Investigating Nitrogen Pollution in the Canoochee River, Evans County, Georgia

Chandra Marie Pitt Brown

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INVESTIGATING NITROGEN POLLUTION IN THE CANOOCHEE RIVER,
EVANS COUNTY, GEORGIA

Chandra Marie Pitt Brown
INVESTIGATING NITROGEN POLLUTION IN THE CANOOCHEE RIVER,

EVANS COUNTY, GEORGIA

A Thesis
Presented to
the College of Graduate Studies of
Georgia Southern University

In Partial Fulfillment
of the Requirements for the Degree
Master of Technology
In the School of Technology

by

Chandra Marie Pitt Brown

December 2002
December 6, 2002

To the Graduate School:

This thesis, entitled “Investigating Nitrogen Pollution in the Canoochee River, Evans County, Georgia,” and written by Chandra Marie Pitt Brown is presented to the College of Graduate Studies of Georgia Southern University. I recommend that it be accepted in partial fulfillment of the requirements for the Masters Degree in Technology.

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Chapter I

Introduction

Water quality throughout the United States is compromised by ever increasing pollution loads. This pollution is categorized by the ease of identifying its sources. Pollution that is readily identified from discrete sources is known as point source (PS) pollution. Due to the ease in identifying PS pollution, it is readily reduced through onsite pollution prevention and remediation. Pollution that does not originate from a defined or discrete source is nonpoint source (NPS) pollution. Since NPS pollution is diffuse throughout an area, determining its origin requires extensive knowledge of the particular pollutant, its pathways to the ecosystem, and its effects on the particular ecosystem.

There has been a significant reduction in PS pollution to Georgia’s rivers and streams since the passage of the Clean Water Act of 1972 and the Georgia Erosion and Sedimentation Act of 1975. Unfortunately, this reduction in PS pollution has not coincided with a reduction in pollution to surface waters. NPS pollution increases have prevented further improvement in air and water quality in recent years. These increases in pollution through nonpoint sources may be addressed through stringent enforcement of the aforementioned Acts (Odum, 1993). Since NPS pollutants are identified as the primary cause of remaining water quality issues, they have become the principal focus in water quality improvement efforts (Gade, 1998).

Nitrogen and its various forms such as ammonia, ammonium, nitrite, and nitrate
are common NPS pollutants that cause deleterious effects on the health of aquatic ecosystems. NPS nitrogen sources include runoff from agricultural fertilizers, residential fertilizers, and deforested areas, sewage, and acid rain (Sprent, 1987). Nitrogen is used as a fertilizer and is beneficial to plant growth in low concentrations; however, when it is found in abundance in aquatic systems, nitrogen becomes a pollutant (Gade, 1998). The elevation of nutrients, nitrogen and phosphorous is a naturally occurring aging process in lentic systems (non-running waters such as lakes). However, the natural eutrophication process is hastened by the addition of nutrients from humans to both lentic systems and lotic systems, or running waters. When nutrients are elevated in waters as the result of human activities, the process is called cultural eutrophication. Eutrophication reduces dissolved oxygen levels in water bodies, and when severe it can result in fish kills, increased suspended particles (turbidity), and a decrease in primary production or a decrease in plant life (Ricklefs, 1993).

Evans County, Georgia (Figure 1) is home to agricultural and industrial operations, as well as residential areas, all of which are potential sources of both PS and NPS pollution. The Canoochee River runs adjacent to many of these potential source areas. Algae blooms and low dissolved oxygen levels in the Canoochee River were reported by landowners in specific areas of the river and are indicators of cultural eutrophication. A preliminary study of potential sources of nitrogen contamination in the surrounding watershed was conducted using Geographic Information Systems (GIS) program ArcView. Local land use practices were mapped using ArcView, and visual surveys were conducted.
The Canoochee River in Georgia

Figure 1. Map of the Canoochee River and Georgia. Evans County is highlighted in red.
Results of the preliminary study led to the development of this larger study to further investigate potential nonpoint sources of nitrogen contamination.

Statement of the Problem

The problem of this study was to determine the source(s) of increased nitrogen levels in the Canoochee River, Evans County, Georgia as an aid to pollution prevention and remediation.

Sub-Problems.

There were two major subproblems of this study. The first was to determine whether significant nonpoint source pollution could be identified as point source pollution (i.e., pollution originating from a discrete source) via water sampling at detailed spatial and temporal scales. The second subproblem was to determine whether surface sources of nitrogen could be differentiated from groundwater sources.

Questions to Be Resolved by the Study

1. Do dissolved oxygen, pH, conductivity and temperature serve as indicators of human impact on surface water?
2. Can surface sources of nitrogen in the Canoochee River be located through determining tributary inputs of ammonia and nitrate?
3. Can sub-surface sources of nitrogen in the Canoochee River be located through increases in nitrate between surface inputs?
4. Is detailed temporal and spatial sampling, in conjunction with nitrate and ammonia/ammonium analysis, an effective means of locating significant contributors to nonpoint source nitrogen pollution from both surface and subsurface sources?

**Terms of the Study**

ammonification: metabolic decomposition of proteins and amino acids with ammonia emitted as a by-product (Ricklefs, 1993)
anoxic: deficient in oxygen, anaerobic (Ricklefs, 1993)
aquifer: permeable layers of rock or sediment that easily conduct groundwater (Tarbuck and Lutgens, 1996)
autotroph: an organism that digests energy from either sunlight (green plants) or inorganic compounds (sulfur bacteria) (Ricklefs, 1993)
baseflow: The component of stream discharge from groundwater seeping into the stream (Fetter, 1994)
calcareous sediments: calcite-rich sediments (Tarbuck and Lutgens, 1996)
confining layer: A rock or sediment layer of low permeability that is above or below an aquifer; it restricts the movement of water to and/or from the aquifer (Fetter, 1994)
denitrification: biochemical reduction, predominantly performed by microorganisms, of nitrogen from nitrate ($\text{NO}_3^-$) ultimately to gaseous nitrogen ($\text{N}_2$) (Ricklefs, 1993)
discharge: the volume of water flowing in a stream or through an aquifer past a precise point at a specific point in time (Fetter, 1994)
discharge area: An area in which groundwater is flowing toward the surface and may

discharge as a spring, seep or baseflow, or by evaporation and transpiration

(Fetter, 1994).

dissolved oxygen: a measurement used to determine the volume of oxygen available in

saturation for chemical reactions (Horne and Goldman, 1994)

drainage basin: the land area from which surface runoff empties into a stream system

(Fetter, 1994)

eutrophication: the process of nourishment of waterbodies through nutrient loading and

primary production (Ricklefs, 1993)

hydraulic gradient: slope of the water table or potentiometric surface, direction of flow of

groundwater (Tarbuck and Lutgens, 1996)

infiltration: the passage of surface water into rock or soil via cracks and pore spaces

(Tarbuck and Lutgens, 1996)

infiltration capacity: the maximum rate at which sediments can take up water (Tarbuck

and Lutgens, 1996)

nitrification: decomposition of nitrogen-containing organic compounds by

microorganisms, producing nitrate (NO₃⁻) and nitrite (NO₂⁻) (Ricklefs, 1993)

nonpoint source pollution: pollution originating from diffuse sources (Odum, 1993)

permeability: the measure of a material's ability to conduct fluid (Tarbuck and Lutgens,

1996)

pH: a range of acidity or alkalinity; the logarithmic scale of the concentration of

hydrogen ions (Ricklefs, 1993)
photosynthesis: usage of the light energy to mix carbon dioxide and water into simple sugars for use as food; performed primarily by green plants and other autotrophs (Ricklefs, 1993)

point source pollution: pollution originating from a discrete source (Odum, 1993)

porosity: the volume of open spaces in a substrate (Tarbuck and Lutgens, 1996)

potentiometric surface: the point to which water will rise in a well cased to a confined aquifer (Fetter, 1988)

primary production: Absorption (gross primary production) or collection (net primary production) of energy and nutrients by green plants and other autotrophs (Ricklefs, 1993)

turbidity: measurement of the amount of sediment and other suspended particles in water (Horne and Goldman, 1996)

watershed: drainage area of a stream system (Ricklefs, 1993)

Limitations of the Study

The following limitations were inherent in this study:

1. The entire reach of the Canoochee River was not studied; sample sites were limited to a section of the river in Evans County, Georgia beginning at the Highway 169 Bridge, Brooks Brewton Park, and ending approximately 11 miles downstream.

2. Chemical testing of water quality was limited to the measurement of dissolved oxygen, pH, specific conductivity, temperature, nitrate, and ammonia/ammonium.
3. Lab analysis of ammonia/ammonium and nitrate were limited to the detectable ranges of ion selective electrodes.

4. No chemical analyses were conducted for the measurement of phosphorous, nitrite, calcium, magnesium, sulfate, biological oxygen demand, chlorine, nor fecal coliform.

5. Detailed discharge measurements were not taken along the Canoochee River sample sites.

6. This study did not determine organic versus inorganic nitrogen.

7. Field measurement accuracy of pH, dissolved oxygen, conductivity, specific conductivity, and temperature were limited by the calibration of the equipment.

Assumptions of the Study

1. The results of this study relate only to the sample sites along the Canoochee River located in Evans County, Georgia within the time frame of the study.

2. The water samples collected were representative of the water quality of the Canoochee River at the sample sites selected for this study.

3. The apparatus and calibration of instrumentation used in the sampling and analysis process was appropriate for the purpose of the study, and conformed to the Standard Methods for the Examination of Water and Wastewater, 20th edition (1998).

Procedures

In cooperation with graduate faculty of the School of Technology’s Master of Technology program, Environmental Studies option, at Georgia Southern University, an
area impacted by pollution was examined. Following a preliminary investigation, it was determined that a study of the potential impact area was feasible. A preliminary review of literature was conducted and a procedure was developed for conducting this study.

In preparation to conduct this study, appropriate water sampling methods were investigated, as were sample analysis techniques. Sample sites along the Canoochee River in Evans County, Georgia were identified followed by a water sampling schedule. Appropriate transport methods were determined for moving the samples from the sample sites to the laboratory for analysis. The ammonia/ammonium samples were preserved with sulfuric acid and, along with the nitrate samples, were placed on ice for transport to the laboratory. Field measurement techniques were practiced and refined for in situ data as were lab analysis techniques that during the course of this project were carried out within 24 to 48 hours of sample collection.

Results from lab analysis and field measurements were compiled into a database along with sample retrieval date, time, and weather conditions. These data were combined with stream discharge measurement from a United States Geological Survey (USGS) gauging station located at one of the sample sites as well as precipitation data from the National Oceanographic and Atmospheric Administration (NOAA). Determining the sources of nitrogen input to the Canoochee River was accomplished by comparing the results of the lab analysis, field data, discharge data, and precipitation data in conjunction with land use practices.

**Summary**

Remediating pollution requires determination of its source. The major
contributors to PS pollution are readily identifiable, whereas the major contributors to NPS pollution are more difficult to determine due to its often diffuse and intermittent nature. Nitrogen is a pollutant of particular concern due to its dynamic nature, and because it leads to cultural eutrophication, resulting in lowered dissolved oxygen levels, increased turbidity, and possible fish kills. This study was designed to determine the major contributing sources of nitrogen pollution in the Canoochee River along an 11-mile reach to aid in pollution prevention and remediation. Included in this design were two subproblems; the first was to determine whether significant nonpoint source pollution could be identified as point source pollution, or pollution originating from a discrete source, by collecting water samples at detailed spatial and temporal scales. The second subproblem was to determine whether surface sources of nitrogen could be differentiated from groundwater sources. The resolution of the original problem and subproblems included determining whether surface sources of nitrogen could be located through determining tributary inputs of ammonia and nitrate and whether sub-surface sources of nitrogen in the Canoochee River could be determined through increases in nitrate between surface inputs. Additionally, the sampling methodology utilizing detailed temporal and spatial sampling, combined with nitrate and ammonia/ammonium analysis, was investigated as an effective means of locating significant contributors to nonpoint source nitrogen pollution from both surface and subsurface sources.

The results of this study were limited by the time frame of the sampling period, the location of the sample sites, and sample analysis techniques. Inherent assumptions of this study include that the water samples collected were representative of the water
quality of the Canoochee River at the sample sites, and that the apparatus and calibration of instrumentation used in the sampling and analysis process was appropriate for the purpose of the study and conformed with the Standard Methods for the Examination of Water and Wastewater, 20th edition (1998).

This study was initiated in response to a preliminary investigation into nitrogen pollution and a land use survey to determine potential sources of nitrogen pollution and to locate sample sites adjacent to these potential sources. Once these sites were chosen, the sampling process was initiated and field measurements were taken at each site for dissolved oxygen, conductivity, salinity, temperature, and pH. Samples were also collected and put on ice to return to the laboratory for analysis. The results of the lab analysis for nitrate and ammonia/ammonium were compiled into a database for further analysis after the completion of the sample collection period.
Chapter II

Review of Literature

In order to determine sources of nitrogen pollution to the Canoochee River, a detailed look at the site-specific geology and hydrology as well as a generalized understanding of nitrogen and its effects, transport, and sources was necessary.

Geology and Hydrology

The Canoochee River is a blackwater river with headwaters beginning in lowland bogs in Emanuel County, GA (Figure 1). According to Vives (Oral Communications, 2000) blackwater rivers have several unique attributes: (1) low pH, ranging from 3.5 to 5.0, (2) low dissolved oxygen levels, and (3) large seasonal variation in flow. The low pH is a result of tannic acids and the humic substances that are abundant in the headwaters of most blackwater rivers. Low dissolved oxygen levels often occur during the warm summer months when flow is significantly decreased as a result of low rainfall. These attributes result in a system that is naturally low in primary producers such as algae and macrophytes.

The 11-mile reach of the Canoochee River in this study is located in Evans County, part of the Coastal Plain Province of Georgia (Figure 1). Evans County itself lies in a portion of this province known as the Coastal Terraces area of Georgia. The Coastal Terraces range in altitude from 100 to 270 feet, and are primarily an inland continuation of terraces accumulated along the Coastal Lowlands and characterized by similar shorelines and sea bottoms left by early Pleistocene advances and retreats of the
the ocean (Krause and Randolph, 1989). The basic geology of this area of Georgia consists of sedimentary rocks and sediment overlying the older crystalline rocks of the piedmont area. The sedimentary rocks of the Coastal Plain are partially made up of sediment eroded from the Appalachian Mountains over approximately the past 200 million years, as well as from limestones created by marine organisms and other processes that occur at sea (Department of Geology, 2002). Evans County lies in the Vidalia Upland District of the Coastal Plain (Figure 2), characterized as a moderately dissected area with a well-developed dendritic stream pattern on gravelly, clayey sands. Floodplains in the Vidalia Uplands are narrow, excluding along the major rivers that have a wide expanse of swamp bordering both sides of the channel (Clark and Zisa, 1976).

The average annual rainfall for Evans County from 1961-1990 was 42.5 inches (www.nationalatlas.gov, July 2001). The National Oceanic and Atmospheric Administration (NOAA) lists 2000, at only 35.91 inches, as the ninth driest year on record for Savannah, Georgia since 1895 (http://nndc.noaa.gov/?home.shtml, July 2001). Maximum rainfall amounts given by Krause and Randolph (1989) occur during summer thunderstorms in July and August, and the minimum rainfall occurring during October and November. Recharge to aquifers from rainfall primarily takes place during the non-growing season when evapotranspiration is the lowest, generally October through March. Krause and Randolph (1989) cite the average annual runoff for 1941-70 as 12 in/yr for Evans County. Evapotranspiration rates range from 33-32 in/yr.
Figure 2. The Physiographic Regions of Georgia. Evans County lies in the Vidalia Uplands Province of the Coastal Plain Region. From: Clark and Zisa, 1976.
The hydrogeology of Evans County is similar to that of Treutlen County as described by Krause and Randolph (1989). The uppermost aquifer system begins with a surficial aquifer that overlies the upper confining unit of the Floridan Aquifer (Figure 3). This surficial aquifer system is made up of post-Miocene age, unconsolidated fine to very coarse, well-sorted sand that generally becomes more phosphatic and calcareous at depth. Intermingled with these beds of fine sand are areas of poorly sorted sand, clayey silt and sand, and at depth, argillaceous limestone. Water in the surficial aquifer system is generally unconfined or under semi-confined conditions. The configuration of the water table is commonly a subtle replica of the land surface and is close to land surface in low-lying zones (along streams and in swamps). The water table is also near the land surface in areas where the surficial aquifer has shallow beds of more clay rich material that has lower permeability. Comparatively steep gradients in the water table border major streams, whereas more gentle gradients are located in the expansive interstream areas.

Krause and Randolph (1989) note that infiltrating precipitation is the primary source of recharge to the surficial aquifers. The infiltration rate is relatively high for these unconsolidated sand aquifers (www.nationalatlas.gov, July 2001). Once in the surficial aquifer, water moves laterally down gradient and flows into streams, ponds, wetlands, etc., and some moves vertically downward to the Upper Floridan Aquifer. Water is also lost from the surficial system by evapotranspiration and transpiration and returned to the atmosphere. Because of its proximity to the surface, the water level in the surficial aquifer responds quickly to rainfall and varies seasonally in conjunction with rainfall and evapotranspiration. The surficial aquifer operates as a source or as a sink to
Figure 3. Water movement from the surficial aquifers through the upper confining unit of the Floridan aquifer system. Water may move in both directions through the upper confining unit.

(From: Miller, 1990).
the underlying Floridan aquifer system. In zones where the water table in the surficial
aquifer is above the potentiometric surface of the Floridan, the surficial aquifer serves as
a source and recharges the Floridan, as water is moving vertically downward through the
upper confining unit of the Floridan. When the head gradient is reversed (heads are
higher in the Floridan than the surficial aquifer), the surficial aquifer serves as a sink for
water discharging from the Floridan. In the Evans County area, the potentiometric
surface of the Floridan is located below the surficial water table, resulting in the
downward movement of water from the surficial aquifer to the Floridan aquifers. Figure
4 shows the recharge areas of surficial aquifers for the Evans County area.

The upper confining unit of the Floridan Aquifer in Evans County, according to
Krause and Randolph (1989), is mostly the Hawthorn Formation of late and middle
Miocene age. All layers between the surficial aquifer and the Upper Floridan aquifer
compose this unit and include clays of very low permeability as well as local areas of
sand beds of moderate permeability. In some areas, major updip rivers (such as the
Ocmulgee, Oconee, and Ogeechee) breach this confining limit, but the extent to which
the confining limit is breached is unknown. Krause and Randolph (1989) estimate the
leakance through the upper confining unit in Evans County as $10^6$ to $10^5$ feet per day per
foot.

According to Krause and Randolph (1989), the Upper Floridan aquifer (Figure 5)
in Evans County consists mainly of the Ocala Limestone and equivalents of the late
Eocene Age. The Ocala Limestone is very fossiliferous and has high effective porosity
Figure 4. Recharge areas in Evans County. Recharge areas are indicated by strips of yellow. Source: Environmental Atlas of Georgia. Created by Chandra Brown, January 2002.
Figure 5. Upper and Lower Aquifer System. Evans County is located in Southeast Georgia. The surficial aquifer system lies above the upper confining unit. Notice that the middle semiconfining unit may not separate some areas of the Upper and Lower Floridan. (From Miller, 1990).
and permeability. Additionally, secondary permeability caused by the movement of groundwater along bedding planes, joints, fractures, and other areas of weakness has contributed to the high permeability of the Ocala. The Lower Floridan aquifer consists primarily of middle to lower Eocene carbonate rocks, more dolomitic and less fossiliferous than the Upper Floridan, with permeability being greatest in areas of weakness, such as bedding planes.

A hard, low-permeability limestone, called the middle semiconfining unit, confines the Lower Floridan. This semiconfining unit is breached by faults or fractures that enhance the movement of water between the Lower and Upper Floridan in localized areas. Because the Lower Floridan is a minor source of water in the region, few wells have been drilled into the system, and relatively little is known about the geology of the Lower Floridan aquifer (Krause and Randloph, 1989).

The Nitrogen Cycle

Understanding the pathways of nitrogen in the ecosystem is crucial to determining its anthropogenic sources. Keeney (1986) discusses key biological transformations of nitrogen in its cycle (Figure 6). Inorganic forms of nitrogen are immobilized or assimilated by plants and microorganisms to form organic nitrogen compounds. Organic nitrogen is decomposed through the processes of ammonification or mineralization into ammonium. Nitrification (the oxidation of ammonium to nitrite) occurs with the help of microbes. The mitigation of nitrate or nitrite to dinitrogen oxide and nitrogen gas (denitrification) is another crucial part of the nitrogen cycle. Nitrogen fixation is the reduction of nitrogen gas to ammonia.
Figure 6. A Model of the Nitrogen Cycle in Terrestrial Systems. Solid arrows represent the flows and exchanges mediated and controlled by organisms. Dashed lines indicate flows resulting from physical forces or human activity. (From Odum, 1993).
Transforming atmospheric nitrogen ($N_2$) to ammonia ($NH_3$) is the first step in the nitrogen cycle according to Ricklefs (1993). This process is known as nitrogen fixation and is conducted only in the presence of bacteria such as *Azotobacter*, *Rhizobium*, and blue-green algae (cyanobacteria). According to Giddens (1985), in terrestrial soils in Georgia, legumes are the best source of nitrogen fixation ($N_2 \rightarrow NH_3$). In aquatic systems, nitrogen fixation, according to Horne and Goldman (1994), is carried out mostly by blue-green algae. However in wetlands, nonlegumes, such as wax myrtle, as well as blue-green algae provide this important function. The enzyme required for $N_2$ fixation is called nitrogenase. This enzyme reduces $N_2$ gas to ammonia by the following process detailed in Sprent (1987):

$$8H^+ + N_2 + 8e^- \rightarrow 2NH_3 + H_2$$

The energy used to process this reaction is generally derived from photosynthesis, but may sometimes be from chemosynthesis. Ricklefs (1993) defines ammoniaification as the hydrolysis of proteins and oxidation of amino acids resulting in the production of ammonia ($NH_3$). Sprent (1987) notes that nitrogen fixing organisms are important in agriculture and forestry because they carry out nitrogenase reduction that helps to restore nitrogen in soils that is removed by crop plants, animals, and fire.

Ricklefs (1993) describes the next step in the nitrogen cycle, nitrification, the oxidation of nitrogen from ammonia ($NH_3$) to nitrite ($NO_2^-$) to nitrate ($NO_3^-$) that is performed by specialized bacteria: *Nitrosomonas*, *Nitrosococcus*, *Nitrobacter*, and *Nitrococcus*. This process ($NH_3 \rightarrow NO_2^- \rightarrow NO_3^-$) requires the presence of oxygen.
saturated, anoxic soils and sediments, nitrate (NO$_3^-$) and nitrite (NO$_2^-$) can behave as electron acceptors or oxidizers, and reverse this process causing denitrification (NO$_3^-$ $\rightarrow$ NO$_2^-$ $\rightarrow$ NO). In terrestrial systems, this process occurs in soil depleted of oxygen and is carried out by bacteria such as Pseudomonas denitrificans. Additional reactions in the denitrifying process result in gaseous nitrogen (NO $\rightarrow$ N$_2$O $\rightarrow$ N$_2$). In a study by Giddens (1985), it was found that as much as 80% of the applied nitrogen was lost as gaseous nitrogen in seven days in high moisture soil when sucrose was applied.

In aquatic systems, the nitrifying and denitrifying processes are closely tied according to Horne and Goldman (1994). In most aquatic systems denitrification rates are higher than nitrogen fixation rates, the loss from the system is made up by nitrogen input from rainfall and streams. Denitrification is performed by anoxic bacteria that reduces nitrate instead of dissolved O$_2$ during respiration at low oxygen levels in sediments (NO$_3^-$ $\rightarrow$ N$_2$). The gaseous nitrogen (N$_2$) is released from the soils and enters the water, eventually making its way to the atmosphere. Denitrification is an energy demanding process requiring the presence of organic carbon to take place. However, nitrification (the oxidation of ammonia) produces energy for the bacteria to perform denitrification. Horne and Goldman (1994) liken the nitrification-denitrification relationship in aquatic systems to a factory assembly line in which ammonia from organic matter is oxidized to nitrate. Nitrate is then converted to N$_2$. However, these two processes must occur in different areas because denitrification occurs under anoxic conditions, but nitrification requires oxygen. Generally speaking, nitrification occurs in
the upper 5 cm of mud and nitrate either diffuses up to the water or down to the anoxic zone where it is denitrified.

The processes of nitrification/denitrification in aquatic environments may also occur in the presence of blue-green algae according to Horne and Goldman (1994). Most biologically available nitrogen is found as nitrate that is taken up by algae and used for growth; the algae die and are then deposited in sediments where the process of nitrification/denitrification occurs once more. Most denitrification occurs in the sediments, particularly in wetlands, whereas most nitrogen fixation occurs in the plankton.

Nitrogen exists in abundance in natural ecosystems. The atmosphere is primarily composed of nitrogen gas (N₂), as 79% of the total atmosphere is N₂ (Sprent, 1987). Nitrogen is crucial to the growth of most living matter, consisting of about five percent nitrogen by dry weight. Nitrate (NO₃⁻) and ammonia (NH₃) are not always available in sufficient amounts in natural waters and may limit plant growth (nitrogen limitation). Nitrogen limitation occurs most frequently in ocean and in lakes in warm climates as well as in ecosystems where phosphorous and silicon occur naturally in large quantities. Nitrogen limitation also occurs in aquatic systems where pollution has increased phosphorous relative to nitrogen (Horne and Goldman, 1994). Most nitrogen enters unpolluted aquatic systems from precipitation as either ammonia or nitrate, since only a few bacteria can convert nitrogen gas (N₂) into a biologically available form (nitrate or ammonia). Nitrate is usually the most common form of combined inorganic nitrogen in
streams, and its concentration and supply rate are closely connected with land use practices in the watershed (see section on land use and nonpoint source nitrogen pollution).

According to Horne and Goldman (1994), ammonia is present in aquatic systems and saturated soils primarily in the ionic form known as ammonium (\(\text{NH}_4^+\)). This ion is much more reactive than nitrate due to its higher chemical energy and its positive charge that enables it to form bonds with negatively charged clays. In contrast, nitrate (\(\text{NO}_3^-\)) makes its way to surface waters through subsurface flow and runoff and is easily leached through soils due to its negative charge (Shirmohammadi et al., 1991). Increases in both \(\text{NH}_4^+\) and \(\text{NO}_3^-\) forms of nitrogen in surface waters may be caused by natural alterations in the vegetation of the drainage basin due to fires, floods, or human-caused clearing (e.g. forestry, agriculture, urban development). Such elevated levels of nitrogen in surface waters result in nitrogen pollution.

**Effects of Nitrogen Pollution**

Nitrogen is one of the most widespread nonpoint source pollutants responsible for eutrophication and nutrient enrichment of water bodies. However, nitrogen as a nonpoint source pollutant is difficult to isolate not only because of its dynamic characteristics in the nitrogen cycle and ease of transportation, but also because there are various natural and anthropogenic origins of nitrogen. Excessive nitrogen in surface waters results in eutrophication, while elevated levels of nitrate in drinking water may cause human and animal health problems (Gade, 1998). The adverse health effects of nitrate in humans are due primarily to nitrite that is formed by the reduction of nitrate by intestinal flora in
infants (as well as in some animals). Nitrite itself acts as an oxidant, changing the Fe$_2^+$ of hemoglobin to Fe$_3^+$. This oxidized hemoglobin cannot transport oxygen and causes the toxic effect cyanosis that is detected when approximately 5% of the hemoglobin is converted into oxidized hemoglobin (Keeney, 1983). The physical manifestation of cyanosis is a bluish discoloration of the skin and mucous membranes (Turkington, 1999). Toxic effects in livestock are similar to those in humans. However, animals usually require a higher dose of nitrate and toxicity is quite rare (Keeney, 1983).

Gade (1998) cites the over-enrichment of surface waters with nitrogen and other nutrients as a main cause of decreased water quality. The water quality effects include enhanced algal blooms, increased aquatic macrophyte growth, and dissolved oxygen depletion. Generally these effects are more apparent in lentic (lakes) than lotic (streams) water bodies because the pollutants are not as easily transported in still bodies as they are in running bodies. Because the effects of over enrichment are more readily observed in lakes than other bodies there has been a move to classify lakes according to their trophic status.

A primary problem associated with over-enrichment of nitrogen in waterbodies is the accelerated eutrophication of streams and lakes. Eutrophication is the natural process of lentic bodies of water evolving from their original oligotrophic (nutrient poor) state to a more productive eutrophic state. The addition of nitrogen, phosphorous, and other nutrients required for the production of algae and other aquatic plants are key elements of the process of eutrophication, as the nutrients cause an increase in the growth of aquatic
plants (Warren, 1971). This natural eutrophication is accelerated by the addition of pollutants from man-made sources, or cultural eutrophication (Odum, 1993).

Gade (1998) notes that an important indicator of advanced eutrophication is large algal blooms. These algal cells inevitably die and decompose via bacterial decay that consumes large quantities of dissolved oxygen, often resulting in oxygen deficiency for the water body. With increases in the eutrophication of a water body, the rate of respiratory activity of many animals suffers and is reduced. Ultimately, rates of development and survival also change. Effects in streams caused by the increase in nutrients include changes in the flora, the growth of periphyton and macrophytes, decreases in clear-water fish, and an increase in turbidity levels (Hynes, 1970). The clear-water fish are displaced due to the increase in turbidity that allows more heat to be absorbed by the increase in particulate matter in the stream. These clear-water fish are then replaced by warm-water species. Therefore, this over enrichment of water bodies negatively affects the varying demands of the water supply, such as fisheries, recreation, aesthetics, and drinking water (Vighi and Chiaudani, 1987).

Pathways of Nitrogen to Surface Waters

Nitrogen pollution occurs when nitrogen levels in soil and solution exceed denitrification. The different forms of nitrogen enter aquatic systems to contribute to nitrogen pollution through different pathways. Because ammonia (generally ionized as ammonium) binds to negatively charged clays and organic matter, it is generally kept at soil cation exchange sites. In other words, ammonium is generally held in the soil, and is not prone to leaching below the root zone. After ammonium is in the soil, it may nitrify
and erode with soil or reenter the soluble nitrogen fraction through overland flow. Nitrate enters the soil and becomes part of the soil nitrogen cycle, or reappears in the surface water down-slope through runoff or groundwater discharge.

It is difficult to assess exactly how the nitrogen arrives in the water body, especially given the dynamic nature of the nitrogen cycle. Gade (1998) states that in addition to existing in its natural state in soil and the atmosphere, nitrogen is transported to surface waters by means of erosion, overland flow from runoff, and leaching. Various meteorological, soil, geologic, land use, and management factors also affect how nitrogen reaches these surface waters.

Erosion.

Nitrogen may erode with soil particles to enter surface waters. Ammonium binds to negatively charged clays and organic matter, so it is primarily kept at soil cation exchange sites. After ammonium is in the soil, it may nitrify and erode with the soil or reenter the soluble nitrogen fraction (Keeney, 1983). Because nitrate is negatively charged, it generally does not bind with soil particles, and is not prone to contribute to nitrogen pollution via erosion.

Runoff from overland flow.

In addition to organic nitrogen transported with the eroded soil, surface runoff resulting from overland flow also consists of soluble nitrogen, generally ammonium and nitrate (Gade, 1998). Keeney (1983) notes that precipitation is also a significant source of inorganic nitrogen (5-10 kg/ha/yr), and under normal conditions, more nitrogen is added in precipitation than is lost in surface runoff and groundwater baseflow. In areas
devoid of nitrogen pollution, the nitrogen cycle is balanced as this excess nitrogen input is offset by denitrification losses. However, when the precipitation rate surpasses the infiltration capacity of the soil, the resulting overland flow is able to pick up supplementary inorganic nitrogen from plant residues. Therefore, in a given area, the more land in agricultural production, the higher the ratio of inorganic nitrogen to total nitrogen.

Leaching to Groundwater.

According to Hynes (1970), nitrogen exists in aqueous form as ammonium (NH₄⁺), ammonia (NH₃), nitrite (NO₂⁻), and nitrate (NO₃⁻). Nitrate is the most fully oxidized form and the most readily used form by plants. Because it is so fully oxidized, nitrate is generally the form of nitrogen found in running water, excepting areas impacted by pollution where ammonia (NH₃) is the more likely form. The main sources of nitrate to surface waters are rainfall and runoff from overland flow. However, Shirmohammadi et al. (1991) suggest that nitrate is largely introduced into surface water through groundwater. The low adsorption potential of nitrate is caused by its being repelled by negatively charged clays due to its negative ionic charge, and results in high leaching rates through the soil mixing zone by infiltrating water. This leaching results in nitrate in shallow subsurface flow.

Under normal stream conditions, the concentration of nitrate concentration is low because it is readily absorbed by plants (Hynes, 1970). This is documented by the increased algal growth in rivers where they flow through areas naturally and artificially rich in nitrate and phosphate. Seasonal fluctuations in nitrate levels also occur due to
plant uptake, since uptake is less in winter than during peak growing seasons in summer. Ricklefs (1993) found in the Bay of Quinte, Ontario that particulate and dissolved organic nitrogen increased from winter to summer, whereas nitrate decreased. These changes denote that the main difference between the cycling of nitrogen in the summer and winter was the rate of uptake of nitrate by phytoplankton. Ricklefs interprets these results as indicating that nitrate uptake is increased in the summer due to amplified phytoplankton production.

If nitrate in the soil is not absorbed by plants or denitrified by bacteria, it will be leached below the root zone and make its way to the groundwater system that eventually discharges into surface waters. Keeney (1986) notes that several studies in Illinois, Georgia, Texas, and Florida have found that groundwater beneath irrigated agriculture sites is generally higher in nitrate than beneath noncropped or nonfertilized sites. Hubbard et al. (1984) found that nitrate levels in groundwater beneath central pivot irrigation systems in the Georgia coastal plain were much higher than beneath forested areas (20 mg/L versus 1 mg/L).

Keeney (1986) observed that nitrate moves to the groundwater under saturated conditions in the direction of the infiltrating water from precipitation and/or irrigation. The rate and direction of nitrate movement in soils is roughly related to the amount of nitrate in soil solution and the direction and rate of the infiltrating water. This concept assumes that all pores are interconnected, that soil solution in the connected pores share in the transfer process, and that soil solution is pushed ahead of the soil water. This theory of nitrate movement through soils is further developed by Jury (1978) and Keeney
(1983). It is known as 'piston flow' or miscible displacement model. Since pore size is rarely homogenous and pore discontinuity common, this model has major problems, as these situations are unlikely to occur *in situ*. Additionally there is a lack of research to determine nitrate movement through horizontally layered soils, as is common *in situ*, all of which makes estimating the actual nitrate release from soils to groundwater very difficult. However, the research shows that nitrate moves readily through soils and is prevalent in groundwater. Once nitrate is in groundwater, it is transported to surface water via shallow aquifer systems (see Figure 7).
Figure 7. Nitrogen movement to surface water. Pathways include erosion, overland flow from runoff, and leaching to groundwater.
Figure 7 shows the different pathways of nitrogen to surface water. Ammonia/ammonium, and nitrate may reach surface water via overland flow from runoff or erosion. Nitrate also leaches to the groundwater and enters the surface water via the shallow aquifer system. Once nitrate is in the groundwater, removal through denitrification is not very likely because below the root zone, little organic carbon and denitrifying bacteria exist to perform the process (Keeney, 1986). Denitrification also requires anaerobic or anoxic conditions rarely found in shallow aquifers. Keeney concedes that denitrification may occur in groundwater, however, no definitive evidence of such a process actually taking place has been presented. Therefore, much of the groundwater contamination eventually results in surface water contamination.

Nonpoint Source Pollution

Nitrate and ammonium from agricultural, residential, and industrial sources provide excess nitrogen to aquatic systems through runoff and groundwater discharge; the resulting pollution is known as nonpoint source pollution. Giddens (1985) maintains that tilling soils can greatly increase the chances of nitrogen losses from the soil. Additionally nitrification (the process of converting \( \text{NH}_3 \) to \( \text{NO}_3^- \)) is rapid in most soils in Georgia when the application rate of nitrogen is below 100 kg/ha. A study by Petrovic (1990) on nitrogen losses from turfgrass operations indicated that uptake of nitrogen from soils by plants varies greatly with location, type of nitrogen applied, application rate and timing, type of plant, soils, etc. According to Petrovic (1990), processes that prevent nonpoint source pollution from nitrate leaching to groundwater are (a) irrigating only to replace the moisture lost through evapotranspiration (b) limiting application of excess
nitrogen to sandy soils, and (c) using slow-release nitrogen sources. These processes would greatly reduce the likelihood of nitrogen pollution from nonpoint sources.

The sources of nonpoint nitrogen pollution described above are characterized by Novotny and Chesters (1981). They found that nonpoint-source pollution enters surface waters in a dispersed and periodic fashion and generally coincide with precipitation events. The NPS pollutants are generally from vast land areas with the pollutants being carried overland to surface waters. Because the land area from which the pollutant originates is so large, nonpoint-sources are not easily observed from the point of origin, and the path the pollutant takes to the surface waters is not readily identified. Other studies, such as the ones by Petrovic (1990) and Shirmohammadi et al. (1991), indicate that groundwater contribution of nitrate to surface waters from over application at surface sites may be a primary contributor to nitrogen loads in surface waters.

Land Uses Related to Nitrogen Pollution

Land use in a watershed can be an indicator of potential contributing sources of nitrogen pollution. Nitrogen pollution is derived from many different land uses: agriculture (e.g. fertilizers), municipal sewage treatment, livestock production (e.g. manure), residential (e.g. lawn fertilizer and septic tanks), and industry. Keeney (1983) lists irrigated agriculture as a particularly likely culprit in nitrate contamination of groundwater in humid areas, such as Georgia, where variable rain events on soils already saturated from irrigation can leach nitrate to the groundwater. This leaching occurs because the negatively charged nitrate ion is repulsed by negatively charged clay particles (with a few exceptions), leading to nitrate leaching if the nitrate is not absorbed
by vegetation. Denitrification is directly related to available carbon supply in carbon-limited conditions. Because the area below the rooting zone in the soil (the vadose zone or unsaturated zone, and the aquifer) is generally low in organic carbon and denitrifying bacteria, it may be assumed that denitrification is not a mechanism of nitrate removal in this area. According to Keeney (1983), there is no evidence of subsurface denitrification in sandy soils low in organic matter (such as those in the study area) most likely due to the highly aerated environment and low carbon availability.

Keeney (1986) suggests several methods for the control of nitrogen loss through agricultural nonpoint-sources. First, there should be an adherence to the agricultural Best Management Practices (BMPs) to reduce erosion and runoff. Additionally, irrigation should be used efficiently in order to minimize leaching of nitrate into groundwater. Cropping sequences should be employed that use cover crops that would make use of residual nitrate. Finally, nitrification and urease inhibitors should be used when applicable as well.

According to Dutweiler and Nicholson (1983) nearly 80 percent of total nitrogen and phosphorous found in U.S. bodies of water were ascribed to agricultural nonpoint sources. Table 1 shows the total percentages of phosphorous and nitrogen originating from point and nonpoint sources for the U.S. Since such an overwhelming amount of pollution comes from sources not readily recognizable or remediated, it is imperative that research be conducted to help alleviate this stress on the surface waters.
Table 1

Annual discharge of phosphorous and nitrogen to waterways from point and nonpoint sources in the U.S. (From Duttweiler and Nicholson, 1983).

<table>
<thead>
<tr>
<th>Source</th>
<th>Percentage of Total Phosphorous</th>
<th>Percentage of Total Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point Sources</td>
<td>15.3%</td>
<td>13.9%</td>
</tr>
<tr>
<td>Agricultural Nonpoint-Sources</td>
<td>84.7%</td>
<td>86.1%</td>
</tr>
</tbody>
</table>

Keeney (1986) notes that intensively managed forage and grazed grasslands may be the source of significant nitrate in groundwater. Grasslands and croplands have yearly biomass cycles that result in nitrate being left behind in the soil profile, leaving it at risk of being leached during low production time for the vegetation. This period corresponds to the cooler season when precipitation and groundwater recharge rates are high. The characteristic large channels caused by roots and wormholes make pastured soil particularly susceptible to nitrate leaching. Row crop agriculture (i.e., intensively farmed annuals) involves tilling or some other seedbed preparation that disturbs the soil leading to greater nitrate loss to groundwater and greater ammonia loss in runoff.

Other types of agriculture, especially livestock production, contribute significant amounts of nitrogen to surface and ground water. Lowrance et al. (1985) studied four coastal plain watersheds in Georgia and found that the agricultural watersheds contained 1.5 to 4.4 times more nitrate in stream flow than forested areas. Veervoort et al. (1998) noted that poultry production is a driving economic force in many areas of the United
States. In 2001, Georgia produced over 1 billion broilers with an estimated value of 2.5 billion dollars (www.nass.usda.gov/charts/brlpdi99.gif). Among the by-products of this industry is the combination of manure and bedding known as poultry litter, with an estimated 1.4 billion kilograms of just bedding material produced in Georgia during 1993 (Walthall and Noefe, 1998). These wastes pose risks to the environment, even more so by the usually localized production of poultry (Vervoort, 1998). The most prevalent disposal method has traditionally been to spread the poultry litter over pastures, so that the high nutrient contents of the litter (mostly phosphorous and nitrate) can serve as a fertilizer for the plants (Walthall and Noefe, 1998). While these benefits for plants are certainly an excellent way to recycle wastes, ground and surface water pollution by nitrate and orthophosphates has been connected to the over-application of animal wastes (Vervoort, 1998). Excessive rates of land application of animal wastes can lead to nitrate accumulation in the soil profile as well as in the ground water. Denitrification serves to remove much of the nitrogen, but poultry manure is higher in total and available nitrogen than that of other livestock animals and is more susceptible to leaching (Keeney, 1986). However, as noted by Keeney (1986), denitrification is naturally low in well aerated soils with low organic content. Such conditions are prevalent in the Coastal Plain of Georgia, resulting in the increased risk of nitrate contamination of groundwater below poultry waste disposal sites.

Keeney (1986) lists human sewage as another contributing source of nitrogen to surface waters. Sewage treatment plants have begun selling sewage sludge (i.e. the biosolid byproduct of human waste treatment) to farmers as fertilizers. Because this
sludge has generally gone through extensive aerobic or anaerobic digestion to get rid of organic matter, the organic nitrogen is generally mineralized at a slower rate than that of animal manure. Therefore, nitrate in the sewage sludge is not readily leached to groundwater. According to Keeney, sludge application in row agriculture, especially when growing grains, is an effective means of nitrogen use, because when it is applied at an optimum rate for maximum yield, sewage sludge does not result in substantial nitrate leaching below the root zone. However, sewage effluent carries slightly different consideration, such as the proper water-loading rate to prevent leaching as opposed to the proper nutrient-loading rate.

Effluent from sewage treatment plants and livestock operations is usually applied to the land in three ways: (a) at very high rates to highly permeable soils (high infiltration rate), (b) by controlled release at moderate loading rates to impermeable soils on a slope in order to treat at the soil-plant boundary (overland flow), or (c) at slow rates onto crop land (crop irrigation). Each of these methods may also be referred to collectively as land application systems (LAS). The high infiltration method results in direct groundwater recharge; therefore, nitrate contamination of the ground water is almost assured. However, proper manipulation of effluent loading rates can result in nitrogen removal by nitrification-denitrification. This method is particularly appropriate for arid areas where the water can be used for ground water recharge. Overland flow treatment should not generally result in leaching to groundwater, but may result in surface water contamination if the loading rates are not appropriately matched for the area. Crop irrigation is usually accomplished with overhead sprinklers and involves a high degree of
management to maximize yield and minimize nitrate leaching. Forested lands are also used in waste application (both sewage sludge and effluent) but loading rates must be properly attuned to the ecological and nutritional requirements of the forest stand. Special delivery systems must be created to prevent damaging the forest, and vegetation must be carefully selected to maximize nitrogen uptake and biomass production.

Septic systems are another form of human waste disposal that may contribute to nitrogen pollution in both surface and subsurface water. Keeney (1986) notes that approximately 30% of households and small rural establishments in the U.S. use septic tanks. The average effluent from a septic tank has 50 to 70 mg-N/L, seventy-five percent of which is ammonium and 25% is organic nitrogen (Starr and Sawhney, 1980). According to Keeney, this effluent is generally released to the soil in a gravel-filled subsurface bed or trench (0.4 to 0.6 m below surface), where most of it infiltrates into the unsaturated zone. The effluent reaches the unsaturated zone through a restrictive layer known as the crust. Water recycling through evaporation or transpiration is practically nonexistent below the root zone; therefore, infiltration to groundwater is certain. Moreover, aerobic conditions exist below the crust unless the system is constructed in an inappropriate site, such as in a high water table site. In these aerobic conditions, pathogens are eliminated through sorption and die-off, organic carbon is mineralized to carbon dioxide, and organic nitrogen compounds are mineralized to ammonium and then nitrified. Consequently, most nitrogen-removal processes (volatization, immobilization, and plant uptake) have been eluded. Denitrification is the most likely removal process at this point. However, for denitrification to occur, organic matter must be present that is
not very common. Most monitoring studies indicate very little nitrogen removal in the aerobic vadose zone below septic systems. According to Keeney (1986), the most practical means of alleviating nonpoint source nitrogen pollution due to septic systems is to zone areas to limit residence density or to expand municipal sewers.

Other possible sources of nitrogen pollution include industrial discharges, petroleum processing wastes, and acid precipitation (Keeney, 1986). Possible contributing sources for the study area are shown in Figure 8.
Figure 8. Land use in the study area. The sample sites are numbered and major land uses are identified by color. Possible sources of nitrogen pollution are identified by polygons with stripes.
The majority of the study area of this investigation is used for agricultural purposes, with some residential and industrial uses. Note the position of the poultry processing plant and sewage treatment plant (municipal LAS) in Figure 8. The poultry processing plant utilized a crop irrigation LAS in the area around the plant for effluent disposal. The sewage treatment plant utilized a crop irrigation LAS in the area noted. The sample sites were chosen in order to determine if either of these plants contributed significant nitrogen concentrations to surface water.

**Previous Studies**

The geology and hydrology of the study area are significant factors in nitrogen pollution of surface water. As mentioned previously, groundwater can be a significant contributor of pollution to surface water when nitrate moves downward through sandy soils to surficial aquifers and then laterally to streams. A major study in groundwater/surface water interactions in a region similar to Evans County was conducted by the USGS in the Suwanee River in the Georgia/Florida Coastal Plain (Berndt et al., 1998). This study found that groundwater affected water quality in the Suwannee River. In this case, the period in which groundwater makes up the largest percentage of stream discharge in the Suwannee River is during low flow when groundwater discharges to the river through springs and upward movement through the riverbed (i.e. riverbed leakage). The peak period for river water inflow to the Upper Floridan aquifer occurs during high flow when water from the Suwannee River recharges segments of the aquifer.
Areas studied along the Suwannee by Berndt et al. (1998) included a 33-mile stretch where inflow to the river is exclusively from groundwater. Eleven springs in this stretch were measured and accounted for 40 percent of the flow increase along this area. The other 60 percent of the increase in flow was determined to be from unmeasured groundwater inputs from springs and riverbed leakage. The average nitrate concentration in measured springs was 1.7 mg/L and the range was from 1.3 to 8.2 mg/L. The nitrate load in the river increased 3,700 kilograms per day along the river reach; the majority of this increase occurred along the lower reaches of the river. The disproportionate increase in the lower reaches of the river from groundwater sources was determined to be caused by the effects of land use on groundwater.

This USGS study also investigated nitrate inputs from surficial aquifers. The average concentration of nitrate in groundwater in agricultural areas was 4.2 mg/L. The average nitrate concentration in the Upper Floridan aquifer was <0.05 mg/L whereas the average nitrate concentration in surficial aquifers in urban areas was 0.95 mg/L. These results indicated that nitrate concentrations were related to the depth of the wells sampled in addition to land use. For example, the higher concentrations were found in shallow wells in agricultural areas. This trend shows that nitrogen sources at the land surface significantly affect groundwater concentrations of nitrate. The primary source of nitrate to the groundwater was found to be from fertilizers and animal waste in the row-crop agricultural area. In addition to land use, determining factors of the concentration of nitrate in the groundwater were also related to geology, soils, and topography. Well-drained sandy soils that have a low water-nutrient holding capacity were found to
increase the likelihood of leaching nitrate to groundwater. It should be noted that nitrate was the most common nutrient detected in groundwater.

Other investigations found similar relationships between surficial aquifers, land use and nitrate contamination. A study by Shepherd and Bhogal (1998) on sandy soils indicated that application of poultry litter during September and October resulted in nitrogen leaching to groundwater due to increased rainfall. Additionally, applications above 10 tons/ha increased the amount of nitrogen leaching to the groundwater. As described previously, because of nitrate's negative ionic charge, it is repulsed by positively charged soil particles, giving it a low adsorption potential. Therefore, nitrate is easily leached out of the soil mixing zone by infiltrating water and is more likely to be introduced to surface water bodies through shallow groundwater flow than through overland flow (Shirmohammadi et al., 1991). Hence, nitrate contamination of groundwater leads to contaminated drinking and surface waters. This contamination, however, may be prevented in sandy soils by increasing retention time of nitrogen thereby increasing denitrification and preventing contamination of surface waters through leaching and runoff (Surampalli, 1997-98). Increased retention time in soils may be aided through determination of agronomic rates to insure that no excess nitrogen is available for leaching or runoff.

Summary

The study area lies in the Vidalia Uplands section of the Coastal Plain physiographic province. The hydrology and geology of the study area is important because it affects the pathways of nitrogen to surface water. The basic geology of this
area of Georgia consists of sedimentary rocks and sediment overlying the older crystalline rocks of the piedmont area. The hydrology of the study area consists of a series of aquifers. The uppermost aquifer system begins with a surficial aquifer that overlies the upper confining unit of the Floridan Aquifer. Precipitation is the main source of recharge to the shallow aquifer system. Once in the surficial aquifer, water moves laterally down gradient and flows into streams, ponds, wetlands, etc., and some moves vertically downward to the Upper Floridan Aquifer. Because of its proximity to the surface, the water level in the surficial aquifer responds quickly to rainfall and varies seasonally in conjunction with rainfall and evapotranspiration. The surficial aquifer operates as a source or as a sink to the underlying Floridan aquifer system.

Determining the pathways of nitrogen to surface water requires an understanding of the nitrogen cycle. In the nitrogen cycle, nitrogen gas from the atmosphere (N\textsubscript{2}) or from fertilizers or other waste is immobilized or assimilated by plants and microorganisms to form organic nitrogen compounds. Nitrogen fixation is the reduction of nitrogen gas to ammonia. Organic nitrogen is decomposed through the processes of ammonification or mineralization into ammonium. Nitrification (i.e., the microbial oxidation of ammonium to nitrite) occurs with the help of microbes. The mitigation of nitrate or nitrite to dinitrogen oxide and nitrogen gas (i.e., denitrification) returns nitrogen to the atmosphere.

Nitrogen pollution in surface water results when nitrogen is introduced at a higher rate than denitrification can occur. Nitrogen may reach surface waters through nitrate (NO\textsubscript{3}\textsuperscript{-}) in groundwater and runoff as well as from ammonia (NH\textsubscript{3})/ammonium (NH\textsubscript{4}\textsuperscript{+})
through surface runoff and erosion. Land use and geology are closely connected to the occurrence of nitrogen pollution. For example, areas with high recharge rates and sandy soils are prone to nitrogen leaching to groundwater. Additionally, land uses such as agriculture, septic systems, and urban runoff contribute excess nitrogen to surface waters through runoff, leaching, and erosion.
Chapter III

Methodology

The problem of this study was to determine the source(s) of nitrogen input into the Canoochee River in Evans County. Subproblems were to determine whether significant nonpoint source pollution could be identified as originating from a discrete source and to determine whether surface sources of nitrogen could be differentiated from groundwater sources. The problem of this study was to determine the source(s) of nitrogen input into the Canoochee River in Evans County. Subproblems were to determine whether significant nonpoint source pollution could be identified as originating from a discrete source and to determine whether surface sources of nitrogen could be differentiated from groundwater sources.

Study Design

The study design was developed under faculty guidance. Using a combination of faculty expertise and preliminary research conducted for the Review of Literature, it was hypothesized that testing for ammonia and nitrate in the river and tributaries would verify sources of nitrogen pollution to the Canoochee River in the study area. It was further hypothesized that the pathways of nitrogen to the river could be determined by conducting detailed spatial and temporal sample collection in conjunction with nitrate and ammonia sample analysis. Conducting the study in such a manner required careful site selection.
Site Selection

In order to determine appropriate locations for sample sites, a land use survey of the watershed in Evans County was conducted through site visits and using Geographic Information System (GIS) maps (Figure 8). Suspected sources of nitrogen pollution were identified through this preliminary land use survey. Several locations were considered as potential major contributors of nitrogen pollution: (1) a subdivision that utilized a central septic system that was thought to be overloaded, (2) the municipal sewage treatment plant, (3) the poultry processing plant. The sample sites were chosen for their accessibility and their proximity both upstream and downstream from suspected inputs of nitrogen. Each of the suspected inputs was situated upstream from site 4, where nuisance algae blooms were present.

The main river sample sites 1, 2, 3, 4 on the Canoochee River were sampled on a weekly basis (every 5-10 days). Site 1 was chosen as the background site, because it was located upstream from any suspected major contributors of nitrogen. Site 2 was originally chosen because it was located just upstream of possible input from the poultry processing plant and downstream of the sewage treatment plant. Subsequent fieldwork showed that the mouth of the tributary that drains the poultry plant, and at which sample site 5 is located, was incorrectly plotted on the USGS topographic map (Figure 9). Because site 2 actually lies downstream of the tributary at site 5 and not upstream, both the sewage and poultry plants influence nitrogen levels at site 2. Sites 3 and 4 are both downstream of the poultry plant with site 3 being the closest downstream
Figure 9. Topographic map of study area and sample sites. Weekly sites were chosen due to proximity to suspected nitrogen inputs.
Site 4 was included in the weekly sampling rounds to ensure that there was no other major source of nitrogen downstream from the poultry plant. Since this site was the location of extensive algae blooms, it was included to monitor the water quality associated with the bloom itself. Figure 10 shows the extensive algae blooms at site 4 on August 15, 2000.

The other sample sites (5, 6, 7, 8, 9, 10, 11, 12, 13) were sampled on a seasonal basis. All of these sample sites, with the exception of site 7 (Figure 9), were located on tributaries to the Canoochee River and were measured seasonally to determine tributary input of nitrogen pollution to the Canoochee River. Site 7 was included in the seasonal sampling due to low nitrogen levels (similar to those found at site 1) during the preliminary study period.

Sites 6 and 10 were chosen to measure inputs from Cedar Creek, a tributary of the Canoochee. Site 11 was chosen to measure possible inputs from an unnamed tributary that drained a cattle farm that emptied into the Canoochee downstream from site 3 and upstream from site 4. Site 12 was chosen to measure possible surface inputs of nitrogen from an unnamed tributary draining the poultry processing plant LAS fields. Site 13 was added to measure possible inputs of nitrogen from a tributary draining poultry farms.

Site 5 was included in the weekly monitoring after relatively high ammonia and nitrate levels were repeatedly found at this site, about 1/3 of the way through the 12 month sample period. Adding this sample site to the weekly sampling
sites added very little time to the sampling trips, as site 5 was easily accessible and in close proximity to site 2. Sites 8 and 9 are the tributaries to the larger stream at Site 5. The tributary at site 8 drains the municipal sewage treatment plant LAS, and site 9 drains the poultry processing plant and sewage treatment plant LAS. Figure 11 shows the mixing zone of these two tributaries upstream from site 5.
Figure 10. Algae bloom Site 4, 8/15/00.

Figure 11. Mixing zone of sites 8 (on right) and 9 (on left). The water draining the municipal plant was much lighter in color than that draining the poultry processing plant.
Field Sampling Methodology

The field sampling methodology used in this study was adapted from the U.S. Environmental Protection Agency's (EPA) Region 4 Environmental Investigations Standard Operating Procedures and Quality Assurance Manual as well as the EPA Office of Water Quality publication Volunteer Stream Monitoring: A Methods Manual. Each site was sampled by collecting a grab sample. Grab samples are individual samples collected at a single location at a specific time (EPA Region 4, 1997). These grab samples were collected following the procedures outlined in Volunteer Stream Monitoring: A Methods Manual (Figure 12). This sampling method was duplicated in situ with several modifications: (a) sample sites accessible by bridge (1, 2, 6, 7) were sampled using a plastic bucket on a rope gently lowered below the surface water and returned to the bridge for analysis and collection, (b) the sample site accessible only from the bank (3) was sampled with the bucket and by gently lowering it below the surface of the water, and then returning it to the bank for analysis and collection. Sample sites accessible through wading (4, 5, 8, 9, 11, 12, 13) were sampled in the manner illustrated in Volunteer Stream Monitoring: A Methods Manual in order to reduce the impact of disturbed sediments on sample quality. The only exception to this methodology was instead of collecting the sample in the screw-cap bottles, the samples were collected in the bucket and brought to the bank for in situ analysis and collection for lab analysis.
Figure 12. Sampling procedures using a bucket. Adapted from Volunteer Stream Monitoring: A Methods Manual Chapter 5, Collecting Samples For Screw-Cap Bottles.

Water samples were collected in the plastic bucket either by wading into the middle of the stream, lowering on a rope from a bridge, or from the side of the bank, depending on site accessibility.
Once the samples were collected, the bucket was gently placed on the ground for in situ analysis using an Orion 210A pH meter, and an YSI 85 Multi-Parameter dissolved oxygen (DO), conductivity, temperature, salinity, and specific conductivity probe. The pH meter was calibrated every 2 hours during sampling and the Multi-Parameter probe was calibrated at each sample site. The pH, dissolved oxygen, conductivity, specific conductivity, temperature and salinity as well as the time and general weather conditions and visual water characteristics were recorded at each sample site. A sample was then collected and placed in two 125 ml sterile polyurethane sample bottles, one bottle for nitrate and the other for ammonia analysis.

The sample bottles were prepared in the laboratory prior to sample collection, with the ammonia sample bottles being acidified with 2 ml of concentrated sulfuric acid. The bottles were acidified because at low pH ammonia (NH₃) is converted to ammonium (NH₄⁺). This process prevents ammonia gas from being lost from the sample in transit to the lab through denitrification. All of the sample bottles were labeled as to collection date, site number, and NH₃ or NO₃⁻. After collecting the ammonia and nitrate samples from the bucket, the sample bottles were promptly put on ice for transport to the laboratory.

Lab Analysis

Upon arrival at the lab, all samples were placed in a refrigerator to await lab analysis via nitrate ion selective electrode and ammonia gas sensing electrode analysis. Lab analysis was conducted in Georgia Southern University’s Hydrogeochemistry
Laboratory by experienced faculty. Sodium hydroxide was added to the ammonia samples to raise the pH to 12, thereby converting ammonium (NH$_4^+$) to ammonia (NH$_3$). All samples were analyzed in the lab within 48 hours of sample collection, the recommended holding time. Duplicate samples were taken in situ on occasion to verify field techniques and lab analysis accuracy. Duplicate samples are two or more samples collected from a common source (EPA Region 4, 1997). Experienced faculty in Georgia Southern University’s Hydrogeochemistry Laboratory conducted all lab analysis via ion selective analysis and gas sensing electrodes (Methods 4500-NH3 D and 4500-NO3- D) in accordance with *Standard Methods for the Examination of Water and Wastewater*, 20th edition (1998).

**Analytical Results**

The results from the field and lab analysis were entered into a master database for further study. Stream discharge and precipitation data were included in the database. The discharge data was collected by the USGS from a gauging station located just upstream from sample site 2 on the Canoochee River near US Highway 301. The gauging station was situated downstream from the confluence of the tributary at site 5 and the Canoochee River. The precipitation data was collected from the National Oceanic and Atmospheric Administration (NOAA). This data included only the precipitation data for the Claxton, Georgia area.
Statistical Analysis.

Statistical analysis was conducted on the data once all data collection ceased. The statistical software JMP was used to conduct these analyses. Statistical data was computed solely for the weekly river sites, as these sites contained enough data points \((n>20)\) to result in meaningful statistics. Analysis of variance (ANOVA) model II tests were conducted to determine if there were statistically significant spatial and temporal differences in nitrate and ammonia among the sample sites. ANOVA tests the null hypothesis that there is not any added variance among sample means at each of the sample sites. If the means among all of the sample sites vary significantly, then the null hypothesis is rejected (Sokal and Rohlf, 1997). All tests used a significance level of \(p < 0.05\). If \(p\) was less than 0.05, then the null hypothesis was rejected, meaning that there was a difference in the means among sample sites, and the data set was viewed as displaying a statistically significant relationship.

In order to determine if there was a relationship between discharge and ammonia concentration, discharge and nitrate concentration, precipitation and ammonia concentration, and precipitation and nitrate concentration, pairwise correlations were conducted for each river sample site. The purpose of conducting correlation analysis was to determine and estimate an association between the two data sets. Correlation analysis was not used to determine a causal relationship between the data sets, but rather to see if there was a relationship between the two variables (Sokal and Rohlf, 1997). All tests used a significance level of \(p<0.05\). Stronger relationships have a correlation coefficient
closer to "1.00, whereas weaker relationships have a correlation coefficient closer to 0.00.

**Graphical Analysis.**

Precipitation and discharge were plotted over time and compared to determine if they were related. Dissolved oxygen, pH, conductivity, and temperature variations between sample sites and over time were analyzed through graphs and plotted in conjunction with discharge and precipitation data. Nitrate was plotted by sample site over the study period and examined in conjunction with precipitation. Only the main river sample sites were graphed with discharge data, as discharge data was unavailable for each of the tributary sites. The discharge data is from the gauging station near site 2 and was used for each of the other river sample sites; actual discharge at these points may have varied over the sample period. The same analysis was conducted for the ammonia data for each of the sample sites.

**Summary**

This study was designed to locate sources of nitrogen via nitrate and ammonia analysis. Sample sites were chosen on the river and its tributaries following a land use investigation using GIS maps and site visits. Accessibility and location relative to potential major sources of nitrogen were key considerations in choosing sample sites. Subsequent to a preliminary sampling period of two weeks, four main sample sites were chosen along the river to be monitored on a weekly basis (every 5-10 days) and nine sample sites were chosen to be monitored on a seasonal basis.
Sample collection methodology was modified from *Volunteer Stream Monitoring: A Methods Manual* and *Environmental Investigations Standard Operating Procedures and Quality Assurance Manual*. Samples were collected either from a bridge, the bank, or by wading. After collection, the samples were analyzed in situ for pH, temperature, dissolved oxygen, conductivity, specific conductivity, and salinity via field probes. Then the samples were placed in prepared sample bottles and put on ice for transport to the laboratory for nitrate and ammonium analysis via nitrate ion selective electrode and ammonia gas-sensing electrode. All of the data, including sample site, date, and time of collection, were recorded in a master database for statistical analysis via JMP software and graphical analysis via Microsoft Excel and Grapher. Nitrate and ammonia concentration were compared spatially and temporally using the statistical software and graphs. Temperature, pH, dissolved oxygen, conductivity, and salinity were compared at each sample site over time and to discharge and precipitation data collected from the USGS and NOAA, respectively.
Chapter IV

Findings

The problem of this study was to determine the source(s) of nitrogen input into the Canoochee River in Evans County. The subproblems were (a) to determine whether significant nonpoint source pollution could be identified as originating from a discrete source and (b) to determine whether surface sources of nitrogen could be differentiated from groundwater sources. In order to determine the sources of nitrogen and to differentiate between groundwater and surface water contributions of nitrogen, a detailed spatial and temporal sampling study was designed. Sample sites were chosen for their proximity to suspected sources of nitrogen pollution. Four main river sites were sampled on a weekly basis and 9 sites sampled on a seasonal basis. Temperature, dissolved oxygen, pH, conductivity were analyzed in the field using field probes, whereas ammonia and nitrate were analyzed in a laboratory by faculty. Results of the analyses were entered into a database for graphical and statistical analysis.

Precipitation, Discharge, Temperature, Dissolved Oxygen, pH, and Conductivity

Dissolved oxygen, pH, temperature, salinity and conductivity were in order to help characterize each sample site. Precipitation and stream discharge, however were available for only a single site within the study area. Graphical analysis was conducted to
delineate differences in dissolved oxygen, pH, conductivity and temperature between the sample sites, but statistical data were not calculated for these data sets. Salinity data was recorded, but not analyzed graphically due to the lack of variation between the sample sites. Since the sample area included freshwater only, salinity measurements were rarely found and did not generate meaningful data.

Precipitation and discharge were graphed in order to determine if there was a relationship between precipitation and discharge in the study area (Figure 13). These data were from single collection points located in the study area. The discharge monitoring station was located on the Canoochee River upstream from sample site 2, and the precipitation data were for the city of Claxton, Georgia, located at 32°10'N/81°54'W. From this figure, it can be seen that not all spikes in discharge correspond to precipitation events in the study area. These anomalies, circled in red, may be due to precipitation occurring upstream in the drainage basin but not at the precipitation station in the study area. It is also possible that discharge from an unknown source in the study area was responsible for these anomalous increases in stream discharge.

Temperature in the river was fairly uniform between sample sites and followed a seasonal pattern with higher temperatures in the summer months and a gradual cool down over the fall and winter (Figure 14). Temperature did not vary greatly between sample sites. Dissolved oxygen levels in the river followed a similar seasonal pattern with the lowest dissolved oxygen levels occurring during the summer months (Figure 15). However, dissolved oxygen levels also had considerable spatial variation. The lowest
dissolved oxygen levels in the river occurred consistently at site 4, where the algae blooms were the most prevalent.

The pH at each of the river sample sites was variable over the sampling period. Figure 16 shows pH at sites 1, 2, 3, and 4 over the sample period. Site 1 generally had a lower pH than the sites downstream from the sewage treatment plant and the poultry processing plant. The largest variation in pH occurred during the summer months when stream discharge was the lowest (Figure 17). During this period, pH at sample sites 2, 3, and 4 was significantly higher than that at site 1. Figure 18 shows pH and precipitation at the river sites over the study period. Precipitation events appeared to impact pH at sites 2 and 3 more than at site 1 or site 4. On September 26, 2000 for example, the pH at sites 2 and 3 decreased dramatically during an extended precipitation event. A similar decrease occurred in December 2001. Figure 19 shows pH over time for all of the sample sites. Sites 5, 8, 9, and 12 had more elevated pH in general than the other sites.

Conductivity data for the river sites shows sites 2, 3, and 4 had higher conductivity than site 1 (Figure 20). The greatest disparities in conductivity were found during low flow levels in sites downstream from the poultry processing plant (Figure 21). Tributary sites that drained the poultry processing plant and sewage treatment plant (5, 8, 9, and 12) were found to be higher in conductivity readings than the river sites or other tributaries (Figure 23).
Figure 13. Discharge and precipitation over study period. Most discharge peaks corresponded to precipitation in the study area. The areas circled in red indicate days on which an increase in discharge did not correspond to a precipitation event in the study area.
Figure 14. Temperature in river sites over study period. Temperature followed a seasonal pattern among all of the sample sites with very little variation between the sites.
Figure 15. Dissolved oxygen and discharge. Dissolved oxygen drops occurred during the summer months when discharge was low and temperatures were high. The lowest dissolved oxygen levels occurred at site 4 where the nuisance algae blooms were present.
Figure 16. pH in the river over the study period. Variation in pH was the most noticeable during the summer months. Sites downstream from the sewage treatment plant and poultry processing plant had a more alkaline pH.
Figure 17. Discharge and pH at the main river sites over the study period. Differences between pH at sample sites were more pronounced during low flow periods. Peaks in discharge during low flow resulted in pH in downstream sites returning to natural levels.
Figure 18. pH at the main river sites and precipitation over the study period. On several occasions following precipitation events, pH decreased in river sites downstream from the sewage treatment and poultry processing plants. Site 1 did not appear to be impacted by precipitation.
Figure 19. pH over time at all sample sites. Tributaries draining the poultry processing plant consistently had the highest pH, most likely due to return flow of Floridan aquifer water from municipal and industrial users. The pH of Floridan aquifer water ranges from 7-8.
Figure 20. Conductivity in river sites. Conductivity was consistently higher in the sites below the sewage treatment and poultry processing plants.
Figure 21. Precipitation and conductivity in main river sites. Differences in conductivity were the most noticeable during low flow periods. Conductivity spikes in the river at sites downstream from the poultry processing plant occurred after precipitation events during low flow periods on several occasions. However, some of these spikes occurred when there was no precipitation in the study area (circled in red).
Figure 22. Discharge and conductivity. Variability in conductivity was most apparent during low flow. In general, sites 2, 3, and 4 had higher conductivity than site 1. Spikes in conductivity occurred occasionally in conjunction with spikes in discharge. These spikes in discharge did not always occur in conjunction with precipitation in the study area (circled in red).
Figure 23. Conductivity at all sites over study period. Conductivity was significantly elevated in tributaries that drain the poultry processing plant.
Sources of Ammonia

The sampling procedure preserved ammonia (NH$_3$) as ammonium (NH$_4^+$) then ammonium (NH$_4^+$) was later converted back to ammonia (NH$_3$) for analysis. Therefore, total ammonium/ammonia concentrations will herein be referred to simply as ammonia concentration, and reported as NH$_3$-N. The resulting data for ammonia concentration were entered into a database and analyzed graphically. Ammonia data for the river sites were analyzed statistically with discharge and precipitation data to determine if a relationship existed.

Figure 24 illustrates how ammonia concentrations were highly variable among the sample sites. For example, sites 5 and 9 were located on tributaries that drained the poultry plant and had the highest concentrations of ammonia, whereas tributary sites outside the influence from the poultry processing plant had very low ammonia levels. Figure 25 shows ammonia concentrations at sample sites on seasonal sampling events. Sample sites 5, 12, and 9 had the highest concentrations on each sampling date and were located on tributaries that drain the poultry processing plant. Sites 9 and 5 drain both the poultry processing plant and the sewage treatment plant, however, site 8 only drains the sewage treatment plant (see Figure 8 for map).
Figure 24. Ammonia concentrations over study period at each sample site. Tributaries draining the poultry processing plant contained much higher concentrations of ammonia than river sites and other tributaries in the study area.
Figure 25. Ammonia concentration in watershed on sampling dates. The highest levels of ammonia in the drainage basin occurred during the summer in tributaries draining the poultry processing plant. The highest ammonia levels in the river occurred during the fall sampling event. (See Figure 9 for sample location).
Since ammonia contributions from site 8 are negligible in comparison to the contributions at site 9, the sewage treatment plant contribution to ammonia concentration in this tributary was minimal. The tributary along which sites 8, 9, and 5 are located empties into the Canoochee River just upstream from site 2. Ammonia concentrations at site 2 are higher than those at site 3, with the exception of on February 24, 2001 when the ammonia concentration at site 12 was higher than that at sites 5, 8, and 9 (see Figure 8 for map).

In addition to this spatial variability, ammonia concentrations increased on similar days in the river sites. The data indicate that the tributary input of ammonia had a small impact on ammonia concentrations in the river sites. Figure 26 shows the ammonia concentration data for the main river sites (Sites 1, 2, 3, and 4). Site 1 was generally lower in ammonia than the sites downstream from tributaries draining the poultry processing and sewage treatment plants (Table 2).

Table 2

<table>
<thead>
<tr>
<th>Site Number</th>
<th>Number of Samples Collected</th>
<th>Average (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>40</td>
<td>0.072</td>
</tr>
<tr>
<td>Site 2</td>
<td>40</td>
<td>0.263</td>
</tr>
<tr>
<td>Site 3</td>
<td>40</td>
<td>0.197</td>
</tr>
<tr>
<td>Site 4</td>
<td>34</td>
<td>0.217</td>
</tr>
</tbody>
</table>
Figure 26. Ammonia concentrations at main river sites during sampling period. Ammonia varied among samples, but the sites downstream from the poultry processing plant and sewage treatment plant (2, 3, and 4) had the highest concentrations.
While site 1 was generally lower in ammonia over the study period (see Table 2 and Figure 26), statistical analysis indicated that the main factor influencing ammonia concentration in the river was temporal rather than spatial. An analysis of variance (ANOVA) test using ammonia data from river sample sites indicated that ammonia concentration does not vary significantly among sample sites (F=2.001, df=3, 150 Prob >F =0.1164). However, an ANOVA test on ammonia data from river sample sites indicated that the ammonia concentration in the river varied significantly by day (F=3.3877, df=39, 114 Prob >F= 0.000). This statistical relationship prompted further examination of the temporal relationship between ammonia and sample site.

The relationship between discharge and ammonia was expressed graphically in figure 27. Pronounced spikes in ammonia concentration take place when discharge is low. There also appears to be a relation between discharge and ammonia spikes during periods of low flow. To further investigate the relation between discharge and ammonia concentration spikes, precipitation data was analyzed to determine if the precipitation events could be responsible for the temporal variation in ammonia concentration among river sites. Ammonia concentrations in both the river and tributaries often spiked after rain events (Figures 28 and 29). In order to determine if these spikes were significantly related to precipitation event, a pairwise correlation test was run using ammonia concentration at the river sites and the sum of the precipitation within 3 days of a sampling event. While there is not a strong correlation between discharge and ammonia
concentration at river sample sites downstream from the poultry processing plant, there is a strong correlation between precipitation events and ammonia at site 1 (Table 3).

Table 3

**Ammonia concentration correlation to precipitation and discharge at river sample sites.**

<table>
<thead>
<tr>
<th>Site</th>
<th>Count</th>
<th>Correlation Coefficient</th>
<th>Probability*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>Precipitation</td>
<td>40</td>
<td>0.6945</td>
</tr>
<tr>
<td></td>
<td>Discharge</td>
<td>40</td>
<td>-0.0763</td>
</tr>
<tr>
<td>Site 2</td>
<td>Precipitation</td>
<td>40</td>
<td>-0.0369</td>
</tr>
<tr>
<td></td>
<td>Discharge</td>
<td>40</td>
<td>-0.2280</td>
</tr>
<tr>
<td>Site 3</td>
<td>Precipitation</td>
<td>40</td>
<td>-0.0657</td>
</tr>
<tr>
<td></td>
<td>Discharge</td>
<td>40</td>
<td>-0.2509</td>
</tr>
<tr>
<td>Site 4</td>
<td>Precipitation</td>
<td>34</td>
<td>0.2153</td>
</tr>
<tr>
<td></td>
<td>Discharge</td>
<td>34</td>
<td>-0.1547</td>
</tr>
</tbody>
</table>

**Note.** *Indicates Significant Relationships (p<0.05)
Figure 27. Ammonia-N concentration and discharge at main river sites. Large ammonia spikes corresponded with discharge during low flow when ammonia concentration at the downstream sample sites increased in conjunction with discharge. Red circles indicate days when there were increases in discharge and there was no precipitation.
Figure 28. Precipitation over the study period and ammonia concentration at river sample sites. Several of the spikes in ammonia corresponded to precipitation events. The only occasion of high ammonia concentration at site 1 occurred after a lengthy precipitation event. The red circles indicate days when there were increases in ammonia and there was no precipitation in the study area. These days correspond to increases in discharge in Figure 27. On these days site 1 had low ammonia, indicating that the ammonia spikes were a local occurrence.
Figure 29. Ammonia concentration and precipitation at tributaries. The ammonia levels in the tributaries draining the poultry processing plant had the highest ammonia levels. Ammonia level in these tributaries corresponded to most precipitation events, however, some spikes occur when there is no precipitation event in the study area, indicating a localized input of ammonia.
This correlation is not repeated at any of the other river sample sites, even though, graphically, there appears to be a connection between precipitation events and ammonia concentration.

Sources of Nitrate

In comparison to ammonia concentrations, the nitrate concentrations in the river varied both temporally and spatially. Figure 30 depicts nitrate concentration throughout the watershed. As seen with the ammonia data (see Figure 29), the tributaries that drained the poultry processing plant had the highest levels of nitrate. As also seen with the ammonia data, the tributary contribution of nitrate did not dramatically increase the nitrate levels in the river. However, as with the ammonia data, the average nitrate concentration in the river sites increased downstream from the poultry processing plant (Table 4).

Table 4.

Average Nitrate Concentration in River Sites

<table>
<thead>
<tr>
<th>Site Number</th>
<th>Number of Samples Collected</th>
<th>Average (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>40</td>
<td>0.110</td>
</tr>
<tr>
<td>Site 2</td>
<td>40</td>
<td>0.168</td>
</tr>
<tr>
<td>Site 3</td>
<td>40</td>
<td>0.445</td>
</tr>
<tr>
<td>Site 4</td>
<td>34</td>
<td>0.268</td>
</tr>
</tbody>
</table>
A comparison of the river nitrate concentration with discharge indicated a significant relationship (Figure 31). As discharge decreased, nitrate concentrations in the river below the poultry processing plant increased. ANOVA test on this data shows that nitrate concentration at river sites varies significantly by discharge by site (F=5.9795, df=3, 146, Prob>F=0.0007) and by day (F=1.9269, df=38, Prob>F=0.0044).

ANOVA analysis also indicated that nitrate varied significantly by discharge (high flow vs. low flow) at the main river sites (F=23.2071, df = 1, 148, Prob>F = 0.000). Nitrate concentrations were the highest when discharge was the lowest. During the low flow period, sites 3 and 4 consistently had the highest concentrations of nitrate (Figure 31). A pairwise correlation test indicated that there was a strong correlation between nitrate concentration and discharge at site 3 and at site 4. There was not a strong correlation between nitrate concentration and flow at site 1 or site 2 (Table 5).
Table 5

Relationship Between Nitrate Concentration and Discharge and Precipitation at River Sites.

<table>
<thead>
<tr>
<th>Site Number</th>
<th>Count</th>
<th>Correlation Coefficient</th>
<th>Probability*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge</td>
<td>38</td>
<td>-0.1575</td>
<td>0.3450</td>
</tr>
<tr>
<td>Precipitation</td>
<td>38</td>
<td>0.0497</td>
<td>0.7672</td>
</tr>
<tr>
<td>Site 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge</td>
<td>39</td>
<td>-0.1799</td>
<td>0.2730</td>
</tr>
<tr>
<td>Precipitation</td>
<td>39</td>
<td>0.0394</td>
<td>0.8118</td>
</tr>
<tr>
<td>Site 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge</td>
<td>39</td>
<td>-0.4209</td>
<td>0.0076*</td>
</tr>
<tr>
<td>Precipitation</td>
<td>39</td>
<td>-0.1766</td>
<td>0.2821</td>
</tr>
<tr>
<td>Site 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge</td>
<td>34</td>
<td>-0.5148</td>
<td>0.0018*</td>
</tr>
<tr>
<td>Precipitation</td>
<td>34</td>
<td>0.1125</td>
<td>0.5264</td>
</tr>
</tbody>
</table>

Note. *Indicates significant relationships ($p<0.05$).
Figure 30. Nitrate-N in watershed for sample period. The highest nitrate levels occurred in tributaries draining the poultry processing plant. In the river, site 3 was consistently high in nitrate.
Figure 31. Nitrate-N at river sites and discharge. Nitrate was diluted in the river during high flows. During low flow, Site 3 was consistently high in nitrate. However, peaks in discharge during low flow did not correspond to peaks in nitrate.
There was not a significant relationship between nitrate concentration and precipitation at the main river sampling sites. Figure 32 depicts the precipitation and nitrate concentrations for the main river sites and supports the statistical findings that there was not a significant relationship between nitrate and precipitation events in the main river sites. Figure 33 shows the precipitation data graphed in conjunction with the nitrate data for all of the sample sites. Precipitation did not affect nitrate at any of the sample sites.

Figure 34 shows nitrate concentration throughout the watershed on seasonal sampling dates. During low flow (sample date: August 15, 2000), nitrate concentration in the river increased substantially from site 2 (0.05 mg/l NO$_3^-$ - N) to site 3 (1.08 mg/l NO$_3^-$ - N). However, there was no tributary input of nitrate between these two sample sites (site 12 did not contribute any nitrate to the river). On this date, nitrate concentration decreased from site 3 to site 4 (1.08 to 0.05 mg/l NO$_3^-$ - N). Sites 5 and 9 also had high concentrations of nitrate, but did not raise the nitrate concentration in the river at site 2.

On November 18, 2000, the highest concentrations of nitrate were found in tributaries draining the poultry processing plant. Sample sites 2 and 3 had equal concentrations of nitrate, and sites 5, 9, and 12 contributed the highest levels of nitrate to the river. On February 24, 2001, nitrate was not detectable in the river sites, but tributaries 5, 9, and 12 had high concentrations of nitrate.
Figure 32. Precipitation events and nitrate concentration in the river sites. The only spike in nitrate concentration at site 1 was found after a large precipitation event. However, precipitation did not impact nitrate concentrations at other sites or on any other occasion.
Figure 33. Nitrate concentration and precipitation at all sample sites. Nitrate concentration was not considerably impacted by precipitation at any of the sample sites over the study period.
Figure 34. Nitrate concentrations at sample sites on watershed sampling events. Nitrate increased drastically on 8/15/00 from site 2 to site 3, with no surface input at site 12. Site 8 was located on the tributary that drained the sewage treatment plant, therefore the highest concentrations of nitrate were consistently found downstream and in tributaries from the poultry processing plant.
Summary

The pH, conductivity, and dissolved oxygen showed evidence of human impact at the river sites downstream from the sewage treatment and poultry processing plants (sites 2, 3, and 4). These parameters also varied between the tributaries draining the poultry processing plant (sites 9, 5, and 12) and the remaining tributaries (sites 6, 8, 10, 11, and 13). In the river sites, the pH and conductivity values were higher downstream from the poultry processing and sewage treatment plants. Several occurrences of significantly lowered pH in the river corresponded to precipitation events during low stream flow. The pH and conductivity in tributaries draining the poultry processing plant and sewage treatment plant were significantly higher than those in the river and other tributaries.

Temperature and dissolved oxygen levels in the river followed a seasonal pattern with the lowest oxygen levels occurring during the summer months, the period of highest water temperatures. The lowest dissolved oxygen levels in the river occurred at site 4, where the algae blooms were the most prevalent.

Ammonia concentrations at the sample sites varied both temporally and spatially over the study period. While ANOVA analysis of ammonia concentration at river sites did not result in a statistically significant spatial relationship, there was a significant relationship between precipitation events and increases in ammonia concentration at the background site (site 1). The spatial relationship between ammonia and river sample site was also shown through graphical analysis (Figure 26) and by comparing averages over the study period (Table 2). The average ammonia concentration at site 1 was lower than at the downstream river sample sites. Tributary data also indicated a spatial relationship
between ammonia and sample site, as the highest ammonia concentrations occurred in
tributaries draining the poultry processing plant.

While the ammonia concentration correlated to precipitation events at site 1, this
temporal relationship was not repeated at the downstream river sites. Ammonia
concentration at sites 2, 3, and 4 did not statistically correlate with precipitation events or
discharge. However, graphical (Figure 26) and statistical ANOVA analysis indicated
that there was a statistically significant relationship between river sample site and sample
date. Since this temporal relationship with ammonia in the downstream sample sites did
not correlate to discharge or precipitation events, the ammonia spikes in downstream
river sites were associated with other discrete events in the study area.

Nitrate concentrations at the sample sites varied temporally throughout the study
period, but were consistently higher in the localized area around the poultry processing
plant than anywhere else. Nitrate concentrations were consistently higher in the river
during low flow periods, but did not correspond to precipitation events. The nitrate
concentration at site 3 was sustained over a long period of time during low flow. Nitrate
levels were the highest in tributaries draining the poultry processing plant. However, the
largest increase in nitrate concentrations in the river occurred at a time when no tributary
input of nitrate was taking place.
Chapter V
Summary, Conclusions, Recommendations

The problem of this study was to determine the source(s) of nitrogen input into an 11 mile reach of the Canoochee River in Evans County. Subproblems were to determine whether significant nonpoint source pollution could be identified as originating from a discrete source and to determine whether surface sources of nitrogen could be differentiated from groundwater sources. The questions to be resolved in this study included (a) determining if dissolved oxygen, pH, conductivity and temperature at the sample locations indicated human impacts, (b) identifying sources of nitrogen, (c) verifying whether surface sources could be distinguished from groundwater sources of nitrogen, and (d) determining if the study design was an effective method of locating significant nonpoint sources of nitrogen.

Dissolved Oxygen, pH, Conductivity, and Temperature as an Indicator of Human Impact

Several of the parameters measured \textit{in situ} at each of the sample points served as indicators of human impact on the Canoochee River. The pH and conductivity increased dramatically downstream from the poultry processing and sewage treatment plants and in tributaries that drained the poultry processing plant (Figures 18 and 20). Moreover, dissolved oxygen was lower in these locations (Figure 15). Since pH in blackwater rivers is naturally low (approximately 4 to 6), due to tannins in the water, the higher pH in the
area draining the municipal area, where the average pH in these tributaries ranged from 6.67 - 7.04, served as an indicator of human impact. This rise in pH was likely the result of return flow of Floridan aquifer water from the spray fields of the poultry processing and sewage treatment plants. Both the municipality and the poultry processing plant used the Floridan Aquifer for sources of water. This water with a more alkaline pH (pH 7 - 8) was introduced into the stream from the spray fields (either through runoff to or surficial aquifer flow) and mixed with the lower pH water to raise the pH in the streams. The increased conductivity in the downstream river sites and in the tributaries around these plants served as an additional indicators of human impact.

Dissolved oxygen in the Canoochee River also served as an indicator of nutrient loading due to human activity. Site 4 (see Figure 9) exhibited the lowest dissolved oxygen levels during the summer when algae blooms were present. Dissolved oxygen levels dropped well below the threshold (3.0 mg/l) for fish habitat on several occasions during the summer months (Horne and Goldman, 1994). Although this site displayed visual signs of nutrient pollution, this site was not the location of the highest nitrogen levels. The lack of nitrogen in the water samples could be attributed to nitrogen uptake by the algae blooms. As the algae blooms decay, the dissolved oxygen levels at this site would be lowered as a result of eutrophication (see Chapter II). The impact of the nitrogen pollution on this site was evident by visual characteristics and chemical constituents other than nitrogen levels.
There was no evidence to support that temperature was an indicator of human impact. The fluxes in temperature at each of the sample sites followed a natural, seasonal pattern (Figure 14).

Surface Water Sources of Nitrogen to the Canoochee River

It was found that runoff to tributaries was the primary surface water source of nitrogen to the Canoochee River in the study area. Tributaries draining the poultry processing plant had high concentrations of nitrate and ammonia relative to other tributaries in the drainage basin. Moreover, the volume of water in the river influenced the degree to which the ammonia and nitrate concentrations from the tributaries would impact the river. For example, during low flow periods, spikes in the concentration of ammonia concentration due to tributary input were more substantive in the river than during high flow periods. The relationship between discrete precipitation events and ammonia concentrations was more discernible during the summer months when the discharge in the river was lower than during the spring and winter months.

While ammonia concentrations at the river sites varied throughout the study area, as often found with NPS pollution (pollution originating from diffuse sources), the tributaries draining the poultry processing plant consistently had the highest concentrations of ammonia, indicative of PS pollution (pollution from a discrete source). In the main river sites (1, 2, 3, and 4), there was a temporal relationship between ammonia and the sample site, but this relationship does not significantly correlate with
precipitation or discharge, except at site 1 where there is a significant correlation between precipitation and ammonia. The data from site 1 supports previous research that indicated that ammonia is often introduced into aquatic environments through runoff associated with precipitation (see Chapter II). The sites that do not correlate to precipitation events are those sites downstream from the poultry processing plant and the sewage treatment plant. The analysis of ammonia data from the tributaries provided no specific evidence to indicate that the loading in the tributaries, and, subsequently, the river was solely related to precipitation. It is more likely that an independent variable, such as application rates on spray fields and/or sewage spills contributed to the increase.

During high stream flow, ammonia was diluted in the river; during low flow, ammonia concentration was diffuse. However, there was no correlation between ammonia concentration and discharge in the main river sites, even though the peaks in ammonia concentration are much more pronounced during low flow (Figure 27). The placement of the monitoring station could have a relationship on the lack of correlation between discharge and ammonia. The USGS discharge monitoring station was located downstream from the tributary that drained sites 5, 8, and 9. There was no significant statistical correlation between sample sites and discharge. However, on November 25, 2000 (as well as June 30, 2000) there was an increase in discharge that corresponds to a subsequent spike in ammonia concentration at sites 2, 3, and 4 (Figure 27). This increase
in discharge is prior to any major precipitation event in the immediate drainage basin (Figure 13) but does correspond with a large spike in ammonia concentration at site 5 (19.32 mg/l NH$_3$-N).

There are two possible explanations for the spikes in ammonia concentration. Either some event at the sewage treatment or poultry processing plants increased the flow of ammonia laden water into this tributary at site 5 or a precipitation event elsewhere in the watershed that was not monitored contributed ammonia to the river. The later appears to be the case on July 26, 2000 (Figure 28). The spike at site 1 occurred after a precipitation event in the study area, but may have been related to runoff from precipitation upstream in the drainage basin. On June 30, 2000 and November 29, 2000 the peaks in ammonia occurred only at sites 2, 3 and 4 on dates prior to precipitation in the study area. Since site 1 did not spike on these dates, the ammonia input originated from a localized source downstream from site 1 and upstream from sites 2, 3 and 4.

Overall, the high concentration of ammonia in the tributaries did not significantly raise the ammonia concentrations in the river sites downstream of their confluence with the river (Figure 35). The lack of influence of the tributary input of nitrogen to the river could be due to the volume of water in the tributaries relative to the volume of water in the river. The greatest increases in ammonia concentration in the river occurred during low flow. In figure 35, ammonia increased from 0.01 mg-N/l to 0.17 mg-N/l from site 7 to site 2. This increase was due to ammonia input from the tributary at site 5. However, during high flow, although the tributaries draining the poultry processing plant had very
high concentrations of ammonia and nitrate, the concentrations could be diluted in the river (Figure 30). It is also possible that the ammonia in the tributaries was converted to nitrate due to higher dissolved oxygen levels in the river. However, nitrate concentrations in the river did not appear to be affected by tributary input, as the major increases in nitrate in the river occurred at site 3 on days when the tributary input of nitrate from site 12 was negligible (Figure 34).
Figure 35. Map of ammonia in study area. From August 15, 2000. The highest ammonia concentrations were found in tributaries draining the poultry processing plant. Ammonia concentration in the river rose slightly from these impacts.
The major variable in ammonia concentration in the river sites was temporal. This was indicated graphically (Figure 26) by the occurrence of ammonia spikes and statistically by the significant relationship between ammonia concentration among all river sample sites and day. However, the major factor that affected tributary ammonia concentration was land use, because the tributaries that drained that poultry processing plant consistently had the highest concentrations of ammonia in the watershed (Figure 24). Nitrate concentrations in these tributaries were also considerably higher than in any of the other tributaries sampled. Although the poultry processing plant did not directly discharge the effluent from their processes to the Canoochee River or tributaries, the high concentration of ammonia and nitrate in the tributaries that drained the poultry processing plant would indicate that the plant was a discrete source of nitrogen via surface water to the Canoochee River.

**Delineation of Groundwater Sources of Nitrogen**

Through graphical (Figure 32) and statistical analyses (Table 5) it was determined that precipitation events had no direct affect on nitrate concentrations in the river or at tributary sample sites. Therefore, the nitrate contamination of the river and tributaries was not due to runoff associated with precipitation. Statistical data also indicated that nitrate concentration varied spatially. There was a significant correlation between nitrate concentration and discharge at sites 3 and 4 (Table 5). Additionally, the inverse relationship between discharge and nitrate concentration at the river sites indicated that
nitrate is higher during low flow. Since runoff was not a significant pathway of nitrate to the river, groundwater must have been the most substantial source of nitrate to the river.

The hypothesis that groundwater is the major contributing source of nitrate to the Canoochee River is further supported by data from the watershed sampling event on August 15, 2000 as shown in Figure 34 and Figure 36. In these figures it can be seen that, nitrate concentration in the river increased 10 fold from site 2 to site 3 without any surface input on this date (Figure 36). The data from this study period indicated that sites 3 and 4 had significantly higher concentrations of nitrate than the other river sample sites, even though the tributary with the highest concentration of nitrate, site 5, and was upstream of site 2 (Figure 9).
Figure 36. Drainage map showing nitrate concentration in the Canoochee River and its tributaries on August 18, 2000. Nitrate concentration (in red) increased dramatically from site 2 to site 3 without any surface input of nitrate.
In addition to the increase in nitrate concentration from site 2 to site 3, as shown in figure 36, the sustained elevation of nitrate levels at site 3 and site 4 during low flow indicated that there was an ongoing, substantial input of nitrate to the river (Figure 31). This elevation in nitrate in the river occurred between sites 2 and 3 during low flow and on occasions when there was no surface input of nitrate. Because there were sustained periods of elevated nitrate concentration at site 3 at a time when there was no surface input of nitrate, the increase in nitrate between sites 2 and 3 must have been from groundwater input of nitrate (Figure 34 and Figure 36).

Since the poultry processing plant lies between sites 2 and 3 and this is the area where nitrate is entering the river via groundwater baseflow, the poultry plant was determined to be the most substantial source of nitrogen to the Canoochee River in the study area. The impact of contaminated groundwater from the poultry plant spray fields was most severe during the summer months when stream discharge was low and water temperature is high. It was during these months that algae growth was at its maximum and groundwater was the dominant component of stream discharge. Therefore, nitrate contaminated groundwater could have an appreciable impact on nitrate concentration in the river and result in excessive algae growth.

The concentrated and sustained nature of this groundwater input of nitrate to the Canoochee River affected nitrogen levels in the river more substantially than runoff or tributary inputs. The groundwater input of nitrate was particularly problematic because it occurs at the time of maximum algae growth and at a time of slow stream discharge. In
addition, nitrate is the form of nitrogen most readily available for plant growth. Since the nitrate input from groundwater was the most significant during the growing season, large algae blooms and subsequent low dissolved oxygen levels severely impacted the area downstream from the poultry processing plant.

**Effectiveness of Study Method**

By collecting detailed spatial and temporal samples and analyzing for both ammonia and nitrate, the results of this study indicate that the most significant contribution of nitrogen pollution to the Canoochee River during the study period was from nitrate in groundwater draining a poultry processing plant. This method would be appropriate for use in other drainage systems in which the pathways of nitrogen pollution to surface water are unknown. The detailed temporal and spatial scales of this study method allowed the results to be analyzed in conjunction with discrete precipitation events, land use, and long-term discharge measurements. In order for this sampling method to be effective, sites were carefully selected to include all potential tributary input of nitrogen as well as river sites downstream from tributary inputs. Sample sites were of sufficient spatial scale to detect a nonpoint source as a point source and monitoring tributary inputs assisted in the delineation the nonpoint source. This study also showed that ammonia was found primarily in surface water inputs, whereas nitrate dominated groundwater inputs. Since ammonia is typically restricted to surface water, and nitrate may be found in both surface water and groundwater, surface water sources of nitrogen can be delineated from groundwater sources by monitoring for ammonia and
nitrate. Groundwater input of nitrate was observed when there was an increase in nitrate in the river between sample sites, without any tributary input of nitrate. In addition to careful selection of sample sites for detailed spatial analysis, the temporal scale of this study was sufficient to detect short term nitrogen inputs. This study design may be applied to other areas in order to delineate surface and groundwater sources of nitrogen to surface waters.

Recommendations for Further Study

Although this study demonstrated the effectiveness of ammonia and nitrate analysis in differentiating surface and subsurface inputs of nitrogen, additional studies are needed to refine this method. Analysis of additional chemical species such as phosphorous, chloride, and sulfate is necessary in order to determine the extent and source(s) of nutrient loading in the Canoochee River. Isotope analysis of the nitrogen would also help to determine the exact source of nitrogen (human or animal). Discharge data for the tributaries would help to determine the significance of the tributary inputs of nitrogen relative to the groundwater inputs. A study should be initiated in which detailed discharge data of the Canoochee River in the vicinity of the suspected groundwater input is collected in conjunction with ammonia and nitrate analysis. This data would help to further delineate the exact location(s) and significance of groundwater contributions of nitrate to the Canoochee River in the area of the study. Detailed data should be collected
as to the type, size, and impact of algae blooms in the Canoochee River to determine. This data should be collected in conjunction with nutrient analysis to further determine the impact of nutrient loading on the ecology of the Canoochee River.

Similar studies should be conducted in other reaches of the Canoochee River to determine the extent of nutrient pollution via surface and groundwater. Other pollution, such as mercury, should be investigated as well. In other studies, the fish in the Canoochee River were found to be contaminated with mercury (Georgia Department of Natural Resources, 2002). A study of heavy-metal contamination on the Canoochee River would be useful to determine sources and recommend remedial actions. Should any subsequent study reveal additional contaminants of the Canoochee River, the sources should be thoroughly investigated and remediated according to appropriate governing water policies. In addition to supplementary studies on the Canoochee River, this study should also be replicated on other rivers to determine its usefulness in other water bodies.

Summary

The purpose of this study was to determine sources of nitrogen pollution in the Canoochee River in Evans County over the study period. In order to determine the sources of nitrogen in the Canoochee River, sample sites were established on the river and its tributaries. Tributaries draining a poultry processing plant and a sewage treatment plant were found to have the highest concentrations of ammonia and nitrate in
the watershed. However, these tributaries did not significantly increase the nitrogen levels in the river over the study period due to the low volume of water in these tributaries relative to the river.

Dissolved oxygen, pH, and conductivity indicated human impact in the river sites downstream from the municipal area and in tributaries draining the poultry processing plant. The most downstream site (site 4) had the lowest dissolved oxygen levels and was the site of algae blooms during the summer. However, this site did not have the highest levels of nitrogen due to nitrogen uptake by the algae. The pH in the area around the poultry processing and sewage treatment plants was elevated in comparison to the other sites and was likely due to the return flow of Floridan Aquifer water from municipal and/or industrial uses.

The source of nitrogen of greatest impact to the Canoochee River over this study period was groundwater from a poultry processing plant. This hypothesis is substantiated by the consistent increase in nitrate downstream from the poultry processing plant, without a subsequent increase in surface water inputs. Moreover, this increase in nitrate concentration at the river sites occurred on a date when there was no surface input of nitrate into the river. The groundwater contribution of nitrate was substantial due to the fact that when the algae growth is at a maximum in the summer months, groundwater is the dominant component of stream discharge. In addition, because stream flow is low at this time, dilution of the contaminated groundwater is minimal.
Ammonia concentrations in the river were diffuse throughout the watershed. The spikes of ammonia concentration that occurred throughout the river sites on specific dates were evidence of the diffuse nature of this input of nitrogen. However, ammonia concentrations in the river did correlate statistically to precipitation events, except at site 1. However, there was some correspondence between precipitation events and ammonia concentrations in the river. The highest concentrations of ammonia occurred in tributaries draining a poultry processing plant. Although these tributaries had concentrated levels of ammonia and nitrate, their impact on the nitrogen levels in the Canoochee River was low in comparison to the impact of contaminated groundwater due to dilution of this input in the river. Ammonia concentrations in the river downstream from tributaries draining the poultry processing plant spiked on similar days, but these spikes were not sustained over long periods of time. The nitrate contribution from groundwater downstream from the poultry processing plant, however, was sustained over most of the low flow period, and was more highly concentrated.

The study method proved effective in determining sources of nitrogen over the study period and would be useful in similar circumstances. Nitrate and ammonia analysis allowed for the delineation of surface and subsurface sources. Subsurface sources of nitrogen were located when nitrate between river sites increased without any tributary input of nitrogen. Additional studies should be conducted in the Canoochee River and on other rivers using this study design to verify its usefulness in determining surface and groundwater contributions of nitrogen to surface waters.
References


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