Spatial and Temporal Trends and the Role of Land Use/Cover on Water Quality and Hydrology in the Fish River Watershed

by

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Abstract

This study focuses on exploring linkages between land use/cover (LULC) and water quality/quantity at both spatial and temporal scales in the Fish River watershed. The Fish River, in coastal Alabama, is of critical importance to the health of Weeks Bay, a designated Outstanding National Resource Water. The study takes place across ten subwatersheds within the Fish River's watershed boundaries. Dominant LULCs in the watershed include row-crop agriculture and medium density residential areas. Significant urbanization has occurred across all subwatersheds between 1995 and 2008. Grab samples and stormflow ISCO automated samples were taken and processed to determine concentrations of ammonium + ammonia (NH_4+NH_3 -N), Nitrate (NO_3^--N), Total Phosphorus (TP) and Total Suspended Sediment (TSS). Discharge rates were established at each site in order to better quantify subwatershed flows. Spatial comparisons between subwatersheds were linked to water quality and flow trends over time. Data from previous studies in the mid-1990s were compared with this study's collected data to determine changes in nutrient and sediment levels over time. Only 2 sites showed significant changes in hydrology between the two study periods. Sites with large increases in urbanized land uses had substantially higher TSS concentrations. Nitrate levels between study periods showed a general decrease, while TP concentrations and loads increased significantly between the two time periods. A shift in the nitrogen-phosphorus balance in the Fish River and its tributaries may result in eutrophication of Weeks Bay. The introduction of different crops

along with rapidly increased population growth and urbanization are causing substantial changes in the water quality balance within the Fish River and ultimately Weeks Bay.

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1. Introduction

1.1. Introduction

Different land use/cover (LULC) conditions have long been known to influence water quality and hydrology (Bormann *et al*. 1999, Basnyat *et al*. 1999, Bledsoe and Watson 2001, Lehrter 2003, MacCoy 2004, Helms 2008). Consequences of LULC changes over time far outweigh any effects caused by climate changes (Vorosmarty *et al*. 2000). The Southeastern United States is predominately comprised of agricultural, silvicultural and urban land uses which can each impact water quality and hydrology in different ways (Brown et al. 2005). Urbanization and increased agricultural land use can have serious impacts on the health of an ecosystem. While these LULCs can affect the quality and quantity of runoff from a watershed, such adverse impacts can be mitigated by the type and size of riparian buffers that separate the LULC and the water body (Vidon 2010). Water quality is of critical concern when watersheds transition to agricultural and urbanized landscapes. Urbanization of a watershed and an increase in impervious surfaces can result in the reduction of infiltration rates, increasing surface flow and reducing groundwater release preventing naturally occurring pollutant processing (Dunne and Leopold 1978, Arnold and Gibbons 1996, Schoonover *et al*. 2006, Ma *et al*. 2010). Disturbances in the natural hydrologic pattern of a watershed can have serious ecological consequences such as loss of habitat and increases in sediment (Finkenbine et al. 2000). In urbanized watersheds, runoff from impervious surfaces provides most of the nutrient and sediment input into a water body. Increased agricultural usage and leaking septic systems can also have significant effects on nutrient levels. Increases in the amount of row crop agriculture within a watershed have been found to alter nutrient concentrations significantly (Murgulet and Tick 2008). Fertilizer application on crops can either leach through the soil and enter the groundwater or pass through the water column as runoff (Miller-Way *et al*. 1996, Novoveska 2005, Chandler *et al.* 1998). Urban and agriculture LULCs are known to be major contributors of nitrogen and phosphorus (Carpenter et al. 2000, USEPA 2000, Tong and Chen 2002).

Nutrient and sediment inputs to freshwater streams are greatly influenced by local LULC conditions. The nutrient balance within an aquatic system is critical to maintaining ecological health. Nitrogen and phosphorus are considered the two most important nutrients in a freshwater environment. A shift in the nitrogen/phosphorus balance may cause serious changes in local flora and fauna. Excessive loading and high concentrations of nitrogen and phosphorus in coastal systems can result in algal blooms, lowering dissolved oxygen levels and ultimately causing eutrophication and decreased productivity (Frick 1996, Miller-Way *et al*. 1996, Basnyat 1998, Freeman *et al*. 2007). Channel erosion due to urbanization can result in excessive amounts of sediment downstream (Paul and Meyer 2001). Heavy metals and nutrients can bind to these eroded sediment particles resulting in the potential degradation of stream biota (Arnold and Gibbons 1996, Callender and Rice 2000, USEPA 2000).

In the Southeast U.S., fewer studies have been conducted in the Atlantic and Gulf Coastal Plain than in the Piedmont or Appalachian regions. Historically, the Coastal Plain has been utilized for silvicultural and agricultural purposes. Recently, there has been a rapid expansion of coastal populations in the late 20th and early 21st centuries. The growing population has lead to rapid expansion of urban areas, potentially degrading ecological systems (Martinez *et al.* 2007).

Nitrate (NO_3^-) and phosphorus concentrations in the Coastal Plain are generally known as being lower and higher, respectively than in the Piedmont region (Berndt *et al* 1998). Linking water quality and changing LULC has proven difficult for certain water quality constituents in the Coastal Plain compared with the Piedmont. For example; nitrate relationships to changing LULC were stronger in the Piedmont than the Coastal Plain, whereas total suspended sediment (TSS) and total phosphorus (TP) relationships were more greatly impacted by Coastal Plain LULCs (Weller *et al.* 2003). As data collection in the Coastal Plain has been historically limited, it is important to continue to study the interactions between LULC and water quality.

There are two main approaches to determine water quality conditions in a watershed: modeling and field sampling. There are many different models available that provide estimations of water quality with varying LULC; however, many models require collected data from field studies to accurately determine water quality conditions. While physically-based models can provide estimations of conditions in a watershed, they also generally over-parameterize which can cause additional uncertainty (DeFries *et al.* 2004). The collection of water quality samples in the field has been and will continue to be of great benefit to estimating how water quality interacts with changing LULC. Sampling can be limited by available resources so it is important to determine the best sampling design which will provide sufficient data. Water quality sampling can be done at two distinct domains to establish the linkages between LULC and water quality: spatial and temporal domain. Spatial sampling allows samples to be collected at many different locations within a certain, short time frame (typically 1 to 2 years). One can then provide linkages between different LULC at these locations and determine possible interactions between LULC and water quality. Temporal sampling can be done at the same location over a long period of time, where LULC changes over time. This technique helps one understand how changes in LULC over time can cause changes in water quality conditions.

When assessing water quality *in-situ*, it is important to collect samples that are representative of actual stream conditions. Many water quality studies sample primarily during baseflow conditions and do not gather sufficient storm event samples. A major problem with sampling only once during a day is that compounds are constantly added and diluted in the water column, making it difficult to accurately estimate a representative concentration (Round 1991). Sampling of this type can skew results towards those that occur during baseflow conditions. Overland runoff occurs only during storm events, so it is of vital importance that water quality data are collected during both baseflow and stormflow conditions. Grab sampling has been the standard sampling technique used by many previous studies (Basnyat 1998; Chandler *et al.* 1998; Lehrter 2003; Schoonover 2005). Sampling can be improved by collecting multiple samples with an automated sampler; this is especially important when gathering data during storm events. However, the collection of multiple samples over time is more difficult to implement and much costlier to process. Automated samplers are often very expensive and analysis of multiple samples can be time-consuming and costly.

In addition to collecting water quality samples, it is important to monitor flow conditions at sites throughout a watershed. Measured flow data at the subwatershed level allows one to more accurately depict hydrologic conditions at a smaller scale. Establishing flow conditions can provide useful data with regards to changes in base/stormflow. The collection of flow data also helps determine an accurate assessment of the nutrient/sediment load passing through the system. Nutrient loads can be directly related to the LULC conditions within a watershed (Lehrter 2003). This relationship is of great concern especially in coastal areas where rivers drain ecologically important bays and estuaries. Excess nutrient and sediment loads in estuarine systems can result in eutrophication, causing a negative impact on biota, degradation of natural habitats, and a negative impact on the local fishing and tourism industries (Murgulet and Tick 2008).

1.2. The Fish River Watershed

The Fish River watershed is located in southern Baldwin County in coastal Alabama (Figure 1.1). This watershed drains into Weeks Bay which was classified as one of three Outstanding National Resource Waters (ONRWs) in the state of Alabama in February 1992. These waters are classified as having:

"no new point source discharges or expansion of an existing point source discharge to waters of, or tributary to, Outstanding National Resource Waters shall be allowed if such discharge would not maintain and protect water quality within the Outstanding National Resource Water." (Miller-Way et al. 1996)

Historically, water quality research has been fairly sparse in the coastal plain of the United States. Recent population shifts from inland cities to the coast have spurred aquatic health concerns which have led to studies being undertaken in coastal watersheds. The Fish River watershed has had a substantial increase in population. Population increases typically lead to urbanization leading to water quality concerns. Several previous studies occurred in this region in the 1990s/2000s. These studies and the changing trends in land use of coastal Alabama provide an opportunity to conduct a water quality study which samples both spatially and temporally.

Previous studies have documented water quality concentrations at various sites in the Weeks Bay watershed; however, there have been no studies that monitored real-time flow in the tributaries of the Fish River. The U.S. Geological Survey (USGS) have been monitoring flow at the intersection of Hwy. 104 and the Fish River. This station encompasses approximately 44% of the Fish River watershed (Chandler *et al.* 1998). This USGS station also provides the only rain gauge located within the watershed's boundary. Lehrter's study (2003) estimated flow data for un-gauged watersheds using the HSPF model; however, measured flow data at sampling sites should provide a better representation of the actual hydrology.

The Geological Survey of Alabama (Chandler *et al.* 1998) collected water quality samples from 1994-1998 at many locations in the Fish River and Magnolia River watersheds. They analyzed samples for many water quality parameters including NO_3^-, TP and TSS. Their results showed that water quality is closely linked to physiographic and LULC characteristics.

Prakash Basnyat (1998) conducted a dissertation study through Auburn University and collected biweekly samples from 1995-1996 at locations throughout the Fish River watershed. These were analyzed for NO_3^- and TSS at Auburn University. Basnyat found that forested land typically acts as a NO_3^- sink and that residential/urban areas are responsible for the majority of NO_3^- entering the system with agriculture areas as a secondary source.

John Lehrter (2003) conducted a dissertation from the University of Alabama and collected water quality samples every three weeks from 2000-2002. Nitrogen, phosphorus, organic carbon and TSS export rates were determined for the Fish River. Agricultural areas were found to be a source of dissolved inorganic nitrogen (DIN) and total nitrogen (TN) while forested wetland areas also had high levels of TN load. TP was highest in subbasins with intermittent and low flow as well as in forested wetland areas. Urbanized areas had high TSS export rates. Lehrter's study took place during drought conditions where water quality conditions may be very different from those occurring during moderate to wet years; therefore, data from this study were not compared temporally with other studies.

1.3. Objective

This current study focuses on how water quality (NO_3^-, TP and TSS) varies spatially and temporally with differing LULC in the Fish River watershed. Determining the sources of pollutants is important for future management plans. Evaluating increasing or decreasing trends over time regarding the nutrient balance is critical to establishing how LULC changes affect water quality in the area. We will determine whether or not the analysis of collected data at the spatial scale can act as a surrogate for predicting future changes in water quality with changing LULC.

Objective: To determine temporal and spatial linkages between LULC and water quality/quantity using data from previous studies (1994-1998) and data collected from the current study (2008-2010).

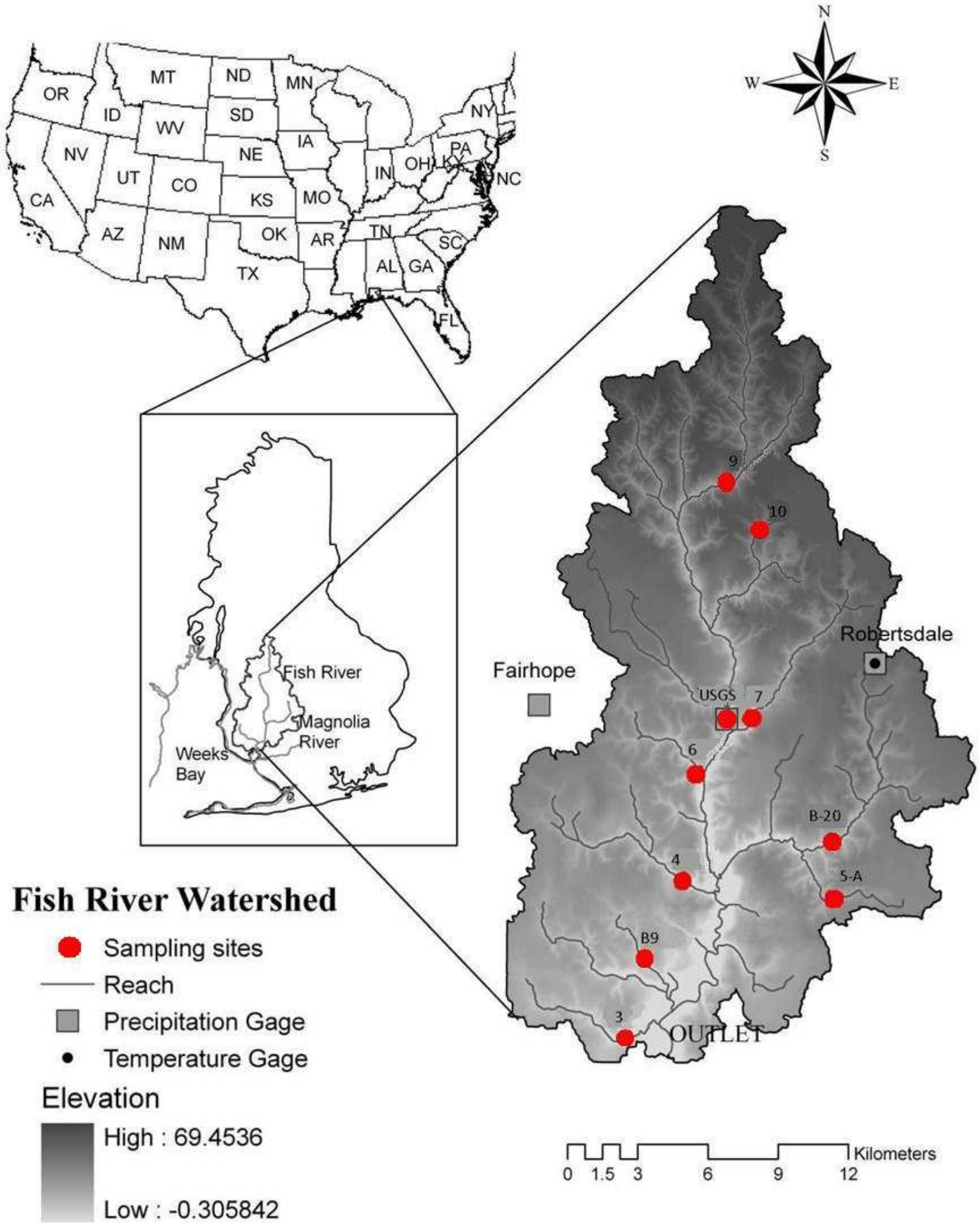


Figure 1.1. Location of Fish River Watershed with sampling sites for the 2008-2010 study period.

2. Methods

2.1 Study Area

The Weeks Bay watershed is located in southern Baldwin County, Alabama and drains into Weeks Bay which is a sub-estuary of Mobile Bay (Figure 1.1). The watershed is divided into the Fish River and Magnolia River watersheds. The Fish River watershed is approximately 408.6 km^2 in size and is located between the towns of Stapleton, Fairhope and Foley, AL (Basnyat 1998). The Fish River watershed encompasses approximately 73% of the freshwater draining into Weeks Bay (Schroeder 1996, Novoveska 2005). The watershed is located in a humid subtropical region of the Gulf Coast. Summer temperatures are typically warm and humid with winters being mild with the occasional cold spell. The average annual precipitation of the region is 1676 mm per year (South Alabama Regional Planning Commission 2004; Stallman et al. 2005). Hurricanes, tropical storms, winter storms and summer showers account for the different forms of precipitation in this region (Chandler *et al.* 1998). The average annual air temperature is approximately 20^{o}C with an average January temperature of 10.5^{o}C and an average July temperature of 28^{o}C.

The Fish River watershed is located on the coastal plain in the southeastern United States. Soils in this area are ultisols and are derived from fluvial and marine sediment eroded out of the Appalachian and Piedmont plateaus (ACES 2008). There are three distinct soil series in our study area: Dothan, Greenville, and Troup. Dothan soils consist of approximately 86% sand, 7% silt and 7% clay. Greenville soils are made up of 68% sand, 20% silt and 12% clay. Troup soils consist of 86% sand, 4 % silt and 10% clay. The textural classification for the Dothan and Troup soils is loamy sand whereas the Greenville soil is classified as sandy loam (McCuen 2005). Slope conditions within the study area typically range from 0-2%. Elevation throughout the Fish River watershed ranges from 0-65 meters with highest elevations in the northern portion of the watershed.

The Geological features of the Fish River are from the Tertiary period of the Cenozoic era. They are predominately made up of the Citronelle formation with the Alluvial formation formed around stream deposits (Basnyat 1998). The Citronelle formation is composed of sand and gravel beds with depths of up to 67 meters (Hinkle 1984).

There are two distinct physiographic districts located within the Fish River watershed: the Southern Pine Hills and Coastal Lowlands. The Southern Pine Hills district is characterized by broad, round hills of low relief. Soil leaching and high organic matter often result in tea-colored waters known as blackwater streams. The Coastal Lowlands district is located between the Southern Pine Hills and the estuarine system of Weeks Bay. Coastal Lowland stream channels are typically heavily vegetated and have extensive root systems. (Chandler *et al.* 1998)

Water quality and flow data were collected at 10 sampling locations between October 2008 and March 2010 (Figure 2.3). There was no specific sampling interval established as attempts were made to capture representative samples during both baseflow and stormflow conditions. Intervals between sampling visits varied from several days to weeks depending on the occurrence of storm events. Sample sites were selected based upon the location of previous studies' sampling sites and ease of access.

2.2 Previous Studies in the Weeks Bay Watershed

Several studies have been conducted within the Fish River watershed since the mid 1990s related to water quality. These studies include the following: Geological Survey of Alabama (Chandler *et al.* 1998); dissertations by Prakash Basnyat (Basnyat 1998) and John Lehrter (Lehrter 2003); and theses by John Cartwright (Cartwright 2002) and Lucie Novoveska (Novoveska 2005).

The Geological Survey of Alabama (Chandler *et al.* 1998) concluded that water quality in the Weeks Bay watershed is linked specifically to each subwatershed's physiographic and LULC condition. Chemical and physical characteristics of streams vary considerably at the subwatershed level (Chandler *et al.* 1998). Samples were collected monthly between 1994 and 1998 at tributaries throughout the Fish and Magnolia River watersheds and analyzed for various water quality parameters including: specific conductance, air and water temperature, turbidity, pH, dissolved oxygen, chloride, sulfate, ammonia (NH_3), total Kjeldahl nitrogen (TKN), nitrite (NO_2), NO_3^-, total NO_2-NO_3^- (NO_x), orthophosphate (PO_4), TP, total dissolved solids (TDS), TSS, biochemical oxygen demand, fecal coliform and fecal streptococcus bacteria. Biological sampling and habitat analysis were also performed in this study. Sampling sites were located in two separate physiographic regions: Coastal Lowlands and Southern Pine Hills. In regard to nitrogen, higher TKN and lower NO_x concentrations were more typical in Coastal Lowland streams compared with Southern Pine Hill streams (Figure 2.1). This difference is likely due to lower dissolved oxygen levels, higher BOD content, and higher mineral content in Coastal Lowland streams. Coastal lowland streams typically have more pockets of standing water in wetland areas allowing plants to assimilate more nitrogen, lowering NO_x levels.

Prakash Basnyat (1998) completed a dissertation at Auburn University focusing on the effect of LULC on sediment and nutrients in the Fish River watershed. Sampling sites were selected at various locations within subwatersheds of the Fish River system. NO_3^- and TSS were the main parameters tested regarding LULC impacts on water quality. Samples were collected, on average, every two weeks from early spring 1995 to late spring 1996. Basnyat's results showed that forested areas acted as a NO_3^- sink. Residential/urban built-up areas were responsible for the largest contribution of NO_3^- into the system with active agriculture as the second largest contributor. Water quality responded well to passive forests and grasslands that were located adjacent to streams. For the purposes of his study, there was no attempt to distinguish between wetland and grassland areas. Basnyat (1998) suggested that by maintaining adequate riparian zones and other best management practices (BMPs), water quality concerns from LULC activity can be mitigated.

John Lehrter's (2003) dissertation from the University of Alabama focused, in part, on the effect of LULC, geomorphology, and climate on nutrient export in several coastal watersheds. Nitrogen, phosphorus, organic carbon and TSS export rates were determined for three coastal watersheds, one of which being the Fish River watershed. Loads were derived from empirical and model-based flow estimations and measured concentrations of water quality parameters. Samples were collected every three weeks between January 2000 and January 2002. While the majority of samples were collected during baseflow, data were also collected during a few storm events. Agricultural areas resulted with the highest DIN and TN while forested wetland areas also had high levels of TN load. TP was highest in subbasins with intermittent and low flow as well as in forested wetland areas. Urbanized areas had the highest TSS export rates especially in the wetter year of 2001. As this study took place during a drought, care should be taken when attempting to compare this study's results with others.

Many of the water quality problems in the Fish River have been site specific and time-related (Chandler *et al.* 1998). Determining which subwatersheds have the greatest impact on downstream systems is of critical importance. Previous studies in the Fish River watershed have not evaluated water quality over a long period of time. Temporal trend analysis is of significant importance when focusing on LULC change over many years. If a trend is established, forecasts can be made to better predict how further LULC change will affect the watershed. Water quality data collected by the GSA and Basnyat were used in this study to determine temporal changes in trends; however, Lehrter's data were not used as these were collected during drought conditions and would not necessarily be comparable to data collected from 1994-1998 and 2008-2010. (Figure 2.2)

2.3 Sampling Sites

Sampling sites were chosen to capture data from major tributaries and a variety of LULC types. Commonality with previously studied sites and ease of access were also taken into consideration. In total, 10 sampling sites were selected (Figure 2.3, Table 2.1 and Table 2.2). The site with the largest drainage area is Site 70 (USGS) which encompasses much of the northern portion of the Fish River watershed and is approximately 141.3 km^2. Sites 9 and 10 also drain into site 70 (USGS). Site 10 has the smallest drainage area among all the sampling sites with an area of only 5.45 km^2. Site 9's subwatershed accounts for the largest percent forested area (38.9%) with site 5A's subwatershed the smallest percent area (6.2%). Site 4's subwatershed is the most urbanized (combination of low/medium/high density residential/commercial/industrial/transportation land) (36.2%) with site 5A's subwatershed having the least (6.0%). Site 5A's subwatershed also has the highest percentage of agricultural area (73.3%) with site 9 having the lowest (10.6%). Site 9 also had the most wetland area (12.7%) with site 10 having the least (0.7%). As can be seen from Table 2.1 and Table 2.2, we have a gradient in terms of area and LULC distributions. Descriptions of individual sampling sites and their subwatersheds are given below:

Site 9 – Fish River at U.S. HWY. 90, Lat. 30°38'11s N, Lon.87°47'58s W: Site 9 is located where Highway 90 crosses over the Fish River in the northern-most section of the Fish River watershed. This sub-watershed covers the area between Stapleton in the north, down to Highway 90 where our site is located. The site 9 watershed is approximately 43.9 km^2 in size. The 2008 LULC characteristics are approximately the following: 11% agriculture, 6% pasture, 39% forest, 18% urban (9% connected impervious) and 26% other (shrubland, grassland, wetlands, etc.).

Site 10 – Corn Branch, downstream of culvert on County Rd. 64, Lat. 30°37'05s N, Lon.87°47'08s W: Site 10 is located on Corn Branch where County Road 64 crosses the stream to the West of the town of Loxley. The sub-watershed covers the area between the Fish River and Loxley. The site 10 watershed is approximately 5.45 km^2 in size. The 2008 LULC characteristics are approximately the following: 45% agriculture, 22% pasture, 11% forest, 21% urban (8% connected impervious) and 1% other (shrubland, grassland, wetlands, etc.).

Site 7 – Perone Branch, downstream of bridge on Hwy. 104, Lat. 30°32'44s N, Lon.87°47'18s W: Site 7 is located where Highway 104 crosses over the Perone Branch, south of Loxley and west of Silverhill. The watershed is approximately 24.8 km^2 in size. The 2008 LULC characteristics are approximately the following: 39% agriculture, 7% pasture, 22% forest, 22% urban (8% connected impervious) and 10% other (shrubland, grassland, wetlands, etc.).

Site 6 – Pensacola Branch, upstream of bridge on County Rd. 48, Lat. 30°31'26s N, Lon.87°48'44s W: Site 6 is located in the central-western part of the watershed. The site was installed upstream of County Road 48 on the Pensacola Branch. The site 6 watershed is approximately 12.7 km^2 in size. The 2008 LULC characteristics are approximately the following: 33% agriculture, 20% pasture, 20% forest, 15% urban (5% connected impervious) and 12% other (shrubland, grassland, wetlands, etc.).

Site 4 – Cowpen Creek, downstream of bridge on County Rd. 33, Lat. 30°28'59s N, Lon.87°49'07s W: Site 4 is located south and west of site 6 between the town of Fairhope and the Fish River. The site is located downstream of the County Road 33 bridge and Cowpen Creek. The site 4 watershed is approximately 30.8 km^2 in size. The 2008 LULC characteristics are approximately the following: 29% agriculture, 7% pasture, 18% forest, 36% urban (14% connected impervious) and 10% other (shrubland, grassland, wetlands, etc.).

Site B20 – Polecat Creek, upstream of bridge on County Rd. 55, Lat. 30°29'54s N, Lon.87°45'01s W: Site B20 is located in the central and eastern section of the Fish River watershed. B20 is located upstream of where County Road 55 crosses over Polecat Creek. The sub-watershed covers the area between site 7's watershed and Robertsdale and includes the city of Silverhill. The B20 watershed is approximately 42.7 km^2 in size. The 2008 LULC characteristics are approximately the following: 39% agriculture, 14% pasture, 18% forest, 19% urban (8% connected impervious) and 10% other (shrubland, grassland, wetlands, etc.).

Site 5A – Baker Branch, upstream of bridge on County Rd. 55, Lat. 30°28'34s N, Lon.87°45'03s W: Site 5A is located south of the B20 watershed and west of Summerdale. 5A was installed upstream of the bridge on County Road 55 on Baker Branch. Site 5A watershed is approximately 10.5 km^2 in size. The 2008 LULC characteristics are approximately the following: 73% agriculture, 9% pasture, 6% forest, 6% urban (3% impervious) and 6% other (shrubland, grassland, wetlands, etc.)

Site B9 – Green Branch, downstream of culvert on Danne Rd, Lat. 30°26'58s N, Lon.87°50'07s W: Site B9 is located in the southwestern portion of the Fish River watershed. B9 is located on Green Branch, downstream of the culvert on Danne Road. The B9 watershed is approximately 8.3 km^2 in size. The 2008 LULC characteristics are approximately the following: 55% agriculture, 3% pasture, 12% forest, 25% urban (11% connected impervious) and 5% other (shrubland, grassland, wetlands, etc.).

Site 3 – Turkey Branch, downstream of bridge on Hwy. 181, Lat. 30°25'19s N, Lon.87°50'37s W: Site 3 is located southwest of Site B9 where Hwy. 181 intersects Turkey Branch. The site 3 watershed is approximately 17.3 km^2 in size. The 2008 LULC characteristics are approximately the following: 67% agriculture, 8% pasture, 8% forest, 13% urban (5% connected impervious) and 4% other (shrubland, grassland, wetlands, etc.).

Site 70 (USGS) – Fish River on Hwy 104, Lat. 30°32'44s N, Lon.87°47'53s W: Site 70 (USGS) is the USGS station located on Highway 104 where the road crosses over the Fish River. This sub-watershed covers the majority of the area north of Highway 104. The site 70 (USGS) subwatershed is approximately 141.3 km^2 in size. The 2008 LULC characteristics are approximately the following: 27% agriculture, 6% pasture, 32% forest, 17% urban (7% connected impervious) and 18% other (shrubland, grassland, wetlands, etc.).

2.4 Land Use / Cover (LULC) in the Fish River watershed

LULC data were generated by GIS Spatial Analysts at Auburn University. LULC types were established for both 1995 and 2008. Individual subwatersheds have varying percentages of each LULC classification; however, the overall theme is that the Fish River watershed is impacted mainly by row-crop agriculture with some forested patches and urban development.

A Landsat TM image acquired on March 25, 2008 covering Weeks Bay was purchased from USGS Earth Resource Observation and Science (EROS) and geo-referenced to DOQQ corresponding to the GRS 1980 spheroid, NAD 83 datum and UTM projection with RMSE of less than 0.5 pixels. Unsupervised classification was then performed, producing 100 spectral clusters. Each spectral cluster was visually checked against the Landsat imagery as well as the ancillary data such as aerial photographs, existing LULC data, national wetland inventory, etc., and was labeled with the land cover type it represents. All unlabeled pixels remaining from the last step were then subjected to additional unsupervised classification, and each cluster was assigned with specific land cover type. Post refinements were performed, especially for developed areas, including commercial/transportation/industrial, high residential, medium residential and low residential by comparing the original TM images with aerial photographs of 2005 and LULC data of 2005 developed by Baldwin County as well as ground truth data, the obliviously misclassified areas were manually corrected. Nearest neighbor functions were performed on the final classification image using a 3x3 window, producing a smooth LULC image. An overall accuracy of 85.43% was achieved. (Shufen Pan, personal communication)

The imperviousness fractions of the subwatersheds are quantified using the method provided by Neitsch *et al.* (2005). This method establishes a weighted coefficient for each type of urban land use. The method provides both the estimated average total impervious area as well as the average directly connected impervious area (Table 2.3). Establishing the directly connected impervious areas helps to more accurately assess the impact that impervious surfaces can have on water quality.

Table 2.2 and Table 2.2 show that there have been significant change in LULC between 1995 and 2008; the majority of which being related to local urbanization and increasing populations of nearby towns. Agriculture has remained relatively stable between time periods across most of the subwatersheds. Agriculture also makes up for the majority of land use in most subbasins. Sod farming was defined in the agriculture LULC category as water quality output from these areas closely resemble those from other agricultural practices. Pasture land has increased marginally at most subwatersheds. Forested land has varied widely between study periods depending upon the individual subbasin in question. The majority of change that has occurred is in urbanized landscapes, particularly with regards to medium-density residential areas. Urban (residential/commercial/industrial/transportation) areas have increased by 10-20% total area (doubled in size) across the watershed. Decreases in LULC proportions exist primarily in shrubland, grassland, and wetland landscapes. Removal of these types of LULC combined with an increase in urban landscapes may lead to degradation of water quality.

Figure 2.4 shows the changes in crop types from 2008-2009. It is important to recognize that different crop types require different management practices including fertilizer application and land disturbances. Certain crops may require more or less NPK fertilizer application. Storm events following fertilizer application can result in additional nutrients entering the streams through runoff.

2.5 Storm Event Sampling

Four ISCO 3700 Portable Automated Samplers were used during this study. These samplers can collect up to 24 one-Liter samples at programmed intervals during a rain event. The ISCOs were programmed to sample during significant rainfall events and collected samples at varying time periods in order to capture a representative series of samples. The first 6 samples were set to collect every 20-minutes with the second set of samples collecting every 40-minutes. This style of sampling intended to capture more samples on the rising limb of a hydrograph. It is important to capture a greater number of samples on the rising limb as most pollutants are washed off surfaces and into streams during the beginning of large rain events. This process is referred to as the "*first flush effect*" (Figure 2.5) (Borah *et al.* 1999). By sampling at longer intervals in the second set, we attempted to capture substantial portion of the falling limbs of the hydrographs. The automated samplers were installed at four sites for the collection of storm-event samples. The sites selected were representative of all major LULC conditions. An ISCO 1640 Liquid Level Actuator was used to activate the sampler after a significant increase in stage height. The Actuator was installed several inches above where baseflow levels typically occurred. When the water level rose to the installed Actuator, an electronic pulse was sent to the ISCO sampler, enabling the start of the sampling period. Figure 2.6 shows an example of sampling during and after storm events.

Event mean concentrations were calculated for storm events where multiple samples were collected. Discharge levels were determined for that sample's specific time interval. For each sample, flow was multiplied along with concentration. These values were then summed together and divided by the sum of the total flow to determine a single event mean concentration.

$$\mathbf{EMC} = \frac{\sum_{i=1}^{N} c_i q_i}{\sum_{i=1}^{N} q_i} \qquad (1)$$

where:

EMC = Event Mean Concentration [M/L^3]

c_i = Instantaneous concentration of water quality constituent [M/L^3]

q_i = Instantaneous flow discharge [L^3/T]

N = total number of samples

ISCO storm event samples were collected at sites 7, 6, 4 and B20. Due to problems with sampler malfunctions we were only able to collect multiple automated samples for five storm events at sites 7 and 6, three automated sample events for site 4, and one automated sample event for site 5-A.

Each storm's EMC and the associated grab sample were compared to determine if any relationship may exist. A mean absolute bias was determined for each water quality constituent:

$$\mathbf{B_i} = \frac{\mathbf{G_i - EMC_i}}{\mathbf{EMC_i}} \qquad (2)$$

where:

B_i = Relative bias

G_i = Concentration of the i^{th} grab sample taken after storm event

EMC_j = Event Mean Concentration from multiple samples during storm

Mass Balance Error (MBE) was used to summarize values for each water quality constituent and is defined as

$$\mathbf{MBE} = \frac{\sum \mathbf{G_i} - \sum \mathbf{EMC_i}}{\sum \mathbf{EMC_i}}$$

2.6 Grab Sampling

At least one grab sample was collected at each site on arrival. One-Liter samples were collected in pre-washed polypropylene bottles at 0.6 depths to ensure a representative sample was collected. Samples were stored in a cooler until analysis. Grab samples, along with ISCO automated samples were analyzed within 24 hours at the Weeks Bay Reserve Laboratory for ammonium + ammonia (NH_4+NH_3), Nitrate (NO_3^-N), and Nitrite (NO_2^-). Total Phosphorus (TP) and Total Suspended Sediment (TSS) were analyzed at the School of Forestry and Wildlife Sciences Water Laboratory at Auburn University.

2.7 Flow Monitoring

Stage levels were monitored using both Level Troll pressure transducers manufactured by In-Situ Inc. and Solinst Levelogger pressure transducers. The pressure transducers were located below the stream surface in a calm section of the channel. By comparing atmospheric pressure to subsurface water pressure, the transducer determines relative gauge height. The stage was then associated with discharge measurements taken during sampling visits to determine a stage-discharge relationship. Discharge data was measured using a Marsh-McBirney, Inc. Flo-Mate Model 2000 Portable Flowmeter. The Flo-Mate measures flow using the Faraday law of electromagnetic induction. This law states that as a conductor moves through a magnetic field, a voltage is produced. The magnitude of this voltage is directly proportional to the velocity at which the conductor moves through the magnetic field. When the flow approaches the sensor from directly in front, then the direction of the flow, the magnetic field, and the sensed voltage are mutually perpendicular to each other. Hence, the voltage output will represent the velocity of the flow at the electrodes. The sensor is equipped with an electromagnetic coil that produces the magnetic field. A pair of carbon electrodes measure the voltage produced by the velocity of the conductor, which in this case is the flowing liquid. The measured voltage is processed by the electronics and output as a linear measurement of velocity (Marsh-McBirney 1990).

Flow was measured using the 0.2, 0.6, and 0.8 velocity method for stream cross-sections originally developed by the USGS (Olson and Norris, 2007). This method determines the cross-sectional area of the stream by taking flow measurements at 0.6 depths for every 10% flow increase across the channel. At locations deeper than 0.7 meters we measured flow readings at 0.8 and 0.2 depth and averaged the two readings with the 0.6 depth measurement in order to gain the most accurate result possible. (Figure 2.7)

Due to physical constraints of measuring discharge during very high flows, it was necessary to use a different method to estimate flow during peak events. The Manning's equation was used to generate estimations of flow above the highest measured values on the stage-discharge curve. The Manning's formula is defined as:

$$\mathbf{Q} = \frac{\mathbf{1}}{\mathbf{n}} * \mathbf{A} * \mathbf{R}^{\frac{\mathbf{2}}{\mathbf{3}}} * \sqrt{\mathbf{S}} \tag{3}$$

where:

Q = flow (m^3/s)

R = hydraulic radius, i.e. Area / Wetted Perimeter (m)

S = slope, estimated as bedslope (S_0)

n = Manning's roughness coefficient

A = Cross-sectional area

Each site's cross-sections were derived throughout the channel and its floodplain. Cross-sectional areas and wetted perimeters were then calculated for each 1 millimeter increment in stage measured by our installed pressure transducers. Manning's n values for all depths were derived by calculating measured discharge values and solving for n.

$$\mathbf{n = f(h)} \tag{4}$$

where:

h = depth

Once Manning's equation was applied to determine flow during peak events, these values were used for depths at which our rating curve could not accurately estimate. Each site's observed flow values consist of flow estimated values from the rating curve during low and moderate flows, while flow estimations from Manning's equation are used for high flows.

Several analytical methods were used to determine the overall hydrologic patterns within the Fish River watershed. Baseflow Index was calculated using the WHAT (Lim *et. al* 2005) model to determine the proportion of baseflow occurring during the study period. The Richards-Baker Index (RB) is used to determine a stream's flashiness, or the frequency and rapidity of short-term changes in streamflow. The method to determine RB is described in Baker *et al.* (2004).

$$\mathbf{RB} = \frac{\sum_{i=1}^{N} |Q_i - Q_{i-1}|}{\sum_{i=1}^{N} Q_i} \qquad (5)$$

where:

Q_i = average daily flow (m^3/s)

2.8 Chemical Analysis

Samples were analyzed at the Weeks Bay Reserve Laboratory for Ammonium/Ammonia (NH_4/NH_3), Nitrate (NO_3^-) and Nitrite (NO_2^-). Total Phosphorous (TP) and Total Suspended Sediment (TSS) analysis was conducted at the Auburn University Water Laboratory in the School of Forestry and Wildlife Sciences. All analysis was completed in accordance with the methods outlined in Standard Methods for the Examination of Water and Wastewater (1998).

Ammonium/ammonia (NH_4/NH_3) was analyzed using the 4500-NH_3 Phenate Method. This method generates an intensely blue compound, indophenol, which is created by the reaction of ammonia, hypochlorite, and phenol catalyzed by sodium nitroprusside. The samples were then read by a spectrophotometer at 640 nm with a light path of 1 cm. Samples were analyzed no more than 24 hours after collection due to the possibility of interference within the sample.

Nitrate (NO_3^-) was analyzed using the 4500-NO_3^- Cadmium Reduction Method. This method uses cadmium granules treated with copper sulfate packed in a glass column which reduces the sample to nitrite. The NO_2^- produced is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylediamine dihydrochloride (NADL) to form a colored dye which can be measured colorimetrically using a spectrophotometer at 543 nm with a light path of 1 cm. NO_3^- is determined by subtracting the NO_2^- values from the calculated NO_3^- values.

Nitrite (NO_2^-) determination occurred using the simple 4500-NO_2^- Colorimetric Method. This method uses a similar coupling of diazotized sulfanilimide with NADL to produce a reddish purple dye which is then measured using a spectrophotometer at 543 nm with a light path of 1 cm.

Total Phosphorous (TP) was determined using the Molybdate-blue method to determine water phosphorus (Murphy and Riley, 1962; Watanabe and Olsen, 1965). 100 ml samples were evaporated until no liquid remained. HNO_3 (Nitric acid), H_2O_2 (3% hydrogen peroxide) and HCl (Hydrochloric acid) were then added following the methods directions. The resulting solution was filtered through Whatman 42 filter paper and combined with a secondary reagent and deionized water. The sample was then measured on the spectrophotometer at 700 nm with a light path of 1 cm. The double digestion results are then compared to the standard curve to calculate total phosphorus.

Total Suspended Sediment (TSS) was determined using the 2540 Total Suspended Solids Dried at 103-105^{o}C method. A thoroughly mixed sample was filtered through a weighed standard glass-fiber filter which was then dried at 103-105^{o}C and weighed to determine an estimate of total suspended solids. The oven-drying and weighing was repeated three times to produce a reliable result.

2.9 Estimation of constituent loadings

Monthly nutrient and sediment loads were calculated using the Load Estimator program (LOADEST) (Runkel et al. 2004). LOADEST is widely utilized in estimating constituent loads in rivers and streams (Dornblaser and Striegl 2007; Eshleman *et al.* 2008; Maret *et al.* 2008). Data variables, such as time, flow, nutrient and sediment concentrations are entered into the regression model which, in turn, provides an output of estimated loads. The LOADEST model runs 10 different regressions with the given input data and uses the best fitting model to determine loading. The model output is given as Adjusted Maximum Likelihood Estimation (AMLE), Maximum Likelihood Estimation (MLE) or Least Absolute Deviation (LAD). This study used the AMLE generated output.

2.10 Trend Analysis

Kendall's Tau (Helsel and Hirsch 2002) is used to determine water quality trends in time. Kendall's Tau is used to measure the strength of a monotonic relationship between two independent values. Tau is easily computed by ordering all data pairs by the chronological order of the x (date) values. For each date (x), we have an associated load value (y). When moving from one x value to the next, we determine whether the next y value is greater than, less than, or equal to the previous y value. If there is a positive correlation, the y's will increase more often as x increases. If there is a negative correlation, the y's will decrease more often as x increases. A test statistic, S, measures this monotonic dependence:

$$\mathbf{S = P - M} \tag{6}$$

where:

P = number of positive values

M = number of negative values

Kendall's Tau correlation coefficient is then calculated:

$$\boldsymbol{\tau} = \frac{\mathbf{2S}}{\mathbf{N(N-1)}} \tag{7}$$

N = total number of values

To determine significance, the large sample approximation Z_s is calculated using the following equation:

$$\mathbf{Z}_{\mathrm{s}} = \frac{\boldsymbol{S-1}}{\sqrt{\frac{\boldsymbol{N}}{\mathbf{18}} * (\boldsymbol{N}-\mathbf{1}) * (\mathbf{2}\boldsymbol{N}+\mathbf{5})}} \tag{8}$$

The p-value is then computed from a normal distribution table.

Spearman's Rho was also used to verify the validity of Kendall's Tau test. The Spearman test is similar to Kendall's Tau, however with Spearman's Rho, differences between data values ranked further apart are given more weight (Helsel and Hirsch, 2002). Kendall's tau and Spearman Rank were both determined using Microsoft Excel.

Table 2.1. LULC percentages in study sites for 1995.

1995	9	10	7	6	4	B20	5A	B9	3	70 USGS
Subwatershed Area (km^2)	43.9	5.4	24.8	12.7	30.8	42.7	10.5	8.3	14.3	141.3
Agriculture	10.3	47.1	36.5	37.5	25.9	37.6	68.4	55.3	60.0	27.9
Pasture	5.9	16.4	6.4	18.1	7.3	12.8	8.0	7.8	8.1	5.9
Urban (total)	8.4	10.2	9.7	8.4	18.9	11.2	4.5	11.0	5.2	7.6
Low Residential	0.1	0.3	0.1	0.4	0.4	0.1	0.1	0.1	0.4	0.1
Medium Residential	4.2	6.8	6.8	7.2	10.5	6.4	3.0	7.6	4.1	4.8
High Residential	0.1	0.0	0.1	0.6	2.3	0.1	0.0	2.6	0.0	0.1
Commercial/Industrial/Trans.	4.1	3.2	2.7	0.2	5.7	4.5	1.5	0.7	0.7	2.7
Impervious (total)	5.0	5.2	4.9	3.3	10.2	6.3	2.4	5.0	2.2	4.1
Impervious (directly connected)	4.5	4.6	4.2	2.6	8.7	5.5	2.1	4.0	1.8	3.6
Forest (total)	48.2	9.2	20.7	15.6	9.5	12.0	2.2	4.5	3.6	34.0
Evergreen Forest	39.9	5.2	14.4	6.2	4.5	6.8	0.9	2.3	1.1	26.6
Deciduous Forest	0.0	0.0	0.5	0.0	0.0	0.3	0.0	0.0	0.9	0.0
Mixed Forest	8.3	3.9	5.8	9.4	4.9	4.9	1.3	2.2	1.7	7.4
Water	0.1	0.0	0.6	0.0	0.2	0.1	0.0	0.0	0.4	0.1
Bare Land	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Shrub	8.2	7.8	11.7	5.9	15.6	9.2	5.5	4.7	3.6	9.0
Grass	1.6	4.7	5.2	3.5	12.6	6.5	3.3	8.5	10.6	2.3
Wetland (total)	17.2	4.5	9.1	11.0	9.9	10.7	8.0	8.2	8.6	13.0
Forested Wetland	15.8	4.4	8.2	10.1	8.3	10.0	6.7	5.7	8.5	12.0
Shrub Wetland	0.5	0.1	0.9	0.9	1.5	0.6	1.2	2.4	0.1	0.4
Emergent Wetland	0.9	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.6

Table 2.2. LULC percentages in study sites for 2008.

2008	9	10	7	6	4	B20	5A	B9	3	70 USGS
Subwatershed Area (km^2)	43.9	5.4	24.8	12.7	30.8	42.7	10.5	8.3	14.3	141.3
Agriculture	10.6	44.8	38.9	33.4	28.9	38.6	73.3	54.9	67.1	26.6
Pasture	5.6	22.2	7.3	20.2	7.2	14.2	8.5	2.7	8.3	6.4
Urban (total)	18.0	21.1	22.4	15.1	36.2	19.4	6.0	25.1	13.2	17.2
Low Residential	1.9	1.7	3.8	1.7	4.3	2.8	0.8	3.4	0.6	2.1
Medium Residential	7.7	15.2	14.4	10.4	19.1	9.5	2.7	11.2	9.5	9.3
High Residential	0.6	0.8	0.4	0.9	6.1	0.9	0.0	4.5	0.8	0.5
Commercial/Industrial/Trans.	7.8	3.4	3.8	2.1	6.6	6.2	2.4	6.1	2.2	5.3
Impervious (total)	10.0	9.3	9.3	6.5	16.9	9.6	3.2	12.4	6.0	8.5
Impervious (directly connected)	8.9	7.7	7.9	5.4	14.1	8.4	2.8	10.5	5.0	7.4
Forest (total)	38.9	11.0	21.9	19.6	18.2	17.6	6.2	11.7	7.8	32.2
Evergreen Forest	33.4	9.5	18.5	15.9	17.0	13.9	5.6	11.5	6.8	28.2
Deciduous Forest	0.0	0.0	0.5	0.0	0.0	0.4	0.0	0.0	0.6	0.0
Mixed Forest	5.5	1.4	3.0	3.7	1.3	3.4	0.6	0.2	0.4	4.0
Water	0.1	0.0	0.6	0.3	0.4	0.3	0.2	0.1	0.1	0.3
Bare Land	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0
Shrub	12.3	0.2	1.5	0.7	1.6	0.9	0.3	1.4	0.4	5.2
Grass	1.8	0.0	1.3	3.3	3.5	2.3	3.1	2.7	0.7	1.5
Wetland (total)	12.7	0.7	6.1	7.5	3.9	6.7	2.4	1.5	2.5	10.6
Forested Wetland	9.6	0.6	5.7	7.4	3.3	6.0	1.7	1.2	2.1	8.5
Shrub Wetland	1.4	0.0	0.1	0.0	0.1	0.1	0.1	0.3	0.2	0.8
Emergent Wetland	1.8	0.1	0.4	0.0	0.5	0.7	0.6	0.0	0.1	1.3

Table 2.3. Range and average impervious fractions for different urban land types. Adapted from Neitsch *et al*. (2005).

Urban Land Type	Average Total Impervious	Range Total Impervious	Average directly connected impervious	Range directly connected impervious
Residentail-High Density *(>8 unit/acre or unit/2.5 acre)*	.60	.44 - .82	.44	.32 - .60
Residentail-Medium Density *(1-4 unit/acre or unit/2.5 acre)*	.38	.23 - .46	.30	.18 - .36
Residentail-Med/Low Density *(>0.5-1 unit/acre or unit/2.5 acre)*	.20	.14 - .26	.17	.12 - .22
Residential-Low Density *(<0.5 unit/acre or unit/2.5 acre)*	.12	.07 - .18	.10	.06 - .14
Commercial	.67	.48 - .99	.62	.44 - .92
Industrial	.84	.63 - .99	.79	.59 - .93
Transportation	.98	.88 - 1.00	.95	.85 - 1.00
Institutional	.51	.33 - .84	.47	.30 - .77

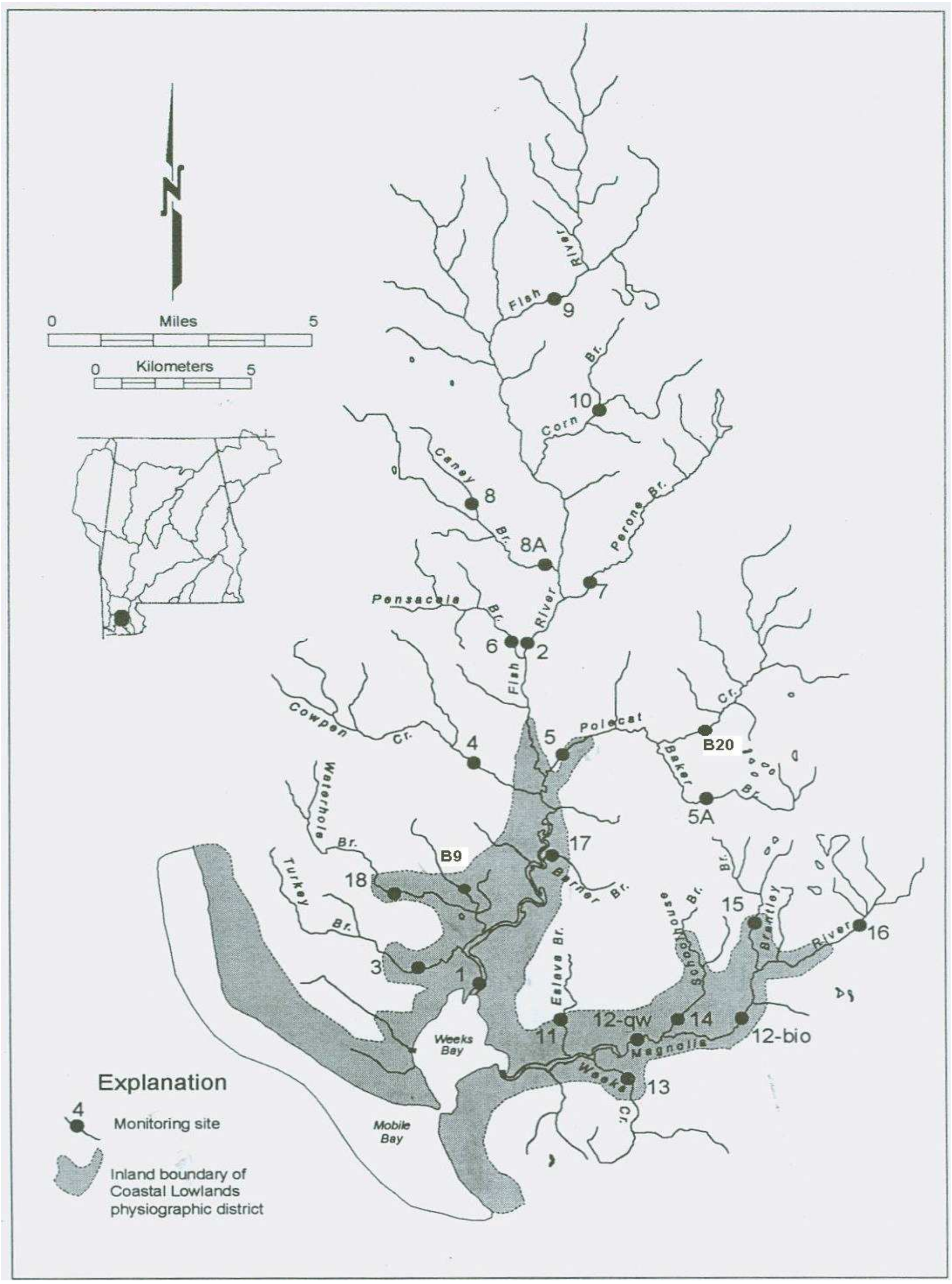


Figure 2.1. Physiographic map of the Weeks Bay watershed. Sites 9, 10, 7, 6, 4, B20 and 5A were studied during 2008-2010 and are located in the Southern Pine Hills physiographic region. Sites 3 and B9, again sampled during 2008-2010, were located in the Coastal Lowlands physiographic region. (Chandler *et al.* 1998)

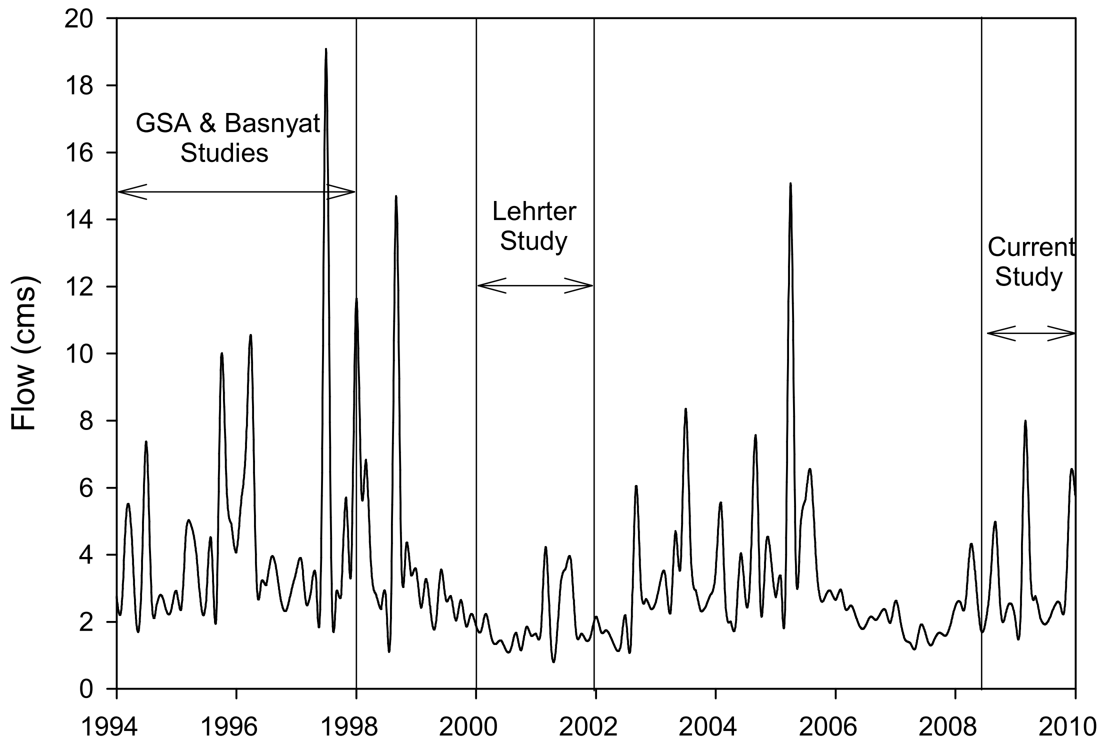


Figure 2.2. Site 70 USGS monthly flow from 1994 to 2010. Lehrter's study in 2000-2002 occurred during drought conditions.

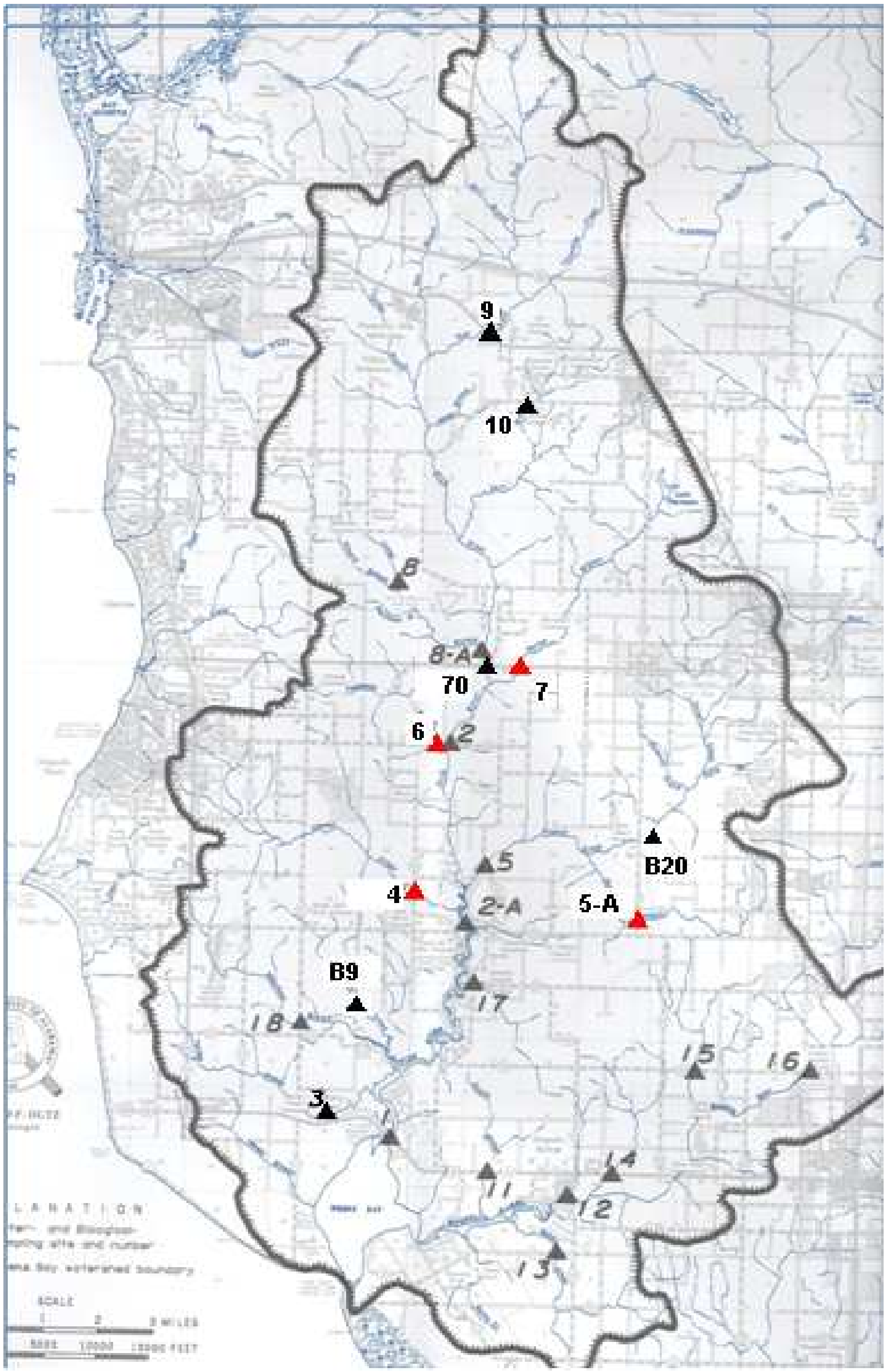


Figure 2.3. Site locations within the Weeks Bay watershed. Red triangles indicate current sites with automatic samplers; black triangles indicate sites monitored without current automated samplers; grey triangles indicate sites previously studied. (Map modified from the Geological Survey of Alabama)

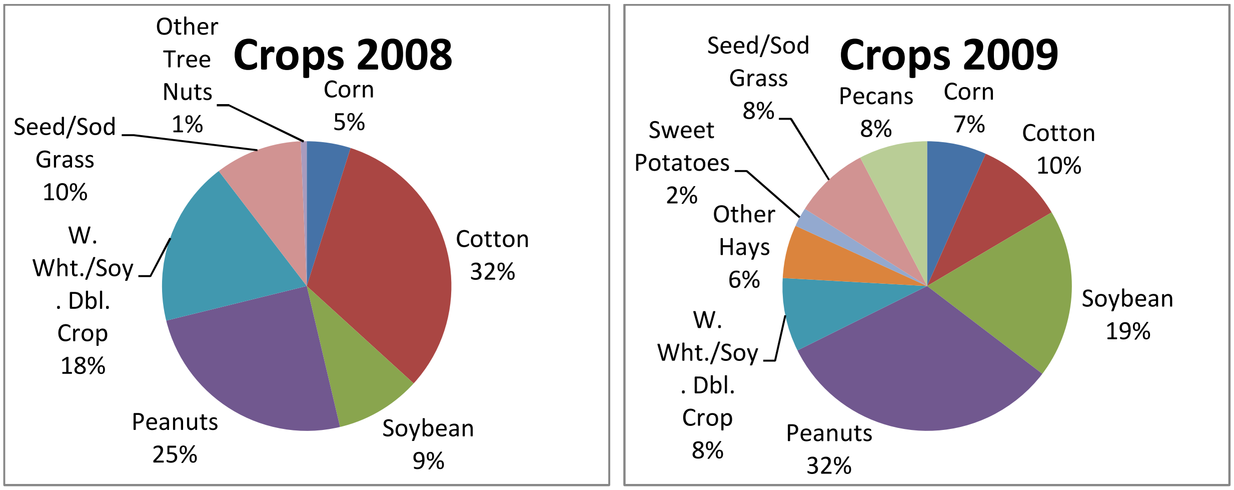


Figure 2.4. Changes in major crop types in the Fish River watershed between 2008 and 2009 (USDA 2008, USDA 2009).

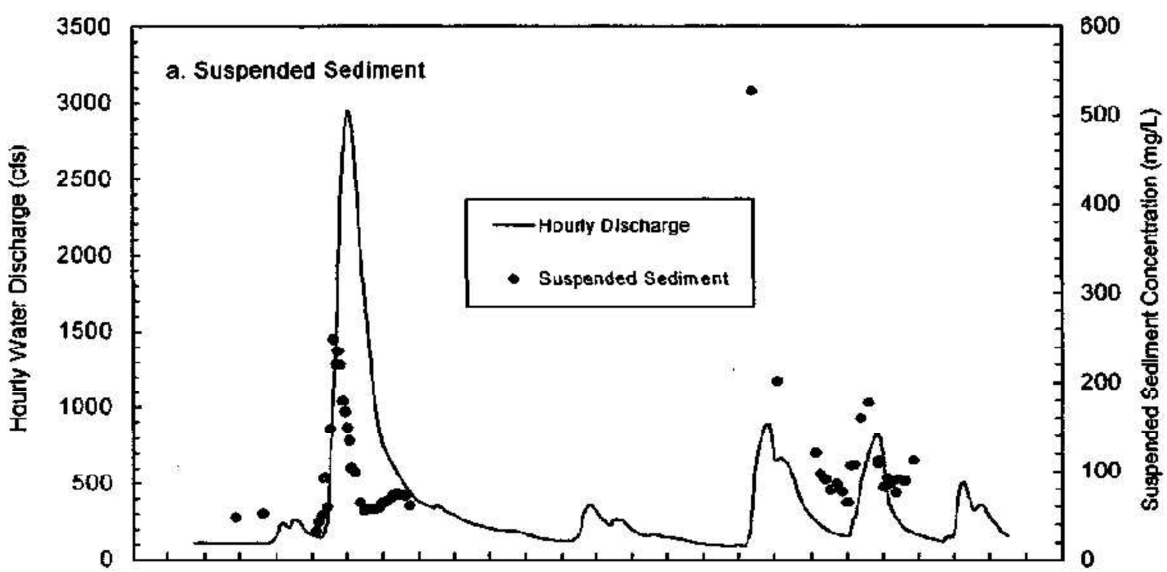


Figure 2.5. Example hydrograph showing the “first flush effect” for suspended sediment (Borah et al. 1999).

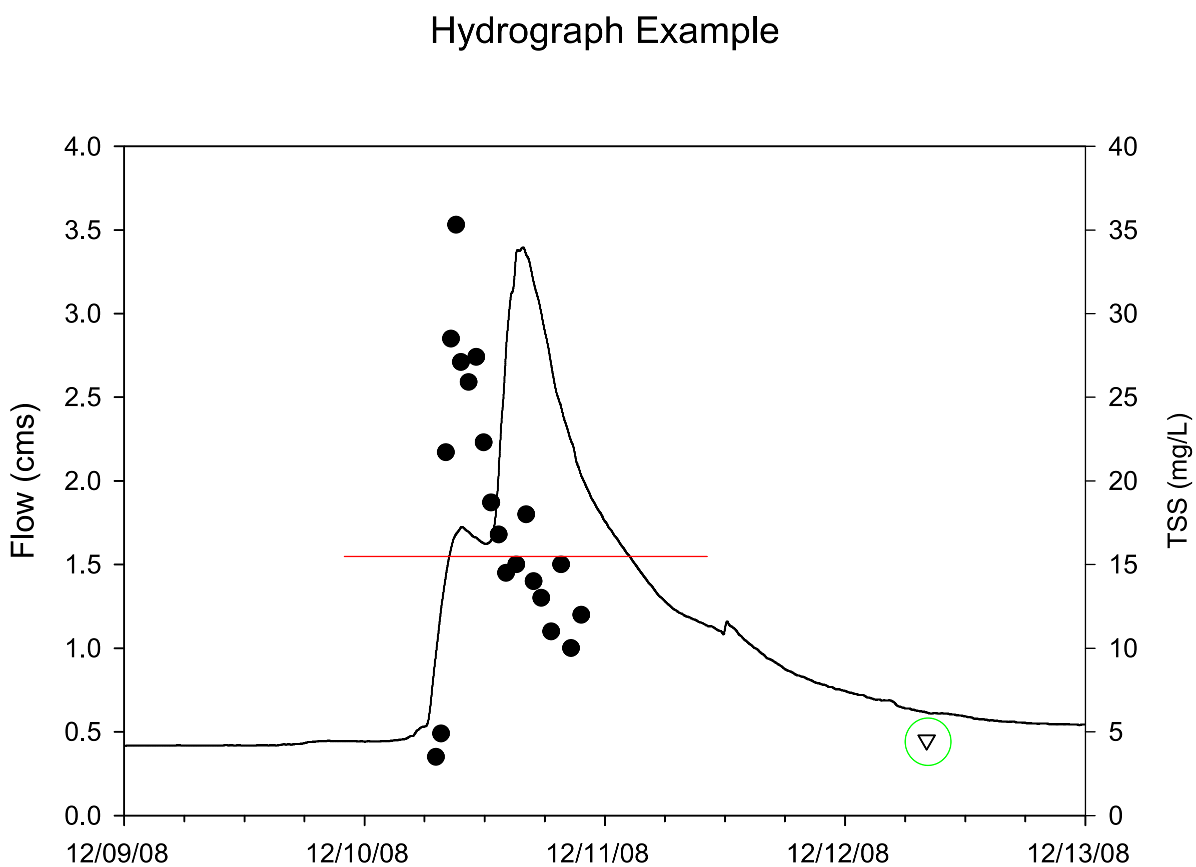


Figure 2.6. Example hydrograph showing ISCO samples of TSS (black circles) taken during event with grab sample (open triangle) taken at a later time.

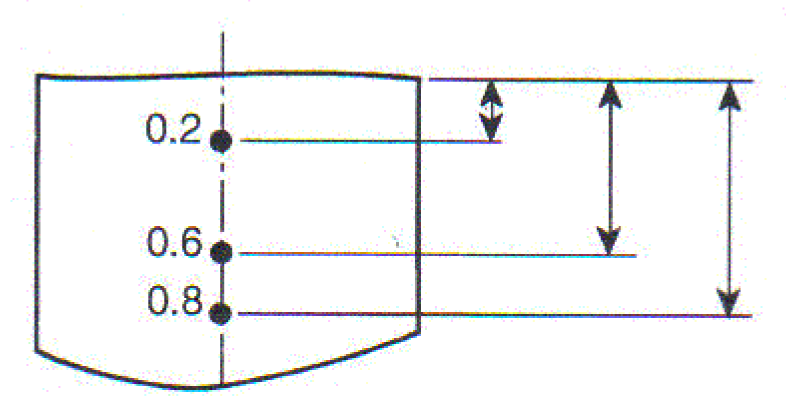


Figure 2.7. Cross-sectional area stream profile for measuring velocity along with 0.2, 0.6 and 0.8 depths. (Marsh-McBirney 1990)

3. Results

3.1 Automated vs. Grab sampling

Event Mean Concentrations (EMCs) were established for several storm events from samples taken during the 2008-2010 period for sites 7, 6, 4 and 5A. A limited number of storm events were sampled due to few available field samplers and occasional malfunctions. Grab samples were also taken and analyzed for sediment/nutrient concentrations. A relationship between the automated samples and grab samples taken at a later time was hypothesized. As expected, concentrations of TSS and TP decreased for the post-storm grab samples compared with the associated EMC. No strong relationships existed, however, between grab and storm-event samples for TSS and TP. NO_3^- and NH_4/NH_3 had a stronger correlation between the EMC and associated grab sample. It is important to note that these relationships are only based upon a few sampled storm events and more data would be needed to determine any relationships between storm-event samples and a post-storm grab sample.

Table 3.1, Table 3.2, Table 3.3, and Table 3.4 show the relationships and P_{bias} between NO_3^-, TP, TSS and $NH_4 + NH_3$ concentrations from stormflow EMCs and grab samples taken after the event. Grab sample collection time after the storm event varied from a few hours to 1 day after the associated stormflow samples.

Table 3.1 shows NO_3^- concentrations for the different collection periods for all sites. P_{bias} results show both negative and positive differences between samples; however, the variation was very small with a Mass Balance Error (MBE) of -1.84%. Figure 3.1 also shows that NO_3^-

concentrations show a strong relationship between grab samples and the EMC. Table 3.2 shows TP P_{bias} results were mostly negative, meaning grab samples were typically lower than EMCs. The MBE was approximately -42% which shows that post-storm event grab samples were typically 42% lower than EMC concentrations. While the grab results were lower than the EMCs, Figure 3.2 shows there may be a relationship between the two sampling techniques. Table 3.3 shows TSS P_{bias} results were mostly negative indicating grab samples having lower concentrations than the EMC. A MBE of -59% shows that grab samples were substantially lower than the EMCs. Like the TP results, Figure 3.3 may show a relationship between the two sampling styles. Table 3.4 shows the NH_4 + NH_3 P_{bias} results. Many of the grab samples show a close relationship to the associated EMC however, there was one sample which showed very high concentrations of NH_4 + NH_3. Figure 3.4 also shows that NH_4 + NH_3 concentrations exhibit a strong relationship between grab samples and EMCs. While it is possible that this one high concentration value may be a result of laboratory error, this sample was also processed for other water quality parameters without yielding any outlying results. It is thought that NH_4 + NH_3 levels are typically very low with the exception of occasional pockets of high concentrations in the water column. Values of zero in grab samples show that these samples had concentrations below the detection limit and MBE values should not be used to represent any association.

These results show that for different water quality constituents, one grab sample following a storm event will likely have different results compared with the EMC of that storm. NO_3^- concentrations showed the best relationship between EMC and grab samples. This is likely due to the nitrate having a more consistent relationship with flow than other water quality parameters. Grab samples of TP and TSS are severely underestimated when compared with EMCs; therefore, it is of critical importance that studies take into consideration multiple sampling techniques during storm events. Results showed that merely obtaining one grab sample event either during a storm or immediately after will not provide enough data to summarize water quality conditions for individual storms. Multiple sample collection during storm events is recommended for a more accurate picture of water quality.

P-values show that a relationship may exist between grab samples and EMC concentrations. This relationship was very strong with NO_3^- and NH_4 + NH_3 parameters. A larger dataset would be needed to accurately assess whether or not a relationship could be established for TP and TSS values.

3.2 Temporal Trends

3.2.1. Precipitation

Measured precipitation values at the USGS gauge were compared between 1994-1998 and 2008-2010 to determine any significant difference in rainfall. Kendall tau analysis showed a p-value of 0.5 meaning there is no significant difference in monthly rainfall totals between the two study periods. Establishing any precipitation differences between the study periods is important when determining trends over time. We can conclude that any significant change in flow or water quality is not directly linked to overall changes in precipitation.

3.2.2 Flow

No previous studies collected flow data at the subwatershed scale; therefore, we estimated flow using the SWAT model. SWAT is a physically based watershed scale model.

Harsh Singh, a master's student at Auburn University, produced flow estimates for the 1994-1998 and the 2008-2010 study periods at each sampling site. Comparative analysis found that SWAT-generated flow and observed flow correlated sufficiently enough at the USGS station to warrant use of SWAT model derived flow (Singh 2010).

Average monthly flow data were statistically analyzed using Kendall's tau and Spearman's Rho methods (Helsel and Hirsch 2002). Flow trend statistics show that the majority of sites showed no significant change in flow between the two study periods. Exceptions to this include sites 6 and B9 which showed significant decreases in flow ($p < 0.05$) (Table 3.5, Figure 3.5). The specific cause of this change in flow pattern is unknown; however, changes in LULC is the most likely culprit. Site B9's watershed has also seen a change in forest stand age. Young planted pines dominated the area in 1995, whereas in 2008 we have a well established 15 year old stand. This change in forest age may have had a significant effect on the hydrology of such a small watershed (Table 2.1 and Table 2.2). Established forested areas use more water than non-forested or newly planted forest areas resulting in a decrease in flow. Site 6 may have seen a shift in hydrologic pattern due to the recent local urbanization which can significantly alter the baseflow/stormflow relationship.

Richards-Baker flashiness indices for model estimated flow were determined for all sites for both the 1994-1998 and the 2008-2010 data collection periods. Multi-linear regression analysis was used to determine any relationship to LULC for both time series. We determined a significant negative relationship between flashiness and pasture land (p-value = 0.003), and a positive relationship for urban land (p-value = 0.03) and impervious surfaces (p-value = 0.02) in

2008-2010 (Table 3.6). There were no significant relationships found for the 1994-1998 study period. These results show that urbanization and an increase in impervious surfaces may cause higher flashiness in a watershed.

Baseflow Index (BFI) was calculated for each site to determine the proportion of flow passing through a channel considered to be baseflow. The baseflow separation model WHAT was used for these calculations. Multi-linear regression analysis was used to determine relationships between BFI and LULC (Table 3.6). 1994-1998 results showed marginally significant results for all parameters when impervious areas were not considered (p-values 0.05-0.06). When imperviousness was considered, no significant relationships were found. The 2008-2010 results showed negative significant relationships for pasture (p-value = 0.01) and impervious areas (p-value = 0.09). These values show that as pasture and impervious landscapes increase, the proportion of baseflow as total streamflow decreases.

3.2.3 N, P and TSS Loadings

Since loading results were generated for the 1994-1998 study period using SWAT estimated flows (Singh, 2010) for consistency; it was important to derive SWAT estimated flows for the current study period to determine loads, rather than using measured flow data. The 2008-2010 flow values were determined with the SWAT model using the 2008 LULC data (Singh 2010).

Previous data were analyzed and compared with current values to determine any possible water quality trends between the time periods. Data from the 1994-1998 period includes both GSA's and Basnyat's results. Kendall's Tau and Spearman's Rho (Helsel and Hirsch 2002) were used to determine the significance of increasing/decreasing trends over time with a significant p-value of 0.05 between the study periods (Table 3.7, Table 3.8, Table 3.9).

The majority of sites show a significant decreasing trend in NO_3^- loads over time (Figure 3.6). TP load results show a significant positive trend between study periods for most sites (Figure 3.7). TSS statistical analysis show mostly decreasing trend results with the exception of site 4 which has a significant increase in load over time (Figure 3.8).

3.2.4. Flow-adjusted loads

Water quality constituent concentration is known to be correlated to discharge (Hirsch *et al.* 1982). These relationships can vary from site to site and with different constituents. Changes in flow may mask or exaggerate perceived changes in water quality; therefore, it is important to remove the flow effect by establishing flow-adjusted loadings.

Loading values were estimated using the LOADEST model. For each site and constituent, the model produces a separate equation which it then uses to estimate load. The equation for the 2008-2010 period can be compared with the equation for the 1994-1998 collection period. This comparison filters out the effect of flow resulting in any difference between the two equations being caused by changes in LULC.

While NO_3^- results had strong relationships to flow, TP and TSS loading results from some sites did not have as close a relationship. These results are not shown in the figures as flow-adjusted loadings would not be accurately portrayed. When attempting to filter out the flow effect, it is important to determine if a relationship between flow and loading actually exists.

Figure 3.9 and Figure 3.10 show the comparisons between the 2008-2010 equations and the 1994-1998 equations. The NO_3^- results show typically higher nitrate loadings for the 1994-1998 model compared with the results using the 2008-2010 model. TSS results show decreases over time at sites 9 and 7 with increases over time for sites 6 and 4. These results are consistent with findings presented in earlier subchapters. Site 6 and 4 have had substantial increases in urbanization and these flow-adjusted figures provide further evidence that the high TSS results are due to a change in LULC conditions. It is also interesting to note that site 6 had a significant decrease in flow between the study periods (Table 3.5) but did not see a significant increase in TSS between study periods (Table 3.9). We can see, however, in Figure 3.10 that when the flow component is removed, site 6 does show an increasing trend in TSS.

3.3 Spatial Linkages

3.3.1 Water Quality

Water quality samples were collected at each site throughout the 2008-2010 study period during both baseflow and storm events. ISCO samplers were set up at sites 7, 6, 4 and 5A; however, equipment malfunctions led to a variety of sample numbers for each site (Table 3.10). Numbers also varied slightly between nutrient analyses due to either insufficient sample amount or laboratory error leading to a removed sample. Stormflow ISCO samples were translated into event mean concentrations (EMC) as described in the methods section. Water quality and discharge results are shown in Table 3.11, Table 3.12, Table 3.13, Table 3.14 and Table 3.15.

NH_4/NH_3 average and median concentrations were relatively low for all sites (< 0.1 mg/L). Occasional high concentrations did occur for individual samples during storm events at sites 7 and 6. Other samples during the same storms show a variety of NH_4/NH_3 concentrations. This indicates that conditions during storm events may be highly variable with occasional pockets of high concentrations within the water column.

NO_3^- concentrations varied from site to site with highest average and median concentrations at sites 7, B20 and 70 (USGS). The highest concentrations typically occurred at site 70 (USGS). There is a point discharge a short distance upstream from this location: the Loxley Wastewater Treatment Plant. Data were not available for the discharged treated sewage; however, McGechan *et al.* 2005 shows that secondary effluent discharges of NO_3^- typically have concentrations of approximately 17 mg/L. This is the likely cause of the higher NO_3^- concentrations at site 70 (USGS).

TP concentrations are high at all sites throughout the watershed. Results show average concentrations between 0.7-1.0 mg/L with maximum values as high as 3.3 mg/L. The highest value occurred at site 5A. This could be due to the large proportion of agriculture (73%) upstream from this site. High TP concentrations such as these may be caused by runoff from recently applied fertilizers.

TSS concentrations were relatively low for most sites (< 10 mg/L), with the exception of sites 6 and 4. These results showed high concentrations of average and median TSS indicating sedimentation is an ongoing problem at these two sites. Since the majority of the texture of the soil in the Fish River watershed consists of sand, TSS rates should remain relatively low. This is due to sand particles being larger and settling out quicker than silt and clay. Site 4 has a particularly high proportion of urbanized land (36%). Urbanization at this site, combined with substantial decreases in wetlands, grasslands and shrublands is the likely cause of increased sedimentation.

The section below provides a summary and discussion of flow and water quality data for each site followed by a section providing comparative analysis. The linkages between water quality and LULC are discussed in further detail later.

Site 9 2008-2010 Measured Water Quality and Hydrology

Median daily flow at this site was 0.44 m^3/s with the highest measured flow of 5.15 m^3/s. The highest estimated flow using Manning's equation was 31 m^3/s. Nitrate concentrations were between 0 – 0.45 mg/L and had decreasing concentrations with increasing flow for both baseflow and stormflow samples. Ammonia/Ammonium concentrations were between 0 – 0.1 mg/L with no clear relationship to flow. Total Suspended Sediment levels were between 0-15 mg/L with an average of 5.7 mg/L and a median of 5.2 mg/L and had a positive correlation to increasing flow with storm-event samples. Total Phosphorus levels had a positive insignificant relationship to flow during storm-event sampling. The mean concentration of TP was approximately 0.9 mg/L with a range of 0.002 – 1.84 mg/L.

Site 10 2008-2010 Measured Water Quality and Hydrology

Median daily flow conditions were 0.004 m^3/s with only one high flow measurement of approximately 1.7 m^3/s. The highest estimated flow over the study period was approximately 24.7 m^3/s. Nitrate concentrations were sporadic and ranged between 0.04 – 1.5 mg/L. There was no obvious relationship between nitrate and flow. Ammonia/Ammonium concentrations were between 0 – 0.26 mg/L with no clear relationship to flow. Total Suspended Sediment levels were between 6 – 51.7 mg/L and had a positive relationship to increasing flow during storm-events. Total Phosphorus levels also had a positive insignificant relationship with increasing flow during storm-event sampling. The mean concentration of TP was approximately 1.1 mg/L with a minimum of 0 mg/L and a maximum of 2.7 mg/L.

Site 7 2008-2010 Measured Water Quality and Hydrology

Median daily flow conditions were 0.48 m3/s with the highest measured flow of 2.5 m^3/s. The highest estimated flow using manning's equation was approximately 6.9 m^3/s. The mean nitrate concentration was 1.0 mg/L with a range between 0.02 – 1.7 mg/L and had decreasing concentrations with increasing flow during baseflow and storm events. Ammonia/Ammonium concentrations were between 0 – 0.8 mg/L with no clear relationship to flow. Total Suspended Sediment levels had a strong positive relationship with increasing flow during storm events. The range of TSS concentration was between 0 -182 mg/L. Total Phosphorus levels had a slight positive insignificant relationship to increasing flow during storm events. The mean concentration of TP was 0.7 mg/L with a minimum of 0 mg/L (below detection limit) and a maximum of 2.4 mg/L.

Site 6 2008-2010 Measured Water Quality and Hydrology

Median daily flow conditions were 0.15 m3/s with the highest measured flow of 1.8 m^3/s. The highest estimated flow using manning's equation was 28.5 m^3/s. The mean nitrate concentration was 0.48 mg/L with a range between 0.2 – 1.4 mg/L and had decreasing concentrations with increasing flow during storm events. Ammonia/Ammonium concentrations were between 0 – 1.2 mg/L with no clear relationship to flow. Total Suspended Sediment levels rose strongly with increasing flow during both baseflow and storm flow periods. The range of TSS concentration was between 2.7 - 314 mg/L. Total Phosphorus levels remained relatively consistent regardless of flow but did increase with increasing flow during baseflow conditions. The mean concentration of TP was 0.9 mg/L with a minimum of 0 mg/L (below detection limit) and a maximum of 2.5 mg/L.

Site 4 2008-2010 Measured Water Quality and Hydrology

Median daily flow conditions were 0.17 m3/s with the highest measured flow of 4.3 m^3/s. The highest estimated flow using manning's equation was 32.8 m^3/s. The mean nitrate concentration was 0.45 mg/L with a range between 0.1 – 1.2 mg/L and had strong decreasing concentration trends with increasing flow during storm events. Ammonia/Ammonium concentrations were between 0 – 0.17 mg/L and had a positive insignificant relationship to flow during storm events. Total Suspended Sediment levels rose steadily with increasing flow. The range was between 0 - 260 mg/L. Total Phosphorus levels had no discernable relationship with flow. The mean concentration was 0.84 mg/L with a minimum of 0 mg/L (below detection limit) and a maximum of 2.26 mg/L.

Site B20 2008-2010 Measured Water Quality and Hydrology

Median daily flow conditions were 0.6 m3/s with the highest measured flow of 8.5 m^3/s. The highest estimated flow using manning's equation was approximately 23.8 m^3/s. The mean nitrate concentration was 0.7 mg/L with a range between 0.03 – 1.5 mg/L and had decreasing concentrations with increasing flow for both baseflow and stormflow conditions.

Ammonia/Ammonium concentrations were between 0 – 0.35 mg/L with variable concentrations regardless of flow. Total Suspended Sediment concentrations increased strongly with increasing flow for stormflow periods. The range of TSS concentration was between 0-47 mg/L. Total Phosphorus levels had a positive insignificant relationship with increasing flow during storm events. The mean concentration of TP was 0.7 mg/L with a minimum of 0 mg/L (below detection limit) and a maximum of 2.4 mg/L.

Site 5A 2008-2010 Measured Water Quality and Hydrology

Median daily flow conditions were 0.09 m3/s with the highest measured flow of 0.68 m^3/s. The highest estimated flow using manning's equation was approximately 7.01 m^3/s. The mean nitrate concentration was 0.5 mg/L with a range between 0.1 – 1.2 mg/L and had decreasing concentrations with increasing flow during storm events. Ammonia/Ammonium concentrations were between 0 – 0.14 mg/L with a positive insignificant relationship to flow for both baseflow and stormflow periods. Total Suspended Sediment concentrations increased with increasing flow for all samples. The range of TSS concentration was between 0-37 mg/L. Total Phosphorus levels had a positive insignificant relationship with flow during both baseflow and stormflow conditions. The mean concentration of TP was 0.6 mg/L with a minimum of 0 mg/L (below detection limit) and a maximum of 3.3 mg/L.

Site B9 2008-2010 Measured Water Quality and Hydrology

This site's flow patterns were seasonal in nature. Median daily flow conditions were 0 m3/s with the highest measured flow of 0.67 m^3/s. The highest estimated flow using manning's equation was approximately 11.5 m^3/s. Unlike other sites, nitrate concentrations showed an increasing relationship to increasing flow during storm events. The mean nitrate concentration was 0.06 mg/L with a minimum value of 0 mg/L and a maximum of 0.33 mg/L. Ammonia/Ammonium concentrations were between 0 – 0.2 mg/L and had no strong relationship to flow. Total Suspended Sediment levels ranged between 1.9 - 30 mg/L and showed consistent concentrations regardless of flow. Total Phosphorus levels were also consistent with increasing flow. The mean concentration was approximately 0.8 mg/L with a minimum of 0.18 mg/L and a maximum of 1.6 mg/L.

Site 3 2008-2010 Measured Water Quality and Hydrology

Median daily flow conditions were 0.003 m3/s with the highest measured flow of 0.31 m^3/s. The highest estimated flow using manning's equation was approximately 45 m^3/s. Nitrate concentrations showed a slight trend with decreasing nitrate concentrations and increasing flow. The range of nitrate concentrations was between 0 – 0.54 mg/L and had a mean of 0.21 mg/L. Ammonia/Ammonium concentrations were between 0 – 0.12 mg/L with a slightly decreasing insignificant relationship with increasing flow. Total Suspended Sediment concentrations increased with increasing flow especially during stormflow periods. The range of TSS concentration was between 0.7-24.3 mg/L. Total Phosphorus levels remained consistent with increasing flow during both baseflow and stormflow events. The mean concentration of TP was 1.05 mg/L with a minimum of 0.2 mg/L and a maximum of 1.9 mg/L.

Site 70 (USGS) 2008-2010 Measured Water Quality and Hydrology

Median daily flow conditions were measured as 2.2 m^3/s with the highest USGS approximated average daily flow of 111 m^3/s. The mean nitrate concentration was 1.2 mg/L with a range between 0.2 – 2.0 mg/L and had a very strong decreasing relationship of concentration to increasing flow for all flow conditions. Ammonia/Ammonium concentrations were between 0 – 0.15 mg/L with a significant positive relationship to storm flow. Total Suspended Sediment concentrations increased with increasing flow during storm events only. The range of TSS concentration was between 2-67 mg/L. Total Phosphorus levels remained stable with increasing flow. The mean concentration of TP was approximately 0.8 mg/L with a minimum of 0.1 mg/L and a maximum of 2.0 mg/L.

Summary - 2008-2010 Measured Water Quality and Hydrology

Nitrate concentrations were highest at sites 7 and 70. The Loxley wastewater treatment plant also discharges to the Fish River upstream of site 70, increasing nitrate levels. Nitrate typically has a strong negative relationship with increasing flow, especially during storm events. This held true for all sites with the exception of site B9 which showed an increasing relationship to increasing flow during storm events. This is likely due to site B9 having very low to almost non-existent flow conditions during most of the year. Nitrate typically enters the stream in groundwater and with minimal baseflow lower nitrate concentrations would be expected. This is further established by site B9 having the least amount of nitrate concentration by an order of magnitude over other sites within the Fish River watershed.

Ammonia/ammonium concentrations were very low for all sites. Most site conditions did not have any distinct relationship to increasing flow. TSS conditions were by far the highest at sites 6 and 4. The channel conditions at these sites are incised streams with steep stream banks. Urbanization and a decrease in wetlands, grasslands and shrublands are likely the cause of sedimentation within sites 6 and 4's subwatersheds. TSS was strongly correlated to increasing flow for most sites with significant relationships regarding storm flow.

TP concentrations were typically higher than nitrate levels at most sites. Maximum concentrations of over 3 mg/L were found in samples from site 5A. This may be due to the high percentage of agricultural land upstream from this site along with recent fertilizer application to the upstream lands prior to the sampling visit. TP shows no significant relationships to flow with the exception of site 6 during baseflow at which there is an increasing trend in TP with increasing flow. This may be accounted for by the associated link regarding flow and TSS at this site.

3.3.2 LULC vs. Concentration

Direct linkages were difficult to determine relating water quality and LULC in this watershed. The lack of a strong LULC gradient at the subwatershed level combined with a small samples size is the most likely reason that relationships are not clear. The use of multi-linear regression analysis did not yield strong relationships, even at p=10%, due to the diversity of LULC types across each subwatershed.

Graphical representations of the relationships between concentrations and loads and the various LULC types can be found from Figure 3.11 to Figure 3.22. Baseflow concentrations of NH_4+NH_3 did not show clear trends regarding LULC in the figures (Figure 3.11). NH_4+NH_3 linkages to LULC are difficult to estimate due to the very low concentrations that exist within water columns. Stormflow concentration figures do show some clear trends in the agriculture and urban figures (Figure 3.12). NH_4+NH_3 concentrations steadily increase until approximately

50% agricultural LULC, from which point concentrations level out or decrease. This pattern is indicative of a threshold effect, where concentration patterns change at a certain LULC proportion.

Baseflow NO_3^- comparisons with urban and impervious LULC show an increase until approximately the 17% and 7% level, respectively. A slight decrease in concentration is shown beyond these points (Figure 3.13). Stormflow concentrations show a similar pattern for forested land cover as in baseflow. Urban and impervious land uses also show a similar spike in concentration at the same locations (Figure 3.14). This effect appears to show the impact urbanization has on water quality. After urbanization reaches a certain threshold in percent land, a balancing effect appears to mitigate some of the water quality constituents. For example, as a community continues to develop, infrastructure is put in place (i.e. water treatment plants, retention ponds) that can actually stabilize or even decrease pollutants in the local systems.

Baseflow and stormflow TP figures, in comparison with LULC, show a high variation across most of the sites. No good relationships exist regarding concentration of TP and LULC (Figure 3.15 and Figure 3.16).

Baseflow TSS results show a steadily increasing trend with regards to urban and impervious areas (Figure 3.17). Stormflow results, however, do not show strong relationships between concentration and LULC %. (Figure 3.18)

Multi-linear regression analysis was conducted with the Statistical Analysis Software (SAS version 9.0) to determine any significant linkage between water quality and various LULC types. Backwards selection at $\alpha = 0.10$ was used to find significant relationships. Average and median water quality concentrations were log-transformed to normalize the dataset. Proportions of agriculture, pasture, total urban, directly connected impervious, total forest, and forested wetland LULCs were arc-sin transformed as per Sokal and Rohlf (1995). Analysis was done separately for the different urban and impervious LULCs as these are directly linked to each other. Water quality data were separated into baseflow and stormflow values to better determine linkages during different hydrologic conditions.

Regression analysis did not find any strong relationships directly linking LULC to water quality for either the current study or the 1994-1998 studies. Future studies in the coastal region should consider locations that provide a better defined LULC gradient. This is difficult to accomplish at the watershed scale and it is believed that smaller study sites may provide more accurate linkages.

3.3.3 Load per unit area vs. LULC

Loading values were divided with subwatershed area in order to determine which subwatersheds are contributing more nutrients and sediment per unit area. NH_4+NH_3 results show an increase in load with regards to agriculture until the 40% level. Beyond this point, there is a steady decrease in total load. This may be due to lower urbanized areas in higher percentage agricultural subbasins. The pasture figure shows an increase and then flattening trend beyond the 10% mark (Figure 3.19). NO_3^- loading results show similar patterns to the concentration results regarding urban and impervious land uses (Figure 3.20). TP loading amounts showed little change in average levels of Kg/ha/day, however, variation increased substantially with increasing agriculture land use. The result is opposite when comparing load to forested land use;

variation in load decreases as forested land cover increases. A similar pattern to forested LULC is shown in forested wetland areas (Figure 3.21). TSS load comparison (Figure 3.22) to LULC type is very similar to the TP results. Relationships between LULC and water quality are difficult to quantify when subwatersheds have a broad mix of land use.

Comparisons of both concentration and loads to LULC type did not yield many clear relationships to increasing land use/cover. This is attributed to a lack of LULC gradients across the selected subwatersheds. Each land use type affects water quality in different ways before arriving in a water body. Planners should take this into consideration when developing management strategies intended to limit the addition of pollutants into the Fish River system.

Site 6 contributes the bulk of TSS load into the system per area. Sites B9 and 3 remain the smallest contributors for the majority of the sampling period (Figure 3.23). Sites 7 and 70 (USGS) are contributing the most amount of nitrate into the system. Sites B9 and 3 are contributing the least amount (Figure 3.24). Figure 3.25 shows that sites 6, B20 and 7 contribute the most ammonium/ammonia per area load. B9 and 3 are contributing the least amount of ammonium/ammonia per area into the system. Several sites contribute the majority of TP load per area into the watershed system; however, B9 and 3 are consistently the lowest contributors of nutrients and sediment (Figure 3.26).

A seasonality pattern appears in the loading results. Nutrient and sediment levels are peaking in early spring while typically declining during late summer months. These patterns often reflect the precipitation amounts for different times of year; however, agricultural management practices may also be impacting loads entering the system. Fertilizing crops, ploughing fields, and many other practices are often conducted at the start of the main growing season (early spring). Spring frontal systems can often be forecast several days ahead of time and should be taken into account before certain practices are applied.

Table 3.1. NO_3^- concentrations of stormflow (SF) samples against grab samples with variation between sets.

Site	SF Date/Time	SF (mg/L)	Grab Date/Time	Grab (mg/L)	P_{bias}
7	11/29/08 17:32 - 22:12	1.154	12/1/08 10:45	1.063	-8%
7	12/10/2008 05:41 - 13:01	0.784	12/11/08 13:20	0.625	-20%
7	3/16/2009 09:24 - 11:24	0.255	3/16/09 13:20	0.235	-8%
7	7/23/2009 9:08 - 15:28	0.911	7/23/09 17:37	1.051	15%
6	11/29/2008 18:23 - 11/30/08 07:03	0.473	12/1/08 11:20	0.450	-5%
6	12/10/2008 06:37 - 15:37	0.495	12/11/08 12:29	0.574	16%
6	2/13/2009 18:57- 2/14/08 08:57	0.415	2/15/09 16:40	0.480	15%
6	3/16/2009 02:42 - 12:42	0.236	3/16/09 13:45	0.212	-10%
4	11/29/2008 19:41 - 11:30 03:01	0.680	12/1/08 12:40	0.600	-12%
4	12/10/2008 09:58 - 12/10/08 17:18	0.311	12/11/08 10:25	0.360	16%
4	3/16/2009 03:14 - 13:04	0.108	3/16/09 14:30	0.120	11%
5A	11/28/2008 16:42 - 11/29/08 02:02	0.447	12/1/08 14:15	0.384	-14%
	avg	**0.522**	**avg**	**0.513**	
				mbe	-1.84%

Table 3.2. TP concentrations of stormflow (SF) samples against grab samples with variation between sets.

Site	SF Date/Time	SF (mg/L)	Grab Date/Time	Grab (mg/L)	P_{bias}
7	11/29/08 17:32 - 22:12	0.448	12/1/08 10:45	0.420	-6%
7	12/10/2008 05:41 - 13:01	0.479	12/11/08 13:20	0.483	1%
7	3/16/2009 09:24 - 11:24	1.843	3/16/09 13:20	0.440	-76%
7	7/23/2009 9:08 - 15:28	1.631	7/23/09 17:37	1.515	-7%
6	11/29/2008 18:23 - 11/30/08 07:03	1.261	12/1/08 11:20	0.199	-84%
6	12/10/2008 06:37 - 15:37	0.708	12/11/08 12:29	0.557	-21%
6	2/13/2009 18:57- 2/14/08 08:57	0.616	2/15/09 16:40	0.548	-11%
6	3/16/2009 02:42 - 12:42	2.118	3/16/09 13:45	1.206	-43%
4	11/29/2008 19:41 - 11:30 03:01	0.562	12/1/08 12:40	0.312	-45%
4	12/10/2008 09:58 - 12/10/08 17:18	0.513	12/11/08 10:25	0.309	-40%
4	3/16/2009 03:14 - 13:04	1.572	3/16/09 14:30	0.613	-61%
5A	11/28/2008 16:42 - 11/29/08 02:02	0.383	12/1/08 14:15	0.475	24%
	avg	**1.011**	**avg**	**0.590**	
				mbe	-41.67%

Table 3.3. TSS concentrations of stormflow (SF) samples against grab samples with variation between sets.

Site	SF Date/Time	SF (mg/L)	Grab Date/Time	Grab (mg/L)	P_{bias}
7	11/29/08 17:32 - 22:12	7.0	12/1/08 10:45	3.3	-53%
7	12/10/2008 05:41 - 13:01	82.3	12/11/08 13:20	20.4	-75%
7	3/16/2009 09:24 - 11:24	69.1	3/16/09 13:20	76.3	10%
7	7/23/2009 9:08 - 15:28	34.9	7/23/09 17:37	17.9	-49%
6	11/29/2008 18:23 - 11/30/08 07:03	72.3	12/1/08 11:20	9.3	-87%
6	12/10/2008 06:37 - 15:37	163.7	12/11/08 12:29	28.4	-83%
6	2/13/2009 18:57- 2/14/08 08:57	197.6	2/15/09 16:40	31.9	-84%
6	3/16/2009 02:42 - 12:42	168.2	3/16/09 13:45	119.0	-29%
4	11/29/2008 19:41 - 11:30 03:01	12.6	12/1/08 12:40	4.2	-67%
4	12/10/2008 09:58 - 12/10/08 17:18	88.4	12/11/08 10:25	24.6	-72%
4	3/16/2009 03:14 - 13:04	113.9	3/16/09 14:30	78.2	-31%
5A	11/28/2008 16:42 - 11/29/08 02:02	3.3	12/1/08 14:15	2.7	-18%
	avg	**84.4**	**avg**	**34.7**	
				mbe	-58.93%

Table 3.4. $NH_4 + NH_3$ concentrations of stormflow (SF) samples against grab samples with variation between sets.

Site	SF Date/Time	SF (mg/L)	Grab Date/Time	Grab (mg/L)	P_{bias}
7	11/29/08 17:32 - 22:12	0.001	12/1/08 10:45	0.000	-100%
7	12/10/2008 05:41 - 13:01	0.015	12/11/08 13:20	0.022	43%
7	3/16/2009 09:24 - 11:24	0.033	3/16/09 13:20	0.039	18%
7	7/23/2009 9:08 - 15:28	0.056	7/23/09 17:37	0.053	-6%
6	11/29/2008 18:23 - 11/30/08 07:03	0.001	12/1/08 11:20	0.008	640%
6	12/10/2008 06:37 - 15:37	0.020	12/11/08 12:29	0.020	-1%
6	2/13/2009 18:57- 2/14/08 08:57	0.118	2/15/09 16:40	0.627	430%
6	3/16/2009 02:42 - 12:42	0.030	3/16/09 13:45	0.049	66%
4	11/29/2008 19:41 - 11:30 03:01	0.008	12/1/08 12:40	0.000	-100%
4	12/10/2008 09:58 - 12/10/08 17:18	0.022	12/11/08 10:25	0.020	-12%
4	3/16/2009 03:14 - 13:04	0.030	3/16/09 14:30	0.033	11%
5A	11/28/2008 16:42 - 11/29/08 02:02	0.011	12/1/08 14:15	0.000	-102%
	avg	**0.029**	**avg**	**0.072**	
				mbe	152.13%

Table 3.5. Flow trend values for each sampling site between 1994-1998 and 2008-2010 study periods: Kendall's Tau, Spearman's Rho and p-values ($p < 0.05$ in bold).

FLOW	Kendall's Tau	p-value	Spearman rho	p-value
9	-0.01	0.846	-0.02	0.832
10	0.08	0.287	0.13	0.271
7	-0.08	0.275	-0.14	0.228
6	**-0.15**	**0.047**	**-0.23**	**0.039**
4	0.08	0.312	0.12	0.303
B20	-0.03	0.770	-0.05	0.735
5A	-0.03	0.706	-0.04	0.752
B9	**-0.25**	**0.002**	**-0.36**	**0.001**
3	0.05	0.482	0.08	0.465
70 USGS	-0.07	0.363	-0.10	0.362

Table 3.6. Richards-Baker (RBI) and Baseflow Index (BFI) multi-linear regression results for 1994-1998 and 2008-2010 data.

	Ag	Past	Urb	For	Imp	Wetf	grass	shrub	r^2	Equation	p-value
RBI 94-98	.	.	.	.	x	.	.	.	.	.	.
RBI 94-98	.	.	x	.	.	.	.	.	.	.	.
RBI 08-10	.	0.00	0.03	.	x	.	.	.	0.77	-0.037 + 0.0249 past + 0.0122urb	0.01
RBI 08-10	.	0.00	x	.	0.02	.	.	.	0.81	-0.093 + 0.0272past + 0.0346imp	0.00
BFI 94-98	0.06	0.06	0.06	0.06	x	0.06	0.06	0.05	0.95	80.9 -0.807ag-.802pas-.745urb-.811for-.773wet-.820grs-.884shr	0.16
BFI 94-98	.	.	x	.	.	.	.	.	.	.	.
BFI 08-10	.	0.04	.	.	x	.	.	.	0.44	0.766 - 0.0114past	0.04
BFI 08-10	.	0.01	x	.	0.09	.	.	.	0.64	0.920 - 0.0137past - 0.0168imp	0.03

Table 3.7. NO_3^- trend values for each sampling site between 1994-1998 and 2008-2010 study periods: Kendall's Tau, Spearman's Rho and p-values ($p < 0.05$ in bold).

NO_3^-	Kendall's Tau	p-value	Spearman rho	p-value
9	-0.02	0.806	-0.31	0.760
10	0.05	0.501	0.07	0.525
7	**-0.25**	**0.001**	**-0.40**	**0.000**
6	**-0.18**	**0.019**	**-0.31**	**0.007**
4	**-0.16**	**0.041**	**-0.26**	**0.020**
B20	**-0.47**	**<0.0001**	**-0.72**	**<0.0001**
5A	**-0.34**	**<0.0001**	**-0.49**	**<0.0001**
B9	-0.10	0.368	-0.13	0.413
3	0.04	0.599	0.05	0.635

Table 3.8. TP trend values for each sampling site between 1994-1998 and 2008-2010 study periods: Kendall's Tau, Spearman's Rho and p-values ($p < 0.05$ in bold).

TP	Kendall's Tau	p-value	Spearman rho	p-value
9	**0.37**	**<0.0001**	**0.55**	**<0.0001**
10	**0.42**	**<0.0001**	**0.59**	**<0.0001**
7	**0.47**	**<0.0001**	**0.66**	**<0.0001**
6	**0.30**	**0.000**	**0.47**	**<0.0001**
4	0.11	0.156	0.15	0.196
B20	.	.	.	.
5A	**0.43**	**<0.0001**	**0.61**	**<0.0001**
B9	.	.	.	.
3	**0.48**	**<0.0001**	**0.66**	**<0.0001**

Table 3.9. TSS trend values for each sampling site between 1994-1998 and 2008-2010 study periods: Kendall's Tau, Spearman's Rho and p-values ($p < 0.05$ in bold).

TSS	Kendall's Tau	p-value	Spearman rho	p-value
9	**-0.25**	**0.001**	**-0.39**	**0.000**
10	**-0.30**	**0.000**	**-0.47**	**<0.0001**
7	-0.14	0.076	-0.19	0.097
6	-0.02	0.750	0.00	0.990
4	**0.16**	**0.035**	**0.24**	**0.035**
B20	-0.08	0.429	-0.13	0.409
5A	**-0.19**	**0.021**	**-0.27**	**0.030**
B9	0.01	0.91	-0.01	0.959
3	**-0.36**	**<0.0001**	**-0.32**	**0.004**

Table 3.10. Sample counts for each site for 2008-2010 study. Baseflow (x) and stormflow (y) samples (x,y).

Site	NH_4/NH_3	NO_3^-	TP	TSS
9	9,10	9,10	8,10	7,10
10	4,7	4,7	4,8	4,8
7	11,16	11,16	9,14	9,14
6	9,17	9,17	7,17	7,17
4	9,12	9,12	8,12	8,12
B20	9,11	9,11	8,12	8,12
5A	10,10	9,10	9,11	9,11
B9	4,6	4,6	4,7	4,7
3	7,7	8,7	7,8	8,8
70 USGS	12,7	12,7	11,7	9,7

Table 3.11. Discharge values (m^3/day/ha) for each site 2008-2010.

Site	Mean	Median	Minimum	Maximum
9	12.98	8.66	5.90	609.89
10	6.35	0.63	0.63	3910.55
7	20.22	16.73	12.20	240.21
6	18.34	10.19	5.43	1937.28
4	12.08	4.77	1.40	922.61
B20	18.21	11.94	0.40	481.55
5A	12.34	7.40	0.00	576.63
B9	6.22	0.00	0.00	1192.69
3	9.15	0.18	0.06	2725.51
70 USGS	20.18	13.70	9.17	678.89

Table 3.12. NH_4/NH_3 concentrations (mg/L) for each site 2008-2010.

Site	Mean	Median	Minimum	Maximum
9	0.029	0.012	0.000	0.103
10	0.086	0.073	0.000	0.263
7	0.068	0.029	0.000	0.825
6	0.070	0.028	0.000	1.223
4	0.024	0.025	0.000	0.165
B20	0.053	0.018	0.000	0.345
5A	0.032	0.003	0.000	0.142
B9	0.049	0.037	0.000	0.183
3	0.047	0.046	0.000	0.118
70 USGS	0.032	0.011	0.000	0.153

Table 3.13. NO_3^- concentrations (mg/L) for each site 2008-2010.

Site	Mean	Median	Minimum	Maximum
9	0.288	0.275	0.000	0.449
10	0.395	0.455	0.036	1.531
7	1.010	1.077	0.016	1.662
6	0.476	0.470	0.170	1.360
4	0.446	0.373	0.068	1.192
B20	0.709	0.695	0.032	1.453
5A	0.460	0.444	0.013	1.199
B9	0.064	0.031	0.000	0.334
3	0.210	0.187	0.000	0.535
70 USGS	1.195	1.199	0.169	2.034

Table 3.14. TP concentrations (mg/L) for each site 2008-2010.

Site	Mean	Median	Minimum	Maximum
9	0.860	1.049	0.002	1.838
10	1.050	0.728	0.000	2.674
7	0.696	0.506	0.000	2.375
6	0.921	0.706	0.000	2.476
4	0.843	0.785	0.000	2.255
B20	0.732	0.637	0.000	2.370
5A	0.798	0.583	0.000	3.289
B9	0.782	0.677	0.181	1.618
3	0.861	0.786	0.155	1.894
70 USGS	0.823	0.672	0.099	2.043

Table 3.15. TSS concentrations (mg/L) for each site 2008-2010.

Site	Mean	Median	Minimum	Maximum
9	5.7	5.2	0.0	15.2
10	17.7	14.5	6.7	51.7
7	26.6	9.6	0.0	181.9
6	122.0	111.1	2.7	313.8
4	65.7	65.0	0.0	260.3
B20	9.1	5.9	0.0	47.2
5A	6.0	3.9	0.0	37.0
B9	11.6	9.7	1.9	30.0
3	8.7	9.2	0.7	24.3
70 USGS	18.1	9.8	2.0	67.0

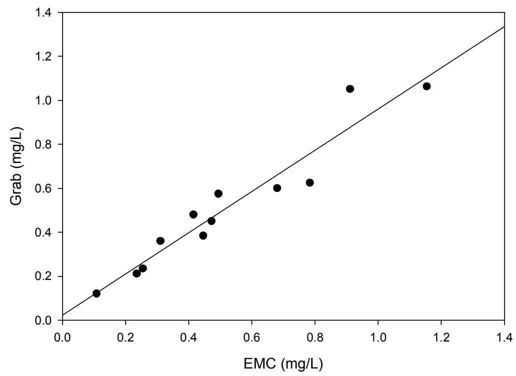


Figure 3.1. NO_3^- EMCs plotted against grab sample concentrations. P-value <0.0001.

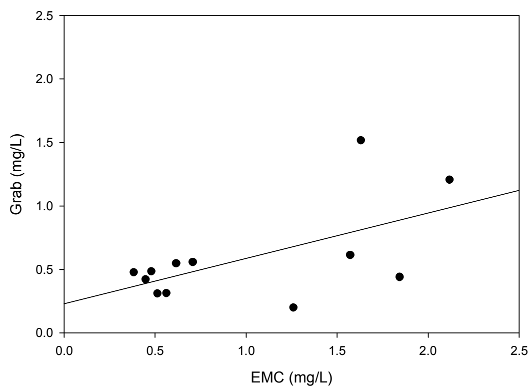


Figure 3.2. TP EMCs plotted against grab sample concentrations. P-value = 0.0452.

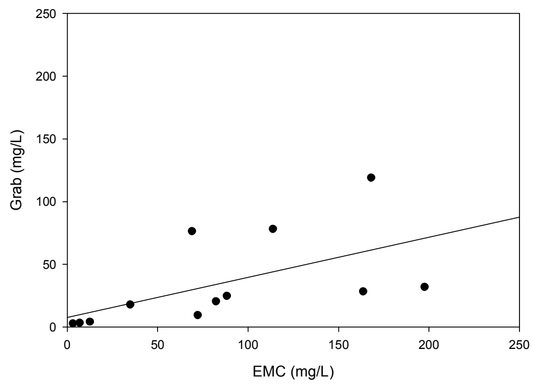


Figure 3.3. TSS EMCs plotted against grab sample concentrations. P-value = 0.0523.

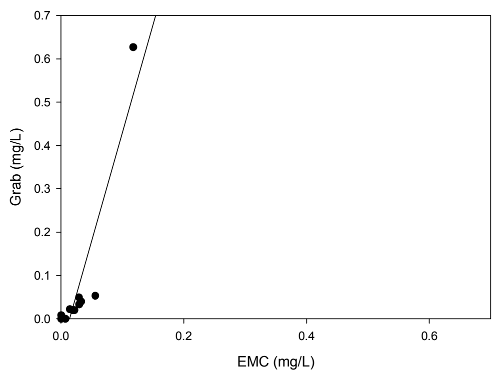


Figure 3.4. $NH_3 + NH_4$ EMCs plotted against grab sample concentrations. P-value <0.0001.

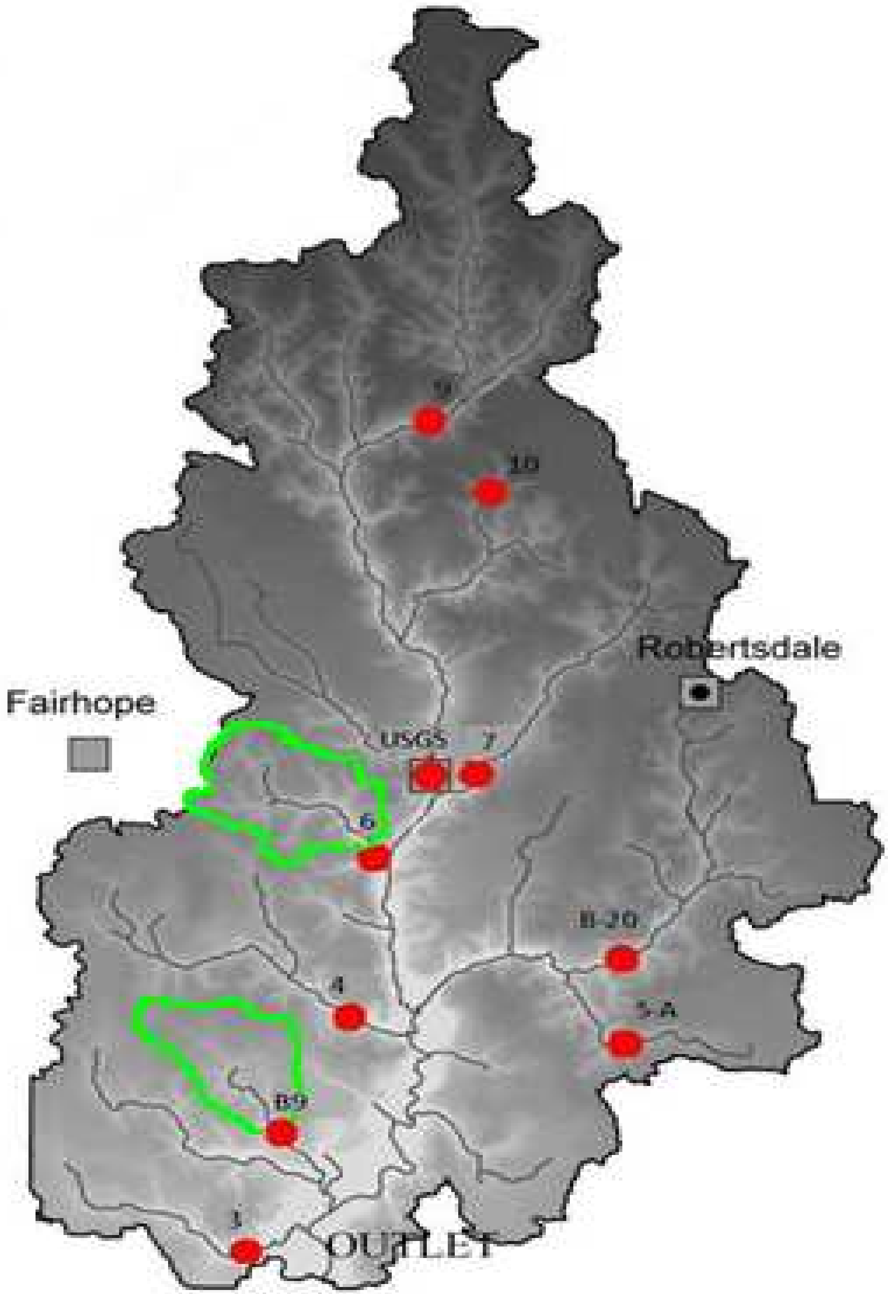


Figure 3.5. Significant decreases in flow at subwatershed level indicated by green. Site locations in red.

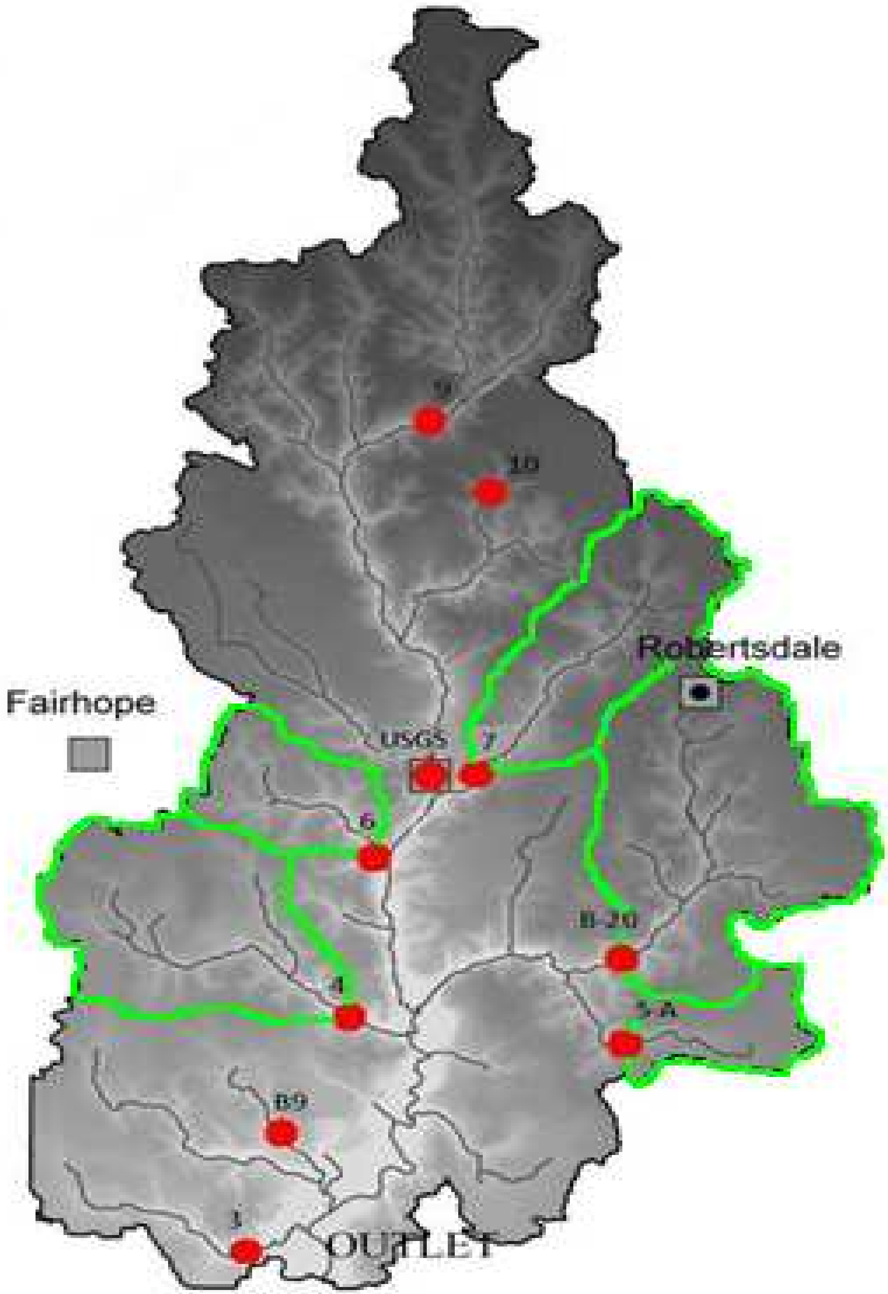


Figure 3.6. Significant decreases in nitrate at subwatershed level indicated by green. Site locations in red.

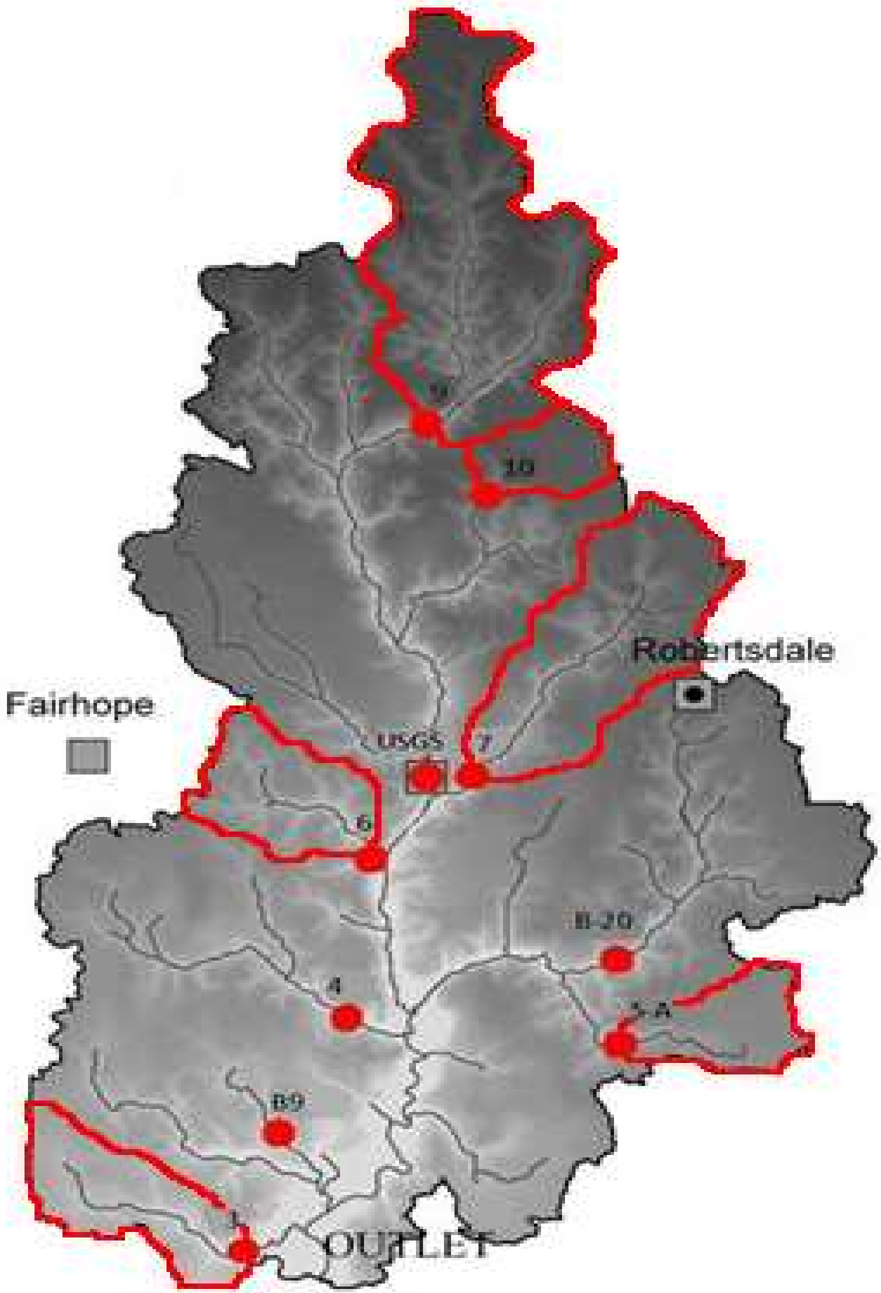


Figure 3.7. Significant increases in TP at subwatershed level indicated by red.

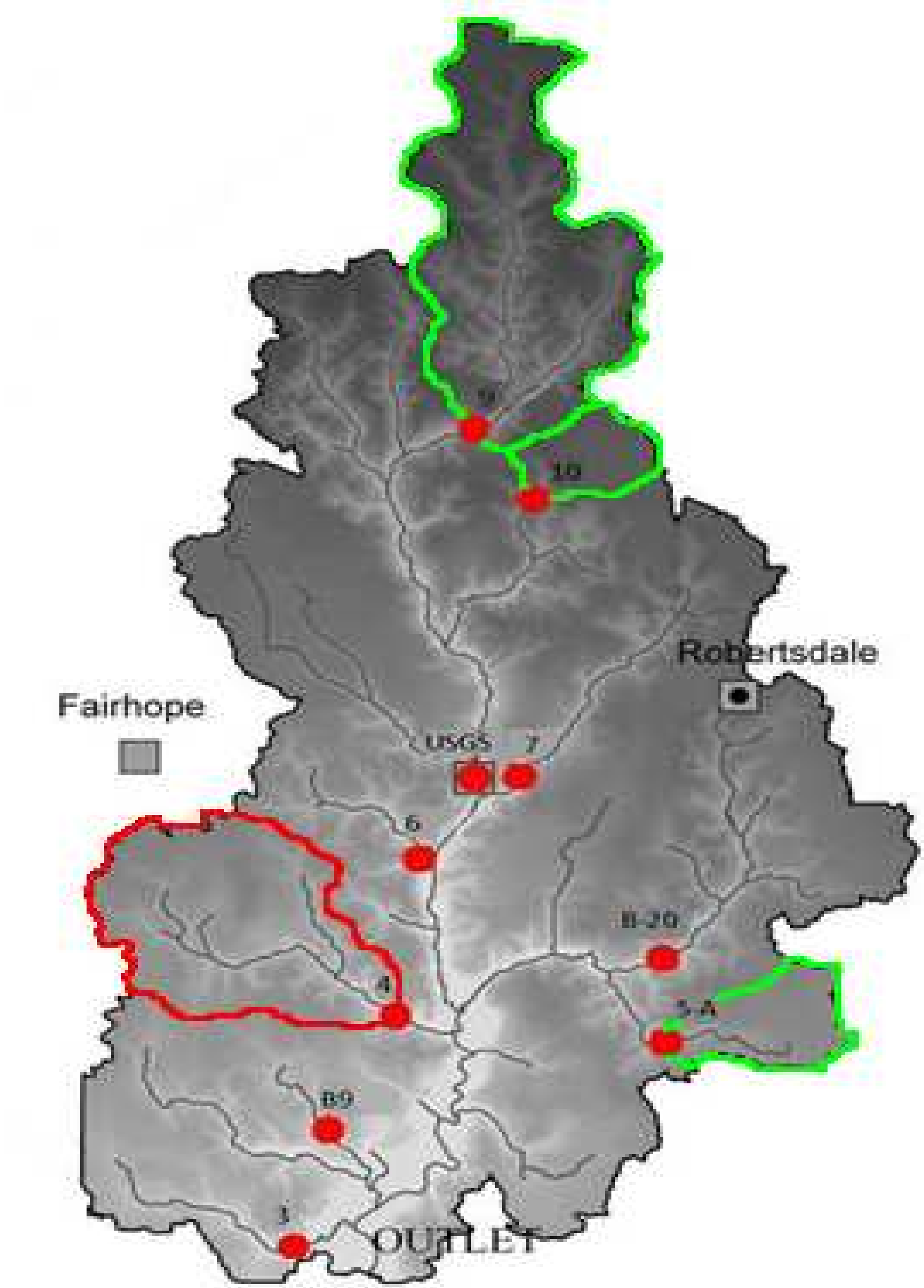


Figure 3.8. Significant decreases in TSS at subwatershed level indicated by green. Significant increases over time indicated by red.

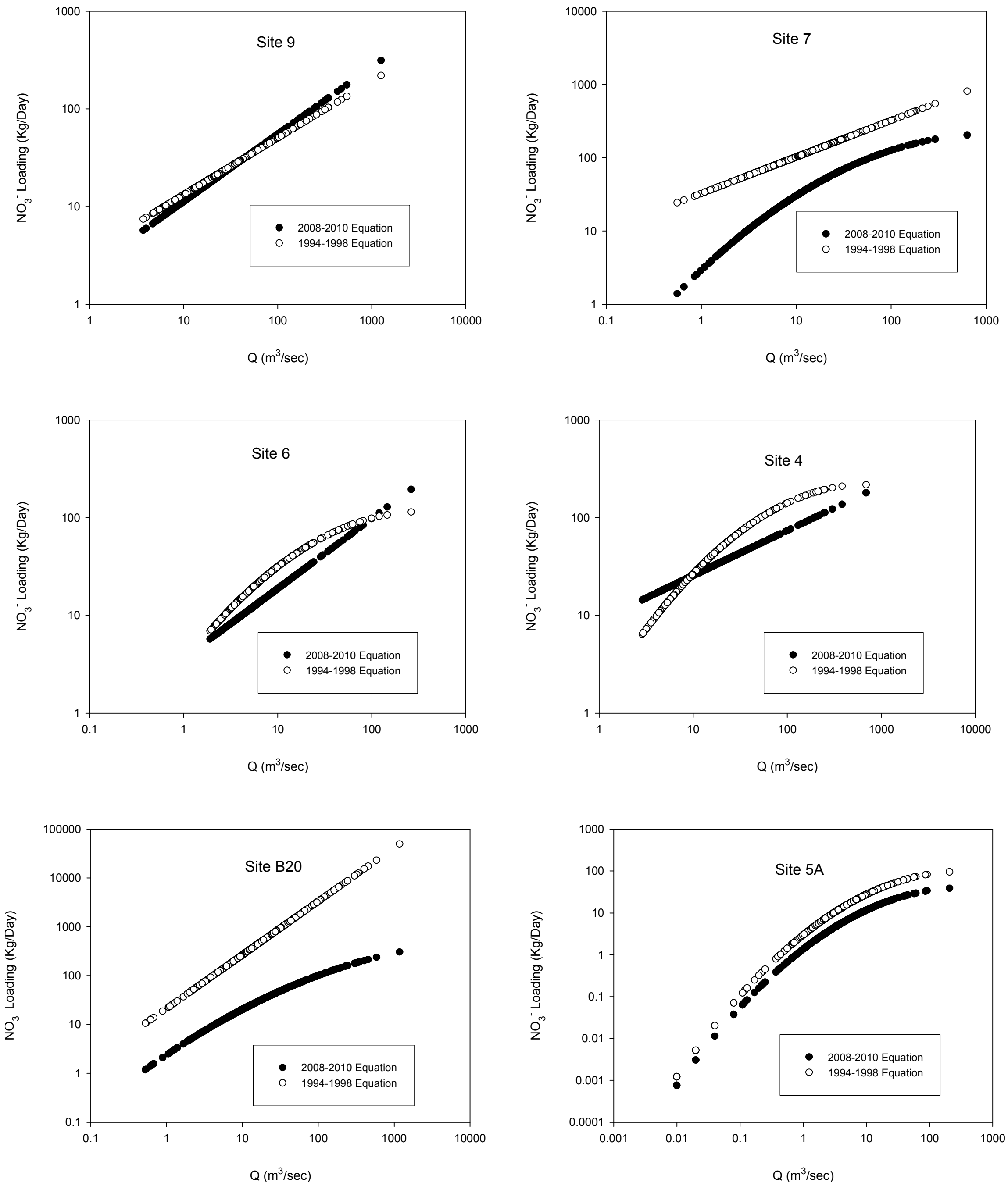


Figure 3.9. Flow-adjusted NO_3^- data for 2008-2010 showing differences between using model equation from the two study periods.

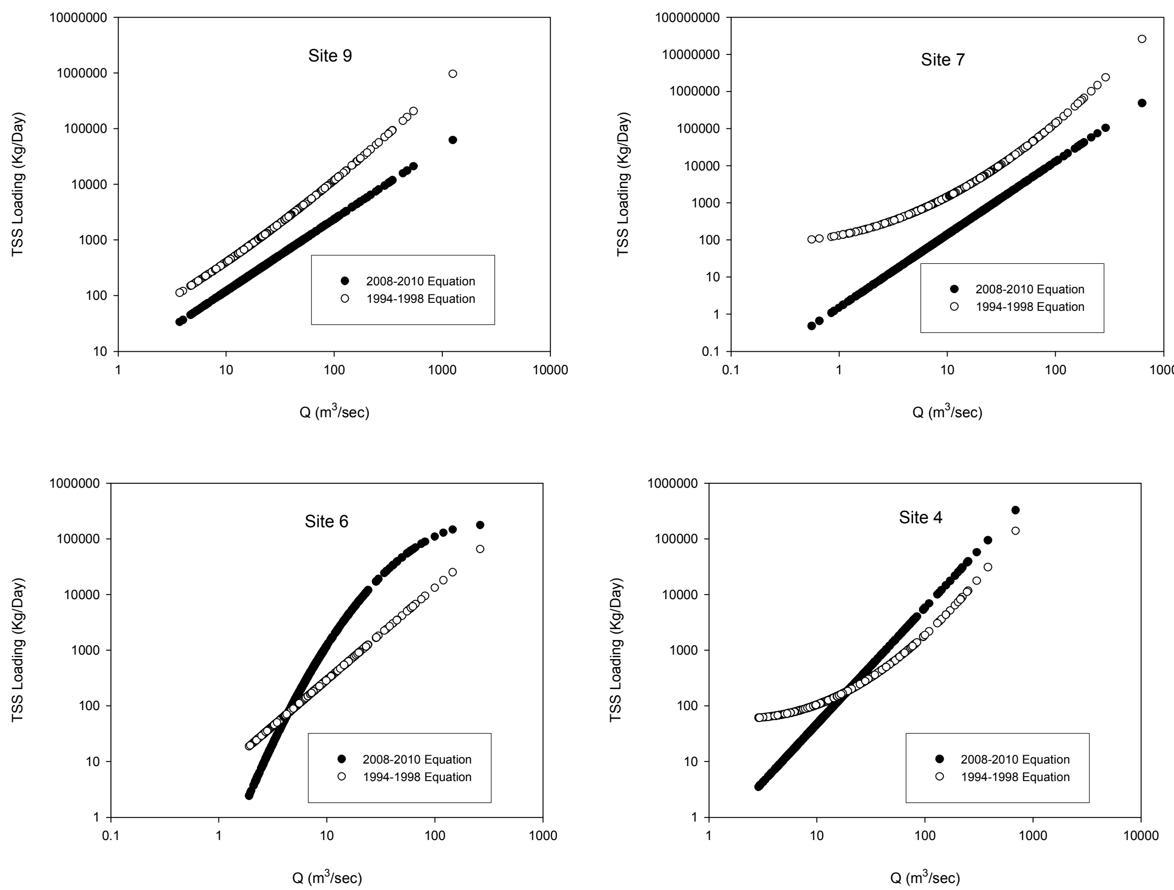


Figure 3.10. Flow-adjusted TSS data for 2008-2010 showing differences between using model equation from the two study periods.

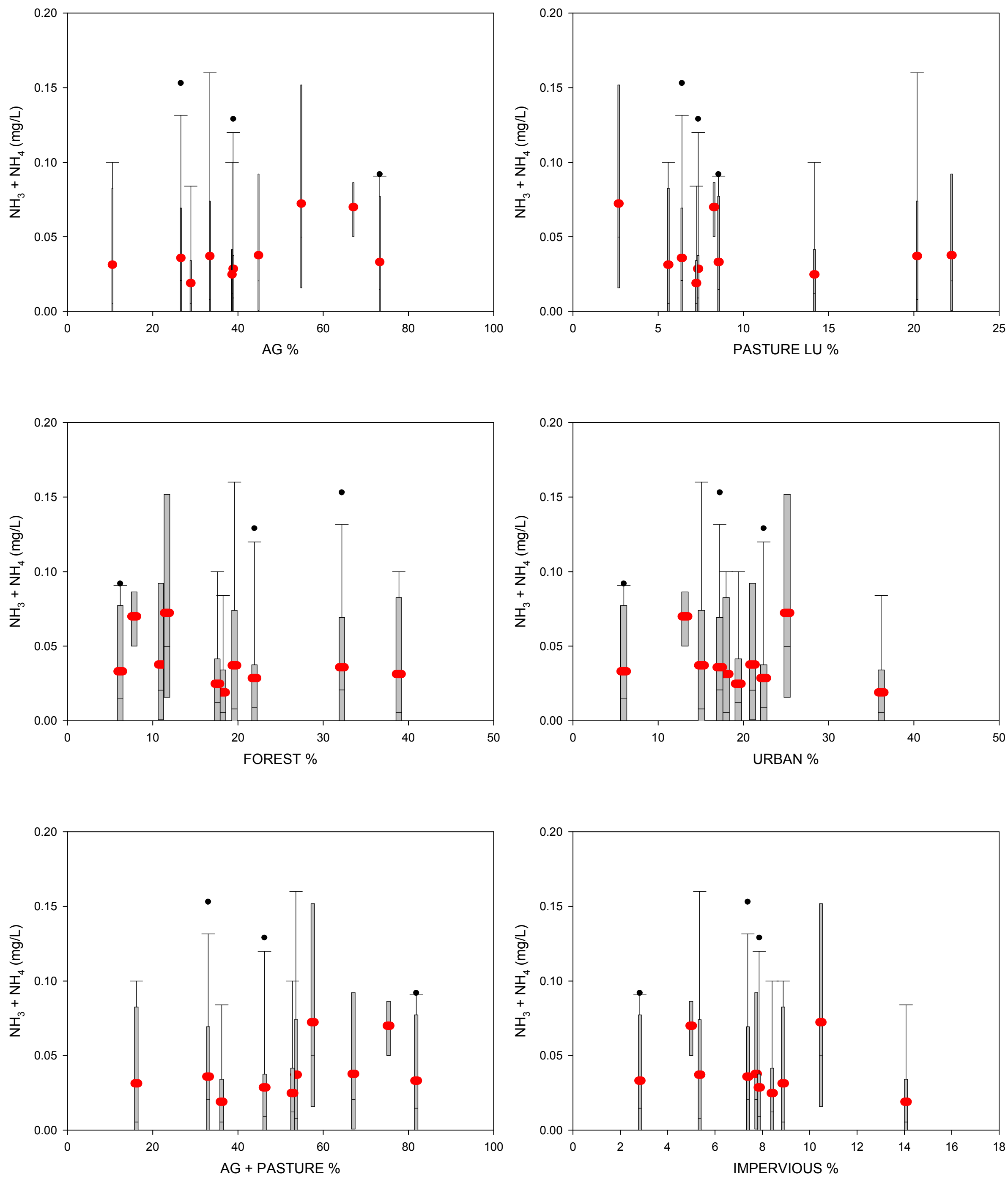


Figure 3.11. Baseflow $NH_3 + NH_4$ concentrations plotted against LULC fractions.

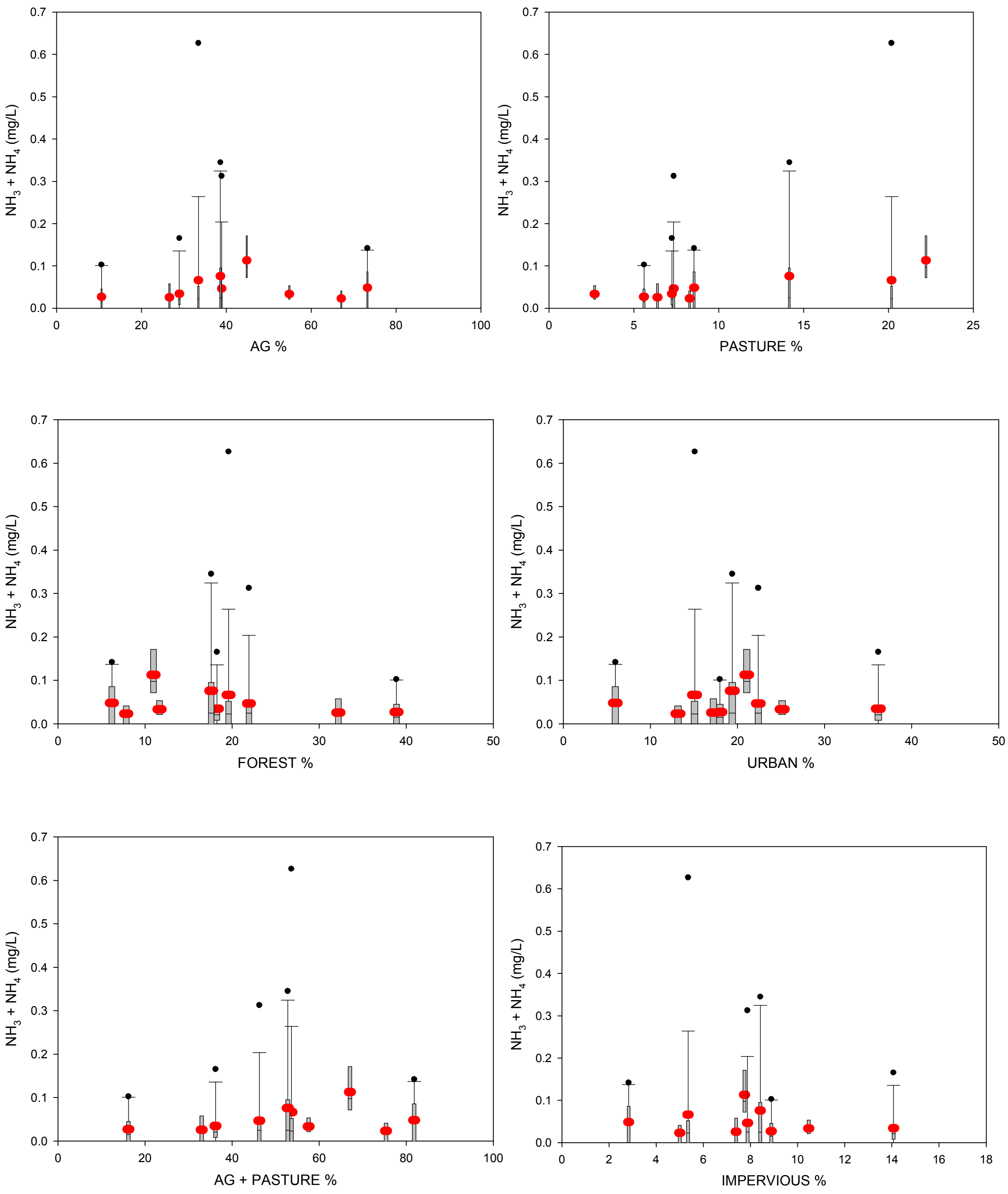


Figure 3.12. Stormflow $NH_3 + NH_4$ concentrations plotted against LULC fractions.

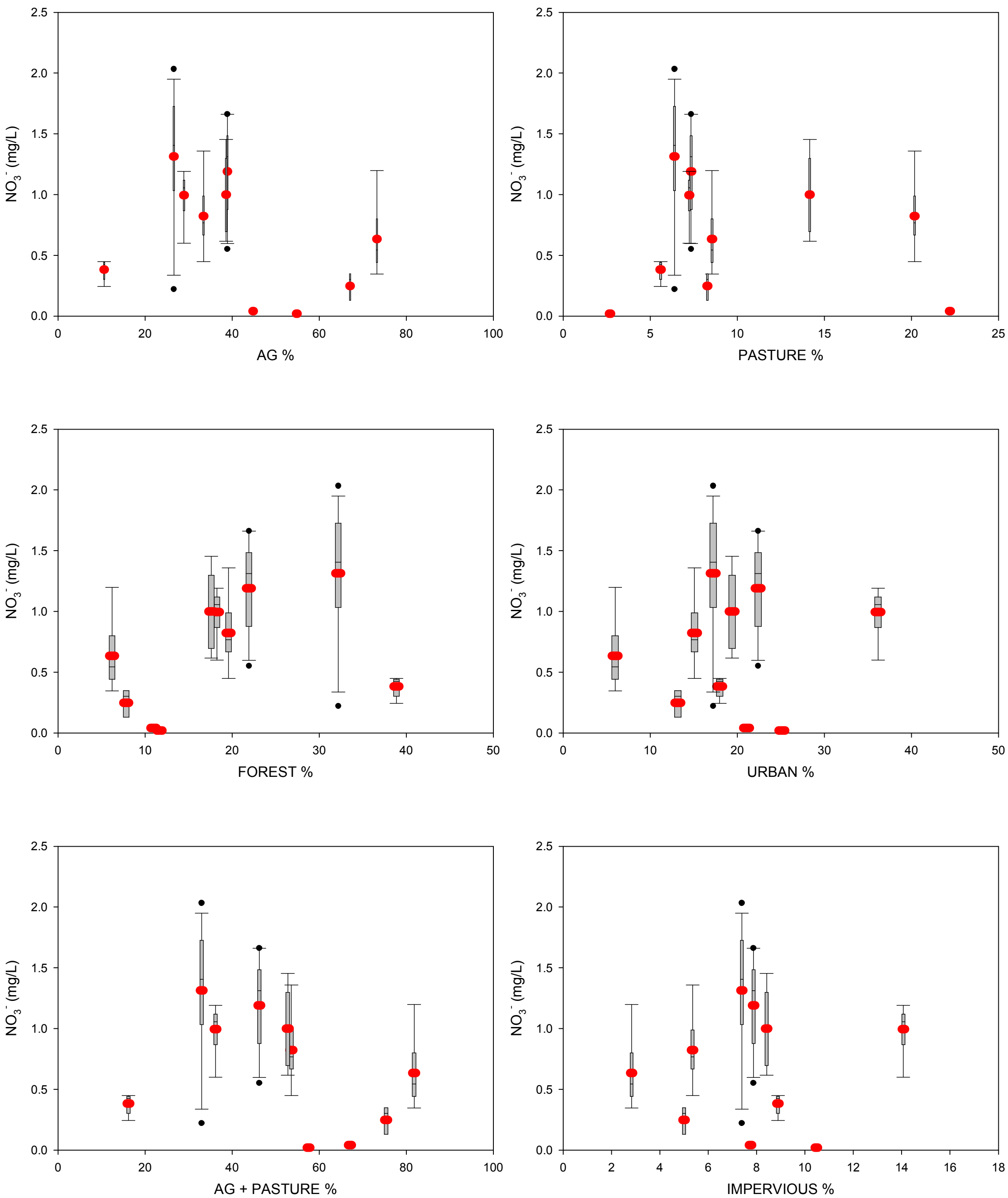


Figure 3.13. Baseflow NO_3^- concentrations plotted against LULC fractions.

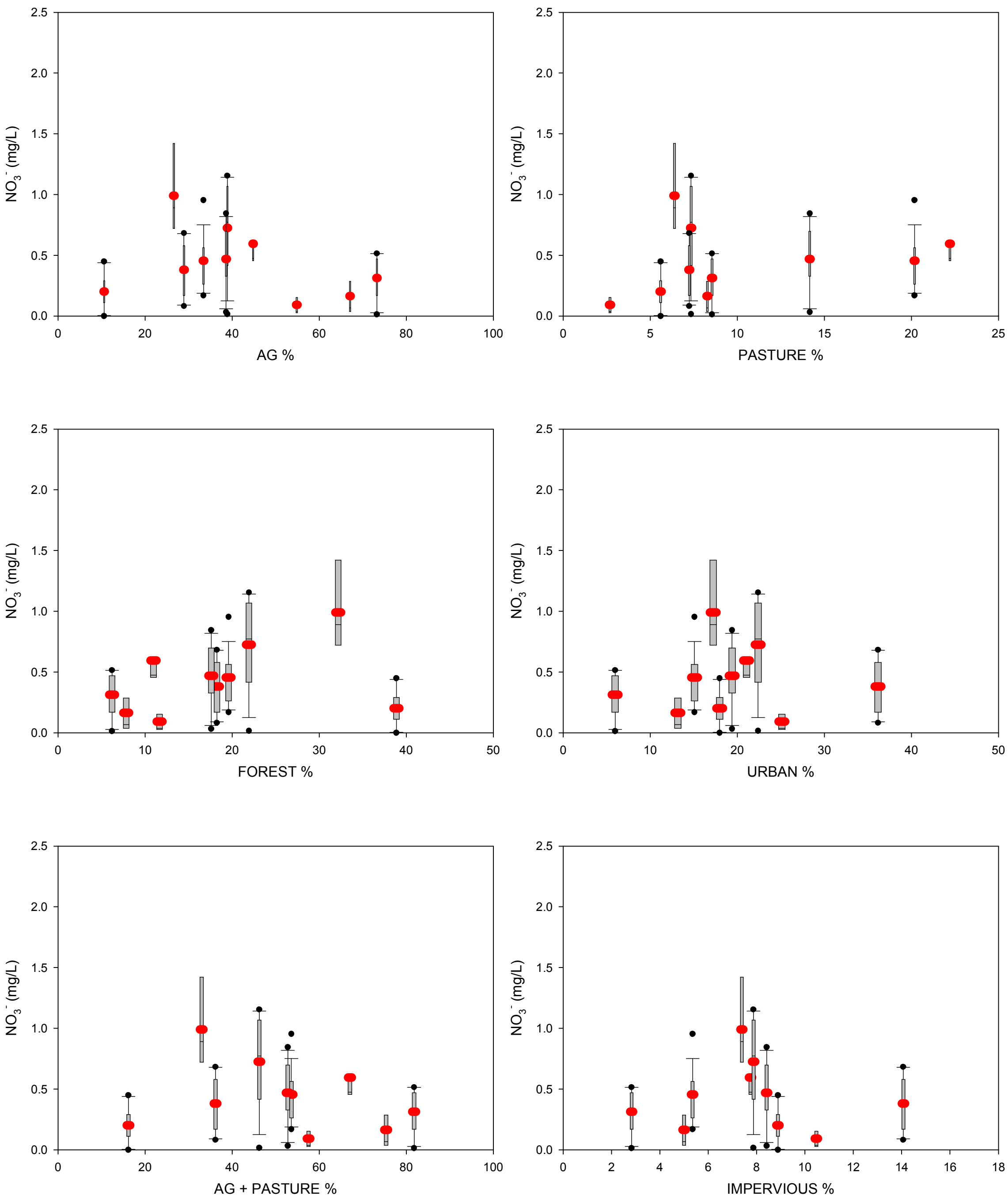


Figure 3.14. Stormflow NO_3^- concentrations plotted against LULC fractions.

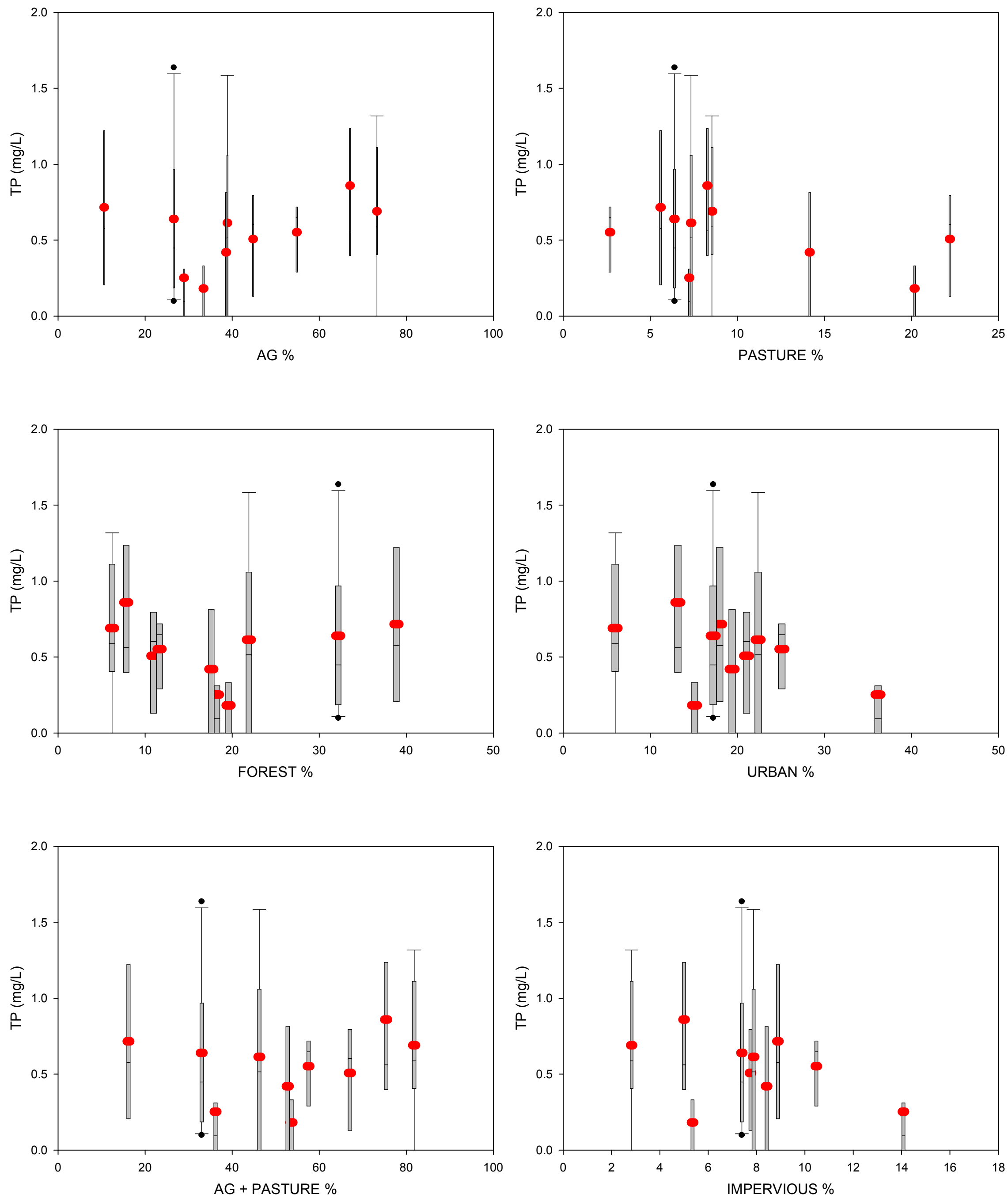


Figure 3.15. Baseflow TP concentrations plotted against LULC fractions.

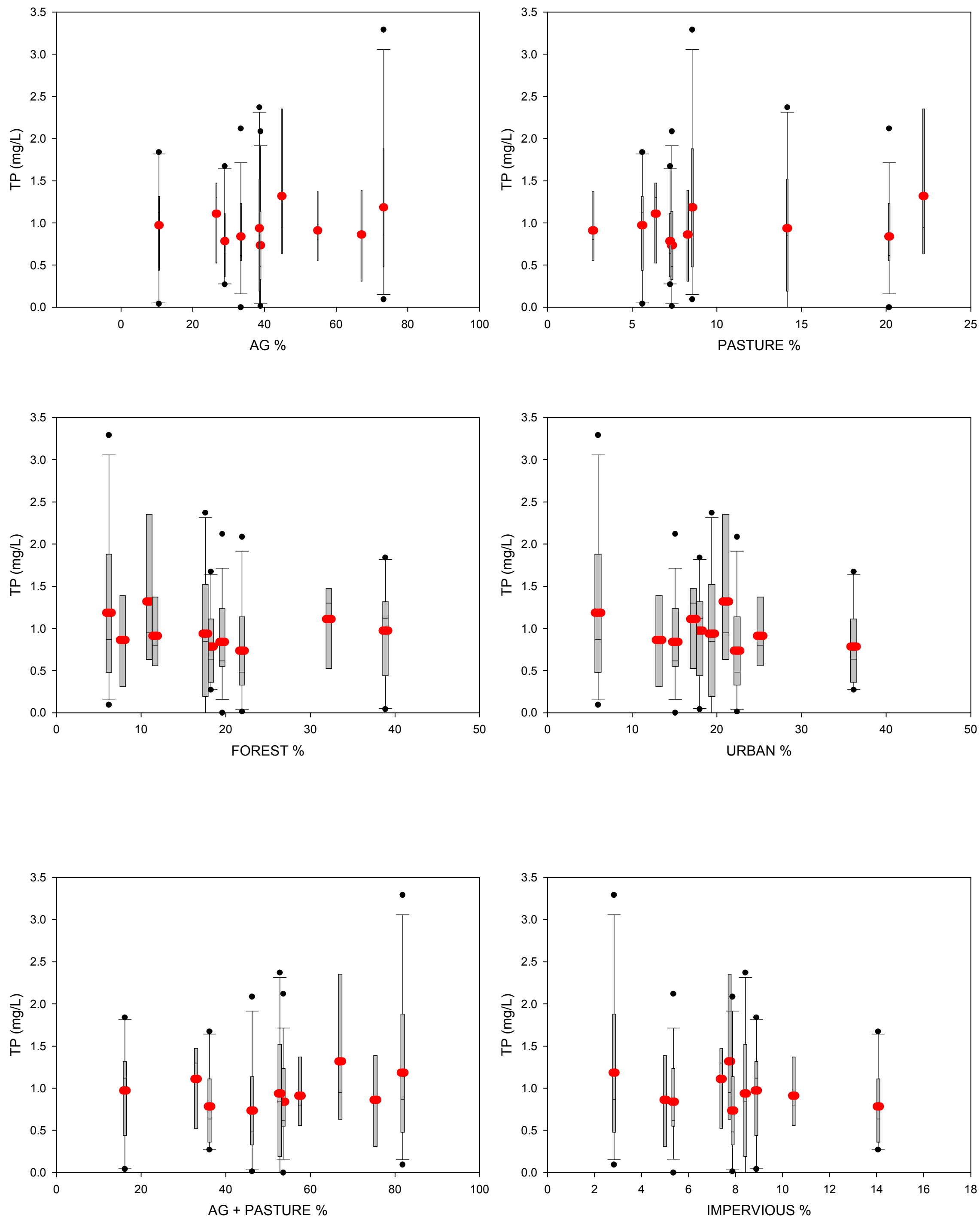


Figure 3.16. Stormflow TP concentrations plotted against LULC fractions.

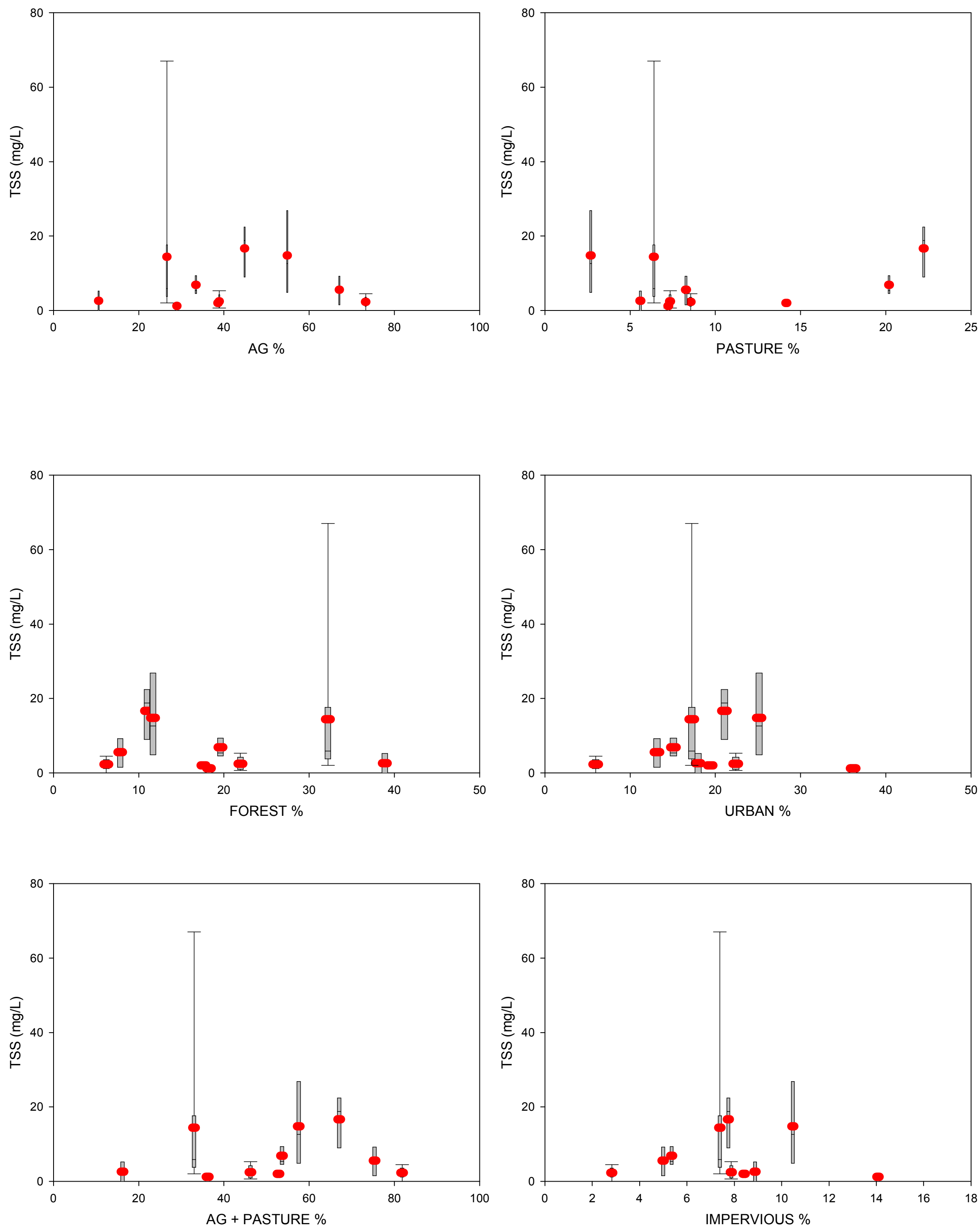


Figure 3.17. Baseflow TSS concentrations plotted against LULC fractions.

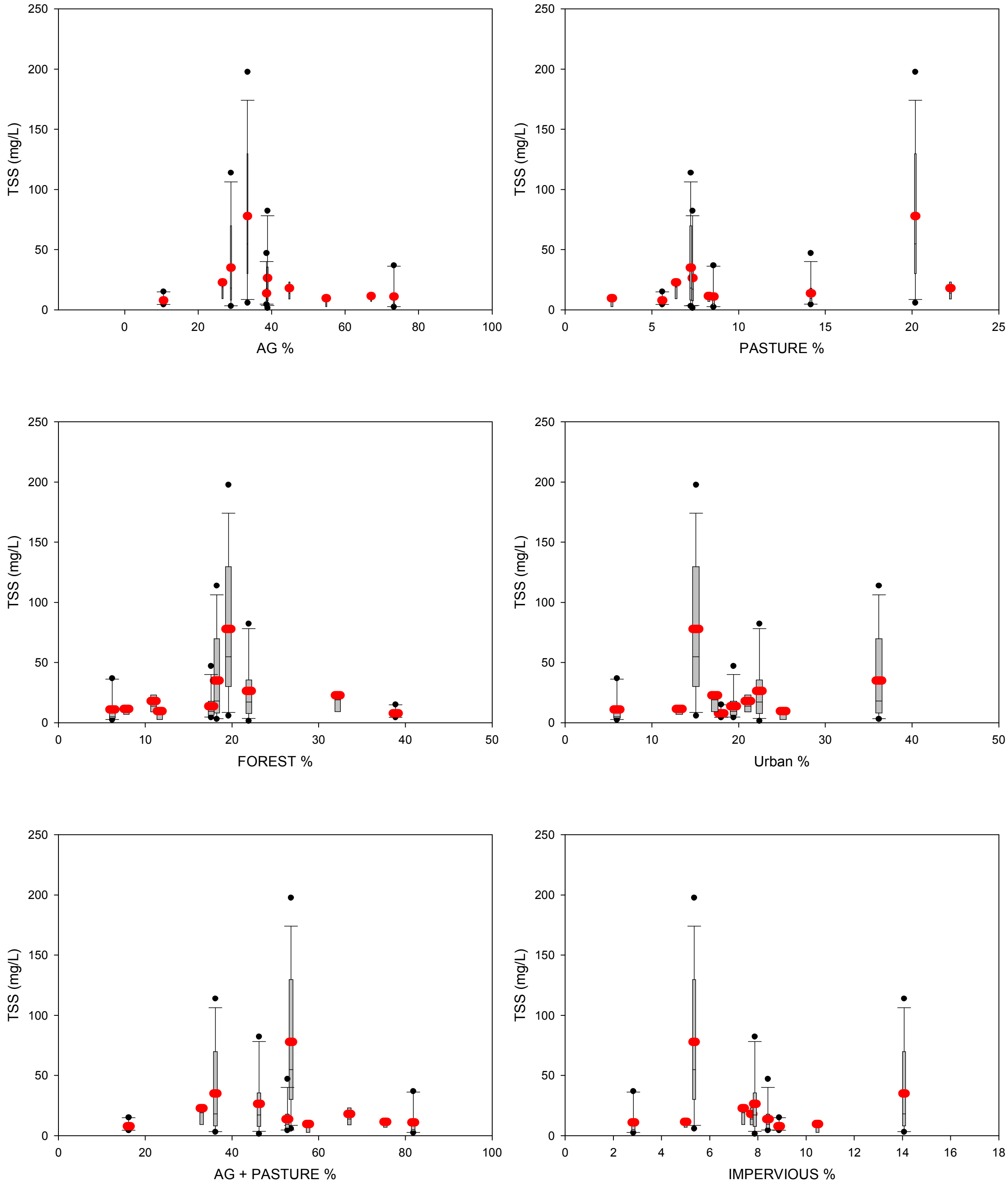
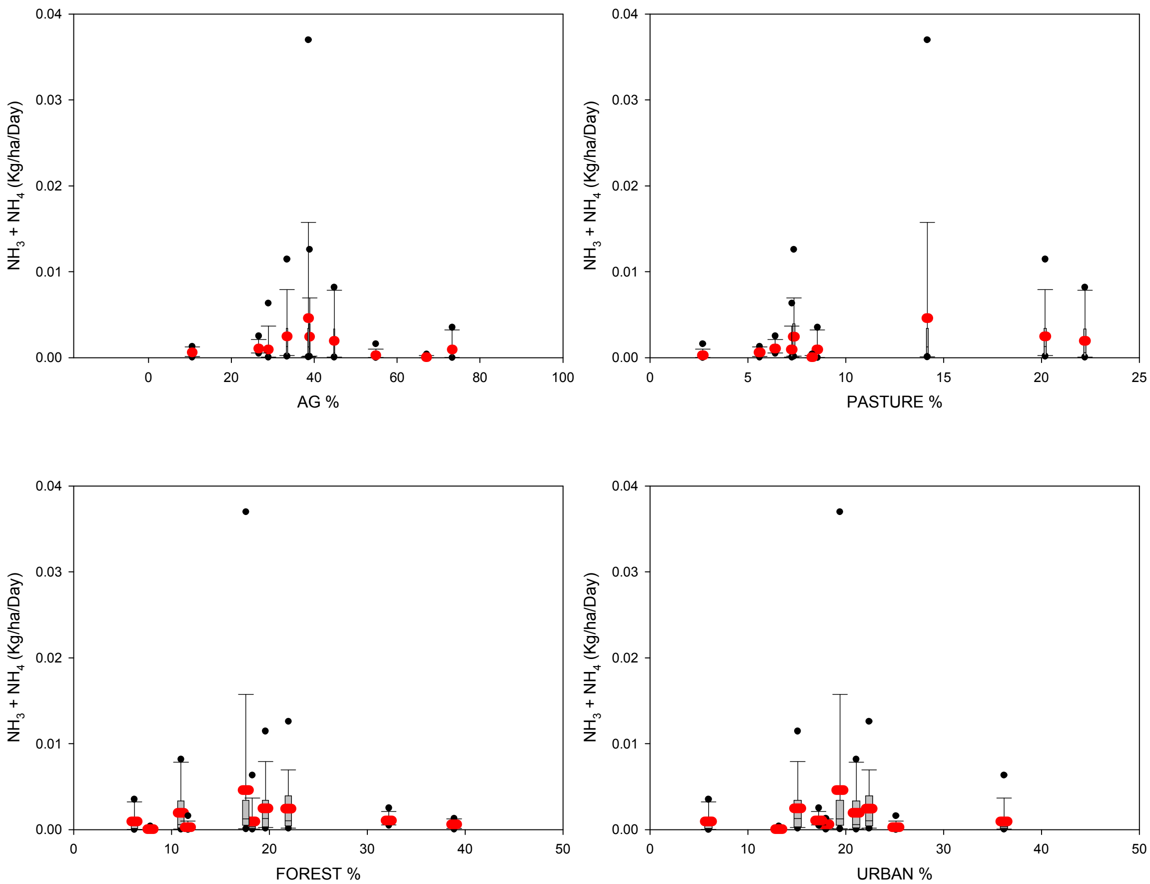


Figure 3.18. Stormflow TSS concentrations plotted against LULC fractions.



NH3 + NH4 (Kg/ha/Day)
0.04
0.03
0.02
0.01
0.00
0
20
40
60
80
100
AG %
0
5
10
15
20
25
PASTURE %
0
10
20
30
40
50
FOREST %
URBAN %

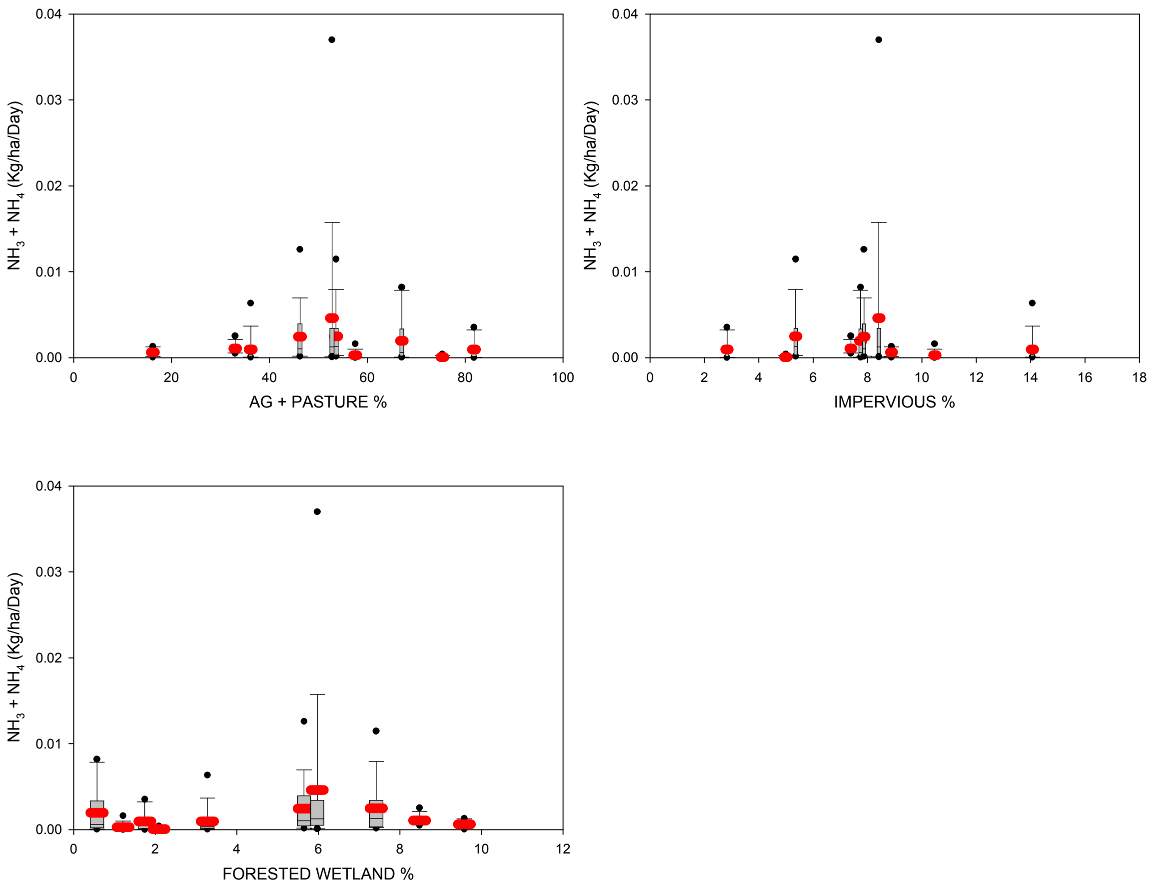
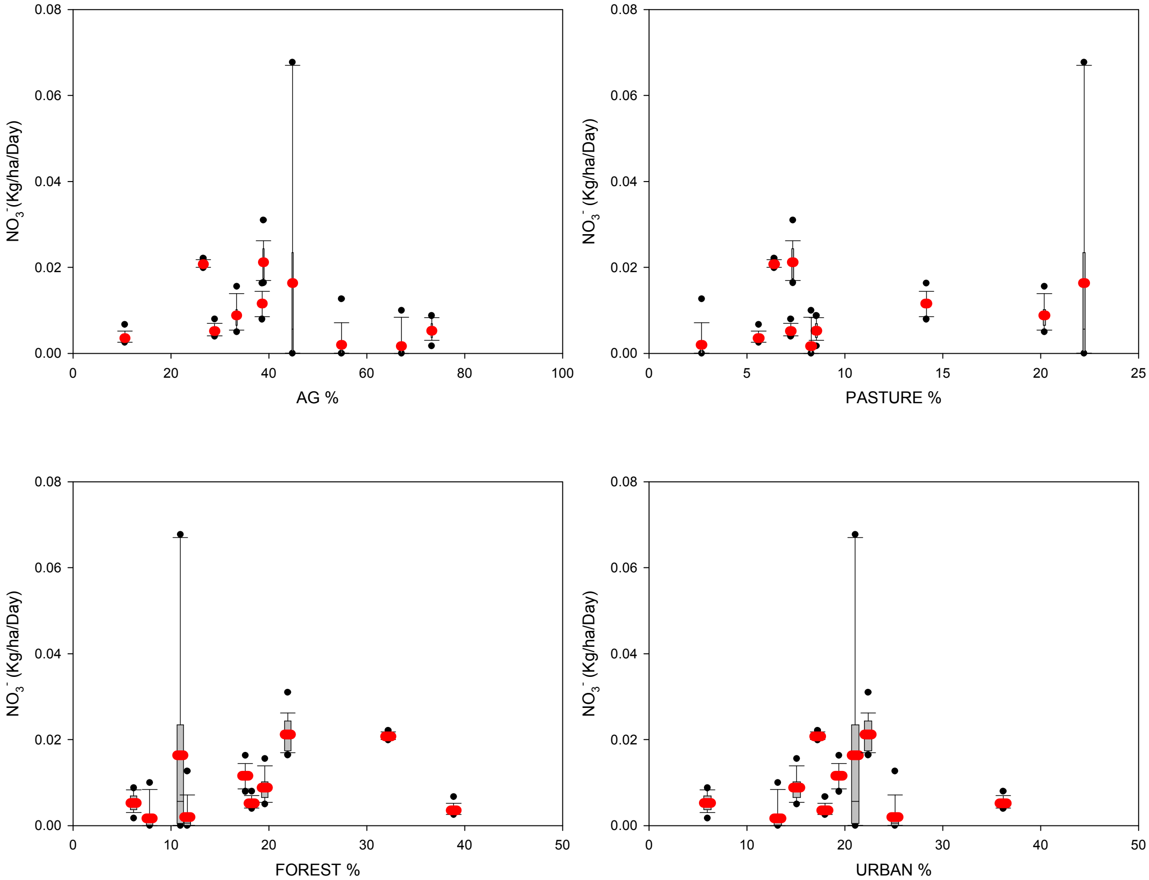


Figure 3.19. Monthly load (kg/ha/day) $NH_3 + NH_4$ plotted against LULC fractions.



NO3- (Kg/ha/Day)
AG %
PASTURE %
FOREST %
URBAN %

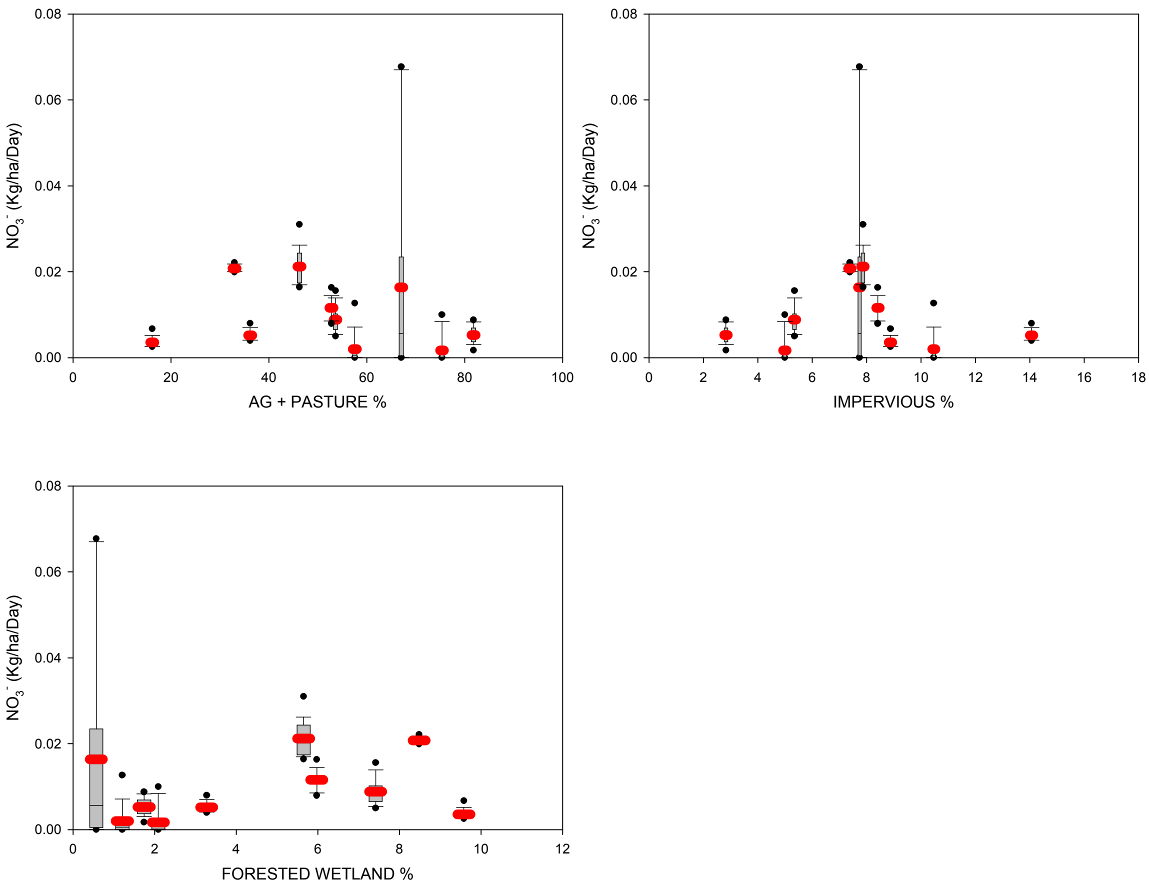
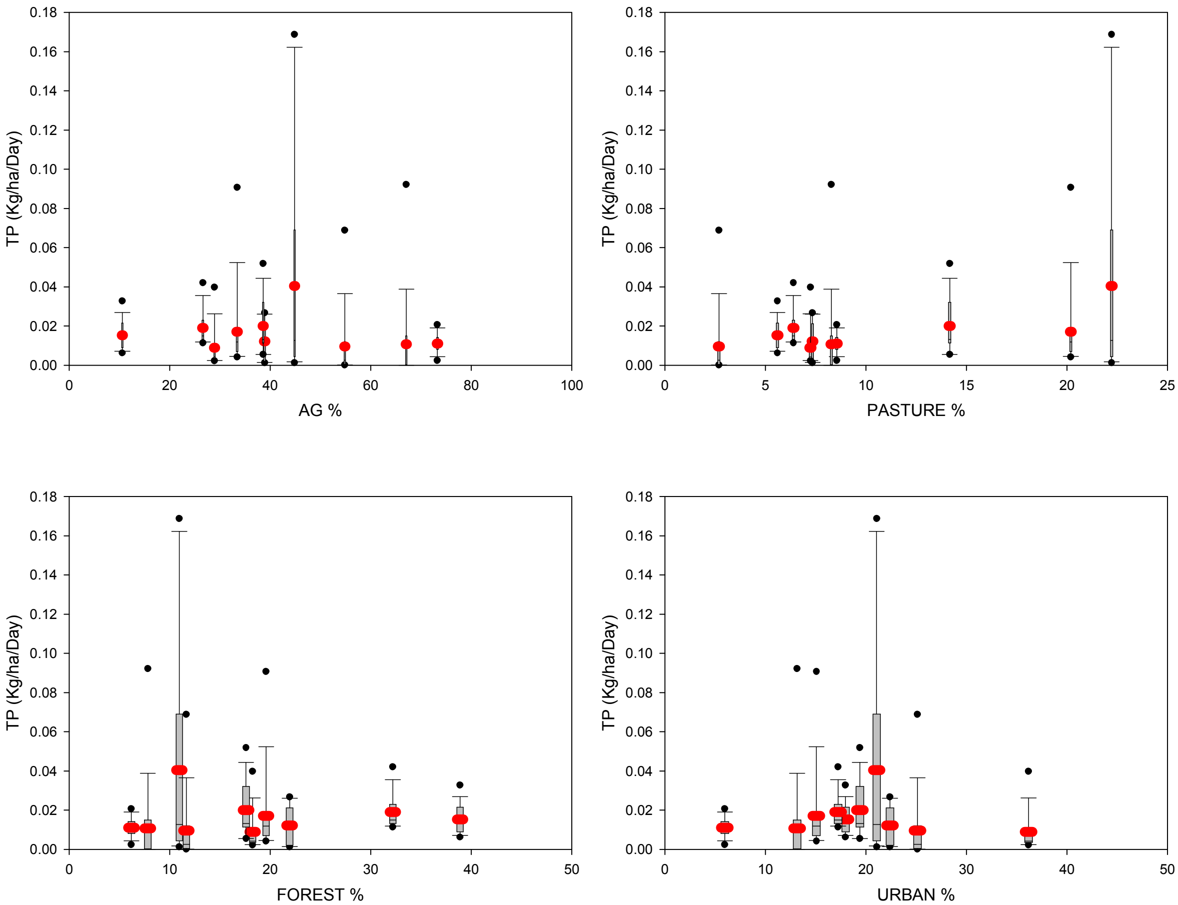


Figure 3.20. Monthly load (kg/ha/day) NO_3^- plotted against LULC fractions.


TP (Kg/ha/Day)
AG %
PASTURE %
FOREST %
URBAN %

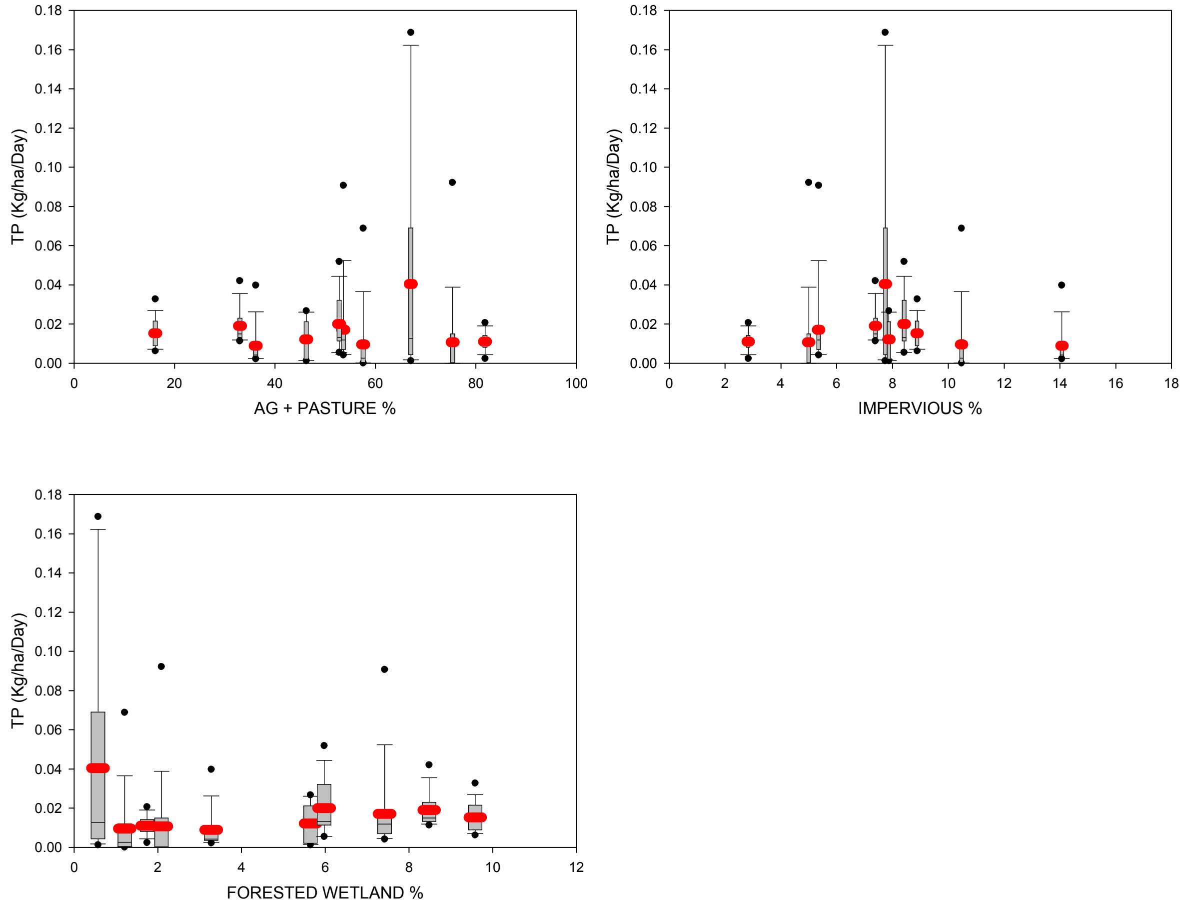
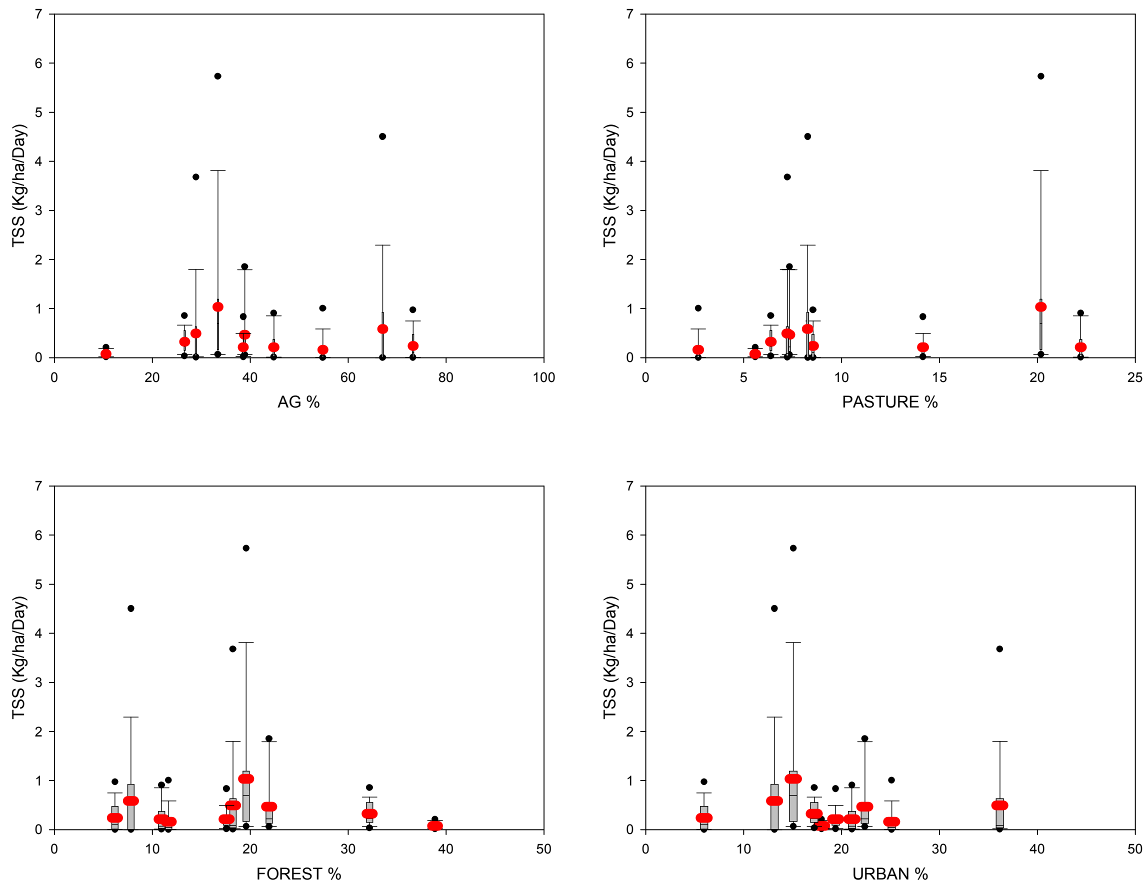


Figure 3.21. Monthly load (kg/ha/day) TP plotted against LULC fractions.



TSS (Kg/ha/Day)
AG %
PASTURE %
FOREST %
URBAN %

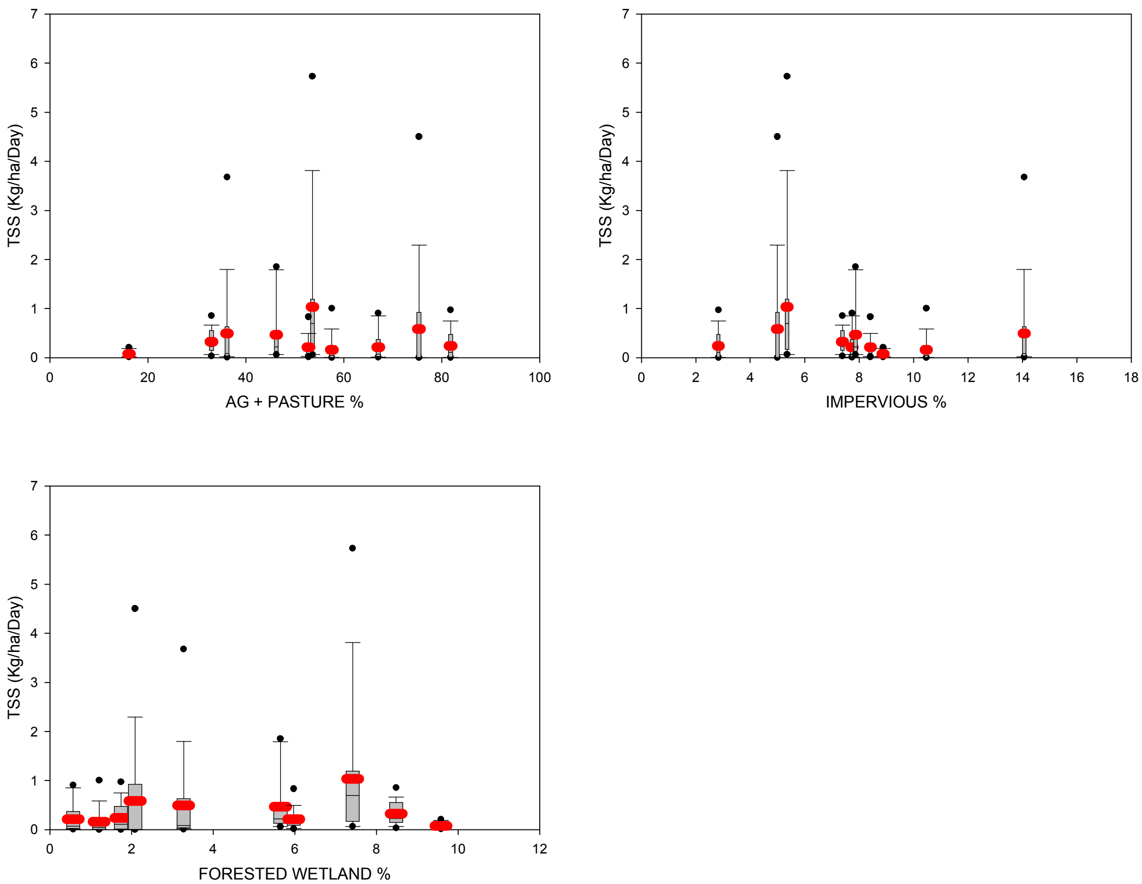


Figure 3.22. Monthly load (kg/ha/day) TSS plotted against LULC fractions.

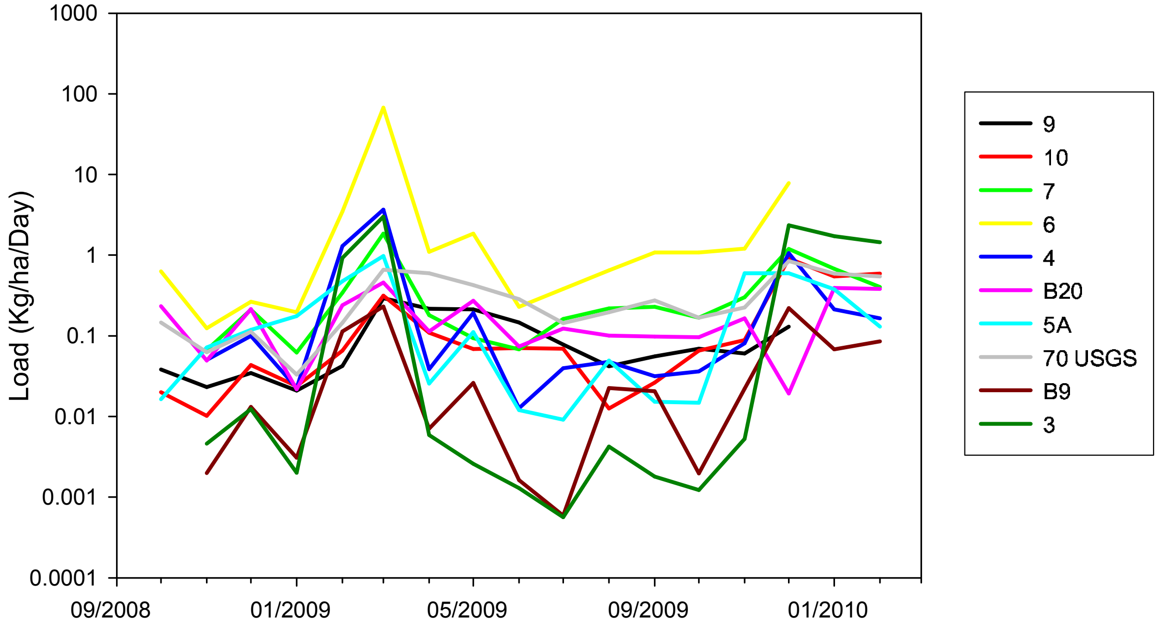


Figure 3.23. TSS area-weighted load seasonality (Kg/ha/Day)

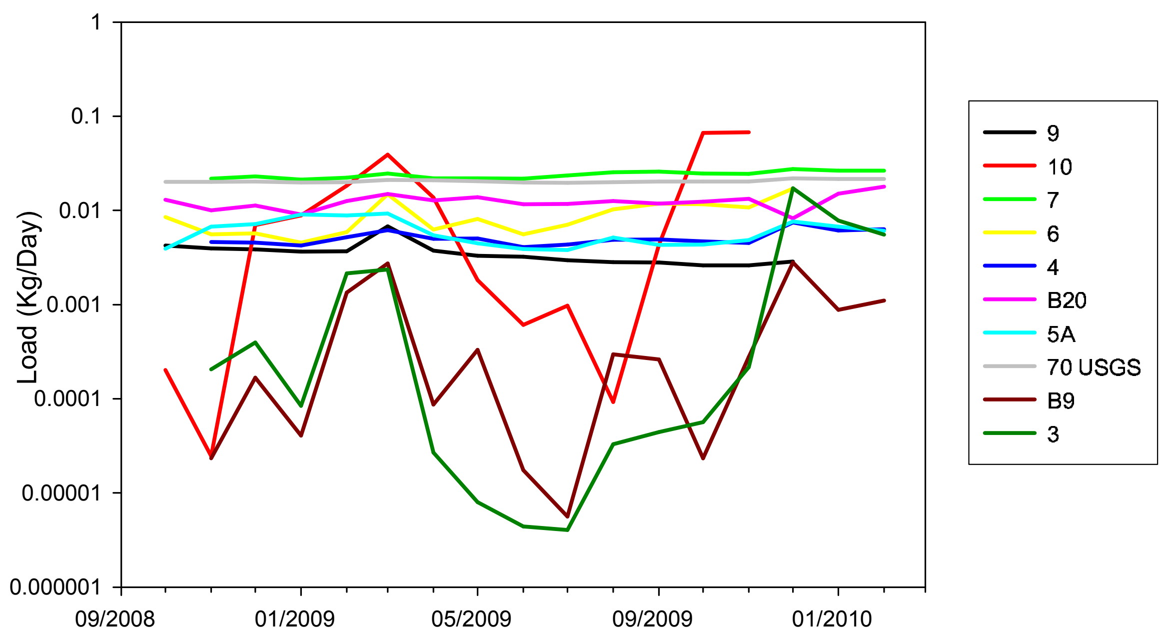


Figure 3.24. NO3 area-weighted load seasonality (Kg/ha/Day)

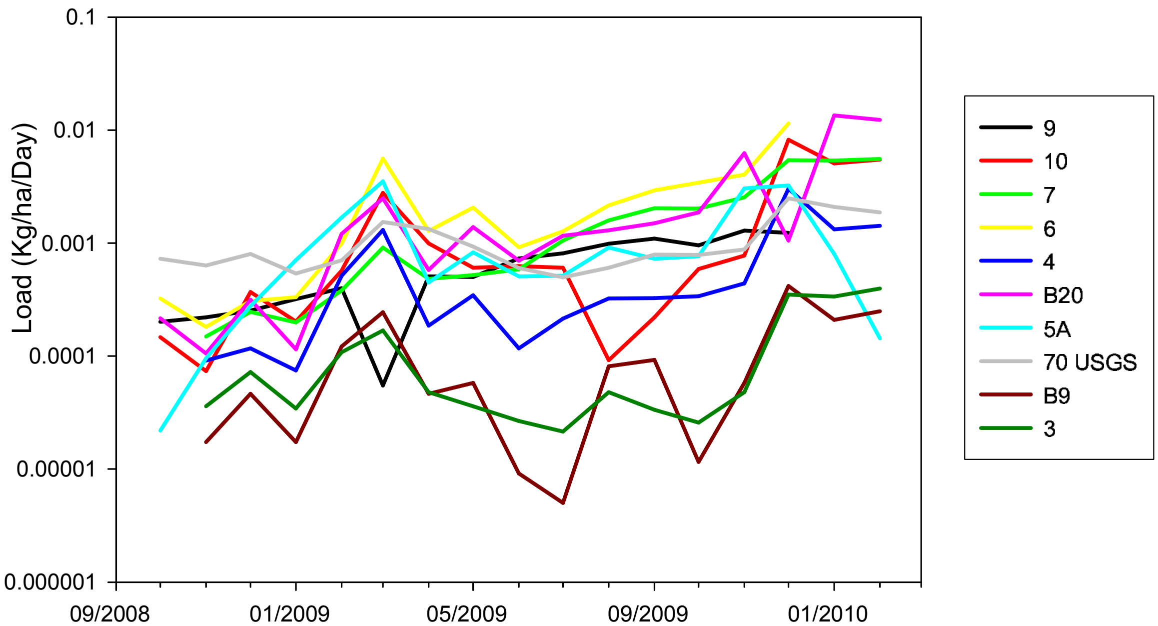


Figure 3.25. NH3+NH4 area-weighted load seasonality (Kg/ha/Day)

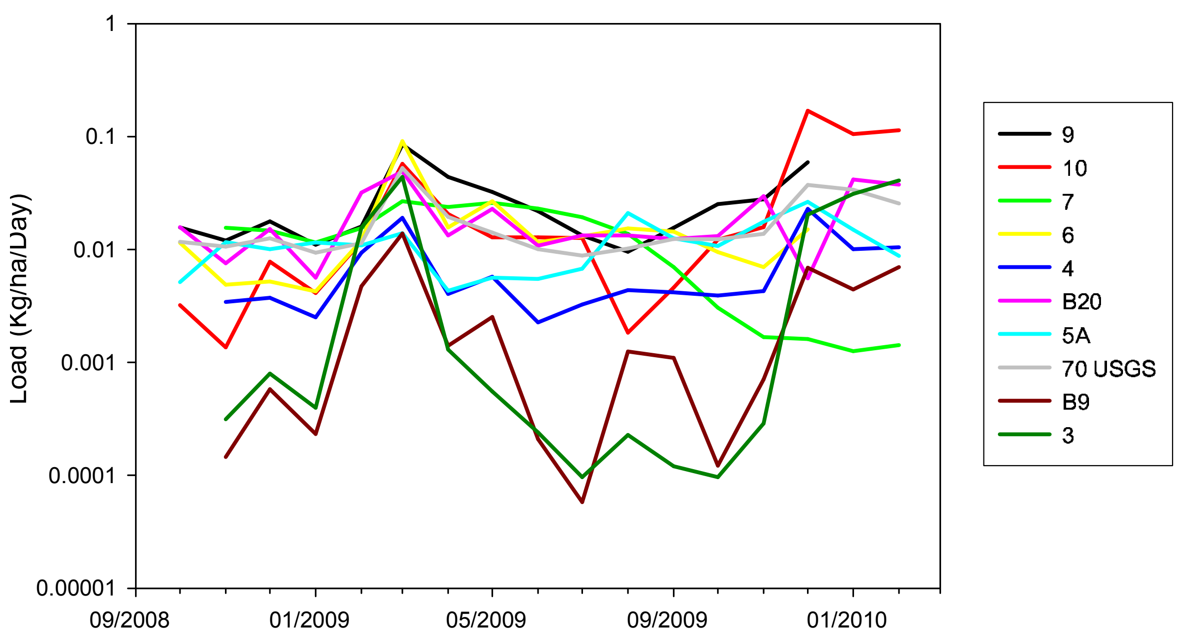


Figure 3.26. TP area-weighted load seasonality (Kg/ha/Day)

4. Summary and Conclusions

4.1 Summary

Land Use / Land Cover (LULC) of the Fish River watershed has significantly changed between the two study periods. Urban land has increased from 3-16% (1995) to 6-36% (2008) of the sub-watershed area. Impervious surfaces have increased similarly from 2-10% (1995) to 3-17% (2008) area. Agricultural land, forested land and pasture land have also increased. Other LULCs, such as shrub land, grassland and wetland have all declined. Directly connected impervious areas have almost doubled since 1995. The substantial increase of urban areas is primarily based around pre-existing towns and city areas (Cartwright 2002). With increasing population, the number of septic systems and the total wastewater output delivered into the Fish River increases. The Loxley wastewater treatment plant directly inputs treated wastewater into the Fish River upstream of site 70 (USGS). This may be one reason for elevated nutrient concentrations at this site. Leaking septic systems are a common occurrence and can be associated with higher nutrient levels in nearby water bodies.

Comparisons between automated sampling and grab sampling during stormflow showed that merely obtaining one grab sample either during a storm or immediately after will not provide enough information on water quality conditions for individual storms. NO_3^- concentrations showed the best relationship between EMC and grab sample concentrations. This is likely due to nitrate having a more consistent relationship with flow than other water quality parameters. Grab samples underestimated concentrations of TP and TSS when compared with associated EMCs. Multiple sample collection during storm events is recommended for a more accurate picture of water quality, especially regarding concentrations of TP and TSS.

There have been no significant changes in precipitation between the two study periods. It can be concluded that any significant change in flow or water quality is not directly linked to overall changes in precipitation. Flow trend analysis showed no significant change for most sites in the watershed with the exception of sites 6 and B9 which showed significant decreases in flow between the 1994-1998 and the 2008-2010 study periods. This decrease may be due to an increase in forested land in these subwatersheds combined with possible anthropogenic effects of developing land to urban areas. The Richards-Baker flashiness indices show that urbanization and an increase in impervious surfaces is causing higher flashiness within the watershed. Baseflow indices showed that as pasture and impervious land increases, the proportion of baseflow as total streamflow decreases, meaning a higher proportion of runoff enters streams from pasture land. Flow-adjusted results show a decrease in nitrate loadings between the two study periods and an increase in TSS loadings in the heavily urbanized sites.

Ammonia/ammonium concentrations were very low for all sites (< 0.1 mg/L). Storm events may cause highly variable conditions with occasional pockets of high concentrations within the water column. Site 4 concentrations had a positive correlation to flow during storm events. This may be linked to the heavily urbanized conditions in site 4's subwatershed. The site 4 watershed has the highest percentage of low and medium-density residential areas. These landscapes typically have large lawns that receive fertilization, possibly impacting nutrient levels in nearby streams. Site 5A concentrations had a positive correlation to flow during all flow conditions. The site 5A subwatershed is the most heavily farmed subbasin with 73% of the area existing as cropland. Ammonia-based fertilizers may be the cause of increases in ammonia/ammonium entering the channel in runoff during storm events.

Nitrate concentrations were highest at sites 7 and 70. A combination of agriculture and urban LULC is likely the reason for the higher nitrate concentrations. The Loxley wastewater treatment plant also discharges in the Fish River upstream of site 70, increasing nitrate levels. Nitrate typically had a strong negative relationship with increasing flow, especially during storm events. This was true for all sites with the exception of site B9 which showed an increasing relationship to increasing flow during storm events. This is likely due to site B9 having very low to almost non-existent flow conditions during most of the year (intermittent stream). Nitrate typically enters the stream in groundwater and with minimal baseflow low nitrate concentrations would be expected. This is further established by site B9 having the least amount of nitrate concentration by an order of magnitude over other sites within the Fish River watershed.

TP concentrations were typically higher than nitrate levels at most sites. Highest concentrations were found at sites 10 and 5A with a maximum concentration of over 3 mg/L at site 5A. This is likely due to the abundance of agricultural land upstream from this site. Mean TP concentrations ranged between 0.7-1.0 mg/L for all sites with maximum values as high as 2.0-3.3 mg/L. The highest amounts of TP loading were from sites 70 (USGS) and 9. Flow rates were highest at site 70 (USGS) and site 9 had the third highest flow rates. High flow combined with high concentrations would result in highest amount of TP load. Urbanized land may also be contributing to higher TP levels in the watershed. Berndt *et al*. (1998) found that urban and agricultural lands typically produced much higher phosphorus concentrations than mixed-use landscapes in the Southeastern U.S. The high levels of phosphorus in the Fish River watershed appear to have increased over time along with the increase in urban and impervious lands.

TSS concentrations were relatively low for most sites, with the exception of sites 6 and 4. Site 6 contributes the most TSS load per area out of all other sites over the entire sampling period. Urbanization and a decrease in wetlands and grasslands are likely the cause of sedimentation within these subwatersheds. Urban areas are well known to have streams with elevated suspended sediment levels (Wahl *et al.* 1997). Watersheds with an abundance of pasture land may also produce higher levels of TSS due to lower streambed stability (Schoonover *et al.* 2007). TSS levels in the Fish River watershed showed a strong positive correlation to increasing flow for most sites. Most median TSS concentrations were less than 10 mg/L.

It was difficult to determine any direct linkages between water quality and LULC in this watershed. The lack of a LULC gradient at the subwatershed level is most likely the reason that relationships are not clear. A larger sample size would also benefit any further studies interested in determining a direct linkage. The use of multi-linear regression analysis also proved problematic and did not yield strong relationships due to the diversity of LULC types across each subwatershed.

Sites 7, 6, 4, B20 and 5A showed a significant decrease in nitrate load, with sites 9 and B9 showing insignificant decreases and sites 10 and 3 showing insignificant increases between the study periods. TSS loading trend results showed a significant decrease for sites 9, 10, 5A and

3. All other sites showed insignificant decreases with the exception of site 4 which showed a significant increase in TSS. Site 4's TSS results are likely due to the severe increase in urbanized landscapes combined with decreases in grasslands and wetlands within the subwatershed. TP loading results showed a significant increase for all sites with the exception of site 4 which showed an insignificant increasing trend.

4.2 Conclusions

When conducting water quality experiments, it is important to determine the best sampling technique available with the resources at hand. Multiple samples taken during storm events can help provide a better overall picture of water quality conditions. However, expense and time constraints can limit the number of samples one can adequately process.

Since flow in the Fish River and in the majority of subwatersheds has not statistically changed between the two study periods in question, we can conclude that nutrient and sediment load changes may be tied to LULC and management practices. At locations where flow reductions did occur, small scale anthropogenic impacts would be the most likely explanation for these changes. Another possible cause could be due to urbanization and increased imperviousness causing hydrological changes with regards to flashiness and baseflow index.

We have seen major shifts in the relationship between nitrates and phosphorus in most of the tributaries of the Fish River. Phosphorus has historically been the limiting nutrient for phytoplankton growth within the Fish River watershed (Miller-Way et al. 1996). An increase in TP combined with a decrease in nitrates in a P-limited system can cause ecological imbalance resulting in algal blooms and eutrophication (Miller-Way et al. 1996, Basnyat 1999, Vidon

2010). In comparison to water quality levels in the piedmont plain; Berndt et al. (1998) found that nitrate and phosphorus levels were lower and higher, respectively, than levels in the coastal plain region. As nitrate concentrations in the 2008-2010 study period are shown to be similar to TP levels, the N:P ratio may have lowered. This becomes important when developing management plans to mitigate any eutrophication problems in the Fish River and Weeks Bay.

The substrate in the Fish River watershed is very permeable and dissolved nutrients may have a greater effect on groundwater. Watersheds with little slope and very sandy soils may have greater groundwater leaching of dissolved nutrients such as nitrate. The majority of nitrates running off landscapes may enter the groundwater system as opposed to directly entering the stream channel. Murgulet and Tick (2008) conducted a study of groundwater nitrate levels in 2006 and 2007. They found nitrate concentrations in the shallow aquifer's groundwater to be an order of magnitude higher than stream concentrations collected in 2008-2010 (Figure 4.1). This study took place during a severe drought period, whereas the 2008-2010 study period was considered to be moderately wet. The nitrate concentration difference between the studies is likely due to differing local hydrologic conditions. Groundwater nitrate levels differed substantially from year to year due to variance in precipitation, local aquifer pumping, and changes in recharge and discharge. Other studies conducted typically show an increase in nitrates over time with increasing urbanized and impervious landscapes (Crim 2007, Lewis *et al*. 2007, Basnyat *et al*. 1999). While this study shows a significant decrease in nitrate levels compared with previous studies, further research would be necessary to determine nitrate conditions and sources and their relationship with changing LULC. With regards to nitrate transportation throughout the Fish River watershed, nitrate may be leaching through the permeable substrate and entering groundwater in larger amounts than what is found in streamflow. Annual variation of nitrate concentration should be taken into account when establishing temporal trends. Concentrations also vary spatially throughout the region. Murgulet and Tick (2008) concluded that agricultural areas, sewer/septic breakthrough and animal waste are the most likely sources of nitrate.

As the watershed is highly impacted by agricultural land use, an alteration of crop type may have played a role in changing the nutrient balance. Organic P, a major constituent of TP, readily attaches itself to sediment particles; yet, while our results show a substantial increase in TP, there has been no similar increase in suspended sediment. As crops continue to rotate and change in the future, it will be critical to determine how water quality evolves with the changing landscape.

There have been substantial increases in urbanization throughout the Fish River watershed. A combination of urbanization and changes in crop types is the most likely cause of the possible shift in the nitrate-phosphorus balance. The introduction of peanut farming in the late 1990s / early 2000s and the growing sod farming industry are possible sources of heavier fertilizer application in the watershed. Most fertilizer application is based upon a soil test; however, typical application of fertilizer for peanuts in this area is 0-40-40 pounds N-P_2O_5-K_2O per acre (Adams and Mitchell, 2000). This shows that while nitrogen application is not necessary, phosphorus is typically applied. Sod farming also uses a large amount of fertilizer application compared with other crops (80-40-40 pounds N-P_2O_5-K_2O per acre).

Urbanization may be linked to significant increases in sedimentation at site 4. A decrease in grassland and wetland landscapes may be further damaging water quality conditions in this subwatershed. The bulk of sediment and nutrient entering the system occurs during large storm events and care must be taken to ensure BMPs are implemented, specifically during seasons with heavy precipitation. Further analysis over extended periods of time should be conducted in this region to determine ongoing impacts of LULC changes.

This study showed that when conducting water quality and hydrology assessments, it is important to determine both spatial and temporal conditions of a watershed. Fluctuations in land use/cover can significantly alter water quality and hydrology at the spatial and temporal scale. It is difficult to determine direct linkages between LULC and water quality in mixed-use watersheds; however, the majority of coastal landscapes have a broad variety of land use and further research should be applied landscapes continue to evolve.

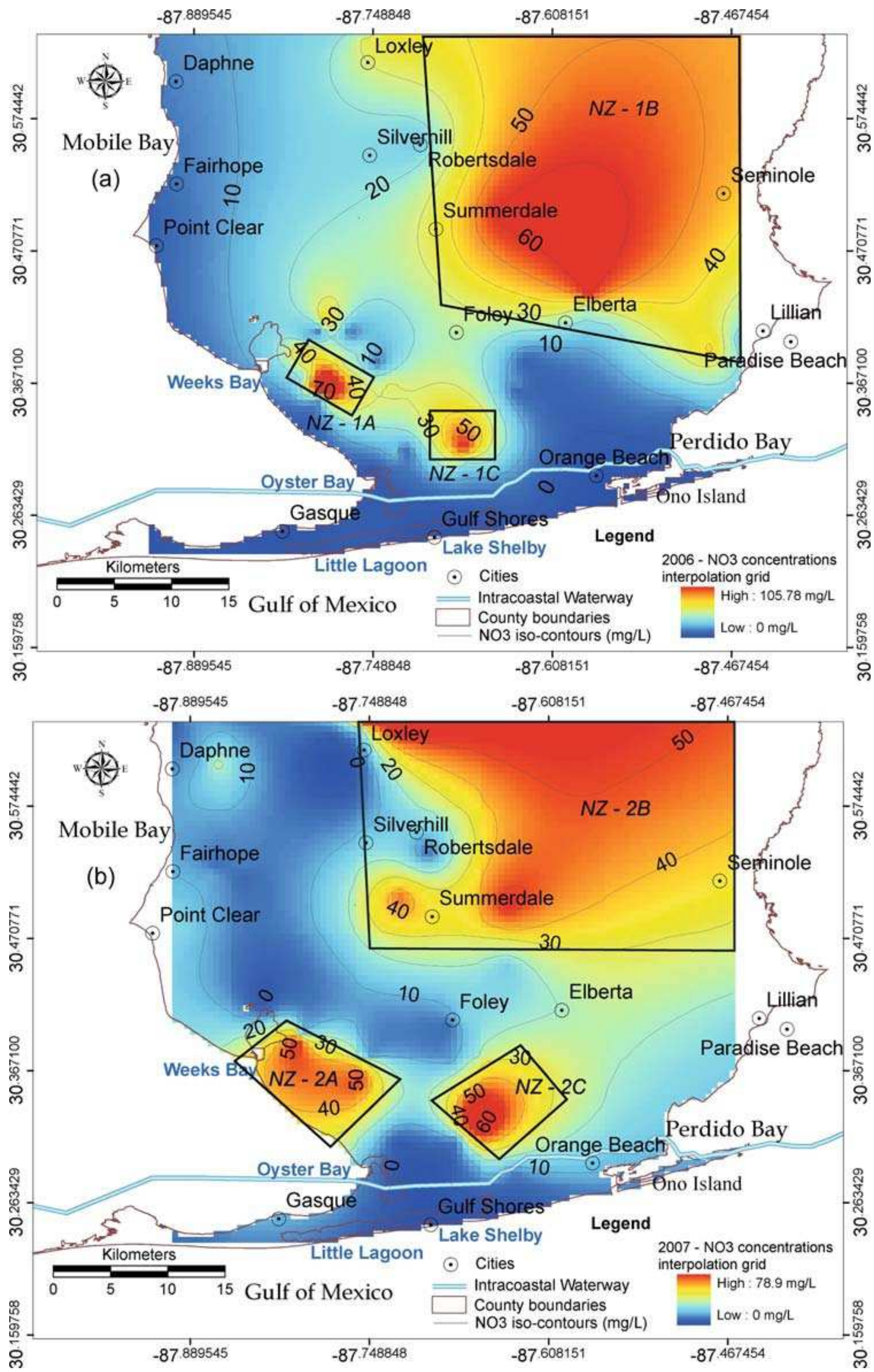


Figure 4.1. Iso-concentration maps of nitrate concentrations in the shallow aquifer zone (A2) for 2006 (above) and 2007 (below) in lower Baldwin County. The location of the Fish River is north of Weeks Bay and West of Robertsdale and Summerdale. (Adapted from Murgelet and Tick, 2008)

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