasons (e.g., 9/12-10/12, 9/13-10/13). In general, spatial variability in Δt was exceptionally high (CV>1) during wet dormant periods along hillslopes, irrespective of storm characteristics (e.g., storm 7, 8, 27). Furthermore, spatial variability was more for the large storms that occurred during dry dormant seasons (e.g., storm 4, 19) along hillslopes (Figures 3.3d, 3.4d and 3.5d). The sequential order of Δt during most of events revealed increases in Δt for the landscape positions with depth along H1 suggesting matrix flow (Figure 3.3d). But, for a few landscape positions, we observed abrupt decrease Δt with depth (e.g., MS30) during large storms (>100 mm) along H1 (Figure 3.3d). For H2 and H3, large numbers of probes exhibited abrupt changes in Δt with depth during storms, and these patterns were independent of storm characteristics (Figures 3.4d and 3.5d). Most notably, the frequency of occurrence of such patterns was higher during wet dormant seasons and early growing seasons.

3.4.3 Inter-comparison of Lag times (Δt) for Groundwater, Soil moisture, and Runoff Responses

Patterns of Δt for shallow groundwater were highly variable among hillslopes and storms, and they exhibited significant differences between dormant (median Δt = 3.5 hr) and growing (median Δt = 8.5 hr) seasons (Wilcoxon P=0.001, Figure 3.6). Lag times were smaller for NS (median Δt = 5.5 hr) than for HS (median Δt = 9.5 hr) wells (Wilcoxon, P=0.01). Furthermore, median Δt observed for each NS well was significantly different among hillslopes (Wilcoxon P<0.05), and similar patterns were also noted among HS wells (Wilcoxon P<0.001). Among NS wells, Δt was smallest for H2 (median Δt = 2.5 hr), and among HS wells, Δt was smallest for H3 (median Δt = 5.5 hr; Figure 3.6). A few of these wells demonstrated strong correlations between Δt of runoff and Δt of NS well for H1.
(Spearman’s \( \rho =0.59, P<0.001 \)), NS well for H2 (Spearman’s \( \rho =0.43, P=0.01 \)), and HS well for H3 (Spearman’s \( \rho =0.66, P<0.001 \)). Furthermore, during few events, \( \Delta t \) of runoff coincided with NS wells for H1 and H2, and HS well of H3 (Table 3.6), suggesting the intimate connection between these wells and runoff.

We found distinct patterns of hillslope scale hydrologic response to storms when we compared the lags of soil moisture and groundwater with runoff lag at the catchment outlet (Table 3.6). We broadly characterized the hydrologic responses into three main behaviors based on which hydrologic variable peaked first, runoff, soil moisture, or shallow groundwater. The frequency of occurrence of each behavior varied by hillslope: runoff peaked first for 58% of events for H1, soil moisture peaked first for 48% of events for H2, and groundwater peaked first for 24% of events for H2. It was only during large storms (>100 mm) that all hillslopes exhibited similar hydrologic responses, where soil moisture peaked first. These sequential patterns of lags between soil moisture and runoff led to hysteresis in soil moisture and runoff relationship during storms (Figure 3.7). Hysteresis was highly variable during storms and not necessarily season or event dependent as suggested by other studies [e.g., McGuire and McDonnell, 2010; Penna et al., 2011].

3.4.4 Relationships between Response Patterns and Topography, Storm Properties and Antecedent Conditions

We investigated relationships between topographic variables and soil moisture responses (\( \Delta s, \Delta t \)) to storm events among the hillslopes. Significant relationships between spatial pattern of \( \Delta s \) and profile curvature was only noted during large storms (e.g., storms 17) across hillslopes (Spearman’s \( \rho =-0.4, p<0.05 \)). In contrast, significant relationships
between spatial patterns of $\Delta t$ and topography variables were noted during most of the storms (Table 3.7). However, the relationship varied with seasons and hillslopes.

We found significant relationships between soil moisture response ($\Delta s$, $\Delta t$) and storm characteristics and antecedent moisture conditions (Figure 3.8). Significant relationships occurred more frequently for $\Delta s$ than for $\Delta t$ and during dormant seasons more frequently than growing seasons. In particular, storm properties were positively correlated to $\Delta s$ and negatively correlated to $\Delta t$, and antecedent moisture condition was negatively correlated to $\Delta s$ and $\Delta t$ for most landscape positions (Figure 3.8). Similar findings have been reported by other hillslope scale studies that investigated the spatiotemporal temporal controls of soil moisture response to storm events for forested headwater catchments [e.g., Kim 2009].
3.5 Discussion

3.5.1 Spatiotemporal Controls of Soil Moisture Response (magnitude and timing)

3.5.1.1 Absolute Changes in Magnitude (Δs) of Soil Moisture

Soil moisture responses varied with time and among study hillslopes (Figures 3.3b, 3.4b, 3.5b). These variations can be linked to topographic characteristics of the hillslopes, to observation depth, and also to antecedent moisture conditions. Overall, large response percentages and higher values of Δs observed for shallower soils could be attributed to high infiltration rate (>60 mm hour⁻¹) for shallower soils of Coweeta [e.g., Price et al., 2010]. Large spatiotemporal variability in Δs for shallow soils can be attributed to variability in infiltration rates, which could be influenced by changing antecedent moisture conditions in space and time (Figures 3.3, 3.4, 3.5) [e.g., Gray and Norum, 1967; Liu et al., 2011]. In particular, the moisture gradient along the soil profile will have large influence on the patterns of infiltration rate. Wet antecedent conditions along the soil profile may affect the moisture gradient, leading to reduce the penetration depth of the wetting front compared to the penetration depth during dry antecedent conditions. In other words, during dry conditions, for similar storm type, we may see large changes in Δs with depth than during wet conditions.

For H1, most of the landscape positions exhibited gradual decline in Δs with depth suggesting the soil matrix flow to be the dominant mechanism through which wetting front moved through the soil (Figure 3.3b). During large storms, abrupt increases in Δs with depth at certain landscape position (e.g., US₃₀, MS₃₀) could be attributed to activation of preferential flow paths [e.g., Sidle et al., 2000; 2001]. We speculate that extremely wet
conditions enabled physical linkages between soil pores of different sizes, leading to
activation of preferential flow paths. Furthermore, both landscape positions (e.g., US and
MS) were located in relatively steep area, where the chances of triggering preferential flow
or lateral flow is much higher than shallow area on the same hillslope.

For H2 and H3, several landscape positions (e.g., US30, MS30, LS100) showed increase
in Δs with depths, suggesting high occurrence of preferential flow during most of the storms,
irrespective of storm properties (Figures 3.4b, 3.5b). These specific landscape positions at
certain depths were superimposed by soil layers that exhibited persistently wet antecedent
conditions throughout the study period along H2 (e.g., US20, MS10, MS20, LS60; Figure 3.4b).
Similar observations were also made at some landscape position along H3 (e.g., LS60, LS100;
Figure 3.5b). It is possible that when wetting front percolates down, wet antecedent
conditions may offer resistance to the wetting front, resulting in the activation of preferential
flow vertically or laterally [e.g., Whipkey and Kirkby, 1978]. This phenomenon may explain
spatial patterns of Δs for some landscape positions of H3 (e.g., LS; Figure 3.5b).

There were a few landscape positions along H3 that showed abrupt patterns of Δs
with depth (e.g., US and MS; Figure 3.5b), but these landscape position were not
superimposed by relatively high antecedent conditions as mentioned above. The abrupt
patterns in Δs with depth for these positions may be attributed to the relative locations of
those landscape positions (e.g., US and MS) along H3. Both landscape positions (US, MS)
were located in the vicinity of a hollow with one of the greatest topographic convergence
among study hillslopes, where most flow paths of the large and steep hillslope converged
(Table 3.2). These long, converging flow paths have the potential to quickly mobilize
subsurface flow, leading to the activation of preferential flow paths and influencing the spatiotemporal patterns of Δs. This particular mechanism, in combination with relatively dry antecedent conditions for most of the landscape positions (Table 3.3), could potentially explain the large values of Δs observed for H3 relative to other study hillslopes (Figures 3.3a, 3.4a, 3.5a). Although topographic variables were not significantly correlated with Δs for H3, the large temporal variability at LS could be attributed to its large drainage area relative to other landscape positions in the study. During storm conditions, we did not detect significant topographical control on the patterns of Δs for all hillslopes, but it is critical to recognize that topography may have influenced the antecedent conditions that were highly correlated to Δs.

3.5.1.2 Lag Time (Δt)

Study hillslopes demonstrated unique spatiotemporal patterns of soil moisture lag responses (Figures 3.3d, 3.4d, 3.5d). In general, these lag time provided crucial insights about how quickly wetting front moved along soil profile with changing antecedent conditions, storm properties and topography. Studies have shown that antecedent condition exerts strong control on the hydraulic conductivity; wetter the antecedent conditions, higher the conductivity and shorter the lag time. This phenomenon was also evident in our data, where lag times were shorter for wetter landscape positions than drier landscapes positions. Furthermore, during wet dormant seasons, lag time was relatively shorter than dry growing seasons across landscape positions and depths.

In particular, most of the landscape positions where matrix flow was the dominant mechanism exhibited gradual increases in lag time with depth (Figures 3.3c, 3.4c, 3.5c), suggesting the time required to fulfill the saturation deficit in shallower soils before the
greater depths reach peak [e.g., Whipkey, 1965]. For the landscape positions where preferential flow frequently occurred, we did not observe gradual increases in Δt with depth indicating the variability in sources and flow paths that contributed to landscape positions during storms (Figures 3.3c, 3.4c, 3.5c). However, smaller Δt for deeper soils does not necessarily indicate the presence of preferential flow given that deeper soils generally have higher antecedent moisture conditions and saturate earlier than shallower soils (Figures 3.3c, 3.4c, 3.5c). These results highlight the importance of antecedent moisture conditions in determining the spatial patterns of Δt along the study hillslopes. It is consistent with prior work on this topic [e.g., Dunne, 1978; Haga et al., 2005].

We noted large spatial variability in Δt along hillslopes (CV>1) for storms that occurred during wet dormant period or early growing seasons (e.g., storm 7, 8, 27, Table 3.6; Figures 3.3c, 3.4c, 3.5c). Extremely wet antecedent conditions are more likely to initiate lateral flows during storms [e.g., Grayson et al., 1997], irrespective of storm properties, leading to influence the flow paths that contribute to individual landscape position and resulting in high spatial variability of Δt.

We found significant topographic influence on the spatial patterns of Δt, although strength varied with seasons and hillslopes (Table 3.7; Figure 3.8). More specifically, topography has the potential to influence availability of soil water, encourage wetness and increase the velocity of subsurface flow at certain landscape conditions [e.g., Moore et al., 1988; 1993]. The shortest lag time and largest spatiotemporal variability observed along H3 could be attributed to its large drainage area (Table 3.1). The large drainage area of H3 has the potential to quickly mobilize large amount of subsurface flow along H3, which not only
resulted into short lag times for the landscape positions but led to soil saturation at some depths prior to peak rainfall (Figure 3.5c). Overall, these results suggest the strong influence of storm properties, antecedent moisture condition and topography on the patterns of Δt along steep hillslopes with deep soils.

3.5.2 Spatiotemporal Heterogeneity in Hydrologic Responses along Hillslopes

Earlier studies at Coweeta have shown that subsurface flow is the dominant runoff generation process [e.g., Hewlett, 1961; Hewlett and Hibbert, 1967], mostly due to high infiltration rates [e.g., Price et al., 2010] and large storage capacities of these deep, forested soils. The sequential order of Δt for soil moisture, groundwater and runoff further revealed the spatial and temporal heterogeneity in hydrologic responses that varied with antecedent conditions and storm properties along study hillslopes (Table 3.6). Furthermore, these distinct patterns also highlighted the hysteric relationships (e.g., runoff and soil moisture, soil moisture and groundwater) that varied with time during storm events (Figures 3.7, 3.8).

The characterization of hydrologic responses on the basis of lag times helped us to broadly categorize and understand some of the common behaviors of the hillslope in these forested catchments. Hillslope H1 exhibited the slowest response among the three study hillslopes, where runoff peaked earlier than soil moisture and groundwater for a large proportion of storms (58%), and this could be attributed to the dominance of matrix flow for most of the landscape positions in H1 (Table 3.6, Figure 3.3). On the other hand, for H2, either soil moisture (48%) or groundwater (24%) peaked first compared to runoff. The early saturation of H2 could be due to large occurrence of preferential flow paths for several landscape positions and convergent topography of the hillslope that further encourages soil
water accumulation along H2 (Table 3.1, 3.6; Figure 3.4). Not only did groundwater peak first for 24% of storms for H2, but the NS well also exhibited the shortest median lag (2.5 hr) for the 39 storms (Table 3.6, Figure 3.6). It is possible that preferential flow paths in shallow soils facilitated subsurface flow without affecting the soil matrix (Figures 3.9 c-d), leading to early peak in response for the NS well. A few other studies have reported similar findings elsewhere [e.g., Harpold et al., 2010].

With few exceptions, during most of the events, soil moisture and groundwater lagged behind runoff, suggesting no contribution of the study hillslopes to peak runoff (Table 3.6). The study period included some of the unusually wet conditions for the catchment, but a large area of the study hillslopes remained disconnected from the stream and did not contribute to peak runoff during the selected storms. Only during few events [e.g., 17, 25, 27; Table 3.6], lags of NS wells coincided with the runoff lags suggesting the potential contribution of near stream area to peak runoff (Table 3.6). These results are in agreement with the variable source area concept [e.g., Hewlett and Hibbert, 1967; Hewlett and Nutter, 1970] and also have been reported by other studies in various catchments [e.g., McGlynn and McDonnell, 2003; Harpold et al., 2010; Haught and van Meerveld, 2011]. In an exceptional case, the lag for shallow groundwater at the hillslope well in H3 coincided with the runoff lag, and both peaked earlier than the near-stream well in H3 (Table 3.6). This behavior could be due to the landscape position of this well at the base of a large, steep hillslope with the potential to mobilize large amounts of subsurface flow rapidly through pressure wave propagation [e.g., Rodhe and Seibert, 2011]. These results highlight the heterogeneities in
hydrologic responses within a catchment and suggest the knowledge gained from a hillslope may not be generalized for other hillslopes in the same catchment.
3.6 Conclusions

We observed large spatiotemporal variability in the soil moisture response to storm events along three instrumented hillslopes at Coweeta. Our findings suggest that storm characteristics exert strong control on the patterns of $\Delta s$ and $\Delta t$, and topography exerts strong influence on the spatial patterns of $\Delta t$. These results suggest that the combination of several variables might influence the spatiotemporal patterns of soil moisture responses to rainfall. Understanding these spatiotemporal patterns of soil moisture response during storms and their controls could be beneficial in modeling soil moisture and catchment responses to precipitation.

The sequential order of $\Delta t$ for soil moisture, groundwater and runoff revealed the spatial and temporal heterogeneity in hydrologic responses that varied with antecedent conditions and storm properties. During most of the storms, runoff peaked earlier than groundwater and soil moisture suggesting little or no contribution from study hillslopes to peak runoff, even during record wet conditions at Coweeta. These results advance our understanding of soil moisture response to storms and could be beneficial for understanding runoff generation for humid forested catchments.
3.7 References


Moore I.D., GJ Burch and DH Mackenzie (1988), Topographic effects on the distribution of surface soil water and the location of ephemeral gullies Trans ASAE (31), 1383-1395.


### Table 3.1 Soil bulk density across landscape positions and depths

<table>
<thead>
<tr>
<th>Position</th>
<th>Depth (cm)</th>
<th>H1 (g/cm(^3))</th>
<th>H2 (g/cm(^3))</th>
<th>H3 (g/cm(^3))</th>
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<td>1.51</td>
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</tbody>
</table>

“-” represent locations were soil samples were bad

Upslope (US), Midslope (MS), Lowserslope (LS), and Near Stream (NS) H1, H2 and H3 were three instrumented hillslopes as shown in Fig 3.1
Table 3.2 Summary (means) of topographic variables for instrumented hillslopes in WS02.

<table>
<thead>
<tr>
<th>Hillslopes</th>
<th>DA (m²)</th>
<th>Elevation (m)</th>
<th>Slope (Degree)</th>
<th>TWI Ln (m)</th>
<th>GTC</th>
<th>DFC (m)</th>
<th>DFC/GTC (m)</th>
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<th>Profile Curv.</th>
</tr>
</thead>
<tbody>
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<td>4.76</td>
<td>0.48</td>
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DFC (Flow path length from Creek); GTC (Gradient to Creek); TWI (Topography Wetness Index)
Table 3.3 Mean soil moisture (coefficient of variation) during the study period

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Table 3.5 Response percentage for monitored locations

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Median Lags*

|       | 1.5 | 3.3 | 5.3 | 2.5 | 3.5 | 2.0 | 5.5 |

SM (Soil Moisture), NS (Near Stream), HS (Hillslope), SL (Sequence of lags). "-" represents missing data and sequence was only reported when data sets were available for all three time series.

*For the entire study period
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“-” represents non-significant relationships (P>0.1)
Figure 3.1 Showing delineated hillslopes with landscape positions of soil moisture probes and groundwater wells in WS02.
Figure 3.2 Precipitation and runoff measured at 30 min intervals for WS02. Rainfall data were recorded at the rain gauge (RG20). Red filled circle represents flow condition prior of storm arrivals.
Figure 3.3 Magnitude (a, b) and lag time (c, d) of soil moisture responses to selected storm events for H1. Circle diameter shows relative magnitude of response. Color shows antecedent moisture conditions (AMC) prior to the event. Light gray rectangular box represents missing data.
Figure 3.4 Magnitude (a, b) and lag time (c, d) of soil moisture responses to selected storm events for H2. Circle diameter shows relative magnitude of response. Color shows antecedent moisture conditions (AMC) prior to the event. Light gray rectangular box represents missing data.
Figure 3.5 Magnitude (a, b) and lag time (c, d) of soil moisture responses to selected storm events for H3. Circle diameter shows relative magnitude of response. Color shows antecedent moisture conditions prior to the event.
Figure 3.6 Lag time (Δt) of groundwater response to storm events for instrumented hillslopes. The size of circles represent lag (hours) and color represents antecedent wetness condition (i.e., groundwater stage prior to the event) for each well. NS (Near stream) and HS (hillside) represent the location of wells along hillslopes. Gray color represents missing data for the well.
Figure 3.7 Hysteresis between volumetric water content (VWC) and runoff during two events; storm 12 (a, b), and storm 29 (c, d), for H1 and H2.
Figure 3.8 Relationship between $\Delta s$ and storm characteristics (a), and $\Delta t$ and storm characteristics (b) for all study hillslopes. Significant Spearman's $\rho$ correlations ($P<0.05$) shown in color. Storm properties include storm depth (SD), storm period (SP), mean intensity (MI), peak intensity (PI), and antecedent moisture condition (AMC).
**Figure 3.9** Hysteresis between volumetric water content (VWC) and runoff (a, c) and soil moisture and groundwater stage (b, d) during an event (storm 12) for hillslopes H1 and H2. Runoff peaks first, followed by soil moisture and groundwater on H1 (a-b), and groundwater peaks first, followed by runoff and soil moisture on H2 (c-d). These patterns can be inferred from Table 3.6 using the sequences of lags.
CHAPTER 4

Shallow Groundwater Responses to Storms and Implications for Runoff in the Southern Appalachian Mountains

Abstract

The spatiotemporal patterns of shallow groundwater are central to understanding runoff generation in humid headwater catchments. We investigated the spatial patterns of shallow groundwater response (magnitude and timing) to storms for 22 wells along 12-instrumented hillslopes across four forested catchments of the southern Appalachian Mountains. We examined the relationship between observed patterns of groundwater response and storm properties, topography and antecedent wetness conditions (i.e., groundwater stage prior to storm). We further identified groundwater-runoff relationships, including corresponding lag relationships, during storms among varying landscape positions. We found large variability in groundwater responses (magnitude and timing) in space and time among the study hillslopes. The spatial patterns of groundwater responses were highly correlated with storm properties, including depth and intensity, and also with antecedent wetness. Topographic controls on response timing were evident during most storms, but only the largest storms elicited groundwater response magnitudes that were correlated with topographic variables. The groundwater-runoff relationships and the corresponding lags varied with storm characteristics and among landscape positions. These results highlighted the potential source areas that may contribute to peak runoff at the catchment outlet during storms. The study advances our understanding of shallow groundwater dynamics and the groundwater response to storms in the southern Appalachian Mountains and similar forested catchments elsewhere.
4.1 Introduction

Spatiotemporal patterns of shallow groundwater exert strong control on runoff generation in small headwater catchments [Seibert et al., 2003; McGlynn and McDonnell, 2003a]. These patterns have important implications for source areas within catchments that contribute to peak runoff during stormflow conditions. Shallow groundwater is also important because it sustains hydrologic connectivity between unchannelized hillslopes and adjacent streams [Jencso et al., 2009; Detty and McGuire, 2010] while also influencing solute movement through catchments [e.g., McGlynn and McDonnell, 2003b; Pacific et al., 2010], vegetation dynamics [e.g., Baird et al., 2005], and natural hazards [e.g., Montgomery et al., 2002]. Given the important role of shallow groundwater in a wide range of catchment processes there has been extensive work documenting and assessing physical processes that influence shallow groundwater response along hillslopes [Ragan 1968; Dunne and Black, 1970; Freeze, 1974; McGlynn et al., 2004; Jencso et al., 2009; Rodhe and Seibert, 2011; Emanuel et al., 2014]. However, due to the complexity of shallow groundwater responses and the inherent heterogeneity of many landscapes, we continue to struggle to understand generalized behavior of shallow groundwater responses as they relate to catchment-scale processes [Wagener et al. 2007; cf. Bachmair and Weiler, 2011].

The magnitude and timing of shallow groundwater responses to storm events have been explored in relation to surface topography [Dunne and Black, 1970; Anderson and Burt, 1978; Detty and McGuire, 2010; Rinderer et al., 2015], bedrock [Meerveld and McDonnell 2006 a-b], soils [Fannin et al., 2000; Anderson et al., 2010; Penna et al., 2014], and vegetation [Bachmair et al., 2012; Dhakal and Sullivan, 2014]. These studies and others
provide fundamental insight into factors influencing shallow groundwater responses and runoff generation within a catchment. Many of these studies were conducted in catchments with relatively shallow soils (< 2 m) or where snowmelt constituted a significant hydrologic input. Fewer studies have evaluated groundwater responses in largely snow-free and humid regions, where hydrologic inputs are dominated by frequent storms. The southern Appalachian Mountains occupy such a region, and the relatively steep slopes and deep soils found throughout their headwaters provide a unique contrast to shallow-soil and snowmelt-dominated catchments. Investigating groundwater responses to storms in the southern Appalachian Mountains has the potential to advance our understanding of shallow groundwater influences on runoff generation by providing a contrast to these existing studies.

A large body of literature concludes that shallow groundwater is inextricably linked with the runoff generation for small headwater catchments [cf. Bachmair and Weiler, 2011]. Field-based studies reveal that runoff dynamics are often correlated with shallow groundwater stages close to the stream, but this correlation fades with distance away from the stream [Seibert et al., 2003; Detty and McGuire, 2010; Haught and van Meerveld, 2011]. These studies collectively provide important insight into the relationship between groundwater stages and runoff generation in space and time. Little attention has been given to how such relationships vary through time with storm characteristics and topographic variables. It remains unclear how the spatial characteristics of hillslopes interact with varying storm properties to influence the strength of groundwater-runoff relationship, particularly for forested catchments with relatively deep soils and steep terrain. Furthermore, how these relationships vary in space and time within and across catchments.
This study analyzes shallow groundwater responses to storms at 22 locations situated within four catchments representing different combinations of landscape variability. We seek to understand how storm characteristics influence shallow groundwater responses and how these responses vary for hillslopes with different areas, aspects and vegetation types. We also seek to understand how these shallow groundwater responses are related to catchment-scale hydrologic responses for the same storms. With this in mind, our study addressed the following specific questions: How do shallow groundwater responses to storms vary across a range of landscape conditions in steep, forested headwaters characterized by humid and temperate climatic conditions? How do these shallow groundwater responses relate to runoff responses?
4.2 Study Site

This study was conducted at the Coweeta Hydrologic Laboratory (hereafter, Coweeta) located in the Nantahala National Forest of western North Carolina, USA (35°03’N, 83°25’W). The Coweeta basin (Figure 4.1) contains 26 experimental and reference catchments covering a total of 21.85 km² and ranging in elevation from 680 m to 1500 m above mean sea level. Coweeta Creek, to which the 26 catchments eventually drain, lies within the headwaters of the Tennessee River.

The climate is classified as maritime and humid temperate with cool summers and mild winters, including frequent short period rainfall events distributed year-round [Swift et al., 1988]. Mean annual precipitation at a climate station near the outlet of Coweeta Creek (CS01) was 1791 mm from 1937 to 2011. Mean annual temperature at CS01 was 12.6°C for the same time period. A standard estimate of the growing season is April 15 through October 14 [Swift et al., 1988].

The study focuses on two pairs of catchments, with each pair containing one catchment dominated by broadleaf deciduous forest (WS02, WS18) and another dominated by *Pinus strobus* (white pine) forest (WS01, WS17). The catchments (Figure 1) are part of a long-term experiment to evaluate the effects of forest type on catchment water balances [Swank and Douglass, 1974]. Catchments WS01 and WS02 are south-facing catchments (SFC), and WS17 and WS18 are north-facing catchments (NFC). The deciduous-dominated catchments were abandoned to secondary ecosystem succession in 1920 and are considered hydrologic reference catchments. The pine-dominated catchments were completely cleared in 1950 and replanted with white pine, and they are considered treatment catchments in the
paired experiment. Each of the four catchments areas is on the order of 10 ha. Table 4.1 summarizes area and other spatial characteristics of the study catchments. Between 2010 and 2011, three hillslopes in each catchment were instrumented with shallow wells. These hillslopes cover a range of topographic variables including drainage area, slope, and aspect. Table 4.2 summarizes the topographic variables for all of the instrumented hillslopes.

Soils within the catchments are mostly sandy loam and belong to the Chandler series. Soils can be as deep as 6 m and are underlain by deeply weathered saprolite. The Coweeta basin has two major bedrock formations, the Tallulah Falls Formation and the Coweeta Group [Hatcher, 1971]. Both formations are predominantly metamorphic and crystalline [Hatcher 1974; 1979].
4.3 Methods

4.3.1 Geospatial Analysis

The National Center for Airborne Laser Mapping (NCALM) collected light detection and ranging (LIDAR) data for Coweeta Hydrologic Laboratory in 2010. The NCALM datasets included 1 m x 1 m digital elevation models (DEMs) of the bare earth surface and the top of the vegetation canopy. We resampled the 1 m x 1 m bare earth DEM to 5 m resolution to avoid the confounding effects of microtopography on geospatial algorithms used to represent subsurface drainage patterns from surface topography [Seibert and McGlynn, 2007]. The topographic variables computed at 5 m resolution included, elevation, slope, drainage area, topographic wetness index (TWI), plan curvature, profile curvature, flow path length to the stream, and gradient to creek (GTC). We used the multidirectional flow accumulation algorithm of Seibert and McGlynn [2007] to estimate the drainage area of each 5 m pixel.

4.3.2 Data Collection

The study period for this project was October 1, 2011 through Dec 31, 2013. Stream discharge was measured continuously by the US forest service (USFS) using V-notch weirs at the outlet of each catchment. Rainfall was also recorded by the USFS at 30-minute intervals, at a rain gauge (RG20) in south facing catchment (SFC) and a rain gauge (RG96) in north facing catchment (NFC). The RG96 and RG20 were located in a clear-cut area at an elevation of 887 m and 817 m in WS17 and WS2, respectively.

We monitored shallow groundwater stages in 12 instrumented hillslopes (three hillslopes per catchment). For each hillslope, we installed wells to monitor the water table in
shallow, unconfined aquifers located in near stream (NS) and hillslope (HS) landscape positions (Figure 4.1). Wells on a hillslope in a catchment are referred as watershed name (e.g., WS01) followed by hillslope number (H1-H3, where 1 being the most downstream hillslope and 3 being the most upstream hillslope). Groundwater stage was measured at 30-minute intervals using capacitance rods with ±1 mm accuracy (Tru-Track, Inc., Christchurch, NZ). Wells were constructed using both a portable, gas-powered auger with a flight diameter of 4.8 cm, and a sledgehammer-driven steel rod having a diameter of 3.8 cm (1-1/4 inch). Well screening consisted of 3.8 cm inner-diameter PVC conduit (schedule 40) slotted from approximately 10 cm below ground to the completion depth. Wells were open at the bottom. Completion depth was assumed to be bedrock and ranged from 0.9 m to 3.5 m below the surface. Bentonite clay was packed around each well at the soil surface to prevent surface runoff or direct precipitation from entering wells.

4.3.3 Data Analyses

Storms were identified manually using data from both rain gauges. The following criteria were applied for event selection: i) 30-minute rainfall equaled or exceeded 0.5 mm, and ii) total event rainfall exceeded 20 mm. We identified 72 distinct storms that met the above criteria during the study period, and out of those we selected 40 storms for which complete hydrologic datasets were available immediately before, during and for 3 days after each storm.

We calculated several response metrics from measurements at each well for the selected storm events. We defined a minimum threshold for groundwater response as 3 mm of rise in 30 minutes (three times the uncertainty of the capacitance rod). The response
percentage was defined as the percentage of storms that generated detectable response in each well. The initial response rainfall \((P_i)\) was defined as the total amount of rain occurred before the onset of response during storms. The initial response time \((T_i)\) was defined as time required to initiate the response since the arrival of storm. The absolute rise \((AR)\) in stage for a well was defined as the difference between minimum and maximum stage during a storm, where the difference was greater than or equal to 10 mm. The time to peak \((T_p)\) was defined as difference between the time at initiation of well response and time of peak well response. The peak to peak \((T_{p2p})\) was defined as the time difference between the time of peak rainfall and time of peak well response. The slope of rise \((S_r)\) was defined as the change in well stage divided by the time it took to reach peak. Antecedent wetness conditions \((AWC)\) were defined as the groundwater stage 1 hour prior to the arrival of storm. This could also be used as a means to understand the deficit in local storage. We tested for significant differences between distributions and medians of datasets using the Kolmogorov–Smirnov test (hereafter, KS) and Wilcoxon Rank-Sum (hereafter, Wilcoxon) test, respectively. We assessed correlations between storm characteristics, groundwater responses and topographic variables using Spearman’s rank correlation \(\rho\).

We calculated positive lag correlation \(\rho_l\) from lag 0 to lag 10 between groundwater stages and runoff for selected storms. Prior to estimating lag correlations, time series were de-trended to remove serial auto-correlations following Chatfield (2004). During each storm, we identified the strongest significant correlation \(\rho_{\text{max}}, P < 0.05\) and its corresponding lag \(l_{\text{max}}\) for each well. Lag 0 means both groundwater and runoff responses are nearly synchronous \((\pm 30\) minutes\), and positive lag means runoff peaks before groundwater.
4.4 Results

4.4.1 Annual Dynamics of Rainfall, Runoff and Groundwater and Storm Characteristics

During the 26-month study period, NFC received an annualized average 2616 mm yr\(^{-1}\) of precipitation, and SFC received an annualized average 2387 mm yr\(^{-1}\) of precipitation. Median 30-minute rainfall did not differ significantly between NFC (median: 1.60 mm) and SFC (median: 1.61 mm). On an annual basis, runoff from the catchments averaged 732 mm yr\(^{-1}\) (WS01) and 945 mm yr\(^{-1}\) (WS02) for SFC, and 811 mm yr\(^{-1}\) (WS17) and 1294 mm yr\(^{-1}\) (WS18) for NFC (Figures C1-C4). The median half-hourly runoff was also significantly higher (Wilcoxon p<0.05) for deciduous catchments (WS02, WS18) than for their paired pine catchments (WS1, WS17).

Groundwater stages were highly variable in space and time during the study period (Figures C1-C4; Table 4.3). In general, stages were higher for NS wells than for HS wells, while variability was greater for HS wells than NS wells (Table 4.3). Overall, groundwater stages were highest for WS18, lowest for WS01 and the largest temporal variability in stages was noted for WS17.

Characteristics of the 40 storms are summarized in Table 4.4. Medians of properties for the 40 storms did not differ significantly between NFC and SFC (Wilcoxon P>0.05). Storm magnitudes ranged from 20 mm to 179 mm, and their periods ranged from 2.5 to 38 hours. Peak intensities ranged from 3 mm 30 min\(^{-1}\) to 28 mm 30 min\(^{-1}\). Twenty-six events occurred during the dormant season, and the remaining 14 events occurred during the growing season. Storm depth and period were significantly correlated at both rain gauges (p>0.61, P<0.001).
4.4.2 Shallow Groundwater Response Metrics across Catchments

We observed large spatiotemporal variability in groundwater responses for the selected storm events (Figures 4.2, 4.3, 4.4). Table 4.5 summarizes the response percentages for all wells across catchments. In general, NS wells in NFC had larger response percentages than NS wells in SFC (Table 4.5). Some wells never responded to storm events, possibly because the groundwater stages were consistently higher such as HS wells of WS17H3 or consistently lower such as HS wells of WS2H1 (Table 4.3). We also observed strong correlations among some groundwater response variables including relationships between absolute rise and slope of rise, and time to peak and peak-to-peak time (Table 4.6). These relationships were similar in both SFC and NFC. The remainder of this section highlights key findings related to the distributions of response metrics among NS wells and HS wells within each catchment, and between NS and the corresponding HS wells within each study hillslope.

The median $P_i$ (i.e., total amount of rain prior to the onset of a groundwater response) was significantly different among HS wells within each study catchment, but no such patterns existed for NS wells (Figures 4.2a, 4.3a). Similar spatial patterns were noted for median $T_i$ (Figures 4.2b, 4.3b). Within paired catchments, $P_i$ was significantly higher for pine catchments (WS01) than deciduous catchments (WS02; Wilcoxon $P=0.01$) only for SFC. Similarly, median $T_i$ was significantly higher for WS01 (5 hours) than for WS02 (3 hours; Wilcoxon $P<0.001$). The $P_i$ was significantly higher for SFC than NFC (Wilcoxon $P=0.01$) but $T_i$ was indistinguishable between SFC and NFC (Wilcoxon $P>0.05$).
Among all catchments, the median absolute rise for NS wells was relatively low and less variable than it was for HS wells (Figures 4.2c, 4.3c). Similarly, the $T_p$ was significantly short for NS wells that were relatively shallow than the corresponding HS wells (Wilcoxon $P<0.05$; Figures 4.2d, 4.3d). The median absolute rise was significantly less for WS01 (37 mm) than for WS02 (130 mm), and significantly greater for WS17 (186 mm) than for WS18 (46 mm; Wilcoxon $P<0.001$). No significant differences were noted for $T_p$ within paired catchments, but $T_p$ was significantly higher for SFC than NFC (Wilcoxon $P<0.001$). These results suggest that aspect, as a proxy for energy availability in these catchments, may exert significant control on both groundwater response magnitude and timing. The spatial patterns of $T_{p2p}$ were similar to $T_p$ and the positive values of $T_{p2p}$ suggest that groundwater always peaked after rainfall (Figures 4.2e, 4.3e). The median $S_r$ was not significantly different between NS wells and HS wells with few exceptions of deeper wells (e.g., WS18H3; Figures 4.2f, 4.3f). The $S_r$ was significantly higher for WS02 than WS01 (Wilcoxon $P<0.001$) and significantly higher for WS17 than WS18 (Wilcoxon $P<0.001$).

Figures 4.5 and 4.6 demonstrate the spatiotemporal patterns of response magnitude (absolute rise) and timing (e.g., $T_i$, $T_p$) for varying seasons and precipitation characteristics. Seasonal differences (growing versus dormant) were only noted for $T_i$ (Wilcoxon $P=0.02$) and $T_p$ (Wilcoxon $P=0.003$) for wells in SFC. No seasonal differences were noted in response metrics for NFC. We observed remarkably high spatial variability ($CV>1$) in $T_p$ for storms during wet dormant and early growing seasons (Figures 4.5, 4.6). Similarly, spatial variability in absolute rise was higher during dormant seasons ($CV>1.2$) than during growing seasons ($CV<1$). Some of the large spatial variability in absolute rise, $P_i$, and $T_i$ were
associated with large storms that occurred during dry growing seasons or early dormant seasons (e.g., Storm 4, Storm 40; Figures 4.5, 4.6). Similarly, low spatial variability in absolute rise, $P_i$, and $T_i$ were noted for relatively small but high-intensity storms (e.g., storm 14, storm 34; Figures 4.5, 4.6). Besides a few large storms (e.g., Storm 4), $P_i$ did not exhibit much spatial variability. An exception to this result was that one HS well (WS2H3) exhibited the smallest $P_i$ and shortest $T_i$ throughout the study period.

4.4.3 Spatiotemporal Controls on the Groundwater Response

The magnitude and timing of groundwater responses were correlated with storm properties for most of the wells, but the relationship was stronger and more frequent for NS wells or wells located on large hillslopes (DA $> 10^4$ m$^2$; Figure 4.7). Groundwater responses were also correlated with AWC, and the relationship was stronger for HS wells than for NS wells (Figure 4.7). In general, groundwater response magnitude was positively correlated with storm depth, peak and mean intensity, and it was negatively correlated with AWC. In other words, higher antecedent wetness yielded smaller groundwater responses. The response timing variables ($T_i$, $T_{p2p}$, $T_p$) were negatively correlated with AWC, peak intensity and mean intensity, and positively correlated to storm depth. The $S_r$ was positively correlated with storm depth, mean intensity and peak intensity, and it was negatively correlated with AWC. The strength of these relationships varied among wells. These findings highlight important connections between climate and groundwater responses across all landscape positions.

We found strong relationships ($\rho >0.70$, $p<0.05$) between groundwater response magnitude and topographic variables (e.g., drainage area, slope) during the largest storm events, although groundwater response timing was correlated with TWI and slope during
most of the storms. We detected relatively weak relationship between absolute rise and drainage area and TWI, and $S_r$ and GTC. Significant relationships between median groundwater response timings ($T_i$, $T_p$) and topographic variables (e.g., slope, TWI) were observed in all catchments (Table 4.7).

### 4.4.4 Relationship between Shallow Groundwater and Runoff across Catchments

We found large spatiotemporal variability in the distributions of $\rho_{\text{max}}$ (-0.61 to 0.90) and $l_{\text{max}}$ (0 to 10) in all four catchments (Figure 4.8). In general, significant values of $\rho_{\text{max}}$ were observed for wells with relatively large drainage areas. Negative $\rho_{\text{max}}$ values were observed for HS wells more frequently than NS wells (Figure 4.8). With few exceptions, $l_{\text{max}}$ was zero for NS wells. Hillslopes with small drainage areas had high variability in lags than hillslopes with larger drainage areas (Figure 4.8). Wells in NFC exhibited significant peak correlations at lag 0 more frequently than wells in SFC. These results highlight the combined role of landscape position and aspect in mediating the spatial patterns of groundwater-runoff relationships over time.

For most of the storms, $\rho_{\text{max}}$ was relatively high for NS wells compared to their adjacent HS wells (Figure 4.8). During small storms (<35 mm), $\rho_{\text{max}}$ were only detected for some NS wells or wells with relatively large drainage area, and lags were relatively long (Figure 4.8). During some of these events, a few HS wells exhibited negative $\rho_{\text{max}}$ with long lags. During high intensity events (>20 mm 30min$^{-1}$), $\rho_{\text{max}}$ was high compared to lower-intensity storms and the corresponding lags were zero for most wells. During large events (>90 mm), high $\rho_{\text{max}}$ with zero lags were noted for most of the wells (Figure 4.8). We observed a significant positive correlation (p<0.05) between storm depth and $\rho_{\text{max}}$ for most of the
wells, but no such patterns were noted with other storm properties. No significant correlation (p<0.05) was noted between storm period and $I_{\text{max}}$. These results indicate the strong influence of storm depth on the groundwater-runoff relationship in these headwater catchments.
4.5 Discussion

4.5.1 Spatiotemporal Control of Groundwater Responses

4.5.1.1 Rainfall Requirements for Groundwater Responses

Our analysis showed that the rainfall requirements to elicit groundwater responses ($P_i$) were significantly higher for SFC than NFC (Figures 4.2, 4.3). These results point to the important role of aspect in mediating hydrological processes within catchments [e.g., Emanuel et al., 2014; Smith et al., 2014]. Our findings suggest that within catchments, $P_i$ is not solely controlled by antecedent wetness conditions, but it is also influenced by topographic conditions (Figures 4.4, 4.5, 4.6). During most of the storms, NS wells with relatively high stages responded at about the same time, leading to no significant difference in $P_i$ among them (Figures 4.5, 4.6). In contrast, HS wells with relatively low stages and greater depths than their corresponding NS wells had greater $P_i$ than their corresponding NS wells (Table 4.3; Figures 4.5, 4.6). These results suggest the role of local storage deficit associated with HS wells that need to be sufficed before groundwater can respond to storms. One exception was a HS well (e.g., WS2H3) with the largest drainage area and high TWI which exhibited the smallest $P_i$, irrespective of the storm properties. Due to the topography of landscape positions, HS wells received large amount of sub-surface flow in short time and responded earlier than their corresponding NS wells, leading to very small values of $P_i$, regardless of the storm properties (Figures 4.5, 4.6). These results are counterintuitive, as we generally presume that NS wells will require less rain to respond due to their high antecedent conditions. Nevertheless, these results suggest that rainfall requirements to generate groundwater responses depend on the both topography and antecedent conditions.
4.5.1.2 Absolute Rise of Groundwater

We observed large spatiotemporal variability in the absolute rise of groundwater in response to storms (Figures 4.5, 4.6). In general, the low temporal variability observed for absolute rise in NFC highlights the role of aspect and relatively wet antecedent condition throughout the study period. For most of the hillslopes, higher values of absolute rise for HS wells relative to NS wells could be due to the large storage capacities and low AWC that characterized HS wells (Figures 4.2, 4.3; Table 4.3). The spatial patterns of absolute rise also depended upon the responsiveness of each well, which could be influenced by the topography and soil properties of the landscape position. The large magnitude of absolute rise observed for WS17 and WS02 corresponded to some of the highest Sr (Figures 4.2, 4.3), suggesting that hillslopes in these catchments were able to mobilize relatively large amount of subsurface flow in a shorter duration compared to other catchments. This can be possible when either hillslope is contributed by significantly larger drainage area as noted in WS02, or activation of preferential flow paths or presence of macropores along hillslopes [e.g., Sidle et al., 2001].

Our analysis suggests that the strength of topographic control varied with storm characteristics and antecedent wetness conditions. It is possible that subsurface flow initiated during large storms can increase wetness state and hydrologic connectivity of hillslopes [e.g., Burt and Butcher, 1985, Jencso et al., 2009], leading to strong topographic control on spatial pattern of absolute rise. In particular, topographic conditions such as, high TWI or large drainage area encourage the convergence and accumulation of shallow groundwater,
influencing patterns of absolute rise during storms (Table 4.7). Few prior studies have evaluated topographic controls on absolute rise during storms. Recently, Penna et al. [2014] reported relatively strong topographical controls (TWI and slope) on absolute rise for two hillslopes in a pre-alpine headwater catchment with shallow soils (< 2 m depth). When combined with our findings at Coweeta, these results indicate that the strength of topographic control on groundwater response to storms might be sensitive to soil depth.

Our analysis suggests that storm characteristics (e.g., storm depth, mean intensity and peak intensity) influence the temporal patterns of absolute rise for wells with relatively large drainage areas (Figure 4.7). It is possible that due to persistently high groundwater stage and shallow soils (Table 4.3), NS wells respond early and reach their peaks rapidly, leading to close connections between groundwater responses and storm properties. The significant relationship between groundwater response and storm depth and storm intensities indicate that groundwater response for some of these wells may not be hydrologically limited as observed in other landscapes [e.g., Fannin et al., 2000]. We also detected strong influence of antecedent wetness condition on absolute rise suggesting that groundwater stage prior to storm can have strong influence on absolute rise in these catchments.

4.5.1.3 Timing of Groundwater Response

Groundwater response timing exhibited distinct patterns in space and time (Figures 4.5, 4.6). In general, due to similar wetness conditions and well depths, no significant differences in T1 were noted among most of the NS wells (Figures 4.5, 4.6; Table 4.3). In contrast, significant difference in T1 observed among all HS wells could be due to the high variability in well depths (Table 4.3) or differences in topographic variables among their
landscape positions. Spatial variability in response times were lower prior to the onset of response \(T_i\), but once the response was triggered, \(T_p\) exhibited much larger spatial variability than \(T_i\) (Figures 4.5, 4.6). These differences in response timing \(T_p\) could be attributed to variability in sources and flow paths contributing to shallow groundwater on individual hillslopes as well as differences in storage deficits that we can approximate from AWC.

Our analysis suggests that storm characteristics (e.g., storm depth, peak and mean intensities) and AWC exerted strong control on response timings across study catchments. During high intensity events (> 22 mm 30 min\(^{-1}\)), response times were short (Figures 4.5, 4.6), suggesting rapid movement of the wetting front due to high infiltration rates characteristic of forest soils at Coweeta [Price et al., 2010]. Some of the large variability in response timing was noted for event with small depth (<35 mm) and low mean intensity (<6 mm hr\(^{-1}\)), indicating the potential role of soil properties in influencing the spatial patterns of response timings (Figures 4.5, 4.6). These soil properties have been shown to influence groundwater responses in other headwater systems [Penna et al., 2014]. Furthermore, large spatial variability observed in response timings (CV>1) during relatively large events occurring in relatively dry times (e.g., storm 4) points to the heterogeneity in antecedent conditions or activation of preferential flow paths as noted by others [e.g., Harpold et al., 2010]. These are some of the storms when spatial variability was high for all response metrics (e.g., absolute rise, \(P_i\); Figures 4.5, 4.6). As an exception, greater spatial variability was noted for \(T_p\) and \(T_{p2p}\) but not for other response variables, during wet dormant or early growing seasons. This variability could be attributed to the threshold-activated flow paths
due to extremely wet conditions [e.g., Sidle et al., 2000; 2001]. Studies have shown that occurrences of lateral flow in soil profile are more likely to happen under extremely wet condition than drier antecedent conditions [Grayson et al., 1997], and the patterns of lateral flow can contribute to the spatial variability in response timings within a catchment.

During large storms, we found significant topographic controls on response timing for both south and north facing catchments. During large storms, slope, drainage area, and TWI all encouraged the potential availability of water and wetness state, and influenced the patterns of groundwater response timing. However, the topographic control was weaker for a few median response timings, and local slope was the only common variable that exhibited significant relationship with response timing for north and south facing catchments (Table 4.7). These results point to the heterogeneity in shallow groundwater dynamic and their associated topographic controls, where the combination of topographic relationships was noted. We also found significant control of DFC (i.e., flow path length from stream) on the patterns of $T_p$. We speculate that flow path length might influence antecedent conditions of the landscape position and that could affect the patterns of $T_p$ for wells.

4.5.2 Relationship between Runoff and Groundwater

The spatiotemporal patterns of $\rho_{\text{max}}$ and the corresponding $l_{\text{max}}$ during storms demonstrate strong influence of storm depth and topographic variables on shallow groundwater and runoff relationships through time (Figure 4.8). In general, high occurrence frequency of $\rho_{\text{max}}$ was noted for NS wells or HS wells with relatively large drainage area ($>10^4$ m$^2$). Similarly, for these wells, during most of the storms, $l_{\text{max}}$ was zero suggesting that groundwater and runoff peaked around the same time and the corresponding landscape
positions may have contributed to peak runoff (Figure 4.8). These results point to the intimate connection between runoff and groundwater that does not necessarily depend upon the proximity to stream but could also be sensitive to drainage area of the wells. However, other HS wells with small drainage areas exhibited relatively weak $\rho_{\text{max}}$ and large $l_{\text{max}}$, suggesting that groundwater-runoff relationships do decline away with distance from the stream and those landscape positions may not have contributed to peak runoff during storms. Furthermore, high spatiotemporal variability found in $l_{\text{max}}$ for HS wells could be due to dry antecedent wetness conditions. Other studies have reported similar behavior in other landscapes with different hydro-climatic conditions [e.g., Haught and Meerveld, 2011].

Small storms (<35 mm depth) are more likely to generate less subsurface flow, leading to weak or non-significant groundwater-runoff relationships (Figure 4.8). Some wells exhibited negative $\rho_{\text{max}}$, indicating that runoff peaked and began to decline while groundwater continued to rise in these landscape positions. High intensity events (> 20 mm 30min$^{-1}$) can generate relatively greater amount of subsurface flow in relatively short time than small storms, leading to strong $\rho_{\text{max}}$ in space. During large storms (>90 mm), most of the wells exhibited strong relationships with positive lags (for wells with small drainage areas) or zero lags (for wells with large drainage areas), implying that large storms may not only influence the strength of groundwater-runoff relationships, but also minimize the spatial variability of the relationships. Furthermore, these results also indicate the strong control of storm depth and topography on the source areas that may contribute to peak runoff during storm at the catchment outlet.
4.6 Conclusions

The patterns of shallow groundwater response (magnitude and timing) to storms exhibited large variability in space and time across instrumented hillslopes. Significant differences in responses (e.g., absolute rise, $P_i$, $T_p$) between south and north facing catchments indicated the role of aspect in influencing shallow groundwater dynamics for these headwater catchments. During most of the storms, we found relatively strong controls of storm properties and antecedent conditions on the spatial patterns of groundwater rise and response timings. We also detected strong effects of topography on response timings during many storms, but the absolute rise of groundwater was only linked to topographic control during large storms. The spatiotemporal patterns of $\rho_{\text{max}}$ and $l_{\text{max}}$ suggest that storm depth and landscape position influenced groundwater-runoff relationships during storms. This study advances our understanding of shallow groundwater dynamics during storms for forested catchments of the southern Appalachian Mountains, which are characterized by humid climate and relatively deep soils. Our work complements previous findings by others working in different climates and topographic settings, and it contributes to this growing body of research by highlighting the role of topography and storm properties on shallow groundwater dynamic and its relationship with runoff.
4.7 References


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to precipitation in humid areas, in Forest Hydrology, edited by W. E. Sopper and H.


Table 4.1 Summary of landscape variables for study catchments

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<th>Landscape Variables</th>
<th>WS01</th>
<th>WS02</th>
<th>WS17</th>
<th>WS18</th>
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<tbody>
<tr>
<td>Minimum Elevation (m)</td>
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<td>707</td>
<td>739</td>
<td>719</td>
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<td>1005</td>
<td>1031</td>
<td>983</td>
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<td>817</td>
<td>815</td>
<td>796</td>
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<tr>
<td>Mean Slope (Degree)</td>
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<td>29</td>
<td>28</td>
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<tr>
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<td>0-62</td>
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<td>12</td>
<td>13</td>
<td>12</td>
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<td>Dominant Aspect</td>
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<td>North</td>
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Table 4.2 Spatial characteristics for the study hillslopes.

<table>
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<tr>
<th>Hillslopes</th>
<th>DA (m²)</th>
<th>Elevation (m) (Mean)</th>
<th>Slope (Degree) (Mean)</th>
<th>TWI ln (m) (Mean)</th>
<th>GTC (Mean)</th>
<th>DFC (m) (Mean)</th>
<th>DFC/GTC (m) (Mean)</th>
<th>Plan Curv. (Mean)</th>
<th>Profile Curv. (Mean)</th>
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Gradient to Creek (GTC), Topography wetness Index (TWI, logₑ m), DFC (Flow path length, m), Drainage Area (DA, m²);
Table 4.3 Summary of physical measurements and distribution of shallow groundwater stages for the study wells.

<table>
<thead>
<tr>
<th>Groundwater Wells</th>
<th>Well Depth (m)</th>
<th>Distance from Stream (m)</th>
<th>Inter Quartile Range (P_{75}-P_{25}) (m)</th>
<th>*Detectable water present in the wells (%)</th>
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<tbody>
<tr>
<td>WS01T1NS</td>
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<td>99</td>
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<td>56</td>
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<td>97</td>
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*duration for which groundwater was above the measuring capacitance rod
Table 4.4 Storm characteristics for rain gauges RG20 and RG96 located in South and North Facing catchments.

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<th>(Rain Gauge 20)</th>
<th>(Rain Gauge 96)</th>
<th>Peak Intensity (mm 30 min⁻¹)</th>
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141
Table 4.4 Continued

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<th>Peak Intensity (mm 30min⁻¹)</th>
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Table 4.5 Groundwater response percentages for study wells.

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<td>H3HS</td>
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*Response (%) represents the percentage of storms that generated detectable response at each well.
Table 4.6 Correlation matrix (Spearman’s ρ) among groundwater response variables for south facing catchments.

<table>
<thead>
<tr>
<th>Rho (p&lt;0.01)</th>
<th>Absolute Rise</th>
<th>Sr</th>
<th>Ti</th>
<th>Tp</th>
<th>Tp2p</th>
<th>Pi</th>
</tr>
</thead>
<tbody>
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<td>AR</td>
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<td>0.30</td>
<td>0.06*</td>
<td>0.18</td>
</tr>
<tr>
<td>Sr</td>
<td>0.60</td>
<td>1.00</td>
<td>-0.25</td>
<td>-0.51</td>
<td>-0.54</td>
<td>0.09*</td>
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<tr>
<td>Ti</td>
<td>-0.08*</td>
<td>-0.25</td>
<td>1.00</td>
<td>0.18</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>Tp</td>
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<td>-0.51</td>
<td>0.18</td>
<td>1.00</td>
<td>0.78</td>
<td>0.05*</td>
</tr>
<tr>
<td>Tp2p</td>
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<td>-0.54</td>
<td>0.43</td>
<td>0.78</td>
<td>1.00</td>
<td>-0.05*</td>
</tr>
<tr>
<td>Pi</td>
<td>0.18</td>
<td>0.09</td>
<td>0.32</td>
<td>0.05*</td>
<td>-0.05*</td>
<td>1.00</td>
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* Not significant (P > 0.05)
### Table 4.7 Correlation between topographic variables and groundwater response

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<th>Slope (Degree)</th>
<th>GTC</th>
<th>TWI (ln m)</th>
</tr>
</thead>
<tbody>
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<td></td>
</tr>
<tr>
<td>$T_{p2p}$</td>
<td>0.52(0.09)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_p$</td>
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</tr>
<tr>
<td>AR</td>
<td>0.57(0.07)</td>
<td></td>
<td></td>
<td>0.51(0.1)</td>
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<tr>
<td>$S_r$</td>
<td>-</td>
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<td>-</td>
<td>-0.65(0.03)</td>
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</table>

<table>
<thead>
<tr>
<th>NFC</th>
<th>$\rho$ (P value)</th>
<th>Slope (Degree)</th>
<th>DA (m$^2$)</th>
<th>DFC (m)</th>
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</thead>
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<td>0.75(0.01)</td>
<td></td>
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<td>$T_{p2p}$</td>
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<td>$T_p$</td>
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<td></td>
<td>0.61(0.05)</td>
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</tr>
<tr>
<td>AR</td>
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<td></td>
<td>0.56(0.08)</td>
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</tr>
<tr>
<td>$S_r$</td>
<td>-</td>
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</table>

“-” represents no significant relationship (P>0.1)
Figure 4.1 Showing the map of WS02 (a), WS01 (b), WS18(c), and WS17 (d) with delineated hillslopes and landscape positions of groundwater wells.
Figure 4.2 Distribution of groundwater response metrics, $P_i$ (a), $T_i$ (b), AR (c), $T_p$ (d), $T_{p2p}$ (e), and $S_r$ (f), to the selected storms for near stream (NS, left side of the panels) and hillslope (HS, right side of the panels) wells for south facing catchments. Filled boxes represent WS01, and open boxes represent WS02. The NS wells (left column) and HS wells (right column) are arranged by increasing drainage area within each group.
Figure 4.3 Distribution of groundwater response metrics, $P_i$ (a), $T_i$ (b), AR (c), $T_p$ (d), $T_{p2p}$ (e), and $S_r$ (f), to the selected storms for near stream (NS, left side of the panels) and hillslope (HS, right side of the panels) wells for north facing catchments. Filled boxes represent WS17, and open boxes represent WS18. The NS wells (left column) and HS wells (right column) are arranged by increasing drainage area within each group.
Figure 4.4 Median groundwater response metrics, $P_i$ (a), $T_i$ (b), AR (c), $T_p$ (d), $T_{p2p}$ (e), and $S_r$ (f) for all wells with the corresponding drainage area for south facing (black filled circle) and north facing (red filled circle) catchments.
Figure 4.5 Spatiotemporal patterns for response metrics, $P_i$ and $T_i$ (a), AR and $T_p$ (b), for the near stream (NS, top panel of each subplot) and hillslope (HS, bottom panel of each subplot) wells in the south facing catchments. The size of circle represents amount for $P_i$ (mm) and Absolute rise (mm), and color represents time (hour) for $T_i$ and $T_p$. The NS and HS wells are arranged by increasing drainage area within each group. Gray cross represents no response during the storms. Gap represents missing data.
Figure 4.6 Spatiotemporal patterns for response metrics, $P_i$ and $T_i$ (a), AR and $T_p$ (b), for the near stream (NS, top panel of each subplot) and hillslope (HS, bottom panel of each subplot) wells in the north facing catchments. The size of circle represents amount for $P_i$ (mm) and Absolute rise (mm), and color represents time (hour) for $T_i$ and $T_p$. The NS and HS wells are arranged by increasing drainage area within each group. Gray cross represents no response during the storms. Gap represents missing data.
Figure 4.7 Spearman correlations ($\rho$) between response metrics, storm characteristics and antecedent wetness conditions for near stream (NS) and hillslope (HS) wells. Color represents significant correlations ($p<0.05$).
Figure 4.8 Variation of $\rho_{\text{max}}$ and $l_{\text{max}}$ with storm depth for near stream and hillslope wells along select hillslopes in WS01 (a, b), WS02 (c, d), WS17 (e, f) and WS18 (g, h). Color represents $l_{\text{max}}$ from zero (dark blue) to 10 (light yellow).
CHAPTER 5

Hydro-Climatological Influences on Long-Term Dissolved Organic Carbon in a Mountain Stream of the Southeastern United States

Abstract

In the past decade, significant increases in surface water dissolved organic carbon (DOC) have been reported for large aquatic ecosystems of the Northern Hemisphere and have been attributed variously to global warming, altered hydrologic conditions, and atmospheric deposition among other factors. We analyzed one of the longest DOC records (1988-2012) available for a forested headwater stream in the United States and documented two distinct regimes of stream DOC trends. From 1988-2001, annual mean volume-weighted DOC concentration (DOC$_{vw}$, mg L$^{-1}$) and annual DOC flux (kg ha$^{-1}$ yr$^{-1}$) declined by 34% and 56%, respectively. During 1997-2012, the decline in DOC$_{vw}$ and DOC flux increased by 141% and 165%, respectively. Declining DOC$_{vw}$ from 1988 to 2001 corresponded to a decline in growing season runoff, which has the potential to influence mobilization of DOC from uplands to streams. Increasing DOC$_{vw}$ from 1997 to 2012 corresponded to increased precipitation early in the growing season, and an increase in number and intensity of short-duration fall storms capable of mobilizing long-accrued DOC from forest litter and soils. Rising air temperature, atmospheric acid deposition and nitrogen depositions did not offer any plausible explanation for the observed bi-directional annual trends of stream DOC$_{vw}$. Our study highlights the critical role of long-term datasets and analyses for understanding impacts of climate change on carbon and water cycles and associated functions of aquatic and terrestrial ecosystems.
5.1 Introduction

Headwater streams constitute almost 70% of the total length of streams in the United States [Leopold et al., 1964]. These streams can influence the global carbon cycle by outgassing CO$_2$ [Buttman and Raymond, 2011] and by transporting large amounts of organic carbon to downstream environments [West et al., 2011; Reichstein et al., 2013]. Headwater streams are intimately linked with their surrounding terrestrial ecosystems, and highly sensitive to biogeochemical processes within their contributing areas [Lowe and Likens, 2005]. Due to interactions between headwater streams and the surrounding terrestrial ecosystems [Gomi et al., 2002; Beckman and Wohl et al., 2014], headwater streams receive most of their organic carbon in the form of dissolved organic carbon (DOC) [e.g., Meyer and Tate, 1983]. In forested headwater streams, DOC influences energy supplies [Aitkenhead-Peterson et al., 2003], trophic resources [Hall and Meyer, 1998] and water quality [Stewart and Wetzel, 1981; McKnight, 1981]. Furthermore, DOC not only dominates the carbon cycle of headwater streams [Dahm 1981], but it also mediates biogeochemical cycles of nitrogen [Bernhardt and Likens, 2002], phosphorus [Ardón et al., 2006] and other elements. At high concentrations, DOC imparts color to the stream and protects microorganisms from ultraviolet radiation [Curtis and Schindler, 1997].

In the past two decades, studies focusing on Northern Hemisphere sites have reported significant increases in freshwater DOC concentration and export (Table 5.1). Several of these studies have investigated potential drivers of long-term DOC patterns, but no single driver has been implicated among all studies. Some of the major drivers include rising air temperature [Freeman et al., 2001], hydrological change [e.g., Eimers et al. 2008a-b],
recovery from acidification [Monteith et al., 2007], nitrogen deposition [Finlay, 2005], and land use land cover change [Aitkenhead-Peterson et al., 2009]. However, many of these studies were conducted on large, freshwater bodies such as lakes and rivers of mid to high latitudes, many of which are heavily influenced by wetlands and snowmelt-dominated runoff. Fewer studies have investigated long-term (>10 years) trends of stream DOC and associated potential drivers for humid mountainous watersheds [Lutz et al., 2012]. But, Lutz et al. [2012] was limited in the data sets and used a combination of observed and modeled DOC time series for the analysis.

Here, we analyzed a 25-year DOC record along with ancillary hydro-climatic and atmospheric deposition data for a forested headwater stream in the Appalachian Mountains of the southeastern United States. Long-term datasets provided a unique opportunity to understand the possible impacts of climate change on carbon and water cycles in streams that are more sensitive to anthropogenic forcing [Lowe and Likens, 2005]. Our objectives were to quantify and evaluate long-term trends of DOC concentration and flux in the stream over the period 1988 through 2012, and to investigate the potential drivers responsible for the observed DOC trends.
5.2. Study Site and Methods

5.2.1 Study Site

The study was conducted at Coweeta Hydrologic Laboratory (hereafter Coweeta), a US Forest Service Experimental Forest and an NSF Long-Term Ecological Research (LTER) site, located in the Southern Appalachian Mountains of North Carolina, US (35°03’N, 83°25’W; Figure D1). The climate is classified as maritime-humid temperate with frequent, short and small rainfall events distributed year-round [Swift et al. 1988]. Since the 1934, Coweeta has been monitoring long-term precipitation and temperature at a low elevation (685m) climate station (CS01) and has observed annual precipitation of 1802 mm and annual temperature of 12.87 °C for 63-year period of record (1950-2012).

The study watershed (WS27) has a drainage area of 39 hectares and elevations ranging from a minimum of 1061 m at the outlet to a maximum of 1455 m at the ridge. The watershed is characteristic of the region’s headwaters with a mean channel bed slope of 33%, a mean areal slope of 55% and soil depths <2 m. Soils in WS27 are predominantly coarse-loamy and belong to chandler soil series. In general, high elevation Coweeta streams are cold in nature, highly depleted in nutrients and have low ionic strength [Swank and Waide, 1988]. Runoff for the second-order perennial stream (Hard Luck Creek) draining WS27 is currently monitored using an instrumented 120° v-notch weir and has a mean annual runoff of 1658 mm for the 63-year period of record (1950-2012). Since 1992, precipitation has been monitored at a climate station (CS77) located within WS27 at an elevation of 1398 m. Mean annual precipitation for the 21-year period of record (1992-2012) at CS77 is 2363 mm. The watershed is considered a reference watershed for paired watershed studies at Coweeta and
has not been harvested since 1929. Two vegetation communities are present within WS27; a northern hardwood community is dominated by Quercus rubra, Betula allegheniensis and Betula lenta, and a mixed oak community is dominated by Quercus spp. and Carya spp. [Elliott et al., 1999]. The bedrock underlying WS27 is metamorphic and comprises biotite, gneiss, metasandstone, and schists [Velbel, 1985]. Unfractured bedrock beneath WS27 is highly impermeable, suggesting that runoff measured at the weir accurately represents total water drainage from the study watershed [Swift et al., 1988].

5.2.2 Methods

Dissolved organic carbon concentrations were measured in water samples (n~1000) collected weekly to bi-weekly from WS27 between 1988 and 2012. Water samples were collected from the stream immediately upstream of the weir pond, filtered using a Gelman A/E glass fiber filter with pore size of 0.3 µm and refrigerated until analyzed. Samples were analyzed for DOC using two different methods: i) an Oceanography International Organic Carbon analyzer using persulfate oxidation (1988-2001), ii) a Shimadzu TOC- 5000A Total Carbon Analyzer (2001-2012) using high temperature combustion. Dissolved organic carbon concentrations obtained from the persulfate method (PS) were converted into DOC concentrations from high temperature combustion (HTC) method using the regression equation $HTC = 0.87 \times PS - 0.07$; $r^2 = 0.6$, $p < 0.05$, where the 95% CI for slope ranged from 0.72 to 1.008 and the 95% CI for the intercept ranged from -0.14 to -0.003. These ranges are comparable to other studies juxtaposing both methods [Benner and Hedges 1993]. This regression-based approach for converting DOC values from HTC to PS is consistent with other work at Coweeta summarized by Meyer et al. [2014].
To assess potential bias ($\Delta$DOC=HTC-PS) in our time series due to the change in methods, we evaluated a dataset of 106 surface water samples collected at biweekly intervals from September 1999 to August 2000 from Coweeta streams, which were analyzed for DOC using both of the instruments. Mean stream DOC concentrations were not significantly different between HTC (0.31±0.28 mg L$^{-1}$) and PS (0.44±0.23 mg L$^{-1}$). The mean bias ($\Delta$DOC) for 106 samples was -0.13 mg L$^{-1}$, and the mean absolute difference was 0.11 mg L$^{-1}$. The lower quantile and upper quantile of bias was -0.06 mg L$^{-1}$ and -0.18 mg L$^{-1}$, respectively. The bias was insensitive to DOC concentration (Spearman $\rho = -0.18$, P >0.05), due in part to the relatively low DOC concentrations found in Coweeta waters. These results suggest that although differences were observed between the two methods, the distribution of the bias is generally small relative to the average annual trends. The observed bias was consistent with results from other freshwater studies comparing these two methods [Kaplan 1992], which attribute the systematic bias to incomplete oxidation of recalcitrant DOC in the PS method, error in the removal of inorganic compounds during degassing in the HTC method, and altered solubility of organic acids during the acidification process. Overall, the methodological difference is believed to account for ~ 5% of total uncertainty in DOC estimates from freshwater systems [Kaplan, 1992]. The difference in methods may affect the overall magnitude of DOC reported in this study, but unlikely to affect the direction of DOC trends at Coweeta.

For each month, the volume-weighted DOC concentration ($\text{DOC}_{\text{vw}}$) was calculated as:
\[ DOC_{vw} = \frac{\sum_{j=1}^{n} C_j Q_j}{\sum_{j=1}^{n} Q_j} \]

where \( C_j \) is the DOC concentration of a biweekly sample (mg L\(^{-1}\)) and \( Q_j \) is the instantaneous runoff (L sec\(^{-1}\)) at the time of sampling. Monthly DOC flux was calculated by multiplying monthly \( DOC_{vw} \) by monthly mean runoff for WS27. We assessed DOC patterns on both monthly and water year (WY) basis. We used the water year definition of Meyer et al. [2014], which is November 1 of the water year to October 31 of the following year (e.g. WY 1989 is 1 November 1989 though 31 October 1990). No DOC samples was collected in 1998 and 2002.

Daily runoff (WS27), daily precipitation (CS77) and daily air-temperature (CS01) were acquired from the Coweeta data portal (http://coweeta.uga.edu). We used daily mean runoff to compute the monthly and annual runoff. To study climatic patterns, we used the monthly averages of daily mean temperatures and the monthly averages of daily maximum temperatures from CS01. To understand the temporal trends of precipitation corresponding to the period of DOC record within the study watershed, we used monthly precipitation totals from CS77. Similar to runoff, an annual estimate of precipitation was computed as the sum of monthly precipitation values for each WY. Runoff ratio was calculated as the ratio of annual runoff (WS27) to annual precipitation (CS77). From 1988 until CS77 was established in 1992, we calculated precipitation using a simple regression model: \( Y=1.1057*X+7.022 \) (\( r^2 =0.95 \)), where \( Y \) is modeled monthly precipitation (mm) for the missing months of CS77 and \( X \) is observed monthly precipitation (mm) at CS17, a climate station located in nearby watershed. Discharge data were missing for four months (August - October) in the WY 2002,
four months (November - February) in WY 2003, and 30 days (January - February) in the WY 2012.

Trend analysis on all datasets was performed at annual and monthly time scales, using Mann-Kendall test [MKT; Mann 1945; Kendall 1975], and the rate of change (i.e., slopes) of significant trends were estimated using Sen Slope (SS) method [Sen, 1968]. MKT is a robust statistical test due to its insensitivity to the shape of distribution and outliers of the time series. Where any gaps in time series variables occurred, we used linear least squares regression to estimate the trend slope. The Kendall correlation coefficient (τ) was also used to quantify the relationships between potential drivers and DOC for the study period. We performed Wilcoxon rank sum tests [Wilcoxon, 1945] to evaluate differences between median values of two time series.

We performed a breakpoint analysis to identify the period of time in which trends in stream DOC changed direction. The breakpoint analysis involved computing correlation statistics (one-sided τ and a corresponding p value) for the DOC time series both before and after a potential breakpoint year. We systematically tested each year from 1989 to 2011 to determine whether it met the following criteria for a breakpoint in the time series. We considered a breakpoint in the time series to occur near the maximum sum of |τ| values before and after the potential breakpoint year where both p values were significant. We allowed for uncertainty in the analysis by computing summed |τ| to two significant digits only, allowing us to identify a range of consecutive years during which the trend in DOC changed direction. A Bonferroni adjustment for testing two simultaneous, one-sided correlations yielded a critical p value of 0.05 (0.10/2) [e.g., Schroeter, 2008].
5.3. Results

5.3.1 Temporal Trends in Stream DOC Concentrations and Fluxes

The breakpoint analysis identified a breakpoint in stream DOC trends between 1997 and 2001, with a declining trend in stream DOC\textsubscript{vw} (\(\tau = -0.66, p < 0.05\)) with a linear slope of -0.04 mg L\textsuperscript{-1} yr\textsuperscript{-1} from 1988 to 2001 followed by a rising trend in stream DOC\textsubscript{vw} (\(\tau = 0.72, p < 0.05\)) with a linear slope of 0.09 mg L\textsuperscript{-1} yr\textsuperscript{-1} from 1997 to 2012 (Figure 5.1). Using the linear rates of decline and increase, we estimated a decline of 34% (1988-2001) followed by an increase of 141% (1997-2012) in annual mean DOC\textsubscript{vw} (Figure 5.1). The lowest annual DOC\textsubscript{vw} was observed in 2000 (0.88 mg L\textsuperscript{-1}), during the breakpoint-defined interval (1997-2001). We separated all data sets into pre (1988-2001) and post (1997-2012) intervals to investigate the drivers influencing rising and declining trends in DOC\textsubscript{vw} during each of these intervals.

To further understand trends in DOC\textsubscript{vw}, we compared the temporal patterns of DOC\textsubscript{vw} at a monthly scale for the 1988-2001 and 1997-2012 intervals. For both intervals, significant changes in monthly mean DOC were observed for the growing season months of April and June, and the early fall months of September, and October (Wilcoxon, \(p<0.05\)) (Figures 5.2a-d). A bi-directional trend in mean monthly DOC\textsubscript{vw} was only observed for the month of September (Figure 5.2). For September, we observed a declining trend in DOC\textsubscript{vw} (1988-2001; \(\tau = -0.60, p < 0.05\), linear slope=-0.09 mg L\textsuperscript{-1}) followed by a rising trend in DOC\textsubscript{vw} (1997-2012; \(\tau = 0.67, p < 0.05\), linear slope=0.17 mg L\textsuperscript{-1}) that was consistent in shape to the declining and rising behavior of annual mean DOC\textsubscript{vw} during the 25-year study period (Figure 5.1).
Annual DOC flux declined from 1988 through 2001 ($\tau = -0.60$, $p < 0.05$) with a linear slope of -1.49 kg ha$^{-1}$ yr$^{-1}$. The declining trend was followed by rising DOC from 1997 through 2012 ($\tau = 0.75$, $p < 0.05$) with a linear slope of 1.81 kg ha$^{-1}$ yr$^{-1}$ (Figure 5.3). Based on linear slopes, we computed a decline of 56% between 1988 and 2001 followed by an increase of 165% in annual DOC flux between 1997 and 2012 (Figure 5.3). We also compared seasonal and monthly trends in DOC flux for the 1988-2001 and 1997-2012 intervals and did not detect any significant changes in mean monthly fluxes (Wilcoxon, $p > 0.05$) between both intervals.

5.3.2 Hydro-Climatological Trends

We identified a significant change ($\tau = 0.23$, $p < 0.05$) in annual maximum air temperatures of 1.25 °C over the 25-year period with a Sen Slope (SS) of 0.05 °C year$^{-1}$ (Figure D2). Summer months in particular became warmer, with trends in monthly maximum air temperatures during the 25-year study period observed for June ($\tau = 0.45$, $p < 0.05$) and August ($\tau = 0.34$, $p < 0.05$).

We observed a decline in runoff of 22 mm yr$^{-1}$ ($\tau = -0.28$, $p < 0.1$) and runoff ratio ($\tau = -0.32$, $p < 0.05$), but no significant trends were detected for annual precipitation ($p > 0.05$), during the study period (Figures 5.4). The declining trend in annual runoff suggested a decline of 550 mm (SS of -22 mm yr$^{-1}$) in annual runoff from 1988-2012, which was further supported by declining runoff ratios (Figure 5.4).

We found no significant differences in monthly precipitation or monthly runoff between the two time intervals (Wilcoxon, $p > 0.05$). During the 1988-2001 interval, we identified significant declining trends in monthly runoff for the months of August ($\tau = -0.39$, p
September ($\tau=-0.45$, $p<0.05$) and October ($\tau=-0.45$, $p<0.05$) (Figure 5.5). During the 1997 – 2012 interval, April precipitation increased significantly ($\tau=0.43$, $p<0.05$) (Figure 5.5). We also observed an increase in extreme precipitation for the month of September (Figure 5.5), which was previously documented by Laseter et al. [2012] at a lower elevation climate station within the Coweeta basin (Figures 5.6 a-b). Laseter et al. [2012] found rise in the number of high intensity storms ($75^{th}$ and $85^{th}$ percentile) from 2000 onward (Figure 5.6), which were attributed to tropical storm activity.

5.3.3 Stream DOC and Discharge

Instantaneous discharge and DOC concentrations at the time of sampling covered a wide range of flows under base flow and storm flow conditions (Figure 5.7); however, we found no significant correlation between sampled DOC concentration and instantaneous discharge for the entire 25-year study period. When we examined samples during two intervals separately, we found that stream DOC concentrations during 1997-2012 were 35% higher on average than DOC concentrations during 1988-2001, despite the approximately same mean instantaneous discharge of 20 L sec$^{-1}$ (Figure 5.7). During the month of September, we found that mean instantaneous discharge increased by 32% from the 1988-2001 interval to the 1997-2012 interval, and mean instantaneous stream DOC increased by 55% from the earlier interval to the later interval as well. Mean instantaneous DOC also increased during the months of April, June and October from the earlier interval to the later interval, but the changes were less than that of September (Figure 5.7). We found a strong correlation between runoff during the growing season months and annual mean DOC$_{vw}$ ($\tau=0.46$, $p<0.05$) and annual DOC fluxes ($\tau=0.53$, $p<0.05$), respectively, during the
1988-2001 interval. For the same interval, a stronger correlation ($\tau = 0.53$, $p < 0.05$) was observed between the runoff from the month of September and annual mean DOC$_{vw}$. 
5.4 Discussion

5.4.1 Rising Air Temperature

Generally, higher air temperature increases microbial activity, leading to increased DOC production in aquatic ecosystems [Freeman et al., 2001; Evans et al., 2005]. In forested headwater streams, temperature exerts a strong control over the seasonal variability of DOC formation and consumption [e.g., Cronan and Aiken, 1985; Mulholland and Hill, 1997]. High air temperature during the growing season increases microbial decomposition in forest soils, leading to increased DOC formation [Liechty et al., 1995]. At Coweeta, maximum annual air temperature increased by 1.25 °C during the 25-year study period (Figure D2). These annual trends were accompanied by significant increases in mean and maximum air temperatures during the growing season months of June. Increasing June temperatures may have contributed to significantly higher DOC$_{vw}$ in June for the later interval (1997-2012).

Air temperature can also influence the transport of DOC from uplands to stream indirectly by altering the water balance of the watershed. Specifically, rising air temperatures can cause increased atmospheric demand for water vapor, which may increase evapotranspiration when soil water supplies are sufficient to meet vegetation requirements [Emanuel et al., 2007; Emanuel et al., 2010; Wang and Dickinson, 2012]. These influences of temperature on DOC can elicit complex behavior by counteracting each other or by operating at different temporal scales.

5.4.2 Hydrological Changes

Several field studies highlight relationships between runoff and DOC concentrations and fluxes in aquatic ecosystems [Tate and Meyer, 1983; McDowell and Likens, 1988; McGlynn and McDonnell, 2003]. Significant declines in annual runoff and runoff ratios at
Coweeta (Figure 5.4c) suggest drier conditions, potentially linked to rising air temperatures (Figure D2). Earlier work at Coweeta, Tate and Meyer [1983] reveals that biological activities responsible for DOC formation and consumption are most active during the growing season due to favorable conditions for in-stream biological activity, litter decomposition and leaching in soils. During the 1988-2001 interval, we observed decline in monthly runoff for some of these growing season months (Figure 5.5), and detected significant correlations between growing season runoff and annual mean DOC$_{vw}$ and DOC fluxes. However, September exhibited much stronger correlation between the monthly runoff and annual mean DOC$_{vw}$ for the same duration. These correlations were indicative of strong seasonal control of runoff on annual patterns of mean DOC$_{vw}$ [Eimers et al., 2008b]. Declining runoff during the growing season (Figure 5.5) might be associated with reduced transport of labile DOC from uplands to the stream. Furthermore, as the watershed experienced drier conditions, landscapes within the watershed might be less likely to establish hydrologic connectivity with the stream, and further influencing the ability of these landscapes to contribute new DOC to the stream [Stieglitz et al., 2003].

The role of runoff in mobilizing DOC has been widely recognized in various ecosystems [Eimers et al., 2008b; Winterdahl et al., 2011; Lutz et al., 2012; Oni et al., 2013]. Eimers et al. [2008b] reported that seasonal runoff changes had a direct impact on modulating the annual DOC dynamics for Canadian wetland-dominated watersheds. Winterdahl et al. [2011] emphasized the role of runoff in mobilizing DOC from uplands to nearby streams in the forested headwater of Sweden. Oni et al. [2013] reported that runoff explained significant variability in DOC for both upland and wetland-dominated watersheds.
of Sweden. Our study joins these studies to further support the direct linkages between runoff and DOC$_{vw}$, which could potentially explain the declining annual patterns of DOC$_{vw}$ observed during the 1988-2001 interval.

During the 1997-2012 interval, both DOC$_{vw}$ and precipitation increased in April (Figures 5.2; 5.5), along with increase in mean monthly DOC$_{vw}$ and changes in monthly precipitation patterns (i.e., rise in high intensity storms, Laseter et al., 2012) for September (Figures 5.2c; 5.6b). Increasing precipitation in April might have promoted high productivity during that month. Furthermore, the timing of September storms were crucial, when most of the growing months were dry, because subsurface flow generated during these storms [e.g., Hewlett and Hibbert, 1967] might have mobilized DOC that became available during the growing season due to rapid decomposition [Meyer and Tate, 1993]. Also, these storms might have provided enough hydrologic connectivity to wash out fresh leaf-litter available during the month of October, when leaf-fall generally begins at Coweeta. The Experimental studies in other Coweeta streams have demonstrated a direct link between DOC concentration and amount of decomposing leaves in the stream [Meyer et al., 1998]. A number of field studies have analyzed the relationship between DOC and storms, focusing on event based DOC flushing in Coweeta [Meyer and Tate, 1983] and other ecosystems [e.g., McDowell and Likens, 1988; Hinton et al., 1997; Dhillion and Inamdar, 2013]. McDowell and Likens [1988] attributed the consistent flushing of high DOC concentrations during multiple storms to freshly fallen leaves in a forested stream of New Hampshire. A few studies have also suggested that the strength of the flushing signal is even stronger after prolonged dry periods [Worrall et al., 2004a; Inamdar et al., 2008].
5.4.3 Other Potential Drivers

In general, other drivers that may influence the long-term patterns of stream DOC include land use and land cover changes [Aitkenhead-Peterson et al., 2009], recovery from acidification [e.g., Monteith et al., 2007], and nitrogen deposition [Findlay, 2005]. We evaluated some of these drivers for WS27 but were unable to implicate any of them as controls on observed long-term patterns of stream DOC. In particular, WS27 is a reference watershed for the Coweeta basin, so no land use and land cover changes occurred at our study site during the study period.

Studies show an inverse relationship between atmospheric [SO$_4^{2-}$] and stream DOC [e.g., Evans et al., 2005; Monteith et al. 2007]. These studies suggest that increase in atmospheric [SO$_4^{2-}$] (i.e., acidification) suppresses the solubility of organic compounds in soil solution, resulting in restraining the formation and consumption of DOC in soils and streams [Thurman 1985; Clark et al., 2005; Hruska et al., 2009]. Annual mean volume-weighted [SO$_4^{2-}$] from the National Atmospheric Deposition Program (NADP) wet-deposition site at Coweeta (http://nadp.sws.uiuc.edu; NC25) declined at an average rate of -0.02 mg L$^{-1}$ yr$^{-1}$ ($\tau$ = -0.52; $p < 0.001$) during the study period (Figure D3). These data suggest that the watershed has been recovering from acidification since at least 1988 or earlier. Steadily declining [SO$_4^{2-}$] might be expected to cause steadily rising stream DOC [e.g., Erlandsson et al., 2011]. But, no such pattern was observed in stream DOC for WS27 (Figure 5.1). Although a lag in recovery of DOC from acidification might be expected, such a long lag (> 10 years) seems highly unlikely given observations of recovery in other sites [Evans et al. 2005]. Recovery from acidification may provide part of an explanation for
long-term trends in DOC at Coweeta, but given the bi-directional nature of the DOC trends acidification recovery alone is unlikely to explain our observations.

Annual mean concentrations of [NO$_3^-$] of wet deposition from the same NADP site declined gradually ($\tau = -0.48$; $p<0.001$; Figure D3) for the study period. Furthermore, no significant trend was detected for annual mean concentrations of [NH$_4^+$] at the site during the 25-year period (Figure D3). These observations suggest a minor decline in inorganic nitrogen deposition for the watershed during the study period. Laboratory and field experiments provide equivocal evidence of direct [Pregitzer et. al., 2000], inverse [Park et. al., 2002], or no relationship [Magil et. al., 2000] between DOC and nitrogen deposition. A long-term surface water DOC export study in Hudson River suggested that high rates of nitrogen deposition could accelerate microbial decomposition, leading to release of humic substance and contributing to the formation of DOC [Findlay, 2005]; however, given that nitrogen deposition at Coweeta declined during the 25-year study period, it is unlikely that this trend is linked to observed patterns in stream DOC.

Among the potential drivers of long-term stream DOC discussed in this paper, hydro-climatological factors emerge as the most likely source of the bi-directional trends observed in WS27. Other studies have reported bi-directional or periodic trends in long-term DOC, Hejzlar et al. [2003] found bi-directional trends in dissolved organic matter in an upland stream, which was attributed to variability in streamflow, air temperature and atmospheric deposition. Recently, Lutz et al. [2012] attributed the observed rising and declining patterns in stream DOC to changes in runoff and runoff source areas for a forested watershed in Tennessee, US. Together with our results, these studies demonstrate the potential for hydro-
climatological factors to elicit or contribute to non-monotonic trends in long-term stream DOC.

5.4.4 Implications and Limitations

Our results provide evidence of strong linkages between long-term DOC trends and hydro-climatological variability. Annual maximum air temperatures are increasing at Coweeta [Figure D2; Ford et al., 2011; Laseter et al., 2012], a trend that is consistent with global model predictions for the southeastern United States [IPCC 2013]. Based on evidence of positive feedbacks between air temperature and soil microbial activity [Davidson et al., 2000; Heimann and Reichstein, 2008], continued temperature increases may be accompanied by increases in terrestrial DOC production, which may eventually contribute to rising concentrations of stream DOC.

General circulation models predict that precipitation could become more extreme with increases in short duration, high intensity storms for much of the United States, including the Southeast [IPCC 2013]. Intense storms can significantly reduce the residence time of DOC within watersheds and flush a larger proportion of DOC from soils into stream channels [Dhillon and Inamdar, 2013]. Over the long-term, changes in storm characteristics (e.g., frequency, intensity, duration) may impact global DOC dynamics, larger carbon budgets and overall ecosystem response [Knapp et al., 2008], even if annual precipitation magnitude remains unchanged through time. In general, changing climatic patterns can severely affect the availability, formation, consumption and transport of DOC in mountainous watersheds. Changing DOC patterns can have impacts on the closely coupled watershed nitrogen cycle [Bernhardt and Likens, 2002] and overall stream chemistry. Due to
the close coupling between headwater streams and their surrounding landscapes [Gomi et al., 2002], these changes may influence the healthy functioning of aquatic and terrestrial ecosystems.

Our study, along with other long-term datasets published in recent years [Argerich et al., 2013; Meyer et al., 2014], highlights the potential complexity of long-term trends in stream biogeochemistry. In particular, these studies illustrate the ability of long-term trends to vary in magnitude or even direction depending on the length of record or the period of record chosen for analysis. Collectively, these studies suggest caution while interpreting trends from a given time series and call for building and maintaining long-term datasets to understand more fully long-term ecological and hydrological responses of watersheds and their streams to environmental change. It stands to reason that such multi-decadal datasets will only increase in value as benchmarks for scientific research and for management and policy decisions.
5.5 References


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### Table 5.1 List of recent studies reporting long-term changes in surface water DOC

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<thead>
<tr>
<th>Geographical Location</th>
<th>Ecosystems</th>
<th>Time period</th>
<th>Length of DOC Record (yr)</th>
<th>Sampling Frequency (No)</th>
<th>Mean DOC (mg.L⁻¹)</th>
<th>DOC-Trend reported/site*</th>
<th>Change reported</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>Forested Watershed</td>
<td>1988-2012</td>
<td>25</td>
<td>Bi-weekly</td>
<td>1.45</td>
<td>(-) (+) (+) 216 sites</td>
<td>0.04 mg L⁻¹ yr⁻¹</td>
<td>This study</td>
</tr>
<tr>
<td>UK</td>
<td>Rivers</td>
<td>1977-2002</td>
<td>NA</td>
<td>Weekly-Monthly</td>
<td>NA</td>
<td>(-) 55 sites (0) 44 sites</td>
<td>0.06 mg L⁻¹ yr⁻¹</td>
<td>Worrall &amp; Burt, 2007</td>
</tr>
<tr>
<td>USA</td>
<td>Forested Watershed</td>
<td>1988-2006</td>
<td>15</td>
<td>Weekly</td>
<td>0.7</td>
<td>(-) (+)</td>
<td>0.09 mg L⁻¹ yr⁻¹</td>
<td>Lutz et al., 2012</td>
</tr>
<tr>
<td>Canada</td>
<td>Wetland-dominated watershed</td>
<td>1980-2001</td>
<td>22</td>
<td>1.3-1.9/week</td>
<td>3.4-10.6</td>
<td>(+)</td>
<td>0.05-0.15 mg L⁻¹ yr⁻¹</td>
<td>Eimers et al., (2008a)</td>
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<tr>
<td>UK</td>
<td>Terrestrial Bio-Reserve</td>
<td>1993-2002</td>
<td>10</td>
<td>Weekly</td>
<td>14-37</td>
<td>(+)</td>
<td>0.14 mg L⁻¹ yr⁻¹</td>
<td>Clark et al., 2005</td>
</tr>
<tr>
<td>UK</td>
<td>Rivers, Lakes, Reservoirs</td>
<td>1962-2002</td>
<td>10-38</td>
<td>Daily-Yearly</td>
<td>NA</td>
<td>(+)/153 sites (0)/45 sites</td>
<td>0.17 mg L⁻¹ yr⁻¹</td>
<td>Worrall et al., 2004b</td>
</tr>
<tr>
<td>Finland</td>
<td>Headwater catchment</td>
<td>1990-2003</td>
<td>14</td>
<td>NA</td>
<td>NA</td>
<td>(+)</td>
<td>0.19-0.21 mg L⁻¹ yr⁻¹</td>
<td>Futter et al., 2008</td>
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<tr>
<td>Sweden</td>
<td>Forested Watersheds</td>
<td>1989-2008</td>
<td>14</td>
<td>Weekly-Monthly</td>
<td>7.2-18.7</td>
<td>(+) 2 sites (0) 2 sites</td>
<td>NA</td>
<td>Winterdahl et al., 2011</td>
</tr>
<tr>
<td>Europe</td>
<td>Forested Watershed</td>
<td>1993-2007</td>
<td>15</td>
<td>Weekly</td>
<td>18.8-20.2</td>
<td>(+)</td>
<td>0.42-0.43 mg L⁻¹ yr⁻¹</td>
<td>Hruska et al., 2009</td>
</tr>
<tr>
<td>UK</td>
<td>Rivers</td>
<td>1988-2002</td>
<td>15</td>
<td>Monthly-Quarterly</td>
<td>NA</td>
<td>(+)</td>
<td>0.06 to 0.51 mg L⁻¹ yr⁻¹</td>
<td>Evans et al., 2005</td>
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<tr>
<td>Germany</td>
<td>Wetlands</td>
<td>1987-2009</td>
<td>23</td>
<td></td>
<td>1.3-7.3</td>
<td>(+)</td>
<td>NA</td>
<td>Knorr, 2013</td>
</tr>
</tbody>
</table>

*(+), (-), (0) = Increasing, decreasing and no trend respectively. Photosynthetically active radiation (PAR)
<table>
<thead>
<tr>
<th>Geographical Location</th>
<th>Ecosystems</th>
<th>Time period</th>
<th>Length of DOC Record</th>
<th>Sampling Frequency (No)</th>
<th>Mean DOC (mg.l⁻¹)</th>
<th>DOC-Trend reported/site*</th>
<th>Change reported</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finland</td>
<td>Rivers</td>
<td>1975-2010</td>
<td>36</td>
<td>10,854</td>
<td>12</td>
<td>(0) 4-61 (+) 64-67</td>
<td>9.2% for the period</td>
<td>Räike <em>et al.</em>, 2012</td>
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<tr>
<td>USA</td>
<td>Lake and Streams</td>
<td>1992-2001</td>
<td>10</td>
<td>NA</td>
<td>NA</td>
<td>(+) Catskill</td>
<td>4.7µmolyr⁻¹</td>
<td>Burns <em>et al.</em>, 2006</td>
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<tr>
<td>UK</td>
<td>Peatlands</td>
<td>1988-2000</td>
<td>13</td>
<td>NA</td>
<td>NA</td>
<td>(+) Adirondack</td>
<td>7.6 µmolyr⁻¹</td>
<td>Freeman <em>et al.</em>, 2001</td>
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<tr>
<td>Canada</td>
<td>Boreal lakes</td>
<td>1978-1998</td>
<td>21</td>
<td>5-24</td>
<td>1.8-5.1</td>
<td>(+)</td>
<td>Ice-free PAR² period : 33.6%</td>
<td>Hudon <em>et al.</em>, 2003</td>
</tr>
<tr>
<td>North America, Europe</td>
<td>Lakes and streams</td>
<td>1990-2004</td>
<td>15</td>
<td>NA</td>
<td>NA</td>
<td>(+) 363</td>
<td>0.02-0.1 mg L⁻¹ yr⁻¹</td>
<td>Monteith <em>et al.</em>, 2007</td>
</tr>
<tr>
<td>UK</td>
<td>Forest/wetland catchments</td>
<td>1987-2006</td>
<td>12-16</td>
<td>Weekly to biweekly</td>
<td>2.19-11.59</td>
<td>(0) C4&amp;C7</td>
<td>0.15-0.79 mg L⁻¹ yr⁻¹</td>
<td>Dawson <em>et al.</em>, 2008</td>
</tr>
<tr>
<td>USA</td>
<td>Rivers</td>
<td>1996-2010</td>
<td>2-14</td>
<td>Monthly</td>
<td>1.0-7.5</td>
<td>(+) 0.476 mg.l⁻¹ of increase/1°C T</td>
<td>0.476 mg.l⁻¹ of increase/1°C T</td>
<td>Tian <em>et al.</em>, 2013</td>
</tr>
</tbody>
</table>

*(+), (-), (0) = Increasing, decreasing and no trend respectively. Photosynthetically active radiation (PAR)
Figure 5.1 Trends for annual mean volume-weighted dissolved organic carbon (DOC<sub>vw</sub>) for a 25-year period (1988-2012) in WS27 at Coweeta Hydrologic Laboratory, NC. Solid red lines show linear trends, dashed line shows the breakpoint interval (BI) (1997-2001), black error bars in the DOC<sub>vw</sub> represent standard error based on the number of samples collected during the study period.
Figure 5.2 Monthly trends of volume-weighted dissolved organic carbon concentration (DOC\textsubscript{vw}) for the months of April (a), June (b), September (c), and October (d) during a 25-year period (1988-2012). Dashed lines and double arrows show the duration of lengths for which trends were significant (p<0.05).
Figure 5.3 Trends for annual dissolved organic carbon flux for a 25-year period (1988-2012) in WS27 at Coweeta Hydrologic Laboratory, NC.
Figure 5.4 Trends in annual precipitation (a), annual runoff (b), and annual runoff ratio (c), for WS27 from 1988 to 2012. Solid red lines show the SS estimates, and red dashed lines represent 95% confidence interval for the SS estimates.
Figure 5.5. Trends for monthly precipitation and monthly runoff for the months of April (a, b), June (c, d), September (e, f), and October (g, h) during a 25-year period. Symbols represent type of data, precipitation (open circle) and runoff (filled circle). Dashed lines and double arrows show the duration of lengths for which trends were significant (p<0.05).
Figure 5.6 Total number of storms observed in the month of September (a), and percentage (%) of storms exceeding 75th percentile (17 mm) (b), during 1988-2008. Data provided by Laseter et al., (2012), and gap represents no storms exceeding 75th percentile for that particular year.
Figure 5.7 Raw (non-volume weighted) dissolved organic carbon (DOC) concentration from weekly and biweekly samples (n~1000) shown with instantaneous discharge at the time of sampling for all months (a), and for the individual months of April (b), June (c), September (d), and October (e). Black open circle and grey marker show study intervals 1988-2001 and 1997-2012, respectively.
CHAPTER 6

Conclusions

This dissertation provides a holistic understanding of how climate, topography and vegetation can mediate hydrologic processes that influence runoff generation, and how hydro-climatological changes can influence biogeochemical process in the catchments of Coweeta. These forested catchments are characterized by humid and temperature climate, steep terrain and deep soils. This dissertation builds on the wealth of data and findings of prior studies at Coweeta, and it contributes to the legacy of catchment hydrology research at Coweeta.

The scientific contribution of this dissertation is three-fold. First, each of the four body chapters addresses a critical question that is relatively understudied. Although the chapters are entirely independent of each other, they all revolve around the same overarching goal. Second, chapter 2 highlights the role of catchment structure for a small headwater streams, and chapters (3-4) provide insight into patterns of response timing and magnitude while emphasizing the subtle differences in their controls in space and time. Third, chapter 5 emphasizes the potential role of climate-induced hydrological changes on temporal patterns of stream dissolved organic carbon (DOC), and it calls for more long-term studies to truly understand the impact of climate change on water quantity and quality of these forested catchments.

Chapter 2 quantifies the role of internal catchment structure and hydrologic conditions on patterns of baseflow that vary in space and time for two headwater streams of Coweeta. We derive a topographic metric (i.e., incremental contributing area) as a means to
understand the role of hillslope arrangement in determining spatial patterns of runoff. We test this idea using a novel Monte Carlo simulation to verify that spatial patterns of baseflow $^{18}$O is linked to the unique arrangement of hillslopes within a catchment. This study underlines the utility of stable isotopes for investigating patterns of baseflow.

Chapter 3 assesses the soil moisture response to storms (both magnitude and timing) and its relationships with topography and storm properties for three forested hillslopes. Our findings suggest that strength of the relationships vary with season and among hillslopes. The characterization of hydrologic responses using lag times assists us to broadly categorize and understand some of the common behaviors of the hillslope in these forested catchments. This could be useful in identifying and understanding generalized rainfall-runoff processes for un-gauged catchments with similar landscape and climate elsewhere. This study can have implication for modeling soil moisture for humid forested catchments with deep soils.

Chapter 4 provides insight on shallow groundwater responses (magnitude and timing) to storms across 12 instrumented hillslopes. Some of these response patterns are significantly different between south and north facing catchments suggesting the strong influence of aspect on the shallow groundwater dynamics. Furthermore, the response patterns are correlated to storm properties, topography, and antecedent wetness conditions (i.e., groundwater stage prior to the storm). Topographic control on the magnitude of groundwater response is weak and only noted during wet conditions. These results run contrary to studies conducted in catchment with shallow soils, implying that deeper soils at Coweeta may influence groundwater responses in this environment. The study shows that the strength of groundwater-runoff relationships varies with storm depth and topography. The patterns of
lags suggest that the potential sources that contribute to peak runoff at catchment outlet are not necessarily limited to near-stream areas but can also be influenced by storm properties and topography. This work has implication for understanding runoff generation and modeling shallow groundwater responses for forested catchments with deep soils located in humid, temperate climates.

Chapter 5 shows bi-directional patterns (a decline followed by an increase) in stream DOC concentration and flux for a high-elevation catchment at Coweeta. These temporal patterns appear to be more sensitive to climate-induced hydrological changes than by any other drivers that we analyze. This work also indicates that the trend is sensitive to the length of record used in the analysis. Furthermore, the study highlights the critical role of long-term datasets in understanding the influence of climate change on carbon and water cycles. Overall, this dissertation offers insight into hydrological processes that can influence runoff generation from hillslope to catchment scales. The dissertation is weaved around a wide array of questions, but together they advance our understanding of runoff generation and biogeochemical cycling in these humid, forested catchments. This dissertation contributes to catchment hydrology and has implication for both water quality and water quantity of the forested catchments.
A. Correlation Matrix of Topographic Variables and Phase Diagrams for Chapter 1
Figure A1. Correlation matrix (Pearson’s r) between five landscape variables in WS01 (a), and WS02 (b). Correlations were calculated between hillslope scale median values of landscape variables. White color represents non-significant relationships (p>0.05). Diagonal values (left to right) are correlation of landscape variable with itself. Abbreviations are: Hillslope Size (HSIZE), Flow path lengths (DFC), Gradient to creek (GTC), Elevation (Elv).
Figure A2 Isotopic composition ($\delta^{18}O$ and $\delta^2H$) of baseflow, groundwater, soil water, and precipitation samples for both study catchments. Local meteoric water line (LMWL) and global water lines (GMWL) shown for reference. Inset shows groundwater and baseflow samples relative to LMWL. Baseflow was sampled from 33 locations along streams, groundwater was sampled from 12 shallow wells, soil water was sampled from 5 lysimeters (WS02 only) and precipitation was sampled from high and low elevation rain gauges.
B. An Example of Soil Moisture Data used in the Analysis of Chapter 2
Figure B1 Time series of volumetric water content for an upslope position along H1 (a), H2 (b), and H3 (c), at four depths (10, 30, 60, 100 cm) in WS02. Gaps show missing data. Color represents depths from lighter (greater) to darker (shallower).
C. Groundwater Elevations Recorded across 12 Instrumented Hillslopes
Figure C1 Time series of runoff and rainfall (a), with groundwater stage for wells in WS02 (b-d). Gaps show missing data for a particular well and runoff.
Figure C2 Time series of runoff and rainfall (a), with groundwater stage for wells in WS01 (b-d). Gaps show missing data for a particular well.
Figure C3 Time series of runoff and rainfall (a), with groundwater stage for wells in WS17 (b-d). Gaps show missing data for a particular well.
Figure C4 Time series of runoff and rainfall (a), with groundwater stage for wells in WS18 (b-d). Gaps show missing data for a particular well.
D. Study Site, Air Temperature and NADP Data
Figure D1 Watershed 27 at Coweeta Hydrologic Laboratory in Otto, NC, USA showing the 25 m contours, tree height, streams, outlet, and the climate station.
Figure D2 Trends for the annual maximum daily air temperature observed during study period (1988-2012) at CS01. Solid red line represents SS and dashed lines represents 95% confidence interval for the SS estimates.
Figure D3 Trends for annual mean concentration of $\text{SO}_4^{2-}$ (a), $\text{NO}_3^-$ (b), $\text{NH}_4^+$ (c), for atmospheric wet deposition collected from CS01 available via National Atmospheric Deposition Program (NADP; http://nadp.sws.uiuc.edu; NC25) for the 25 year study period (1998-2012). Solid red line represents SS and dashed lines represents 95% confidence interval for the SS estimates.