Prepared in cooperation with the City of Durham, Public Works Department,
Stormwater Services Division

Using Stable Isotopes of Nitrogen and Oxygen to Identify Sources of Nitrate in Three Creeks, Durham County, North Carolina, 2011–12

Scientific Investigations Report 2014–5171

Cover. Top left: Cabin Branch Creek above mouth near Fairintosh, North Carolina (photo by Kristen Bukowski McSwain, USGS).
Top right: Third Fork Creek at Woodcroft Parkway near Blands, North Carolina (photo by P. Shawn Spivey, USGS).
Bottom: Ellerbe Creek at Club Boulevard at Durham, North Carolina (photo by Kristen Bukowski McSwain, USGS).

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Conversion Factors and Datums

Inch/Pound to SI

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi ²)	2.590	square kilometer (km ²)
Flow rate		
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (μg/L).

Abbreviations

ANOVA	analysis of variance
BMP	best-management practice
ECONet	Environment and Climate Observing Network
GMWL	Global Meteoric Water Line
H	hydrogen
N	nitrogen
NC CHRONOS	North Carolina Climate Retrieval and Observations Network of the Southeast Database
NCDENR	North Carolina Department of Natural Resources
NTU	nephelometric turbidity unit
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
O	oxygen
P	phosphorus
SSD	Stormwater Services Division
USGS	U.S. Geological Survey
VSMOW	Vienna Standard Mean Ocean Water

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Abstract

A preliminary assessment of nitrate sources was conducted in three creeks that feed nutrient impaired Falls and Jordan Lakes in the vicinity of Durham County, North Carolina, from July 2011 to June 2012. Cabin Branch, Ellerbe Creek, and Third Fork Creek were sampled monthly to determine if sources of nitrate in surface water could be identified on the basis of their stable isotopic compositions. Land use differs in the drainage basins of the investigated creeks—the predominant land use in Cabin Branch Basin is forest, and the Ellerbe and Third Fork Creek Basins are predominantly developed urban areas. Total nutrient concentrations were below 1 milligram per liter (mg/L). All measured nitrate plus nitrite concentrations were below the North Carolina standard of 10 mg/L as nitrogen with the highest concentration of 0.363 mg/L measured in Third Fork Creek. Concentrations of ammonia were generally less than 0.1 mg/L as nitrogen in all creek samples. More than 50 percent of the total nitrogen measured in the creeks was in the form of organic nitrogen. Total phosphorus and orthophosphate concentrations in all samples were generally less than 0.2 mg/L as phosphorus. The isotopic composition of surface water ($\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$) is similar to that of modern-day precipitation. During July and August 2011 and May and June 2012, surface-water samples displayed a seasonal difference in isotopic composition, indicating fractionation of isotopes as a result of evaporation and, potentially, mixing with local and regional groundwater. The dominant source of nitrate to Cabin Branch, Ellerbe Creek, and Third Fork Creek was the nitrification of soil nitrogen. Two stormflow samples in Ellerbe Creek and Third Fork Creek had nitrate sources that were a mixture of the nitrification of soil nitrogen and an atmospheric source that had bypassed some soil contact through impermeable surfaces within the drainage basin. No influence of a septic or wastewater source was found in Cabin Branch. Results from this study suggest that it is possible to distinguish sources of nitrogen and biogeochemical processes on nitrate using stable isotopes of nitrogen and oxygen in small creeks of Durham County, North Carolina.

Introduction

Falls Lake reservoir in the Neuse River Basin and Jordan Lake reservoir in the Cape Fear River Basin have been included in the North Carolina Department of Natural Resources (NCDENR), Division of Water Resources (formerly the Division of Water Quality) 303(d) list of “impaired” waters due to violations of the State chlorophyll-*a* standard caused by excessive nutrient inputs (North Carolina Department of Environment and Natural Resources, 2010a). The North Carolina Environmental Management Commission has adopted nutrient-management strategies for both reservoirs that call for comprehensive controls to reduce nitrogen (N) and phosphorus (P) loads from various sources in the drainage basin, including urban stormwater, wastewater, and agriculture (North Carolina Department of Environment and Natural Resources, 2010b–d).

Stable isotopes of hydrogen and oxygen in water and of nitrogen and oxygen in nitrate are useful to identify water sources in some complex hydrologic settings (Kendall, 1998; Kendall and others, 2007). There are two stable isotopes of nitrogen: ^{14}N and ^{15}N . All nitrogen compounds contain both isotopes, but because of isotopic fractionation the isotopes are incorporated into compounds in differing ratios. Commercial fertilizers, animal and septic waste, precipitation, and soil are common sources of nitrate in urban areas, and each source may have a distinguishable isotopic $^{15}\text{N}/^{14}\text{N}$ ratio (Heaton, 1986; Kendall, 1998). Further, the ratio of light (^{14}N) to heavy (^{15}N) nitrogen isotopes in the water can often be used to characterize a mixture of sources or identify processes such as denitrification. Additionally, under some conditions, variations in hydrogen (H) and oxygen (O) stable isotopes of water (^{16}O and ^{18}O , and ^1H and ^2H , respectively) affected by precipitation can be used to differentiate relatively “older” groundwater stored within a drainage basin from the more variable “new” storm precipitation components of surface-water runoff (Bullen and Kendall, 1998).

From July 2011 to June 2012, the U.S. Geological Survey (USGS) in cooperation with the City of Durham, Public Works Department, Stormwater Services Division (SSD), conducted

a study to determine if sources of nitrate in three creeks could be identified on the basis of their isotopic compositions. The City of Durham, SSD, is tasked with implementing best-management practices (BMPs) to reduce nutrient inputs from stormwater in both the Falls Lake and Jordan Lake drainage basins. Cabin Branch and Ellerbe Creek, located above the Falls Lake reservoir in the Neuse River Basin and Third Fork Creek located above Jordan Lake in the Cape Fear River Basin were investigated for potential sources of nitrate, such as precipitation, soil organic matter, synthetic fertilizers, human septic waste, and animal manure.

Purpose and Scope

This report presents a preliminary assessment of sources of nitrate in three small creeks that feed nutrient-impaired Falls and Jordan Lakes in Durham County, North Carolina. Results from chemical and isotopic analyses of surface-water samples were used to characterize in-stream water-quality conditions. Additionally, this report assesses the possibility of using stable isotopes to characterize nitrate sources and possible transport pathways within low-order streams in other areas.

Description of the Study Area

The three stream study sites are located in the Piedmont Physiographic Province within Durham County, North Carolina (fig. 1; table 1). A ridgeline separates Durham County into two river basins, with about 70 percent of the county land area within the Neuse River Basin and 30 percent within the Cape Fear River Basin. Cabin Branch and Ellerbe Creek in the Neuse River Basin are located upstream from Falls Lake, a water-supply reservoir for the City of Raleigh. Third Fork Creek is located in the Cape Fear River Basin upstream from Jordan Lake, a water-supply reservoir for the towns of Cary and Apex.

Streambed composition differed at the sampling site on each creek and geology is a major factor in streambed

composition, in addition to many others factors. The Cabin Branch drainage basin is located within the Carolina Terrane and Durham subbasin of the Deep River Mesozoic basin (Phillips and others, 2010). The streambed of Cabin Branch is composed of metavolcanic rocks, ranging in size from pebbles to boulders, that are resistant to weathering. The Ellerbe Creek and Third Fork Creek drainage basins are underlain predominantly by sandstones, siltstones, and mudstones of the Durham subbasin of the Deep River Mesozoic basin, formerly called “Triassic basin” (North Carolina Geological Survey, 1985; Bradley and others, 2010). In order to control flooding resulting from the low porosity and permeability of the surrounding clayey soils and increasing impervious surface area within the drainage basin, much of the natural channel of Ellerbe Creek was straightened and channelized by the U.S. Army Corps of Engineers in the early 1960s (North Carolina Department of Environment and Natural Resources, 2003). The stream channel located near the Ellerbe Creek streamgage was converted into a uniformly shaped concrete-lined channel during the Corps of Engineers modifications. In contrast, the streambed of Third Fork Creek is composed primarily of sand-sized particles that shift easily under high flows.

On the basis of the 2006 National Land Cover Database (Fry and others, 2011), some differences in land use are noted among the three study drainage basins. The smallest drainage basin (Cabin Branch) is predominantly forested (58.3 percent) with a lesser amount of developed urban area (26.7 percent) (fig. 2). Ellerbe Creek (fig. 3) and Third Fork Creek (fig. 4) have similar land use within each drainage basin, consisting predominantly of developed urban area (82.6 and 85.3 percent, respectively) with a lesser amount of forested land coverage (14.2 and 9.8 percent, respectively). On-site septic systems are the primary wastewater-treatment systems used in the Cabin Branch drainage basin. Within the Ellerbe Creek and Third Fork Creek drainage basins, however, wastewater treatment by way of sewerage is provided by water reclamation facilities operated by the City of Durham. There were no wastewater-treatment plant discharges within the investigated drainage basins upstream from the sampling locations.

Table 1. Stream sites sampled monthly from July 2011 to June 2012 for nutrients and stable isotopes in Durham County, North Carolina.

[NAD 83, North American Datum of 1983; mi², square miles]

Stream site	USGS station number	Station name	Latitude	Longitude	Drainage area (mi²)
			NAD 83		
Falls Lake drainage basin, Neuse River Basin					
Cabin Branch	0208525105	Cabin Branch above Mouth near Fairintosh, NC	36°05'36.7"	78°51'58.9"	3.45
Ellerbe Creek	0208675010	Ellerbe Creek at Club Boulevard at Durham, NC	36°01'09.8"	78°53'41.2"	6.01
Jordan Lake drainage basin, Cape Fear River Basin					
Third Fork Creek	02097280	Third Fork Creek at Woodcroft Parkway near Blands, NC	35°55'21.5"	78°57'08.7"	14.79

Figure 1. Locations of investigated stream sites and precipitation gage in Durham County, North Carolina.

Figure 2. Land use in the Cabin Branch drainage basin, Durham County, North Carolina (land-use data modified from Fry and others, 2011).

Figure 3. Land use in the Ellerbe Creek drainage basin, Durham County, North Carolina (land-use data modified from Fry and others, 2011).

Figure 4. Land use in the Third Fork Creek drainage basin, Durham County, North Carolina (land-use data modified from Fry and others, 2011).

Methods of Data Collection and Analysis

This section provides a description of the methods used to conduct a preliminary assessment of the sources of nitrate in Cabin Branch, Ellerbe Creek, and Third Fork Creek. The methods used to collect streamflow and precipitation data, and to collect and analyze water-quality samples are described.

Surface-Water and Precipitation Data Collection

Stream stage and streamflow data at Ellerbe Creek and Third Fork Creek were available through the USGS National Water Information System (NWIS) during the study as part of the USGS streamgaging network. Fifteen-minute and daily mean stream stage and streamflow values were retrieved through the NWIS database at <http://waterdata.usgs.gov/nc/nwis> for the July 2011 to June 2012 study period. Continuous streamflow data were not available at Cabin Branch, so instantaneous-streamflow measurements were conducted at Cabin Branch during each sampling visit, using a SonTek FlowTracker Handheld-ADV® (Acoustic Doppler Velocimeter). Precipitation data for the study area were obtained through the North Carolina Climate Retrieval and Observations Network of the Southeast Database (CHRONOS) for the DURH Environment and Climate Observing Network (ECONet) station (fig. 1) located at the North Durham Water Reclamation Facility State Climate Office of North Carolina (State Climate Office of North Carolina, 2012).

Water-Quality Sampling and Analyses

Surface-water sampling and field-processing methods specified by the USGS (U.S. Geological Survey, 2006) were implemented in this study. Each of the three creeks were sampled on an approximately monthly basis for physical properties, nutrients, and stable isotopes. Two sets of samples were collected under stormflow conditions (September 28, 2011, and February 23, 2012). The equal-width increment sampling method was used when streamflow rates allowed, otherwise grab samples from the center of flow were collected, composited in a polycarbonate churn splitter, processed, and preserved. At the time of sampling, the physical properties of dissolved oxygen, pH, specific conductance, and water temperature were measured using a multiparameter data sonde. Additionally, turbidity was measured in the field, using a portable turbidimeter when available. Precipitation and streamflow data, notated with the 12 sampling events for the study sites, are shown in figure 5.

Chemical analyses for nutrients were performed at the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado, following methods outlined by Fishman (1993) and Patton and Kryskalla (2011). Nutrient

analyses included dissolved nitrate plus nitrite, dissolved ammonia, total ammonia plus organic nitrogen (also known as total Kjeldahl nitrogen), dissolved orthophosphate, and total phosphorus. Concentrations of the nitrogen species are reported in milligrams per liter as nitrogen (N) and concentrations of phosphorus are reported in milligrams per liter as phosphorus (P). The nitrate concentration values presented in this report were measured as dissolved nitrate plus nitrite. Because nitrite typically represented a small fraction of the total concentration, the reported values are presented and discussed as nitrate. The total organic nitrogen concentration was calculated by subtracting ammonia from the total Kjeldahl nitrogen. Samples for analysis of dissolved constituents were filtered through a 0.45-micron disposable capsule filter, using a peristaltic pump.

In October 2011, the NWQL changed methodology for determination of nitrate in filtered water from the cadmium reduction method described in Fishman (1993) to a colorimetric enzymatic reduction automated discrete analyzer method (Patton and Kryskalla, 2011). Water samples collected from July 20 to September 28, 2011, were analyzed using the cadmium reduction method, and samples collected on October 26, 2011, were analyzed using the enzymatic reduction method. Water samples collected from November 28, 2011, to June 29, 2012, were analyzed using both the cadmium reduction and enzymatic reduction methods for statistical comparison.

Because there were not 12 months of water samples analyzed for nitrate concentration by the cadmium reduction (11 samples) or enzymatic reduction methods (9 samples), an independent-samples t-test comparison was done to determine if there was a difference in the long-term mean measured concentration between the methods (Helsel and Hirsch, 1992). At the 95-percent confidence level (p -value=0.05), there were no statistically significant differences between results provided by the two analytical methods used to determine nitrate concentrations in the samples collected at Cabin Branch (p -value=0.385), Ellerbe Creek (p -value=0.967), or Third Fork Creek (p -value=0.953) during the study. Consequently, the nitrate concentrations measured by the enzymatic reduction method on samples collected on October 26, 2011, were used in place of the missing cadmium reduction concentrations. Statistical analyses of nitrate presented later in this report were based on concentrations determined with the cadmium reduction method.

Quality-control samples, including replicate samples and field blanks, were collected and reviewed throughout the study to document potential bias and variability in data that may result during the collection, processing, shipping, and handling of environmental samples. Replicate samples were collected as split samples or concurrent samples. Concurrent samples were collected simultaneously, whereas split samples were produced by compositing concurrent samples into a churn splitter and dividing the contents into two separate samples. To determine if equipment cleaning or sample processing procedures may have contaminated samples, inorganic blank water was processed in

Figure 5. Daily total precipitation at the North Carolina State Climate Office DURH Environment and Climate Observing Network station and hydrographs of streamflow measured at Cabin Branch, Ellerbe Creek, and Third Fork Creek, Durham County, North Carolina, July 2011 to June 2012.

the field with the same equipment used for the environmental samples and analyzed for nutrients. Approximately 20 percent of the total number of samples collected during the study were replicate samples and field blanks.

No major quality-assurance problems were observed for the analytical data obtained during this study. Results of replicate and blank samples analyzed for nutrients are given in table 2. Replicates generally indicated good analytical repeatability, with all sample concentrations within 0.01 milligram per liter (mg/L), except for total phosphorus and nitrate by enzymatic reduction, both of which were within 0.07 mg/L in one sample. Three blank samples were analyzed for nutrients, with most concentrations generally below the reporting level. One blank sample was contaminated with trace amounts of nitrate and another with trace amounts of total phosphorus. However, the concentration of these constituents was about one order of magnitude lower than that measured in the environmental samples, suggesting that contamination in the blanks did not affect the results from environmental samples.

Isotopic Characterization

Stable isotopes are measured as a ratio of the two most abundant isotopes of an element. By convention, stable-isotope ratios are reported as per mil (parts per thousand or ‰) deviation from a standard reference using the δ (delta) notation:

$$\delta(\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1,000 \quad (1)$$

where R is the isotope concentration ratio ($^{15}\text{N}/^{14}\text{N}$, $^2\text{H}/^1\text{H}$, or $^{18}\text{O}/^{16}\text{O}$) of a sample or standard (Kendall and Caldwell, 1998). Vienna Standard Mean Ocean Water (VSMOW) is the international isotopic standard used for H and O isotopes, and atmospheric air is the standard for N isotopes. Both VSMOW and atmospheric air have arbitrarily defined delta values of 0‰ (Kendall, 1998).

Stable Isotopes of Water

Stable isotopes of water ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$) in surface-water samples were analyzed by the USGS Stable Isotope Laboratory, Reston, Virginia. Analyses were performed using a VG Micromass 602 hydrogen dual inlet, double-collecting isotope-ratio mass spectrometer, following methods outlined in Révész and Coplen (2008a and 2008b). Results are reported with an analytical error within two standard deviations (2σ)

of $\pm 0.2\text{‰}$ for ^{18}O and $\pm 2.0\text{‰}$ for ^2H . The isotope ^2H is called deuterium. A linear correlation between $\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ in precipitation samples collected from a worldwide network of stations within the Global Network for Isotopes in Precipitation (<http://www.iaea.org/water>) has been established to create a Global Meteoric Water Line (GMWL). The GMWL is represented by the linear relation (Craig, 1961):

$$\delta^2\text{H}_{\text{H}_2\text{O}} = 8 \times \delta^{18}\text{O}_{\text{H}_2\text{O}} + 10 \quad (2)$$

Stable Isotopes of Nitrogen and Oxygen

Surface-water samples with measurable concentrations of nitrate were analyzed for stable isotopes of nitrogen and oxygen ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$) by the USGS Stable Isotope Laboratory, Menlo Park, California, using a Micromass IsoPrime continuous flow mass spectrometer and following the Sigman-Casciotti microbial denitrifier method (Sigman and others, 2001; Casciotti and others, 2002). Stable isotopes are reported with an analytical error (2σ) of $\pm 0.5\text{‰}$ for $\delta^{15}\text{N}_{\text{NO}_3}$ and $\pm 1.0\text{‰}$ for $\delta^{18}\text{O}_{\text{NO}_3}$.

Statistical Analysis of Water-Quality Data

The statistical variability in the water-quality data is summarized using truncated box plots (Helsel and Hirsch, 1992). Box plots are used to statistically categorize data, indicate the degree of data dispersion and skewness, and identify outliers, and can be an effective means of visual comparison between datasets. The box encompasses the interval between the first and third quartiles (25th and 75th percentiles), with the median (50th percentile) represented by a horizontal line within the rectangular box. The 10th percentile and 90th percentile of the dataset are represented by a whisker attached to a vertical line drawn from the first and third quartiles, respectively, to those values.

The nonparametric Kruskal-Wallis one-way analysis of variance (ANOVA) comparison test on ranked data was used to determine if any statistically significant relation among the medians of water-quality constituent values or concentrations existed among the three sampling sites at the 95-percent confidence level ($p\text{-value}=0.05$) (Helsel and Hirsch, 1992). If the Kruskal-Wallis ANOVA test indicated a significant difference in median concentrations among the sampling sites, followup tests were conducted to evaluate pairwise differences among the three groups. A Tukey-Kramer multiple comparison test was used to determine which populations were different (Tukey, 1977).

Table 2. Concentrations of nutrients in quality-assurance samples collected from streams in Durham County, North Carolina. Values in bold red indicate relative percent difference of replicate samples exceeded 10 percent or the measured concentration of field blank sample exceeded the method detection limit established by Fishman (1993) and Patton and Kryskalla (2011).

[N, nitrogen; P, phosphorus; mg/L, milligrams per liter; NM, not measured; <, less than]

Station name	Station number	Sample type	Sample date	Sample time	Ammonia	Nitrate plus nitrite, cadmium reduction method
					(mg/L as N)	
Third Fork Creek	02097280	Concurrent	Sept. 28, 2011	14:15	0.089	0.364
	02097280	Replicate	Sept. 28, 2011	14:16	0.091	0.363
Ellerbe Creek	0208675010	Split	Dec. 29, 2011	11:15	0.019	0.247
	0208675010	Replicate	Dec. 29, 2011	11:16	0.018	0.245
Cabin Branch	0208525105	Concurrent	May 30, 2012	15:15	0.037	0.034
	0208525105	Replicate	May 30, 2012	15:16	0.038	0.038
Cabin Branch	0208525105	Concurrent	June 29, 2012	13:30	0.018	0.023
	0208525105	Replicate	June 29, 2012	13:31	0.018	0.022
Ellerbe Creek	0208675010	Field blank	Oct. 26, 2011	10:36	<0.010	NM
Cabin Branch	0208525105	Field blank	Jan. 30, 2012	12:46	<0.010	0.025
Cabin Branch	0208525105	Field blank	June 29, 2012	13:32	<0.010	<0.020

Water-Quality Sampling Results

This section presents a summary of the results of physical properties, nutrients, and stable isotope sampling of surface water collected approximately monthly. An overview and statistical summary of the physical properties and nutrient concentration results are provided to characterize water-quality conditions at the stream sites. Results of stable isotopes of hydrogen, oxygen, and nitrogen measurements are discussed to assess the possibility of using stable isotopes to characterize nitrate sources and possible transport pathways within low-order streams.

The NCDENR adopted in-stream water-quality standards (North Carolina Department of Environment and Natural Resources, 2007) for four of the constituents measured in this study: pH (less than 6.0), dissolved-oxygen concentration (less than 5.0 mg/L), turbidity (greater than 50 nephelometric turbidity units), and nitrate concentration (greater than 10 mg/L). The three creek study sites are in nutrient-sensitive waters classified for water-supply use and are subject to the most stringent standards established by NCDENR to protect freshwater aquatic life, water supply, and human health. Results of analyses of monthly water-quality samples collected from Cabin Branch, Ellerbe Creek, and Third Fork Creek are listed in table 3. Concentrations shown in bold red font in table 3 indicate that the sampled constituent did not meet a NCDENR water-quality criterion at that location.

Physical Properties

Statistical summaries of measured streamflow and physical properties for all sampling events at each site are listed in table 4 and shown in figure 6. Streamflow at the time of sampling ranged from a low of 0.06 cubic foot per second (ft³/s) in Cabin Branch to a high of 17 ft³/s in Third Fork Creek (table 4), reflecting the increase in drainage areas of the study sites (table 1). Water temperatures ranged from a low of 4.9 degrees Celsius (°C) in Cabin Branch to a high of 29.1 °C in Ellerbe Creek (table 4). The overall range in water temperatures at the sites reflected seasonal variations in atmospheric temperature. Measurements of specific conductance ranged from 87 microsiemens per centimeter (μS/cm) at 25 °C at Cabin Branch to 284 μS/cm at Third Fork Creek (table 4), with no discernable relation between specific conductance and streamflow. Overall, little variation occurred in pH among the three sites, with median pHs ranging from 6.1 in Cabin Branch to 6.6 in Ellerbe Creek (table 4). Although the pH measurements collected in Ellerbe Creek met the NCDENR water-quality standard, two observations in Cabin Branch (September 2 and December 23, 2011) and one in Third Fork Creek (April 25, 2012) fell below the standard of 6.0 (table 3). Dissolved-oxygen concentrations ranged from 3.8 mg/L in Third Fork Creek (measured November 28, 2011, and is less than the standard of 5 mg/L) to 13.0 mg/L in Ellerbe Creek (table 3). Turbidity was measured during 9 of the 12 sampling events.

Table 2.—Continued

Nitrate plus nitrite, enzymatic digestion method	Total phosphorus	Ortho- phosphate	Total ammonia plus organic nitrogen	Total organic nitrogen	Station number	Station name
(mg/L as N)	(mg/L as P)		(mg/L as N)			
NM	0.254	0.070	0.77	0.68	02097280	Third Fork Creek
NM	0.195	0.073	0.73	0.64	02097280	
0.240	0.092	0.045	0.47	0.45	0208675010	Ellerbe Creek
0.243	0.089	0.045	0.46	0.44	0208675010	
0.131	0.056	0.012	0.61	0.57	0208525105	Cabin Branch
0.058	0.056	0.012	0.61	0.57	0208525105	
<0.040	0.042	<0.004	0.56	0.54	0208525105	Cabin Branch
<0.040	0.045	0.005	0.55	0.53	0208525105	
<0.040	0.007	<0.004	<0.07	<0.07	0208675010	Ellerbe Creek
<0.040	<0.004	<0.004	<0.07	<0.07	0208525105	Cabin Branch
<0.040	<0.004	<0.004	<0.07	<0.07	0208525105	Cabin Branch

The turbidity standard of 50 nephelometric turbidity units (NTU) was exceeded in one measurement collected on September 28, 2011, at Third Fork Creek during a stormflow event.

Comparison testing revealed some statistically significant differences between the more urban stream sites (Third Fork Creek and Ellerbe Creek) and the more forested site (Cabin Branch) (fig. 6). The median specific conductance in Third Fork Creek was significantly greater than that in Cabin Branch (p -value=0.0005), suggesting a possible relation between specific conductance and drainage area. Ellerbe Creek and Third Fork Creek had median pH levels that were significantly higher than Cabin Branch (p -value=0.0018), which is consistent with Cabin Branch having a more forested drainage area. The median dissolved-oxygen concentration measured in Ellerbe Creek was significantly higher than that in Cabin Branch and Third Fork Creek (p -value=0.0207), likely a result of improved aeration and flow within the concrete-lined channel. Cabin Branch had median turbidity measurements that were significantly higher than Ellerbe Creek and Third Fork Creek (p -value=0.0029), which may be related to low streamflows during sample collection.

Nitrogen and Phosphorus

The continuous cycling of nitrogen and phosphorus within the environment causes variation in total nitrogen and phosphorus concentrations and distribution of their species

fractions in surface water. Various factors influence nitrogen and phosphorus delivery to streams, including urban and agricultural runoff from storm events, groundwater discharge, point sources (such as wastewater outfalls), and nonpoint sources (such as leaking septic tanks). Statistical summaries of the nutrient concentrations by sampling site are shown in figure 7 and listed in table 5.

Nitrogen occurs in surface water as both inorganic nitrogen in the form of dissolved nitrite, nitrate, and ammonia, and as dissolved and particulate organic nitrogen in the form of urea, amino acids, and protein (Hutchinson, 1957). Hydrographs of inorganic and organic nitrogen concentrations measured in Cabin Branch, Ellerbe Creek, and Third Fork Creek are shown in figure 8. All measured nitrate concentrations in surface-water samples were below the NCDENR standard of 10 mg/L, ranging from below the detection limit of 0.02 mg/L in Ellerbe Creek to a high of 0.363 mg/L in Third Fork Creek (table 5). Cabin Branch had the smallest range and median concentration of nitrate, and Third Fork Creek had the largest (table 5). The highest concentrations of nitrate in Ellerbe Creek and Third Fork Creek were measured during stormflow events that occurred on September 28, 2011, and February 23, 2012, whereas the highest concentrations in Cabin Branch were measured on January 30 and February 23, 2012 (table 3). The hydrographs in figure 8 do not display a seasonal component in any of the creeks that might explain the variations in nutrient concentrations.

Table 3. Physical properties, water-quality concentrations, and stable isotope results measured in surface water from Cabin Branch, Ellerbe Creek, and Third Fork Creek, Durham County, North Carolina. Values in bold red do not meet North Carolina water-quality criteria.¹

[ft, feet; NAVD 88, North American Vertical Datum of 1988; ft³/s, cubic feet per second; N, nitrogen; P, phosphorus; mg/L, milligram per liter; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; NTU, nephelometric turbidity units; %, per mil; NM, not measured; <, less than]

Sample date	Sample time	Gage height (ft above NAVD 88)	Instantaneous streamflow (ft³/s)	Ammonia	Nitrate plus nitrite, cadmium reduction method	Nitrate plus nitrite, enzymatic digestion method	Total phosphorus	Ortho- phosphate	Total ammonia plus organic nitrogen
				(mg/L as N)	(mg/L as N)	(mg/L as P)	(mg/L as P)	(mg/L as N)	
Cabin Branch									
July 20, 2011	12:45	NM	0.08	0.111	0.064	NM	0.281	0.157	0.53
Sept. 2, 2011	12:00	NM	0.06	0.012	0.03	NM	0.054	0.009	0.51
Sept. 28, 2011	13:00	NM	0.78	0.023	0.025	NM	0.073	0.011	0.80
Oct. 26, 2011	11:35	NM	0.16	0.033	NM	<0.040	0.051	0.006	0.50
Nov. 28, 2011	12:35	NM	0.29	0.037	0.026	<0.040	0.039	0.009	0.53
Dec. 29, 2011	12:30	NM	1.7	0.024	0.074	0.076	0.042	0.009	0.45
Jan. 30, 2012	12:45	NM	0.99	0.033	0.101	0.115	0.082	0.011	0.62
Feb. 23, 2012	13:00	NM	5.3	0.015	0.077	0.084	0.063	0.011	0.58
Mar. 30, 2012	13:45	NM	1.1	0.066	0.038	0.043	0.098	0.019	0.64
Apr. 25, 2012	13:30	NM	0.70	0.043	0.044	0.055	0.079	0.015	0.60
May 30, 2012	15:15	NM	0.25	0.037	0.034	0.131	0.056	0.012	0.61
June 29, 2012	13:30	NM	0.18	0.018	0.023	<0.040	0.043	<0.004	0.56
Ellerbe Creek									
July 20, 2011	11:00	0.26	0.12	<0.010	0.026	NM	0.039	0.021	0.34
Sept. 2, 2011	12:55	0.26	0.07	0.023	0.042	NM	0.056	0.027	0.39
Sept. 28, 2011	11:45	0.45	3.1	0.011	0.259	NM	0.128	0.048	0.51
Oct. 26, 2011	10:35	0.29	0.27	<0.010	NM	<0.040	0.046	0.025	0.40
Nov. 28, 2011	11:30	0.34	0.90	0.010	<0.020	<0.040	0.057	0.023	0.51
Dec. 29, 2011	11:15	0.38	2.1	0.019	0.247	0.240	0.093	0.045	0.47
Jan. 30, 2012	11:50	0.34	0.73	0.013	0.126	0.143	0.059	0.017	0.39
Feb. 23, 2012	11:45	0.50	6.0	0.011	0.247	0.244	0.072	<0.004	0.53
Mar. 30, 2012	12:10	0.36	1.1	0.035	0.060	0.066	0.061	0.026	0.53
Apr. 25, 2012	12:30	0.34	0.73	0.055	0.219	0.208	0.076	0.030	0.56
May 30, 2012	12:30	0.36	1.1	0.060	0.121	0.141	0.096	0.050	0.49
June 29, 2012	12:40	0.28	0.07	0.021	0.036	<0.040	0.074	0.039	0.53
Third Fork Creek									
July 20, 2011	14:20	1.46	0.64	0.036	0.197	NM	0.133	0.088	0.55
Sept. 2, 2011	13:40	1.34	0.11	0.035	0.073	NM	0.195	0.138	0.38
Sept. 28, 2011	14:15	2.52	16	0.089	0.363	NM	0.254	0.070	0.77
Oct. 26, 2011	13:00	1.85	0.7	<0.010	NM	0.041	0.141	0.058	0.50
Nov. 28, 2011	13:30	1.96	1.6	0.095	0.066	0.071	0.164	0.078	0.64
Dec. 29, 2011	13:20	2.14	8.9	0.035	0.153	0.153	0.125	0.040	0.58
Jan. 30, 2012	14:00	1.88	2.8	0.037	0.081	0.094	0.130	0.036	0.50
Feb. 23, 2012	13:45	2.44	17	0.073	0.294	0.295	0.126	0.027	0.59
Mar. 30, 2012	14:40	1.91	6.7	0.100	0.213	0.229	0.153	0.060	0.70
Apr. 25, 2012	11:45	1.69	2.3	0.085	0.261	0.247	0.127	0.057	0.57
May 30, 2012	14:00	1.58	0.90	0.076	0.245	0.271	0.200	0.122	0.68
June 29, 2012	14:30	1.48	0.27	0.060	0.195	0.168	0.130	0.081	0.50

¹North Carolina Department of Natural Resources, 2007.

Table 3.—Continued

Total organic nitrogen	Water temperature, field (°C)	Specific conductance, field (µS/cm)	pH, field	Dissolved oxygen, field (mg/L)	Turbidity, field (NTU)	Delta oxygen-18 of water	Delta deuterium of water	Delta nitrogen-15 of nitrate	Delta oxygen-18 of nitrate
(mg/L as N)									
(‰)									
Cabin Branch									
0.42	26.9	170	6.9	6.9	NM	-3.3	-19.1	0.8	3.7
0.50	21.9	87	5.8	6.8	NM	-2.6	-16.3	5.6	29.4
0.78	23.8	148	6.0	5.2	32	-3.6	-21.3	7.3	15.3
0.47	12.4	117	6.1	6.2	27	-4.5	-28.7	NM	NM
0.49	13.1	139	6.3	6.9	20	-4.3	-22.9	5.5	2.5
0.42	4.9	138	5.6	10.5	26	-3.7	-17.1	5.9	2.8
0.59	7.1	118	6.5	10.2	50	-4.1	-20.2	5.7	9.0
0.56	12.0	135	6.1	9.4	40	-4.8	-26.3	6.7	4.1
0.58	19.0	140	6.2	7.3	41	-3.2	-17.8	6.2	0.5
0.56	15.7	120	6.1	7.9	38	-3.8	-18.4	7.9	11.8
0.57	25.5	161	6.3	5.8	40	-3.5	-17.8	10.9	14.5
0.54	24.9	144	6.1	5.5	NM	-3.0	-17.6	7.5	23.0
Ellerbe Creek									
0.34	27.6	174	7.3	8.4	NM	-2.3	-14.4	9.2	10.2
0.37	25.8	118	6.7	9.8	NM	-2.5	-15.2	3.4	11.6
0.50	23.6	106	6.5	7.8	23	-5.3	-33.0	-1.7	38.7
0.40	14.2	152	6.3	9.4	4.4	-5.1	-34.1	NM	NM
0.50	13.6	158	6.8	9.7	4.0	-4.0	-22.1	NM	NM
0.45	7.1	156	6.4	12.0	12	-3.8	-16.8	4.0	5.9
0.37	7.4	159	6.5	13.0	16	-4.2	-21.9	6.9	10.8
0.52	10.8	183	6.5	11.0	30	-5.4	-28.0	4.2	17.4
0.50	17.7	222	6.6	9.5	5.0	-3.7	-20.5	6.9	0.9
0.50	14.3	178	6.7	10.1	6.7	-4.0	-22.1	3.6	9.7
0.43	24.7	207	6.5	5.6	6.0	-3.7	-19.9	5.1	-0.4
0.51	29.1	195	7.2	9.9	NM	-2.8	-18.8	NM	NM
Third Fork Creek									
0.51	26.8	275	6.6	6.6	NM	-3.0	-16.1	6.8	2.1
0.35	23.7	173	6.3	5.2	NM	-2.9	-18.4	1.9	15.4
0.68	23.0	170	6.4	6.6	59	-5.3	-32.4	0.7	24.4
0.50	13.3	200	6.5	8.0	8.8	-5.7	-36.7	7.3	1.6
0.55	14.3	138	6.6	3.8	7.1	-4.5	-23.4	4.9	-0.7
0.54	6.8	154	6.3	10.8	28	-4.0	-16.7	5.7	6.5
0.46	7.4	199	6.5	11.5	28	-3.8	-19.6	4.1	8.1
0.52	11.2	246	6.5	9.7	35	-5.2	-28.4	1.4	28.4
0.60	17.9	236	6.6	7.5	18	-3.9	-20.0	7.0	3.9
0.48	12.1	186	5.7	8.3	18	-5.1	-31.3	4.4	4.4
0.60	23.4	205	6.6	5.2	11	-3.5	-18.5	7.0	3.8
0.44	24.9	284	6.8	5.5	NM	-3.1	-16.9	7.2	4.4

Table 4. Summary statistics for streamflow measurements and physical properties in water samples collected at Cabin Branch, Ellerbe Creek, and Third Fork Creek, Durham County, North Carolina, July 2011 to June 2012. Values in bold red do not meet North Carolina water-quality criteria.¹

[ft³/s, cubic feet per second; NA, not applicable; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter, NTU, nephelometric turbidity units]

Statistic	North Carolina ambient water-quality criteria ¹	Cabin Branch	Ellerbe Creek	Third Fork Creek
Streamflow (ft³/s)	NA			
Minimum		0.06	0.16	0.11
25th percentile		0.17	0.17	0.66
Median		0.50	0.82	2.0
75th percentile		1.1	1.9	8.4
Maximum		5.3	6	17
Number of measurements		12	12	12
Temperature (°C)	NA			
Minimum		4.9	7.1	6.8
25th percentile		12.1	11.5	11.4
Median		17.4	16.0	16.1
75th percentile		24.7	25.5	23.6
Maximum		26.9	29.1	26.8
Number of measurements		12	12	12
Specific conductance (µS/cm)	NA			
Minimum		87	106	138
25th percentile		119	153	171
Median		139	167	200
75th percentile		147	192	244
Maximum		170	222	284
Number of measurements		12	12	12
pH	6 to 9			
Minimum		5.6	6.3	5.7
25th percentile		6.0	6.5	6.4
Median		6.1	6.6	6.5
75th percentile		6.3	6.7	6.6
Maximum		6.9	7.3	6.8
Number of measurements		12	12	12
Dissolved oxygen (mg/L)	4.0			
Minimum		5.2	5.6	3.8
25th percentile		5.9	8.7	5.3
Median		6.9	9.7	7.1
75th percentile		9.0	10.8	9.3
Maximum		10.5	13.0	11.5
Number of measurements		12	12	12
Turbidity (NTU)	50			
Minimum		20	4.0	7.1
25th percentile		26	4.7	9.9
Median		38	6.7	18
75th percentile		40	20	32
Maximum		50	30	59
Number of measurements		9	9	9

¹North Carolina Department of Natural Resources, 2007.

Figure 6. The range, median, and quartile statistical values for (A) streamflow, (B) temperature, (C) specific conductance, (D) pH, (E) dissolved oxygen, and (F) turbidity measured during monthly sampling events at Cabin Branch, Ellerbe Creek, and Third Fork Creek, Durham County, North Carolina, and the results of significance testing, July 2011 to June 2012.

Figure 7. The range, median, and quartile statistical values for (A) nitrate + nitrite, (B) ammonia, (C) total organic nitrogen, (D) total phosphorus, and (E) orthophosphate measured during monthly sampling events at Cabin Branch, Ellerbe Creek, and Third Fork Creek, Durham County, North Carolina, and the results of significance testing, July 2011 to June 2012.

Table 5. Summary statistics for nutrients in water samples collected at Cabin Branch, Ellerbe Creek, and Third Fork Creek, Durham County, North Carolina, July 2011 to June 2012.

[mg/L, milligrams per liter; N, nitrogen; P, phosphorus; NA, not applicable; <, less than]

Statistic	North Carolina ambient water-quality criteria ¹	Cabin Branch	Ellerbe Creek	Third Fork Creek
Nitrate + nitrite (mg/L as N)	10			
Minimum		<0.040	<0.020	0.041
25th percentile		0.027	0.037	0.075
Median		0.039	0.091	0.196
75th percentile		0.072	0.240	0.257
Maximum		0.101	0.259	0.363
Number of analyses		12	12	12
Ammonia (mg/L as N)	NA			
Minimum		0.012	<0.010	<0.010
25th percentile		0.019	0.011	0.035
Median		0.033	0.016	0.066
75th percentile		0.042	0.032	0.089
Maximum		0.111	0.060	0.100
Number of analyses		12	12	12
Total organic nitrogen (mg/L as N)	NA			
Minimum		0.42	0.34	0.34
25th percentile		0.47	0.38	0.47
Median		0.55	0.47	0.52
75th percentile		0.58	0.50	0.59
Maximum		0.78	0.52	0.68
Number of analyses		12	12	12
Total phosphorus (mg/L as P)	NA			
Minimum		0.039	0.039	0.125
25th percentile		0.045	0.056	0.128
Median		0.060	0.067	0.137
75th percentile		0.081	0.088	0.187
Maximum		0.281	0.128	0.254
Number of analyses		12	12	12
Orthophosphate (mg/L as P)	NA			
Minimum		<0.004	<0.004	0.028
25th percentile		0.009	0.021	0.044
Median		0.011	0.027	0.067
75th percentile		0.015	0.044	0.086
Maximum		0.157	0.050	0.138
Number of analyses		12	12	12

¹North Carolina Department of Natural Resources, 2007.

Figure 8. Hydrographs of (A) instantaneous streamflow, (B) nitrate plus nitrite, (C) ammonia, and (D) total organic nitrogen measured at Cabin Branch, Ellerbe Creek, and Third Fork Creek, Durham County, North Carolina, July 2011 to June 2012.

Ammonia concentrations ranged from below the detection limit of 0.010 mg/L in Ellerbe Creek and Third Fork Creek to 0.111 mg/L in Cabin Branch (table 5). According to Mueller and others (1995), concentrations of ammonia above 0.1 mg/L may show evidence of anthropogenic effects, and concentrations exceeding 0.2 mg/L may indicate that surface water has been affected by urbanization changes to the landscape. Only one sample at any of the sites exceeded an ammonia concentration of 0.1 mg/L (July 20, 2011, at Cabin Branch; table 3), suggesting no urbanization effect was seen. Concentrations of organic nitrogen ranged from a low of 0.34 mg/L at Ellerbe and Third Fork Creeks to a high of 0.78 mg/L at Cabin Branch (table 5). Ellerbe Creek had the smallest range and median concentration of organic nitrogen during the study, and Cabin Branch had the largest, which are consistent with the primary drainage basin land uses (figs. 2 and 3). More than 50 percent of the total nitrogen in the creeks was in the form of organic nitrogen.

Phosphorus can be found in two main forms in surface water, dissolved inorganic orthophosphate and particulate phosphorus. Measured concentrations of total phosphorus and orthophosphate generally were less than 0.2 mg/L in the three creeks (table 5). Concentrations of total phosphorus ranged from 0.039 mg/L in Cabin Branch and Ellerbe Creeks to a high of 0.281 mg/L in Cabin Branch (table 5). Measured concentrations of orthophosphate ranged from less than the detection limit of 0.004 mg/L in Cabin Branch and Ellerbe Creeks to a high of 0.157 mg/L in Cabin Branch (table 5). Cabin Branch had the greatest range in both total phosphorus and orthophosphate concentrations. The greater total phosphorus and orthophosphate concentrations in Third Fork Creek may be related to the residential use of fertilizers within the drainage basin.

Comparison testing revealed statistically significant differences among the three sites. The median nitrate (p -value=0.0039) and median ammonia (p -value=0.0044) concentrations measured in Third Fork Creek were significantly greater than those in Cabin Branch and Ellerbe Creek, respectively. Third Fork Creek also had median concentrations of phosphorus (p -value=<0.0001) and orthophosphate (p -value=<0.0001) that were significantly higher than those in Ellerbe Creek and Cabin Branch. However, the median organic nitrogen concentration measured at Cabin Branch was significantly higher than that measured at Ellerbe Creek (p -value=0.0292).

Stable Isotopes of Water

The $\delta^2\text{H}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ isotopic compositions of surface-water samples collected from Cabin Branch, Ellerbe Creek, and Third Fork Creek generally corresponded with the GMWL (fig. 9). This correspondence indicates that the water in the creeks has a similar isotopic signature to that of modern-day precipitation that has undergone very little fractionation due to evaporation or other processes after reaching land surface. As water evaporates, preferential removal of the lighter isotopes ^1H and ^{16}O occurs, shifting the stable isotopic composition of the remaining water toward the more positive heavier isotopes ^2H and ^{18}O .

Water samples collected at Cabin Branch, Ellerbe Creek, and Third Fork Creek on July 20 and September 2, 2011, and May 30 and June 29, 2012, however, display a seasonal difference in isotopic composition. These samples plot along a line with a slope of about 3.1 as opposed to 8.0 for the GMWL, suggesting enrichment in heavier isotopes of ^2H and ^{18}O as a result of evaporation. The isotope ratios of H and O in water that have undergone multiple cycles of evaporation become more positive as evaporation proceeds. Samples collected in July and early September 2011 as well as June 2012 are the most enriched with respect to the heavier isotopes at all three creeks, plotting the farthest away from the GMWL. As the lowest streamflows were frequently measured during these drier summer months, these isotopic ratios may also represent mixing with an unknown quantity of local and regional groundwater discharge with a slightly different $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ isotopic composition.

Stable Isotopes of Nitrogen and Oxygen

Although laboratory analysis of nitrate in surface water provides important information on water-quality conditions, additional analytical or environmental (such as land use) data are needed in combination with the nitrate concentrations for evaluating potential differences in nutrient sources. Stable isotopes of nitrate have been used as environmental tracers for examining sources of nitrate among different land uses (Cravotta, 1997; Silva and others, 2002; Xue and others, 2009). Isotopic analysis of nitrate can aid in distinguishing atmospheric and synthetic fertilizer sources from organic fertilizer (animal manure) and septic sources. Isotopic analyses also can provide information on geochemical influences on nitrate in surface water, such as denitrification.

Common fields of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values derived from typical source signatures, as defined by Kendall and others (2007), are displayed in an isotope source plot (fig. 10). If the measured isotope values of nitrogen and oxygen in nitrate plot within one of the boxes outlined in the graph, the source is likely identified, assuming there has been minimal cycling of nitrogen. Bacterial decomposition of organic nitrogen, resulting from the decomposition of plants

Figure 9. Deuterium and oxygen-18 stable isotope values of surface-water samples collected from Cabin Branch, Ellerbe Creek, and Third Fork Creek, Durham County, North Carolina, between July 2011 and June 2012. Samples represented by symbols with open centers were collected on July 20 and September 2, 2011, and May 30 and June 29, 2012.

and animals and their organic waste products, produces soil nitrogen. Typically, nitrate derived from animal and human wastes cannot be distinguished from one another using values of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ alone. It can also be difficult to differentiate between ammonium-bearing fertilizer and soil nitrate on the basis of isotopes alone.

Mixing of water between two or more nitrate sources can result in isotope values that plot between the typical source boxes. Additionally, in situ microbial transformation processes, such as denitrification and assimilation, complicate the interpretation of the isotopic composition of nitrate. Values of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ increase with a 2:1 or 1:1 ratio of nitrogen to oxygen through the loss of ^{14}N and ^{16}O in the fractionation process that occurs during denitrification (Böttcher and others, 1990; Kendall and others, 2007). The $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values of the remaining nitrate can be highly altered, complicating source determination. Kendall and others (2007) suggested that $\delta^{18}\text{O}_{\text{NO}_3}$ values are more

Figure 10. Nitrogen-15 and oxygen-18 stable isotope values and potential sources of nitrogen from surface-water samples collected from Cabin Branch, Ellerbe Creek, and Third Fork Creek, Durham County, North Carolina (modified from Kendall and others, 2007).

useful for separating nitrate sources originating from nitrate-bearing fertilizers and atmospheric deposition of nitrate, whereas $\delta^{15}\text{N}_{\text{NO}_3}$ values are more useful for separating nitrate sources originating from ammonium-bearing fertilizer, soil organic matter, and animal manure or septic waste.

Cabin Branch Nitrogen Sources

Eleven of 12 surface-water samples from Cabin Branch had measurable quantities of nitrate sufficient to allow isotopic analysis. Measured $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values in these samples ranged from +0.8 to +10.9‰ and +0.5 to +29.4‰, respectively (table 3), and are shown on an isotope source plot in figure 10. The average measured $\delta^{15}\text{N}_{\text{NO}_3}$ value was +6.4 and the average $\delta^{18}\text{O}_{\text{NO}_3}$ value was +10.6, which is consistent with nitrification of soil nitrogen as the dominant source of nitrate to Cabin Branch.

Three of the water samples had more positive values of $\delta^{18}\text{O}_{\text{NO}_3}$ than the other eight (collected September 2 and 28, 2011, and June 29, 2012), causing them to plot between the defined source boxes. These three samples were likely

a mixture of nitrate derived from precipitation and natural soil nitrogen, but because the nitrate concentration at Cabin Branch was low, these data do not show evidence of a large direct contribution of atmospheric nitrate to the creek. The July 20, 2011, water sample had the lowest value of $\delta^{15}\text{N}$ and highest concentration of ammonia measured at Cabin Branch (0.111 mg/L), suggesting a source of nitrate that was likely derived from ammonium-bearing fertilizer.

The nearly one-to-one linear relation between the values of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ in water samples collected on April 25 and May 30, 2012, is a unique feature of these data. The slope of the relation between the two samples is 0.91 (fig. 10), which is very close to that expected for partially denitrified nitrate. Although these samples plot in the area for manure and septic waste, they are likely denitrified soil nitrogen. Streamflow was low in April and May 2012 at the time of sampling, which restricted nitrate additions from runoff and precipitation and lengthened travel time within the drainage basin, thus enhancing denitrification. Data collected for this study cannot identify whether denitrification was occurring within the stream environment or within the riparian zone during groundwater transport. Studies by Lehmann and others (2003) and Sebilio and others (2003), however, suggest that the small range of $\delta^{15}\text{N}_{\text{NO}_3}$ affected by fractionation processes (2.8 per mil) at Cabin Branch indicates that the denitrification process was likely limited by nitrate supply.

Ellerbe Creek Nitrogen Sources

Nine of 12 surface-water samples collected from Ellerbe Creek had nitrate concentrations sufficient to allow isotopic analysis. Measured $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values in these samples ranged from -1.7 to +9.2‰ and -0.4 to +38.7‰, respectively (table 3). Figure 10 shows the measured $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values in samples collected from Ellerbe Creek plotted on an isotope source plot. The average measured $\delta^{15}\text{N}_{\text{NO}_3}$ value was +4.6‰ and the average $\delta^{18}\text{O}_{\text{NO}_3}$ value was +11.6‰, which is consistent with nitrification of soil nitrogen as the dominant source of nitrate to Ellerbe Creek. Two water samples collected on September 28, 2011 and February 23, 2012, had large positive values of $\delta^{18}\text{O}_{\text{NO}_3}$ (greater than +15‰), causing them to plot between the defined source boxes. These samples were collected during stormflow events, suggesting that they were likely a mixture of nitrate derived from precipitation and natural soil nitrogen. One water sample collected in July 2011 had a $\delta^{15}\text{N}_{\text{NO}_3}$ value of +9.2‰ and a $\delta^{18}\text{O}_{\text{NO}_3}$ value of 10.2‰, suggesting a possible manure or septic waste source. The remaining six water samples had values of $\delta^{15}\text{N}_{\text{NO}_3}$ between +3.4 and +6.9‰ and $\delta^{18}\text{O}_{\text{NO}_3}$ values between -0.4 and +11.6‰, which is consistent with nitrification of soil nitrogen as the likely source.

In Ellerbe Creek the highest nitrate concentrations were measured in water samples collected on September 28, 2011, and February 23, 2012, when the likely nitrogen source was

the mixing of atmospheric nitrogen from precipitation and soil nitrogen during stormflow events. Precipitation and subsequent stormflow events can mobilize previously deposited atmospheric nitrogen through both wet and dry deposition. Precipitation and runoff dominate the flow during stormflow events in Ellerbe Creek because of the relatively high impervious surface area associated with urban land use. Wet atmospheric deposition samples collected by SSD in a contemporaneous precipitation study with Durham County averaged about 0.21 mg/L nitrate (Morrison and Werner, 2012), which is similar to the stormflow concentrations measured in this study.

Third Fork Creek Nitrogen Sources

Twelve surface-water samples from Third Fork Creek had measurable quantities of nitrate sufficient to allow isotopic analysis. Measured $\delta^{15}\text{N}_{\text{NO}_3}$ values in these samples ranged from +0.7 to +7.3‰, and $\delta^{18}\text{O}_{\text{NO}_3}$ values ranged from -0.7 to 28.4‰ (table 3). Measured $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values in samples collected from Third Fork Creek are shown in figure 10. The average measured $\delta^{15}\text{N}_{\text{NO}_3}$ value was +4.9‰, and the average $\delta^{18}\text{O}_{\text{NO}_3}$ value was +8.5‰, which is consistent with nitrification of soil nitrogen as the dominant source of nitrate to Ellerbe Creek. Three water samples collected on September 2 and 28, 2011, and February 23, 2012, had positive values of $\delta^{18}\text{O}_{\text{NO}_3}$ (greater than +15‰), causing them to plot between the defined source boxes suggesting that they were likely a mixture of nitrate derived from precipitation and soil nitrogen. The other nine water samples had values of $\delta^{15}\text{N}_{\text{NO}_3}$ between +4.1 and +7.3‰ and values of $\delta^{18}\text{O}_{\text{NO}_3}$ ranging between -0.7 and 8.1‰, which suggests a soil nitrogen source.

The highest nitrate concentrations were measured in two water samples collected from Third Fork Creek during stormflow events on September 28, 2011, and February 23, 2012, that had isotopic compositions that were a mixture of precipitation-derived nitrate. As with Ellerbe Creek, the large percentage of urban land use and impervious surface area in the Third Fork Creek drainage basin causes runoff to dominate streamflow during precipitation events. This mixing of the soil nitrogen with runoff containing an atmospheric nitrogen average concentration of 0.2 mg/L (Morrison and Werner, 2012) elevates the nitrate concentration during stormflow events.

Summary and Conclusions

A preliminary assessment of stable isotope data showed varying sources that affect nitrate concentrations among three creeks in Durham County, North Carolina. In the forested Cabin Branch drainage basin, the nitrate concentrations were generally below 0.1 milligram per liter (mg/L) and the dominant source of nitrate was the nitrification of soil nitrogen. Three samples had a nitrate source that was a mixture of precipitation and soil nitrogen; however, nitrate concentrations do not reflect a large contribution of nitrate during stormflow events. High $\delta^{15}\text{N}_{\text{NO}_3}$ values, low nitrate concentrations, and a linear relation between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ of about 1:1 are consistent with the denitrification of soil nitrogen, not the influence of septic or wastewater.

In the more urban Ellerbe Creek and Third Fork Creek drainage basins the nitrate concentration in water samples was more likely to exceed 0.1 mg/L. The dominant source of nitrate for both creeks was the nitrification of soil nitrogen. Two stormflow samples in Ellerbe and Third Fork Creek had elevated nitrate concentrations and $\delta^{18}\text{O}_{\text{NO}_3}$ values greater than 15 per mil, indicating that the source of the nitrate was a mixture of soil nitrogen and an atmospheric source that had bypassed some soil contact through impermeable surfaces within the drainage basin.

Results from this study suggest that in the small drainage basins of Durham County, it is possible to distinguish sources and biogeochemical processes on nitrate using stable isotopes of nitrogen and oxygen. Analyses of stable isotopes of nitrogen and oxygen in nitrate of monthly surface-water samples collected from July 2011 through June 2012 show that the highest nitrate concentrations measured in Cabin Branch, Ellerbe Creek, and Third Fork Creek were generally associated with natural sources of nitrate such as the nitrification of soil nitrogen and atmospheric deposition. These sources may not be as practical to remediate as anthropogenically derived nitrate.

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