STREAM CARBON DYNAMICS IN LOW-GRADIENT HEADWATERS OF A FORESTED WATERSHED

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Abstract—Headwater streams drain more than 70 percent of the total watershed area in the United States. Understanding of carbon dynamics in the headwater systems is of particular relevance for developing best silvicultural practices to reduce carbon export. This study was conducted in a low-gradient, predominantly forested watershed located in the Gulf Coastal Plain region, to (1) investigate spatiotemporal dynamics of carbon concentrations in the headwaters, (2) assess the relationships among stream carbon and nutrient conditions, and (3) quantify carbon export from the entire watershed. Fifteen sites were selected along four first-to-third order streams. Monthly and storm event water samples were collected from December 2005 to September 2007. These samples were analyzed for total and dissolved organic and inorganic carbon, nitrate/nitrite nitrogen, and total and dissolved phosphorus. In addition, instream water quality parameters (dissolved oxygen, temperature, pH) were measured monthly at each site to gather information on stream environmental conditions. The study found a seasonal variation of stream carbon concentration ranging from 9.6 to 30.0 mg/L with the lowest concentrations in January and February. There was a clear increasing trend of dissolved inorganic carbon from the winter to summer months, indicating a critical metabolic role of carbon supply and transport. Over the entire 22 months, the watershed exported a total of 1054.35 t carbon, in a decreasing trend of fluxes from 5.2 to 1.3 kg/ha per month with the increasing drainage area. This information can be useful for designing silvicultural practices that will conserve and maintain ecosystem carbon.

INTRODUCTION

Land use activities by humans have enormously altered the timing, magnitude, and nature of inputs of materials such as sediments, nutrients, and organic matter to aquatic ecosystems. One of the dominant themes in streamwater quality research is the effect of organic materials on eutrophication of coastal waters. Organic carbon interacts with the biogeochemical nitrogen cycle (Campbell and others 2000, Cooper and others 2006, Qualls and others 1991), aids in pollutant transport (Kalbitz and others 2000), and may be a major energy source for microorganisms (del Giorgio and Cole 1998, Marschner and Kalbitz 2003, Tranvik 1992). In forested watersheds, the upper horizons of the soil can contain large amounts of organic matter such as plant litter and soil organic matter degraded by microorganisms (Cory and others 2004). Seventy-five percent of carbon present on land is found as soil organic carbon (Sparks 2003). Consequently, surface runoff and erosion can contribute a large input of carbon to streams.

In aquatic systems, organic carbon is either consumed by the biological community, deposited in the benthic zone, or transformed into atmospheric carbon, all of which can affect streamwater quality. Organic matter is an important part of the aquatic food web, especially in headwater streams where primary production is limited as a result of the canopy cover. Most nitrogen transported by rivers to oceans is associated with organic matter. Therefore, understanding the carbon dynamics in streams and rivers can give a better picture of nitrogen present and the potential for eutrophication.

Headwater streams are particularly important for water quality of an entire watershed because they often drain over 70 percent of the total watershed area. Streams are lotic systems; therefore, upstream effects are ultimately felt downstream.

This study was conducted in the headwater streams of a low-gradient, subtropical watershed located in central Louisiana, USA. The study aimed to (1) investigate spatiotemporal dynamics of organic and inorganic carbon concentrations, (2) assess the relationships among stream carbon and nitrate, and (3) quantify carbon export from the headwater catchment.

METHODS

Study Area

The Flat Creek watershed is located in the western part of the Ouachita River Basin in central Louisiana (fig. 1). The basin drains a total land area of 41 439 km^2, characterized by a flat to slightly rolling topography. Flat Creek's drainage area is approximately 369 km^2. Forestry is the dominant land use in the watershed, occupying 61 percent of land and followed by rangeland with 21 percent (Louisiana Department of Environmental Quality 2001). Climate in this region is subtropical with hot, humid summers and mild winters. Long-term average temperatures range from 2.3 °C to 34.1 °C and long-term average rainfall is about 1500 mm/year. Soils in the area are dominated by poorly drained Guyton (silt loam) series along the Flat Creek and Turkey Creek flood plains, with moderately well-drained Sacul-Savannah (fine sandy loam) soils in the upland areas.

Streamwater Sampling and Laboratory Analyses

Four streams in the Flat Creek watershed were sampled: Spring Creek, Turkey Creek, Flat Creek, and Big Creek. Fifteen sites were visited monthly from January 2006 to September 2007 (fig. 1). *In-situ* water quality measurements, including dissolved oxygen, temperature, conductivity, and pH were taken at each site using an YSI 556 (YSI, Inc., Yellow Springs, OH). During each visit grab-water samples

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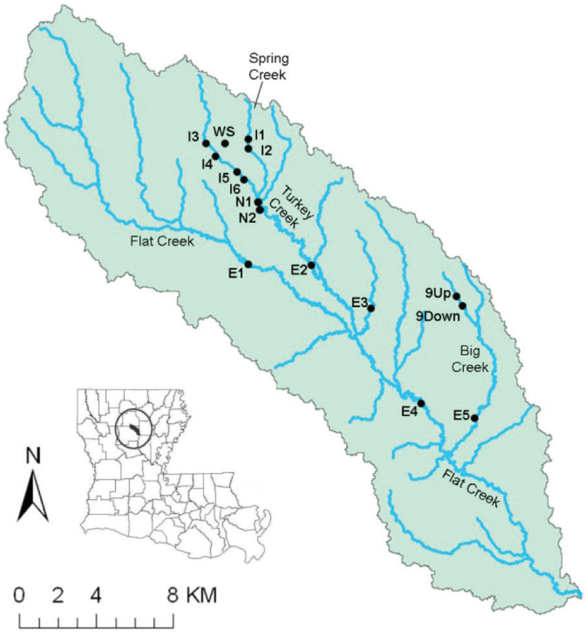

Figure 1—Geographical location of the Flat Creek watershed and water-quality monitoring sites. A weather station (WS) is established between Spring Creek and Turkey Creek.

were collected at each site. In addition, stormwater samples were collected at 6 of the 15 locations with automated Isco samplers (model 6712, Teledyne Isco, Inc., Lincoln, NE). Storm events were defined as enough rain to cause the stream to rise 15 cm in 24 hours. Depending on the rainfall intensity, time since last rainfall, and stream and riparian characteristics, the amount of precipitation for a 15-cm increase of stream level varied.

The laboratory measurements on water samples were conducted in the Wetland Biogeochemistry Institute, Louisiana State University. Water samples were analyzed for total and dissolved organic and inorganic carbon with a Shimadzu Total Organic Carbon Analyzer (model TOC-VCSN, Shimadzu Corporation, Kyoto, Japan) using the combustion/nondispersive infrared gas analysis method. Inorganic carbon and total carbon were measured by the analyzer, and the organic partition was calculated as the difference between total and inorganic carbon. Water for dissolved organic and inorganic carbon analysis was first filtered through a 47-μm glass fiber filter (GF/F Whatman International Ltd., Maidstone, United Kingdom).

Streamflow Measurements and Climatic Observations

Streamflow measurements were collected with a flow meter (SonTek®/YSI Inc., Yellow Springs, OH) and top setting wading rod (Rickly Hydrological Co., Columbus, OH) monthly during baseflow as well as whenever possible during higher flow conditions. Because the streams in the Flat Creek watershed are relatively narrow, most measurements consisted of 5 to 10 cross sections. The autosamplers at the intensive sites record stream level every 15 minutes. Stage-discharge curves developed for sites I1, I3, and I4 were used in conjunction with the stream level to calculate daily discharge. Detailed information about development of the stage-discharge rating curves can be found in Saksa (2007).

Data Analysis

Summary statistics such as mean and standard error were calculated for each month for all stations as well as each site for each sampling month. The number of samples varied with each month (table 1). The number of samples for total carbon

Table 1—Number of samples used in calculating mean and standard error

Month	Total carbon samples	Dissolved carbon samples	Month	Total carbon samples	Dissolved carbon samples
Jan-06	11	11	Jan-07	15	10
Feb-06	8	8	Feb-07	14	15
Mar-06	12	12	Mar-07	15	15
Apr-06	12	12	Apr-07	13	13
May-06	14	14	May-07	15	15
Jun-06	13	5	Jun-07	13	13
Jul-06	13	13	Jul-07	11	12
Aug-06	0	0	Aug-07	11	12
Sep-06	7	5	Sep-07	13	13
Oct-06	9	4			
Nov-06	15	3			
Dec-06	14	11			

is the number of samples for all total carbon concentrations including total inorganic and organic carbon. Similarly, the number of samples for dissolved carbon concentrations refers to dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC).

Carbon mass loading was calculated as:

$$L = e^{(a \,*\, \ln Q + b + \varepsilon)} \tag{1}$$

where
L = loading
Q = discharge
a and b = constants (table 2)
ε = an error term assumed to be evenly distributed

The *a* and *b* terms were adjusted for each site based on the loading to discharge curve (table 2). E4 calculated classically as:

$$L = Q * C \tag{2}$$

where
C = concentration
L = loading
Q = discharge

RESULTS AND DISCUSSION

Seasonal and Spatial Fluctuation of Stream Carbon Concentrations

For the period from January 2006 to September 2007 total carbon (TC) concentration appeared to be lower during two winter months, January and February, than during other months of the year (>22 mg/L). TC was marginally higher during the summer ($P = 0.052$; $t = -1.95$) while total inorganic carbon (TIC), dissolved carbon (DC), and DIC were higher in the summer (May to October) than the remaining of the year (November to April) ($P < 0.001$). Total organic carbon (TOC) was lower in the summer months than the remaining months ($P < 0.001$). Average TC ranged from 9.6 to 30.0 mg/L with the lowest average concentration present in February 2007 and the highest in December 2006. When separating the total carbon into organic and inorganic forms, a much clearer trend of increased inorganic carbon in the summer and increased organic carbon in the spring is apparent (fig. 2). Organic carbon ranged from 8.4 mg/L in February 2007 to 25.3 mg/L in November 2006. Average inorganic carbon ranged from 1.0 mg/L in March 2007 to 13.2 mg/L in June 2006.

Monthly average of dissolved carbon concentrations ranged from 9.9 mg/L in January 2007 to 29.6 mg/L in July 2007. DOC and DIC had a similar trend to TC. DOC ranged from 9.3 mg/L in July 2006 to 28.1 mg/L in July 2007. January 2007 had the lowest DIC (0.3 mg/L) with September 2006 having the highest (14.3 mg/L). A peak in the TIC to TOC ratio is apparent in the summer months from June through October in 2006 (fig. 3). Late October 2006 marked large rains (more than 8 inches within a single week) which indicated the beginning of the "rainy" season typically in the late fall and winter in central Louisiana.

The increased organic carbon observed during the spring may have resulted from an increasing primary production and/or high storm runoff during the season. For the subtropical headwaters of Flat Creek, DOC in quickflow is a more likely reason than primary production for the seasonal pattern present. Headwater streams act as net sinks for carbon and

Table 2—Slope (*a*) and intercept (*b*) for equations to calculate nutrient loading at I1 and I4

Site ID	Nutrient	Intercept	Slope	*R*-squared
I1	TC	0.2992	1.1762	0.96
I4	TC	3.6900	0.9705	0.95
I1	TOC	–1.7486	1.3051	0.95
I4	TOC	1.8050	1.0825	0.95

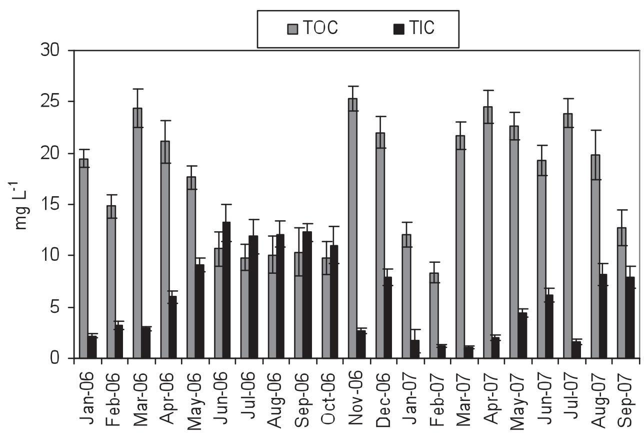

Figure 2—Seasonal fluctuation of total organic carbon (TOC) and total inorganic carbon (TIC) concentrations in the Flat Creek watershed.

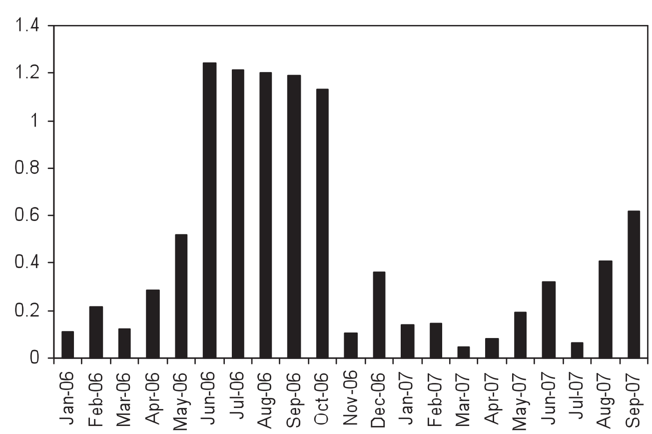

Figure 3—Seasonal trend of the ratio of TIC to TOC in headwater streams in the Flat Creek watershed.

nitrogen since the input is higher than what is processed within the stream (Cooper and others 2006). Also, because of the dense canopy cover in forested headwater streams, primary production has a lesser organic carbon contribution than the contribution from the organic layers of soil that is mobilized in storm events. DOC decreases with soil depth as sorption of dissolved organic matter (DOM) to mineral surfaces occurs in the deeper soil depths (Cory and others 2004); also DOM found in streams is more similar to shallow soil water DOM than the deep soil water DOM (Cory and others 2004). Johnson and others (2006) found that DIC is higher in deeper flow paths in which a 40 to 1 ratio of DIC to DOC existed for emergent ground water. During low flow conditions, which is found in the summer months in Flat Creek, streams receive water from ground water sources and water that has percolated through deeper soil layers enabling most organic carbon to be used by biological sources or abiotically adsorbed to mineral layers (Cory and others 2004) restricting the amount of carbon that is mobile to reach streams. Alternatively, during storm events which occur often in Louisiana during the winter and early spring, quickflow from throughfall, rainfall, and runoff carries rich organic water since it passes through the litter layer and surface soils. Additionally, the rise of streamwater within the banks allows organic materials to enter the water column. The decline in organic carbon in April 2006 to June 2006 shows that TOC is being consumed. DOC decomposition is slower in headwaters, but this process consumes oxygen and converts organic carbon (OC) to inorganic carbon (IC) (del Giorgio and Cole 1998). This fits nicely with the data in which there is a decrease in dissolved oxygen; OC and an increase in IC occurs from spring to summer. Considering spring tends to be a biologically active time, this is expected.

Average TC was lowest at I1 (13.5 mg/L) and highest at I5 (28.6 mg/L^{-}) (fig. 4). Most of the TC was in the dissolved form. Spatially, there was not a clear trend. The local variations, especially local soil characteristics appear to have a larger impact on carbon in the stream than location in the watershed. One site, 9Up, had a large variation due to limited samples collected at this intermittent site. E2 is located downstream of the confluence of Spring Creek (sites I1 and I2) and upper Turkey Creek (sites I3 to I6) and reflects the mixing of lower carbon at Spring Creek and higher carbon at the upper Turkey Creek sites.

Stream Carbon Concentrations during Storm Events

There was not a large difference in organic or inorganic carbon at different stages of the storm hydrograph, but there was a small increase in organic carbon (27.50+3.04 mg/L) in the falling limb (27.50+3.04 mg/L) vs. the rising limb (20.87+1.37 mg/L) and full peak (22.99+1.41 mg/L) (fig. 5). There were no changes in carbon concentrations (20.45 to 20.73 mg/L) during a storm event on January 16, 2007 (fig. 6). However, Spring Creek experienced higher carbon concentrations than Turkey Creek (21.34 mg/L at I1 vs. 18.65 mg/L at I4) during a storm event on October 17, 2006 (fig. 7).

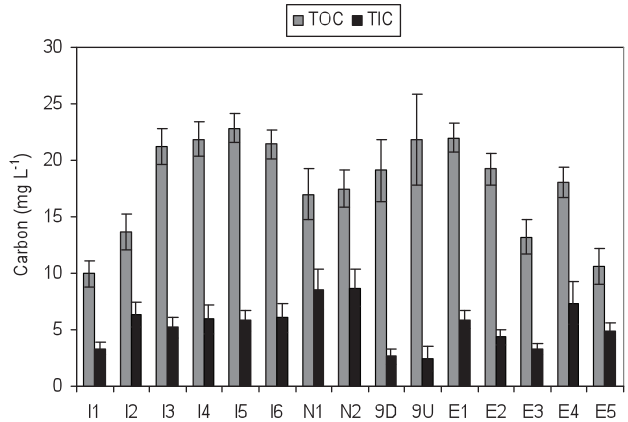

Figure 4—Average total organic carbon and total inorganic carbon concentrations at 15 locations in the Flat Creek watershed. Error bars represent standard error.

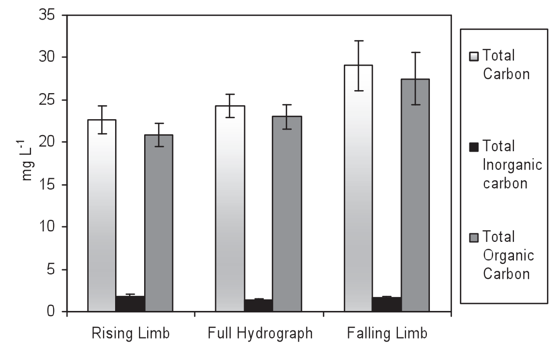

Figure 5—Average total carbon, total inorganic carbon, and total organic carbon during storm events in January 2006 to September 2007 during varying parts of the hydrograph in the Flat Creek watershed. Error bars represent standard error (*n* = 7 for rising limb, *n* = 24 for full hydrograph, and *n* = 5 for falling limb).

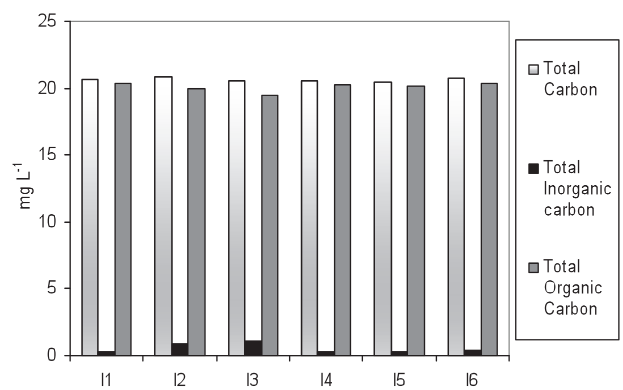

Figure 6—Total carbon, total inorganic carbon, and total organic carbon for all six sites during one storm event on January 15, 2007, in the Flat Creek watershed.

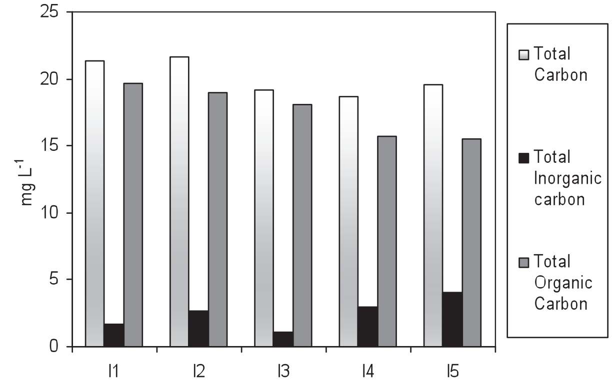

Figure 7—Total carbon, total inorganic carbon, total organic carbon for five sites during one storm event on October 16, 2006, in the Flat Creek watershed.

Previous research suggests that the highest DOC concentration should be during storm events (Cooper and others 2006); however, the DOC concentrations during storm events were only slightly elevated from max DOC measured during monthly water sampling. The literature related to the peak of DOC in the storm hydrograph is contradictory based on our review. Buffam and others (2001) state that the max should occur in the rising limb while Cooper and others (2006) cite various studies that found the max DOC on the falling limb. As stated above, the streams sampled in the study by Buffam and his colleagues had bedrock bottoms, so the streams themselves were not organic matter sources. This greatly contrasts the streams in the Flat Creek watershed. For this reason, it makes sense that Flat Creek's storm data follow more closely to Cooper and others (2006) and not Buffam and others (2001). During a storm event, carbon concentrations did not change among the six sites. This follows what was seen in monthly sampling. This specific storm event on January 16, 2007, followed multiple storm events in December and early January. A storm event on October 17, 2006, broke a long period of dry weather with 16.34 cm of rain. Spring Creek experienced higher carbon concentrations (21.34 mg/L at I1 and 21.65 mg/L at I2) than was seen in the January 16, 2007, storm, and Turkey Creek had lower carbon concentrations (18.65 to 19.57 mg/L). These are small variations and probably are due to differences in runoff and rainfall patterns.

Mass Loading and Transport of Carbon

Carbon loading was calculated using streamflow and concentration for two first-order streams (I1 and I4) and their downstream third-order watershed outlet (E4). Due to the flow conditions of this watershed, it was difficult to develop

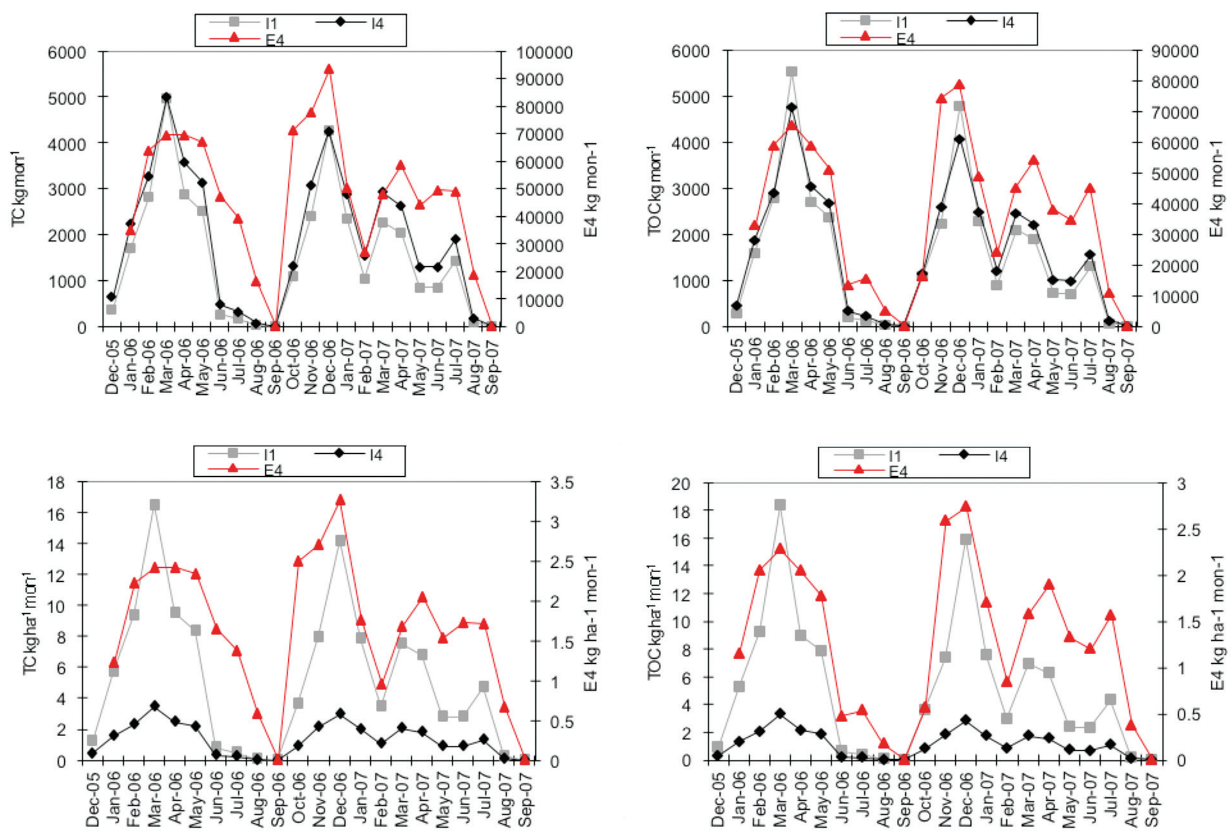

Figure 8—Comparison of mass loading and flux of total carbon and total organic carbon between two first-order (I1 and I4) streams and a third-order stream (E4) in the Flat Creek watershed.

accurate stage-discharge curves (see Saksa 2007). Sites I1 and I4 had the best relationships. The results show that over the 22-month study period total carbon loading at all three sites followed a similar seasonal trend (fig. 8). TC loading at E4 was higher at some points of the study, while I1 and I4 mirrored each other closely. TC loading was highest at E4 (47 925 kg/month) when compared with those at I4 (1905 kg/month) and I1 (1560 kg/month). The loading corresponded to rainfall where the majority of high loads occurred in spring and late fall/winter. I1 is a small stream and responds quickly to little rain. The summer months had low loading which corresponded to a period with little rainfall and low discharge. TOC loading had a similar pattern as that of TC. Loading at I1 had higher peaks than I4 February 2006 and December 2006 (fig. 8). Headwater TOC loading was 1524 kg/month at I1 and 1633 kg/month at I4 (fig. 8). TOC loading at E4 was 36 627 kg/month.

The headwater site, I1, showed higher carbon fluxes because of its smaller drainage size. Total carbon flux from the outlet of the watershed (E4) was 1.7 kg/ha/month, whereas the headwater sites I1 and I4 showed an average carbon flux of 5.2 and 1.33 kg/ha/month, respectively. Similar trends for total organic carbon fluxes were observed, with I1 having average monthly flux of 5.08 kg/ha, I4 having an average monthly flux of 1.14 kg/ha, and E4 having an average monthly flux of 1.28 kg/ha.

Both TC and total inorganic carbon fluxes were about average for a forested watershed in the streams of the Flat Creek watershed. Royer and David (2005) studied DOC loading in an agricultural watershed and found average flux of 3 to 25 kg/ha/year. Using average flux to determine the approximate yearly value, Flat Creek has a range of 16.0 to 62.4 kg/ha/year. This overlaps with the higher end of the range found by Royer and David (2005). An agricultural watershed in the Midwestern United States had DOC loads of 14.1 to 19.5 kg/ha/year (Dalzell and others 2007). It is expected that forests would have higher carbon due to inputs from trees and the organic layer of the soils. Also, agricultural watersheds input nutrients such as nitrate, so carbon would be used by organisms to process the nutrient input. In forested watersheds Dosskey and Bertsch (1994) found a carbon flux of 91.5 kg/ha/year. This is higher than what was calculated for our watershed. Loading in Flat Creek was lower than the Amite, Tangipahoa, and Tickfaw Rivers in Louisiana where these rivers had average annual loading 2404 to 15 780 Mg (Saksa and Xu 2006). Peatlands tend to have the highest organic carbons, and streams in Dee Valley, Scotland, have much higher carbon loads than the Flat Creek watershed. DOC loads in Dee Valley ranged from 1700 to 10 500 kg/km/year (Aitkenhead-Peterson and others 2006).

Relationship between Stream Carbon and Nitrogen

TOC and nitrate/nitrite were compared to see what effects organic carbon has on nutrients, especially nitrate/nitrite. There appears to be two dominating forces in nitrate/nitrite concentrations. The first is storm events. There was a peak in December 2006 (1378 mg/L) that can be attributed to a rain event shortly prior to monthly sampling (fig. 9). Other peaks in nitrate/nitrite, such as in August 2006 or February 2007 correspond to decreased TOC. This is not a definitive relationship, however. There are a number of factors that could be impacting nitrate in addition to storm events and TOC concentrations.

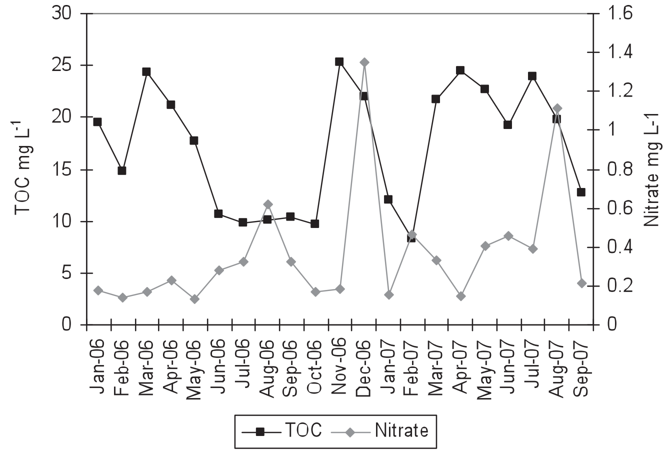

Figure 9—Average nitrate and total organic carbon for all 15 sites from January 2006 to September 2007.

Nitrate can be converted to gases such as N_2O and N_2 through the process of denitrification. The process demands the supplies of carbon and anaerobic conditions (Knowles 1982, Seitzinger 1988). When comparing monthly average nitrate/nitrite concentrations to organic carbon concentrations, there is an interesting pattern that arises (fig. 9). In the spring 2006, organic carbon is elevated; however, nitrate/nitrite is minimal. Straus and Lamberti (2000) found that organic carbon concentrations of 30 mg/L completely inhibited nitrification. TOC in March was 25 mg/L and corresponded to nitrate/nitrite of 0.2 mg/L, which is near the reported value for the detection limit. This inhibition of nitrification appears to be occurring in the spring, when biological activity is high. In the summer when TOC is low, there is a peak of nitrate/nitrite further supporting this theory. In the fall, however, there appears to be a different mechanism at work. TOC is high as is nitrate/nitrite. The peak in TOC corresponds with the start of the rainy season. Nitrate/nitrite peaks in December which also may be a result of increased runoff and organic input from leaf fall. In the early part of 2007 that is reported here, there is a repeat of the relationship seen in the spring of 2006 suggesting that this increased in TOC and decreased nitrate/nitrite is a result of biological activity.

Currently carbon analysis, organic or inorganic, is typically not used in regular water-quality monitoring programs. It has been found that carbon can affect nitrification in streams (Strauss and others 2002) indicating the potential importance of measuring carbon in streams. Carbon in streams, especially headwater streams, tends to reflect neighboring land use through surface runoff, making it a valuable parameter to understand. The general trend in figure 9 may indicate that the carbon concentrations present in the stream may be influencing nitrate/nitrite levels. DOM in streamwater is strongly related to landscape level predictors including loading, transportation, removal, and dilution of DOM (Frost and others 2006). Carbon monitoring may be a beneficial indicator for water quality considering its relationship with nitrogen, a popular indicator for eutrophication and general water quality.

CONCLUSIONS

This study investigated the spatiotemporal dynamics of organic and inorganic carbon concentrations and carbon export in the headwater streams of a low-gradient, subtropical watershed in central Louisiana. Spatial variations did not play a key role in carbon dynamics, but seasonality was a large factor in organic and inorganic carbon levels. TC concentrations in the studied watershed are strongly influenced by storm events and the resulting input from riparian areas. The higher inorganic carbon level in the summer indicates increased metabolism which consumes oxygen. Although carbon is not classified as a classic nutrient like nitrogen or phosphorus, it does play a key role in nitrogen dynamics. High organic carbon is necessary in denitrification, which is becoming an important step in removing excess nitrate from nitrogen saturated forest ecosystems. Making carbon measurements a part of regular water-quality monitoring can give important insights into nitrogen dynamics as well as dissolved oxygen levels. This information can be useful for designing silvicultural practices that will conserve and maintain ecosystem carbon.

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