Spatial and Temporal Dynamics of Stream Water Chemistry in a Headwater Catchment of Central Louisiana

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SPATIAL AND TEMPORAL DYNAMICS OF STREAM WATER CHEMISTRY IN A HEADWATER CATCHMENT OF CENTRAL LOUISIANA

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ABSTRACT

One of the dominant themes of stream water quality research has been the effect of nutrients and organic materials on eutrophication of coastal waters. Despite this prevalence in water quality research, few studies have been conducted on water quality changes in low-gradient watersheds under a humid, warm subtropical climate, such as those in the coastal plains of the Northern Gulf of Mexico. This study addresses: (1) the nutrient conditions in headwater streams of a low-gradient, subtropical watershed, especially as it relates to the suggested criteria by the Environtmental Protection Agency (EPA), (2) organic and inorganic carbon dynamics in the headwaters and how they affects nutrient concentrations, (3) dissolved oxygen (DO) conditions in the headwaters and its dependence on temperature, streamflow, and carbon, and (4) nutrient and carbon transport from the headwater catchment. Monthly in-stream measurements of DO, water temperature, pH and conductivity were conducted at 15 locations within the Flat Creek watershed, a 3rd-order watershed in central Louisiana over a 22-month period spanning December 2005 to September 2007. Monthly and storm event water samples were collected from these locations for chemical analyses of nitrogen, phosphorus, and carbon. The results reveal a seasonal trend of increased inorganic carbon in the dry, summer months, while increased organic carbon was found during the wet winter/early spring months. There was a wide range of monthly DO levels (0.4 to 9.0 mg L^{-1}) with the lowest levels generally occurring from May to July, a period with decreased organic carbon and increased inorganic carbon. Localized conditions were more indicative of dissolved oxygen than stream order in the watershed. Nutrient levels, especially nitrate/nitrite (0.127-1.378 mg L^{-1}) were not meeting EPA's suggested criteria (P25 for nitrate/nitrite is 0.067 mg L^{-1}). There were no spatial relationships in nitrogen, but there was an increasing trend in total phosphorus downstream until a reduction downstream

of beaver dam impacted sites. Annually, the Flat Creek watershed exported 15.36 kg carbon ha^{-1}, 0.0087 kg nitrate/nitrite ha^{-1}, and 0.0022 kg phosphorus ha^{-1}. Nutrient fluxes were largely affected by storm runoff and discharge and showed a decreasing trend with increasing drainage size. This study shows that in the forest-dominated landscape of central Louisiana, it may not be possible to reduce nutrient concentrations sufficiently to limit dissolved oxygen consumption, implying that existing water quality standards may not adequately address natural conditions.

CHAPTER 1: INTRODUCTION

Fresh water is an important renewable natural resource, crucial for the survival of most terrestrial life forms. Not only is the availability of fresh water important, but its quality is vital to aquatic and human health. Water quality can be affected by a range of natural and anthropogenic factors including, among others, geological weathering, sediment runoff, hydrometeorological conditions, land use activities, and industrial and household waste pollution. Pollutants inputted directly into waterbodies from sewage outflows have been greatly reduced through the improvement of wastewater treatment. Although great strides have been made in reducing point source pollution since the passage of the Clean Water Act in 1972, nonpoint source pollution continues to plague waterways because it is harder to identify, isolate, and control (e.g., US EPA, 1998).

Typically, nutrients such as phosphorus and nitrogen and in-situ water measurements including water temperature, dissolved oxygen, pH, and conductivity are used as indicators of water quality. When phosphorus and nitrogen are found in excess, eutrophication is more likely to occur. With eutrophication, primary production of an aquatic ecosystem increases, which can then cause oxygen depletion in the water body, sometimes to the point of anoxia. These anoxic conditions not only kill organisms, but also adjust the speciation of nutrients which further disrupts nutrient cycling.

One of the dominant themes in stream water quality research is the effect of organic materials on eutrophication of coastal waters. Studies have detailed how inorganic nutrient inputs from land-use changes influence the oxygen levels, primary productivity, habitats, and trophic relationships in coastal waters. Organic carbon may have key linkages to water quality within waterbodies, including nutrient availability (e.g., nitrogen) and dissolved oxygen supply.

There is a tendency for increased carbon to inhibit nitrification, which is the process in which ammonium is converted to nitrate (Starry *et al*., 2005). Most nitrogen transported by rivers to oceans is associated with organic matter. Understanding carbon and nitrogen interactions is imperative to gain a full picture of nutrient dynamics.

Headwater streams are an important part of all river basins. They are among the most important characters of water quality for entire stream reaches. About 80% of the total stream length in most drainage networks consists of headwaters (Richardson and Danehy, 2007). Nutrient loading to headwater streams can result in larger scale problems such as coastal eutrophication and declines in regional water quality (Freeman *et al*., 2007). Traditionally, studies on headwater streams have focused on areas with steeper topography, such as the mountainous streams in the US Northwest. Few studies have been conducted on hydrologic responses and water quality changes in low-gradient watersheds under a humid, warm subtropical climate, such those in the coastal plains of the Northern Gulf of Mexico. This is especially true for forested headwaters in low-gradient landscape. Forest management practices, such as timber harvesting, site preparation, and fertilization, can affect stream water quality. Over the past two decades many states have developed forestry best management practices (BMPs) guidelines to minimize negative impacts of forest operations. However, it is largely unknown how effective the BMPs really are in protecting downstream water quality.

To address these issues, an interdisiplinary research was initiated in 2005 in the the Flat Creek watershed in central Louisiana to examine the effectiveness of forestry BMPs in headwater protection. The research employs a two phase approach- pre-harvest and post-harvest in order to assess forest operation impacts on stream water quality, quantity, and ecology. Harvesting was implemented in the fall of 2007. This thesis research utilizes the data collected

between December 2005 and September 2007 to address four critical questions: (1) What are the nutrient conditions in headwater streams of a low-gradient, subtropical watershed that is widely representative in the coastal plain region? (2) How does carbon fluctuate in these headwater streams and in relationship to the nutrient conditions? (3) How do the nutrient and carbon conditions affect the low dissolved oxygen present in the watershed? (4) What is the quantity of nutrients and carbon exported by this low-order watershed to downstream reaches? In these low-gradient streams, the natural conditions of high temperatures, organic matter and low flow create challenging conditions for "good" water quality. Current water quality standards set by the US Environmental Protection Agency (EPA) and Louisiana Department Environmental Quality (LDEQ) do not usually consider natural deterrents to traditional standards of water quality. With high levels of organic matter in these streams, it is expected that carbon plays an important role in nutrient cycling and dissolved oxygen levels. Additionally, since these headwater streams have low flow, storm events are expected to play a key component in nutrient and carbon transport and stream oxygen conditions.

This thesis is divided into six chapters. Chapter 2 provides a literature review emphasizing the current state of research and knowledge on the dynamics of nutrients, carbon and dissolved oxygen in natural headwater systems. Chapter 3 presents the study on nutrient dynamics and transport in the study watershed and discusses how they relate to the nutrient standards proposed by the EPA. Chapter 4 examines seasonal and spatial variations of organic and inorganic carbon and investigates how the carbon dynamics interact with nutrients and low DO present in the watershed. Chapter 5 focuses on the study of dissolved oxygen conditions across the watershed, and assesses how these conditions relate to seasonal fluctuations of carbon and nutrients in these headwater streams. Chapters 3, 4 and 5 are written as stand-alone journal

publications. They have their own introduction, methods, results, and discussion sections, and therefore, there will be some repetition between the chapters.

CHAPTER 2: LITERATURE REVIEW

Management of fresh water resources has been a constant human need and battle. Excess nutrients in waterbodies have caused problems for many decades. The linkage between nutrient enrichment and aquatic productivity was recognized in the early 1900s in Europe (Smith *et al.,* 2006). In the United States, freshwater pollution management did not take off until the 1960's with Rachel Carson's "Silent Spring" drawing attention to environmental concerns. Since then, wastewater and point source pollution management has been the central theme in water quality. Through discharge regulations, point source pollution was mostly controlled. Nonpoint source pollution, runoff from landscape changes such as agricultural, impervious surfaces, and forestry operations, is more difficult to control. Nonpoint source pollution continues to plague waterways because of the difficulty in identifying, isolating, and controlling the source (Ice, 2004). Since there is not one direct source, it is difficult to use daily maximum loads to reduce nonpoint source pollution. Waterbodies act as a sink to chemicals, substances and nutrients in the environment; therefore, it is important to control runoff mechanisms to reduce the harmful effects of a waterbody's natural tendency to receive these chemicals.

Streams are not isolated ecosystems. Rather, they are strongly impacted by surrounding vegetation and land in addition to precipitation and runoff inputs. Due to this combination, it is important to consider stream health from a system-wide watershed approach. Such an approach was used to study a small watershed located on the Fernow Experimental Forest in Parsons, West Virginia and also Hubbard Brook, located in North Woodstock, New Hampshire (Likens *et al*., 1970; Aubertin and Patric, 1974). These studies have served as key research areas where disturbance mechanisms could be applied and studied. It showed that many aspects must be considered when studying stream health including nutrients, sediment and chemical loads,

discharge, runoff, land use near the stream, and the impacts of storm events on these water quality parameters.

2.1 Headwater Streams

Headwater streams are a special and unique subsegment of waterways. They have been defined differently by researchers, depending upon their research focuses and objectives. For instance, Benda and Dunne (1987) define a headwater as the area that is higher than the area where debris flows are deposited; Richardson and Danehy (2007) define headwaters as first order channels that have a small catchment (<100 ha) and a bank full width of less than three meters; However, according to Hack and Goodlett (1960), headwater systems contain four topographic units: (1) hillslopes, (2) zero-order basins, (3) ephemeral or temporal channels emerging from zero-order basins, and (4) first- and second-order stream channels depending on linkages from hillslopes to channels. Other researchers agree that there is not a clear definition of headwater streams, but argue that first and second order streams feed large rivers, thus classified as headwater streams (e.g., Freeman *et al*., 2007). Despite the lack of a clear definition of headwaters, a proper definition is imperative for proper protection under the Clean Water Act (CWA). CWA protects navigable waterways and as was decided by the U.S. Supreme Court in 2001 in the case *Solid Waste Agency of Northern Cook County v. U.S. Army Corps of Engineers* waterways that have a connection to navigable waterways are also protected (e.g., Nadeau and Rains, 2007).

Due to their small size, vast canopy cover, and seasonal intermittence, forested headwater streams are studied far less than other waterbodies (Richardson and Danehy, 2007). Ice and Binkley (2003) comment that although first and second order streams represent 90% of stream networks, they are under-sampled. The research that is available does not focus on the large role

headwaters play in watershed dynamics (Gomi *et al.*, 2002). Despite their size and limited research, they are among the most important character of water quality for entire reaches. About 80% of the total stream length in most drainage networks makes up headwaters (Richardson and Danehy, 2007). Because headwater streams tend to be narrow, interactions with the surrounding land plays a vital role in the processes within the stream. The near complete canopy enclosure makes organic matter input from allochthonous sources more important than primary production (Richardson and Danehy, 2007). Small streams, especially streams with extensive canopy cover limiting primary production, depend on terrestrial energy source input (Triska *et al.*, 1984; Mulholland *et al.*, 1985). Although there is no clear, exact definition of a headwater stream, they tend to be strongly influenced by location and local characteristics.

With many headwaters being intermittent and ephemeral, headwater streams are highly responsive to changing flows and have punctuated fluctuations in discharge (Richardson and Danehy, 2007). Even with the quick response to increased flow, these streams also have a quick recovery time. Nutrient loading to headwater streams can result in larger scale problems such as coastal eutrophication and regional water quality declines (Freeman *et al.*, 2007). A large portion of headwater streams studied is in areas with steeper topography than their downstream counterparts. Few studies have been conducted on hydrologic responses and water quality changes in low-gradient watersheds in a subtropical climate, like the coastal plains of the Northern Gulf of Mexico. Understanding of water quality characteristics of these headwaters is crucial for land use and resources management in the coastal plain region.

2.2 Nutrients and Stream Water Quality

Water quality is multifaceted, in which a complete picture requires data compilation of nutrient concentrations, sediment and chemical loads, and biotic indicator species including

macroinvertebrates and fishes. The combination of these factors must be examined to give an adequate picture of stream health; one factor does not give a complete picture. Nutrients are usually the main parameter used to express water quality. Since nutrients are continuously cycled for use by the entire stream system, relatively small inputs can affect large reaches. Nutrient levels are an important indicator of stream health and are relatively easy to measure; therefore nutrient data are most often used for long-term management strategies (Young *et al.*, 1995). Nitrogen and phosphorus concentrations are used as indicators because they are limiting nutrients in stream rate processes and total biomass. Excess nutrients cause eutrophication, which yield large rates of annual, biological production (Whitton, 1975; Leonard *et al.*, 1979; Howarth *et al.*, 1990; Freedman, 1995). Because ordinarily limiting nutrients are found in excess, algal blooms occur more frequent and are more severe in small streams (Young *et al.,* 1995). This increase in available nutrients allow more algae to grow which in turn blocks sunlight from reaching lower levels of algae growing causing algae death. Decomposition of dead organic matter consumes oxygen in the water, resulting in oxygen depletion.

Nutrient loading of water bodies can occur through point (direct input) or nonpoint (diffuse) sources. Point source pollution includes sewage effluent, and the pollution is usually continuous. Because of direct input and continuous flow from point pollution, management in these cases is easier than for nonpoint sources, since it is clear where the pollution is coming from and at what rate (Carpenter *et al*., 1998). Nonpoint nutrient loading is more difficult to manage, and unfortunately nonpoint pollution is becoming more common. Nutrients from nonpoint sources such as agricultural and urban development runoff, contribute to eutrophication of freshwater systems (Soranno *et al.,* 1996; Carpenter *et al.,* 1998). This accelerated eutrophication is a result of the disturbance caused by sediment and dissolved nutrient input

(Leonard *et al.,* 1979). Watershed characteristics such as regional geology, soil nutrient content, erodibility, topography, and land use impact the potential for nonpoint nutrient loading (Bedford, 1996; Soranno *et al.,* 1996). For example, a stream neighboring steep terrain is more vulnerable since runoff will move at a greater rate over the landscape which reduces infiltration.

Phosphorus is strongly correlated with primary production and is typically most limiting in freshwater systems (Dillon and Kirchner, 1974; Young *et al.,* 1995), thus is the primary factor controlling eutrophication (Kumar, 1992; Soranno *et al.,* 1996). When phosphorus is normally limiting, there is balanced phosphorus cycling within the stream (Newbold *et al.,* 1983; Mulholland *et al.,* 1985; Triska *et al.,* 1989); excess phosphorus disrupts this balance. Phosphorus inputs can come from the sediments or can be deposited directly into the stream (Aspila *et al.,* 1976). Seasonal variation in phosphorus levels can be attributed to input from leaf matter (Mulholland *et al.,* 1985). During autumn leaf fall, phosphorus levels increase in a stream which decreases the demand for phosphorus. There is an overall trend that phosphorus increases with land disturbance, erosion, and impervious surface expansion and development (Soranno *et al.,* 1996). Phosphorus is measured as ionic orthophosphate (PO_4^{-3}) (Freedman, 1995), sediment bound (particulate) phosphate, or total phosphorus (Greenberg *et al.,* 1992; Kumar *et al.,* 1992).

Nitrogen, another critical nutrient for primary production, has a very active biogeochemical cycle among the atmosphere, pedosphere, hydrosphere, and biosphere. The largest source of nitrogen is found in the atmosphere as stable diatomic nitrogen (N_2), which makes up 78% of the atmosphere. The molecule is extremely stable and thus unusable to most organisms (e.g., Alexander *et al*., 2007). Nitrate (NO_3^-) is the largest player in food webs, but a high level of nitrate in water bodies impair the immune system and cause stress in some aquatic species and is, therefore, vital in the study of water quality. Nitrate is produced through nitrogen

fixation by bacteria or nitrification by a multi-step oxidative conversion of ammonium to nitrite to nitrate. Denitrification is the anaerobic process of processing nitrate to N_2. The intermediate molecules include N_2O and NO, which are of important environmental concern. N_2O is one of the top three greenhouse gases after CO_2 and CH_4 in potency. The residence time of N_2O in the atmosphere is 150 years (Zumft, 1997) making this a serious issue.

Nitrogen is constantly cycled between organic and inorganic forms, and anthropogenic effects disrupt this delicate balance of available nitrate for organismal uptake. There is vast evidence that humans are responsible for nearly doubling reactive nitrogen in the environment in the past 50 years. Human activities can affect the N-cycle in streams directly through the input of nutrients (i.e., runoff from fertilizer applied agricultural fields) and input of biological matter from runoff. This input from fertilizer has increased since the Haber-Bosch process has enabled the creation of reactive nitrogen (Smil, 2001). Also the cycle can be changed indirectly by impacting N_2 cycling in the atmosphere (i.e., through fossil fuel burning) (e.g., Smil, 2001; Galloway *et al*., 2004) and through riparian buffer removal. When the riparian buffer is removed there is increased sunlight and decreased oxygen in streams. When there is low oxygen in the water, anaerobic processes of nitrate and nitrite conversion to N_2 gas is preferred over the production of nitrate.

Headwater streams can be driven by both surface runoff and groundwater flow. The increasing concentration of nitrate in groundwater (Burt *et al*., 1988; Spalding and Exner, 1993) and landscapes (e.g., Galloway et al., 2004; Alexander *et al.*, 2007) is a great concern for water quality. Nitrogen is a limiting nutrient in freshwater systems; however, it is the primary limiting factor as the stream approaches an estuary and increases in salinity (Jordan *et al*., 1991). Headwater streams with altered nitrogen concentrations can affect the downstream cycling. This

is especially important since nitrogen in streams is reactive and mobile and can also serve as a vehicle to transport other contaminants downstream (Alexander *et al*., 2007). Because nitrogen is gained from outside of the stream as well as through transport and cycling within the stream, nitrogen observed at a single site is a combination of localized processes and not solely groundwater input (Triska et al., 1989). Nitrogen transport is dependent upon biotic and abiotic controls of nitrogen transformation (Cirmo and McDonnell, 1997). The main factors of nitrogen transformation are age of ecosystem, in-situ decomposition rate, carbon and nitrogen limitation status, soil characteristics, and moisture availability (Cirmo and McDonnell, 1997). Nitrogen concentrations are also correlated to discharge, especially during storm events (Su *et al*., 2006).

Suspended solids and metals increase during storms relative to low-flow stream conditions (Leonard *et al.,* 1979; Rasmussen, 1998) and contaminant concentrations vary with hydrograph stage as well as the season. Early season storms (i.e., the first storms after a dry period) have higher contaminant concentrations than storms later in the season due to storage during the dry season (Kirchner *et al*., 2000; Lewis *et al.,* 2006). These first storms do not change stream flow until the soils reach field capacity (Lewis *et al*., 2006).

2.3 Carbon in Headwater Streams

In aquatic environments, organic carbon is either consumed by the biological community, deposited in the benthic zone, or transformed into atmospheric carbon. In headwaters, the majority of organic carbon comes from allochthonous terrestrial organic matter (e.g., Palmer *et al*., 2001). Inorganic carbon, however, comes from multiple sources including weathering of minerals in soils, in-stream respiration of organic matter, groundwater inputs, and atmospheric draw down (Wetzel, 1992). Despite these multiple sources, researchers found that the dominant source of dissolved inorganic carbon in streams with shallow groundwater inputs was the

groundwater (Palmer *et al*., 2001). Groundwater is rich in carbon dioxide, a major source of inorganic carbon. For organic carbon, land surface processes, climate variation, and anthropogenic activities can all influence organic carbon fluxes. Depending on the season, organic carbon present in a stream may be from two different pools- older organic carbon from soils input from groundwater and newer organic carbon from recent organic matter (Schiff *et al.*, 1997). Organic carbon from increased primary production further enhances oxygen consumption (Trefry *et al.,* 1994).

Although most water quality monitoring programs focus on nitrogen and phosphorus, carbon is increasingly becoming a valuable parameter for water quality. Carbon affects nitrification in streams (Strauss *et al*., 2002) indicating the potential importance of measuring carbon in streams with nitrogen imbalances. Dissolved organic carbon (DOC) can be released as a result of upstream eutrophication from excess nitrogen (Worrall *et al*., 2003). Harriman and colleagues (1998) found a significant relationship between nitrate and DOC concentrations from an upland catchment in the United Kingdom.

2.4 Dissolved Oxygen

Dissolved oxygen (DO) is arguably the most important water quality parameter for organisms. Oxygen is necessary for most organisms to function. Oxygen in water also dictates the speciation of necessary nutrients. Low dissolved oxygen in a water body can result from nutrient or organic matter enrichment due to anthropogenic activities. However, low DO conditions can also be caused by natural environmental variables, such as water stagnation and high temperatures. Dissolved oxygen is classified as a response parameter, not a causal parameter like phosphorus and nitrogen. There are standards set by the Environmental Protection Agency (EPA) for an acceptable oxygen level for the chosen water use. The current

acceptable Total Maximum Daily Load (TMDL) for dissolved oxygen in Louisiana is 5 mg L^{-1} (LDEQ, 2001), but a study by Ice and Sugden (2003) found that 81% of the sites sampled in Northern Louisiana during the summer were below this standard. Most of these streams were classified as having an organic substrate with "slight" or "stagnant" flow, indicating the effect that substrate and stream velocity can have on dissolved oxygen levels.

2.5 Water Quality Standard and TMDLs

The research on water quality in headwater streams has been useful in establishing national and local policies to protect water quality. The Clean Water Act of 1972 is the most comprehensive of these policies. To stay in compliance with Section 303(d) states must develop criteria to maintain levels of pollutants including excessive nutrients. The main method used is total maximum daily loads (TMDL). TMDLs are calculated as the maximum amount of a pollutant, including nutrients like nitrogen and phosphorus, from both point and nonpoint sources that allows for the water body to still meet the designated use. This calculation includes a margin of safety and should consider seasonal variations. Designated uses range from drinking water to recreation uses including swimming and minimal water contact through fishing or kayaking, to fish and wildlife propagation. Water bodies that are impaired are added to the statewide impairment list. These water bodies must have a TMDL and cannot be removed from the list until the TMDL is met. This impairment list is prioritized and usually water bodies with naturally occurring pollution will be lower priority. TMDLs can be easily applied to water bodies that are not meeting water quality standards due to point sources. Nonpoint sources, however, require the understanding of the various sources (i.e., agricultural, urban sources) that are affecting the specific water body and ways to reduce it. In order to reduce these point sources,

cooperation between various government agencies (for water bodies that cross county/state boundaries), private landowners, and the general public is necessary.

EPA has developed a set of suggested water quality criteria for ecoregions across the nation. Ecoregions are created in an effort to divide the waterways of the United States into regions with similar characteristics based on location. These are still coarse divisions and finer divisions may be necessary to account for localized conditions like different vegetation (Ice and Binkley, 2003). These data are to support the development of nutrient criteria (EPA, 2000) such as TMDLs to comply. Data presented include a range of concentrations found for total phosphorus, dissolved phosphorus, and nitrate/nitrite and the 25th percentile (P25) average for each element. Besides the suggested nutrient criteria published by EPA, there are also suggested critical threshold values of nitrogen and phosphorus in the literature. Exceeding these values results in accelerated eutrophication. In late winter these are 0.30 mg L^{-1} and 0.01 mg L^{-1} for nitrate and phosphate, respectively (Whitton, 1975). Kumar and his colleagues (1992) suggest dividing the critical values for P into soluble phosphorus (0.1 mg L^{-1}) and total phosphorus (0.2 mg L^{-1}).

Louisiana Department of Environmental Quality (LDEQ) has recently released a report regarding developing Louisiana's nutrient criteria (LDEQ, 2006). The ultimate goal is to make all waters in Louisiana safe enough for primary and secondary contact recreation and fish and wildlife propagation. To achieve this, the "best attainable criteria" will be determined, which is based on hydrology, geomorphology, and natural organic loading. One of the most important water quality parameters for fish and wildlife is dissolved oxygen. In 1973, a 5 mg L^{-1} DO criterion was established through the state. For determining nutrient criteria, the ecoregions approach is used. This approach is similar to the EPA's approach of dividing regions based on

similar climate, land surface form, soils, vegetation, land use, and hydrologic modifications; however, LDEQ's divisions are finer since they are dealing with a smaller area (one state versus a whole country). There are twelve ecoregions; the Flat Creek watershed, the study area, is in the South Central Plains ecoregion (subecoregion: Southern Tertiary Uplands).

Establishing attainable nutrient criteria is challenging since Louisiana streams are "naturally dystrophic" which is usually a characteristic used to describe lakes or bogs. Dystrophic water bodies have high concentrations of organic matter or humic matter. They are naturally slow with a low gradient and backwaters that are frequently inundated. As of 2004 there were 185 rivers listed as impaired in Louisiana (EPA.gov). The major impairments are oxygen depletion (24%), pathogens (21%), and nutrients (20%).

TMDLs are not a fail-proof method. Often naturally occurring characteristics may make it near impossible for streams to meet TMDL requirements. For example, many streams in Louisiana suffer from low flow, high organic content, and high temperatures for much of the year which contribute to low dissolved oxygen. Lewis *et al.* (2006) propose that the maximum allowable loading for nitrate should be based "probability of occurrence" rather than a mean value. This type of limit can account for the large variation seen during storm events compared to constant values seen during baseflow. There are also seasonal variations for many streams, which may indicate the need for more varied water quality parameter collection. Water quality is largely affected by localized conditions, seasonality, and high flow events (i.e., storms).

CHAPTER 3: COMPARISON OF STREAM NUTRIENT CONDITIONS IN A SUBTROPICAL LOWLAND WATERSHED TO EPA SUGGESTED CRITERIA

3.1 Introduction

Nitrogen (N) and phosphorus (P) are two of the most important nutrients for life in all aquatic systems. However, excessive inputs of these nutrients cause eutrophication, impairing the physical and biological integrity of water bodies (e.g., Whitton, 1975; Leonard *et al.*, 1979; Freedman, 1995; Carpenter *et al*., 1998; Dodds *et al*., 2002). Because ordinarily limiting nutrients are found in excess, algal blooms occur more frequently and are more severe in small streams (Young *et al.,* 1995). Excess nutrients result in overgrowth of aquatic plants and a decline in dissolved oxygen and ecosystem diversity.

Nutrient loading of water bodies can occur through point (direct input) or nonpoint (diffuse) sources. While point source pollution has been effectively controlled, nonpoint source (NPS) pollution continues to plague waterways because of the difficulty in identifying, isolating, and controlling the pollution sources (EPA, 1998 and 2000). Currently, NPS pollution is the leading source of impairment in U.S waterways (EPA, 2000). Land use activities from agricultural and urban development drive nutrient runoff to freshwater systems (Isermann, 1990; Soranno *et al*., 1996; Carpenter *et al*., 1998). Land use and watershed characteristics, such as the local geology, soils, and topography, impact the potential for nonpoint nutrient loading to a waterbody (Bedford, 1996; Soranno *et al*., 1996)

Phosphorus is strongly correlated with primary production and is considered the most limiting nutrient in freshwater systems (Dillon and Kirchner, 1974; Young *et al.,* 1995); therefore, it is the primary factor controlling eutrophication (Kumar, 1992; Soranno *et al.,* 1996). When phosphorus is normally limiting, there is balanced phosphorus cycling within the stream

(Newbold *et al.,* 1983; Mulholland *et al.,* 1985; Triska *et al.,* 1989), thus excess phosphorus disrupts this balance. There is an overall trend that phosphorus increases with land disturbance, erosion, and impervious surface expansion and development (Soranno *et al.,* 1996).

Nitrogen is another critical nutrient for primary production of all aquatic life forms. It has a complex cycle with seven oxidation states as well a variety of conversion mechanisms and environmental storage and transport processes (Galloway, 2004). Being the largest player in food webs, nitrate (NO_3^-) is vital in the study of water quality. Nitrate is produced through nitrogen fixation by bacteria or nitrification by a multi-step oxidative conversion of ammonium to nitrite to nitrate. Denitrification is the anaerobic process of processing nitrate to N_2. The intermediate molecules include N_2O and NO, which are of important environmental concern. N_2O is one of the top three greenhouse gases after CO_2 and CH_4 in potency; however, it is of greater concern because of its role in ozone chemistry. The residence time of N_2O in the atmosphere is 150 years (Zumft, 1997) making this nitrogen gas a serious issue. Nitrogen is constantly cycled between organic and inorganic forms, and anthropogenic effects disrupt this delicate balance of available nitrate for plant uptake. When there is low dissolved oxygen in the water, anaerobic processes of nitrate and nitrite conversion to N_2 gas are preferred over the production of nitrate, which reduces its availability for organism uptake. Although the lack of availability of a necessary nutrient to organisms can be detrimental, in areas with high nitrate concentrations, the conversion of reactive N to unreactive N_2 (denitrification) effectively removes N from the system and reduces the undesirable consequences of excess N such as eutrophication (Davidson *et al*., 2006).

The US Environmental Protection Agency (EPA) has developed a set of suggested water quality criteria for ecoregions across the nation. The ecoregions are further subdivided into

subecoregions to represent more localized conditions. These data are to support the development of nutrient criteria (US EPA, 2000) such as Total Maximum Daily Loads (TMDLs) to comply with the Clean Water Act (CWA) section 303(d). As part of the CWA, designated uses are identified for waterbodies and then criteria are developed to protect this designated use (US EPA, 2000). Data presented include a range of concentrations found for total phosphorus, dissolved phosphorus, and nitrate/nitrite and the 25th percentile (P25) average for each nutrient.

This study was to assess stream nitrogen and phosphorus conditions in low-gradient headwaters in central Louisiana, to determine whether the conditions found meet the criteria suggested by the EPA in its Ambient Water Quality Criteria Recommendations for Ecoregion IX, and to estimate nitrogen and phosphorus transport from the headwater streams to downstream reaches.

3.2 Methods

3.2.1 Study Area

The Flat Creek watershed is located in the western part of the Ouachita River Basin in central Louisiana (Figure 3.1). The basin drains a total area of 41,439 km^2 and is characterized with a flat to slightly rolling topography (Figure 3.2). Forestry is the dominant land use in the Flat Creek watershed, occupying 61% of land and followed by rangeland with 21% (LDEQ, 2001) (Figure 3.3). Flat Creek's drainage area is approximately 369 km^2. Climate in this region is subtropical with hot, humid summers and mild winters. Long-term average temperatures range from 2.3^{o}C-34.1^{o}C (36.2^{o}F to 93.3^{o}F) and long-term average rainfall is about 1,500 mm yr^{-1}. Soils in the area are dominated by poorly drained Guyton (silt loam) series along the Flat Creek and Turkey Creek floodplains, with moderately well drained Sacul-Savannah (fine sandy loam) soils in the upland areas.

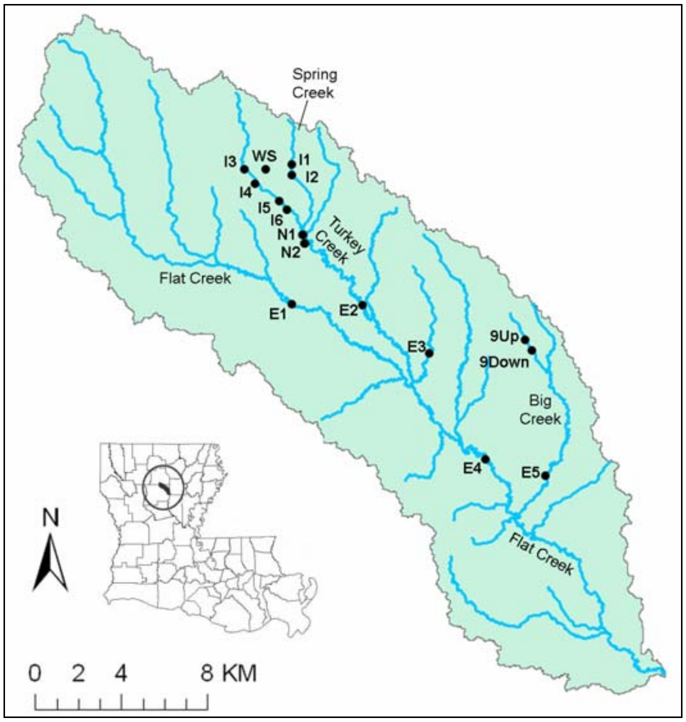

Figure 3.1. Geographical location of the Flat Creek watershed and water quality monitoring sites. A weather station (WS) is established between Spring Creek and Turkey Creek.

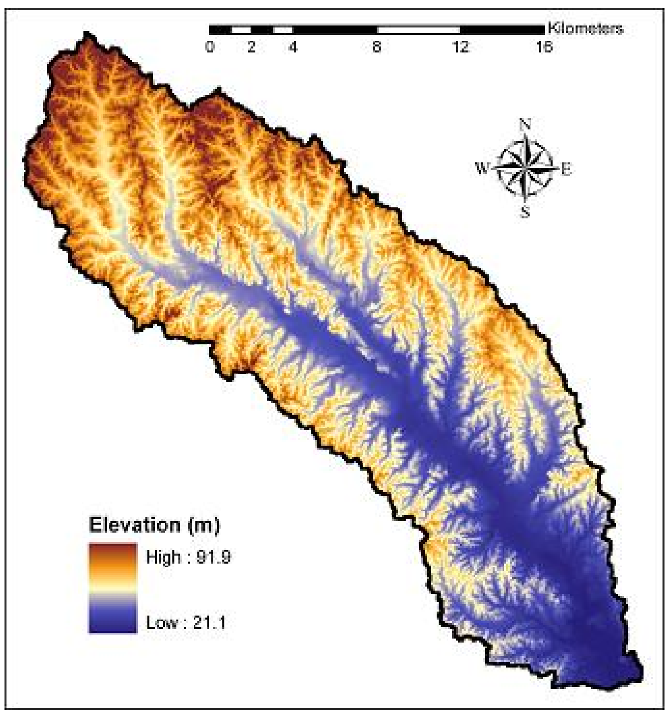

Figure 3.2. Topography of the Flat Creek watershed.

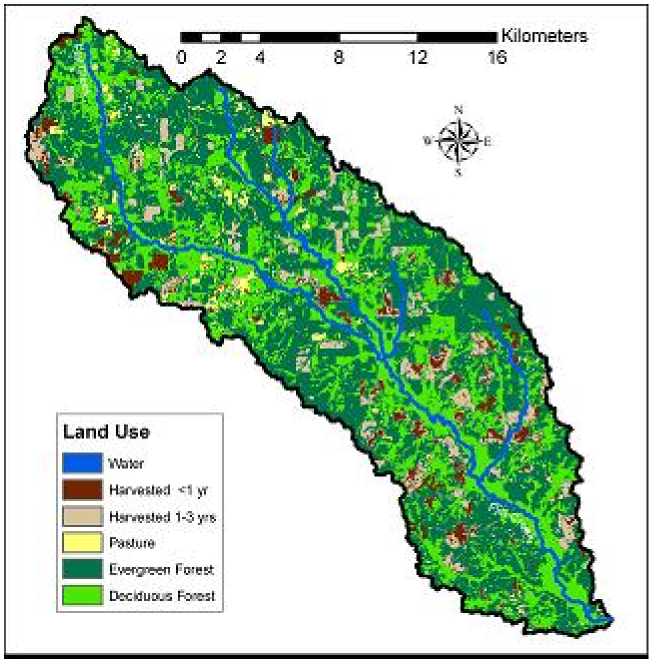

Figure 3.3. Land use conditions of the Flat Creek watershed analyzed from a 2006 Landsat TM5 image (Saksa, 2007).

3.2.2 Water Sampling and Analysis

Five streams in the Flat Creek watershed were sampled: Spring Creek, Turkey Creek, Flat Creek, Fish Creek, and Big Creek. Fifteen sites along these streams were visited monthly from December 2005 to September 2007 (Figure 3.1). In-situ water quality measurements, including dissolved oxygen, temperature, conductivity, and pH were taken monthly at each site using an YSI 556 (Yellow Springs Instruments, Yellow Springs, OH, USA). Monthly water samples collected were analyzed for nutrients including nitrate, nitrite, total Kjeldahl nitrogen (TKN), ammonium, and total and dissolved phosphorus. In addition, storm water samples were collected at six of the fifteen locations with automated ISCO samplers (model 6712, Teledyne Isco, Inc., Lincoln, Nebraska) (Figure 3.4). Each autosampler was set to collect samples when the water level increased at least 15 cm over twenty-four hours. Samples (400 mL) were collected each hour for twenty hours. A composite sample was used for nutrient analysis.

A duplicate and blank (deionized water) were also collected in the field for each sampling event. For most sampling events, the blank had concentrations of total and dissolved phosphorus, nitrate, nitrite, and TKN below detection limits. Ammonium, however, was frequently above detection limits. The duplicate sample (1 site per sampling event) was averaged with the original sample from the representative site. Detection limits (Table 3.1) were reported as half the detection limit and included in calculations.

Table 3.1. EPA methods and the detection limit for each nutrient analyzed. The reported value is half of the detection limit. This value is used in the calculations.

Nutrient	EPA Method	Detection Limit	Reported Value
Total Phosphorus	365.2, 200.7	0.008	0.004
Dissolved Phosphorus	200.7	0.008	0.004
TKN	351.2	5.5	2.75
Nitrate	300.0	0.22	0.11
Nitrite	300.0	0.008	0.004
Ammonium	351.2	0.3	0.15

Water samples were filtered through a 47µm glass fiber filter (GF/F Whatman International Ltd, Maidstone, England). One liter of unfiltered sample and a half liter of filtered sample for each site for each sampling event were sent to Department of Agricultural Chemistry at Louisiana State University AgCenter (Baton Rouge, Louisiana) for analysis. The lab followed EPA protocols for analysis of the concentrations of total and dissolved phosphorus, nitrate, nitrite, TKN and ammonium (Table 3.1; Xu, 2006). TKN had high detection limits, so most of the samples measured were below the detection limit of 5.5 mg L^{-1}. Particulate phosphorus was calculated as the remainder of TP after subtracting dissolved phosphorus.

Figure 3.4. Automated ISCO samplers at one of the six intensive sampling sites in the Flat Creek watershed. A tube connected to the sampler collects water from the stream.

3.2.3 Streamflow Measurements and Climatic Observations

Streamflow was measured during monthly sampling and during storm events using a flow meter (Sontek, Yellow Springs, Ohio) and top setting rod (Rickly Hydrological Co., Columbus, Ohio). The autosamplers at the intensive monitoring sites were set up to record stream water level in a 15-minute interval. The measurements were used to develop stage-discharge curves for sites I1, I3, and I4. In addition, water level loggers were installed at E4 and the records were used to relate daily water level measured at I1. Further details about the hydrologic measurements and the development of stage-discharge rating curves for the study area can be found in Saksa (2007).

Since weather conditions can be variable in a relatively close geographic region, a weather station measuring temperature, precipitation, solar radiation, and wind speed was installed near I4, centrally located to the headwater sites. Data are available in fifteen minute increments averaged to daily and monthly values from December 2005 through September 2007.

3.2.4 Data Analysis

Summary statistics such as mean and standard error were calculated for each month as well as each site. The number of samples varied with each month (Table 3.2) as well as total samples for each site (Table 3.3). T-tests were performed to test the differences between storm and baseflow nutrient concentrations, sites with pooling or nonpooling, perennial and intermittent sites, and seasonally between the summer months and the remaining months (SAS 9.1, SAS Institute Inc., Carey, NC). Coefficient of variation was calculated as

$$CV= (A_1-M)/M \qquad (1)$$

Where A_1 is the actual nutrient concentration for the respective site and month and M is the mean of the nutrient concentration for the respective site.

Table 3.2 Number of samples (N) used in calculating mean and standard error.

Month	N	Month	N
Dec-05	11	Nov-06	15
Jan-06	11	Dec-06	15
Feb-06	12	Jan-07	15
Mar-06	12	Feb-07	15
Apr-06	12	Mar-07	15
May-06	14	Apr-07	15
Jun-06	12	May-07	15
Jul-06	13	Jun-07	13
Aug-06	11	Jul-07	13
Sep-06	8	Aug-07	12
Oct-06	13	Sep-07	13

Loading was calculated as:

$$L= e^{(a*\ln Q + b + \varepsilon)} \qquad (2)$$

where L is loading, lnQ is natural log of discharge, a and b are constants (Table 3.4) and ε is 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 3.4). Although there was a good relationship to calculate loading at I1 and I4, no relationship could be established at E4 since at lower flow conditions, there was high variation in nutrient concentrations. Loading at E4 was calculated classically as concentration multiplied by discharge; however it was assumed that the concentrations measured during monthly sampling represented the entire month.

Table 3.3. Number of samples used in calculating mean and standard error for the representative site.

Site ID	N	Site ID	N
E1	23	I1	21
E2	19	I2	22
E3	20	I3	20
E4	21	I4	21
E5	22	I5	22
9Down	11	I6	22
9Up	7	N1	17
		N2	17

Table 3.4. Slope (a) and intercept (b) for equations to calculate nutrient loading at I1 and I4.

Site ID	Nutrient	Intercept	Slope	R-squared
I1	Total Phosphorus	-3.4504	1.0200	0.91
I1	Dissolved Phosphorus	-3.8325	0.9959	0.92
I1	Nitrate/Nitrite	-3.0902	1.1428	0.78
I4	Total Phosphorus	-0.2353	0.8335	0.88
I4	Dissolved Phosphorus	-4.2074	1.0501	0.73
I4	Nitrate/Nitrite	-0.6893	0.9700	0.73

3.3 Results

3.3.1 Seasonal Variation in N and P Concentrations

Total phosphorus (TP) from December 2005 to September 2007 averaged 0.028 mg L^{-1} - 0.142 mg L^{-1} at the fifteen sites sampled (Figure 3.5). The lowest average TP was in February

2006, while the highest average was in August 2007. All sites had average concentrations within the EPA's reported range (0.0025 mg L^{-1}-1.9 mg L^{-1}) however the total phosphorus in Flat Creek often exceeded the EPA's P-25 for this ecoregion (0.05 mg L^{-1}). TP was significantly higher in the summer months (May-October) with a mean concentration of 0.094 mg L^{-1} compared to the remaining months (November-April) with average TP of 0.058 mg L^{-1} ($t=-5.27$, $p<=0.001$). Dissolved phosphorus averaged 0.014 mg L^{-1} to 0.069 mg L^{-1}, while particulate phosphorus ranged from 0.004 mg L^{-1} to 0.108 mg L^{-1} (Figure 3.5). DP was significantly higher in the summer months (0.040 mg L^{-1}) compared to the remaining months (0.032 mg L^{-1}) ($t=-2.69$, $p=0.008$).

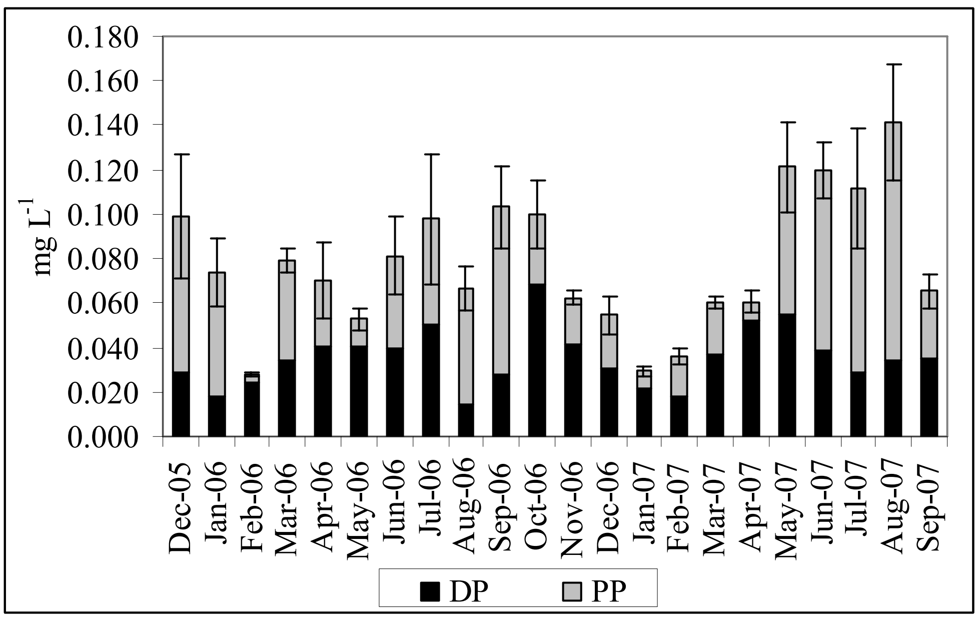

Figure 3.5. Average dissolved phosphorus (DP) and particulate phosphorus (PP) concentrations with standard error of total phosphorus in headwater streams in the Flat Creek watershed.

Average ammonium ranged from the detection limit (0.3 mg L^{-1}, reported as 0.15 mg L^{-1}) to 0.54 mg L^{-1} (Figure 3.6). There were many months where concentrations were at or near detection limits (i.e., January 2006-March 2006; February 2007-April 2007; June 2007-July 2007). Nitrate/nitrite ranged from 0.127 mg L^{-1} to 1.378 mg L^{-1} (Figure 3.6) with a peak in

December 2006 (1.378 mg L^{-1}) and August 2007 (1.137 mg L^{-1}) due to high nitrate (as opposed to high nitrite) measured those months. There was no significant difference in any seasonal variations in nitrite (t=1.09, p=0.2759), nitrate (t=-1.03, p=0.3060), or nitrite/nitrate (t=-0.95, p=0.3413)

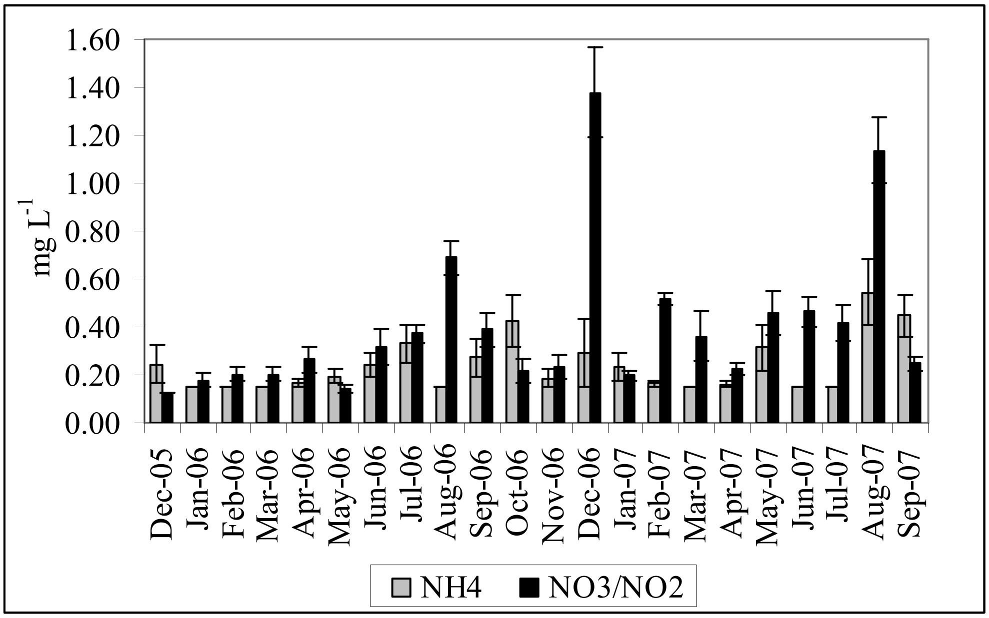

Figure 3.6. Seasonal trend of ammonium and nitrate/nitrite concentration with standard error in headwater streams of the Flat Creek watershed.

3.3.2 Spatial Variation in N and P Concentrations

Among the 15 locations sampled over the 22 months, ammonium concentrations ranged from 0.170 mg L^{-1} at E2 to 0.400 mg L^{-1} at 9D (Figure 3.7). Nitrate/nitrite varied from 0.272 mg L^{-1} at the site nearest the headwater of Turkey Creek (I3) to 0.576 mg L^{-1} at N1 (Figure 3.7). Nitrate/nitrite concentrations appeared to increase from the headwaters to downstream on Turkey Creek (0.272 mg L^{-1} to 0.576 mg L^{-1}) and remained relatively constant in the lower reaches (0.416 and 0.432 mg L^{-1}).

Average total phosphorus concentrations for each site varied from 0.042 mg L^{-1} at I1 to 0.131 mg L^{-1} at I5 (Table 3.5). On Spring Creek, TP increased from 0.042 mg L^{-1} to 0.056 mg L^{-}

[1]. Similar to the nitrate/nitrite pattern found on Turkey Creek, average TP was 0.072 mg L^{-1} at the headwaters and increased downstream at site I5 to 0.131 mg L^{-1}. However, downstream of the confluence of Spring and Turkey Creeks at N1, TP decreased to 0.083 mg L^{-1} and further decreased to 0.062 mg L^{-1} at E2. Flat Creek also had a small increase in average TP from upstream (0.079 mg L^{-1}) to downstream (0.099 mg L^{-1}). Although the two sites sampled on Spring Creek were about the same (0.063 mg L^{-1} upstream vs. 0.060 mg L^{-1} downstream), there was a clearer trend of increasing TP in Turkey Creek (0.051 mg L^{-1} - 0.068 mg L^{-1}). Dissolved phosphorus was relatively constant at most sites. Spring Creek averaged 0.021 mg L^{-1}, whereas Turkey Creek averaged 0.044 mg L^{-1} ranging from 0.036 mg L^{-1} at E2 to 0.059 mg L^{-1} at I5. Flat Creek was 0.043 mg L^{-1} and 0.038 mg L^{-1} at E1 and E4, respectively.

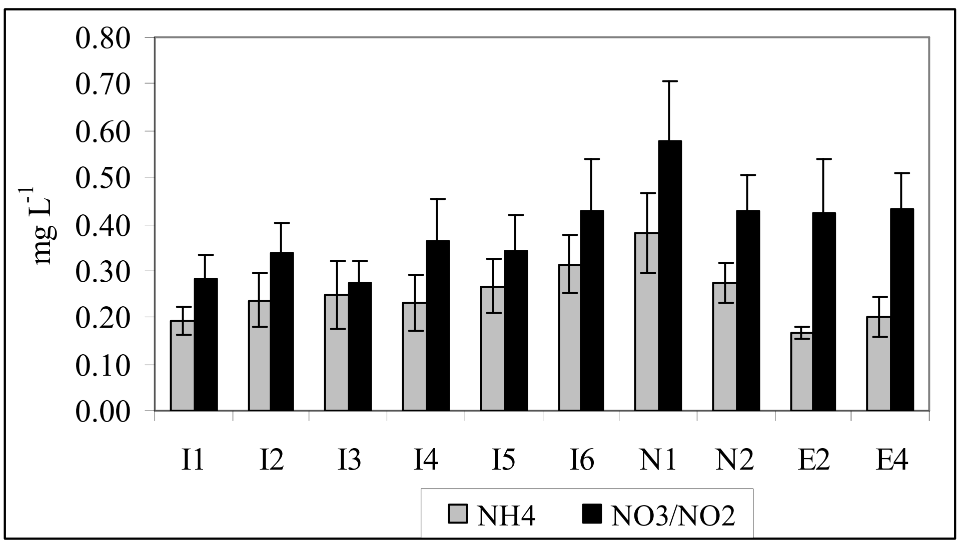

Figure 3.7. Nitrate/nitrite and ammonium variation with standard error from upstream to down stream at Spring Creek (I1 and I2), upper Turkey Creek (I3, I4, I5, I6), lower Turkey Creek below confluence of Spring and Turkey Creeks (N1, N2, E2, E4).

Stream characteristics such as flow permanence affected phosphorus concentrations. The sites with perennial flow showed significantly higher ($p<0.001$) TP (0.0888 mg L^{-1}) and DP (0.0396 mg L^{-1}) than the sites with intermittent flow (0.0599 mg L^{-1} TP, 0.0396 mg L^{-1} DP). No

significant difference in ammonium or nitrate/nitrite was observed between the streamflow conditions. Pools and nonpools also did not have any significant effect on stream nutrient concentrations ($p > 0.2$).

Table 3.5. Spatial patterns of averaged total phosphorus, dissolved phosphorus, and nitrate/nitrite and the respective standard error (SE) at 15 sites in the Flat Creek watershed from December 2005 to September 2007.

Site ID	Stream Order	TP	TP SE	DP	DP SE	NO3/ NO2	NO3/ NO2 SE
Spring Cr							
I1	1st	0.042	0.004	0.022	0.002	0.284	0.050
I2	1st	0.056	0.007	0.021	0.002	0.340	0.061
Turkey Cr							
I3	1st	0.072	0.008	0.036	0.007	0.272	0.050
I4	1st	0.089	0.010	0.039	0.005	0.366	0.088
I5	1st	0.131	0.023	0.066	0.011	0.341	0.080
I6	1st	0.118	0.017	0.043	0.005	0.429	0.111
N1	2nd	0.083	0.012	0.044	0.008	0.576	0.129
N2	2nd	0.077	0.010	0.045	0.004	0.427	0.079
E2	2nd	0.062	0.006	0.038	0.003	0.425	0.115
Flat Cr							
E1	2nd	0.079	0.008	0.042	0.004	0.416	0.091
E4	3rd	0.099	0.021	0.038	0.003	0.432	0.079
Fish Cr (E3)	1st	0.052	0.009	0.022	0.003	0.359	0.094
Big Cr							
9Down	1st	0.051	0.007	0.025	0.005	0.491	0.226
9Up	1st	0.047	0.007	0.021	0.006	0.462	0.153
E5	2nd	0.053	0.005	0.021	0.002	0.442	0.067

To further test for spatial variation, coefficient of variation was used for TP, DP, and NO_3/NO_2 (Figures 3.8 and 3.9). Although it is expected that larger streams would have less variation, this was not seen in Flat Creek for TP and NO_3/NO_2 (Figure 3.8). There were some sampling dates with large concentration variance from the mean, which attributed to a large

positive coefficient of variance (around 3 for TP and DP and around 5 for nitrate/nitrite). DP concentrations remained constant from the upstream sites to downstream sites, however, the variation decreased at the larger drainage area sites such E1 and E4 (Figure 3.9).

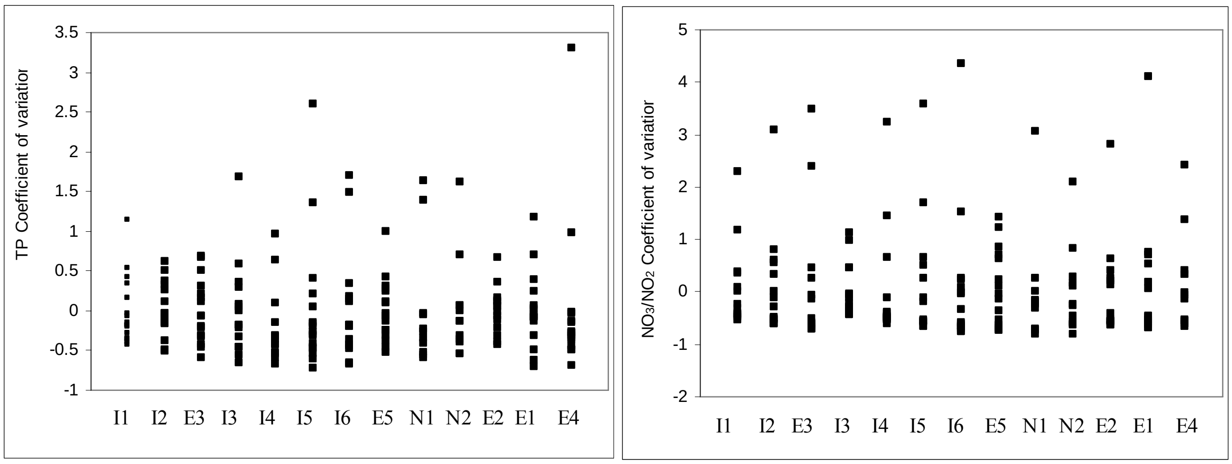

Figure 3.8. Variation of each total phosphorus (TP) (left) nitrate/nitrite (NO_3/NO_2) (right) to their averages in the Flat Creek watershed. Sites are in order of increasing drainage area; however, they are spaced equally apart on the visual to make the results from the smaller streams more viewable.

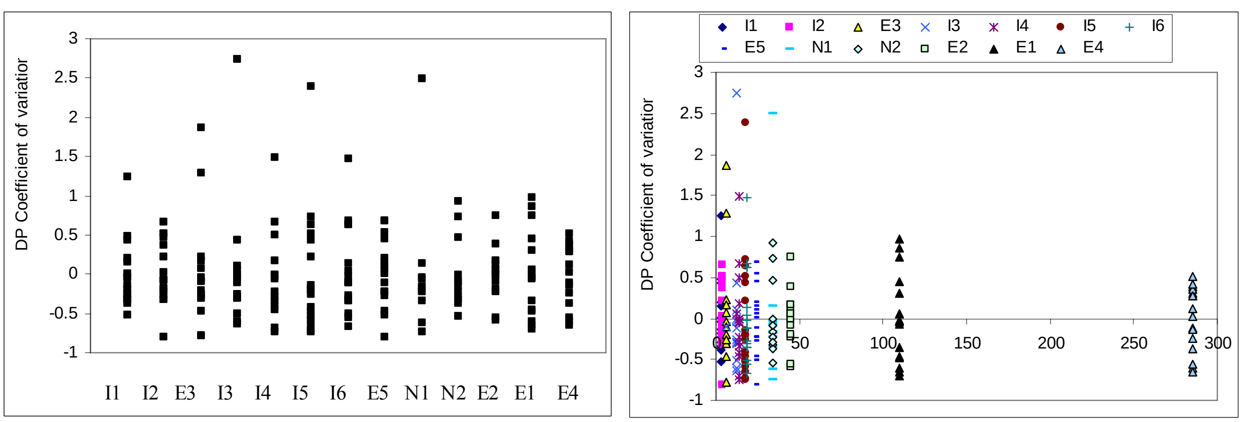

Figure 3.9. Variation of dissolved phosphorus (DP) to the respective site average in order of increasing drainage area.

During storm events, nutrient concentrations for total and dissolved phosphorus were similar at all sites (0.049-0.063 mg L^{-1} for TP and 0.018-0.032 mg L^{-1} for DP) (Figure 3.10). TP and DP was higher during monthly sampling (0.075 mg L^{-1} and 0.036 mg L^{-1}, respectively) than during storm events (0.052 mg L^{-1} and 0.027 mg L^{-1}, respectively) ($p<0.001$). Nitrate/nitrite

concentrations were higher during storm events with an average of 0.572 mg L^{-1} than the monthly sampling events which averaged 0.363 mg L^{-1} ($t=-3.61$, $p<0.001$). Nitrate/nitrite also had large variation between different storms. Average nitrate/nitrite ranged from 0.537 mg L^{-1} at I5 to 0.764 mg L^{-1} at I1 (Figure 3.11).

Table 3.6. Rainfall during storm events in the Flat Creek watershed.

Storm Date	Total Rain (mm)
October 16, 2006	163.4
October 26, 2006	35.8
December 30, 2006	66.3
January 4, 2007	27.4
January 15, 2007	23.4

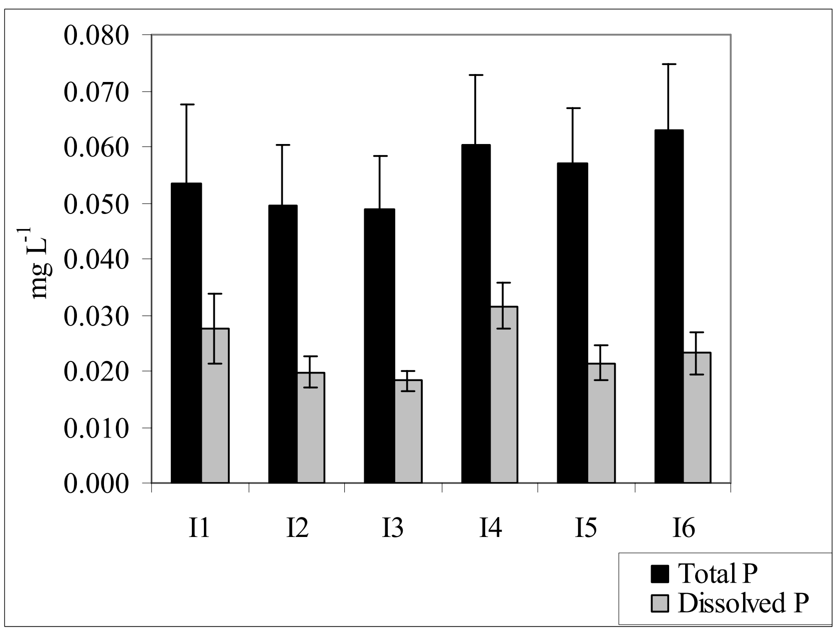

Figure 3.10. Average total and dissolved phosphorus during five storm events (October 16, 2006; October 26, 2006; December 30, 2006; January 4, 2007; and January 15, 2007) in the Flat Creek watershed.

When looking at a single storm on January 15, 2007 in which all six autosamplers triggered, TP showed an increased trend from upstream to downstream (Figure 3.12): TP was

0.028 mg L^{-1} at I1 and 0.036 mg L^{-1} at I2 on Spring Creek, and was 0.036 mg L^{-1} at I3 and 0.103 mg L^{-1} at I6 on Turkey Creek. Dissolved P remained constant, suggesting that most of the increase in phosphorus during the rain storm was probably due to runoff of particulate phosphorus into the streams.

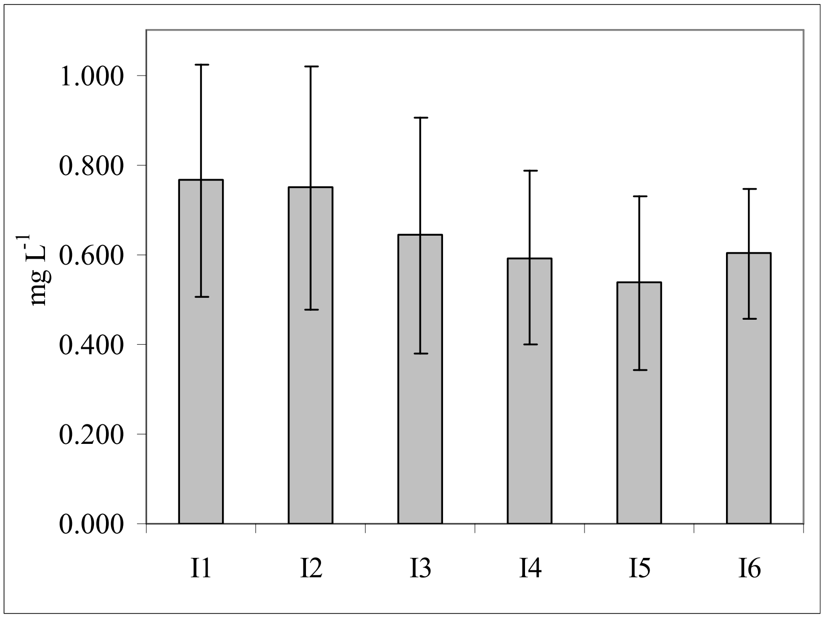

Figure 3.11. Average nitrate/nitrite during five storm events (October 16, 2006; October 26, 2006; December 30, 2006; January 4, 2007; and January 15, 2007) in the Flat Creek watershed.

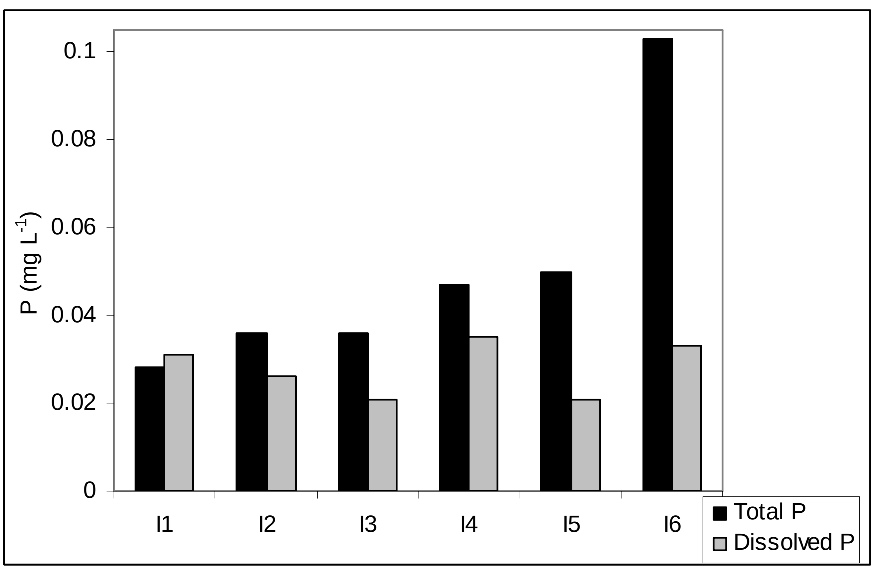

Figure 3.12. Total and dissolved phosphorus concentrations during a single storm event on

January 15, 2007 at six monitoring locations in order of increasing drainage area in the Flat Creek watershed.

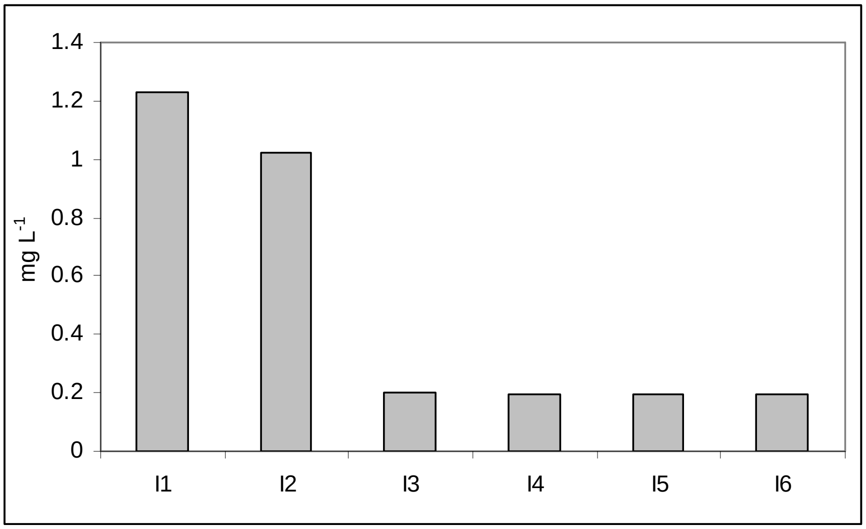

Figure 3.13. Average nitrate/nitrite concentrations during a single storm event on January 15, 2007 at six monitoring locations in the Flat Creek watershed. The sites are in order of increasing drainage area.

3.3.3 Mass Loadings of Nitrogen and Phosphorus

Mass loading of nitrogen and phosphorus were calculated for two 1st order streams (I1 on Spring Creek and I4 on Turkey Creek, Figure 3.1) and their 3rd order downstream outlet (E4 on Flat Creek). Total phosphorus loading was higher at I4 (5.27 kg mon^{-1}) than at I1 (1.74 kg mon^{-1}) for most of the months sampled (Figure 3.14). E4 showed similar loading to I4 (5.25 kg mon^{-1}). The difference in TP loading among the streams was smaller during the summer months during which little rainfall occurred. Similar results in dissolved phosphorus loading from the locations were observed: DP loading was 0.82 kg/month at I1, 2.87 kg mon^{-1} at I4, and 2.22 kg mon^{-1} at E4 (Figure 3.14).

Nitrate/nitrite decreased in spring 2006 and was low during the summer months at both I1 and I4 (Figure 3.15). Average monthly loading at I4 (27.69 kg mon^{-1}) was nearly twice of that at I1 (16.60 kg mon^{-1}). Average monthly nitrate/nitrite loading at E4 was 20.82 kg mon^{-1}.

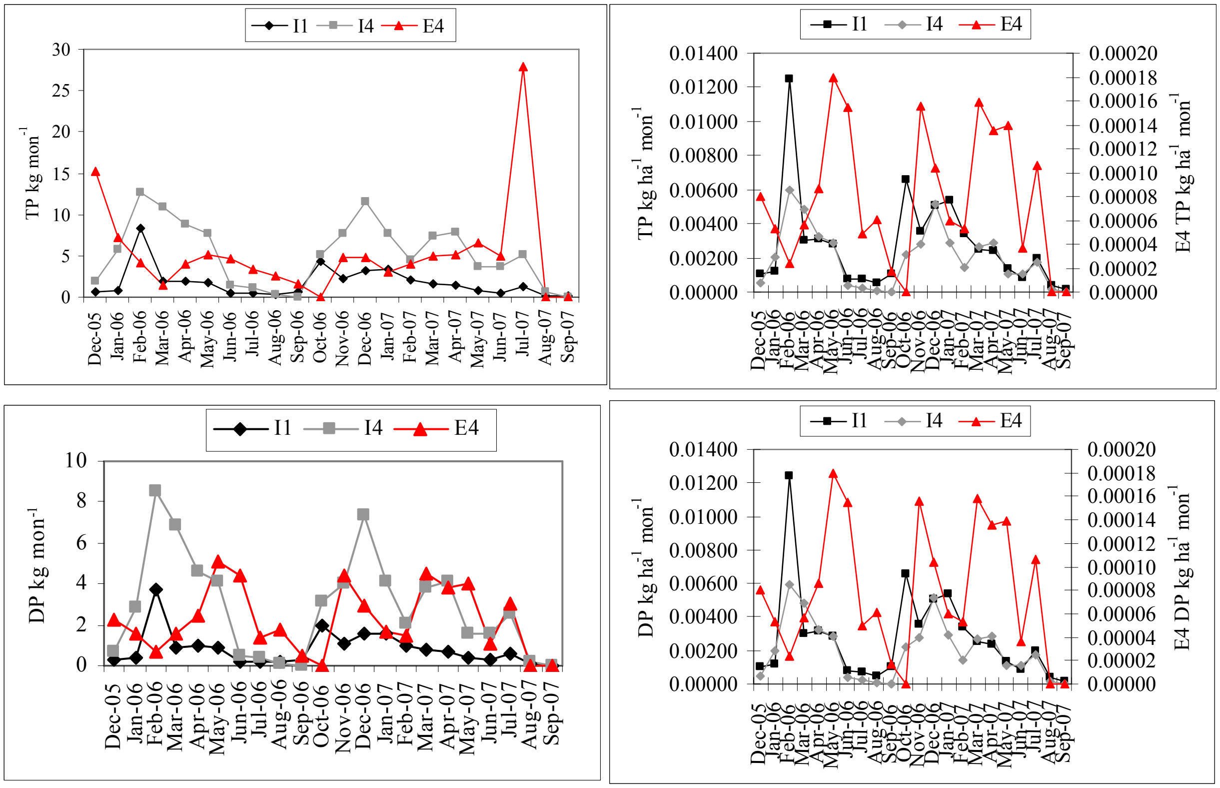

Figure 3.14. Mass loading of total phosphorus (TP) and dissolved phosphorus (DP) in two 1st order (I1, I4) and one 3rd order stream (E4) in the Flat Creek watershed.

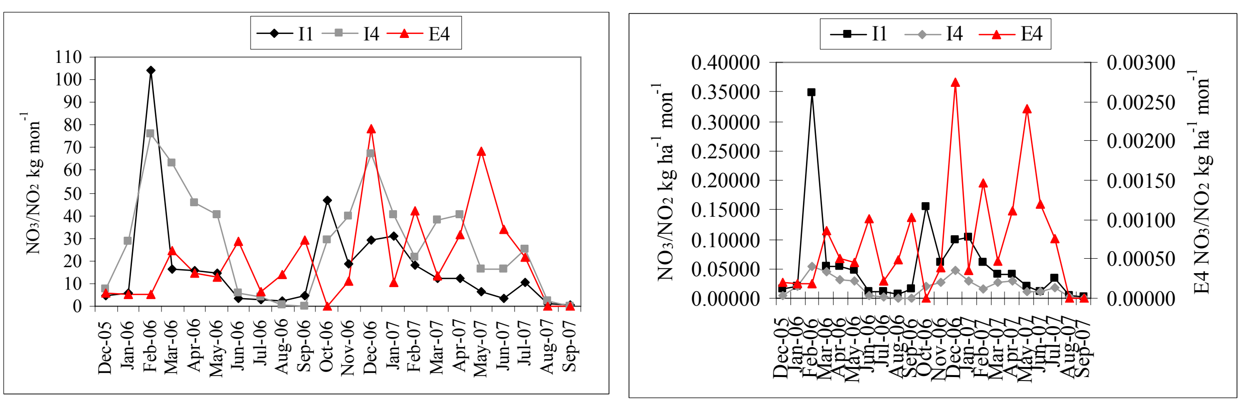

Figure 3.15. Mass loading of nitrate/nitrite (NO_3/NO_2) in two 1st order (I1, I4) streams and one 3rd order stream (E4) in the Flat Creek watershed.

Although I1 had lowest loading, the nutrient fluxes reveal that this upstream location (I1) had the highest rate of nutrient export per unit area. The outlet of the watershed (E4) had an average monthly TP flux of 0.0002 kg ha^{-1}, whereas the headwater site I1 had an average monthly TP flux of 0.0058 kg ha^{-1}. There were similar trends for DP and NO_3/NO_2 with I1 having an average flux of 0.0027 kg ha^{-1} mon^{-1} and 0.0553 kg ha^{-1} mon^{-1}, respectively, and E4 with 0.0001 kg ha^{-1} mon^{-1} DP and 0.0007 kg ha^{-1} mon^{-1} NO_3/NO_2.

3.4 Discussion

3.4.1 Spatiotemporal Variations in Stream Nitrogen Concentration

In their study on nutrient enrichment of the streams and river in the United States, Alexander and Smith (2006) found a distribution of the following percentiles of nitrate/nitrite concentrations: in 10^{th}: 0.11 mg L^{-1}, in 25^{th}: 0.19 mg L^{-1}, in 50th: 0.39 mg L^{-1}, in 75^{th}: 0.82 mg L^{-1}, and in 90^{th}: 2.0 mg L^{-1}. In this study, an average concentration of nitrate/nitrite from all monitoring sites and all sampling dates was calculated as 0.40 mg L^{-1} (0.27 - 0.58 mg L^{-1}; Table 3.5), falling into the 50th percentile in respect to the nitrate/nitrite status of U.S. streams and rivers. Compared to an agricultural watershed in Iowa, Flat Creek has at least an order of magnitude lower nitrate flux (Tomer *et al*., 2003). Nitrate concentrations were lowest at forested watersheds and waters with low oxygen content (Lehrter, 2006), which describes Flat Creek well. In forested watersheds, dissolved organic nitrogen tends to be the dominant form (Lehrter, 2006), even tropical forested watersheds have 60-70% organic N (McDowell and Asbury, 1994). However, Nakashima and Yamada (2005) found that nitrate was the dominating species of total nitrogen in which 70% of total nitrogen was nitrate. Nitrate and dissolved phosphorus concentrations were lower in tropical streams (McDowell and Asbury, 1994) than in Flat Creek;

however, the nitrate and DP fluxes were similar. Based on concentrations alone, this does support why despite being forested, Flat Creek falls in the medium percentile of U.S. streams.

Seasonally, the streams in this subtropical watershed showed little variation in nitrate/nitrite during the entire year, regardless of stream temperature. Most changes in nitrate/nitrite concentration were seen during storm events, indicating that surface runoff plays a critical role in nitrogen transport in this system. Smith and others (2003) found that runoff is the largest indicator for total nitrogen and total phosphorus. When examining nitrate/nitrite loading at I1 and I4, there were two peak seasons - spring and winter. Nitrate/nitrite loading was minimal during the summer due to the little or no stream flow conditions. Zhang and Schilling (2005) postulated that nitrate has temporal variations on a half year cycle although the results in this study indicates that storm events, since they control discharge which is a dominating part of loading, is playing a key role in nitrate/nitrite concentrations. Lehrter (2006) determined that discharge is the major factor that controls concentrations as well as the chemical speciation.

As a result of anthropogenic influences, soils - especially forest soils - in many industrialized nations are reported as nitrogen saturated (Ågren and Bosatta, 1988; Aber *et al*., 1989; Aber, 1992; Aber *et al*., 1998). Nitrogen saturation may be detrimental to water bodies because of potential of increasing nitrate reaching streams (Vitousek *et al*., 1997; Yoh *et al*., 2001), especially as climate changes (Howarth *et al*., 2006). Su *et al*. (2006) investigated correlations between nitrogen and catchment characteristics and found that the vegetation cover was highly correlated to nitrate/nitrite. There is very little change in vegetation cover in the Flat Creek watershed as Louisiana does not experience seasons like the Northern U.S. Considering nitrate/nitrite concentrations were consistent throughout the year, the research by Su *et al*. (2006) supports our results.

Denitrification is an important process since it is the major mechanism to fully remove excess, reactive nitrogen from the environment (Davidson *et al.,* 2006). Denitrification requires supplies of nitrate, organic carbon, and anoxic conditions (Knowles, 1982; Seitzinger, 1988; Claret *et al*., 1998). When dissolved oxygen is low, the condition may favor denitrification (Lehrter, 2006). However, for nitrate to be converted to N_2O or N_2 gas through denitrification, organic carbon must be available. Organic carbon inhibits nitrification, especially at high concentrations (Strauss and Lamberti, 2000). Many environmental factors can affect denitrification rates. Therefore, although organic carbon is available and the oxygen levels in the stream favor denitrification, reduced soil moisture can reduce denitrification. Sexston *et al.* (1985) found peak denitrification with increased soil moisture. In Flat Creek, summer is a period of low rainfall and reduced flows and many streams are intermittent. Although DO was low in the summer favoring denitrification, organic carbon and soil moisture was low. Conditions may also favor denitrification only in microsites (Koba *et al*., 1997). Seasonally, nitrate loading mirrors the trend in organic carbon. This decrease in nitrate in the spring may have more to do with the nitrate being utilized by organisms in the stream. Storm events also affect nitrate/nitrite concentrations. A storm event contributes to the peak in December 2006 (1.378 mg L^{-1}) in which there was a rain event shortly prior to monthly sampling. Other peaks in nitrate/nitrite, such as in August 2006 or February 2007 correspond to a storm event.

3.4.2 Spatiotemporal Variations in Stream Phosphorus Concentration

There was an increasing trend of TP and DP from upstream to downstream at some sites. N1, N2, and E2 on Turkey Creek tended to be lower than sites upstream. E2 is located downstream of the confluence of Spring Creek and Turkey Creek. Phosphorus concentrations at E2 reflected this mixing of water with concentrations higher than Spring Creek and lower than

Turkey Creek. Phosphorus movement tends to coincide with the movement of soil particles, which is transported downstream corresponding with increased total phosphorus shown in this dataset. Beaver dams located between sites I5 and I6 and downstream of I6 likely contribute to the decrease in TP from I6 and N1. Due to blockage of sediment by dams, water quality tends to improve downstream of dams. Beaver dams can trap large volumes of sediment (Butler and Malanson, 2005), as was also observed in this study. Beaver and debris dams reduce organic matter transport downstream, allowing processing to occur in the pool (Bilby and Likens, 1980). Considering phosphorus is usually associated with particles, it is sensible that beaver dams would also block phosphorus from being carried downstream.

Phosphorus was higher in the summer months and at the perennial sites. These two characteristics are interrelated, however. The perennial sites are the only sites with water during the summer. It is expected that high phosphorus is found in winter and early spring, corresponding with rain events, however Lehrter (2006) found that particulate P peaked in the summer months and TP peaked as expected in the winter and spring. Since nitrate/nitrite remained constant throughout the year, it may indicate that P is the limiting nutrient in Flat Creek. The peak in the summer, a period with minimal input from the riparian area, reflects the period of lower growth than spring months. More humid environments are experiencing increasing nitrogen deposition which reduces the nitrogen limitation (Aber *et al.*, 1989).

Phosphorus loading at I1 peaked in February, 2006. TP concentration during this month was low, however discharge was high. There was over 150mm of rainfall in February contributing to the elevated discharge. I1 is a small stream and responds quickly to little rain.

During storm events, total and dissolved phosphorus were lower than the average concentration for baseflow. Phosphorus is usually associated with sediment or other particles. If

phosphorus is not present in the runoff in large amounts (i.e., neighboring land use is agricultural), disturbance of the sediment can also cause increased phosphorus. Nitrate/nitrite was elevated during storm events, however there was large variation at each site. These results follow those of Lewis *et al.* (2006) in which nitrate increased with stream flow and precipitation. Individual storm events can be very different. Although the autosamplers triggered on 15 cm rise per twenty-four hours, hydrometeorological conditions including rainfall amount, intensity, duration and frequency can all impact surface and subsurface runoff, causing leaching of nutrients from soils and thus changing nutrient concentrations. Initial storm events tend to have higher concentrations because contaminants are flushed initially; however, later storms can still deliver nutrients, albeit at lower concentrations (Kirchner *et al*., 2000; Poor and McDonnell, 2007).

3.4.3 Nutrient Exports from the Headwater Areas

Outflow of nitrogen and phosphorus from headwater areas is an important factor affecting water quality conditions downstream. Transport of nitrate downstream can have large scale effects on water bodies. For example, nitrogen exported from the upper Mississippi Catchment is partly responsible for the hypoxic zone in the Gulf of Mexico (e.g., Rabalais *et al*., 2001). Phosphorus, especially particulate, can carry toxicants downstream. Loading was calculated only at the two first order headwater sites and the third order outlet. Due to the flow conditions of this watershed, it was difficult to develop accurate stage-discharge curves (see Saksa, 2007). Sites I1 and I4 had the best relationships. Phosphorus loading varied little from I4 to E4. Since phosphorus is mainly associated with particles, any mechanism that reduces these particles in the water column can have an impact on phosphorus. Downstream of I4, between I5 and N1, there are a number of beaver dams that create pools. In these pools, flow is slowed

which allows particles to settle. This may be why phosphorus loading does not change from the headwater site I4 to the outlet at E4. Nitrogen and phosphorus transport was highest at the upstream site. This stream is a small, highly responsive stream. Although this was a 22 month study spanning two rainy seasons and two dry seasons, rainfall was below average. Nitrate/nitrite totaled 1.217 kg ha^{-1} at the headwater of Spring Creek (I1), where as the lower headwater site on Turkey Creek (I4) was 0.426 kg ha^{-1} and the effective outlet of the watershed was 0.016 kg ha^{-1}. The high input relative to the downstream site indicates that nitrate/nitrite is being used, processed, or stored within the stream. In Oregon at the HJ Andrews Experimental Forest, a forest ecosystem with nearly no agricultural effect, the nitrate input due to rain was larger (0.46 kg ha^{-1} yr^{-1}) than the output (about 0.03 kg ha^{-1} yr^{-1}); but 80% of the total nitrogen output (0.59 kg ha^{-1} yr^{-1}) was organic nitrogen (Vanderbilt *et al.*, 2003). Other studies in forested watersheds also found higher organic nitrogen than inorganic (e.g., McDowell and Asbury, 1994); however, with increasing anthropogenic effects, nitrate is becoming a greater portion of TN fluxes (Howarth *et al.*, 1996). Lewis and others (1999) compared various tropical watersheds. These watersheds had an average total loading of 5.1 kg ha^{-1} yr^{-1} which approximately 70% was dissolved nitrogen. Of this 70%, half was organic and half was inorganic. Nitrate dominated the inorganic portion. The average nitrate loading was 2.43 kg ha^{-1} yr^{-1} which was higher than the temperate forests (0.19 kg ha^{-1} yr^{-1}). It makes sense that Flat Creek, a subtropical watershed is higher than the temperate but lower than the tropical watersheds.

Besides rainfall/runoff inputs of nitrate, groundwater can also contribute to elevated levels; however, in Flat Creek, since nitrate is elevated after storm events and not during the summer when the streams are mostly groundwater fed, this is not an important source. Organic

nitrogen loading would be valuable data to have collected in this study since many studies found that forested watersheds with little agricultural impact is dominated by organic nitrogen (e.g., Vanderbilt *et al*., 2003).

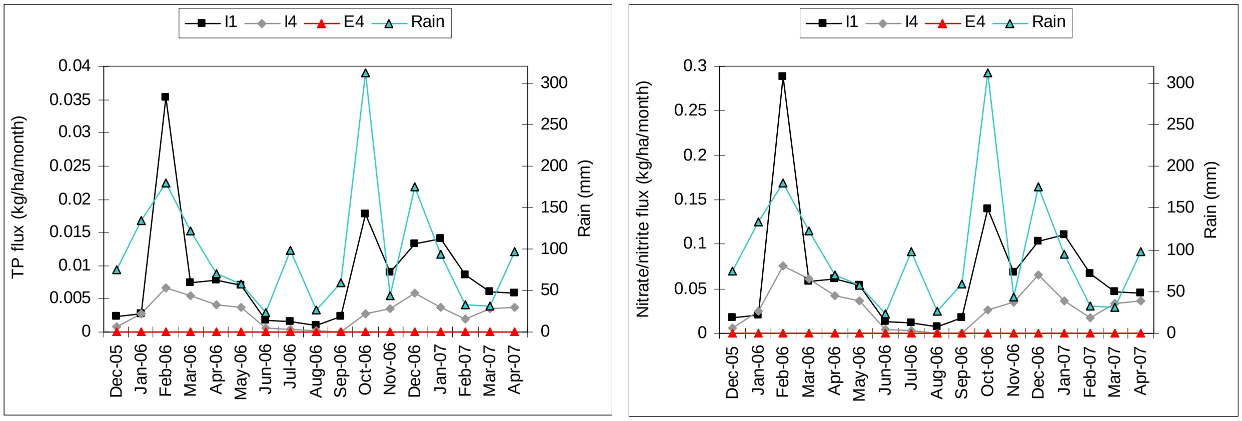

Figure 3.16. Fluxes of total phosphorus and nitrate/nitrite nitrogen in the Flat Creek watershed.

Rainfall was most indicative of nutrient flux, implying that storm runoff plays an important role in exports of nitrogen and phosphorus from the headwater areas (Figure 3.16). Phosphorus accumulation in soils causes increased phosphorus in runoff into surface waters (Bennett *et al*., 2001). Since the peaks in the nutrient flux directly correspond with peaks in rainfall, this supports that runoff is a dominating factor in phosphorus in streams. The headwater site I1 has high nitrogen and phosphorus fluxes, while the downstream outlet at site E4 shows constantly very low nitrogen and phosphorus output. The headwaters are contributing a large amount of nutrients to the entire watershed.

3.4.4 Applicability of EPA Suggested Criteria

The streams in the Flat Creek watershed showed an average total phosphorus concentration of 0.074 mg L^{-1}, ranging from 0.042 to 0.131 mg L^{-1}. These concentrations fall into the range between the 25th and medium percentiles of TP in the US streams and rivers reported by Alexander and Smith (2006). Based on Wetzel's (1983) classification of nutrient

enrichment for lakes, the headwater streams of this subtropical watershed are mesotrophic to eutrophic. Although total phosphorus was within EPA's suggested criteria for this ecoregion, the P25 of 0.05 mg L^{-1} was not met fifteen of the twenty-two months sampled. November 2006-April 2007 marked total phosphorus concentrations at or below the EPA's limit. Even during storm events in which an increase of runoff and thus excess nutrient transport is expected, TP concentrations were lower than monthly sampling events.

Nitrogen, however, exceeded the EPA's P25 of 0.067 mg L^{-1} during every month sampled. The range of nitrate/nitrite (0.127 mg L^{-1} to 1.378 mg L^{-1}) fell within the range reported by EPA for this ecoregion (0.005 mg L^{-1} to 6.245 mg L^{-1}). Although average nitrate/nitrite in the Flat Creek watershed was within this large range reported for this ecoregion by the EPA, it is still an order of magnitude higher than the P25 which would be utilized for regulation. Although this concentration could be a relevant limit for temperate forests, studies show that tropical watersheds have high nitrate input, so the role of climate is especially important in establishing nutrient criteria for Louisiana. With such a small concentration proposed by the EPA, detection limits become an important aspect. The detection limit in this study is 0.22 mg L^{-1} for nitrate alone. Even with a high detection limit, all months except for December 2005 and May 2006 were above the detection limit, therefore higher than EPA's P25. Due to natural conditions, it may not be possible to reduce nitrate/nitrite in Flat Creek to the EPA's P25. The balance of various nitrogen species (i.e., ammonium, nitrate/nitrite) present in a stream can be oxygen dependent (Margolis *et al*., 2001). Louisiana's streams consistently have low dissolved oxygen, which may contribute to nitrate/nitrite levels above EPA's P25. Considering that the sites are in a rural forested area, these streams are experiencing near natural conditions and are not being heavily influenced by land use changes. Lewis and others (2006)

suggest that since annual nitrate increased with stream flow and precipitation (storm events), then the TMDL is not as accurate as "probability of occurrence". TMDLs must take into account spates of nutrients during storm events rather than mean values.

3.5 Conclusions

Stream nitrogen and phosphorus conditions were assessed in a low-gradient 3rd order watershed in central Louisiana. Localized conditions such as beaver dams and runoff affected nutrient levels more than position in the watershed. Based on this dataset, EPA's suggested criteria P25 for nitrate/nitrite may be too low for streams in Flat Creek to attain, whereas the phosphorus criteria appear attainable. Adjusting the criteria for the subtropical climate would yield attainable TMDLs; however nutrient concentration data should be supported with nutrient flux and storm event data. This is especially important for nitrogen since storm events are the major driver of nitrate/nitrite flux.

CHAPTER 4: STREAM CARBON DYNAMICS IN A SUBTROPICAL, HEADWATER CATCHMENT

4.1 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 stream water quality research is the effect of organic materials on eutrophication of coastal waters. In forested streams, dissolved organic carbon has been widely studied (e.g., Mulholland, 1997). Organic carbon inputs from sources like precipitation (Willey *et al.*, 2000), throughfall, and surface and subsurface runoff are frequently greater than the in-situ production of organic carbon.

Organic carbon interacts with the biogeochemical nitrogen cycle (Qualls *et al.,* 1991; Campbell *et al.,* 2000; Cooper *et al*., 2006), aids in pollutant transport (Kalbitz *et al.,* 2000), and may be a major energy source for microorganisms (Tranvik, 1992; del Giorgio and Cole, 1998; Marschner and Kalkitz, 2003). 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 *et al*., 2004). Seventy-five percent of carbon present on land is found as soil organic carbon (Sparks, 2003). Soil organic matter is highly reactive (Sparks, 2003) because of the various structures that compose it. As a result, it can bind important nutrients and serve as an energy source (Frost *et al.*, 2006). Soil organic matter is mainly composed of carbon (approximately 52%-58%), with three additional major components: oxygen (34%-39%), hydrogen (3.3%-4.8%) and nitrogen (3.7%-4.1%) (Sparks, 2003). Because of the large carbon storage in the top soil, surface runoff and erosion can contribute a large input of carbon to streams.

Organic matter reaches aquatic systems through both surface and subsurface runoff. While surface runoff occurs during precipitation events, subsurface flow allows the soluble fraction of organic matter to be leached into water thereby reaching waterbodies (Cory *et al*., 2004). Organic carbon fluxes can also be affected by land surface processes, climate variation, and anthropogenic activities. 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 stream water 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. Organic matter content is typically measured as total organic carbon and dissolved organic carbon, whose concentration has often been found positively correlated with nitrate, nitrite and dissolved organic nitrogen concentrations in natural water bodies.

Studies of dissolved organic carbon (DOC) have a long history, beginning in the early 19th century in Europe with a focus on drinking water quality. Subsequent studies expanded to lake classification using the brown color intensity as an indicator for dissolved organic matter in lake waters (e.g., Birge and Juday, 1927, as cited by Jones, 1992). Since DOC is the most biologically available (Marschner and Kalbitz, 2003) and most mobile form of carbon, it is the most researched fraction of carbon.

Carbon has key linkages to water quality within waterbodies including nutrient availability (e.g., nitrogen) and oxygen levels. Most nitrogen transported by rivers to oceans is associated with organic matter, making the organic carbon to nitrogen ratio for particulate or dissolved pools in those waters a critical parameter in understanding carbon and nutrient cycling. There is a tendency for increased carbon to inhibit nitrification, which is the process in which ammonium is converted to nitrate (Starry *et al*., 2005). It affects nitrification by changing

microbial dynamics, so when carbon is abundant (i.e., a high C:N ratio), heterotrophic microbes outcompete autotrophic nitrifying bacteria for ammonium (Starry *et al.*, 2005). Adjustment of C to N ratio has been an effective measure in controlling inorganic nitrogen in aquaculture facilities and this adjustment is one of the most cost effective methods available (Avinmelech, 1999), which shows the importance of carbon in the control of nitrogen. Organic carbon is indirectly related to the oxygen availability in water (Thunell *et al.*, 2000). Organic carbon from increased primary production further enhances oxygen consumption (Trefry *et al.,* 1994). In natural waters, understanding the carbon dynamics 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% of the total watershed area. Streams are lotic systems; therefore, upstream effects are ultimately felt downstream. Because headwater streams tend to be narrow, interactions with the surrounding land play a vital role in the processes within the stream. The near complete canopy enclosure makes organic matter input from allochthonous sources more important than primary production (Buffam *et al*., 2001; Richardson and Danehy, 2007). Headwater areas act as sinks for carbon and nitrogen as a result of slow decomposition of organic matter (Cooper *et al*., 2006) and continuous cycling of nitrogen.

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.

4.2 Methods

4.2.1 Study Area

The Flat Creek watershed is located in the western part of the Ouachita River Basin in central Louisiana (Figure 4.1). The basin drains a total land area of 41,439 km^2, characterized by a flat to slightly rolling topography (Figure 4.2). Forestry is the dominant land use in the Flat Creek watershed, occupying 61% of land and followed by rangeland with 21% (LDEQ, 2001) (Figure 4.3). Flat Creek's drainage area is approximately 369 km^2. Climate in this region is subtropical with hot, humid summers and mild winters. Long-term average temperatures range from 2.3°C-34.1°C (36.2°F to 93.3°F) and long-term average rainfall is about 1,500 mm yr^{-1}. Precipitation was totaled daily and monthly during the study period (Figure 4.4). Soils in the area are dominated by poorly drained Guyton (silt loam) series along the Flat Creek and Turkey Creek floodplains, with moderately well drained Sacul-Savannah (fine sandy loam) soils in the upland areas.

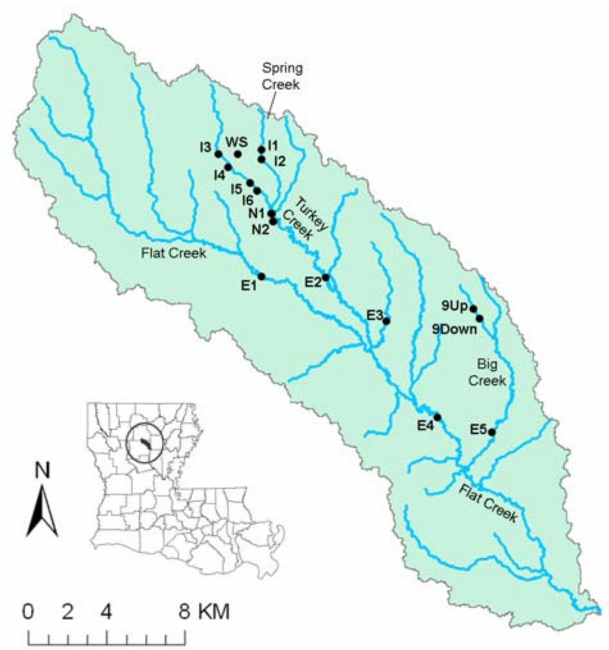

Figure 4.1. Geographical location of the Flat Creek watershed and water quality monitoring sites. A weather station (WS) is established between Spring Creek and Turkey Creek.

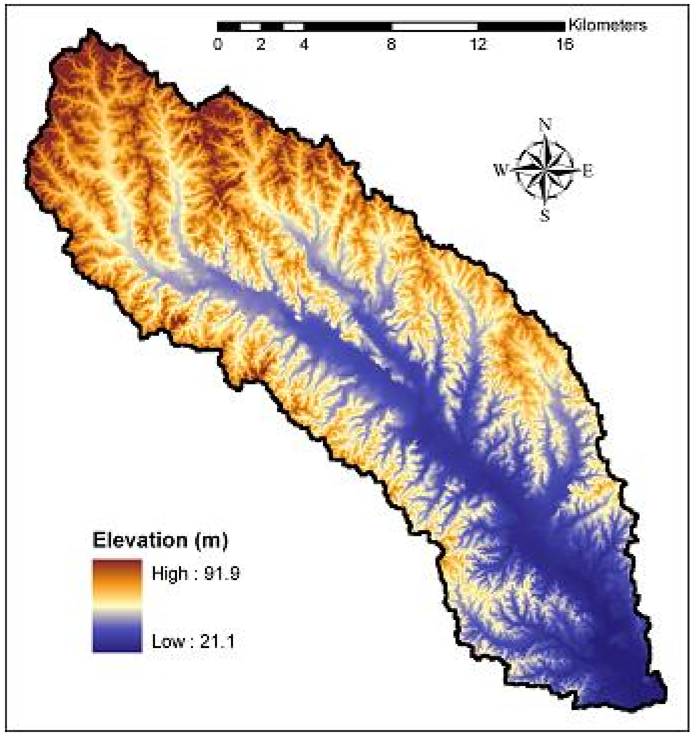

Figure 4.2. Topography of the Flat Creek watershed.

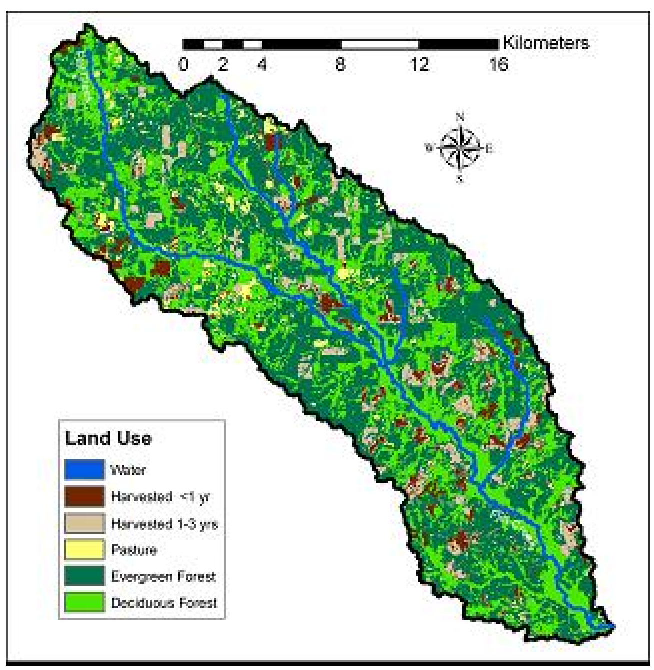

Figure 4.3. Land use conditions of the Flat Creek watershed analyzed from a 2006 Landsat TM5 image (Saksa, 2007).

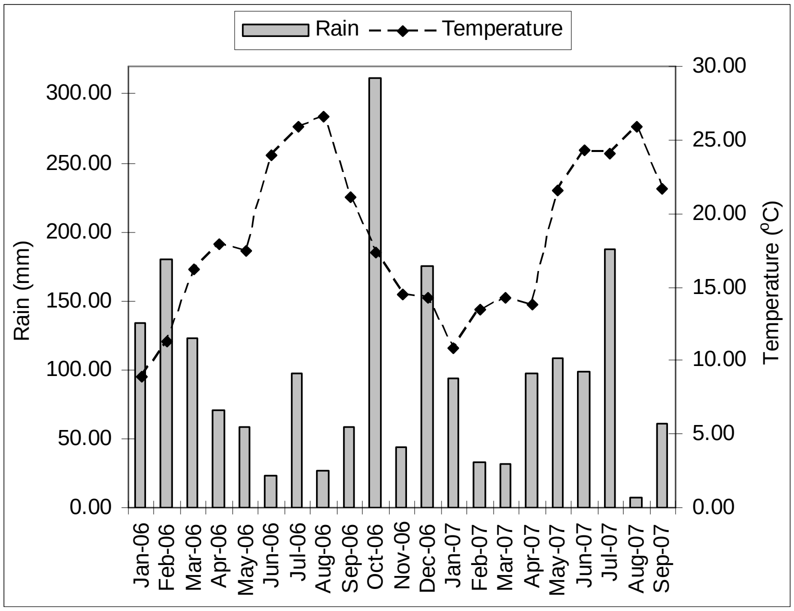

Figure 4.4. Monthly precipitation and average temperatures in the Flat Creek watershed.

4.2.2 Stream Water 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 (Figure 4.1). In-situ water quality measurements, including dissolved oxygen, temperature, conductivity, and pH were taken at each site using an YSI 556 (Yellow Springs Instruments, Yellow Springs, OH, USA). During each visit grab water samples were collected at each site. In addition, storm water samples were collected at six of the fifteen locations with automated ISCO samplers (model 6712, Teledyne Isco, Inc., Lincoln, NE, USA). Storm events were defined as enough rain to cause the stream to rise 15 cm in twenty-four 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.

Water samples were analyzed for total and dissolved organic and inorganic carbon with a Shimadzu Total Organic Carbon Analyzer (TOC-V CSN Shimadzu Corporation, Kyoto, Japan)

using the combustion/non-dispersive infrared gas analysis method. Inorganic carbon and total carbon was 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 47μm glass fiber filter (GF/F Whatman International Ltd, Maidstone, England). The laboratory measurements were conducted in the Wetland Biogeochemistry Institute, Louisiana State University.

4.2.3 Streamflow Measurements and Climatic Observations

Streamflow measurements were collected monthly during baseflow as well as whenever possible during higher flow conditions. Streamflow was measured during monthly sampling using a flow meter (Sontek, Yellow Springs, Ohio) and top setting rod (Rickly Hydrological Co, Columbus, Ohio). Because the streams in the Flat Creek watershed are relatively narrow, most measurements consisted of 5-10 cross-sections. The autosamplers at the intensive sites record stream level every fifteen 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).

An automated weather station was installed between Spring Creek and Turkey Creek (Figure 4.1), centrally located to the headwater sites. The weather station records relevant climatic parameters including temperature, precipitation, solar radiation, and wind speed. Data are available in fifteen minute increments averaged to daily and monthly values from December 2005 through September 2007.

4.2.4 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 4.1). The number of samples for total carbon 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 and organic carbon.

Table 4.1. Number of samples used in calculating mean and standard error.

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

Table 4.2. 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	3.690	0.9705	0.95
I1	TOC	-1.7486	1.3051	0.95
I4	TOC	1.8050	1.0825	0.95

Carbon mass loading was calculated as:

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

where L is loading, Q is discharge, a and b are constants (Table 2) and ε is 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 4.2). E4 calculated classically as:

$$L=Q*C \qquad (2)$$

where C is concentration, L is loading, and Q is discharge.

4.3 Results

4.3.1 Seasonal Fluctuation of Stream Carbon Concentrations

For the period from January 2006 to September 2007 total carbon concentration appeared to be lower during two winter months, January and February, than during other months of the year (> 22 mg L^{-1}) (Figure 4.5). TC was marginally higher during the summer ($p=0.052$; $t=-1.95$) while TIC, DC, and DIC were larger in the summer (May-October) than the remaining of the year (November-April) ($p<0.001$). TOC was smaller in the summer months than the remaining months ($p<0.001$). Average total carbon ranged from 9.6 mg L^{-1} to 30.0 mg L^{-1} 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 (Figure 4.6). Organic carbon ranged from 8.4 mg L^{-1} in February 2007 to 25.3 mg L^{-1} in November 2006. Average inorganic carbon ranged from 1.0 mg L^{-1} in March 2007 to 13.2 mg L^{-1} in June 2006.

To more easily view the trends of organic and inorganic carbon, Figure 4.7 represents the ratio of average total inorganic carbon (TIC) to total organic carbon (TOC). A peak of the ratio is apparent in the summer months from June through October in 2006. 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.

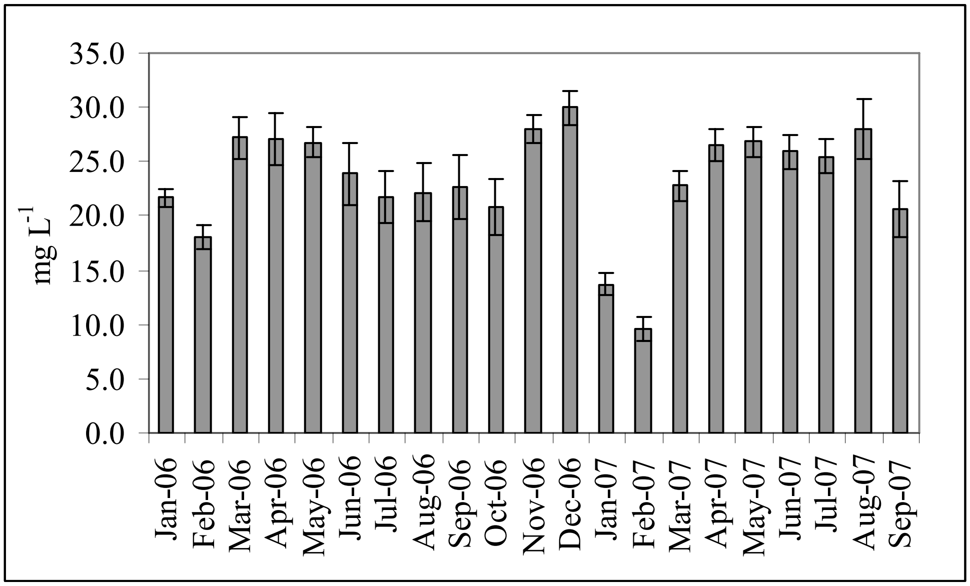

Figure 4.5. Seasonal fluctuation of total carbon concentration in the Flat Creek watershed (Error bars represent standard error).

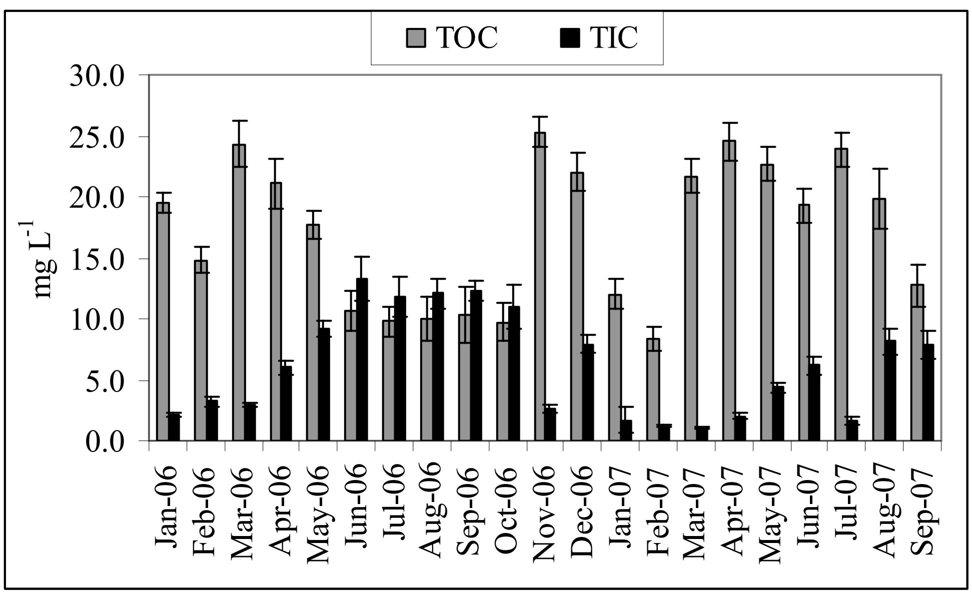

Figure 4.6. Seasonal fluctuation of total organic carbon (TOC) and total inorganic carbon (TIC) concentrations in the Flat Creek watershed.

Most of the total carbon was in the dissolved form (Figure 4.8). Monthly average of dissolved carbon concentrations ranged from 9.9 mg L^{-1} in January 2007 to 29.6 mg L^{-1} in July

2007. Dissolved organic and inorganic carbon had a similar trend to total carbon (Figure 4.9). Dissolved organic carbon ranged from 9.3 mg L^{-1} in July 2006 to 28.1 mg L^{-1} in July 2007. January 2007 had the lowest dissolved inorganic carbon (0.3 mg L^{-1}) with September 2006 having the highest (14.3 mg L^{-1}).

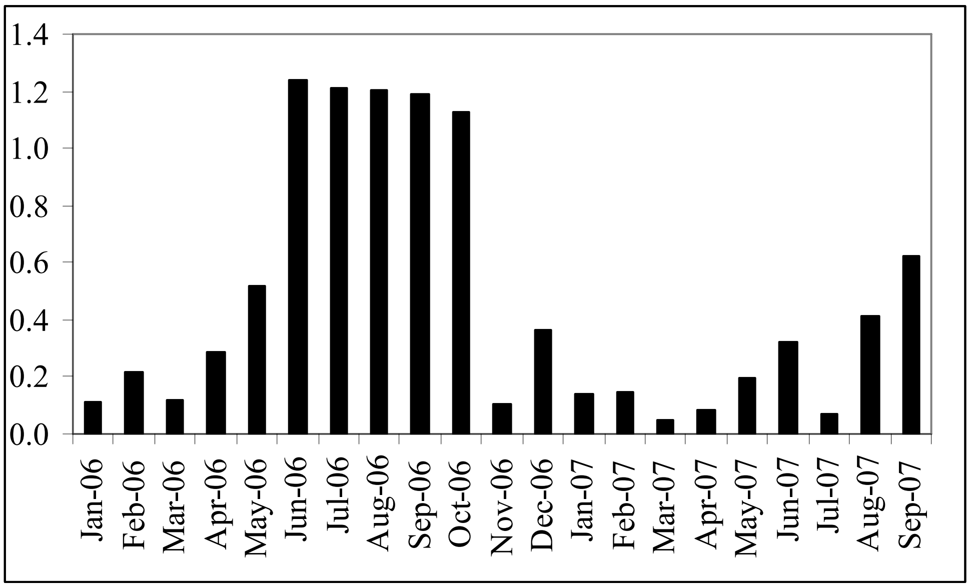

Figure 4.7. Seasonal trend of the ratio of TIC to TOC in headwater streams in the Flat Creek watershed.

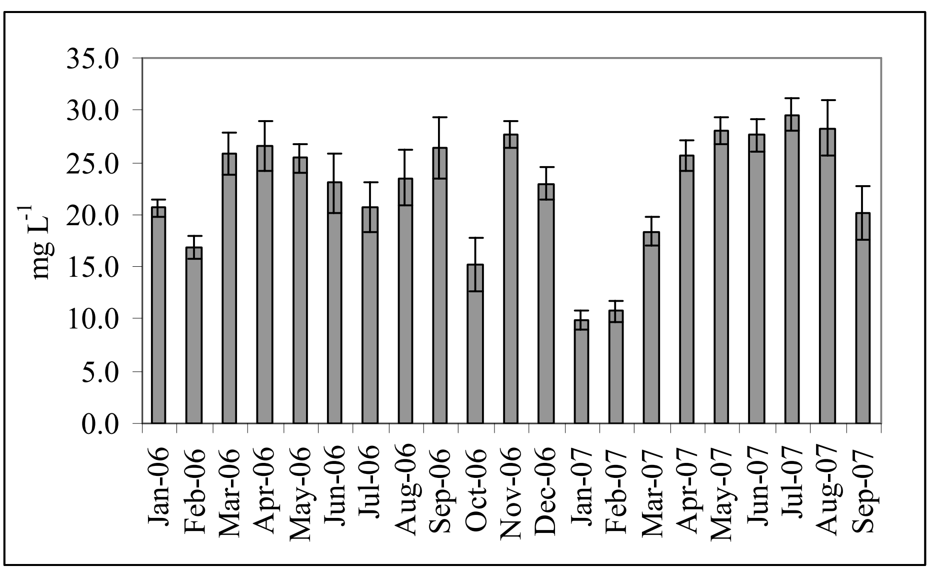

Figure 4.8. Average dissolved carbon concentrations in the Flat Creek watershed. Error bars represent standard error.

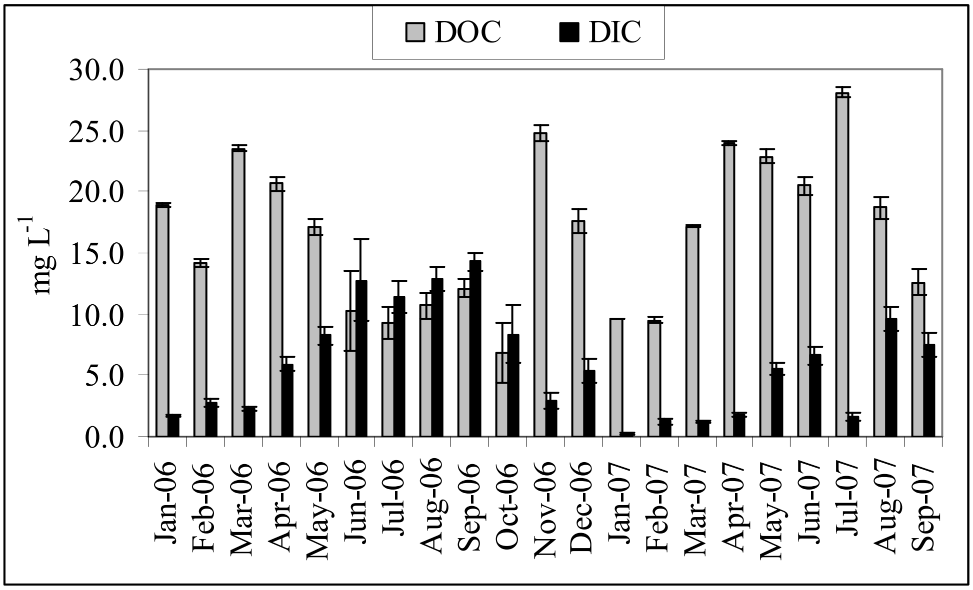

Figure 4.9. Average dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) concentrations in the Flat Creek watershed.

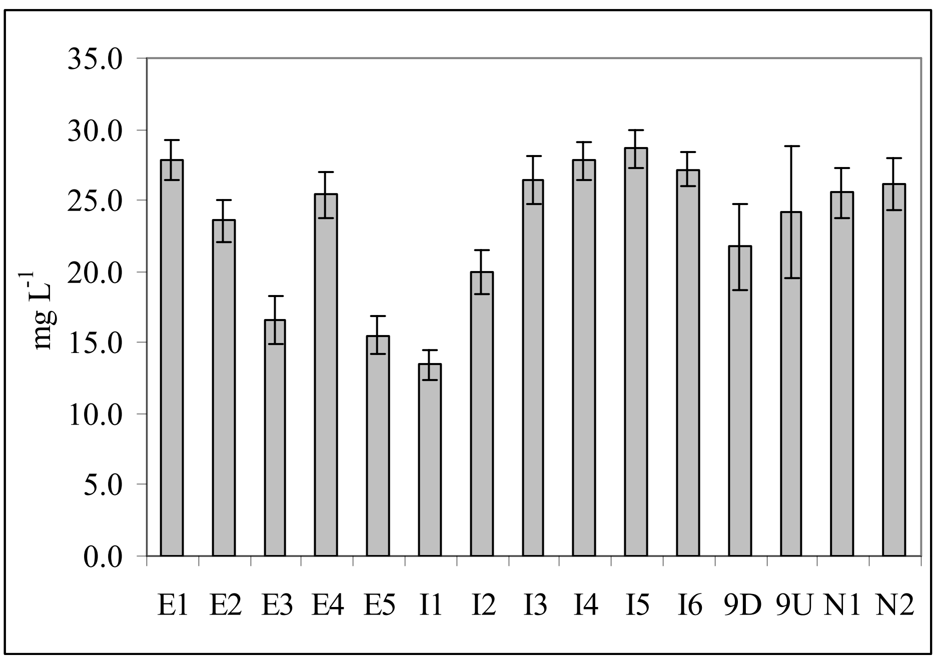

Figure 4.10. Average total carbon concentrations at 15 locations in the Flat Creek watershed. Error bars represent standard error.

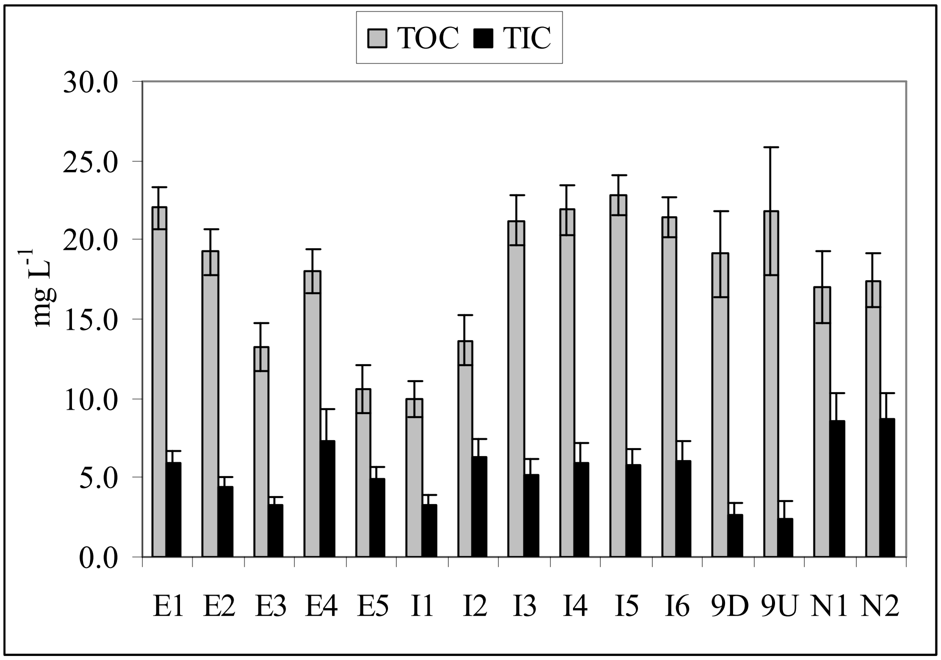

Figure 4.11. Average total organic carbon and total inorganic carbon concentrations at 15 locations in the Flat Creek watershed. Error bars represent standard error.

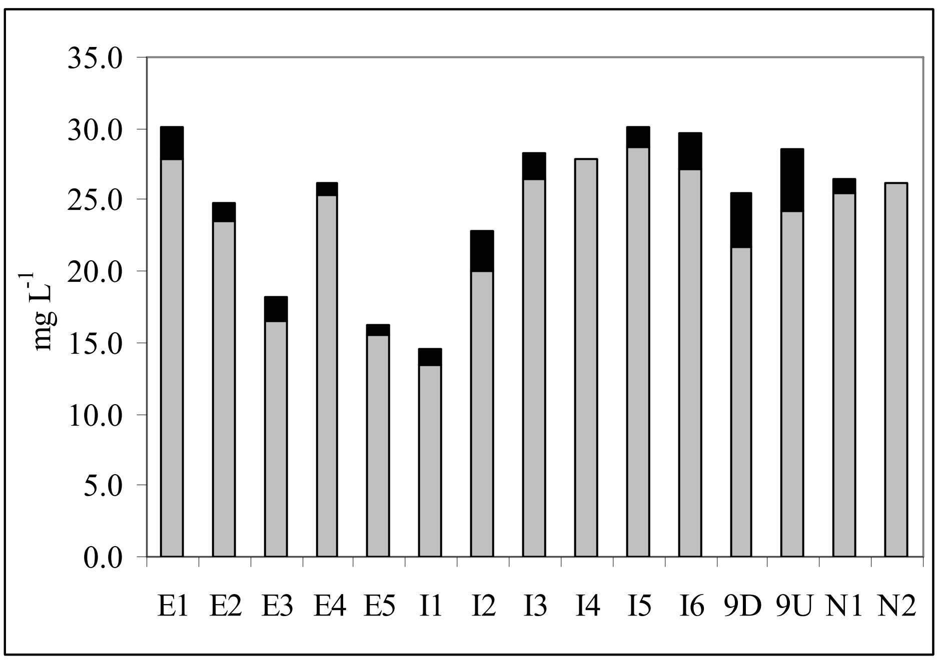

Figure 4.12. Dissolved carbon portion (gray portion) of total carbon (full bar) in the Flat Creek watershed.

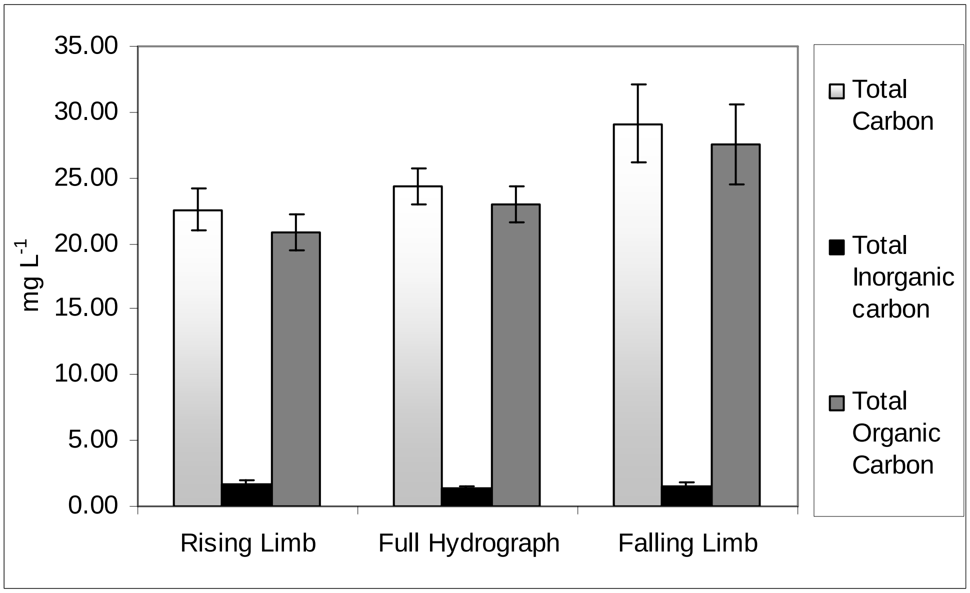

Figure 4.13. Average total carbon, total inorganic carbon, and total organic carbon during storm events in January 2006 to September 2007 during varying parts of the hydrograph in the Flat Creek watershed. Error bars represent standard error (n=7 for rising limb, n= 24 for full hydrograph, and n=5 for falling limb).

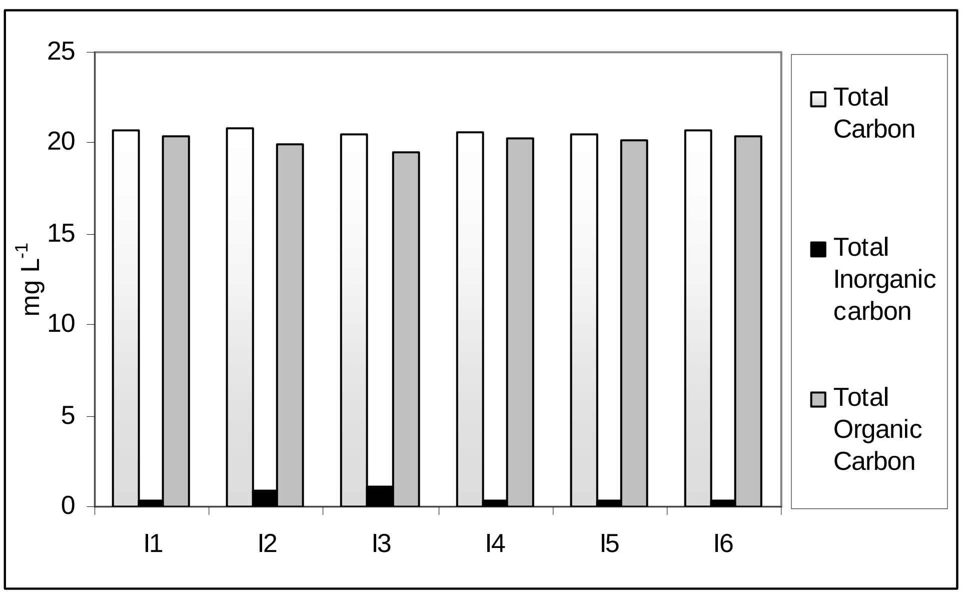

Figure 4.14. Total carbon, total inorganic carbon, and total organic carbon for all six sites during one storm event on January 15, 2007 in the Flat Creek watershed.

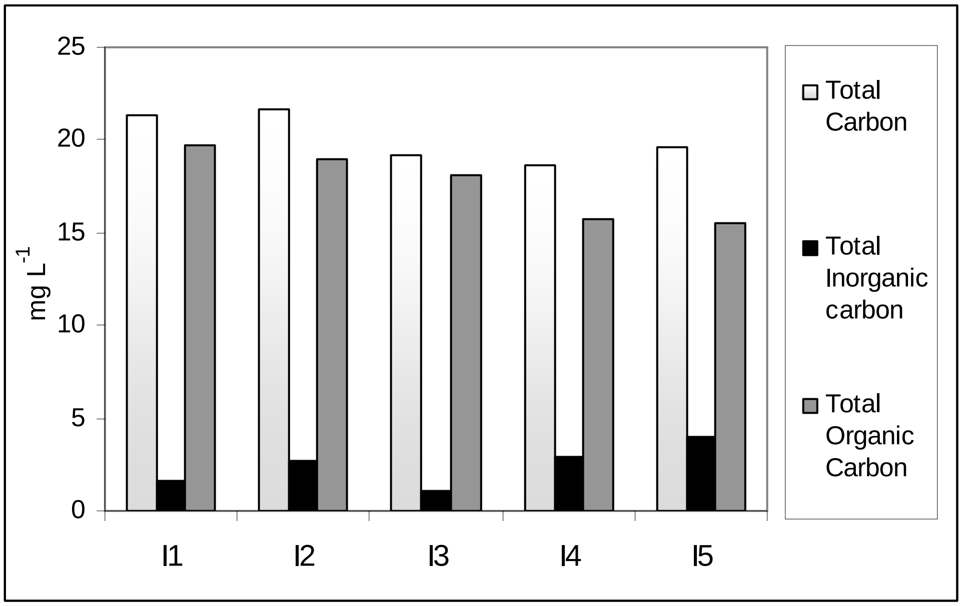

Figure 4.15. Total carbon, total inorganic carbon, total organic carbon for five sites during one storm event on October 16, 2006 in the Flat Creek watershed.

4.3.2 Spatial Distribution of Stream Carbon Concentrations

Figures 4.10 and 4.11 show average concentrations of total carbon and total organic carbon at 15 sampling locations across the Flat Creek watershed. Average total carbon was lowest at I1 (13.5 mg L^{-1}) and highest at I5 (28.6 mg L^{-1}), showing no clear trend with respect to stream order. Most of the stream carbon was in the dissolved form (Figure 4.12).

4.3.3 Mass Loading and Transport of Carbon

Carbon loading was calculated using streamflow and concentration for two 1st order streams (I1 and I4) and their downstream 3rd order watershed outlet (E4). Due to the flow conditions of this watershed, it was difficult to develop accurate stage-discharge curves (see Saksa, 2007). Sites I1 and I4 had the best relationships. The result showed that over the 22-month study period total carbon loading at all three sites followed a similar seasonal trend (Figure 4.16). 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 mon^{-1}) when compared with those

at I4 (1,905 kg mon^{-1}) and I1 (1,560 kg mon^{-1}). 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 (Figure 4.16). Headwater TOC loading was 1,524 kg mon^{-1} at I1 and 1,633 kg mon^{-1} at I4 (Figure 4.16). TOC loading at E4 was 36,627 kg mon^{-1}.

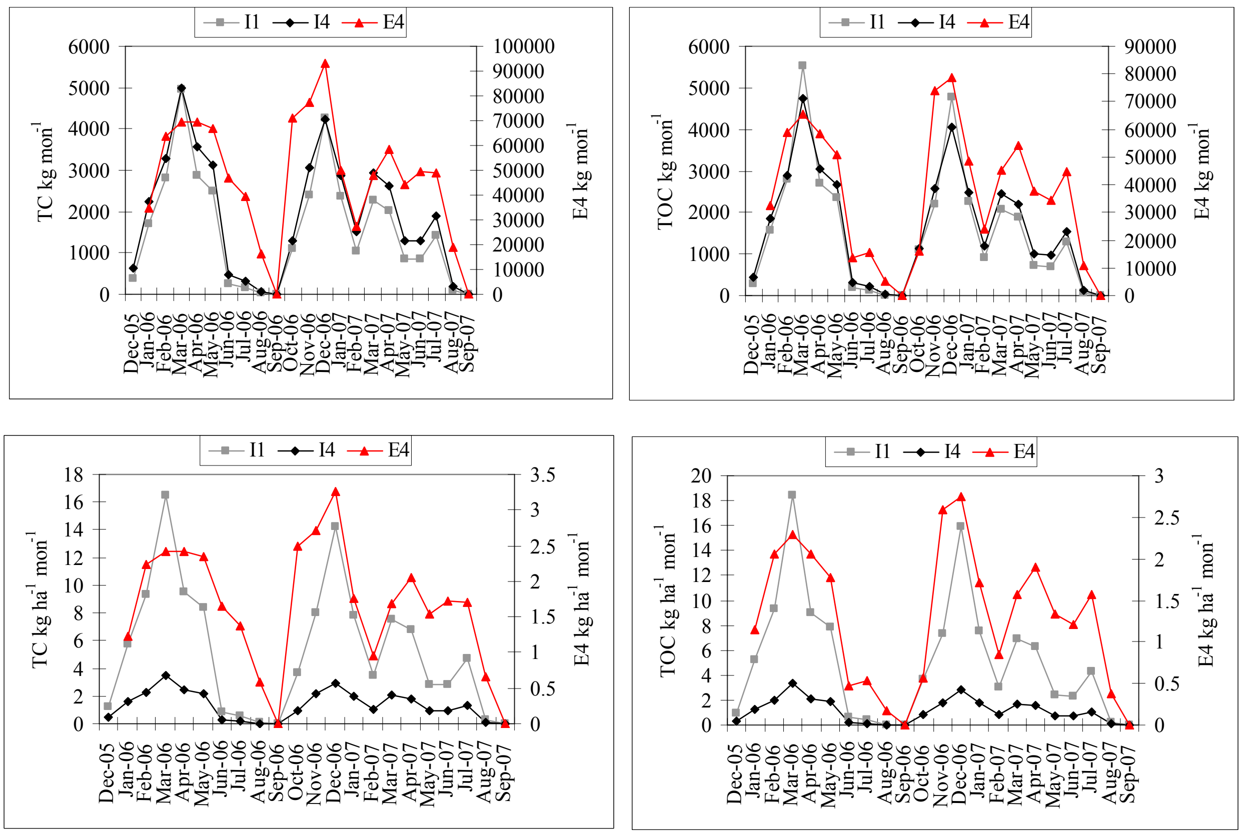

Figure 4.16. Comparison of mass loading and flux of total carbon and total organic carbon between two 1st order (I1 and I4) stream and a 3rd order stream (E4) in the Flat Creek watershed.

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^{-1} mon^{-1}, whereas the headwater sites I1 and I4 showed an average carbon flux of 5.2 kg ha^{-1} mon^{-1} and 1.33 kg ha^{-1}

mon^{-1}, respectively. Similar trends for total organic carbon fluxes were observed, with I1 having average monthly flux of 5.08 kg ha^{-1}, I4 having an average monthly flux of 1.14 kg ha^{-1}, and E4 having an average monthly flux of 1.28 kg ha^{-1}.

4.3.4 Relationship between Stream Carbon and Nitrogen

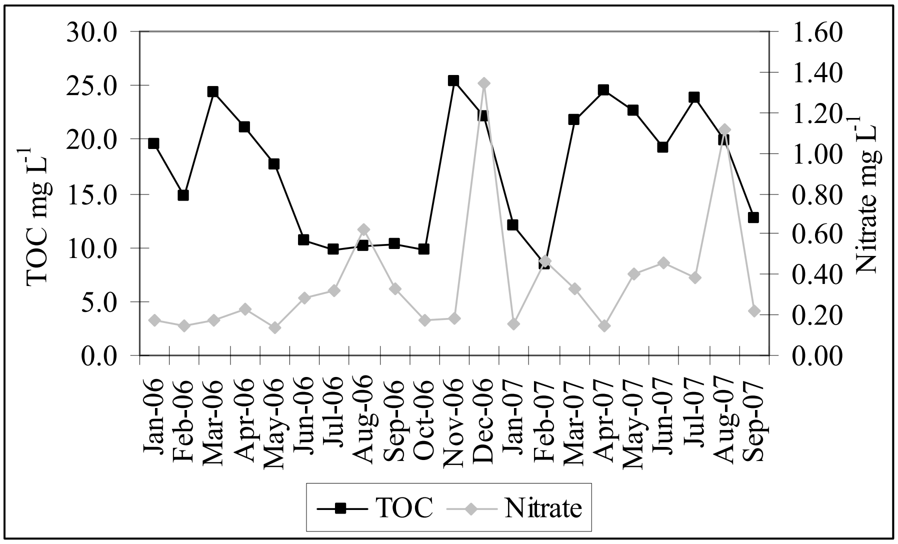

Figure 4.17. Average nitrate and total organic carbon for all fifteen sites from January, 2006 to September 2007.

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 (1.378 mg L^{-1}) that is attributed to a rain event shortly prior to monthly sampling (Figure 4.19). 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.

4.4 Discussion

4.4.1 Seasonal Trend of Organic and Inorganic Carbon

Although total carbon remained relatively consistent over the year, there was a clear seasonal trend of increased inorganic carbon in the summer and of increased organic carbon during the winter and spring months. Increased organic carbon was observed during the spring, which may have resulted from the 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 nitrogen since the input is higher than what is processed within the stream (Cooper *et al.*, 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. Dissolved organic carbon decreases with soil depth as sorption of DOM to mineral surfaces occurs in the deeper soil depths (Cory *et al*., 2004), also DOM found in streams is more similar to shallow soil water DOM than the deep soil water DOM (Cory *et al*., 2004). Johnson *et al.* (2006) found that DIC is higher in deeper flow paths in which a 40:1 ratio of DIC:DOC existed for emergent groundwater. During low flow conditions, which is found in the summer months in Flat Creek, streams receive water from groundwater 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 *et al*., 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 stream water within the banks allows

organic materials to enter the water column. The decline in organic carbon in April 2006- June 2006 shows that TOC is being consumed. DOC decomposition is slower in headwaters, but this process consumes oxygen and converts OC to 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.

In their study on a tropical blackwater stream system in the Amazon, Waterloo and colleagues (2006) found high DOC concentrations during quickflow events that were typical for these types of systems (tropical, blackwater) draining forests. It is interesting to see the dramatic decline in inorganic carbon from October 2006 to November 2006 in which inorganic carbon declined by 25%. More than eight inches of rain fell in one week in October after monthly sampling occurred. If it is expected that increased quickflow, especially after a long dry period, would carry more organic matter, the carbon concentration in November 2006 should reflect an increase in organic matter. Organic carbon more than doubled in November 2006 compared to the month prior. Although organic carbon decreased in December 2006, it is expected since there is a "flushing" effect. Factors affecting DOC release include length of time since soil profile was last flushed, rewetting of the H soil horizon (soil horizon with highest organic content), and event magnitude (Cooper *et al.*, 2006). The rains in October and November did not give a sufficient dry period for organic carbon to accumulate.

Although it is soil type dependent, DOC is expected to have a summer maxima and winter minima as a result of enhanced turnover and release of organic matter from soils (Cooper *et al.*, 2006). This differs with what was seen in Flat Creek. A positive relationship with DOM concentration and proportion of area in total wetlands exists since these wetlands contribute

DOM (Frost *et al.*, 2006). Louisiana has a gentle topography which creates multiple backwaters and less defined stream channels. The backwaters peak in the early spring with the ending of the rainy season. Having these additional wetlands could be contributing to the peak of TOC in spring rather than the summer maxima seen in the study by Cooper and his colleagues (2006).

There was increased TOC in February 2007 to April 2007 compared to the same period the year prior. The winter was wetter in 2007 than 2006, so there was more organic carbon carried to the streams. DOC was higher in wet years compared to dry years in the Rio Negro River Basin in the Amazon (Waterloo *et al.*, 2006). In an experiment by Moller and others (2005) less DOC and DON was released than received in rain water contributing to a net positive, or DOC and DON sink. These results differ from temperate forests, but it is expected that more rapid transformations and mineralization of organic matter occurs under tropical conditions (Moller *et al.*, 2005).

Soils control dissolved organic matter input to streams (Moller *et al.*, 2005). In one study, DOM in stream water was strongly related to landscape level predictors since the predictors affected loading, transportation, removal, and dilution of DOM (Frost *et al.*, 2006). Researchers found that DOM was negatively correlated to watershed area, mean slope, and drainage density suggesting that residence time plays a key role in DOM quantity and type reaching the stream (Frost et al., 2006). Buffam *et al.* (2001) did not find a seasonal pattern in DOC and indicated that the DOC in throughfall was greater than overlandflow DOC. One important difference between Buffam's results and those presented here is stream characteristics. Buffam and his collegues studied streams with bedrock base, so there would be limited organic matter mobile for overland flow to carry to streams. This greatly contrasts Louisiana's streams with the high organic matter and high water table (further mobilizing organic matter). Water

passing through organic matter in soils mobilizes the soluble organic mater thereby increasing DOC and DON in receiving waters (Moller *et al*, 2005).

A majority of carbon measured in this study was in the dissolved form. The sampling method used may preferentially select for dissolved carbon; however, this method is a preferred method to sample nutrients and solids in the water column. Another study also found that dissolved carbon dominated the streams measured. Waterloo and researchers (2006) found DOC was 92%-94% of the total flux. Marschner and Kalbitz (2003) mention that dissolved organic matter is the most bioavailable fraction. This supports the sampling method used was adequate.

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-I6) and reflects the mixing of lower carbon at Spring Creek and higher carbon at the upper Turkey Creek sites.

Although there was not a large difference in organic or inorganic carbon at different stages of the storm hydrograph, there was a small increase in organic carbon in the falling limb. During the falling limb average DOC was 27.33 ± 3.15 mg L^{-1} which was similar to DOC measured in the Rio Negro River Basin during storm events (Waterloo *et al*., 2006). Although it is suggested that the highest DOC concentration should be during storm events (Cooper *et al*., 2006), the DOC concentrations during storm events were only slightly elevated from max DOC measured during monthly water sampling. Concerning the peak of DOC in the storm hydrograph, the literature contradicted each other. Buffam *et al.* (2001) state that the max should occur in the rising limb while Cooper *et al*. (2006) cites various studies that found the max DOC

on the falling limb. As stated above, the streams sampled in the study by Buffam and his collegues 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 *et al*. (2006) and not Buffam *et al.* (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^{-1} at I1 and 21.65 mg L^{-1} at I2) than was seen in the January 16, 2007 storm and Turkey Creek had lower carbon concentrations (18.65 mg L^{-1} -19.57 mg L^{-1}). These are small variations and probably are due to differences in runoff and rainfall patterns.

Both total carbon and total inorganic carbon were about average for a forested watershed in the streams of the Flat Creek watershed. Royer and David (2005) studied dissolved organic carbon loading in an agricultural watershed and found average flux of 3-25 kg ha^{-1} yr^{-1}. Using average flux to determine the approximate yearly value, Flat Creek has a range of 16.0-62.4 kg ha^{-1} yr^{-1}. This overlaps with the higher end of the range found by Royer and David (2005). An agricultural watershed in the Midwestern US had DOC loads of 14.1-19.5 kg ha^{-1} yr^{-1} (Dalzell *et al.*, 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^{-1} yr^{-1}. 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 2,404 Mg 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 1,700-10,500 kg km^{-1} yr^{-1} (Aitkenhead-Peterson *et al.*, 2006).

4.4.2 Carbon and Nitrate Relationship

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 (Figure 4.19). 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^{-1} completely inhibited nitrification. TOC in March was 25 mg L^{-1} and corresponded to nitrate/nitrite of 0.2 mg L^{-1}, 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.

4.4.3 Potential of Using Carbon in Water Quality Testing

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 *et al.*, 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 4.19 may indicate that the carbon concentrations present in the stream may be influencing nitrate/nitrite levels. DOM in stream water is strongly related to landscape level predictors including loading, transportation, removal, and dilution of DOM (Frost *et al.*, 2006). Considering its relationship with nitrogen, a popular indicator for eutrophication and general water quality, carbon monitoring may be a beneficial indicator for water quality.

4.5. 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. Total carbon 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.

CHAPTER 5: DISSOLVED OXYGEN OF HEADWATER STREAMS IN A LOW-GRADIENT SUBTROPICAL WATERSHED

5.1 Introduction

Dissolved oxygen (DO) level in a water body is among the most important indicators of the health of an aquatic ecosystem. Low DO levels can cause fish kills, loss of recreational use from bad smells, and the release of noxious gases from anaerobic bacteria (Liu *et al*., 2007). Nutrient or organic matter enrichment results in low DO in a water body. The frequency of such enrichment has increased with the growing problem of nonpoint source pollution due to anthropogenic activities. However, low DO conditions can also be caused by natural environmental variables, such as water stagnation and high temperatures. Dissolved oxygen in water is a function of temperature, salinity, turbulence, and atmospheric pressure. When water temperature is higher, gases are less soluble (including oxygen). Stream temperature is susceptive to change during seasonal air temperature change, but also by anthropogenic effects, especially any event that results in the vegetation removal of riparian buffers such as timber harvesting, (Brown and Krygier, 1970; Beschta and Taylor, 1988; Jackson *et al*., 2001; Chen *et al*., 2004), thermal pollution (Hoak, 1961; Kinouchi et al., 2007), and flow modification (Caissie, 2006). Turbulence, including flow induced turbulence, in a water body acts to "stir" the water, which brings more oxygen into the water.

Many of Louisiana's freshwater streams are characterized by low flow with high organic content and high temperatures during the summer season which may produce low dissolved oxygen levels. High temperatures reduce the oxygen solubility in water, the low flow reduces turbulence, and the high organic matter consumes oxygen during degradation. These ambient levels of dissolved oxygen are often below levels regarded safe for organisms by the Louisiana

Department of Environmental Quality. The current acceptable Total Maximum Daily Load (TMDL) for dissolved oxygen in Louisiana is 5 mg L^{-1} (LDEQ, 2001), but a study by Ice and Sugden (2003) found that 81% of the sites sampled in Northern Louisiana during the summer were below this standard. Most of these streams were classified as having an organic substrate with “slight” or “stagnant” flow, indicating the effect that substrate and stream velocity can have on DO levels.

The TMDL approach has emerged as a widely-adopted strategy to limit pollution from both point and non-point sources. Development of TMDLs for certain pollutant types may enable watershed managers to enforce constraints on the allowable level of activities concerning that pollutant, making the TMDL approach a protection technique for water quality. If the level of activities or the water quality standards in water bodies violate the recommended values from the TMDL recommendation, a load reduction can be suggested for the watershed, making the TMDL approach a restoration technique. TMDLs are widely used when monitoring streams during land use changes and determining the necessary nutrient reduction to maintain or improve stream health. It is, however, important to note that TMDLs are arbitrary indicators of water quality, and they should not be set at levels which are determined unattainable for natural water conditions. Although the current TMDL for dissolved oxygen in Louisiana is 5 mg L^{-1}, some propose a 3 mg L^{-1} minimum during summer months (LDEQ, 2001). It is argued that the current level is nearly impossible for some streams in Louisiana to maintain, especially during the hot, dry summers, due to naturally occurring conditions.

Organic carbon is indirectly related to oxygen availability in water (Thunell et al., 2000); therefore high organic carbon may be an indicator of low dissolved oxygen in natural stream systems. Carbon sources are locally available within the stream, recycled from upstream

transport, or input from runoff or leaf litter (Thomas *et al*., 2005). Many streams in Louisiana tend to have high levels of organic matter and nutrients (Xu, 2004), so it can also be responsible for decreased dissolved oxygen levels.

This study was conducted to (1) investigate spatial and seasonal dynamics of dissolved oxygen in headwater streams of a low-gradient, forested watershed, (2) identify factors influencing the temperature dependence of dissolved oxygen concentrations, and (3) assess the applicability of dissolved oxygen criterion of 5.0 mg L^{-1} in Louisiana.

5.2 Methods

5.2.1 Study Area

The Flat Creek watershed is located in the western part of the Ouachita River Basin in central Louisiana (Figure 5.1). The Ouachita River Basin drains a total area of 41,439 km^2 with topography progressing from slightly rolling uplands to level floodplains. Flat Creek is a medium sized watershed with a drainage area of approximately 369 km^2, which comprises about 15% of the area in Castor Creek Watershed (Figure 5.2). Land use within the watershed is dominated by forests covering 61% of the area, followed by rangeland at 21% (LDEQ, 2001) (Figure 5.3). Climate in this region is subtropical with hot, humid summers and mild winters. Long-term average temperatures range from 2.3°C-34.1°C (36.2°F to 93.3°F) and long-term average rainfall is about 1500 mm yr^{-1}. Soils in the area are dominated by poorly drained Guyton (silt loam) series along the Flat Creek and Turkey Creek floodplains, with moderately well drained Sacul-Savannah (fine sandy loam) soils in the upland areas.

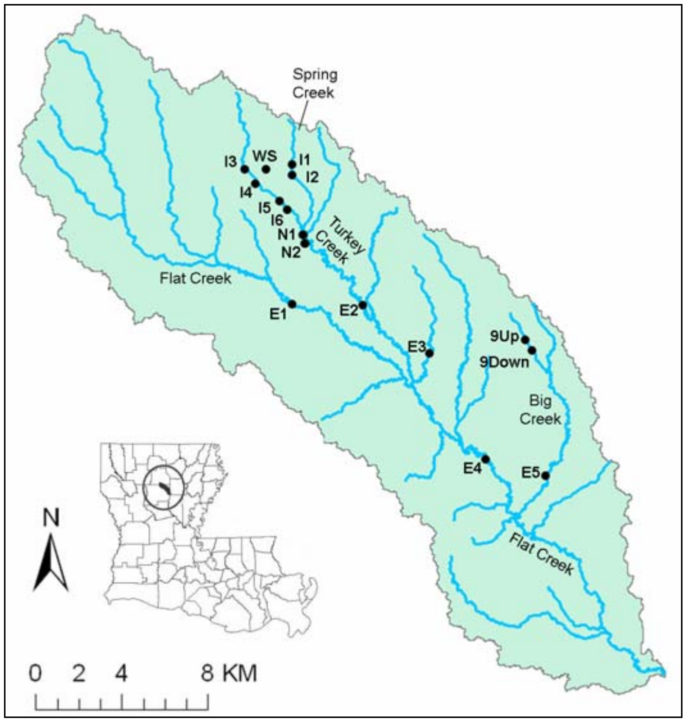

Figure 5.1. Geographical location of the Flat Creek watershed and water quality monitoring sites. A weather station (WS) is established between Spring Creek and Turkey Creek.

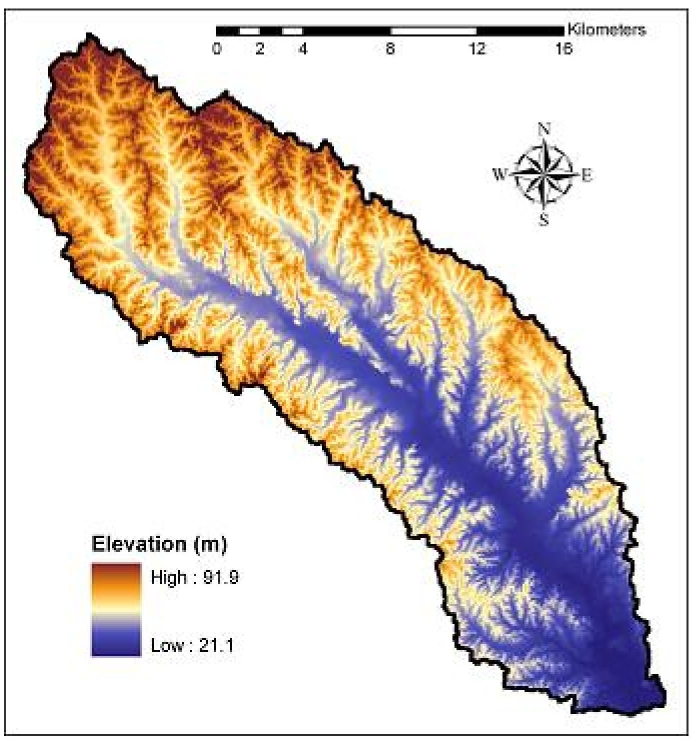

Figure 5.2. Topography of the Flat Creek watershed.

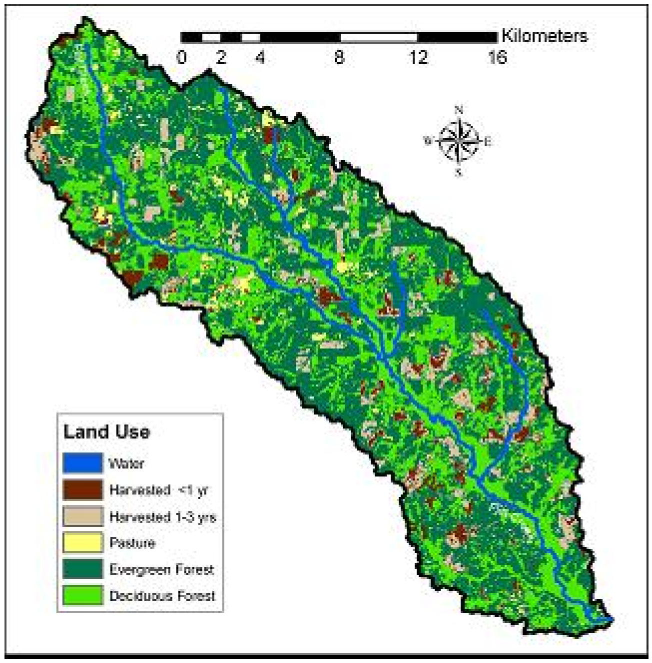

Figure 5.3. Land use conditions of the Flat Creek watershed analyzed from a 2006 Landsat TM5 image (Saksa, 2007).

5.2.2 In-stream Water Quality Measurements

Five streams in the Flat Creek watershed were sampled: Spring Creek, Turkey Creek, Flat Creek, Fish Creek, and Big Creek. Fifteen sites were visited monthly from January 2006 to September 2007 (Figure 5.1). In-situ water quality measurements, including dissolved oxygen, temperature, conductivity, and pH were taken at each site with an YSI 556 multiprobe (Yellow Springs Instruments, Ohio) (Figure 5.3). In addition, two in-stream water quality monitoring sondes (YSI 6920 V2, Yellow Springs Instruments, Ohio) were deployed in Turkey Creek. These sondes measured dissolved oxygen, temperature, conductivity, and turbidity at a 15-min time interval, providing information on daily DO fluctuation over the seasons. Data from these sondes, currently under review, were acquired at periodic intervals between June 2006 and September 2007.

Figure 5.4. Instream measurements were taken at each site monthly. This stream is a typical one in the Flat Creek watershed in late summer/early fall with stagnant water.

5.2.3 Water Sampling and Laboratory Analysis

Monthly water samples were collected at the fifteen monitoring locations and processed in the lab. Water was analyzed for total and dissolved organic and inorganic carbon by a Shimadzu Total Organic Carbon Analyzer (TOC-V CSN Shimadzu Corporation, Kyoto, Japan) using the combustion/non-dispersive infrared gas analysis method. Water for dissolved organic and inorganic carbon analysis was first filtered through a 47μm glass fiber filter (GF/F Whatman International Ltd, Maidstone, England).

5.2.4 Streamflow Measurements and Climatic Observations

Streamflow was measured during monthly sampling using a flow meter (Sontek, Yellow Springs, Ohio) and top setting rod (Rickly Hydrological Co, Columbus, Ohio). Since the streams were relatively small, five to ten cross-sections were used. The autosamplers at the intensive sites record stream level every fifteen 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).

Since weather conditions can be variable in a relatively close geographic region, a weather station measuring temperature, precipitation, solar radiation, and wind speed was installed near I4, centrally located to the headwater sites. Data are available in fifteen minute increments averaged to daily and monthly values from December 2005 through September 2007.

5.2.5 Data Analysis

Summary statistics such as mean and standard error were calculated for each month as well as each site. T-tests were performed on the data comparing sites that had pooling characteristics, seasonal variation, and stream permanence. Coefficient of variation was calculated as

$$CV=(A_1-M)/M \qquad (1)$$

Where A_1 is the actual nutrient concentration for the representative site and month and M is the mean of the nutrient concentration for that site.

5.3 Results

5.3.1 Seasonal and Spatial Variations in Dissolved Oxygen

There was a wide range of DO levels (1.24-8.11 mg L^{-1}) with the lowest DO found during the summer months and the highest DO during the winter months. The summer period (May-October) had significantly lower DO ($t=4.94$; $p<0.001$) than other times of the year (January-April and November-December). The non-summer months had an average DO of 5.77 mg L^{-1}, whereas the summer months had a much lower DO at 2.85 mg L^{-1}. From March to October 2006 and May to September 2007; average DO in the Flat Creek watershed was below the Louisiana DO criterion of 5 mg L^{-1} (Figure 5.6). Each month had wide variation depending on the site. Average DO in September had the narrowest range, but only five sites had flowing

water (DO 0.58-2.4 mg L^{-1}). The other sites were dry or extremely intermittent. January 2006, however, had largest variation in DO from site to site (0.99 mg L^{-1} to 9.03 mg L^{-1}). This distinct, seasonal difference in DO corresponds to the high temperature and reduced rainfall resulting in low flow conditions that normally occur during the summer (Figure 5.7). Average water temperature was lowest in January, 2006 (8.88 ^{o}C) and highest in August, 2006 (26.57 ^{o}C).

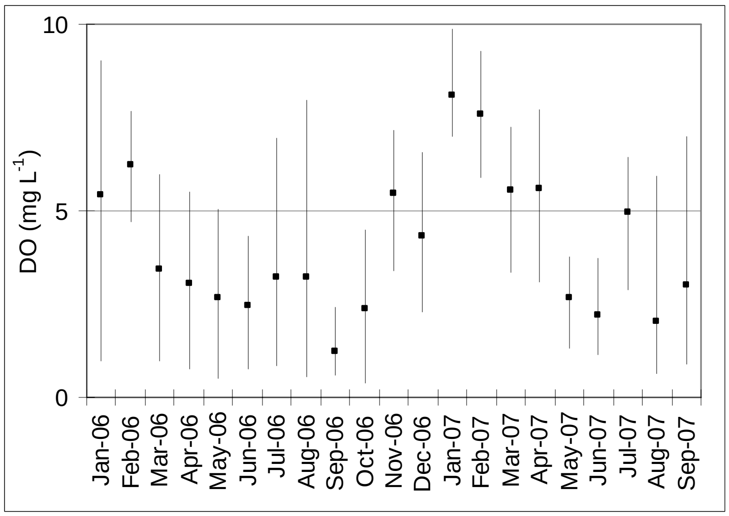

Figure 5.5: Seasonal dissolved oxygen variability. Squares represent the means and lines show the ranges between maximum and minimum values from all 15 sampling sites in the Flat Creek watershed. Current TMDL for DO in Louisiana is indicated by the line at 5.0 mg L^{-1}.

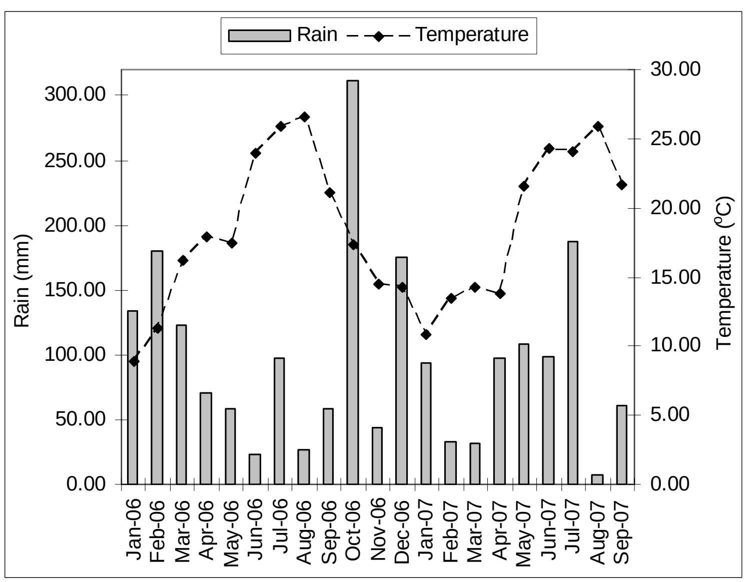

Figure 5.6. Climatic conditions during the study period (January 2006-September 2007) in the Flat Creek watershed.

Intensive monitoring of Turkey Creek showed a diurnal fluctuation in temperature and DO and the lowest DO is found at midday corresponding with the sunniest and warmest part of the day (Figure 5.8). Midday DO was frequently depleted during the summertime.

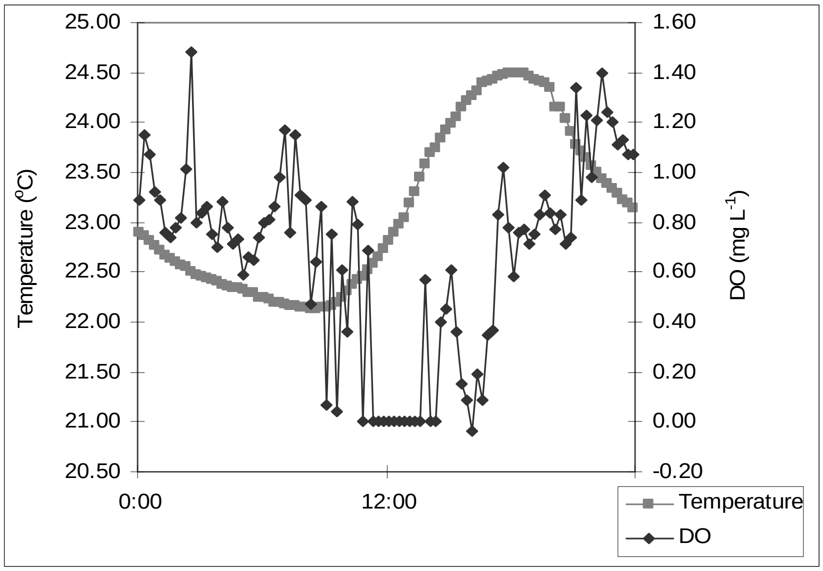

Figure 5.7. Dissolved oxygen and temperature fluctuation during an early fall day (September 12, 2006) at a site on Turkey Creek.

The variation in dissolved oxygen is not related to the location of the site in relationship to the watershed since there is no clear trend in dissolved oxygen and stream order (Figure 5.9). First order streams sampled have average DO between 2.6 mg L^{-1} and 5.7 mg L^{-1} and the second order streams sampled have average DO between 3.7 mg L^{-1} and 5.8 mg L^{-1}. Site E4, the only third order site, had average DO of 5.7 mg L^{-1}. DO does not increase, nor decrease in a clear pattern from upstream, at the headwaters, to downstream, near the outflow (Figure 5.9).

As streams increase in size from the headwaters to the outlet, they usually become more stable, so DO should fluctuate less. We would expect to see a narrower variation in dissolved oxygen at site E4 than at I1, since E4 is larger. To test this, we used coefficient of variation (CV). Although there is some indication that the CV clumps around zero at E4 as compared to

the upstream, first order sites, there is not a large difference in CV (Figure 5.10). Since there are a number of first order streams with similar drainage area, in Figure 5.11 the sites are placed equally apart. I1 and E4 have nearly the same CV pattern.

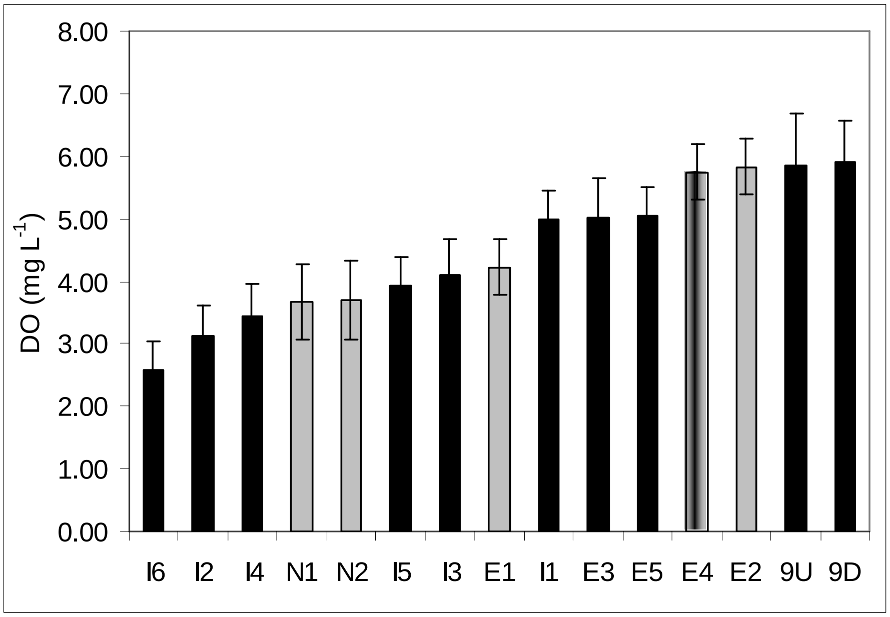

Figure 5.8. Average dissolved oxygen at all 15 sites in order of increasing DO. Black bars represent 1st order streams, grey bars are 2nd order, and site E4 (grey and black bar) is the 3rd order stream.

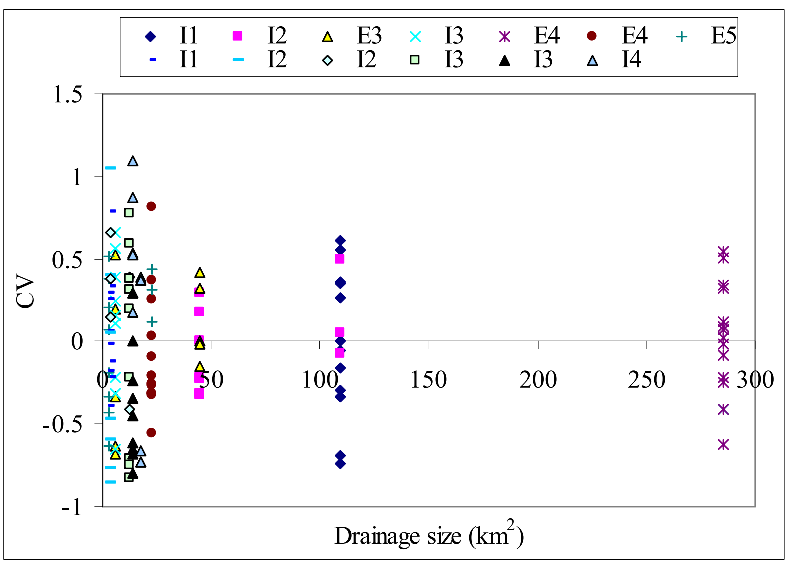

Figure 5.9. Coefficient of variation in dissolved oxygen. Sites are in order of increasing drainage area.

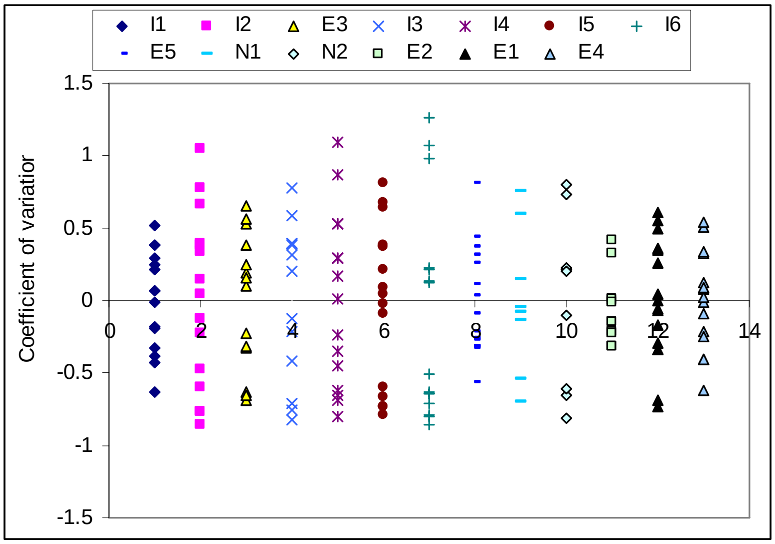

Figure 5.10. Coefficient of variation in dissolved oxygen. Sites are in order of increasing drainage area; however, they are spaced equally for ease of viewing.

5.3.2 Dissolved Oxygen and Stream Conditions

When sites were divided based on stream conditions of pools or nonpools, it is evident that these types of stream conditions are more indicative of oxygen levels than location in the watershed. The lowest DO levels were found at sites with low velocity (Table 5.1). Two sites were classified as pools throughout the year; the remaining sites were either nonpools for the entire year or had pooling conditions for only a small portion of the year. Nonpool sites had significantly higher DO ($t=4.94$, $p<0.001$) ranging from 3.45 mg L^{-1} to 5.89 mg L^{-1} than the pool sites (2.58-3.13 mg L^{-1}). Intermittent sites had significantly higher DO (4.97 mg L^{-1}) ($t=3.66$, $p<0.003$) than the perennial sites (3.92 mg L^{-1}) (Table 5.1). It is important to note that the two sites classified as pools were also perennial.

Since DO is a function of temperature, dissolved oxygen reported as percent saturation (%) can be a more accurate representation. When comparing DO% to DO mg L^{-1} (Figure 5.12), DO in June, July, and August were slightly higher when represented as percent, but overall the

same trends are seen. Since oxygen is less soluble in warmer temperatures, it is expected that the percent saturation in summer would reflect a higher DO level than DO reported as concentration (mg L^{-1}).

Table 5.1. Sites partitioned into pools and nonpools with the respective stream order, flow permanence, and mean DO. Mean discharge is not available for all sites.

Site ID	Order	Flow Permanence	Mean DO (mg L^{-1})	Mean Discharge
Pools				
I6	1st	Perennial	2.58	
I2	1st	Perennial	3.13	
Nonpool				
I4	1st	Perennial	3.45	0.0335
N1	2nd	Perennial	3.68	
N2	2nd	Perennial	3.69	
I5	1st	Perennial	3.92	
I3	1st	Intermittent	4.09	0.0308
E1	2nd	Intermittent	4.23	0.2646
I1	1st	Perennial	4.98	0.0154
E3	1st	Intermittent	5.03	0.0491
E5	1st	Intermittent	5.05	0.0593
E4	3rd	Perennial	5.74	0.7508
E2	2nd	Intermittent	5.83	0.1368
9U	1st	Intermittent	5.84	
9D	1st	Intermittent	5.89	

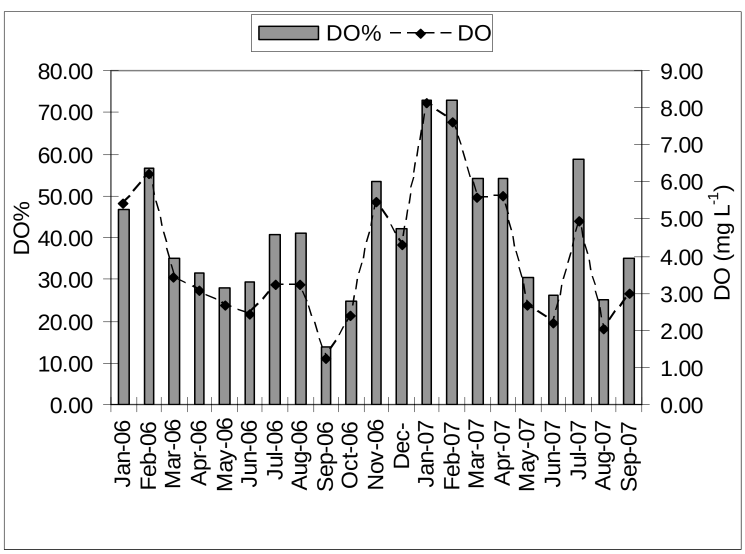

Figure 5.11. Average dissolved oxygen in percent and mg L^{-1} for all 15 sites.

5.3.3 Seasonal and Spatial Variations in Carbon

There were seasonal variations in both average total inorganic carbon (TIC) and total organic carbon (TOC) (Figure 5.13). TOC was high in the spring and fall (i.e., TIC:TOC<1), while TIC was high in the summer months (TIC:TOC>1). Organic carbon ranged from 7.96 mg L^{-1} in February, 2007 to 25.30 mg L^{-1} in November 2006. Average inorganic carbon varied from 1.08 mg L^{-1} in March 2007 to 12.58 mg L^{-1} in June 2006. Late October 2006 marked large rains (more than 8 inches in a single week) which marked the beginning of the "rainy" season typically in the late fall and winter in Louisiana. Since monthly sampling occurred prior to this large rain event, October-November reflects a drastic change in the TIC to TOC ratio caused by an increase in flow and rainfall. The increased inorganic carbon corresponded to decreased DO (Figure 5.13).

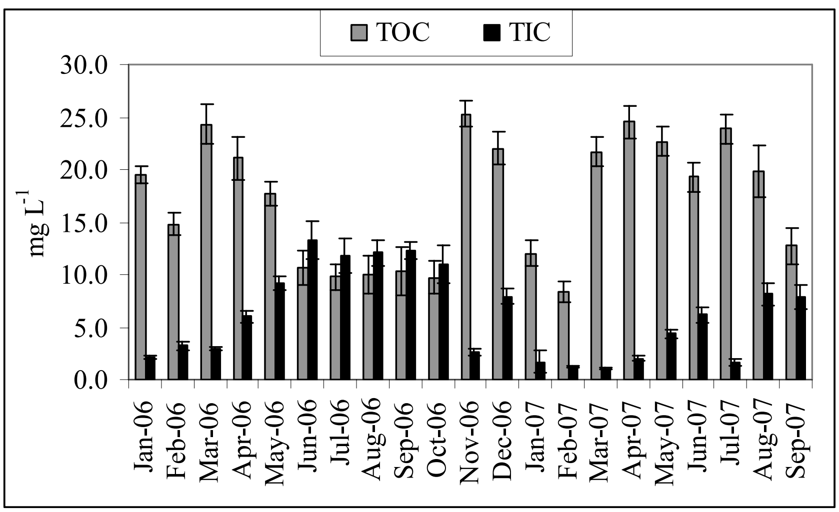

Figure 5.12. Total organic and inorganic carbon in the Flat Creek watershed from January 2006 to September 2007.

5.4 Discussion

5.4.1 Temperature Dependency of Dissolved Oxygen

Flat Creek, a subtropical watershed, has an overall shortage of oxygen which corresponds to the hydrologic regime, seasonally reduced rainfall, and increased temperatures found in this subtropical area. These three characteristics are inherently connected to seasonality. The gentle topography in the area results in overall low flow velocities, which is typical of this area. Lowest flow is found during the summer months in which some of the streams dry completely or become stagnant pools. During the rainy season (late fall/winter), flow increases and temperatures are lower which tends to increase dissolved oxygen in the streams. We saw oxygen concentrations that followed this trend. Flat Creek's extremely oxygen depleted streams during the summer had similar concentrations to a tropical system in Costa Rica. In this system the mean DO prior to flooding was 1.9 $\pm$1.0 mg L^{-1} (Chapman and Kramer, 1994) compared to Flat Creek's summer average of 2.8 $\pm$1.74 mg L^{-1}. Highest DO was found in sites that were nonpooled (characteristic of the hydrologic regime) and during the rainy, non-summer months. There was a strong seasonal effect on dissolved oxygen in which summer months (May-October) had lower dissolved oxygen than the remaining months.

Flow is normally lowest during the summer months, when higher flows could benefit overall oxygen capacity. As a result of this reduced flow and increased temperature, seasonal differences in dissolved oxygen are clearly defined, as found in a similar study by Chapman and Kramer (1994) in which stream DO was reduced during the dry season and higher in the wet season. In their study, seasonal variance explained 40% of the variance in oxygen concentrations (Chapman and Kramer, 1994). Morrill *et al*. (2005) found that water temperature increased 0.6^{o}C-0.8^{o}C for each 1^{o}C increase in air temperature. As temperature increases, oxygen

saturation is achieved at lower concentrations. Chapman *et al*. (1998) correlated DO with both water temperature and rainfall in an Ugandan lake (East Africa). Morrill and others (2005) modeled that when streams with already low DO experienced increased temperatures, DO levels dropped to critical levels that would threaten aquatic species. Temperature plays a large role in the DO seasonal variations. With Louisiana's extended summers, this seasonal impact on DO can be seen for much of the year.

5.4.2 Environmental Conditions Affecting Dissolved Oxygen

Naiman (1983) found that as stream order increases, DO also increases as a result of increased primary production. In this study, all streams sampled were relatively low order (1st-3rd) and there was no clear pattern of increasing DO with increasing order. Spatial variability also did not change from first to third order streams. Other studies have also found DO spatial variation (Chapman *et al*., 1998; McKinsey and Chapman, 1998); however, these variations were not exclusive of seasonality. In the Flat Creek watershed, localized conditions such as pooling, stream intermittence, and flow are far more indicative of dissolved oxygen than location in the watershed.

Localized velocity and morphology influenced DO more than the stream position in the watershed. Local stream morphology has a large effect on DO, as seen in the reduced oxygen present in pools. Distinct characterization of sites as "pool" or "non-pool" is difficult, however. Pooled sites have deep beds with low flow. There are a few sites that were classified as non-pools, but are pools during certain low water levels. For example, I4 is a pool during low water conditions, but is not a pool at other water levels. I4 also experienced the lowest DO levels among non-pool sites. Jiang and others (2007) found a summer formation of a high-nutrient, low-oxygen pool. This pool was a result of organic matter transport to that area, a long residence

time from reduced flow, and high temperature. Although this was in Cape Cod Bay, we see similar characteristics in Flat Creek.

Another local condition that can play a role in DO levels is the flow permanence. This, however, is also related to seasonality. Although perennial streams had lower dissolved oxygen than the intermittent sites, the perennial streams were the only streams with water during this summer period indicating the role seasonality plays in DO in low flowing Louisiana streams. This does not necessarily mean that these intermittent streams have poor water quality; however. Viosca (2007) found macroinvertebrate taxa (EPT taxa) that are DO sensitive and are often used as indicators for good water quality in the intermittent streams.

5.4.3 Carbon and Dissolved Oxygen

Unique characteristics such as gentle topography and high organic matter in this watershed is contributing to the seasonality of DO present in Flat Creek. Dissolved organic carbon fluxes play a critical role in terrestrial ecosystems. They interact with the biogeochemical nitrogen cycle (Qualls et al., 1991; Campbell et al., 2000), aid in pollutant transport (Kalbitz et al., 2000), and may be a major energy source for microorganisms (Tranvik, 1992). In aquatic environments, organic carbon is either consumed by the biological community, deposited in the benthic zone, or transformed into atmospheric carbon. Organic carbon from increased primary production further enhances oxygen consumption (Trefry et al., 1994). Ouyang and others (2006) related DO to various water quality parameters. They found that DO was positively related to total organic carbon. We saw a similar trend in Flat Creek (Figure 5.13) where DO decreased with decreasing TOC and vice versa. The decrease in dissolved oxygen to less than 5 mg L^{-1} began in March, a result of increasing temperature and organic carbon decomposition

present in the stream. Since decomposition of organic materials consumes oxygen. As organic matter is broken down (which is seen in the spring), oxygen will also decrease.

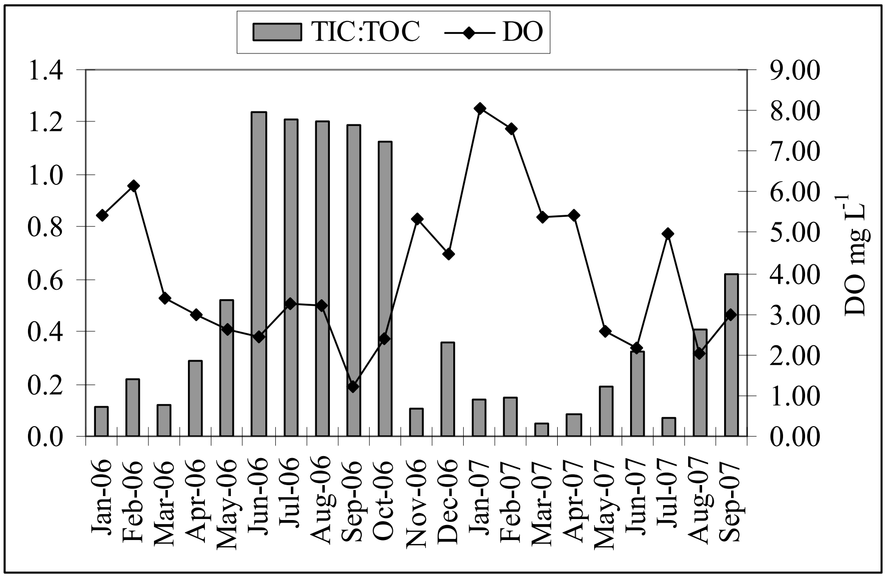

Figure 5.13. Bars represent average total inorganic carbon (TIC) to total organic carbon (TOC) ratio for all fifteen sites in the Flat Creek watershed. Points represent average dissolved oxygen for all 15 sites.

We also observed a shift in the TIC/TOC ratio from organic carbon dominance in January to inorganic carbon dominance in June. As organic carbon decreases, DO decreases indicating that respiration is occurring. Metabolism rates are seasonal and storm related (Roberts *et al.*, 2007). This period of time is also marked with reduced rain and increasing temperatures. Subtropical streams will have periods of lower DO than temperate areas. Higher rates of respiration by microorganisms are found in tropical areas (Chapman and Kramer, 1994) since there is more leaf litter supplying a carbon source. Combined with water stagnation, the increased respiration rates result in oxygen consumption and depletion.

Since rain events increase turbulence of the water bodies, a reduction in storm events will contribute to decreased DO and affect the source of carbon (organic or inorganic) available to the stream. Water levels were observed at their lowest point in the summer season, enhancing the

soil-to-water interaction and potentially increasing inorganic carbon found in the water column. With low precipitation, runoff to the stream is also reduced. Runoff is a source of organic carbon source. Carbon can also be impacted by stream morphology, as pools allow carbon to accumulate which can further decrease DO concentrations.

5.4.4 Applicability of EPA Criteria

This study showed that average DO was below the 5 mg L^{-1} water quality standard from January 2006 to September 2007 at nine of the fifteen sites sampled in the Flat Creek watershed. Average dissolved oxygen levels met state standards for only seven out of the twenty-one months sampled (January, February, November 2006, and January-April 2007), in which water temperatures were also below 15^{o}C (59^{o}F). Based on our observations it is proposed that a DO concentration of 5 mg L^{-1} is not achievable even for natural, undisturbed watersheds in Louisiana. The sampled sites, although they are not in pristine or primary forests, have not been fully harvested in nearly 10 years. In a review of forestry BMP studies in the southeast United States, Aust and Blinn (2004) found that most harvested sites recover within five years. Considering that the sites are in a rural forested area, these streams are experiencing near natural conditions and are not being heavily influenced by land use changes.

The goal of Louisiana Department of Environmental Quality is to determine the "best attainable criteria" (LDEQ, 2006). In our study, changes in DO concentrations were most likely affected by seasonality and therefore the TMDL applied to this area and similar areas in Louisiana should be adjusted accordingly to account for seasonal load allocations for DO. A more achievable goal is 3 mg L^{-1} in the summer months. All sites measured except for one heavily impacted by beaver dams would meet this criteria. With Louisiana's subtropical climate, the summer extends beyond the traditional three month season. With an impractical water

quality standard established in the TMDL, it is difficult to regulate land use changes, and to determine if Forestry Best Management Practices are working effectively.

5.5 Conclusions

This study shows that a subtropical watershed with low flow, high organic material, and long periods of high temperatures is particularly vulnerable to dissolved oxygen levels below standards necessary for stream biological health. The availability of organic carbon in the spring time encourages an environment for metabolic activity resulting in decreasing oxygen availability in the spring and summer. Localized environmental conditions such as the hydrologic regime, stream morphology and permanence are indicative of dissolved oxygen levels and can support water quality surveys. Due to this natural vulnerability and DO levels in some cases are already dangerously low, it is important to monitor water quality during land use changes. TMDLs are often used to track changes in a water body during land use changes; however, established water quality standards must adequately address natural conditions and properly protect or improve existing water quality. In the Flat Creek watershed, a dissolved oxygen TMDL of 3 mg L^{-1} from May-October and a 5 mg L^{-1} criterion during the remaining months is a practical standard that would still protect overall water quality while making a manageable, enforceable standard.

CHAPTER 6: SUMMARY

This study was conducted in a low gradient, subtropical watershed in central Louisiana during the period from December 2005 to September 2007. The watershed is predominantly forested with minimal agricultural and urban land use. The study aimed to investigate stream chemistry conditions in this landscape, widely representative of the Northern Gulf Coastal plain in the United States. Four questions organized this research: (1) What are the natural conditions of nutrients in headwater streams of a low-land watershed, especially as it relates to EPA suggested criteria? (2) Does stream carbon change quantitatively and qualitatively during a year in the headwaters, especially with respect to its relationship with nitrogen and phosphorus dynamics? (3) How does the low-gradient, low-flow condition affect dissolved oxygen levels in these headwaters, and how is the effect related with stream organic matter and temperature conditions? (4) What is the quantity of nutrients and carbon exports from this low-order watershed? Major findings from this research are summarized below.

The streams in the Flat Creek watershed showed a concentration of total phosphorus varying from 0.042 to 0.131 mg L^{-1}, which fall into the range between the 25th and medium percentiles of total phosphorus in the streams and rivers of the United States. Although total phosphorus was within EPA's suggested criteria for this ecoregion, the P25 of 0.05 mg L^{-1} was not met fifteen of the twenty-two months sampled. November 2006 to April 2007 marked total phosphorus concentrations at or below the EPA's limit. Even during storm events in which an increase of runoff and thus excess nutrient transport is expected, TP concentrations were lower than monthly sampling events. There were, however, high nitrate concentrations found in Flat Creek relative to the EPA proposed P25. Nitrate/nitrite was controlled by storm events and organic carbon in streams. Concentrations exceeded the P25 (0.067 mg L^{-1}) set forth by the EPA

with an average nitrate/nitrite concentration of 0.272 mg L^{-1} to 0.576 mg L^{-1}. Although nitrate/nitrite concentrations were within the range measured by the EPA (this was a very wide range), the P25 was lower than the detection limit in this study. Despite this, measurements were frequently measurable, thus above the P25. This is important since the P25 is usually the number used to develop TMDLs. A TMDL as low as the P25 would not be attainable for Flat Creek. A TMDL as a "probability of occurrence" would be more effective than a definitive concentration.

Carbon measured in this study showed interesting patterns of increased organic carbon in the spring with increased inorganic carbon in the summer. This decrease in organic carbon reflects that there is biological activity in the spring that is consuming organic carbon in addition to oxygen. High inorganic carbon in the summer (peak of 13.2 mg L^{-1}) reflects the lack of organic matter input during the summer. Carbon transport in the Flat Creek watershed is dominated by organic carbon. Higher loading occurred at the outlet than the two headwater sites; however, when considering the drainage area, the headwater site on Spring Creek has higher carbon flux due to its small size. Currently carbon analysis, organic or inorganic, is typically not used in regular water quality monitoring programs. Although there has been research on carbon dynamics, using carbon in water quality monitoring programs is rare. Carbon can affect nitrification in streams indicating the potential importance of measuring carbon in streams. In this study we saw that organic carbon in the spring has some impact on nitrate/nitrite concentrations. Spring nitrate/nitrite measured at or near detection limits (0.3 mg L^{-1}). Carbon in streams, especially headwater streams, tends to reflect neighboring land use through surface runoff, making it a valuable parameter to understand. Considering its relationship with nitrogen, a popular indicator for eutrophication and general water quality, carbon monitoring may be a beneficial support indicator for water quality. Furthermore, this research found a high carbon

export (1.28 kg ha $^{-1}$ mon^{-1}) from Flat Creek, implying the importance of assessing carbon transport in headwater streams.

Localized environmental conditions such as stream velocity and morphology are more indicative of dissolved oxygen levels than location within the watershed. Despite this, dissolved oxygen is impacted largely by seasonality and temperature. Oxygen depletion in the early summer is partially a result of organic carbon consumption. After this period of oxygen consumption, characteristics such as high water temperature and low flow further reduces oxygen levels to less than 5 mg L^{-1}. It is evident the Flat Creek watershed is not fully meeting standards by the EPA. With dissolved oxygen below 5 mg L^{-1} for much of the year, the high organic matter and low flow is clearly effecting water quality. This is arguably a natural condition since the major land use is forestry. Forestry land use usually has the lowest incidence of nutrient runoff. Although TMDLs are usually specific to ecoregions, ecoregions are wide classifications that can have a variety of localized environmental conditions. More refined ecoregions would help in having more realistic standards for such areas as Flat Creek. These refined ecoregions in Louisiana have been proposed by Louisiana Department of Environmental Quality for standards being developed for the state of Louisiana. Additionally, a dissolved oxygen TMDL that considers seasonality is a practical standard that would still protect overall water quality while making a manageable, enforceable standard. There are other basins in Louisiana that have already adopted this seasonal standard.

This study is only the first step in an intensive study determining the effectiveness of Louisiana's forestry best management practices. Further study into the water quality in the Flat Creek watershed during land use changes (forest clearcut) is ongoing. Also, long term, intensive

monitoring of DO at two of the sites will give further insight in the DO fluctuations during the land use changes.

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