THE SOURCES AND CYCLING OF NUTRIENTS AND DISSOLVED ORGANIC CARBON IN THE LOWER ACF BASIN AND LAKE SEMINOLE

by

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(Under the Direction of Alan Covich and Steve Opsahl)

ABSTRACT

In shallow reservoirs, the concentrations and transformations of nutrients and dissolved organic carbon (DOC) are determined by natural catchment characteristics, seasonal influences and fluctuations in hydrologic regimes. Examining the factors determining nutrient composition allows for better understanding of how systems process biologically important constituents that potentially affect downstream ecosystems. We examined the factors influencing nutrient and DOC concentrations in large rivers within the lower ACF river basin and estimated the capacity for retention and release within Lake Seminole. This study found that groundwater input and wetland flushing had more prominent effects on nutrient regimes in rivers without upstream reservoirs. Hydrologic variability and seasonal factors appear to control retention dynamics within the reservoir which generally acted as a sink for inorganic nutrients and a source for DOC. Additionally, decomposing *Hydrilla verticillata* appeared to be a source of inorganic nutrients and DOC that likely effects nutrient dynamics within Lake Seminole.

INDEX WORDS: Lake Seminole, hydrologic variability, nutrient cycling, ACF river basin, groundwater, source/sink dynamic, reservoirs, nutrient loading, *Hydrilla verticillata*, macrophyte decomposition

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TABLE OF CONTENTS

CHAPTER 1

LITERATURE REVIEW AND SUMMARY OF OBJECTIVES

Project Overview:

Aquatic ecosystems are sentinels of environmental change due to their low laying position within the landscape and integral role in linking the terrestrial and aquatic biospheres (Gergel et al. 2002, Gergel 2005, Williamson et al. 2008). Unfortunately, these systems are also highly susceptible to degradation via the effects of human impact (Randhir & Hawes 2009, Peters et al. 2008). Nutrient composition in most rivers and lakes now reflects some degree of influence from urban and agricultural change (Ngoye & Machiwa 2004). This study examines the factors responsible for determining nutrient composition in the lower Apalachicola-Chattahoochee-Flint River Basin (ACF) and the shallow, subtropical reservoir Lake Seminole. The purpose of this study was to spatially and temporally evaluate the effects different land use characteristics and hydrologic regimes would have on nutrient and dissolved organic carbon (DOC) dynamics in the lower ACF basin. Also, we strove to characterize the annual physical and chemical characteristics of Lake Seminole and estimate its annual mass balance for N, P and DOC through the creation of a nutrient and hydrologic budget. In addition, we examined the amounts of nutrients and DOC the aquatic invasive species *Hydrilla verticillata* released during decomposition under oxic and anoxic conditions. The following literature review provides a background on factors determining watershed nutrient composition, reservoir nutrient source/sink dynamics and the role of macrophytes in reservoir systems.

Overview of Lake Seminole:

Lake Seminole is a shallow, subtropical, 15,175 ha man-made reservoir located at the border of southwest Georgia and northwest Florida, within the lower Apalachicola-Chattahoochee-Flint (ACF) River Basin System in the Coastal Plain physiographic region of southeastern United States (http://www.sam.usace.army.mil/op/rec/seminole/). The construction of Lake Seminole was commissioned by the Rivers and Harbor Act of 1947 (Grodowitz et al. 2003) and it was open to the public in 1957 with the completion of the Jim Woodruff Lock and Dam (Dalton et al. 2004). The lake is owned and regulated by the United States Army Corp of Engineers and is utilized for the purposes of navigation, hydropower generation and recreation. The impoundment is situated approximately 305 m downstream of the natural confluence of the Chattahoochee and Flint Rivers and acts as the headwater source for the Apalachicola River (Frick et al. 1996). The Chattahoochee River, Flint River and the predominantly groundwater fed Spring Creek are the primary sources of inflow into the reservoir.

In the lower ACF Basin, nutrient composition is heavily influenced by different land use practices. Land cover in the ACF basin is estimated to be 5% urban, 29% agricultural, 58% forested, 5% forested wetlands and 3% water. The main sources of nutrients into the basin come from municipal water effluent, animal manure, fertilizer and atmospheric deposition (Frick et al. 1998). In 1990, approximately 2,500 tons of municipal wastewater effluent, 120,000 tons of animal manure and 82,000 tons of fertilizer was applied within the lower ACF (Frick et al. 1996). The physiography of the lower ACF basin is defined by karst features created from Ocala Limestone which mediates large inputs of groundwater from the Upper Floridian aquifer (Sever 1965, Torak et al. 1996, Dalton et al. 2004, Opsahl et al. 2007). Groundwater in the lower ACF is high in nitrate (at times up to 3500 μg/L) due to agricultural practices and is a significant source of base flow for the Flint River and Spring Creek (Katz et al. 1999, Opsahl et al. 2003, Sims & Opsahl 2007, Allums et al., submitted). The Chattahoochee River has a lower degree of groundwater influence due to less connectivity to the Upper Floridian aquifer but is more affected by urban settings.

Lake Seminole's capacity for nutrient storage and release is of particular importance within the lower ACF because Lake Seminole serves as a gateway for downstream delivery of nutrients and freshwater to the Apalachicola River and Apalachicola Bay ecosystem (Dalton et al. 2004). The Apalachicola Bay is an economically important source of shellfish with 10% of the oysters consumed in the U.S. harvested from the area. It is also provides 35% of the freshwater input into the eastern Gulf of Mexico (http://www.protectingourwater.org/watersheds/map/apalachicola/). Nutrient outflow from Lake Seminole has the potential to greatly impact the Apalachicola ecosystem and therefore, better understanding of the differences in nutrient and DOC sources from the ACF watershed and of Lake Seminole's source/sink dynamics is important for the prevention of degradation to the Apalachicola Bay.

Submerged macrophytes can play a major role in the uptake and storage of nutrients from the water and sediment and, during senescence, can become a major source of nutrients to aquatic ecosystems. *Hydrilla verticillata*, often termed the "perfect aquatic weed", is a highly competitive invasive aquatic macrophyte. It is of great concern within the lower ACF basin and Lake Seminole because of its abundance and resistance to eradication efforts. *Hydrilla* is native to Asia and was first found in the U.S. in 1960 in Florida's Crystal River and is now found as far north as Delaware and as far west as California and Washington (Blackburn et al. 1969, Cook &

Lüönd 1982). *Hydrilla* can grow either rooted within the sediment or as free floating fragments within the water. It can elongate as much as 2.5 cm a day and branches profusely at the water surface thereby effectively intercepting light from other submerged aquatic vegetation (SAV) (Haller & Sutton 1975). *Hydrilla's* tissue is composed of about 90% water which makes it able to produce an abundance of fresh plant material from limited supplies of N, P and C (Langeland 1996). It absorbs nutrients from both the water column and from benthic sediments. It is found in a wide range of water quality conditions including areas that are oligotrophic, eutrophic, saline or with as little as 1% light (Cook & Lüönd 1982, Langeland 1996). *Hydrilla* can have a profound effect on nutrient cycling within reservoirs. Gu (2006) found that the presence of the SAV *Hydrilla verticillata* caused the rates of sedimentation to double compared to non-SAV infested waters. It also is an efficient sink for nutrients and is found to cause the highest rates P removal in comparison to other SAV (Gu 2006). *Hydrilla* also has been determined to have one of the fastest decomposition rates likely due to its highly dissected leaves (Battle & Mihuc 2000) and has been shown to lose as much as 86% of its initial biomass in a three week span (Gu 2006).

Hydrilla was first discovered in Lake Seminole in 1967 and at times, covers as much as 55% of the lake's surface (Eubanks & Morgan 2001). *Hydrilla* affects waterways by severely decreasing flow velocities, clogging river channels, machinery and boat propellers and generally decreasing the recreational qualities of a water body. A variety of techniques, including chemical, biological and mechanical efforts, have been used in an attempt to eradicate *Hydrilla* from Lake Seminole. In 1990, Hydrilla flies (*Hydrellia pakistanae),* which feed on and tunnel through the plant's leaves, were released around the impoundment (Grodowitz et al. 2003). The fly's impact remained low until 1999 when large-scale reductions were observed in many areas of the reservoir indicating that the flies did play a major role in controlling growth. In 1998, the Army Corp of Engineers created the Hydrilla Action Plan which had the objectives of controlling the plant at priority areas, reducing its cover to less than 40% of the lake and restoring native plant communities (Grodowitz et al. 2003). To achieve these goals, the Corp introduced sterile triploid grass carp (*Ctenopharyngodon idella X Aristichthys nobilis*), which are known to consume large quantities of *Hydrilla*, in small areas surrounded by electric barriers. They grass carp proved to be effective at localized *Hydrilla* reduction (Eubanks & Morgan 2001). They also began to apply low doses (10-15 µg/L) of the herbicide Fluridone in the Spring Creek arm of the lake with results ranging from no effect with significant *Hydrilla* re-growth to areas of excellent control where the plant was reduced from 89% to 47% surface water cover (Eubanks & Morgan 2001). Today, a suite of herbicides, along with biological controls such as the triploid grass carp, *Hydrilla flies* and *Hydrilla* weevils, continue to be used in attempts to control *Hydrilla* (personal communication with Donald Morgan, U.S. Army Corp).

Objectives:

This study addresses the following objectives:

Objective 1: Assess the spatial, temporal and hydrologic factors that affect nutrient concentrations within three rivers in the Apalachicola-Chattahoochee-Flint (ACF) river basin.

Objective 2: Characterize the annual physical and chemical characteristics of the Lake Seminole and estimate the annual mass balance for N, P and C through the creation of a nutrient and water budget.

Objective 3: Determine the quantities of nutrients and dissolved organic carbon released from the aquatic invasive species *Hydrilla verticillata* during decomposition.

Completing these objectives will give insight into how land use, hydrologic variability and temporal change affect C, N and P composition of three, large, adjacent watersheds. Examining the effects that passage through a shallow reservoir has on nutrient loads will demonstrate how useful a water and nutrient budget could be for forecasting nutrient and DOC storage and release and the potential consequences to downstream ecosystems. Examining the decomposition dynamics of *Hydrilla* will provide a better understanding of the effects invasive species may have on ecosystem nutrient cycling regimes.

General Literature Review:

Reservoir Nutrient Composition:

The conditions in the lower ACF reflect environmental conditions found in many other catchments. Humans have continually gravitated towards bodies of water and their presence has resulted in the slow, progressive degradation of many aquatic ecosystems (Vitousek et al. 1997, Ngoye and Machiwa 2004, Dodson et al. 2005, Weijters et al. 2009). The transition from undisturbed to human-impacted ecosystems has resulted in few river systems exhibiting "natural" conditions (Wetzel 2001, Strayer et al. 2003, Allan 2004). In 1972, the U.S. Clean Water Act (CWA) was codified with the purpose of regulating the discharge of pollutants and setting water quality standards for all releases to surface waters in the United States. However, non-point source nutrient pollution due to land alteration has continued to be a pressing ecological issue (CWA 1972, Ahn et al. 2008, Irfanullah & Moss 2008). The Environmental Protection Agency (EPA) reported in 2004 that approximately 44% of the streams, 64% of the lakes and 30% of the estuaries around the nation were impaired due to excessive nutrient loading, hydrologic modifications, urban and agricultural runoff and sewage input (EPA 2009).

Water quality and productivity, both indicators of aquatic ecosystem health, are largely controlled by the quality and quantity of nutrients entering the ecosystem (Wetzel 1990, Knoll et al. 2003). Aquatic ecosystems receiving continual, unregulated input of excess nutrient loads eventually exhibit decreases in water clarity and dissolved oxygen concentrations which can ultimately lead to eutrophication and the general degradation of both the ecological and economic ecosystem services the water body provides (Bosch 2008, Williamson et al. 2008). Although a several types of nutrients contribute to such problems, nitrogen and phosphorus have long been of greatest concern due to their important role in primary production (Guildford and Hecky 2000, Zhang et al. 2008). The amount of nitrogen entering waterways has increased from 15.6 Tg/yr in 1890 to 139 Tg/yr in 1990 and is expected to exceed 270 Tg/yr by 2050 as a result of changing agricultural practices (Schaefer & Alber 2007). Phosphorus entering waterways has increased 2.5 to 5-fold in the last 50 years as a consequence of chemical fertilizers, application of animal manure and disposal of raw and treated human waste (Van Herpe & Troch 2000, Schaefer & Alber 2007, Williamson et al. 2008). Today, densely developed areas are positively associated with elevated concentrations of nitrogen and phosphorus (Carpenter et al. 1998, Gergel et al. 2002, Fraterrigo & Downing 2008). Strong relationships existing between urban centers and high fluxes of phosphorus and nitrogen while agricultural lands are associated with increased nitrogen export (Johnson et al. 1997, Vitousek at al. 1997, Aurbuckle & Downing 2001).

Nutrient inputs from watersheds are also influenced by the hydrology and physical characteristics of the catchment (Migliaccio et al. 2007, Li et al. 2008, Fraterrigo & Downing 2008). Hydrology is the primary controller of the linkage between catchment characteristics and water quality dynamics (Johnson et al. 1997) and acts as a critical determinant of the quantity, quality and rate of nutrients delivered into the system. Variations in hydrologic regimes, such as shifts drought to flood conditions, result in a change in the primary transport mechanism for nutrient input into the receiving water (Meixner et al. 2007, Rodriguez-Blanco et al. 2009). Under base-flow conditions, the majority of nutrients are delivered from either upstream surface inflow or, in karst environments, via input from groundwater. Conversely, during high flows, hydrologic controls such as surface runoff and drainage often become the dominate mechanism for nutrient input (Burns et al. 2001, Ocampo et al. 2006, Torak et al. 1996).

Reservoirs as sources and sinks for nutrients:

Reservoirs play an important role in storing and processing nutrient, sediment and organic matter loads due to their large volume, cumulative nature and transitionary location within the river continuum (Stanley & Doyle 2002, Tomaszek & Koszelnik 2003, Ahn et al. 2008, Fraterrigo & Downing 2008). Globally, reservoirs have caused a 700% increase in the standing stock of nutrients by delaying nutrient movement downstream. The amount of water globally held by reservoirs has increased seven fold in the last 40 years (Górniak et al. 2002). Large reservoirs are hot-spots for biogeochemical processes such as denitrification, sedimentation and primary production because of their long residence time, relative to rivers and streams (Harrison et al. 2009). Harrison et al (2009) estimated that these processes cause reservoirs to remove roughly 19.7 Tg/yr of nitrogen, slightly less than a third of the N believed to enter freshwater systems globally every year. The extent to which reservoirs will retain or release nutrients is highly contingent upon the physical characteristics of the reservoir (size, location, depth, water residence time) as well as hydrologic variability, quantity of nutrient loading, abundance of macrophytes and rates of seasonal biological processing (Barko et al. 1988, Shardendu & Ambasht 1991).

Both hydrologic variability and seasonality control the source/sink dynamics within reservoirs. Hydrology determines the rates of sedimentation and nutrient export by altering the natural water residence time of the reservoir (Hillbricht-Ilkowska 1999, Fraterrigo & Downing 2008, Vanni et al. 2001). Studies have documented that floods are one of the most important influences on TN and TP retention and cause the greatest amounts of N and P export (Mhamdi et al. 2007, Irfanullah & Moss 2008, Spieles & Mitsch 2000). Fluctuations from relatively stable low-flow conditions to high flows can decrease the amount of time available for in-reservoir processing and cause resuspension of nutrients trapped within sediment, particularly in shallow reservoir where the sediment layer is easily disturbed when water and wind velocities are high (Trojanowski & Trojanowska 2007, Sobota et al. 2009, Stanley & Doyle 2002).

Seasonal trends, particularly higher temperatures characteristic of the summer season, mediate biological nutrient and carbon fluxes in reservoirs by increasing rates of denitrification and nutrient assimilation by aquatic organisms and macrophytes (Bosch 2008, Lijklema 1994). During the summer, as much as 60% of the NO_3^- imported into reservoirs can be retained because of denitrification (Spieles & Mitsch 2000). Large beds of macrophytes cause nutrient retention by slowing water velocity which promotes sedimentation (Schulz et al. 2003, Sollie & Verhoeven 2008) and the assimilation of large quantities of nutrients into their biomass (Clarke 2002). High temperature can also cause nutrient release by creating anoxic conditions which activates internal P loading in deeper areas of the reservoir (Hillbricht-Ilkowska 1999). The end of the optimal growing season also marks the beginning of another seasonal pulse in which macrophyte decomposition releases nutrients and organic matter back into the ecosystem (Asaeda et al. 2000, Tomaszek & Koszelnik 2003).

Submerged aquatic macrophytes as sources and sinks of nutrients in shallow reservoirs:

Submerged aquatic vegetation (SAV) is an integral part of lentic ecosystems and these plants are considered “biological engineers” because of their influence on the structure, functioning and biogeochemical processes that occur within these habitats (Sand-Jensen et al. 1989, Clarke 2002). In shallow reservoirs, aquatic macrophytes are thought to be responsible for maintaining a clear water state and high water quality through their ability to store nutrients (Takamura et al. 2003, Sollie & Verhoeven 2008). Macrophytes have a significant effect on flow dynamics in shallow lentic systems. Large beds of macrophytes decrease water velocity, increase water residence time and affect rates and patterns of sedimentation by acting as filters and traps for suspended particulate inorganic and organic material (Kufel & Kufel 2002, Knight et al. 2003, Clarke 2002, Schulz et al. 2003). Aquatic macrophytes also affect other physical and chemical parameters of their surrounding waters by altering the availability of dissolved oxygen (DO), light and temperature within the water column (Carter et al. 1991, Titus et al. 2004). Biomass of SAV beds affects the vertical and horizontal distribution of DO in the water column, with concentrations of DO fluctuating in patterns that follow daily and seasonal SAV photosynthesis, respiration and decomposition (Asaeda et al. 2000, Titus et al. 2004).

Macrophytes act as short-term sinks for nitrogen and phosphorus by incorporating these nutrients into their biomass (Kufel & Kufel 2002, Chimney & Pietro 2006). Rooted SAV incorporates nutrients from both the sediment and water column (Asaeda et al. 2000, Clarke 2002, Xie et al. 2004) and, at times, displays “luxury consumption” in which they continually take up N and P even though they have a sufficient amount of nutrients for survival (Kistritz 1978, Demars & Edwards 2007). Biomass, seasonality and environmental variable such as light, temperature and nutrient availability are important factors in determining the nutrient uptake and retention ability of SAV in reservoirs (Pietro et al. 2006, Sollie & Verhoeven 2008). Macrophytes show strong temporal patterns of nutrient uptake and retention starting in the spring growing season, reaching a maximum in the summer and then decreasing during the fall and winter dieback (Kufel & Kufel 2002, Clarke 2002). Howard-Williams (1985) found that plants could assimilate between 900-1500 mg/day of N while denitrification could only remove between 1-80 mg/day. SAV removal of P has been shown to range from between 0 to 7.1 g/day (Knight et al. 2003).

Macrophytes act as sources of nutrients during periods of decay (Park & Cho 2003, Titus et al. 2004, Xie et al. 2004). SAV decomposition is a complex process involving leaching, microbial decay and fragmentation triggered by physical, chemical and microbial processes in the water (Battle & Mihuc 2000, Park & Cho 2003). Plant biomass usually begins to decompose during the late summer and early resulting in nutrients and dissolved organic matter being leached out and released back into the water column (Carpenter 1980, Wetzel 1990, Chimney & Pietro 2006). The quantity of nutrients and DOC released from dying plants can be a considerable source of input for reservoirs (Landers 1982, Asaeda et al. 2000).

Prospectus:

This thesis is divided into three separate studies: Chapter 2) a spatial and temporal evaluation of the effects that different land use characteristics and hydrologic regimes have on nutrient and dissolved organic carbon (DOC), Chapter 3) the annual physical and chemical characteristics of the shallow, subtropical reservoir Lake Seminole and its annual mass balance for N, P and DOC and Chapter 4) the effects that oxic and anoxic environments have on the decomposition of *Hydrilla verticillata*. Chapter 2 is presented in manuscript format, as prepared for submission to the Journal of Environmental Quality. Chapter 3 is presented in manuscript format, as prepared for submission to Hydrobiologia. Chapter 4 is presented in manuscript format, as prepared for submission to Aquatic Botany. Chapter 5 presents a summary and conclusions of these studies.

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CHAPTER 2:

NUTRIENT AND DISSOLVED ORGANIC CARBON CONCENTRATIONS AMONG MAJOR RIVERS WITHIN THE APALACHICOLA-CHATTAHOOCHEE-FLINT (ACF) WATERSHED: THE EFFECTS OF CHANGING FLOW DYNAMICS[1]

[1] McEntire, J.M., S. P. Opsahl, A.P. Covich, S. Wilde and T. Rasmussen. To be submitted to *Hydrobiologia*.

Abstract:

This study examined how different catchment characteristics and hydrologic regimes influenced nutrient and dissolved organic carbon (DOC) dynamics in the three rivers (Chattahoochee River, Flint River and Spring Creek) that discharge into Lake Seminole and how these inflows compare with the outflow from the lake, the Apalachicola River. Lake Seminole is a large, shallow, subtropical reservoir with a short residence time that is affected by the combination of flows from three inflowing rivers. Over an annual cycle, we observed significant differences in mean annual nutrient concentrations among rivers including higher concentrations of NH_4^+ and lower NO_3^- in the Chattahoochee River and higher TN and NO_3^- concentrations in the Flint River and Spring Creek which reflect the major differences in land uses within the drainage basins. TN and NO_3^- were negatively correlated with discharge in the Flint River and Spring Creek, a pattern consistent with dilution of NO_3^- rich ground water by surface runoff during higher flows. Although the Chattahoochee watershed passes through large urban centers, we did not observe higher PO_4^- levels. Instead, the relatively low PO_4^- concentrations in the Chattahoochee River may be due to the presence of large upstream reservoirs which effectively serve as sinks for PO_4^-. Organic matter transported within the Flint River and Spring Creek appeared to reflect the flushing of regional wetlands during high flows and a dilution of DOC by ground water during low flows. In contrast, DOC concentrations in the Chattahoochee River did not correlate with discharge suggesting reduced interactions with flood plains or the influence of increased water residence time in multiple upstream reservoirs. The Apalachicola River was most similar in chemical composition to the Chattahoochee River.

Introduction:

Hydrologic dynamics play a crucial role in determining the linkages between catchment characteristics and water quality and these connections are altered by natural controls and human land use (Johnson et al. 1997, Burt & Pinay 2005, Bracken & Croke 2007, Green et al. 2007, Le Maitre et al. 2007). Flow regimes in natural ecosystems are characterized by free flowing rivers and streams with variations in high and low discharges resulting in interactions between the river and floodplain (Poff et al. 1997, Lytle & Poff 2004). Anthropogenic changes such as the creation of dams, diverting water for human consumption and modifications to surface topography alters the natural flow regime of the system by changing the transport mechanisms, timing and concentration of nutrients flowing through a watershed (Bovee & Scott 2002, Magilligan & Nislow 2005, Fraterrigo & Dowing 2008, Sobota et al. 2009).

Variation in hydrologic regimes result in changes in the primary transport mechanisms for nutrient input into the receiving water by altering the hydrologic flow paths of the nutrients (Novotny 2002, Inamdar & Mitchell 2007, Meixner et al. 2007, Rodriguez-Blanco et al. 2009). In karst terrains such as those found in the Coastal Plain region of southwest Georgia, groundwater is often the largest source of nutrient delivery under base flow conditions, but under high flow conditions, surface runoff becomes the primary mechanisms for nutrient input (Burns et al. 2001, Ocampo et al. 2006, Torak & Painter 2006, Rodriguez-Blanco et al. 2009). Surface runoff during storm events displays a "flashy" response capable of mobilizing high loads of nutrients that have accumulated in the landscape and delivers them to rivers and lakes (Meyer et al. 2005, Walsh et al. 2005, Rosenzweig et al. 2008).

Flood events alter the concentrations of nitrogen, phosphorus and dissolved organic carbon (DOC) observed during base flow and drought conditions due to greater hydrologic connectivity between streams and the surrounding landscape (Novak et al. 2003, Hook & Yeakley 2005, Inamdar 2007, Meixner et al. 2007). Rosenzweig et al (2008) reported that during floods the greater degree of hydrology-landscape interaction was the most important factor controlling nutrient export. Prior studies have documented increased concentrations of phosphorus in runoff from erosion and soil leaching (Novak et al. 2003). Nitrogen dynamics in karst terrains often show initial decreases resulting from the dilution of nitrogen-rich waters followed by increases in concentrations of nitrogen as higher proportions of groundwater return (Buffam et al. 2001, Salvia-Castellvi et al. 2005, Rodriguez-Blanco et al. 2009). DOC concentrations increase during high-flow events as a result of floodplain and wetland flushing (Correll et al. 1999, Golladay & Battle 2002, Hook & Yeakley 2005, Inamdar & Mitchell 2007, Rosenzweig et al. 2008).

The objective of this research was to spatially and temporally evaluate the effect that different land use characteristics and hydrologic regimes impart on nutrient and dissolved organic carbon (DOC) dynamics in the lower Apalachicola-Chattahoochee-Flint (ACF) Basin. Sampling was conducted at the base of the three major watersheds (Chattahoochee River, Flint River, and Spring Creek) before confluence at Lake Seminole to capture an integrated representation of each watershed. The Apalachicola River, the outflow of Lake Seminole, was sampled for comparison to its upstream inflows. We hypothesized that C, N and P concentrations in the lake relative to the three inflowing rivers would be affected in different ways due to the effects of the lake on nutrient uptake and processing.

Methods:

Study Area:

The ACF river basin drains an area of 51,800 km^2 from the Blue Ridge, Piedmont and Coastal Plain physiographic provinces and is located within Georgia, eastern Alabama and north Florida (Frick et al. 1998) (Figure 2.1). The Chattahoochee River and the Flint River are the predominate waterways within the system and converge to form Lake Seminole. Lake Seminole's outflow from the Jim Woodruff Lock and Dam creates the headwater source for the Apalachicola River (Frick et al. 1996). Lake Seminole also receives inflow from a third tributary, the predominantly ground water-fed stream Spring Creek. The lower ACF is situated within the Coastal Plain province in the Fall Line Hills and Dougherty Plain districts. The physiography of the area is defined by karst features created from Ocala Limestone (Dalton et al. 2004, Opsahl et al. 2007). The presence of these features allows for large amounts of internal drainage and surface water/groundwater interactions to occur within the system. The groundwater in the area comes directly from the Upper Floridian aquifer (Sever 1965, Torak et al. 1996, Dalton et al. 2004). The Flint River and Spring Creek receive a large amount of their base flow from the Upper Floridian aquifer.

Land cover in the ACF basin is estimated to be 5% urban, 29% agricultural, 58% forested, 5% forested wetlands and 3% water. The main sources of nutrients into the basin come from municipal water effluent, animal manure, fertilizer and atmospheric deposition (Frick et al. 1998) (Table 2.1). There is a high degree of variability in land use practices among the three major riverine input sources. While the Chattahoochee and Flint rivers have similar geological history and climate, they differ greatly in their distributions of human populations and land-use, as well as the number of dams, sewage treatment discharges and hydrological variability.

Flowing through Metropolitan Atlanta and Columbus, Georgia, the Chattahoochee has the highest density of urbanization at 34%, expected to rise to 60% by 2030 (Frick et al. 1996, Frick et al. 1998). The river also receives large amounts of wastewater inflow from 22 sewage treatment plants along its length. The Chattahoochee has four large storage reservoirs and nine low storage “run-of-the-river” reservoirs. The Flint River has only two “run-of-the-river” reservoirs and Spring Creek’s flow is unimpeded (Frick et al. 1996, Abbott 2005). Agricultural practices account for 49% of the land use in the lower ACF and are predominantly located around the Flint River and Spring Creek corridors (Frick et al. 1996). Spring Creek has only 1.2% urban development along its banks (Frick et al. 1996).

Field Collection and Sample Analysis:

We selected seven sample sites within the lower Apalachicola-Chattahoochee-Flint (ACF) river basin along the Chattahoochee, Flint and Apalachicola rivers and Spring Creek. Surface water grab samples were collected on a bi-monthly basis from May 2008 until September 2008 and on a monthly basis from October 2008 until May 2009. Two sample locations, one upstream and one downstream, were chosen on the Chattahoochee River, Flint River and Spring Creek (Figure 2.1). These sites were selected in order to capture river inflow and river/reservoir transition zones for each of the incoming rivers. Immediately prior to sampling, physical parameter profiles including pH, temperature, dissolved oxygen, % dissolved oxygen, specific conductivity and salinity were taken using a Hach Quanta Hydrolab. Near surface water samples were taken in triplicate in acid-washed polycarbonate 1L bottles that had been rinsed once with river water.

Samples were packed in ice, returned to the Joseph Jones Center and filtered through 0.7 μm glass fiber filters within a 48-hour period. Dissolved organic carbon (DOC) samples were analyzed using a Shimadzu TOC-5050 analyzer. Samples of ammonium (NH_4^+) (Lachat Method 10-107-06-1-G), nitrate (NO_3^-) (Lachat Method 10-107-06-1-B) and phosphate (PO_4^-) (Lachat Method 10-115-01-B) were analyzed on a dual channel Lachat Quick Chem 8000. Total nitrogen (TN) (Lachat Method 10-107-04-1-B) and total phosphorus (TP) (Lachat Method 10-115-01-B) were analyzed on filtered and unfiltered samples following digestion by the Johnes & Heathwaite (1992) method. A CEM MDS-2000 microwave was used to perform the digestions. Dissolved organic nitrogen (DON) and phosphorus (DOP) were calculated as the difference between filtered TN and TP and filtered DIN and DIP. Particulate nitrogen and phosphorus (PN and PP) were calculated as the difference between filtered TN and TP and unfiltered TN and TP and the concentrations include both organic and inorganic nutrients. The detection limit for TN/NO_3^- was 2 µg/L, TP/PO_4^- was 3 µg/L, NH_4^+ was 3 µg/L and DOC was 0.1 mg/L.

The one-year flood recurrence interval discharge was calculated using the largest discharge for each year of record to determine when flood events occurred. Discharge data for each river were obtained from USGS gage stations 02343801, 02358000, 02356000 and 02357150. The recurrence interval (T in years) was calculated:

$$T = (n + 1) / N$$

were *n* is the number of years of record and N is the rank of the particular event (Knighton 1998). If the average discharge during the sampling date was greater than the one-year flood recurrence interval discharge, that date was considered a high-flow event. If the flow was lower than the recurrence interval on the sampling date, that period was considered stable conditions.

Data Analysis:

Statistical analyses were performed using the SigmaPlot 11.0 feature SigmaStats (San Jose, CA). Principal component analysis (PCA) using PC-ORD 4.0 (Gleneden Beach, OR) was performed as an exploratory tool to visualize broad trends in the data. The results from the ordination were interpreted on two axes and examined by designating each watershed with a different symbol and then looking to see if differences between the watersheds were apparent. Based on the results of the PCA, mean values were compared to determine the significance of nutrient concentrations and physical parameters among and within the rivers. Prior to analysis, each nutrient constituent at every sample site was tested to see if the assumptions of normality and homogeneity of variance were met using a Shapiro-Wilk test. Not all of the constituents at each sample sites met the assumptions of normality so a non-parametric one-way analysis of variance (ANOVA) was performed using the Kruskal-Wallis ANOVA on ranks. Significant ANOVAs were followed by Dunn's Method multiple comparisons procedure to determine significant differences between the rivers and river/location interactions. Linear regressions were performed to assess the relationship between nutrient concentration and discharge.

Results:

Hydrology:

Distinct differences in hydrologic conditions were observed during the study period (05/15/2008- 05/15/2009) (Figure 2.2). The Chattahoochee River's annual mean discharge was 247 m^3s^{-1} with an annual low flow of 22 m^3s^{-1} on 07/06/08. The Flint River's annual mean discharge was 204 m^3s^{-1} with an annual low of 49 m^3s^{-1} on 08/11/08. Spring Creek's had an annual mean discharge of 18 m^3s^{-1} with an annual low of 3 m^3s^{-1} on 08/22/08. The Apalachicola River's annual mean discharge (536 m^3s^{-1}) and lowest annual flow (135 m^3s^{-1} on 10/07/08) were slightly higher than the combined average of the three tributaries due to additional groundwater inputs and ungaged runoff contributions in the vicinity of Lake Seminole.

The hydrology of each river responded rapidly to the effects of increased precipitation, showing three distinctive peak discharges following large-rain events. Tropical Storm Fay deposited 42 cm of rain in the southwestern region of Georgia making August 2008 the wettest on record (previously 40 cm in 1977) (http://www.srh.noaa.gov/tlh/climate/2008review.php). During Tropical Storm Fay (Event 1), the high flow (based on results of the recurrence interval data), had peak flows of; 858 m^3s^{-1} in the Chattahoochee; 373.7 m^3s^{-1} in the Flint; and 1194 m^3s^{-1} in the Apalachicola River. Two other major storm events occurred in mid-December 2008 with 16.3cm of rainfall and in late March and early April with 32.3cm of rainfall (GAEMN http://www.griffin.uga.edu/aemn/cgi-bin/AEMN.pl?site=FLSN&report=rf). During the December high flow event (Event 2), peak flows were: the Chattahoochee with 1614 m^3s^{-1}, the Flint with 792.8 m^3s^{-1}; and 2330.4 m^3s^{-1} in the Apalachicola River. The March-April high flow event (Event 3), had peak flows of: 3341.3 m^3s^{-1} in the Chattahoochee; 1803.7 m^3s^{-1} in the Flint; and 3624.5 m^3s^{-1} in the Apalachicola. No data were available for Spring Creek during these high flow events due to the creek overflowing its banks and becoming un-measureable (personal communication, 2009 with Brian McCallum USGS Georgia Water Science Center).

Physical Parameters:

The highest mean annual temperatures were recorded in the Flint River (23.6°C) and the lowest mean annual temperatures occurred in Spring Creek (20.3°C) (Table 2.2) although the differences were not statistically significant (ANOVA, $p = 0.366$). The highest annual mean concentration of DO was observed in the Flint River at the FLINT DOWN location (7.6 mg/L) and the lowest in Spring Creek at the SPRING DOWN location (6.1 mg/L) and these differences were found to be significant (ANOVA, $p = 0.022$). The Flint River had the highest mean annual pH (7.9) and the Chattahoochee River had the lowest mean annual pH (7.4). There was a significant difference in pH between the CHAT DOWN location and all other river locations (ANOVA, p = <0.001). There was a significant difference in conductivity between both Spring Creek locations and the other rivers, excluding the FLINT DOWN site (ANOVA, p<0.0001). The highest conductivity was in Spring Creek (0.219 mS/cm) and the lowest in the Chattahoochee River (0.126 mS/cm). Only near surface (0.5 m) physical parameter data were reported because the parameters from the downstream full depth profiles varied minimally indicating that the rivers at all sites were well mixed at the reservoir-river transition sites.

Multivariate Analysis of Nutrient and DOC concentrations:

The first two axes of the PCA explained 54% of the variation in the data. Points within the ordination biplot represent watersheds and nutrient sample data scores (Figure 2.3). The vectors within the biplot represent the importance of the nutrient constituent in explaining variability in the analysis with longer vectors indicating greater importance and the proximity of the vector to the axis indicating correlations with the principal components. In this study, NO_3^- and TN were strongly positively correlated with Axis 1 while PO_4^-, TP, DOP, DON, DOC and PP were negatively correlated with Axis 1. NH_4^+ was positively correlated with Axis 2 and PN was negatively correlated with Axis 2. Both Spring Creek and Flint River locations trended to be associated with TN and NO_3^- on Axis 1 while the Chattahoochee River sites appeared to associate with the phosphorus constituents on Axis 1. The Apalachicola River and Chattahoochee River trended to associate with NH_4^+ concentrations on Axis 2. The Flint River, particularly the FLINT DOWN location, trended to associate with PN on Axis 2.

Annual Average Nutrient Concentrations:

The highest annual mean concentrations of TN were observed at the SPRING DOWN (2011.8 µg/L) and SPRING UP (1513.5 µg/L) locations (Figure 2.4A). Both Spring Creek locations were significantly different from the Chattahoochee River locations and the Apalachicola River (ANOVA, $p = <0.001$) but were not significantly different than the Flint River locations (ANOVA, $p = >0.05$). Annual mean TN concentrations in the Chattahoochee and Apalachicola Rivers were not significantly different (ANOVA, $p = <0.001$). The lowest annual mean concentration of TN was 713.9 μg/L at the CHAT DOWN site.

NO_3^- represented the majority of the TN present at all locations. The highest annual mean concentrations of NO_3^- were observed at SPRING DOWN (1708.7 μg/L) and SPRING UP (1257.4 μg/L). The Spring Creek locations were significantly different from the Chattahoochee and Apalachicola Rivers (ANOVA, $p = >0.05$) but not from the Flint River (ANOVA, $p = <0.001$). The concentrations of NO_3^- in the Chattahoochee and Apalachicola Rivers were not significantly different (ANOVA, $p = >0.05$) and the annual mean concentrations were similar. The lowest observed annual mean concentration of NO_3^- was 388.6 μg/L at the CHAT DOWN site.

Average annual dissolved organic nitrogen (DON) ranged from 200 to 279 μg/L and varied minimally between the sites (Figure 2.4A). DON was not found to be significant among rivers (ANOVA, $p = >0.05$). NH_4^+ and particulate nitrogen (PN) were the least abundant forms of N. Average annual NH_4^+ concentrations ranged from 9.8 to 46 μg/L. In contrast to nitrate, NH_4^+ in the Apalachicola River and the Chattahoochee was significantly higher than in the Flint River (ANOVA, $p = <0.0001$). There was not a significant difference in NH_4^+ between the Chattahoochee River and Apalachicola River (ANOVA, $p = >0.05$). PN ranged from 59 to 272 μg/L with no significant difference among the rivers (ANOVA, $p = >0.05$).

The mean concentrations of TP ranged from a low of 11.5 μg/L at SPRING DOWN to a high of 31.6 μg/L at CHAT UP (Figure 2.4B). Significant differences were observed between both Chattahoochee River locations and both Spring Creek (ANOVA, $p = <0.001$) but no differences were observed among any of the Chattahoochee and Flint or Apalachicola River locations (ANOVA, $p = >0.05$). There was no significant difference between the FLINT DOWN and Spring Creek locations or between the SPRING UP location and the Apalachicola River (ANOVA, $p = >0.05$). PO_4^- accounted for the majority of the TP but average concentrations remained relatively low, varying from 5.3 µg/L at SPRING DOWN to 11 µg/L at CHAT DOWN. There was no significant difference in PO_4^- between the Flint, Chattahoochee and Apalachicola rivers (ANOVA, $p = >0.05$) but there was a difference between the FLINT UP and CHAT UP sites and Spring Creek (ANOVA, $p = <0.001$). Dissolved organic phosphorus concentrations were similar to PO_4^- concentrations and ranged from 5.8 to 9.1 µg/L over the course of the study period. There was no significant difference in DOP among the rivers (ANOVA, $p = >0.05$). Particulate phosphorus (PP) ranged from 3.7 µg/L in Spring Creek to 13.1 µg/L in the Chattahoochee River. There was not a significant difference in PP among Flint, Chattahoochee and Apalachicola rivers (ANOVA, $p = >0.05$) but there was a difference between the Spring Creek locations and the Chattahoochee and Apalachicola Rivers (ANOVA, $p = <0.001$).

The average annual concentrations of dissolved organic carbon (DOC) ranged from 3.0 mg/L at SPRING DOWN to 5.0 mg/L at CHAT DOWN (Figure 2.4C). Statistical analysis indicated that the only significant differences in average annual DOC concentrations were between the Chattahoochee River locations and SPRING DOWN (ANOVA, $p = <0.001$).

Temporal Patterns of Nutrient Concentrations:

Almost all nitrogen constituents in each river showed substantial temporal variability during periods of relatively stable flow conditions (May through September 2008) as well as during high flows (Figure 2.5). NO_3^- ranged from (149 μg/L to 2135 μg/L in Spring Creek, 283 μg/L to 1463 μg/L in the Flint River, 119 μg/L to 666 μg/L in the Apalachicola River and 94 μg/L to 651 μg/L in the Chattahoochee River). In the Flint River and Spring Creek, significant negative relationships between discharge and NO_3^- concentration were observed (Flint River $r^2 = 0.65$, $p = 0.001$, Spring Creek $r^2 = 0.33$, $p = 0.013$) (Table 2.3). DON in the Flint River ranged from 35 μg/L to 424 μg/L with highest concentration occurring during high flow Event 2 with linear regression showing that there was a positive association between increasing discharge and decreasing DON concentrations ($r^2 = 0.25$, $p = 0.047$). Spring Creek had the largest DON range with the lowest concentration (BD) during May through July 2008 and the highest concentration (586 μg/L) during high flow Event 1. DON in the Chattahoochee River ranged from 128 μg/L to 441 μg/L and from 157 μg/L to 453 μg/L in the Apalachicola River but no clear temporal patterns were evident. NH_4^+ never exceeded 24 μg/L in the Flint River but ranged from 0.0 μg/L to 277 μg/L in Spring Creek. There was a positive association between NH_4^+ and increasing discharge in the Flint River ($r^2 = 0.25$, $p = 0.033$) and a negative association in Spring Creek ($r^2 = 0.24$, $p = 0.04$). However, NH_4^+ concentrations were similar in the Chattahoochee (10 μg/L to 109 μg/L) and Apalachicola Rivers (3 μg/L to 108 μg/L) with no clear relationship to discharge. Particulate nitrogen had the widest ranges in Spring Creek (BD to 2713 μg/L) and in the Flint River (BD to 1113 μg/L) but never exceeded 300 μg/L in either the Chattahoochee or Apalachicola Rivers and did not appear to be a function of discharge.

Phosphorus constituents in each river also showed substantial temporal variability during periods of both relatively stable flow (May through September 2008) and high flow conditions (Figure 2.6). PO_4^- ranged from BD to 20 μg/L in the Chattahoochee River, BD to 32 μg/L in the Flint River, BD to 33 μg/L in Spring Creek, BD to 16 μg/L in the Apalachicola River). There was a significant positive relationship between increasing flow and decreasing PO_4^- in the Apalachicola River ($r^2 = 0.78$, $p = 0.001$) (Table 2.3). However, PO_4^- did not show significant relationships with discharge at any of the other river sites. The Flint River had the largest DOP range with the lowest concentration (3 µg/L) in May 2008 and the highest (42 µg/L) during high flow Event 2 and showed a significant positive relationship with increasing flow ($r^2 = 0.44$, $p = 0.005$). Spring Creek DOP ranged from below detection to 23 µg/L during high-flow Event 2. DOP appeared to increase with increasing flow in the Flint River and Spring Creek but this increase was not found to be statistically significant. DOP ranged from BD to 18 µg/L in the Chattahoochee River and from BD to 11 µg/L in the Apalachicola River with no clear temporal pattern or relation to discharge rates. Particulate phosphorus had the widest ranges in Spring Creek (BD to 58 µg/L) and the Chattahoochee River (2 µg/L to 54 µg/L) but never exceeded 21 µg/L in either the Flint or Apalachicola Rivers and did not vary predictably relative to discharge.

DOC concentrations ranged from 2 mg/L to 11 mg/L in the Flint River, 1 mg/L to 9 mg/L on Spring Creek and between 3 mg/L to 9 mg/L on the Apalachicola River (Figure 2.7). The Chattahoochee River had the lowest range of DOC (3 mg/L to 6 mg/L) after one outliner was excluded. DOC showed minimal temporal variability during periods of stable flow conditions but exhibited large fluctuations in all rivers except the Chattahoochee River when high flows occurred. Increases in DOC coincided with high flow conditions in the Flint ($r^2 = 0.84$, $p = 0.001$) and Apalachicola Rivers ($r^2 = 0.47$, $p = 0.002$) and Spring Creek ($r^2 = 0.32$, $p = 0.015$) but showed no significant relationship with discharge in the Chattahoochee River (Table 2.3).

Discussion:

Influences of catchment characteristics on nutrient concentrations:

Spring Creek and the Flint River had the highest concentrations of TN and NO_3^- with the concentrations of TN appearing to be primarily a function of the abundance of nitrate. The most obvious source of nitrate is intensive agriculture within the watershed. Fifty percent of the land surrounding the Flint is used for agricultural purposes with approximately 10,900 metric tons of fertilizer being applied during the growth season (Frick et al. 1996). Sixty-one percent of the banks around Spring Creek is agricultural land with approximately 9,100 metric tons of fertilizer applied annually (Frick et al. 1996). The agricultural practices in the area are known to contribute to the elevated levels of nitrogen in the groundwater when nitrate from fertilizer percolates through the soil into the water table (Katz et al. 1999, Opsahl et al. 2003, Sims & Opsahl 2007). Both the Flint River and Spring Creek receive large amounts of groundwater-derived nitrate from natural springs situated within the rivers (Torak et al. 1996, Opsahl et al. 2007). During the dry summer and early fall months, Spring Creek's flow is almost entirely fed by groundwater sources causing this river to have the highest mean annual NO_3^- and TN levels. Major increases in TN and NO_3^- concentrations (>500 µg/L) can be seen between the upstream and downstream locations in Spring Creek (Figure 2.4) because of the presence of large springs located in between the two sites. Such large increases from ground water sources exemplify how high ambient ground water nitrate concentrations may be in this area and how influential groundwater sources can be on river nitrogen concentrations. In contrast, nitrogen concentrations in the Chattahoochee River were consistently lower than the Flint River and Spring Creek because of less connectivity to the Upper Floridian aquifer and decreased areas of agricultural land.

We hypothesized that the Chattahoochee River would have the highest concentrations of TP and PO_4^- due to the presence of 22 active wastewater treatment plants (WWTP) and increased residential/commercial run off due to large amounts of impervious surfaces (Frick et al. 1996, Ngoye & Machiwa 2004, Meyer et al. 2005, Walsh et al. 2005, Li et al. 2009). However, average annual TP and PO_4^- concentrations in the Chattahoochee were not significantly higher than the other river systems with the exception of Spring Creek. This result, at least in part, may be due to the presence of 13 reservoirs upstream of the Chattahoochee sample sites (Frick et al. 1996). Dissolved phosphorus is particularly prone to being retained behind dams because of its ability to become absorbed to inorganic particles and settle into the sediment (Müller et al. 2006, Matzinger et al. 2007). Other watersheds that have multiple upstream dams often are associated with a reduction in phosphorus due to either its burial or utilization in the upstream reservoirs (Schindler 1977, Müller et al. 2006). Although the Chattahoochee River has multiple sources of wastewater effluent, it appears as though other factors, such as biotic and abiotic processing contribute to maintaining relatively low phosphorus concentrations in the river.

Nutrient Response to Hydrologic Change:

Decreases in the concentrations of nitrate in Spring Creek and the Flint River during high flows were expected because the ambient nitrate concentrations in these rivers are relatively high and surface water runoff would dilute ground water inputs which are known to have high nitrate concentrations (up to 3500 μg/L; Allums et al., submitted). Occasionally, higher ammonium concentrations were observed in the Apalachicola and Chattahoochee Rivers but these increases did not correlate with discharge. The combination of high biological demand (Dodds 2002) and localized point source inputs are likely the causes of the low, variable concentrations in these rivers. Increases in the concentration of total phosphorus during high flows were expected because concentrations of phosphate are shown to increase during high storm-water flows and surface-water runoff events. Rodriguez-Blanco et al. (2009) found that surface runoff was the main route for transport of P to rivers. In general, the greatest potential for input occurs during high flows (Johnson et al. 1997, Novak et al. 2003).

The positive relationships between discharge and DOC in the Flint River and Spring Creek and a lack of a relationship in the Chattahoochee River reflect fundamental differences in patterns of exchange and/or transport among watersheds. Increases in organic matter during high flows result from flushing of carbon from adjacent forests and wetlands. Overland flooding allows surface water to move through forests and wetlands and flush organic matter out of both soil and the forest floor litter layer (Michener et al. 1998, Hook & Yeakley 2005, Opsahl 2005). In the southeastern Coastal Plain and in other regions, large intact riparian areas were found to be the most important source of storm-flow DOC export (Spruill 2000, Golladay & Battle 2002, McGlynn & McDonnell 2003). Elevated DOC, DON and DOP concentrations during high flows in the Flint River and Spring Creek reflect increased connectivity to regional wetlands and forested floodplains when bank overflows occur (Opsahl 2005, personal communication with Brian McCallum USGS 2009). Michener et al. (1998), during their study of the effects of tropical storms on coastal plain flooding, observed that the Flint River had large loads of DON and DOP because of the mobilization of leaves and other organic matter present in the floodplains. Organic-matter concentrations presumably did not increase in the Chattahoochee River because of a lack of hydrologic connectivity with wetlands and forested floodplains. Also, the potential influences from upstream reservoirs serve to increase residence time within the Chattahoochee watershed and promote greater decomposition of DOC prior to export.

Nutrient Transitions at river/reservoir interfaces and implications for mixing and processing in the Apalachicola River:

We hypothesized that nutrient concentrations would become mixed, processed and altered as they moved through Lake Seminole into the Apalachicola River. The backwater effect of Lake Seminole extends over 50 km up the Chattahoochee River and 60 km up the Flint River (Grodowitz et al. 2003). We were able to capture the initial effects that Lake Seminole had on nutrient concentrations by situating our downstream sample sites at the river/lake backwater transition zone. Within each river, consistently lower nutrient concentrations were observed at downstream sample locations. However, these differences were not found to be statistically significant when averaged over the annual sampling period. For example, in the Flint River, the downstream site (FLINT DOWN) consistently had lower concentrations of all constituents (TN, NO_3^-, PO_4^-, TP, and NH_4^+) except for TON and PP. The Chattahoochee River showed similar trends with CHAT DOWN having lower concentrations of every constituent except for TON and PO_4^-. In contrast, Spring Creek had higher levels of all nitrogen constituents expect TON at the SPRING DOWN site because of several large in-river springs situated between SPRING UP and SPRING DOWN. All phosphorus constituents were lowest at the SPRING DOWN site. Lower phosphate concentrations were also seen in the Apalachicola River and could potentially be a result of the leaching of phosphate that is bound to the soil within the reservoir and is released when an anoxic environment occurs in the deepest waters near the dam (Schindler 1977, Müller et al. 2006, Matzinger et al. 2007). These downstream decreases, which occurred over relatively short distances, are believed to be due to a combination of increased decomposition and settling that occurs at the river/reservoir interface. This pattern indicates that Lake Seminole could be acting as a nutrient sink, particularly for inorganic nitrogen and phosphorus, via biological processing such as nutrient uptake and transformation by aquatic organisms, especially macrophytes (Dodds 2002, Growns et al. 2009).

Conclusion:

Major differences in nutrients and DOC concentrations were observed among the rivers within the lower ACF watershed. These differences were regulated by a combination of hydrologic variability and physical catchment characteristics including river/floodplain exchange as well as the influence of biotic processing that occurred in Lake Seminole prior to discharge into the Apalachicola River. Therefore, Lake Seminole acts as an important site for processing nutrients and serves as a gateway for downstream delivery of nutrients to the Apalachicola River and Apalachicola Bay ecosystem, an economically important source of shellfish (Dalton et al. 2004). More understanding of the differences in nutrient and DOC sources and transformations among watersheds within the ACF under highly variable flows will be needed for the protection of the Apalachicola Bay ecosystem.

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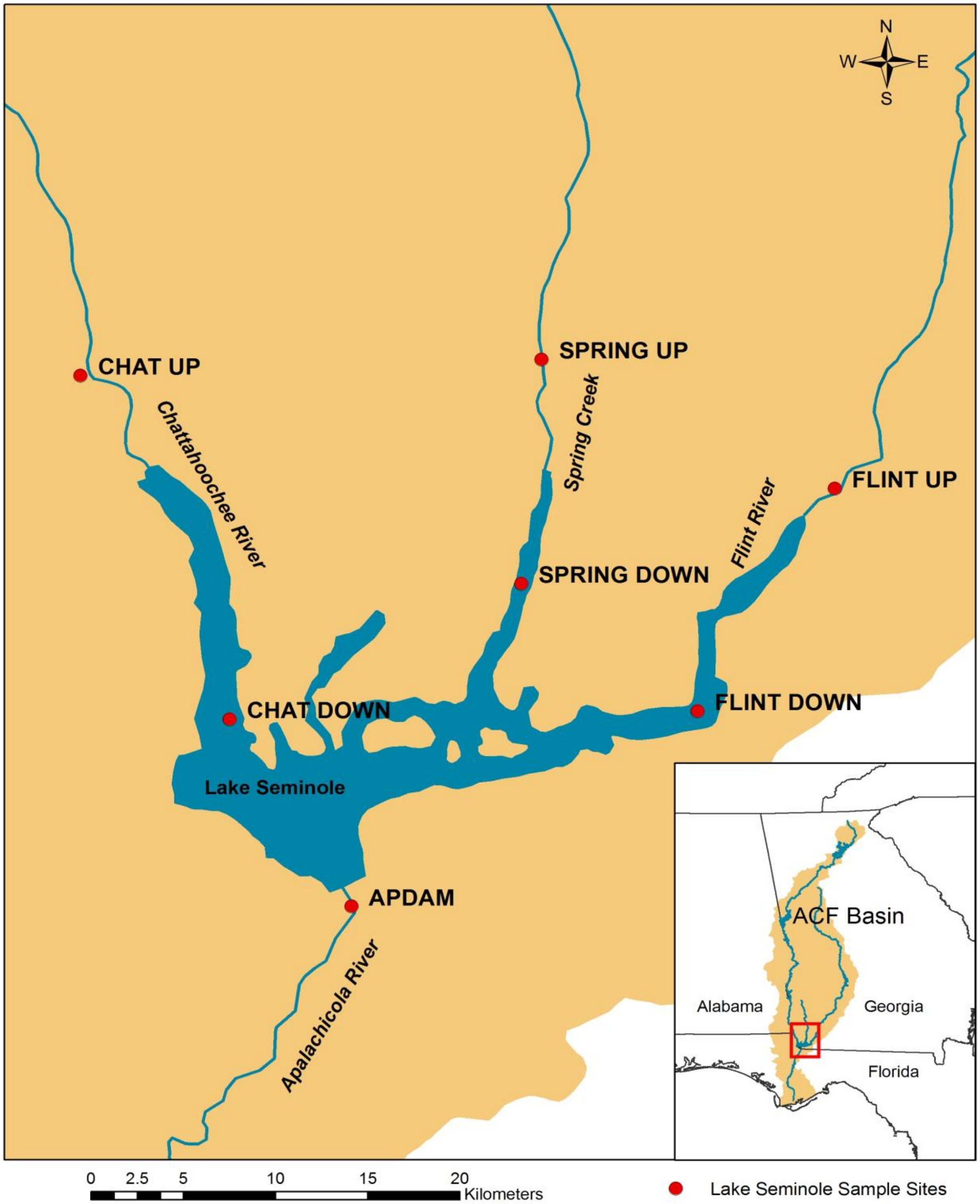

Figure 2.1: Lower Apalachicola-Chattahoochee-Flint (ACF) river basin is located in eastern Alabama, western Georgia and northwestern Florida. The Chattahoochee River, Flint River and Spring Creek converge to form Lake Seminole. Outflow from the Jim Woodruff Lock and Dam acts as the headwater source for the Apalachicola River. Sample sites with gauge station information was available at CHAT UP, SPRING UP, FLINT UP and APDAM.

Table 2.1: Physical characteristics of the three rivers flowing into Lake Seminole and the outflow source, the Apalachicola River.

River	Chattahoochee	Flint	Spring Creek	Apalachicola	Lake Seminole
Length (miles)	430	350	35	106	376
Area Drained (km^2)	8,770	8,460	585	2,600	37,500
% Forested	49	41	32	58	54
% Urban	1.4	4.1	1.2	1.2	1.4
% Agricultural	46	50	61	10	18
% Water	2.5	1.4	2.1	2.3	7.6
% Barren Land	0.2	0.4	0.6	0.3	0.5
Population	51,400	117,000	22,300	25,800	
WWTP	22	4	1	1	0
Reservoirs	13	2	0	0	1
Mean Flow (m^3s^{-1})	247	204	18	534	N/A

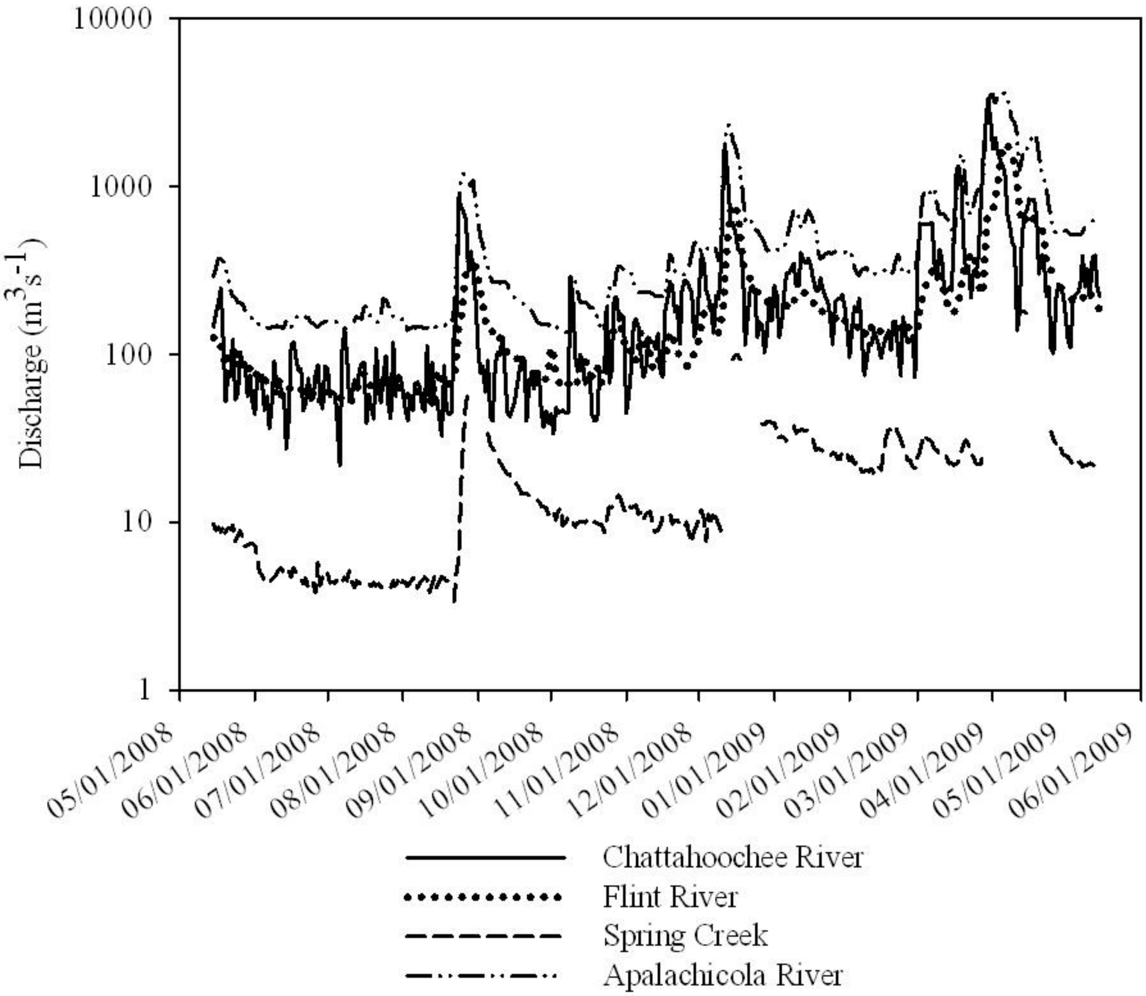

Figure 2.2: Discharge at the Chattahoochee River (USGS 02343801), Flint River (USGS 02356000), Spring Creek (USGS 02357150) and Apalachicola River (USGS 02358000) from May 15, 2008 until May 15, 2009.

Table 2.2: Summary of the physical parameters by annual mean and overall range of the seven sample sites in the lower Apalachicola-Chattahoochee-Flint basin, Georgia, USA. Location of study can be found in Figure 2.1.

Location		Temperature (°C)	DO (mg/L)	pH	Conductivity (mS/cm)
FLINTUP	Range	12.0 - 27.8	6.55 - 8.93	7.58 - 7.88	0.112 - 0.172
	Mean	22.3	7.17	7.8	0.153
FLINTDOWN	Range	12.6 - 29.8	6.99 - 8.73	7.39 - 8.17	0.118 - 0.178
	Mean	23.6	7.64	7.9	0.157
CHATUP	Range	11.8 - 28.6	6.18 - 10.2	7.41 - 7.99	0.091 - 0.141
	Mean	23.0	7.62	7.6	0.126
CHATDOWN	Range	12.1 - 29.3	6.05 - 9.73	7.20 - 7.61	0.092 - 0.146
	Mean	23.4	7.32	7.4	0.128
SPRINGUP	Range	12.2 - 23.8	6.41 - 8.72	7.68 - 7.89	0.163 - 0.253
	Mean	20.3	7.34	7.8	0.219
SPRINGDOWN	Range	12.9 - 26.4	5.48 - 8.19	7.58 - 7.93	0.168 - 0.244
	Mean	21.9	6.13	7.7	0.218
APDAM	Range	12.1 - 28.8	4.18 - 9.26	7.6 - 8.01	0.109 - 0.156
	Mean	23.1	6.23	7.7	0.142

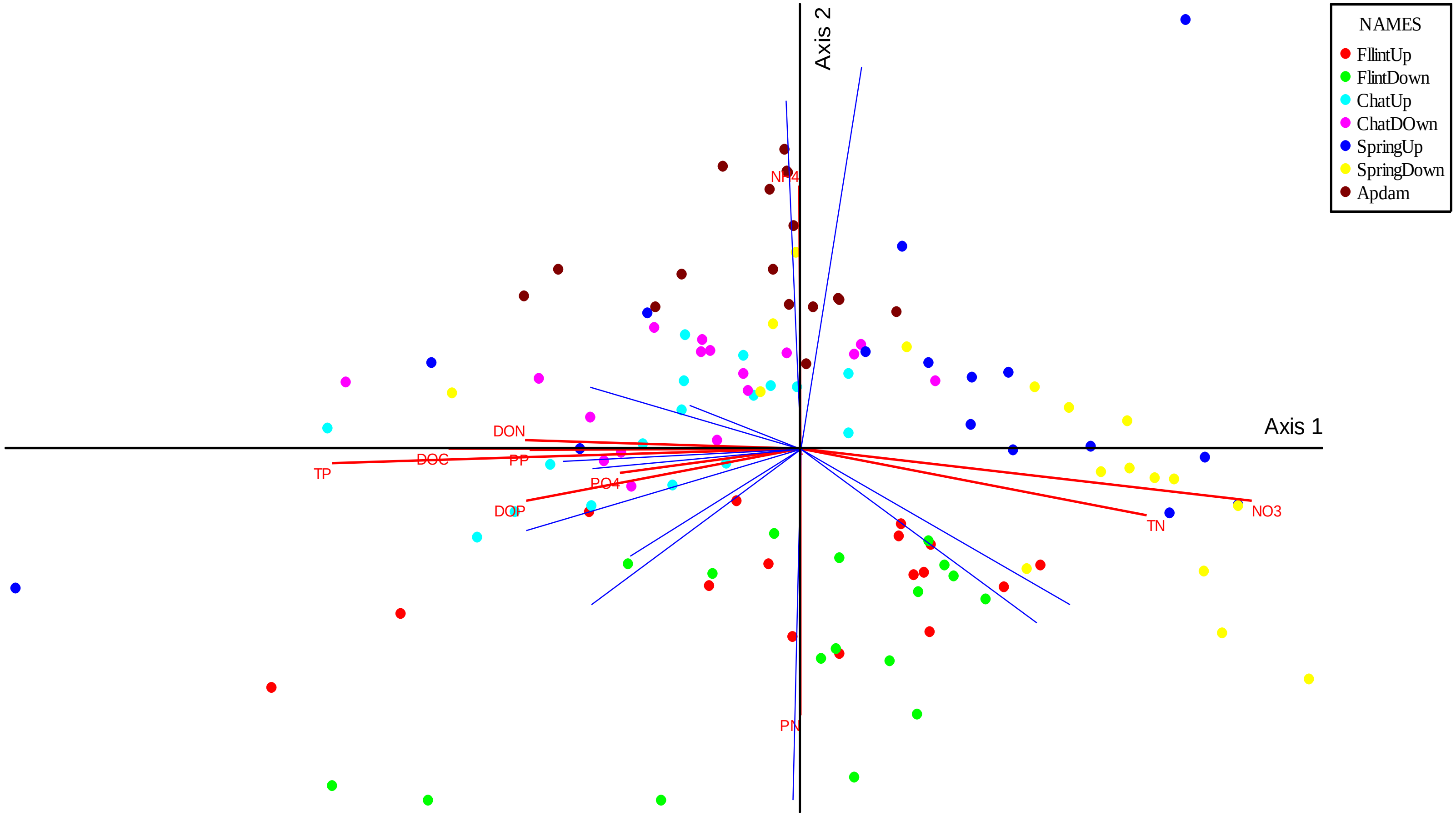

Figure 2.3: Principal component analysis ordination for water quality parameters for the Flint River, Chattahoochee River, Spring Creek and Apalachicola River watersheds indicating the differences in nutrient concentrations between the watersheds.

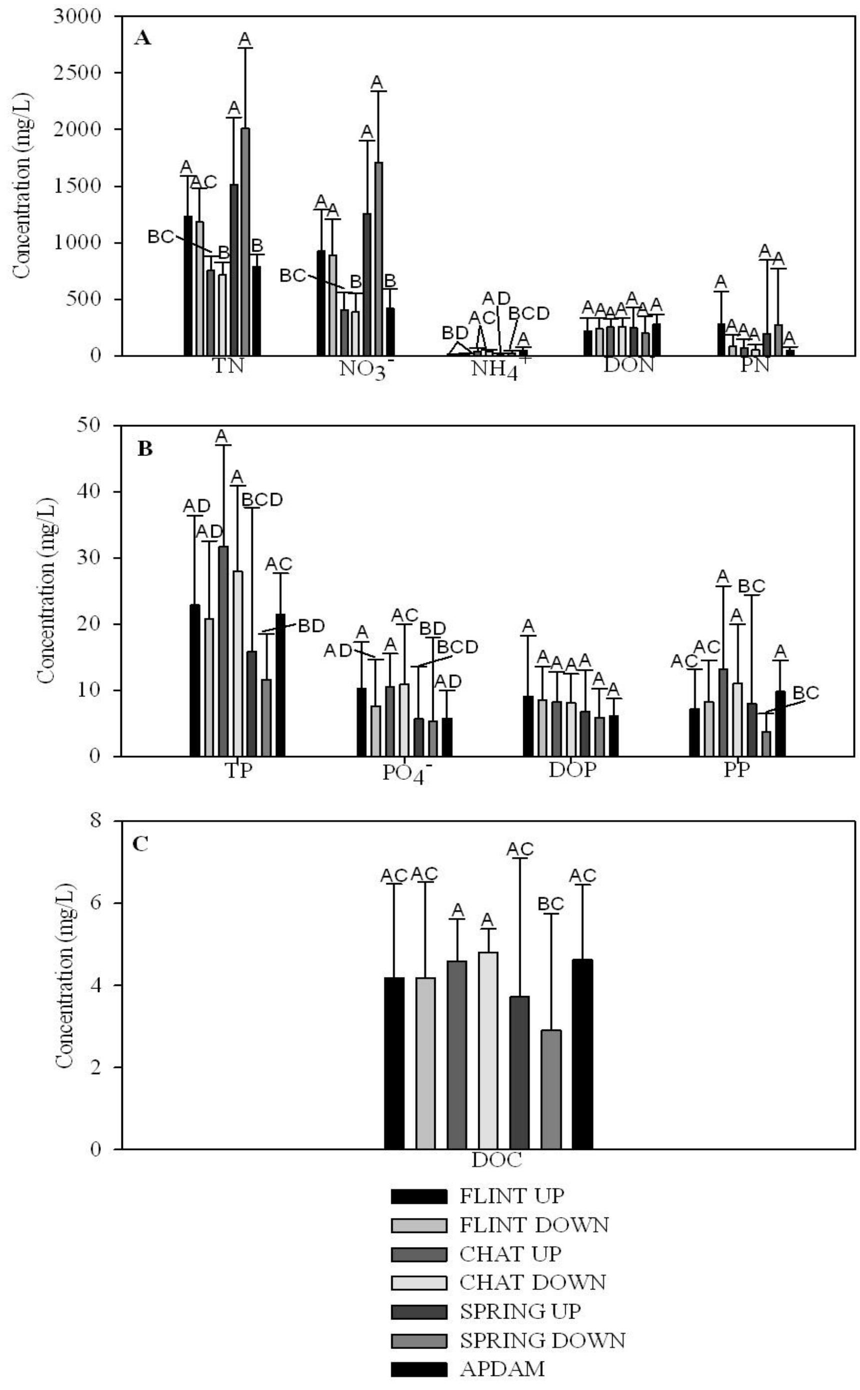

Figure 2.4 a,b,c: (A) Mean annual concentrations for each nitrogen constituent measured as well as the calculated amounts of total organic nitrogen (TON) and particulate nitrogen (PN) at the seven sample sites. Error bars indicate standard deviation. (B) Mean annual concentrations for each phosphorus constituent measured as well as the calculated amounts of total organic phosphorus (TOP) and particulate phosphorus (PP) at the seven sample sites. (C) Mean annual concentrations of dissolved organic carbon (DOC) at each of the seven sample sites.

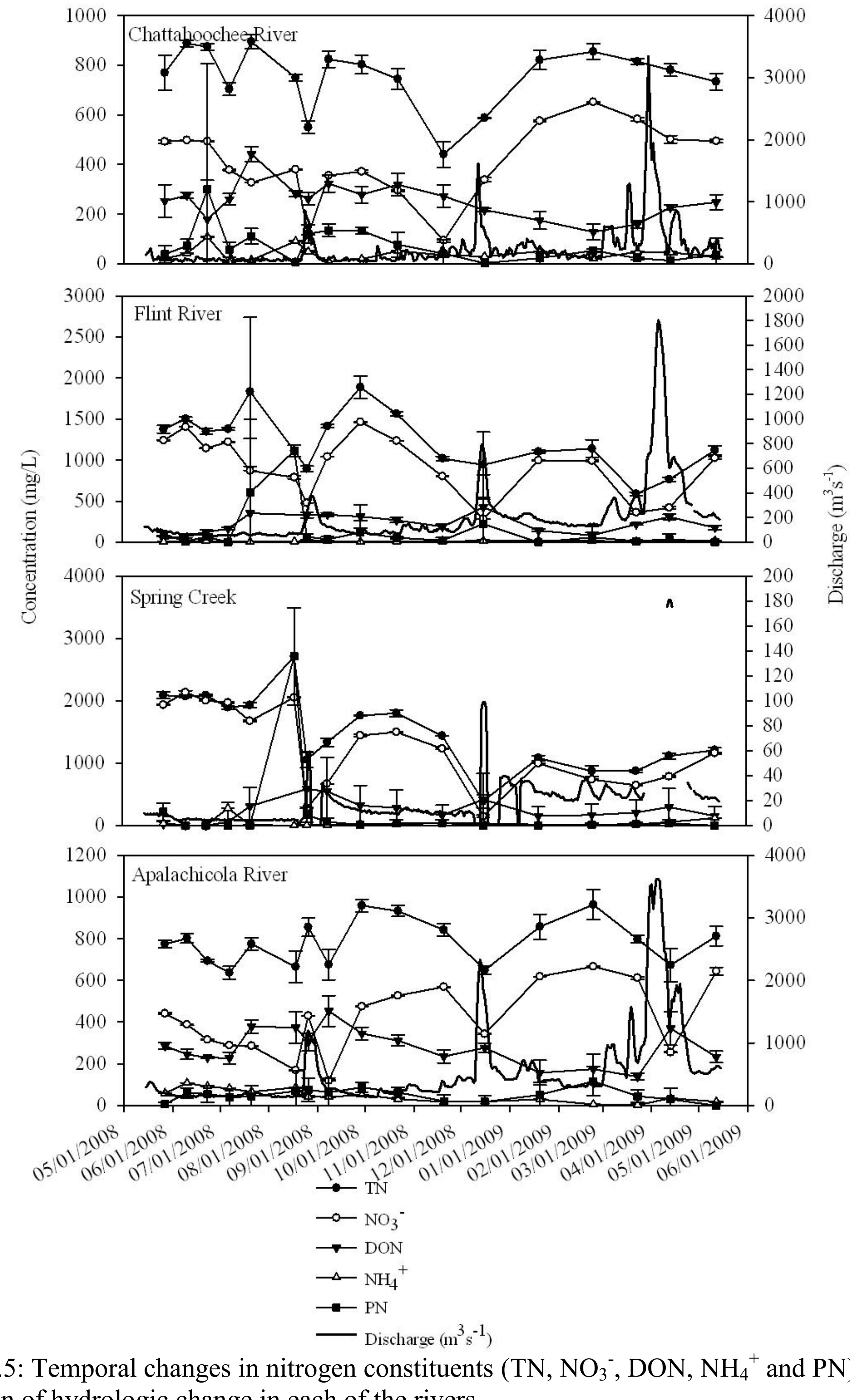

Figure 2.5: Temporal changes in nitrogen constituents (TN, NO_3^-, DON, NH_4^+ and PN) shown as a function of hydrologic change in each of the rivers.

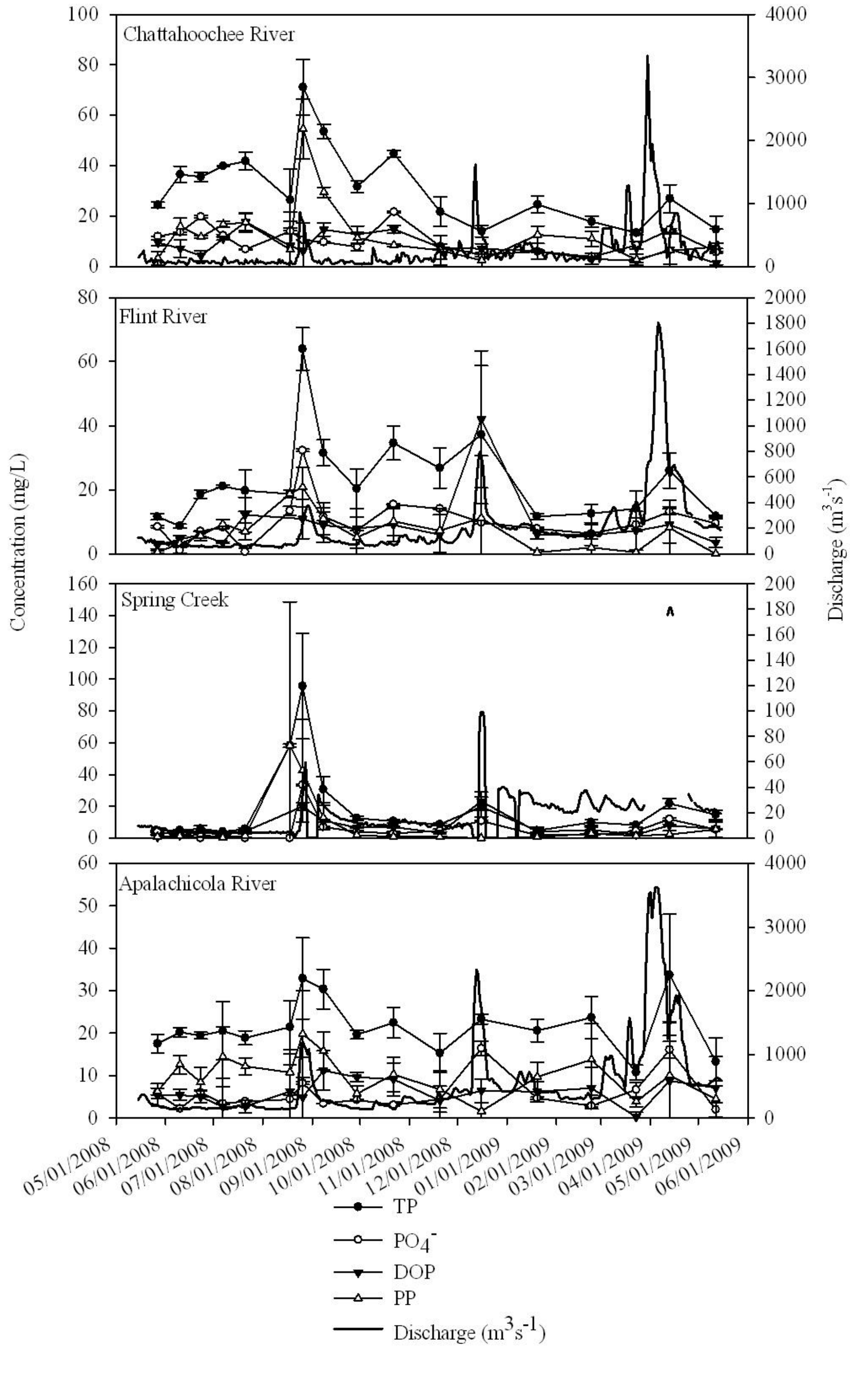

Figure 2.6: Temporal changes in phosphorus constituents (TP, PO_4^-, DOP and PP) shown as a function of hydrologic change in each of the rivers.

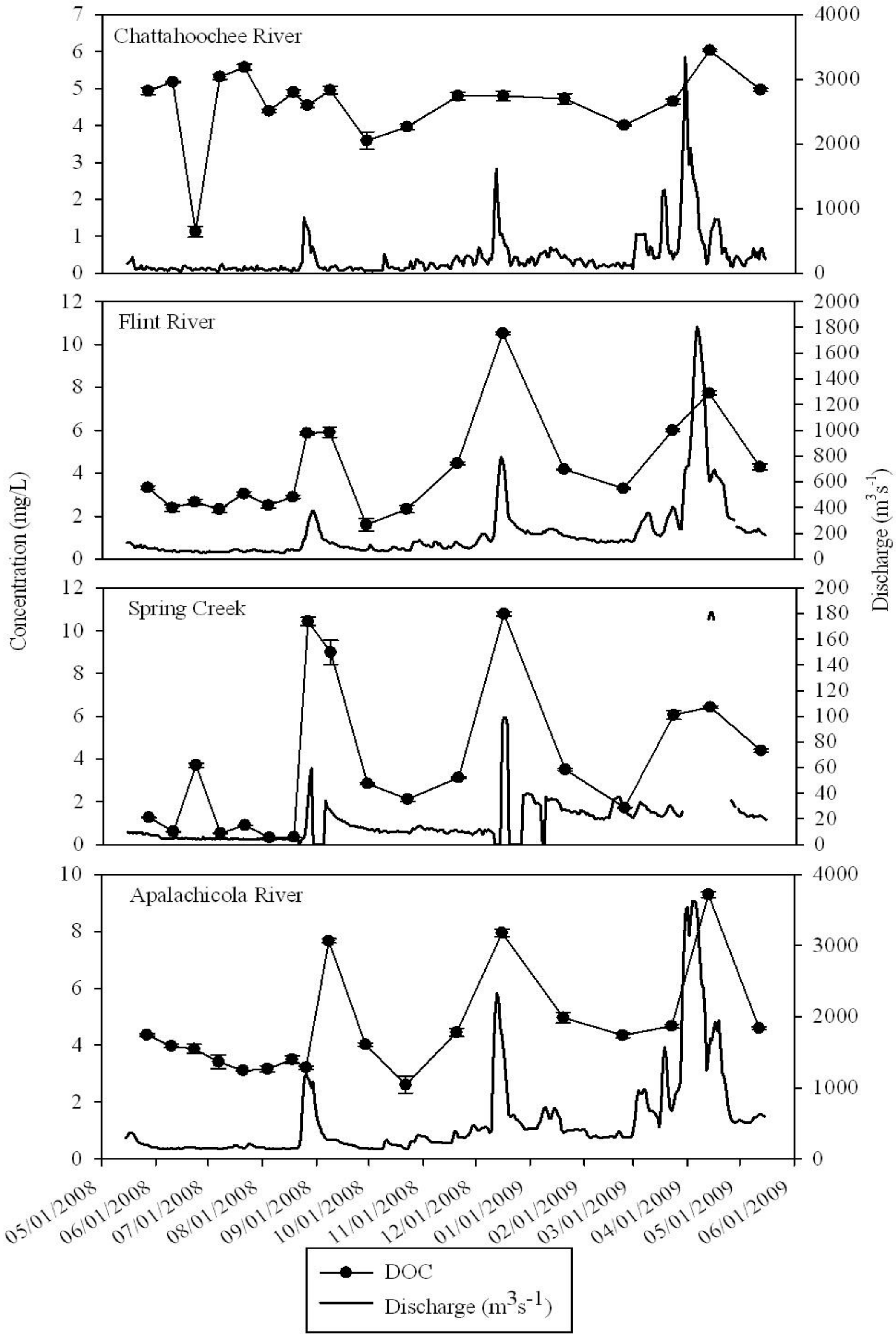

Figure 2.7: Temporal changes in dissolved organic (DOC) carbon concentrations shown as a function of hydrologic change in each of the rivers.

Table 2.3: Results from the linear regression analysis indicating were correlations between discharge and nutrient concentrations occur.

		TN	**NO_3^-**	**NH_4^+**	**DON**	**PN**	**TP**	**PO_4^-**	**DOP**	**PP**	**DOC**
Flint	R^2	0.45	0.65	0.25	0.25	0.18	0.09	0.05	0.44	0.01	0.84
	p-value	0.003 (-)	0.001 (-)	0.033 (+)	0.047 (+)	0.092	0.247	0.376	0.005 (+)	0.739	0.001 (+)
Chattahoochee	R^2	0.29	0.03	0	0.08	0.11	0	0.05	0.18	0.07	0.09
	p-value	0.025 (-)	0.477	0.926	0.276	0.196	0.977	0.355	0.088	0.317	0.235
Spring Creek	R^2	0.3	0.33	0	0.12	0.02	0.02	0.18	0.22	0.01	0.32
	p-value	0.023 (-)	0.013 (-)	0.977	0.183	0.575	0.565	0.078	0.07	0.745	0.015 (+)
Apalachicola	R^2	0.07	0	0.24	0	0.09	0.18	0.78	0	0.04	0.47
	p-value	0.31	0.879	0.040 (-)	0.971	0.256	0.091	0.001 (+)	0.912	0.463	0.002 (+)

CHAPTER 3:

A MASS BALANCE APPROACH TO EVALUATE ANNUAL PATTERNS OF STORAGE AND RELEASE OF NUTRIENTS AND DISSOLVED ORGANIC CARBON IN LAKE SEMINOLE, A SHALLOW SUBTROPICAL RESERVOIR IN THE SOUTHEASTERN USA[2]

[2] McEntire, J.M., S.P. Opsahl, A.P. Covich, S. Wilde and T. Rasmussen. To be submitted to *Hydrobiologia*.

Abstract:

Shallow lakes and reservoirs are biogeochemical hotspots for nutrient processing and are capable of altering the quantity of nutrients delivered to downstream ecosystems. Evaluation of nutrient retention and release dynamics is challenging due to the complex temporal, hydrologic and seasonal factors contributing to variations in allochthonous and autochthonous nutrient input and in-reservoir processing. This study analyzed N, P and dissolved organic carbon (DOC) samples in the context of a hydrologic budget over an annual cycle to assess retention and release of these constituents during passage through Lake Seminole, a large, shallow, subtropical reservoir. Lake Seminole has multiple inputs (Chattahoochee River, Flint River, Spring Creek and groundwater) which contribute to overall system loading, and a single outflow which forms the Apalachicola River. The reservoir has a relatively short water-residence time (1-37 days) and remains generally well mixed. However, the water column does experience summer and fall stratification. Loads of TN into the reservoir ranged from 0.7 t/day to 56.4 t/day with the Flint River delivering the greatest quantities and Spring Creek the lowest. TP ranged from 0.002 t/day in Spring Creek to 3.7 t/day in the Chattahoochee River and DOC loads ranged from 0.13 t/day in Spring Creek to 6287.2 t/day in the Flint River. During high flows, the Flint River became the dominate source of TP and DOC due to regional wetland and floodplain flushing and the Chattahoochee River became the dominate source of TN due to surface water runoff diluting the nitrate rich groundwater in the Flint River. Temporal patterns of loading showed that influxes of NO_3^- and PO_4^- usually exceeded export with high-flow events being an important factor in annual nutrient inputs. Annually, the reservoir appears to be a sink for N and P constituents, only serving as a substantial source of NO_3^- and PO_4^- during high flows. In contrast, the

reservoir appeared to be a source for NH_4^+ and organic matter, particularly DOC, under stable and high flow conditions.

Introduction:

Lakes and shallow reservoirs act as large, transitionary zones for materials transported along river corridors and the surrounding landscape as well as biogeochemical hotspots for nutrient processing and transformation (Hillbricht-Ilkowska 1999, Stanley & Doyle 2002, Fraterrigo & Downing 2008, Williamson et al. 2008, Harrison et al. 2009). With the amount of water held by reservoirs having increased seven fold in the last 40 years, understanding nutrients fluxes through reservoirs is an increasingly important ecological issue (Górniak et al. 2002). Although a reservoir's capacity for retention and release of large loads of nitrogen, phosphorus and dissolved organic carbon (DOC) may have major impacts on the health of downstream ecosystems, their role in modifying nutrient and DOC concentrations has remained poorly quantified (Ahn et al. 2008, Bosch 2008, Yang et al. 2008, Ligon et al. 1995). Only a few studies have comprehensively combined nutrient and DOC sampling with hydrologic budgets to determine the nutrient budget of a reservoir (Nowlin et al. 2005, de Vicente et al. 2006, James et al. 2008). In particular, shallow reservoirs have remained understudied despite their relative abundance and efficient role in nutrient modification. They are predominantly controlled by temporal variability in hydrologic transport rather than seasonal stratification observed in deeper systems (Tomaszek & Koszelnik 2003).

Nutrient and carbon fluxes in reservoirs show seasonal variations which closely follow patterns of annual reservoir productivity (Vanni et al. 2006). Shallow reservoirs act as sites for nutrient retention during the summer growing season when nutrient utilization by aquatic macrophytes and phytoplankton is at its maximum. They can often become sources of nutrients and carbon as macrophytes decompose and release nutrients and organic matter back into the ecosystem (Asaeda et al. 2000, Tomaszek & Koszelnik 2003, Bosch & Allan 2008). Seasonality also mediates biogeochemical nutrient and carbon fluxes. For example, higher temperatures and anoxia during the summer and fall season cause higher rates of permanent N removal via denitrification (Sobota et al. 2009) but may also activate internal P loading (Hillbricht-Ilkowska 1999).

A reservoir's ability to modify material fluxes is also dictated by fluctuations in hydrologic regimes. Processes such as N and P sedimentation, associated with particle settling and carbon burial are evident at the river/lake transition areas where decreases in water velocity occur during transition from a lentic to lotic system (Stanley & Doyle 2002, Bosch 2008, Yang et al. 2008). However, many shallow reservoirs have relatively short water residence time and their nutrient fluxes can be driven by increases in discharge that accompany storm events (Hillbricht-Ilkowska 1999, Fraterrigo & Downing 2008, Vanni et al. 2006). High flow can trigger nutrient and carbon resuspension from the sediment and thereby cause the reservoir to export large loads from the system (Stanley & Doyle 2002, Sobota et al. 2009).

The objective of this study was to characterize the annual physical and chemical characteristics of the shallow, subtropical reservoir Lake Seminole and to understand its annual mass balance for N, P and DOC through the creation of a nutrient and hydrologic budget. Sampling was conducted at the base of the three major inflowing watersheds (Chattahoochee River, Flint River and Spring Creek) before confluence at Lake Seminole, within the lake and in the Apalachicola River, the outflow for Lake Seminole. The purpose was to capture an integrated representation of the nutrient loads before and after the passing through Lake Seminole. A large percentage of Lake Seminole is often covered by aquatic macrophytes, especially *Hydrilla verticillata*, during the growing season. We hypothesized that Lake Seminole acts as a source for N, P and DOC during the fall/winter die back season and a sink for N and P during the spring/summer growing season.

Methods:

Study Site:

Lake Seminole is a shallow, subtropical, 15,175 ha man-made reservoir located at the border of southwest Georgia and northwest Florida, within the lower Apalachicola-Chattahoochee-Flint (ACF) River Basin System in the Coastal Plain physiographic region of southeastern United States (http://www.sam.usace.army.mil/op/rec/seminole/) (Figure 3.1). The impoundment is situated at the confluence of the Chattahoochee and Flint Rivers and acts as the headwater source for the Apalachicola River. Lake Seminole is a run-of-the-river impoundment with 605 km of shoreline. The reservoir has an annual average residence time of 19 days with a maximum of 37 days during periods of relatively low flow and a minimum of 1 day during periods of high flow. The reservoir has a maximum depth of approximately 9.0 m and an average depth of 3.0 m that fluctuates an average of less than 0.6 m (http://www.sam.usace.army.mil/op/rec/seminole). The reservoir receives surface water inflow from the Chattahoochee and Flint Rivers and the predominantly groundwater fed stream, Spring Creek. There is a high degree of variability in land-use practices of the three major riverine input sources. Back-water from Lake Seminole extends over 50 km up the Chattahoochee River and 60km up the Flint River (Grodowitz et al. 2003).

Field Collection and Sample Analysis:

We selected eight sample sites within the lower ACF River Basin along the Chattahoochee, Flint and Apalachicola Rivers, Spring Creek and within Lake Seminole (Figure

3.1). Two sample locations, one upstream and one downstream, were chosen on the Chattahoochee River, Flint River and Spring Creek. These sites were selected to capture river inflow and river/reservoir transition zones for each of the incoming rivers. A site was chosen approximately 30 m in front of the dam within the reservoir to compare surface and bottom water at the deepest location (10 m) within the impoundment. A final location was chosen at the upper end of the Apalachicola River in order to capture Lake Seminole's outflow. Immediately prior to sampling, depth profiles of pH, temperature, dissolved oxygen and specific conductivity were taken using a Hach Quanta Hydrolab. Depth profiles were taken at 2 m intervals at the downstream location on the Flint and Chattahoochee River and within the reservoir. Near surface water samples were taken in triplicate in acid-washed polycarbonate 1L bottles that had been rinsed once with river water. The deep-water samples were taken using a 4-L acrylic Van Dorn sampler. Surface water grab samples were collected on a bi-monthly basis from May 2008 until September 2008 and on a monthly basis from October 2008 until May 2009. Sampling of the eight locations was divided between two consecutive days.

Samples were packed in ice, returned to the Joseph W. Jones Ecological Research Center and filtered through 0.7 µm glass fiber filters within a 48-hour period. Dissolved organic carbon (DOC) samples were analyzed using a Shimadzu TOC-5050 analyzer. Samples of ammonium (NH_4^+) (Lachat Method 10-107-06-1-G), nitrate (NO_3^-) (Lachat Method 10-107-06-1-B) and phosphate (PO_4^-) (Lachat Method 10-115-01-B) were analyzed on a dual channel Lachat Quick Chem 8000. Total nitrogen (TN) (Lachat Method 10-107-04-1-B) and total phosphorus (TP) (Lachat Method 10-115-01-B) were analyzed on filtered samples following digestion by the Johnes & Heathwaite (1992) method. A CEM MDS-2000 microwave was used to perform the digestions. Dissolved organic nitrogen (DON) and phosphorus (DOP) were calculated as the difference between filtered TN and TP and DIN and DIP. Particulate nitrogen and phosphorus (PN and PP) were calculated as the difference between filtered TN and TP and unfiltered TN and TP and the concentrations included both organic and inorganic nutrients. The detection limit for TN/NO_3^- was 2 µg/L, TP/PO_4^- was 3 µg/L, NH_4^+ was 3 µg/L and DOC was 0.1 mg/L.

Water Budget:

A water budget was created using the equation from Dalton et al. (2004):

$$P + SW_{IN} - SW_{OUT} + GW_{IN} - GW_{OUT} - E = \Delta S \qquad \text{(Eq.1).}$$

Where P is precipitation, E is evaporation and ΔS is change in lake storage, SW is surface water and GW is groundwater. The groundwater component was estimated as the residual:

$$GW = \Delta S + E - P - SW_{IN} + SW_{OUT} \qquad \text{(Eq. 2).}$$

Daily discharge data for each river were obtained from USGS gage stations USGS 02356000, USGS 02343801, USGS 02357150, USGS 02358000 (http://water.usgs.gov/waterwatch/?m=real&r=ga). All components of the water balance were converted to cubic meters per second (m^3s^{-1}). Average discharge for each river was determined by taking the average flow of a four day period that included the two sample dates as well as the days before and after sampling. Daily change in lake storage was obtained from U.S.G.S. gage (USGS 02357500). Daily precipitation and evaporation data were taken from the Georgia Automated Environmental Monitoring Network website for Lake Seminole (http://www.griffin.uga.edu/aemn/cgi-bin/AEMN.pl?site=FLSN&report=w). Water residence time was calculated as:

$$RT = \text{Lake Seminole daily storage } (m^3s^{-1}) \;/\; \text{Apalachicola River daily discharge } (m^3s^{-1}).$$

Nutrient Budget:

A nutrient budget was created to estimate the mass load of nutrients entering and leaving the reservoir via surface and groundwater inflows and outflows. Nutrient loads were estimated based on nitrogen, phosphorus and DOC surface water concentrations and river discharges. Nutrient concentrations were converted from µg/L to kg/L (DOC mg/L to kg/L) and discharge was converted from m^3s^{-1} to L/day. Nitrate and phosphate data for groundwater were obtained from unpublished data collected by J. Kilpatrick (Georgia DNA) during their 2000-2001 study of Lake Seminole. NO_3^- concentrations were estimated to be 1027 µg/L and PO_4^- was below detection. Groundwater DOC data were obtained from regional spring discharge sites and DOC was estimated to be 0.3 mg/L (Opsahl unpublished data). Atmospheric nitrate data for precipitation were obtained from http://nadp.sws.uiuc.edu/sites/siteinfo.asp?id=FL14&net=NTN. Nutrient budgets were created for TN, TP, NO_3^-, PO_4^-, DON, DOP and DOC for each of the sample periods. Nutrient loading was calculated as:

Concentration of nutrient (kg/L) x Flow Rate of Individual River + Groundwater (L/day) + Precipitation = Loading (kg/day).

Precipitation was only added to the nitrate loading term. River surface water inflow and groundwater inflow were summed and the Apalachicola River surface water outflow was subtracted to estimate the difference between nutrient inflows and outflows.

Data Analysis:

Statistical analyses were performed using the SigmaPlot 11.0 feature SigmaStats (San Jose, CA). Prior to analysis, each nutrient constituent was tested to see if the assumptions of normality and homogeneity of variance were met using a Shapiro-Wilk test. Not all of the constituents met the assumptions of normality so non-parametric statistics were utilized. A Mann-Whitney rank sum test was performed to analyze the differences between the physical parameters and the nutrient concentrations at the surface and bottom of Lake Seminole. To compare differences in the total nitrogen and total phosphorus loads between the three inflowing rivers, non-parametric one-way analysis of variance (ANOVA) was performed using the Kruskal-Wallis ANOVA on ranks. Significant ANOVAs were followed by Dunn's Method multiple comparisons procedure to determine significant differences between the rivers. Linear regressions were performed to assess the relationship between inflow loads and nutrient retention within the reservoir.

Results:

Water Budget, Hydrology and Climactic Conditions:

Groundwater input accounted for an average of 24% of the total inflow into Lake Seminole with contributions ranging from -11 to 380 m^3s^{-1} (Table 3.1). High groundwater values appeared to coincide with periods of high surface inflows and outflow and are thought to be artificially elevated due to un-gauged surface runoff. Negative groundwater estimates were believed to be caused by a lag in the amount of discharge measured at the Chattahoochee gauge and the amount of water that actually ends up in the reservoir. Negative values could also result from a flow reversal of water back into the aquifer or from other sources of error related to the water budget calculations that are discussed below. Surface water input made up 84% of the inflow into Lake Seminole with precipitation contributing 1% (150 cm annually). Our results are consistent with the water budget of Dalton et al. (2004) who found that surface water inflow accounted for 81% of the inflow, 18% was from groundwater and precipitation contributed 1%. The Chattahoochee River contributed the majority of the river inflow (48%) and had a sampling average discharge of 195 m^3s^{-1}. The Flint River contributed 46% with a sampling average discharge of 187 m^3s^{-1} and the third tributary, Spring Creek delivered 7% with a sampling average discharge of 28 m^3s^{-1} (Figure 3.2). Surface water discharge from the Apalachicola River accounted for 99% of the outflow with evaporation only contributing 1% with an annual mean of 119 cm. Sample average outflow in the Apalachicola River (463 m^3s^{-1}) was slightly higher than the combined average of the three tributaries due to additional groundwater inputs and runoff contributions in the vicinity of Lake Seminole. Changes in lake storage ranged from 4873 m^3s^{-1} and 5853 m^3s^{-1} and its role in the water budget was minimal (ranging from -24 to 143 m^3s^{-1}) relative to surface inflows and outflows.

Physical Parameters:

Depth profiles for temperature, DO, pH and conductivity at the mid-reach CHAT DOWN location showed seasonal patterns of increase and decrease but otherwise appeared to be generally well mixed. Temperature ranged from a low of 10ºC to a high of 31ºC and conductivity ranged from 0.073 mS/cm to 0.157 mS/cm, both varying minimally with increasing depth during each season. DO varied from 5.3 mg/L to 10.0 mg/L and pH varied from 7.0 to 7.6 with both parameters displaying minimal stratification during the summer and fall (Figure 3.3).

Depth profiles for temperature, DO, pH and conductivity at the mid-reach FLINT DOWN location showed seasonal patterns of increase and decrease but appeared to be generally well mixed. Temperature ranged from 11 ºC to 31 ºC and conductivity ranged from 0.113 mS/cm to 0.179 mS/cm with both varying minimally with increasing depth during each season. Notable exceptions included DO which ranged from 5.3 mg/L to 9.1 mg/L and pH which ranged from 7.5 to 8.4 demonstrating seasonal summer stratification (Figure 3.4).

Depth profiles near the dam indicated that stratification occurred during the summer and fall but throughout the rest of the year, the reservoir remained generally well mixed (Figure 3.5). Mean annual water temperature at the lower end of Lake Seminole varied from 11 °C to 31 °C at the surface and from 9 °C to 29 °C in the deep water (10 m) with no significant difference between surface and 10 m temperatures (Mann-Whitney, $p = 0.249$). There was a significant difference between mean annual DO (Mann-Whiney, $p = 0.018$) which varied from 6 mg/L to 10 mg/L at the surface and between 0.6 mg/L to 10 mg/L at 10 m. Mean annual pH ranged from 7.2 to 8 at the surface and from 6.9 to 8.0 at 10 m and differences between surface and 10 m values were found to be statistically significant (Mann-Whitney, $p = <0.001$). Conductivity ranged from 0.079 mS/cm to 1.66 mS/cm at the surface to from 0.086 mS/cm to 1.83 mS/cm at 10 m with no significant difference observed between surface and bottom waters (Mann-Whitney, $p = 0.955$).

Surface and Benthic Nutrient Concentrations:

Nitrogen and phosphorus concentrations within the reservoir displayed wide ranges with some differences in concentrations between the surface and 10 m. TN concentrations ranged from 466.6 µg/L to 1027.7 µg/L (mean 752.2±25 µg/L) at the surface of the water column and from 563.4 µg/L to 1043.3 µg/L (mean 772±57 µg/L) at 10 m with no significant difference between the two (paired t-test, $p = 0.692$) (Figure 3.6A). NO_3^-, which represented the majority of the TN present, ranged from 98.2 µg/L to 887.2 µg/L (mean 369.7µg/L±4 µg/L) at the surface to varied from 149.6 µg/L to 755.8 µg/L (mean 407.3±8 µg/L) at 10 m (Figure 3.6B). Dissolved organic nitrogen varied minimally from 79.1 µg/L to 592.9 µg/L at the surface (mean 286.6±129 µg/L) and from 148.7 µg/L to 465.2 µg/L (mean 265.9±35 µg/L) at 10 m (Figure 3.6C). NH_4^+, which represented the smallest fraction of TN, ranged from 0 µg/L to 48.4 µg/L (mean 15±2 µg/L) at the surface and from 0 µg/L to 119 µg/L (mean 57±4 µg/L) at 10 m (Figure 3.6D).

Total phosphorus concentrations with the reservoir ranged from 6.1 µg/L to 33.5 µg/L (mean 18.0±3 µg/L) and from 6.3 µg/L to 23.9 µg/L (mean 16.4±2 µg/L) at 10 m (Figure 3.7A).

PO_4^-, which represented the majority of the TP present, ranged from 0 to 13.4 µg/L (mean 3.4±0.6 µg/L) at the surface and varied from 0 to 9 µg/L (mean 3.3±0.8 µg/L) at 10 m (Figure 3.7B). Dissolved organic phosphorus (DOP), which represented the smallest fraction of TP, varied from 3.5 µg/L to 10.7 µg/L (mean of 6.7±1 µg/L) at the surface and from 3.6 µg/L and 10.7 µg/L (mean 6.6±0.8 µg/L) at 10 m (Figure 3.7C). DOC in the reservoir varied minimally between the surface 3.3 mg/L to 7.4 mg/L and at 10 m 2.5 mg/L to 9.6 mg/L with annual means of 4.5±0.1 mg/L and 4.6±0.1 mg/L respectively (Figure 3.8).

Temporal Patterns of Nitrogen, Phosphorus and DOC Loading and Export:

Nutrient data used to calculate fluxes are presented in Appendix A. For a detailed discussion about differences among rivers, see Chapter 2. TN loads ranged from between 6.4 t/day to 43.4 t/day in the Flint River, between 2.4 t/day to 35 t/day in the Chattahoochee River and between 0.7 t/day to 17.2 t/day in Spring Creek with a significant difference observed between the Flint and Chattahoochee rivers and Spring Creek (ANOVA, $p = <0.001$) (Figure 3.9). TP loads ranged from 0.03 t/day to 3.1 t/day in the Flint River, 0.07 t/day to 0.1 t/day in the Chattahoochee River and between 0.001 t/day to 0.3 t/day in Spring Creek with a significant difference observed between the Flint and Chattahoochee Rivers and Spring Creek (ANOVA, $p = 0.007$) (Figure 3.9). Dissolved organic carbon (DOC) loads ranged from 5.6 t/day to 271.3 t/day in the Chattahoochee River, between 11.2 t/day to 62.9 t/day in the Flint River and between 0.1 t/day to 99.1 t/day in Spring Creek and a significant difference was seen between the Flint and Chattahoochee Rivers and Spring Creek (ANOVA, $p = <0.001$) (Figure 3.9).

Annually, TN import (10.6 t/day to 112 t/day) almost always exceeded export (7.5 t/day to 88 t/day) with the greatest quantities of total nutrient flux coinciding with high flow events (08/26/08, 12/16/08 and 04/13/09) (Figure 3.10A). NO_3^- influxes ranged from 8.5 t/day to 75.7

t/day with export loads only ranging from 2.2 t/day to 47.1 t/day indicating that the reservoir was most often a sink for NO_3^- (Figure 3.10B). DON imports ranged from 1.5 t/day to 38.1 t/day and export ranged from 2.8 t/day to 43.4 t/day indicating that the reservoir was usually acting as a source for DON, especially during periods of high flow (Figure 3.10C). NH_4^+ influxes ranged from 0.1 t/day to 3.8 t/day with export loads ranging from 0.2 t/day to 4.6 t/day indicating that the reservoir was most often a source for NH_4^+ (Figure 3.10D).

Annually, TP import (0.2 t/day to 3.9 t/day) generally exceeded export (0.08 t/day to 3.3 t/day) with the greatest quantities of nutrient flux again appearing to coincide with periods of high flow (Figure 3.11A). PO_4^- fluxes ranged from inflows between 0.04 t/day to 1.6 t/day and exports ranging between 0.03 t/day and 2.3 t/day, indicating that the reservoir acts as sink for PO_4^- except during high-flow events when the reservoir can serve as a source (Figure 3.11B). DOP imports ranged from 0.05 t/day to 3.0 t/day and export ranged from 0.03 t/day to 1.2 t/day, indicating that the reservoir was usually acting as a sink for DOP (Figure 3.11C).

Annually, between 21.3 t/day to 931 t/day of DOC was imported and between 39.2 t/day and 1216 t/day was exported (Figure 3.12). The reservoir appeared to act as a source for DOC during periods of high flows. Each high flow events also coincided with the greatest total quantities of DOC influx.

Reservoir Nutrient Retention and Release:

Between 14% and 85% of the NO_3^- loads were retained within the reservoir. During high flow events, the amount of NO_3^- released was 20% to 26% higher than the amount retained (Figure 3.13A). In contrast to NO_3^-, only between 0.3% and 22% of the DON loads were retained and between 18% and 120% were exported from the reservoir (Figure 3.13B). Between 19% and 88% of NH_4^+ was retained with between 4% and 931% of the NH_4^+ leaving the reservoir (Figure 3.13C). PO_4^- loads appeared to be similar to NO_3^- with 15% and 86% of PO_4^- loads being retained within the reservoir. During high flows, the amount of PO_4^- being released was 31% and 158% higher than the amount being retained (Figure 3.14A). 1% and 94% of the DOP loads were retained with between 0.6% and 260% being released (Figure 3.14B) and between 4% and 34% of the DOC influxes were retained with 10% and 150% being released (Figure 3.15).

Linear regression analysis showed that there was a significant positive relationship between NO_3^- loads and retention ($r^2 = 0.345$, $p = 0.013$). There was a significant negative relationship between DON loads and retention ($r^2 = 0.264$, $p = 0.042$). NH_4^+ displayed a significant negative relationship between export and retention ($r^2 = 0.224$, $p = 0.047$). Statistical analysis showed that there was a significant positive relationship between PO_4^- exports and retention (r^2=0.614, p = <0.001). There was also a significant positive relationship between DOP loads and retention (r^2 = 0.832, p = <0.001) and a significant negative relationship between loading and retention of DOC ($r^2 = 0.469$, $p = 0.002$) (Table 3.3).

Discussion:

Hydrologic Controls and Pulsed Events Influencing Loading:

The Chattahoochee and Flint Rivers were the dominant sources of nutrient yields primarily due to their larger sizes relative to Spring Creek. While the Chattahoochee River generally had the highest rates of discharge, the Chattahoochee's loading contributions were not often proportional to its water inputs. For example, the highest TN loads were most often observed in the Flint River despite its lower rate of discharge. High TN loads in the Flint River were attributed to intensive agriculture activity and fertilizer application within the watershed and greater amounts of groundwater influence due to the high degree of connectivity to the

Upper Floridian aquifer (Torak et al. 1996, Opsahl et al. 2007). Groundwater input from the aquifer is known to contain high quantities of nitrate due to fertilizer application and its subsequent percolation through the soil and into the water table (Katz et al. 1999, Opsahl et al. 2003, Opsahl et al. 2007). This finding suggests that, during base flow conditions, TN loads are more dependent on the concentrations of nutrients in the river than on discharge rates. TN loads in the Chattahoochee River only exceeded the Flint's during high flow events indicating the possibility of surface water runoff dilution of the nitrate rich groundwater in the Flint (Rodriguez-Blanco et al. 2009). In contrast, the Chattahoochee River was the dominate source of TP and DOC except during two of three high flow events at which time the Flint River became the primary source of both constituents.

Periods of high discharge increased the influxes of nutrients and dissolved organic carbon (DOC) to Lake Seminole with three distinct high flow events occurring during the study. The patterns of N, P and DOC influxes often differed between each high flow event indicating that there were several factors controlling quantities of nutrient loads. High flows caused the loads of TN and NO_3^- delivered to the reservoir to increase between three to five times and TP and PO_4^- to increase between two to four time the amounts usually observed during stable flow conditions. James et al (2008) also found that high flow events caused loads of TN, NO_3^-, TP and PO_4^- in Lake Okeechobee to increase between two and four times the quantity seen under stable flow conditions. These increases are likely due to increased localized surface-water runoff and soil erosion as well as greater amounts of nitrate deposition from precipitation and phosphate from sediment re-suspension (Johnson et al. 1997, Novak et al. 2003, Rodriguez-Blanco et al. 2009). NH_4^+ loads also substantially increased during each high flow events because of re-suspension from sediment and localized point source inputs (Morin & Morse 1999). Interestingly, the highest load of TN, NO_3^- and NH_4^+each occurred during spring (3rd event) suggesting the possibility of increased fluxes due to the onset of agricultural practices and fertilizer application.

During high flow events, dissolved organic carbon (DOC) loads displayed increased influxes similar to the nitrogen constituents and TP during each event. Increased influxes of DOC were expected because of flushing of regional forested riparian zones and wetlands (Michener et al. 1998, Hook & Yeakley 2005, Opsahl 2005). Major differences existed between the patterns of DON and DOP influx. DON followed similar trends as DOC and increased during each high flow event but DOP only showed a substantial increase on one occasion. One possibility for this discrepancy is that groundwater input can be a source of DON but not DOP during high flows when high water tables intersect with the upper soil layer and flush out nutrients buried within (Böhlke et al. 2007, Inamdar et al. 2008, van Verseveld et al. 2008). Another possibility is that the cycling of DOP is more dynamic than bulk DOC and DON and biological uptake and release may more directly influence concentrations as associated retention and release estimates (Kistritz 1978, Landers 1982).

Temporal Patterns of Nutrient Retention and Release:

Annually, the reservoir appeared to be a sink for NO_3^- and PO_4^- and only served as a substantial source under high flow conditions when high discharges decreased water residence time, caused nutrient “flushing” and lessened opportunities for sedimentation and in-reservoir processing (Nõges 2005, van Verseveld et al. 2008, Sobota et al. 2009). NO_3^- and PO_4^- retention was greater during the spring and summer seasons due to increased biogeochemical activity and reservoir productivity including macrophyte growth, nutrient uptake, denitrification and phosphorus burial (Kufel & Kufel 2002, Grizzetti et al. 2003, Irfanullah & Moss 2008, Bosch 2008). In shallow reservoirs, aquatic macrophytes act as short-term sinks for nitrogen and phosphorus by incorporating these nutrients into their biomass (Kufel & Kufel 2002, Chimney & Pietro 2006). Macrophytes show strong temporal patterns of nutrient uptake and retention starting during the spring growing season, reaching a maximum in the summer and then decreasing during the fall and winter dieback (Kufel & Kufel 2002, Clarke 2002). Studies have shown that between 900-1500 mg/day of nitrogen can be taken up by macrophytes (Howard-Williams 1985, Clarke 2002). Lake Seminole has an abundance of aquatic macrophytes including *Hydrilla verticillata*, water hyacinth (*Eichhornia crassipes)*, American water lily (*Nymphaea odorata)*, and Eurasian milfoil (*Myriophyllum spicatum*). *Hydrilla* is particularly efficient at assimilating available dissolved nutrients from both the sediment and water column and at times, has covered as much as 50% of Lake Seminole's surface (Gholson 1984, Grodowitz et al. 2003, Gu 2006, Dhote 2007). Gu (2006) found that in *Hydrilla*-dominated lakes, mean TP concentrations can be reduced from 126 g/L at the inflow site to 106 g/L at the outflow. The abundance of *Hydrilla* during most months and its known absorptive capacity makes it a likely seasonal NO_3^- and PO_4^- sink in Lake Seminole.

Higher summer temperatures are also likely to result in higher rates of microbial uptake for growth and permanent removal of N through denitrification. Studies have shown that denitrification in reservoirs can remove between 7%-16% of the total terrestrial N loads at a rate of between 1-80mg/day (Howard-Williams 1985, Clarke 2002, Seitzinger et al. 2006). Denitrification is largely driven by three key factors: low dissolved oxygen levels, the presence of highly labile organic matter and the availability of nitrate (Groffman et al. 1991, Seitzinger et al. 2006, Dodla et al. 2008). During the spring and summer, Lake Seminole displays low DO concentrations above the dam, has an abundant source of labile organic matter from macrophyte decomposition and receives consistent loads of nitrate from the upstream watershed. In addition, shallow reservoirs are particularly prone to high rates of denitrification because the sediment layer where nutrients are retained are more easily disturbed by human and wind activity (Nõges et al. 1998, Trojanowski & Trojanowska 2007, Irfanullah & Moss 2008). Collectively, these denitrification promoting factors are at a maximum during the spring and summer months which coincides with periods when the highest rates of N retention were observed.

In contrast to NO_3^- and PO_4^-, Lake Seminole appeared to consistently act as a source for NH_4^+, with export often exceeding import, especially during the spring and summer months. A NH_4^+ source dynamic is likely seen during the spring and summer seasons due to relatively low dissolved oxygen concentrations at the bottom of the reservoir that cause the absorptive capacity of the sediment to be reduced that triggers the release of NH_4^+ (Clavero et al. 2000, Quirós 2003). High flow events contribute to NH_4^+ release by causing stores of NH_4^+ that have accumulated in deeper waters to be re-suspended back into the water column (Morin & Morse 1999).

Lake Seminole also consistently acted as a source of DOC and DON during the spring and summer months. We believe this pattern results partly from new inputs of autochthonous carbon from phytoplankton breakdown (Wetzel 2001, Quirós 2003). Aquatic macrophytes are responsible for much of the organic matter production in wetlands and large quantities of organic carbon are released upon the onset of their senescence. However, this senescence and breakdown of organic matter would be a factor mostly during the fall and winter (Wetzel 1990, Clarke 2002, Chimney & Pietro 2006). Other possibilities include high flow events causing organic matter trapped within sediment to be re-suspended into the water column and stores of organic material that have accumulated in the deeper waters near the dam to be released during flood control efforts (Stanley & Doyle 2002, Matzinger et al. 2007, Trojanowski & Trojanowska 2007, Yang et al. 2008).

Budgeting Uncertainties and Limitations:

Although the water budget was constructed with great care, an examination of sources of error is warranted. The USGS gauge located in Columbus, GA is the closest Chattahoochee River gauge to Lake Seminole and was therefore the only logical source of Chattahoochee River flow data. However, this gauge represents one area of concern because of its high degree of daily variability in measured discharge. Variability is believed to occur because the dam at the George W. Andrews reservoir is only a partial dam capable of controlling flows only at low discharges rates and exhibits no significant capacity for storage. Calculating daily flow measurements is a highly complex process at this site because discharge is determine based on the use of two ratings, stage-area and index velocity. Stage value determines the channel area at a surveyed cross-section of the channel reach and the measured index-velocity value determines the mean channel velocity at that cross-section. A range of index-velocities is used to come up with the relation between index-velocity and mean channel velocity (personal comm. with Tony Gotvald, USGS hydrologist, 2009). Also, flow measurements at the Chattahoochee gauge are taken immediately downstream of the dam so discharge rates clearly display the effects of regulation. The Chattahoochee gauge is also much farther north of Lake Seminole in comparison to the other river gauges which could cause a lag in the measured discharge relative to the amount being discharged into the reservoir during sampling. For the Flint River gauge in Bainbridge, the nearest reservoir is much farther upstream and therefore time is available for the effects of regulation to be dampened and less variability in day to day flows will occur. The Flint River gauge at Bainbridge also measures discharge within the river/reservoir interface and thus likely provides a more accurate representation of discharge to the reservoir in comparison to that of the Chattahoochee. Similarly, Spring Creek is an unregulated waterway where daily flow rates vary minimally and discharge is also measured at the river/reservoir interface. The Apalachicola River gauge, located immediately below the reservoir, provides a discharge estimate for surface water outflow from the reservoir with essentially no delay. However, sudden changes in release during the sampling period for which daily discharge was estimated adds uncertainty to the surface water discharge term in the water budget. Our solution to these uncertainties was to estimate a daily discharge using an average of four consecutive days which bracketed each two day sampling events. This method was chosen to more accurately reflect river discharges that were included in each snapshot of the reservoir's water budget.

High-flow events also exhibit a degree of uncertainty due to large quantities of water going unaccounted for because of un-gauged surface runoff and river bank overflow. This error causes the outflow rate from Lake Seminole to appear greater than the inflow rate and results in the groundwater term being artificially elevated in order to make up for the missing inflow quantity. Dalton et al. (2004) estimated that about 4% of their water budget was missing due to un-gauged flows. There is also uncertainty in the quantity of in-reservoir groundwater import and export. Opsahl et al. (2007) found that regional patterns of groundwater inputs varies with higher amounts of influx during the winter and spring and lower amounts during the summer and fall. These findings indicate there is temporal variability in groundwater input but we do not know to what degree these patterns are mirrored within the reservoir. Another source of water budget error could be due to rain/evaporation data only being taken from one gauge station. This limitation suggests that rain events were uniform across the entire reservoir which is not likely the case. Also, the atmospheric deposition gauging station is located in Quincy, FL, 72 km away from Lake Seminole, which may not accurately represent concentrations of nitrate in atmospheric deposition that occurred on Lake Seminole.

Conclusion:

Quantification of fluxes of dissolved constituents based on a water budget demonstrated that the import and export of nutrient and DOC appear to be influenced by hydrologic variability with benthic and pelagic biotic processes likely controlling the nutrient sink and source dynamics seen during the spring and summer months. Lake Seminole acted as an effective trap for NO_3^- and PO_4^- likely due to uptake and storage by aquatic macrophytes during their active growing phase. In contrast, the reservoir appeared to generally be a source of organic matter presumably due to autochthonous inputs occurring within the lake. This study demonstrates that Lake Seminole is an important site for nutrient processing and serves as a gateway for downstream delivery of nutrients to the Apalachicola River and Apalachicola Bay ecosystem, an economically important source of shellfish (Dalton et al. 2004). More understanding of Lake Seminole's source/sink dynamics will provide a stronger basis to predict future patterns of eutrophication in both the reservoir itself and Apalachicola River and Bay.

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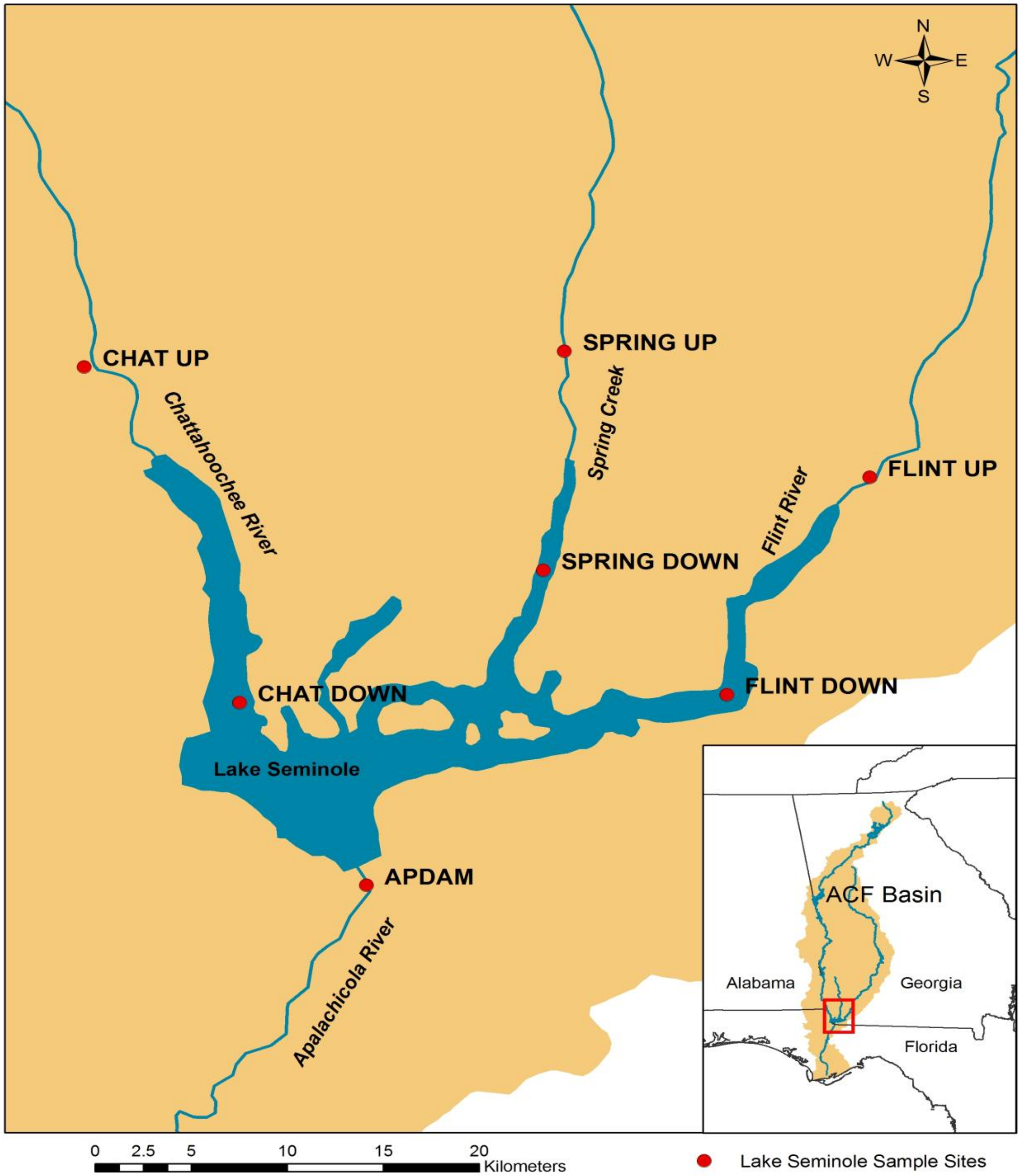

Figure 3.1: Lower Apalachicola-Chattahoochee-Flint (ACF) river basin is located in eastern Alabama, western Georgia and northwestern Florida. The Chattahoochee River, Flint River and Spring Creek converge to form Lake Seminole. Outflow from the Jim Woodruff Lock and Dam serves as the headwater source for the Apalachicola River. Sample sites with gauge station information were available at CHAT UP (USGS 02343801), SPRING UP (USGS 02357150), FLINT UP (USGS 02356000) and APDAM (USGS 02358000).

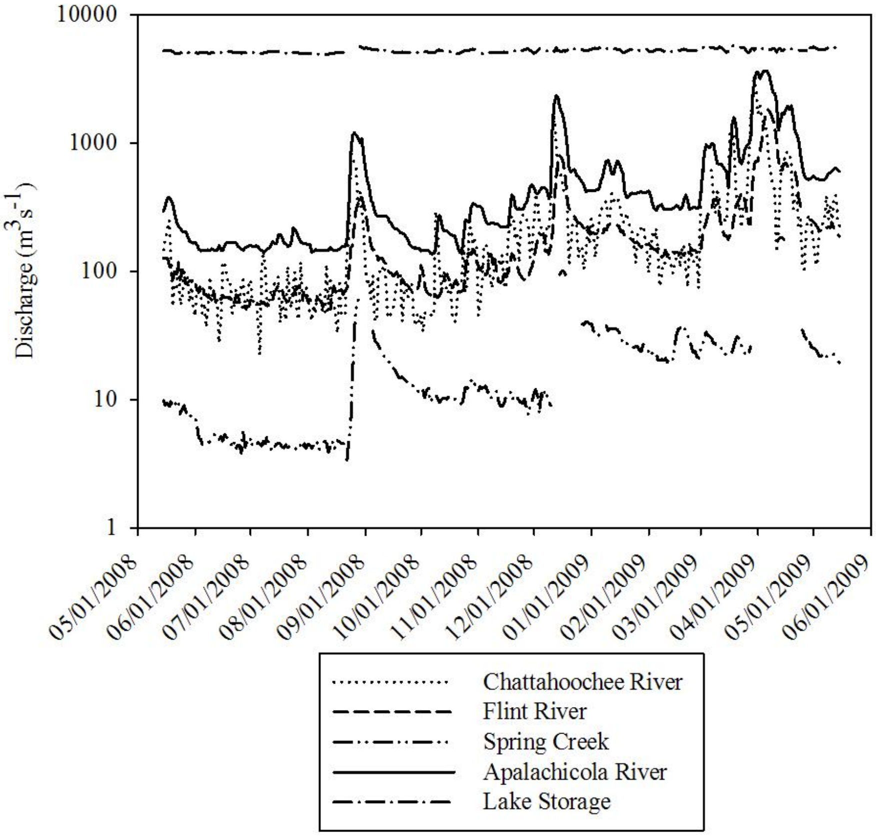

Figure 3.2: Discharge at the Chattahoochee River (USGS 02343801), Flint River (USGS 02356000), Spring Creek (USGS 02357150), Apalachicola River (USGS 02358000) and Lake Seminole storage (USGS 02357500) from May 15, 2008 until May 15, 2009.

Table 3.1: Summary of the annual water budget for the lower ACF basin and Lake Seminole. All measurements are in m^3s^{-1}.

Date	Spring Creek	Chattahoochee River	Flint River	Precipitation	Total River Inflow	Total Inflow	Apalachicola River	Evaporation	Total Outflow	Change in Storage	GW
05/27/08	8	84	85	0	178	178	190	11	201	7	30
06/10/08	5	71	62	13	138	151	146	10	156	18	22
06/23/08	4	58	60	0	122	122	160	9	169	-24	23
07/07/08	5	90	56	2	151	153	144	10	154	20	22
07/21/08	4	66	60	48	131	179	161	9	171	-2	-11
08/04/08	4	52	58	0	115	115	143	9	152	-18	20
08/18/08	5	52	71	0	128	128	150	7	158	5	35
08/26/08	40	600	256	15	897	911	1142	7	1149	143	380
09/08/08	25	83	127	4	235	239	269	8	277	-9	29
09/29/08	12	42	83	0	136	136	149	7	156	2	22
10/22/08	10	105	71	22	186	208	154	3	157	59	8
11/20/08	10	226	123	0	360	360	346	3	349	33	22
12/16/08	96	494	692	0	1282	1282	1586	2	1587	-13	292
01/20/09	27	247	182	0	456	456	390	2	392	64	0
02/23/09	27	123	145	0	296	296	316	4	321	-10	15
03/23/09	26	291	379	0	696	696	762	6	768	-9	62
04/13/09	178	520	663	18	1361	1380	1515	6	1521	51	192
05/12/09	21	311	200	0	532	532	618	9	627	-15	80
Study Period Average	28	195	187	7	411	418	463	7	470	17	69
% of Budget	7	47	45	2			99	1			24

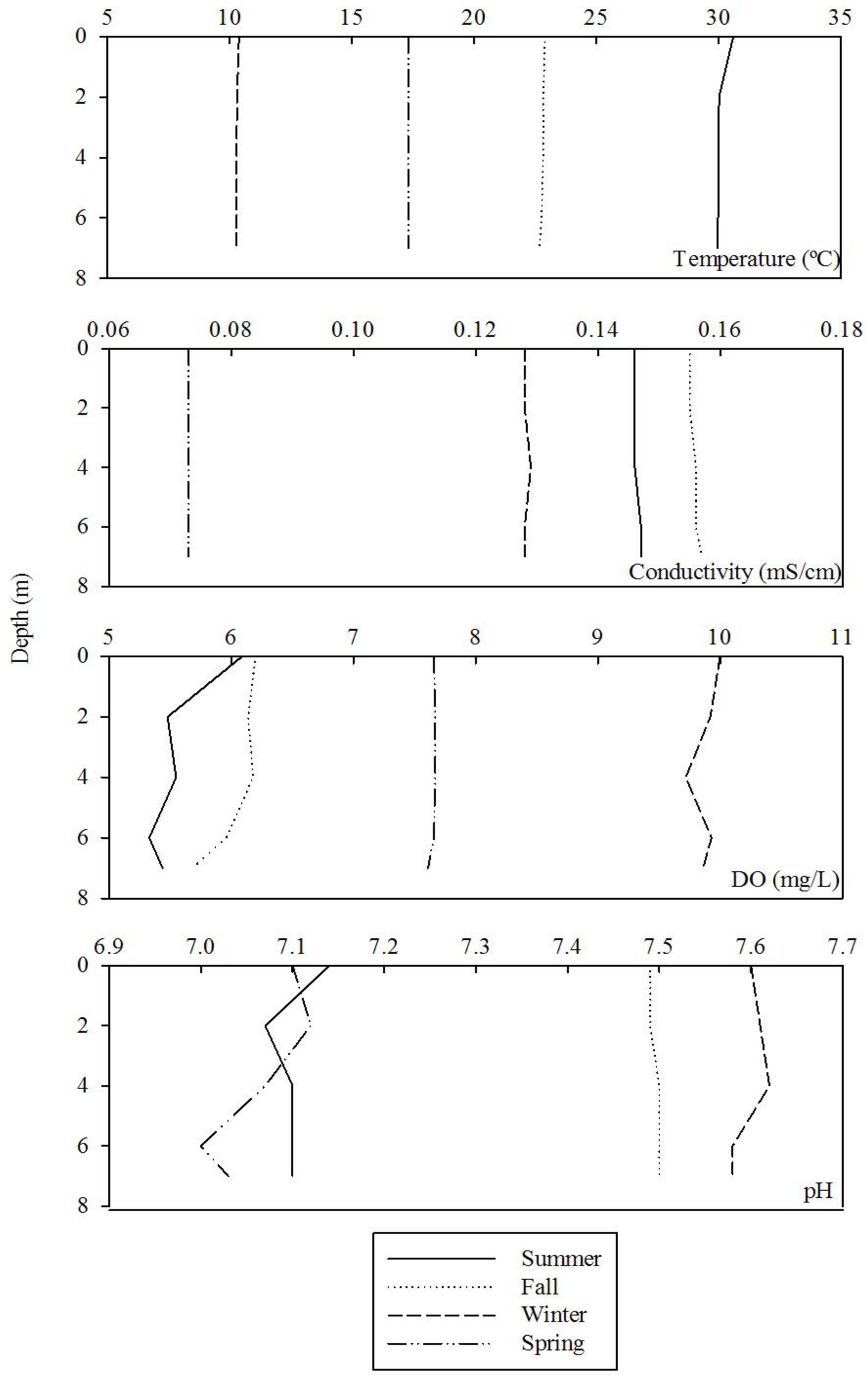

Figure 3.3: Chattahoochee River (CHAT DOWN) temperature, DO, conductivity and pH depth profiles shown by seasons.

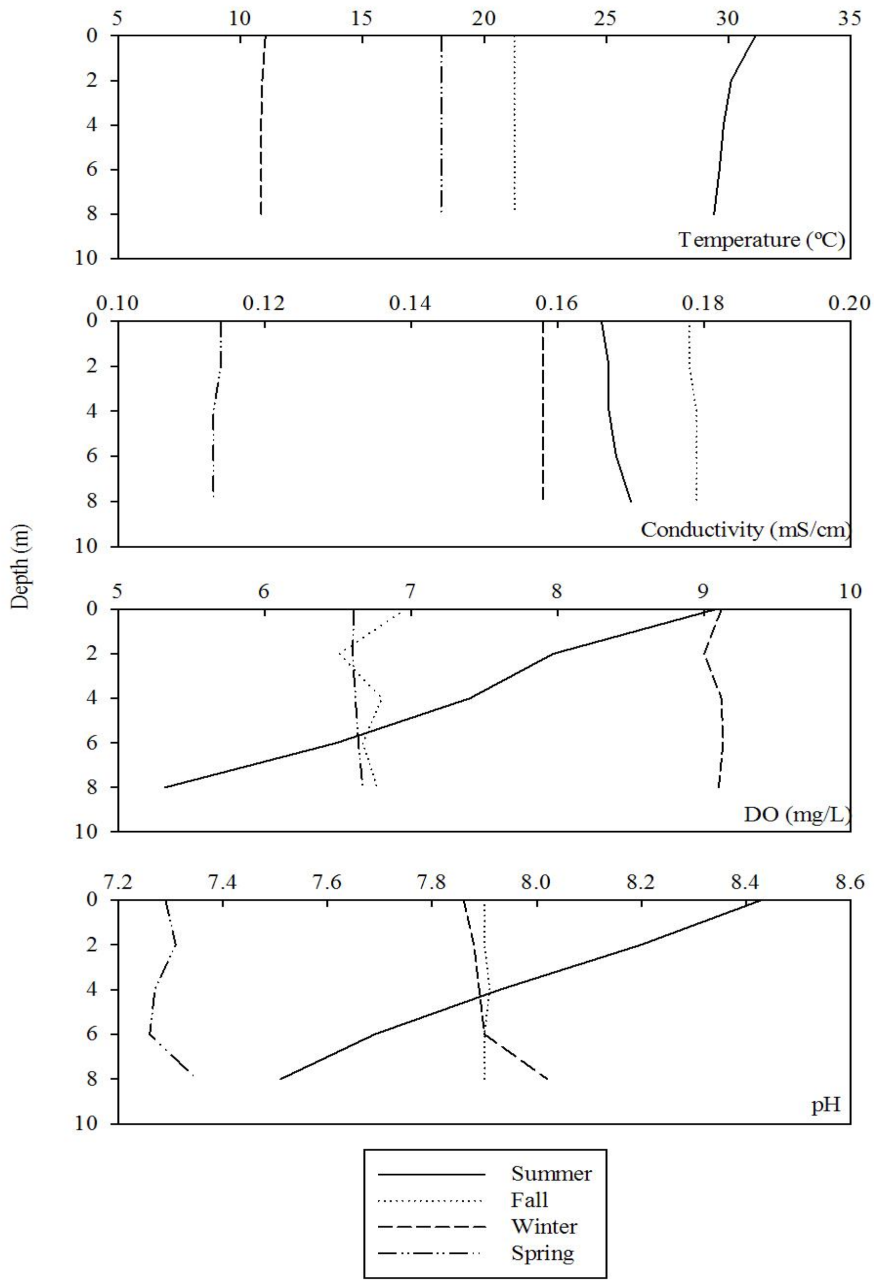

Figure 3.4: Flint River (FLINT DOWN) temperature, DO, conductivity and pH (d) depth profiles shown by seasons.

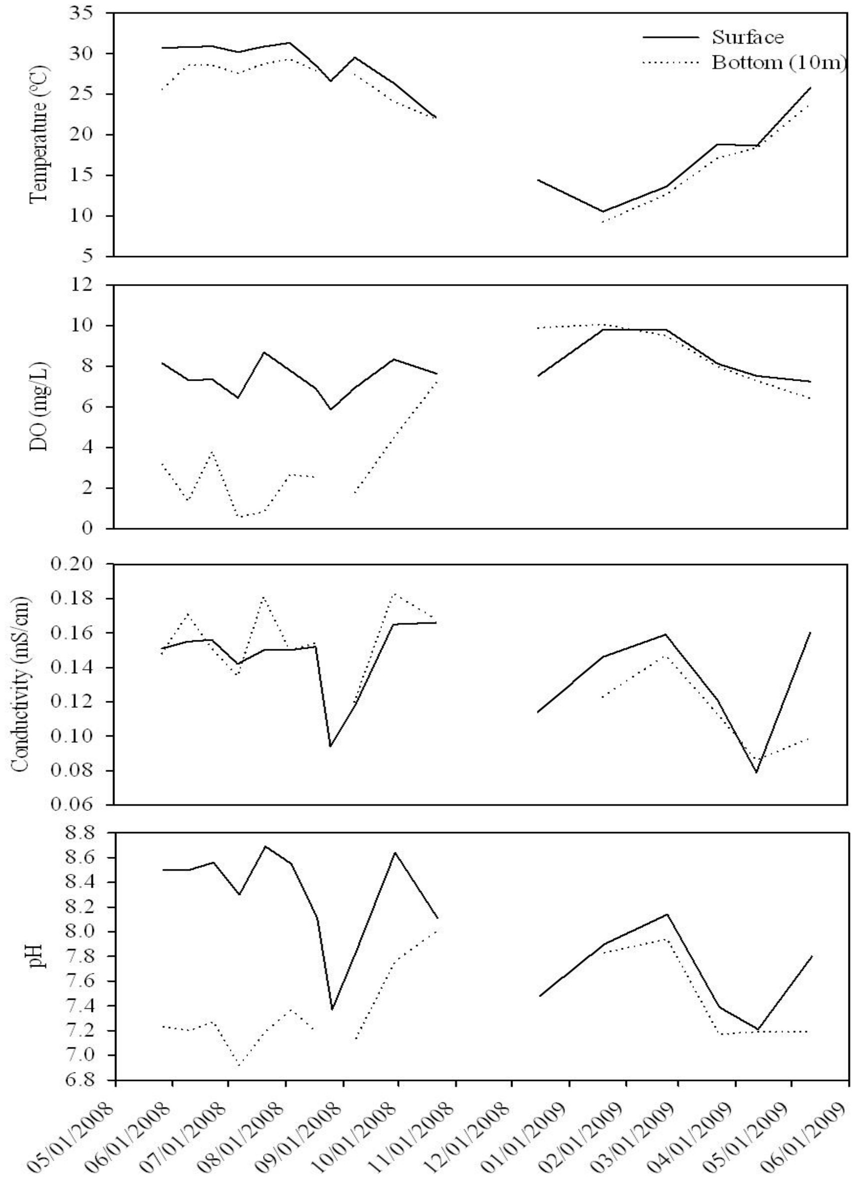

Figure 3.5: Surface and bottom (10m) temporal changes in the physical and chemical parameters of Lake Seminole.

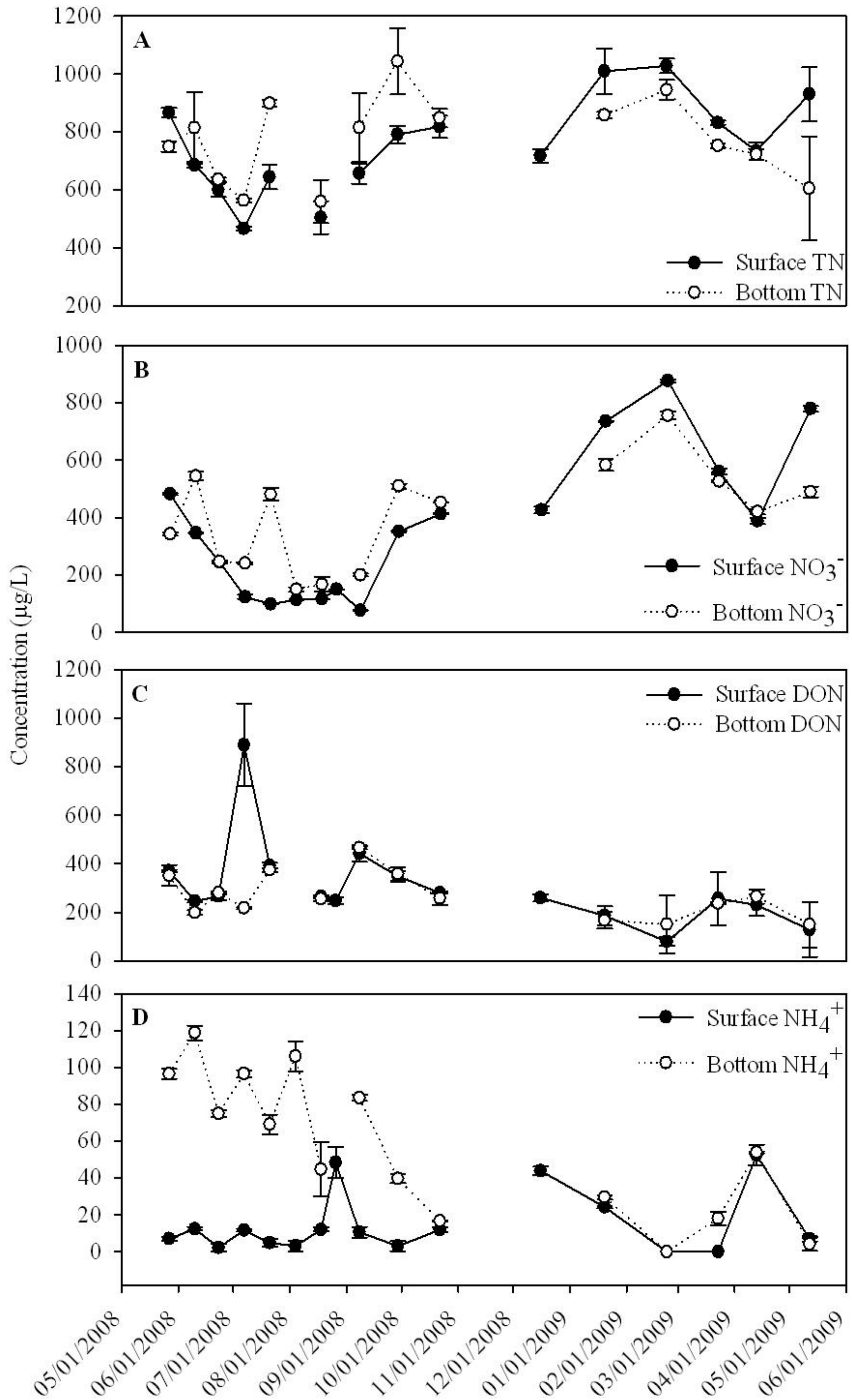

Figure 3.6 A, B, C, D: Temporal changes in the surface and bottom (10m) concentrations of TN, NO_3^-, DON and NH_4^+ (µg/L).

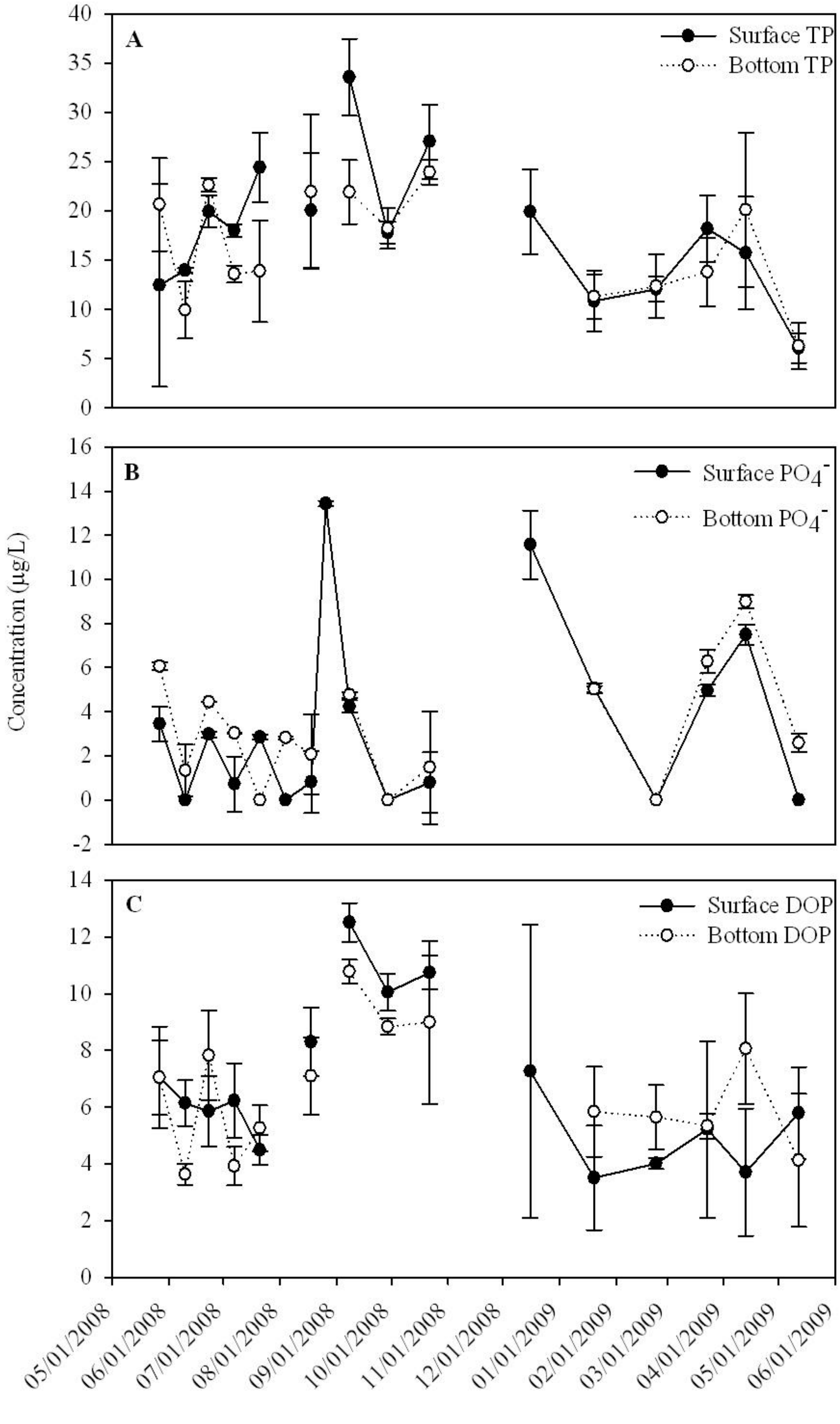

Figure 3.7A, B, C: Temporal changes in the surface and bottom (10m) concentrations of TP, PO_4^- and DOP (µg/L).

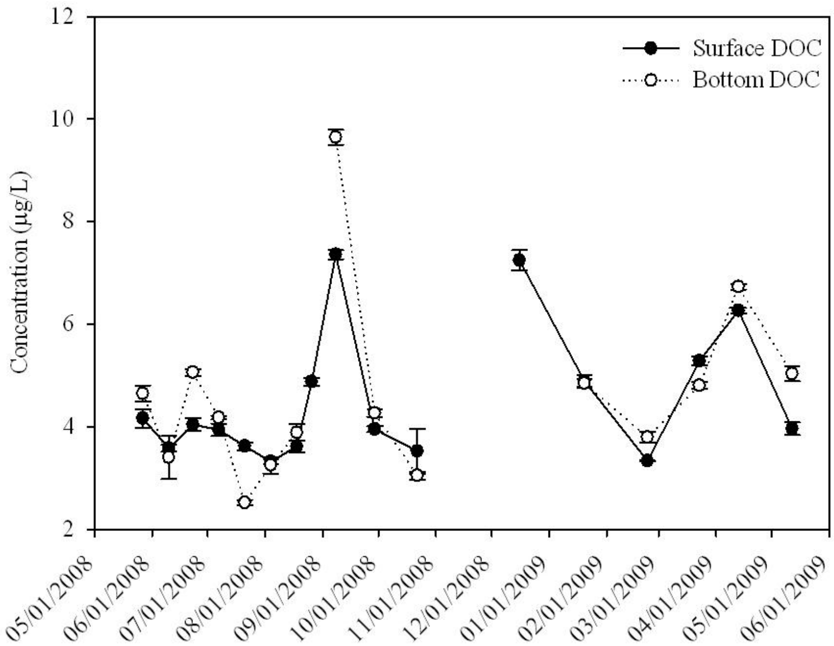

Figure 3.8: Temporal changes in the surface and bottom (10m) concentrations of DOC (mg/L).

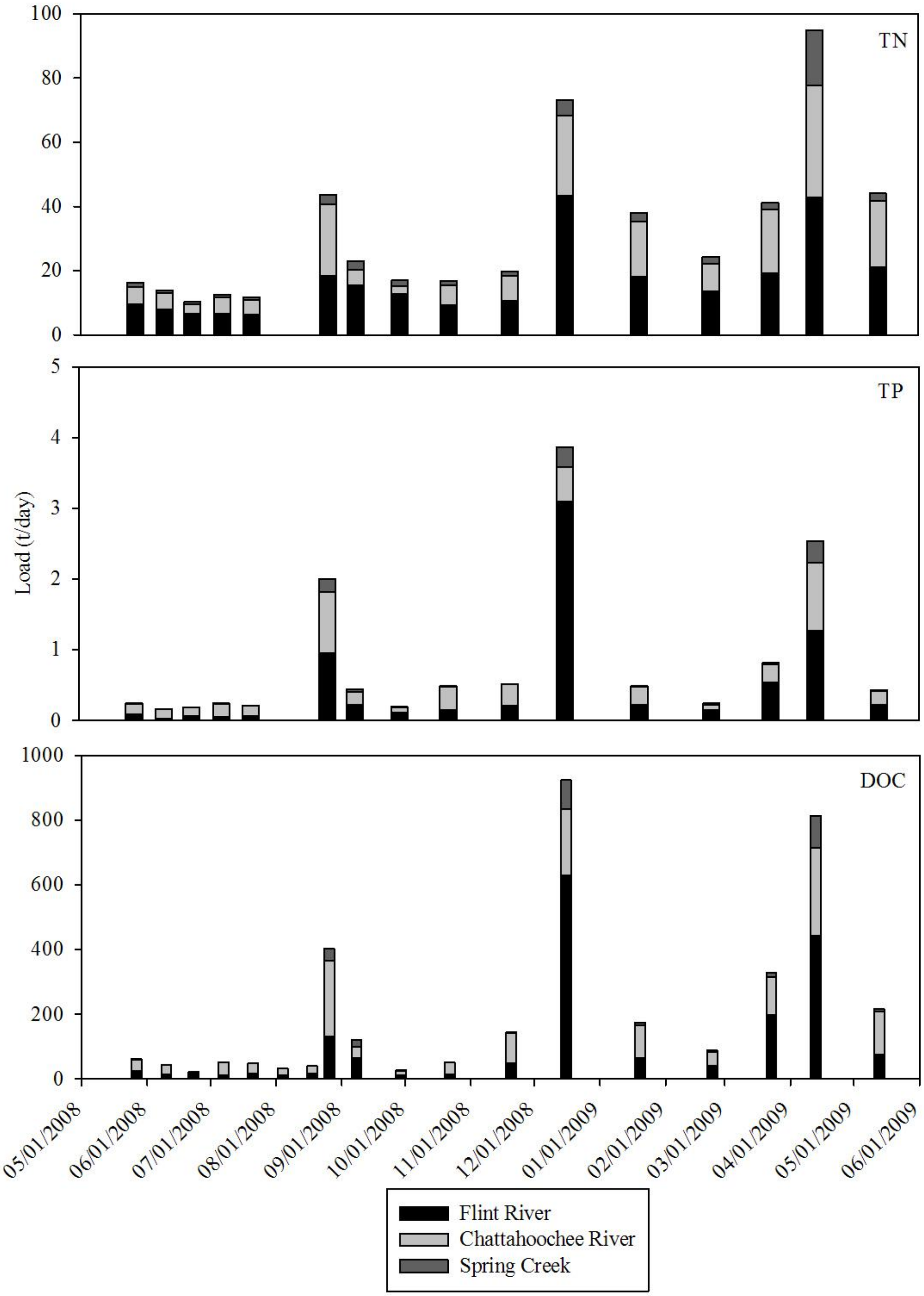

Figure 3.9: Temporal loading (t/day) of TN, TP and DOC by the Chattahoochee River, Flint River and Spring Creek.

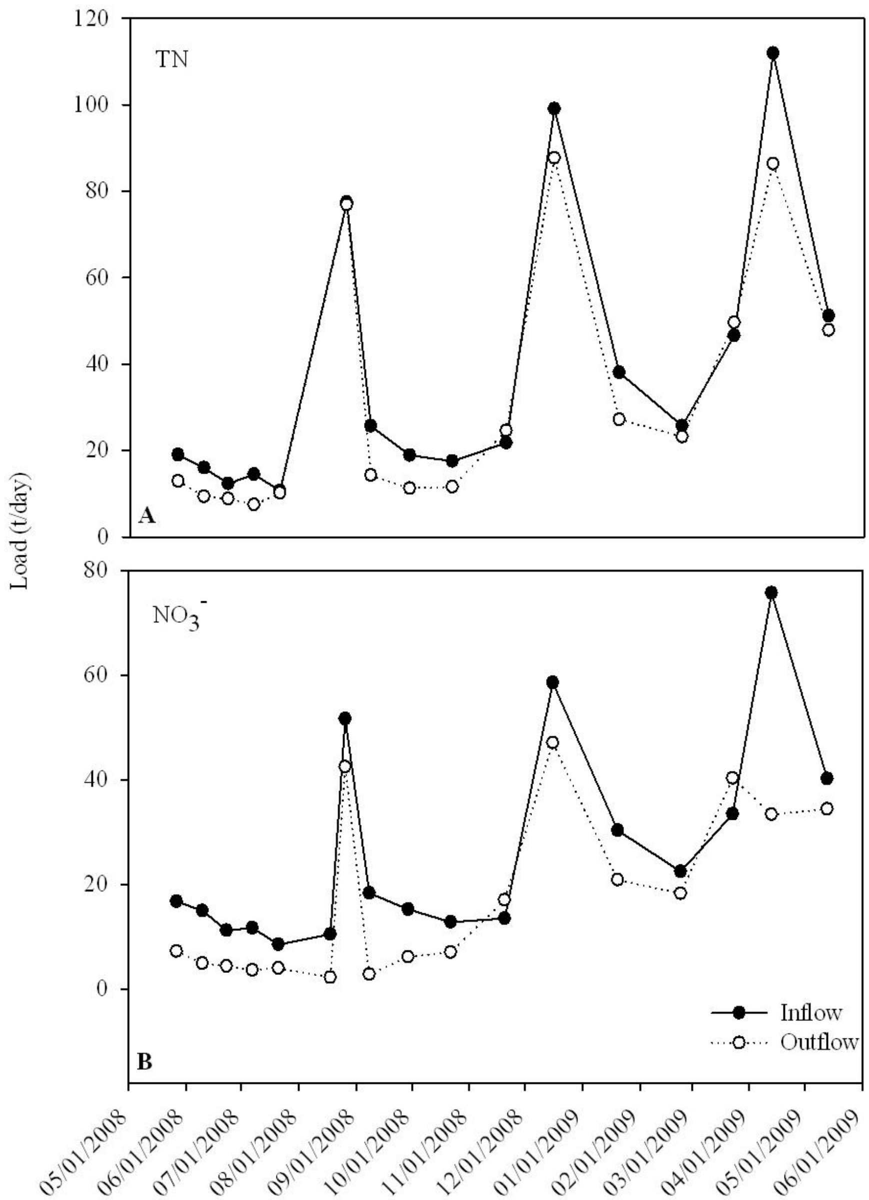

Figure 3.10 A, B: Temporal fluctuations in the import and export of TN (a) (t/day) and NO_3^- (b) into and out of Lake Seminole.

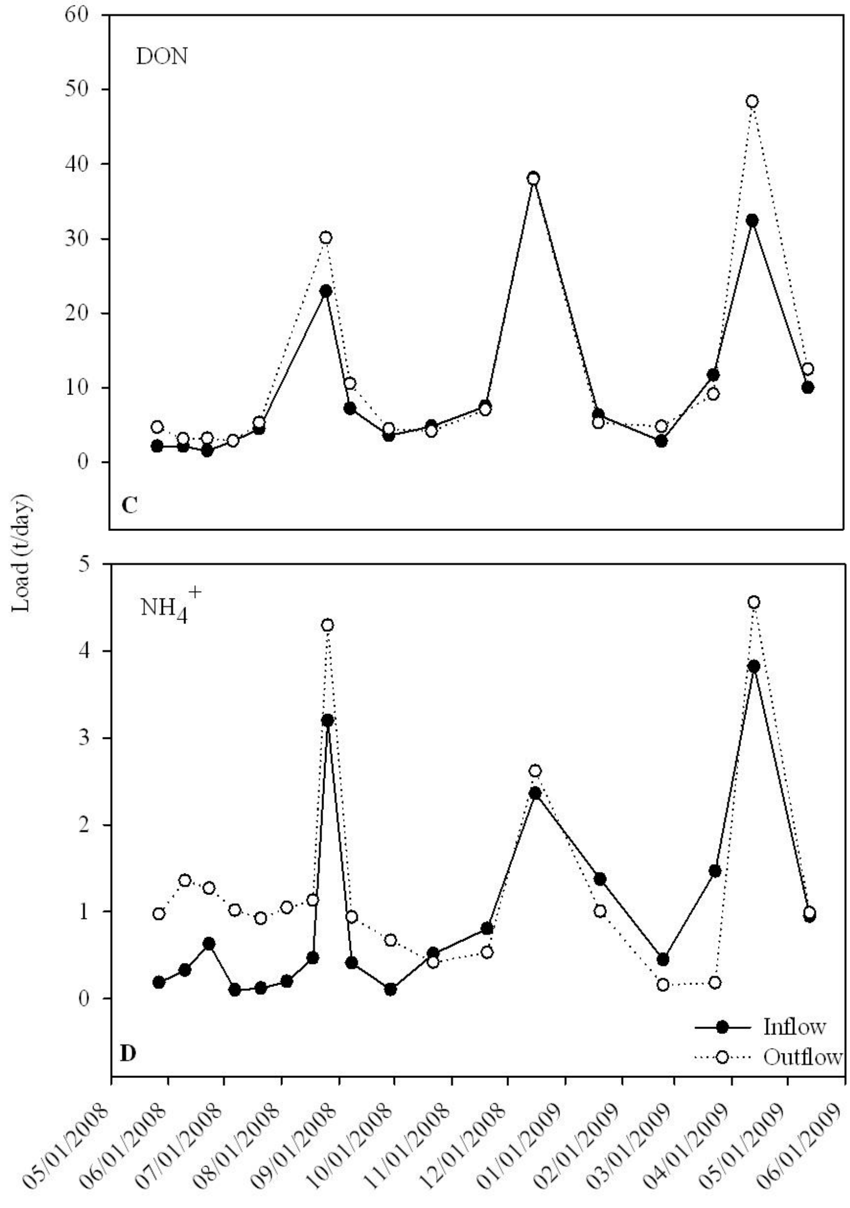

Figure 3.10 C, D: Temporal fluctuations in the import and export of DON (a) (t/day) and NH_4^+ (b) into and out of Lake Seminole.

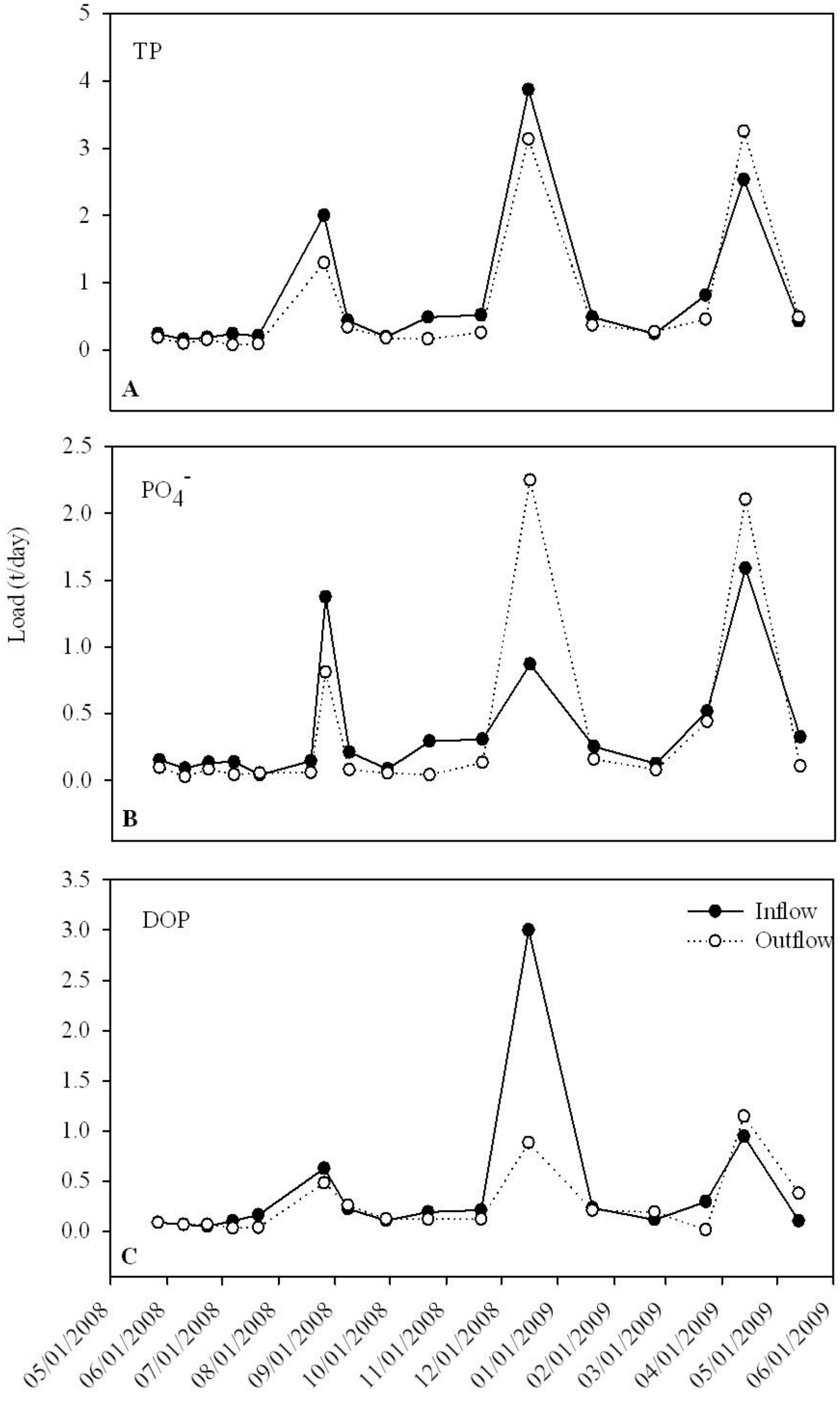

Figure 3.11 A, B, C: Temporal fluctuations in the import and export of phosphorus constituents (t/day) into and out of Lake Seminole.

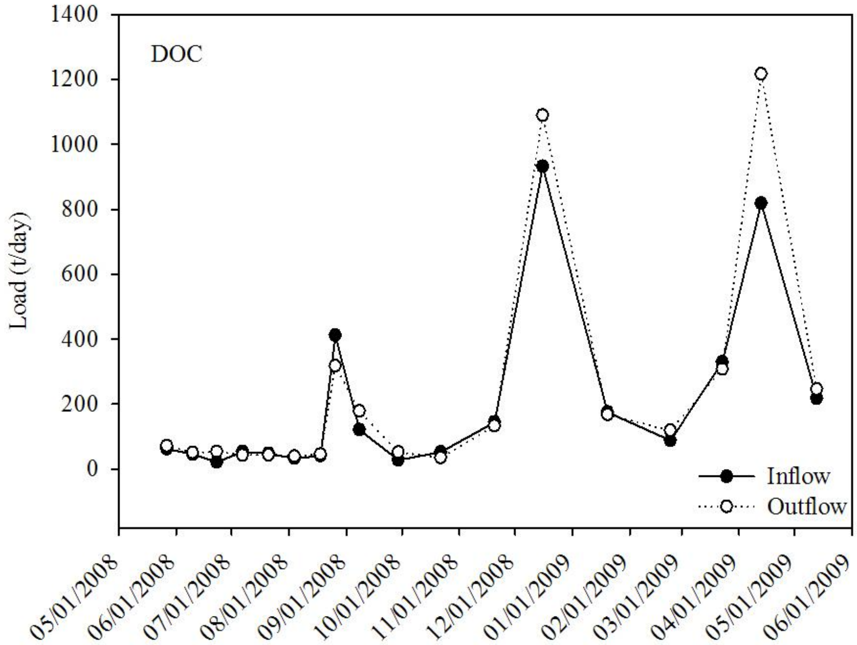

Figure 3.12: Temporal fluctuations in the import and export of DOC (t/day) into and out of Lake Seminole.

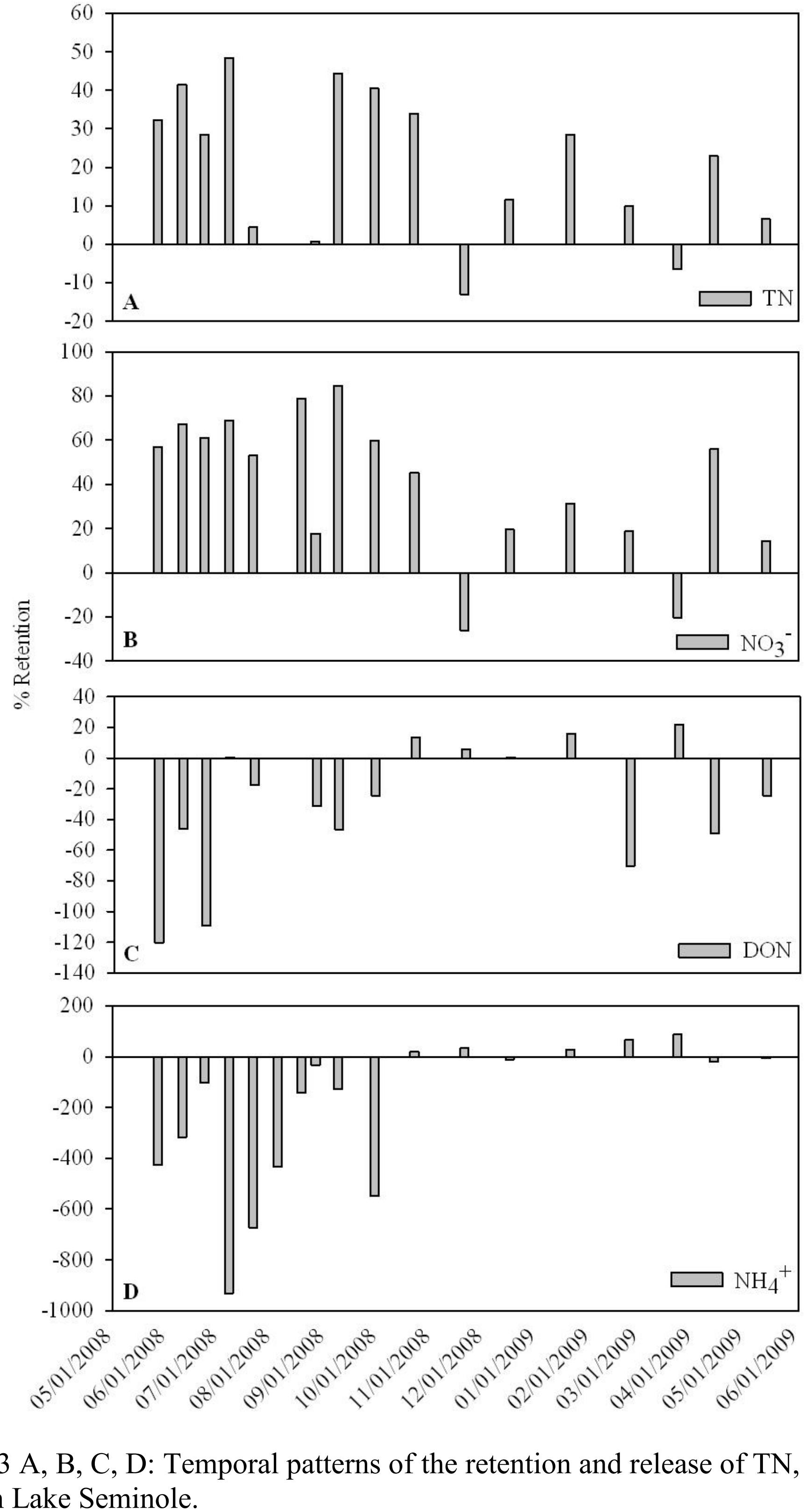

Figure 3.13 A, B, C, D: Temporal patterns of the retention and release of TN, NO_3^-, DON and NH_4^+ from Lake Seminole.

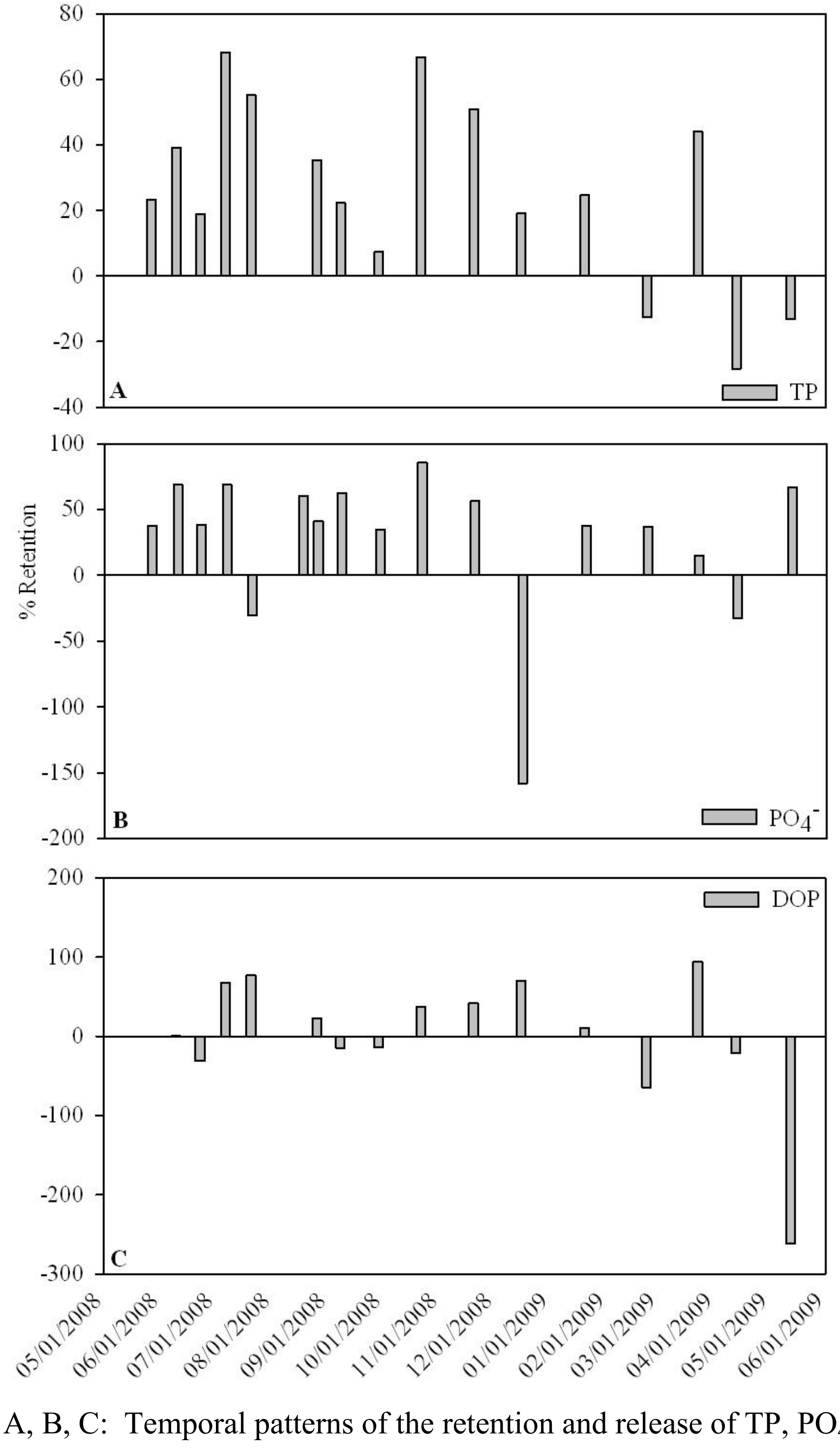

Figure 3.14 A, B, C: Temporal patterns of the retention and release of TP, PO_4^- and DOP from Lake Seminole.

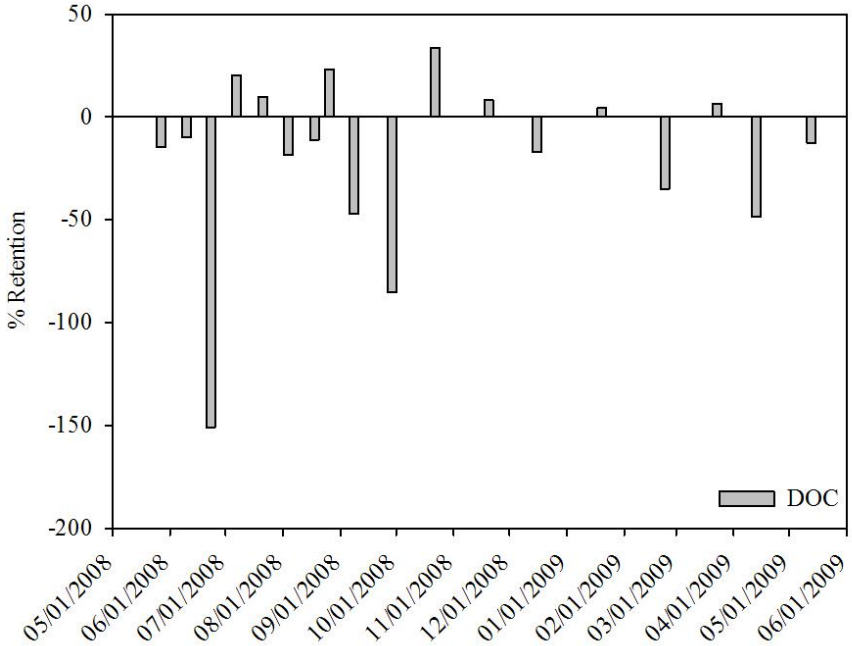

Figure 3.15: Temporal patterns of the retention and release of DOC from Lake Seminole.

Table 3.3: Results from linear regression analysis indicating correlations between nutrient inflow loads and retention occurred.

		Inflow
NO_3^-	r-squared	0.345
	p-value	0.013 (+)
DON	r-squared	0.264
	p-value	0.042 (-)
NH_4^+	r-squared	0.00119
	p-value	0.892 (+)
PO_4^-	r-squared	0.093
	p-value	0.416(-)
DOP	r-squared	0.832
	p-value	<0.001 (+)
DOC	r-squared	0.469
	p-value	0.002 (-)

CHAPTER 4:

NUTRIENT, DISSOLVED ORGANIC CARBON AND BIOMASS LOSS DURING DECOMPOSITION OF HYDRILLA VERTICILLATA UNDER OXIC AND ANOXIC CONDITIONS[3]

[3] McEntire, J.M., S.P. Opsahl, A.P. Covich, S. Wilde and T. Rasmussen. To be submitted to *Aquatic Botany*.

Abstract:

Aquatic macrophytes are an integral part of lentic ecosystems and can represent an important source autochthonous organic and inorganic input during their seasonal decomposition. This study assessed the rate of biomass loss and the quantity of nutrients and dissolved organic carbon (DOC) released from the submerged aquatic macrophyte, *Hydrilla verticillata*, under oxic and anoxic conditions in a controlled laboratory experiment. Fresh clipped *Hydrilla* was placed into aerated and non-aerated containers for an 18 day period. Containers were removed at 2, 4, 6, 9, 13 and 18 day intervals, biomass loss was assessed and the nutrient and DOC concentrations were analyzed. Over 18 days, *Hydrilla* lost 49% of its biomass in oxic conditions and 54% under anoxic conditions. Overall, nitrogen and phosphorus constituents showed different patterns of change during decomposition with net accumulations of TN, NO_3^-, TP and PO_4^- in both oxic and anoxic environments at the conclusion of the experiment. DON and DOP concentrations increased during decomposition but did not exhibit net accumulations at the conclusion. There were significant differences in DOC between oxic and anoxic conditions with concentrations in aerated containers increasing from 2.1 mg/L to 5.5 mg/L but only 1.8 mg/L to 1.9 mg/L in non-aerated containers. Greater DOC accumulation in aerated conditions suggests less efficient microbial breakdown of *Hydrilla*-derived DOC. Less accumulation of DOC under anoxic conditions was possibly due to denitrification.

Introduction:

Submerged aquatic vegetation (SAV) is an integral part of lentic ecosystems and plays an important role in the structure and functioning of these habitats (Clarke 2002, Wang et al. 2008). In shallow reservoirs, aquatic macrophytes are often responsible for maintaining a clear water state and good water quality by acting as seasonal sinks for nitrogen and phosphorus through assimilation and storage of nutrients within their biomass (Kufel & Kufel 2002, Wang et al. 2008, Sollie & Verhoeven 2008, Gu & Dreschel 2008). Despite the efficient uptake of nutrients by SAV, seasonal cycles of decomposition cause retained nutrients to be released back into the ecosystem (Kröger et al. 2007).

Senescing macrophytes represent an important source of organic and inorganic autochthonous nutrient input. The organic material and nutrients released often contribute a major fraction of the total organic material and energy making up the ecosystem's detrital pool and nutrient cycle (Kuehn et al. 1999, Gamage & Asaeda 2005, Davis et al. 2006, Longhi et al. 2008). Clarke (2002) found that SAV decay can account for 18% of the annual TP loading and Battle & Mihuc (2000) found that N input could account for 2.2% of the annual load. Rapid leaching of nutrients from macrophytes begins in the late summer and fall and can last a several days or a few weeks with SAV losing as much as 93% of their biomass, N and P content (Peverly 1985, Davis et al. 2006, Kröger et al. 2007).

Aquatic macrophytes also affect the physical parameters of ecosystems by altering the availability of dissolved oxygen (DO), light and temperature within the water column (Titus et al. 2004, Carter et al. 1991). Temperature and oxygen are the most important factors influencing the rate of nutrient release from decomposing macrophytes (Ogwada et al. 1984). Higher temperatures cause faster rates of leaching due to greater microbial activity (Carpenter & Adams

1979, Chimney & Pietro 2006). Debate exists as to whether oxic or anoxic environments cause faster rates of decomposition. Higher DO concentrations have been shown to exhibit faster decay rates because of the increased abundance of microbes (Nichols & Keeney 1973). In contrast, anoxic environments have been shown to cause more rapid rates of decay because less carbon is assimilated and the less nitrogen is needed for decomposition to occur (Nichols & Keeney 1973).

The purpose of this experiment was to preliminarily determine the rate of biomass loss and the quantity of nutrients and DOC released from the submerged aquatic macrophyte, *Hydrilla verticillata*, under oxic and anoxic conditions in a controlled laboratory setting. *Hydrilla* is a very efficient nutrient sink, has a fast decomposition rate and has been found to loss as much as 86% of its initial biomass in a three week span (Battle & Mihuc 2000, Gu 2006). We hypothesized that there would be significant differences in biomass loss and nutrient release between the oxic and anoxic conditions. Data from this experiment will hopefully aid in determining *Hydrilla's* role in nutrient cycling within Lake Seminole.

Methods:

Field Collection:

A bulk sample of *Hydrilla verticillata* was collected from a stand at Cummings Landing located on the northwest side of Lake Seminole. Lake Seminole is a shallow, subtropical, 15,175 hectare man-made reservoir located at the border of southwest Georgia and northwest Florida, within the lower Apalachicola-Chattahoochee-Flint (ACF) River Basin System in the Coastal Plain physiographic region of southeastern United States (http://www.sam.usace.army.mil/op/rec/seminole/) (Figure 3.1). During collection, 20-L of lake water was collected from within the stand in an acid-washed, polypropylene 20-L carboy. The material was returned to the Joseph Jones Ecological Research Center were the *Hydrilla* was thoroughly rinsed with distilled water to remove periphyton and sediment and the lake water was filtered through an ashed 150 mm glass micro fiber filter using a peristaltic pump. The leaves from the apical tips of the plant were cut into 12 cm strands and blotted with paper towels to remove excess water. From the bulk sample, forty 12 cm wet strands were dried at 70 °C for 48 hours and then weighed to establish a wet/dry weight conversion factor.

Decomposition Experiment and Sample Analysis:

Wet *Hydrilla* from the bulk sample was weighed out into 10 g (wet tissue weight) units and placed into 36 1-L plastic containers that held 750 mL of artificial lake water created following the methods of Smart & Barko (1985) and an inoculation of 250 mL of filtered Lake Seminole water. Smart & Barko (1985) artificial lake water was utilized to maintain consistent initial water nutrient chemistry. The inoculation of lake water was used so that the experiment would include a population of lake microbes. Aquarium bubblers were placed into eighteen of the containers with lids to create oxic environments. The other eighteen containers were sealed to create an anoxic environment. All 36 containers were placed into a dark incubation chamber set to 30 ºC and covered with black plastic bags to prevent the infiltration of light when the door was opened.

Containers were collected at 2, 4, 6, 9, 13 and 18 day intervals. Over this time period, dissolved oxygen (DO) concentrations in each container were measured on a daily basis at roughly 4 p.m. using a Hach Quanta Hydrolab. Observational monitoring was also conducted to assess the physical state of the *Hydrilla* during decomposition and notes were made when signs of senescence began. After removal from the incubation chamber, the contents of the containers were filtered through 45 μm and 500 μm sieves. Particles captured in the 45 μm sieve were considered fine particulate matter and particles collected in the 500 µm sieve were considered course matter. Course and fine *Hydrilla* was dried at 70 °C for 48 hours and then weighed to determine dry weight. All *Hydrilla* was ground using a ball mill grinder and then 0.5 mg subsamples from each container were weighed into preweighed, preashed aluminum pans and ashed at 500 ºC for 30 minutes in a Lindberg Blue muffle furnace.

Water from the containers was filtered through 0.7 µm glass fiber filters. Dissolved organic carbon (DOC) samples were analyzed using a Shimadzu TOC-5050 analyzer. Samples of ammonium (NH_4^+) (Lachat Method 10-107-06-1-G), nitrate (NO_3^-) (Lachat Method 10-107-06-1-B) and phosphate (PO_4^-) (Lachat Method 10-115-01-B) were analyzed on a dual channel Lachat Quick Chem 8000. Total nitrogen (TN) (Lachat Method 10-107-04-1-B) and total phosphorus (TP) (Lachat Method 10-115-01-B) were analyzed on filtered and unfiltered samples following digestion by the Johnes & Heathwaite (1992) method. A CEM MDS-2000 microwave was used to perform the digestions. Dissolved organic nitrogen (DON) and phosphorus (DOP) were calculated as the difference between filtered TN and TP and DIN and DIP. Particulate nitrogen and phosphorus (PN and PP) were calculated as the difference between filtered TN and TP and unfiltered TN and TP and the concentrations included both organic and inorganic nutrients. The detection limit for TN/NO_3^- was 2 µg/L, TP/PO_4^- was 3 µg/L and NH_4^+ was 3 µg/L. DOC was 0.1 mg/L.

Data Analysis:

Statistical analyses were performed using the SigmaPlot 11.0 feature SigmaStats (San Jose, CA). Prior to analysis, each nutrient constituent was tested to see if the assumptions of normality and homogeneity of variance were met using a Shapiro-Wilk test. Not all of the constituents meet the assumptions of normality so Mann-Whitney rank sum test was performed to analyze the differences between biomass loss, dissolved oxygen and nutrient concentrations in aerated and non-aerated conditions.

Results:

Biomass Loss & Dissolved Oxygen:

Initial dissolved oxygen (DO) concentrations at Day 0 were 4.7 mg/L in aerated conditions and 3.1 mg/L in non-aerated conditions (Figure 4.3). Over the 18 day study, DO in aerated containers ranged from 4.5 mg/L to 6.6 mg/L (mean 5.66±0.7 mg/L) and from 1.4 mg/L to 2.1 mg/L (mean 1.74±0.2 mg/L) in non-aerated containers. There was a significant difference between DO concentrations in aerated and non-aerated containers (Mann-Whitney, $p = <0.001$).

Initial decomposition occurred rapidly within the first two days with a 40% biomass loss in aerated conditions and 20% loss in non-aerated conditions (Figure 4.2). Biomass loss continued in both the aerated and non-aerated containers though some variability was observed. By Day 18, 49% of *Hydrilla's* biomass was lost in oxic conditions and 54% was lost under anoxic conditions and the difference was not statistically significant between the two treatments (Mann-Whitney, $p = 0.450$).

Nitrogen, Phosphorus and Dissolved Organic Carbon:

Initial nitrogen constituents were measured prior to the addition of plant material and were as follows: TN 374.2 µg/L, NO_3^- 12.6 µg/L, DON 106.4 µg/L, NH_4^+ 4.7 µg/L and particulate nitrogen (PN) 267.7 µg/L. TN increased from its initial concentration to 2455.7 µg/L in aerated conditions to 1192.6 µg/L in non-aerated containers with increases beginning on day 6 in both environments (Figure 4.4A). NO_3^-, which represented the majority of the TN present, reached concentrations that were higher than TN over the course of the study indicating an unidentified source of error (see discussion below). NO_3^- concentrations increased to 4177.5

μg/L in aerated conditions and to 1424.7 μg/L in non-aerated containers with major increases observed on day 18 in aerated containers and on day 13 in non-aerated containers (Figure 4.4B). Concentrations of DON in oxic conditions were dynamic and increased to 357 μg/L on day two, peaked at 445 μg/L on day 13 and decreased to 130 μg/L at the conclusion of the experiment (Figure 4.4C). DON concentrations in anoxic conditions showed similar trends, increasing from the initial concentration on day 2 (239 μg/L), peaking of on day 6 (423 μg/L) and then steadily decreasing to 89 μg/L at the conclusion of the experiment. Oxic and anoxic NH_4^+ concentrations varied minimally with increases beginning on day 6, peak concentrations of 137 μg/L (aerated) and 112 μg/L (non-aerated) observed on day 9 and then decreases to 46 μg/L and 38 μg/L observed at the end of the experiment (Figure 4.4D). PN, which represented the most minimal fraction of TN, peaked at 113.1 μg/L on day 13 in aerated conditions and showed two distinct peaks on day 6 (268 μg/L) and day 13 (297.4 μg/L) in non-aerated settings (Figure 4.4E).

Initial phosphorus constituents were measured prior to the addition of plant material and were the following: TP 47 μg/L, PO_4^- 0.8 μg/L, DOP 0.8 μg/L and particulate phosphorus (PP) 46 μg/L. TP increased from its initial concentration to a high of 109 μg/L on day 18 in aerated containers. In non-aerated containers, a peak in TP of 163 μg/L was observed on day 6 but TP then decreased to 48 μg/L (Figure 4.5A). PO_4^-, which represented the majority of the TP present, showed a slight increase from initial concentrations on day 2 but then increased minimally until day 18 when it reached a high of 101.1 μg/L in oxic conditions. In anoxic containers, an increase from the initial concentration was observed on day 2, a peak of 51 μg/L was reached on day 6 and then a decrease to 42 μg/L was observed at the end of the experiment (Figure 4.5B). DOP concentrations in oxic conditions showed minimal increases on days 2 and 9 and reached at high of 11 μg/L on day 18. Anoxic DOP concentrations steadily increased from the initial concentration beginning on day 2, reached a peak of 31 μg/L on day 6 and decreased to 8 μg/L at the end of the experiment (Figure 4.5C). PP, which made up the small fraction of TP, increased minimally in aerated conditions to a high of 14.8 μg/L on day 13 and decreased to BD on day 18 and had a peak of 81 μg/L on day 6 before decreasing to BD on day 18 in non-aerated conditions (Figure 4.5D).

Initial DOC concentration measured prior to the addition of plant material was 0.7 mg/L. In aerated conditions, DOC concentrations began to increase on day 2 and reached a high of 5.5 mg/L by the end of the study. In non-aerated conditions, DOC concentrations began to increase on day 2, reached a peak of 3.2 mg/L on day 6 before decreasing to 2 mg/L at the end of the experiment (Figure 4.6). A significant difference was observed between DOC concentrations in aerated versus non-aerated containers (Mann-Whitney, $p = 0.048$).

Discussion:

Biomass Loss and Nutrient and DOC Release during Decomposition

We expected greater rates of biomass loss in aerated containers because higher DO concentrations increase heterotrophic microbial activity and cause faster rates of decomposition (Nichols & Keeney 1973, Thullen et al. 2008). However, we found that there was only a minimal difference in *Hydrilla* biomass loss between the two conditions with 49% lost in aerated containers and 54% lost in non-aerated containers. During decomposition, unexpected increases in biomass were observed. Longhi et al. (2008) suggests that increases in macrophyte biomass during decomposition could be attributed to microbial communities actively taking up elements from the surrounding water and increase the biomass associated with plant tissue. However, the large increase in mass is too great to be explained by an increase in microbial biomass. Alternatively, the use of wet macrophyte material may have caused inaccuracies in the wet/dry conversion factor used to determine initial dry plant biomass (further discussed below).

At the conclusion of the experiment, TN and TP displayed net accumulations in both aerated and non-aerated conditions. Accumulation of TN and TP appeared to be primarily a function of the abundance of NO_3^- and PO_4^- which both showed high amounts of accumulation at the conclusion of the study. NO_3^- and PO_4^- concentrations were expected to rapidly accumulate during decomposition because of rapid initial macrophyte tissue breakdown and the release of soluble materials (Nichols & Keeney 1973, Ogwada et al. 1984, Gamage & Asaeda 2005, Chimney & Pietro 2006). NH_4^+ also appeared to contribute to TN accumulation but to a lesser extent than NO_3^- due to lower concentrations that are likely a result of rapid uptake by the microbial community (Landers 1982, Kistritz 1978). DON and DOP concentrations both displayed expected patterns of decomposition with rapid increases early in the experiment but then declined around day 6 in both aerated and non-aerated environments. In contrast to NO_3^- and PO_4^-, there were minimal amounts of net DON and DOP accumulation at the end of the experiment.

The greatest amounts of dissolved organic carbon accumulation occurred under aerated conditions likely due to greater rates of microbial activity. A possible explanation for less DOC accumulation in non-aerated environments is the occurrence of denitrification. Denitrification is largely driven by three key factors: low dissolved oxygen levels, the presence of highly labile organic matter and the availability of nitrate (Groffman et al. 1991, Seitzinger et al. 2006, Dodla et al. 2008). Each of these factors appeared to be met within the non-aerated treatments and the lower concentrations of NO_3^- observed in the non-aerated treatments at the conclusion of the experiment only serve to further support this possibility. Like DOC, DOP concentrations were also higher in the aerated treatments but DON concentrations were not. This finding suggests that the microbial community is selectively degrading N constituents within the dissolved organic matter (DOM) pool.

Experimental Error and Uncertainty

While this experiment was carefully implemented, certain errors occurred likely due to the fact that this was a trial experiment that strove to mimic a natural process in a controlled laboratory setting. In an attempt to maintain "natural" conditions we chose to use live *Hydrilla* instead of drying the plant matter as is traditional in many other decomposition studies. With the use of wet macrophyte material, we were required to come up with wet/dry conversion factor that would be used to determine the initial dry weight of the plant material. However, the selection of bulk *Hydrilla* for this experiment from the same stand within Lake Seminole consisted of a combination of many separate *Hydrilla* plants which may have been more heterogeneous than expected. Therefore it is not likely that all the material biomass was made up of the same percent of water and we believe the wet/dry conversion ratio was not robust enough to account for these possibly large discrepancies. This would partly explain the unexpected increases in biomass that were observed during decomposition. Another source of error was apparent at the end of the experiment when the concentration of NO_3^- exceeded the concentration of TN in both aerated and non-aerated containers. This situation is impossible and is attributed to analytical error.

Conclusion:

Overall, decomposing *Hydrilla* appeared to be an abundant source of total and inorganic nitrogen and phosphorus and dissolved organic carbon. Due to *Hydrilla's* abundance within Lake Seminole, we believe that inorganic nutrient and carbon release from this macrophyte during decay likely has an effect on the nutrient cycling within the reservoir. *Hydrilla* is also thought to be a source of organic nitrogen and phosphorus and NH_4^+. These constituents are each very dynamic and released in rapid, short lived pulses that are difficult to capture in a laboratory setting but we believe their potentially critical role in the reservoir's nutrient cycling should not be discounted.

Acknowledgments:

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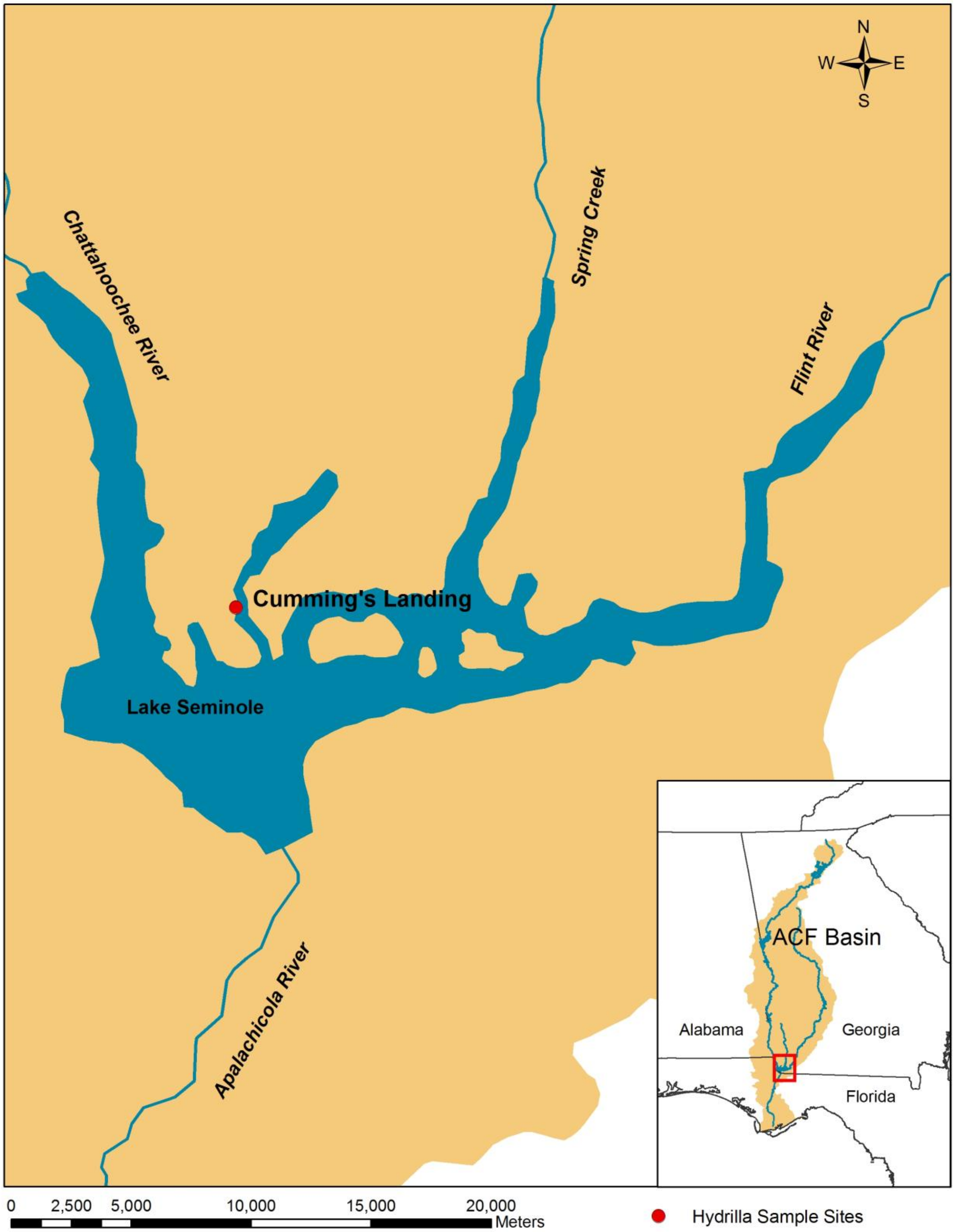

Figure 4.1: Location of the Cumming's Landing *Hydrilla* sampling site on Lake Seminole.

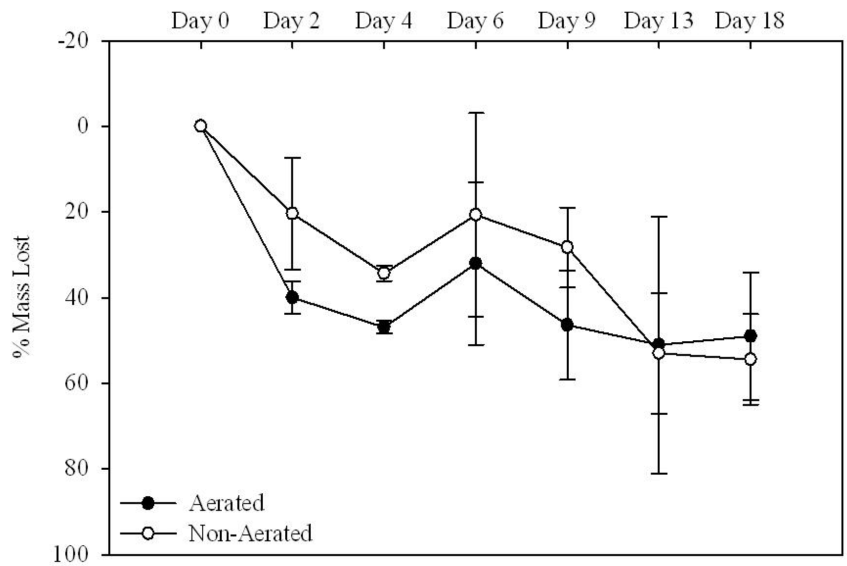

Figure 4.2: Percent of biomass lost over the 18 day experiment in aerated and non-aerated conditions.

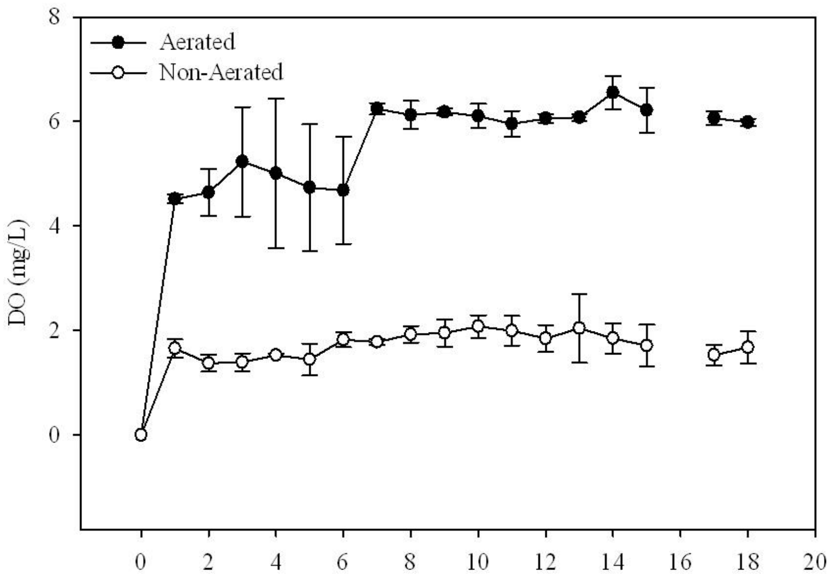

Figure 4.3: Changes in dissolved oxygen (mg/L) in aerated and non-aerated conditions over the 18 day study period.

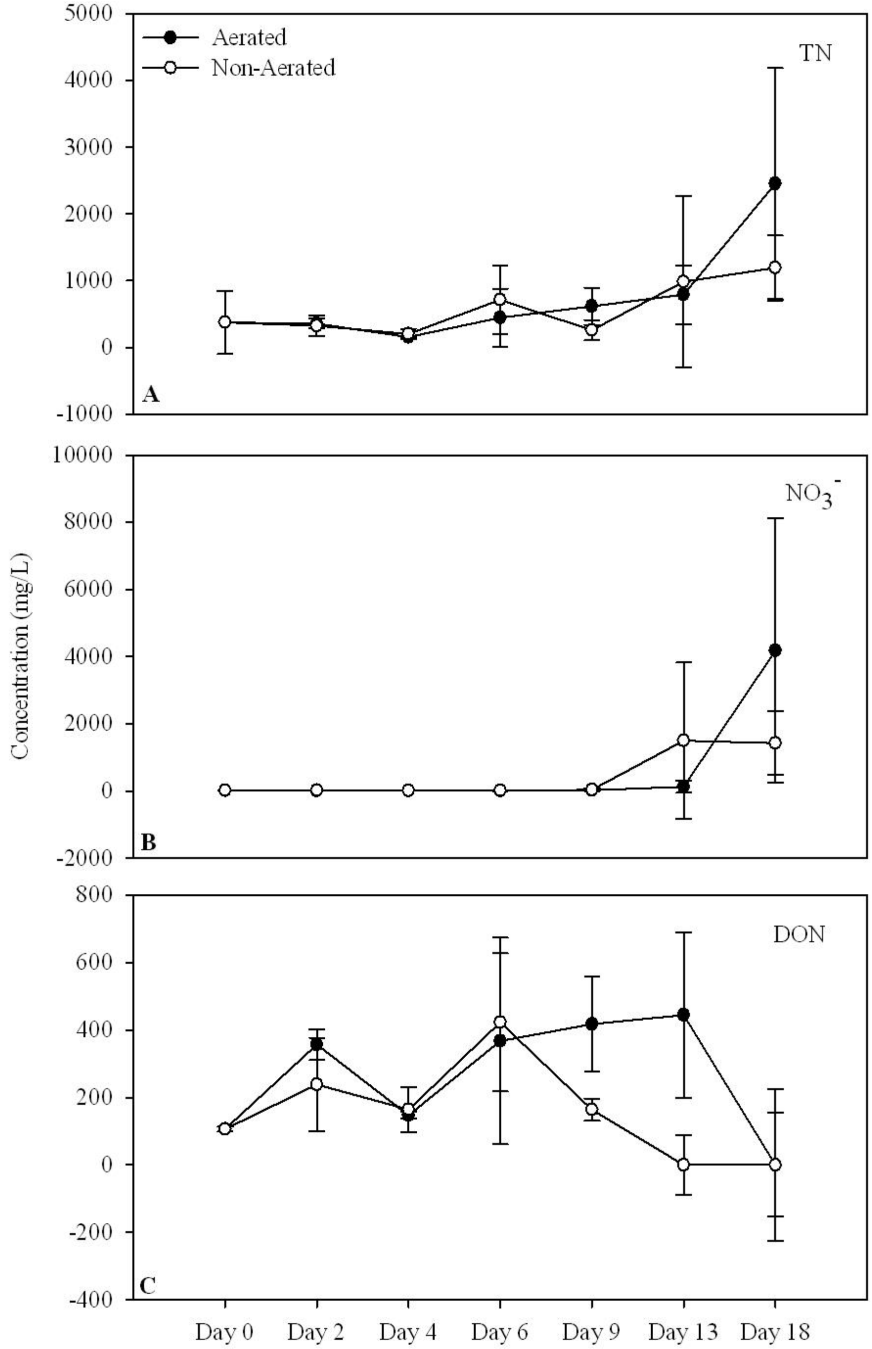

Figure 4.4 A, B, C: Changes in TN, NO_3^- and DOC concentrations (µg/L) in aerated and non-aerated conditions over the 18 day study period.

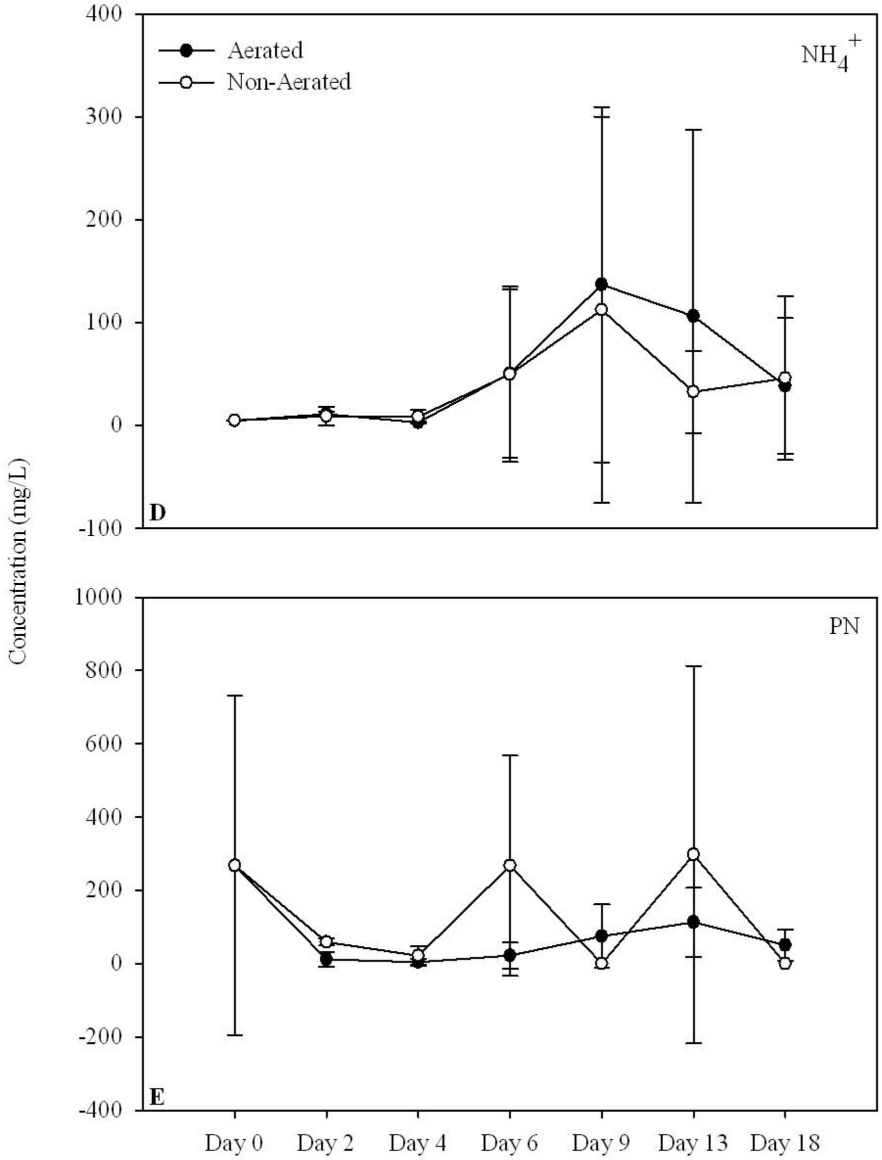

Figure 4.4 D, E: Changes in the NH_4^+ and PN concentrations (µg/L) in aerated and non-aerated conditions over the 18 day study period.

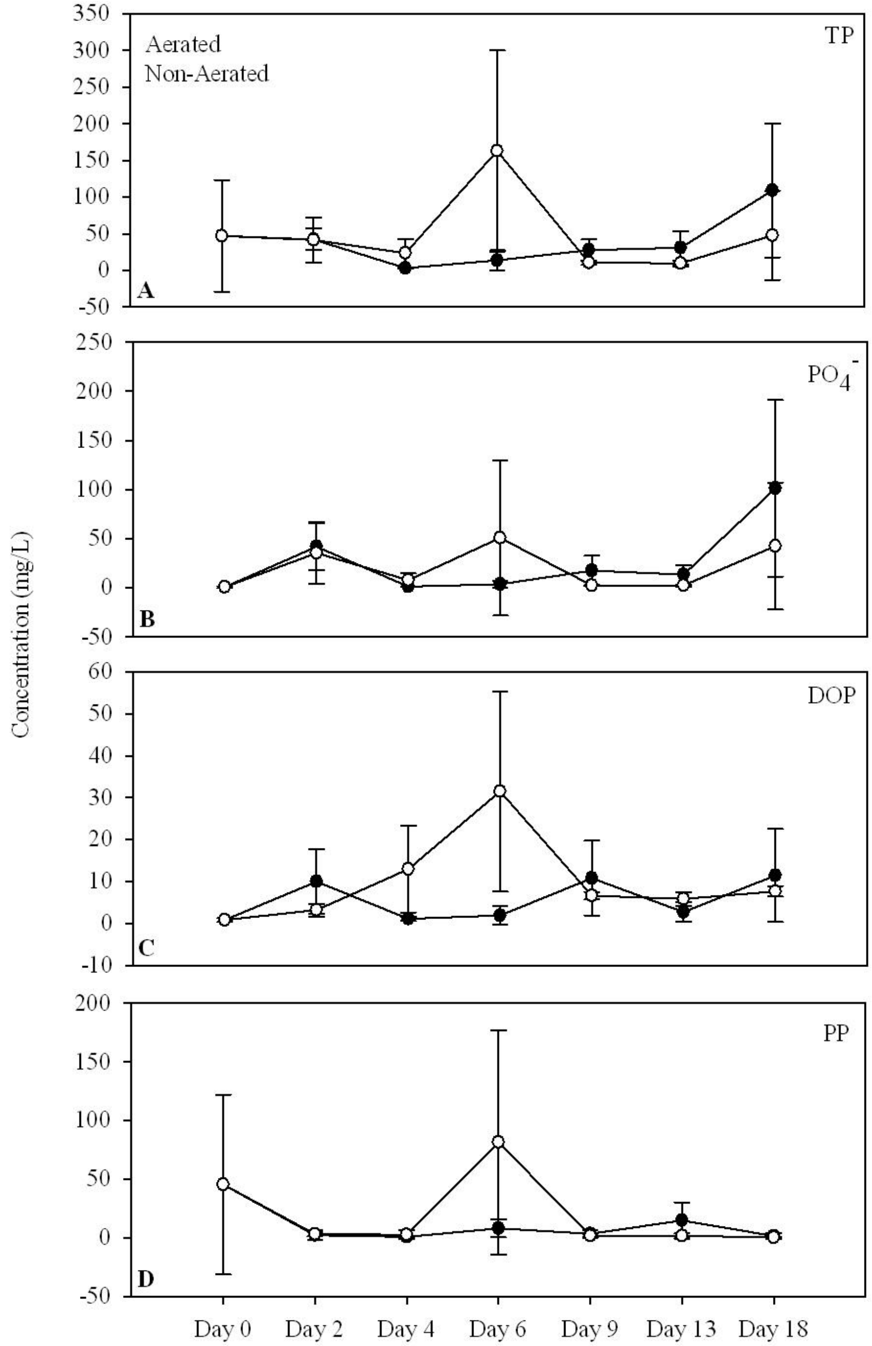

Figure 4.5 A, B, C, D: Changes in the TP, PO_4^-, DOP and PP concentrations (µg/L) in aerated and non-aerated conditions over the 18 day study period.

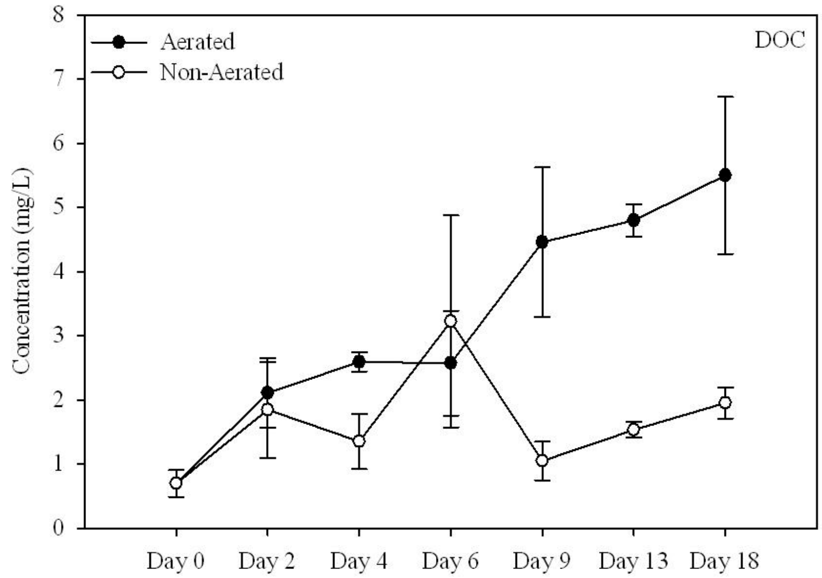

Figure 4.6: Changes in DOC concentration (mg/L) in aerated and non-aerated conditions over the 18 day study period.

CHAPTER 5

CONCLUSIONS

Summary:

Aquatic ecosystems are sentinels of environmental change due to their low laying position within the landscape and integral role in linking the terrestrial and aquatic biospheres (Gergel et al 2002, Gergel 2005, Williamson et al 2008). Due to their cumulative nature and vital importance to humans, nutrient composition and water quality dynamics in most rivers and lakes now reflect some degree of influence from urban and agricultural change (Ngoye & Machiwa 2004). We concluded that nutrient composition and water quality within the lower ACF basin is determined by a complex combination of natural catchment characteristics, human land alteration and shifts in hydrologic regimes.

The mean annual nutrient concentrations in each of the three rivers flowing into Lake Seminole (Flint River, Chattahoochee River and Spring Creek) suggested that surrounding land use practices and natural catchment characteristics greatly influenced nutrient composition. Higher TN and NO_3^- concentrations were observed in the Flint River and Spring Creek due to greater agricultural presence and strong sources of groundwater input while the Chattahoochee River showed more minimal nitrogen concentrations presumably because of less connectivity to the Upper Floridian aquifer. We hypothesized that the Chattahoochee River would have higher concentrations of TP and PO_4^- due to passage through urban settings however, this was not observed suggesting the presence of numerous upstream reservoirs may effectively serve as sinks for phosphate.

This study demonstrated that the magnitude of influence land use practices and catchment characteristics had on nutrient composition were highly contingent on fluctuations in the hydrologic regime. Increases in discharge rates caused the concentration of most nitrogen constituents to decrease due to dilution of groundwater sources by surface runoff. Concentrations of phosphorus and organic material increased during high flows due to erosion and runoff. We found that DOC greatly increased in the Flint River and Spring Creek during high flow events likely due to greater connectivity to wetlands and floodplains. Concentrations of DOC did not increase in Chattahoochee River indicating a reduced degree of interaction with floodplains or the occurrence of nutrient retention in the upstream reservoirs.

Realizing the importance of reservoirs as biogeochemical hotspots for nutrient processing, retention and downstream delivery, this study investigated the capacity for nutrient retention and release in the shallow, subtropical reservoir Lake Seminole. We observed that a complex combination of temporal, hydrologic and seasonal factors influenced the source and sink dynamics within the reservoir. Surface water and groundwater fluctuations appeared to be the primary controllers of nutrient and dissolved organic carbon (DOC) retention and release. High flow events were the most important causes of nutrient and DOC import presumably due to greater localized surface water runoff, soil erosion, sediment re-suspension and wetland and floodplain flushing (Johnson et al 1997, Novak et al 2003).

This study also observed strong temporal patterns of nutrient loading with influxes of NO_3^- and PO_4^- usually exceeding export and export of DOC, DON and NH_4^+ usually exceeding import. Lake Seminole only served as a substantial source of NO_3^- and PO_4^- during high flows, when high discharge decreased water residence time, caused nutrient “flushing” and lessened opportunities for sedimentation and in-reservoir processing (Nõges 2005, van Verseveld et al

2008, Sobota et al 2009). The source and sink dynamics were primarily observed during the spring and summer growing seasons. We believe the seasonal sink was caused by increased biological activity such as macrophyte growth, nutrient assimilation and denitrification that occurred due to higher temperatures and lower dissolved oxygen concentrations. In contrast, we believe that a source dynamic for DOC and DON was observed because of abundant inputs of autochthonous carbon from excess aquatic macrophyte and phytoplankton breakdown. A NH_4^+ source was likely due to relatively low dissolved oxygen concentrations at the bottom of the reservoir causing the absorptive capacity of the sediment to be reduced and trigger the release of NH_4^+ (Clavero et al 2000, Quirós 2003). It is also likely that high flow events caused organic matter trapped within sediment to be re-suspended into the water column and stores of organic material that had accumulated in the deeper waters near the dam to be released during flood control efforts (Stanley & Doyle 2002, Matzinger et al 2007, Trojanowski & Trojanowska 2007, Yang et al 2008).

Finally, in order to preliminarily investigate the role of aquatic macrophytes in reservoir nutrient cycling, we performed a laboratory experiment that investigated the amounts of nutrient and dissolved organic carbon released from decomposing *Hydrilla verticillata*. We found that nitrogen and phosphorus constituents showed different patterns of change during decomposition in oxic and anoxic environments. In both treatments, TN, NO_3^-, TP and PO_4^- showed net accumulations at the conclusion of the experiment. NH_4^+ also accumulated during the experiment but the concentrations remained low likely due to rapid uptake by the microbial community. DON and DOP concentrations increased during decomposition but do not exhibit net accumulations at the conclusion. Greater amounts of DOC accumulation occurred in aerated conditions suggesting more efficient microbial breakdown of *Hydrilla* under higher DO concentrations. Less accumulation of DOC occurred in anoxic conditions possibly due to the effects of denitrification. We concluded that nutrients released from decomposing *Hydrilla* could have a substantial effect on nutrient cycling in Lake Seminole.

Management Implications:

The results of this study confirm that Lake Seminole is an important site for nutrient transformation, retention and release and that the reservoir serves as a gateway for the downstream delivery of nutrients. We found that large loads of nitrogen, phosphorus and dissolved organic carbon are exported from the reservoir, especially during high flow events and believe that these loads could have a substantial effect on the Apalachicola River and Apalachicola Bay ecosystem. The Apalachicola Bay is economically important sources of shellfish with 10% of the oysters consumed in the U.S. harvested from the area. It also provides 35% of the freshwater input to the eastern Gulf of Mexico (http://www.protectingourwater.org/watersheds/map/apalachicola/). Therefore, the nutrient loads from the lower ACF basin have the potential to contribute to coastal eutrophication and the Gulf of Mexico's dead zone. In the future, more understanding of the nutrient and DOC dynamics within the ACF watershed and of the retention and release dynamic within Lake Seminole is needed in order to protect and prevent degradation to the Apalachicola River and Bay.

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APPENDIX A

Table 3.2: Nitrogen, phosphorus and carbon constituent concentrations in the Flint, Chattahoochee, Spring Creek and Apalachicola rivers during each sample period

	TN	NO_3^-	DON	NH_4^+	TP	PO_4^-	DOP	DOC
05/27/08								
Flint	1377	1241	36	4.5	11.6	8.4	2.7	3.3
Chattahoochee	770	492	253	20.7	24.3	11.9	9.4	4.9
Spring Creek	2091	1936	22	0.0	4.7	4.0	BD	1.3
Apalachicola	774	441	286	59.3	17.5	5.8	5.5	4.4
06/10/08								
Flint	1502	1405	78	12.2	8.7	BD	4.5	2.4
Chattahoochee	888	498	276	41.8	36.5	13.6	7.1	5.2
Spring Creek	2073	2136	BD	5.4	4.8	BD	BD	0.6
Apalachicola	802	388	246	107.7	20.2	BD	5.4	4.0
06/23/08								
Flint	1348	1145	121	15.7	18.6	7.0	5.9	2.7
Chattahoochee	874	494	179	109.0	35.5	19.7	4.2	1.1
Spring Creek	2088	2003	BD	5.7	5.9	BD	3.7	3.7
Apalachicola	694	316	230	91.7	19.4	6.0	5.0	3.9
07/07/08								
Flint	1379	1220	164	8.0	21.1	8.3	3.5	2.3
Chattahoochee	704	378	260	7.4	39.8	12.2	11.0	5.3
Spring Creek	1896	1973	55	5.5	4.0	BD	BD	0.5
Apalachicola	637	289	227	81.3	20.5	3.4	2.7	3.4
07/21/08								
Flint	1833	871	352	6.0	19.7	BD	12.2	3.0
Chattahoochee	895	327	442	15.2	41.7	6.7	17.6	5.6
Spring Creek	1930	1677	310	1.8	5.7	BD	4.3	0.9

Apalachicola	775	286	379	66.2	18.9	3.9	2.8	3.1
08/04/08								
Flint		1090		6.7		8.5		2.5
Chattahoochee		325		36.2		10.2		4.4
Spring Creek		1926		10.5		BD		0.3
Apalachicola		175		84.5		5.2		3.2
08/18/08								
Flint	1113	1090		8.8	18.7	13.4		2.9
Chattahoochee	750	325	284	91.1	26.4	13.9	8.1	4.9
Spring Creek	2713	1926		0.0	58.1	BD		0.3
Apalachicola	665	169	374	87.0	21.4	4.4	6.3	3.5
08/26/08								
Flint	894	477	329	23.9	63.9	32.3	10.9	5.9
Chattahoochee	550	117	262	49.9	71.0	10.5	6.1	4.5
Spring Creek	1056	275	586	24.2	95.7	33.4	19.8	10.4
Apalachicola	855	431	305	43.5	32.9	8.2	4.9	3.2
09/08/08								
Flint	1413	1041	335	17.8	31.5	11.6	8.9	5.9
Chattahoochee	824	356	323	10.3	53.5	9.6	14.6	5.0
Spring Creek	1335	669	547	63.9	30.6	6.9	10.9	9.0
Apalachicola	676	120	453	40.3	30.4	3.4	11.2	7.7
09/29/08								
Flint	1889	1463	312	4.8	20.3	7.3	7.9	1.6
Chattahoochee	803	372	279	19.2	31.7	7.7	12.7	3.6
Spring Creek	1764	1445	320	0.0	12.5	4.0	6.6	2.9
Apalachicola	959	475	345	52.0	19.7	4.3	9.7	4.0
10/22/08								

Flint	1564	1235	268	7.3	34.5	15.4	9.0	2.3
Chattahoochee	744	295	320	51.6	44.8	21.6	14.7	4.0
Spring Creek	1802	1498	285	0.0	10.6	2.9	6.9	2.1
Apalachicola	933	527	311	31.4	22.4	3.1	9.1	2.6
11/20/08								
Flint	1019	802	189	10.7	26.8	14.1	6.0	4.5
Chattahoochee	441	94	273	35.4	21.7	7.9	7.5	4.8
Spring Creek	1439	1232	163	0.0	8.6	4.6	3.3	3.1
Apalachicola	842	569	235	17.7	15.3	4.5	4.1	4.4
12/16/08								
Flint	943	284	425	17.2	37.2	9.7	42.0	10.5
Chattahoochee	588	338	217	29.8	13.9	4.6	6.9	4.8
Spring Creek	390	149	418	7.0	19.7	10.7	23.1	10.8
Apalachicola	649	344	277	19.1	23.3	16.4	6.5	7.9
01/20/09								
Flint	1103	996	142	17.2	11.6	7.8	6.0	4.2
Chattahoochee	821	576	175	50.5	24.5	5.9	6.1	4.7
Spring Creek	1082	998	150	10.0	4.7	BD	4.0	3.5
Apalachicola	858	619	157	29.8	20.6	4.7	6.2	5.0
02/23/09								
Flint	1139	992	83	17.6	12.5	6.3	5.9	3.3
Chattahoochee	855	651	129	20.7	17.7	3.8	2.9	4.0
Spring Creek	873	738	169	2.7	9.9	BD	5.2	1.7
Apalachicola	963	667	175	5.7	23.7	2.9	7.1	4.3
03/23/09								
Flint	589	361	219	7.8	14.1	9.1	7.1	6.0
Chattahoochee	814	583	160	48.2	13.3	8.4	BD	4.7

Spring Creek	876	645	208	0.0	8.1	4.4	BD	6.1
Apalachicola	798	612	138	2.8	10.8	6.7	BD	4.7
04/13/09								
Flint	764	420	308	20.8	26.0	13.1	9.1	7.7
Chattahoochee	780	501	227	46.3	26.9	14.5	6.8	6.0
Spring Creek	1115	785	296	35.6	21.7	11.9	7.9	6.4
Apalachicola	674	255	370	34.8	33.7	16.1	8.8	9.3
05/13/09								
Flint	1120	1026	177	11.7	11.7	9.5	3.5	4.3
Chattahoochee	734	494	248	27.3	14.6	5.6	BD	5.0
Spring Creek	1208	1162	152	5.4	14.8	5.4	5.7	4.4
Apalachicola	813	644	233	18.5	13.3	BD	7.1	4.6