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An Analysis of Spatiotemporal Variations of Water Quality in the Little River Watershed and Their Connection with Land-Cover Patterns

A Thesis Presented for
the Master of Science
Degree
The University of Tennessee, Knoxville

Thomas Edward Burley
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Dedication

I dedicate this thesis to El, whose faith in me gave me faith in myself. I also dedicate this thesis to my parents, Bill and Donna, who raised me to strive for the next level and to always do my best.

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Abstract

The Little River supplies drinking water to Blount County, Tennessee, and supports several state and federally listed species. The upper, southeastern area of the Little River watershed is fed by protected sources originating in the Great Smoky Mountains National Park. In the lower, northwestern part, however, the watershed has been affected by anthropogenic land-cover and land-cover change in recent years. These changes may have impacted water quality in the Little River watershed over the past 20 years.

The objectives of this study were: (1) to elucidate the spatiotemporal patterns of water quality, (2) to understand the Little River watershed's land-cover patterns, and (3) to quantify the relationships between land-cover patterns and water quality. Existing water quality data for the past 20 years from different sources were compiled and analyzed using multivariate statistical analysis. Principal component analysis (PCA) was used to identify the associations among water quality parameters. Cluster analysis (CA) was used to group sampling sites with respect to water quality pattern. Discriminant analysis (DA) was used to identify which water quality indicators best represent the differences between the clusters derived from CA. Land-cover data were analyzed to determine types and proportions of different land-cover types upstream from water quality sampling sites. The results of the analyses were visualized using Geographic Information Systems (GIS).

The results show that specific conductance, turbidity, and ammonia nitrogen best reflect the processes influencing data set variability (dissolved solids, seasonal influences, and nutrients, respectively). The results also suggest that water quality differs between samples from the upper and lower parts of the watershed and that the four parameters dissolved oxygen, total phosphorus, ammonia nitrogen, and total suspended solids define spatial groups of sample sites with similar water qualities. There is a spatial relationship between patterns of land cover and patterns of water quality. Higher proportions of anthropogenic land cover (e.g., urban) occur within the same sub-watershed as degraded water quality measures. The results suggest that anthropogenic land cover influences spatial variations of water quality in the Little River.

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Chapter 1 Introduction

1.1 Problem Statement

Blount County, Tennessee is one of the most rapidly developing counties in the state (Ezzell et al. 2005). The Little River (LR) is an important resource which supplies drinking water and recreation to residents of Blount County, Tennessee. Its origins are in the Great Smoky Mountains National Park (GSMNP) and it flows northwestward through Blount County towards the Tennessee River. The portions of the LR in the Park are of outstanding quality largely because of the protected lands through which that portion of the river flows. However, as the LR makes its way through Blount County, water quality becomes degraded (Ezzell et al. 2005). The part of the watershed near the GSMNP, the middle area of the watershed, and the northwestern area of the watershed near the Tennessee River shall hereafter be referred to as the “upper part”, the “middle part,” and the “lower part,” respectively (relative to the direction of flow of the LR main stem). Activities such as mining, construction, and timber harvesting cause landscape changes that modify natural hydrologic processes. Tributaries experience an increased loading of pollutants carried by runoff from modified lands. These pollutants, commonly known as nonpoint source (NPS) pollutants, are responsible for much of the water quality degradation experienced today as a result of human land use and land-cover change (Omernik 1977; Gilliland and Baxter-Potter 1987; USEPA 1993).

The LR watershed has experienced considerable land-cover change. Areas previously covered with eastern hardwood forests are now farms, shopping centers, and neighborhoods. These changes are not expected to decrease. Blount County's population is expected to grow by over 30 percent to nearly 145,000 residents by the year 2030 (Ezzell et al. 2005). The LR is already experiencing water quality issues such as a decline in biodiversity, nitrate problems, habitat alteration, siltation, and pathogen problems (TDEC 2006b; TDEC 2006c).

Water quality reflects land cover and is highly influenced by changes in land cover at the watershed level (Hyde 1982; Arnold and Gibbons 1996; Jones et al. 2001; Goonetilleke et al. 2005). Addressing NPS pollution requires an understanding of the relationships among land cover, water quality, and the factors that influence these relationships (Randhir et al. 2001). Climatic and seasonal influences affect NPS pollution and subsequent patterns of water quality (Vega et al. 1998). Anthropogenic changes can exacerbate natural processes and can also create new problems as well. These factors together comprise the management challenges facing both the residents of Blount County and the organizations responsible for overseeing the quality of water in the LR.

1.2 Research Questions and Hypotheses

The primary objective of this thesis is to analyze the spatiotemporal variations of water quality and their relationship with land cover in the LR watershed. The primary research questions are:

1. What are the spatiotemporal patterns of water quality in the LR Watershed?
2. What are the patterns of land cover in the LR Watershed?
3. What are the relationships between land cover and water quality in the LR Watershed?

In this thesis, multivariate water quality data are analyzed to determine associations among parameters and spatial patterns across the watershed. Geographic Information System (GIS) spatial analysis techniques are used to delineate the study area subwatersheds and to

quantify select landscape indicators known to be associated with NPS pollution. Areal proportions of land-cover change and recent proportions of land cover are calculated to determine types and extents in the LR. Multivariate analysis results and tests of significance are synthesized to determine whether or not upper part and lower part water quality and land cover are significantly different.

- My hypotheses include:
- There is a strong relationship between patterns of water quality and seasonal variations of precipitation and streamflow.
 - There is a strong relationship between spatiotemporal patterns of water quality and land cover patterns.
 - Seasonal variations of precipitation show a relationship with water quality in areas having storm runoff-inducing land cover types.

Chapter 2 Review of Relevant Literature

2.1 Watersheds as an Analytical and Management Framework

"We must not divorce the stream from its valley in our thoughts at any time. If we do, we lose touch with reality" (Hynes, 1975 as quoted in Turner et al. 2001).

A watershed is the area of land that drains to a common outlet (Dingman 2002). Watersheds are shaped by local topography and are composed of many smaller subwatersheds that contribute drained water from the land area within them. Water moves across the watershed land surface as runoff and picks up various materials and chemicals. This water then flows to streams, rivers, reservoirs, and lakes. Consequently, surface water quality will reflect watershed-level land cover, geology, topography, and natural landscape-scale processes.

Runoff processes are important for water quality planning and management (Dunne and Leopold 1978). Human modifications to watersheds alter naturally occurring hydrological processes. Development activities such as deforestation and road construction lead to poor soil drainage. As a result, these areas often become saturated during rainfall and yield storm runoff. Areas that produce runoff also typically yield sediment, nutrients, bacteria, and other pollutants, which are transported to streams and rivers. Changes in the types and magnitude of runoff are a direct result of land-surface modification. Diminished storage and infiltration capacity creates a decreased lag time between the beginning of rainfall events and the occurrence of peak flows. At the same time, groundwater recharge is necessary for supplying base flows during dry periods. Less stored water results in reduced base flows, which, besides affecting supply quantity, affect water quality (Dunne and Leopold 1978).

The watershed approach provides a naturally occurring hierarchical framework for planning and management. Researchers and policymakers focus on watersheds as the primary analysis unit for water-quality studies (NRC 1997; US Congress 2002). Multi-scale biological and ecological processes require an analytical framework that can scale itself up or down appropriately. Site-specific analyses can be synthesized into broader-scale assessments while still maintaining a connection to the finer scale where management actions are implemented (e.g., best management practices or BMPs).

The incorporation of watersheds into land-use planning and management has evolved considerably in the United States. The Federal Water Pollution Control Act was amended in 1965 to encourage states to use watersheds and river basins as spatial units for managing water pollution (NRC 1997). The 1969 National Environmental Policy Act was the impetus for the development of the precursors of current watershed analysis methods (Montgomery et al. 1995). The Federal Water Pollution Control Act of 1972 took this focus further by requiring states to devise plans for achieving water quality standards for watersheds in their state taking into account both point and nonpoint sources of pollution. Legislation and amendments to the United States Clean Water Act are a result of an increased understanding of the connections between water quality and landscape patterns and processes. In 1991 the US Environmental Protection Agency (USEPA) implemented a "watershed protection approach" for its water quality management programs which it continues to use today (NRC 1997).

2.2 Land Use and Land Cover

The link between land cover and water quality is well documented at the watershed level (Hyde 1982; Tong and Chen 2002; Tang et al. 2005) and is complex spatially and temporally (Turner et al. 2001). Landscape changes driven by human activity impact sediment and nutrient budgets in watersheds as well as biotic and abiotic properties of stream ecosystems (Turner et al.

2001; Gergel et al. 2002). The impacts of land cover and land-cover change on hydrologic processes have been identified as a major focal area for research for the future (DeFries and Eshleman 2004).

Understanding the relationship between land cover and water quality is critical for understanding the spatiotemporal patterns and trends of water quality (Ning et al. 2006). Water quality is highly dependent on the landscape's natural ability to regulate flows and to filter out impurities (O'Neill et al. 1997). Land cover surrounding a stream can provide useful information about the likely condition of water in that stream and can even serve as an indicator of risk (Wickham et al. 2000). Landscape indicators that quantify the amount of land converted to human uses (e.g., proportion of riparian urban land cover) often explain water quality variations among watersheds (Gergel et al. 2002).

Certain land cover types have minimal impacts to water quality. For example, undisturbed forest lands, rangelands, and natural grasslands have almost no impact on water quality. Vegetation cover on such lands shields soils from rainfall thus preventing excessive runoff except during the most extreme events. Precipitation can permeate the soil more readily which helps to maintain the hydrologic cycle. Riparian land cover is important because riparian systems serve as natural buffers for protecting streams. Vegetated riparian buffers can help control the transport of nutrients and sediments as well as other pollutants from urban runoff into freshwater streams; freshwater is particularly sensitive to adjacent land cover (Turner et al. 2001). The removal of vegetation from riparian buffer areas permits increased transport of sediment, nutrients from fertilizers, and industrial chemicals into streams.

Adjacent agricultural land cover is a useful indicator of water quality and likely risk (Turner et al. 2001; Ebert and Wade 2004). Agriculture supplies nutrients from fertilizers and livestock waste, pathogens from livestock such as bacteria and manure applications, pesticide chemicals, and sediment from land clearing and crops. Agriculture occurring on steep slopes is also an important indicator of risk. Nine percent is a common definition of a steep slope where soil erosion begins to increase, as per Natural Resource Conservation Service guidelines (McCool et al. 1987), and has been used in similar studies (e.g. Smith et al. 2001). In addition to rainfall, irrigation serves as a direct application of a transporting medium to lands which have readily available pollutants. Past agricultural activities such as the application of DDT and chlordane, still persist, with concentrations occurring in sediment, surface waters, and freshwater biota (USGS 1999).

Urban land cover is known to be detrimental to water resources. Urbanized areas contribute pollution from sources including automobiles, development, industry, and impervious surface cover (O'Neill et al. 1997). Stormwater runoff during precipitation events provides a transport mechanism for NPS pollutants. Urban runoff can be similar to raw sewage in terms of chemical and biological makeup (Rogers 1991). Studies have shown that a proportion of urban land cover as little as 5 to 10 percent can result in stream degradation (Arnold and Gibbons 1996). A proportion of as little as 5 percent overshadows most impacts resulting from agricultural land cover (Baker 2003). Increased risk of nitrogen and phosphorus loading in streams and lakes is also a result of urban land cover (Wickham et al. 2003).

Impervious surface, or any surface that prevents the infiltration of water into soil, is arguably one of the greatest land-cover threats to water resources (Arnold and Gibbons 1996). Human development drives the increase of impervious surfaces in a watershed and generally correlates highly with population density. Consequences of such development include water supply modification, increases in water demand, and changes in water quality (DeFries and Eshleman 2004). Humans and species, both of which are dependent on such resources, are affected by such changes. Ten percent coverage of impervious surface area is generally acknowledged as the threshold where water quality degradation begins to occur (Figure 2.1). Arnold and Gibbons (1996) note several studies which have affirmed the ten percent cover threshold.

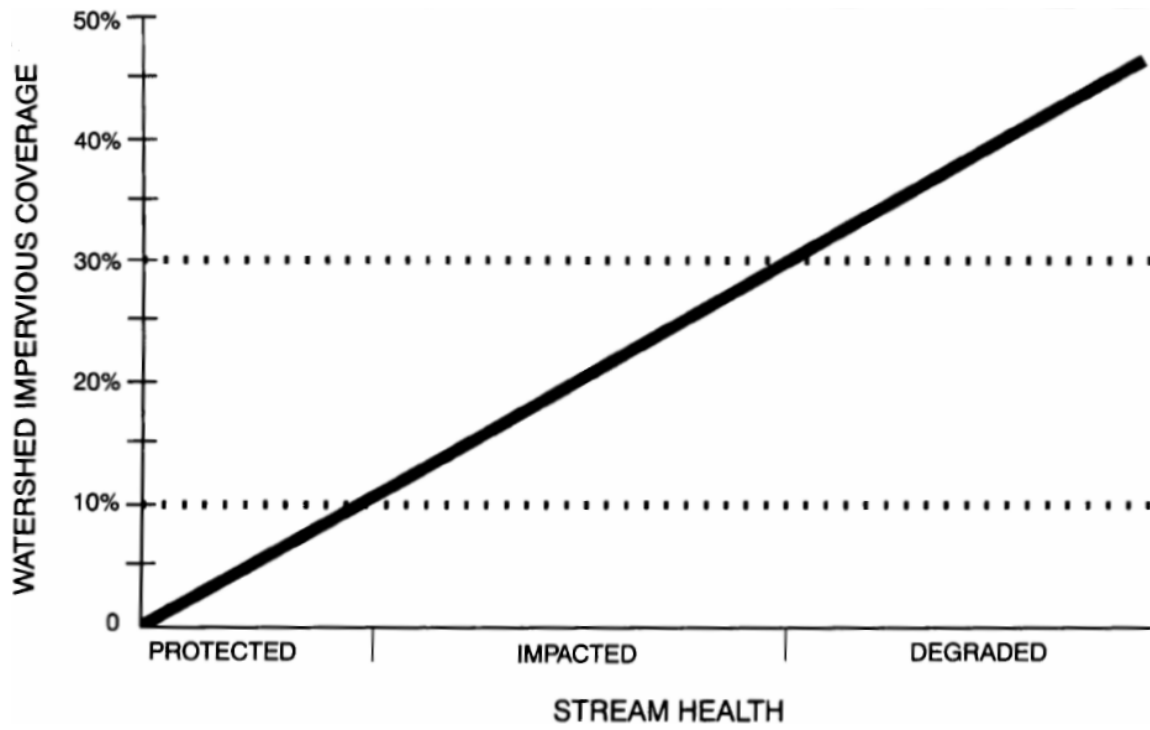


Figure 2.1. Relationship of Impervious Surface Coverage to Stream Health (adapted from Schueler 1992)

Increased impervious surface proportions impact the hydrological cycle and subsequent water quality. Velocity and volume of runoff increase since rainwater cannot penetrate downward through impervious surfaces. Impacts include increased flood frequency and flash flooding, changes in streamflow and groundwater recharge, changes in evapotranspiration rates, increases in environment temperatures (e.g., the urban heat island effect), and habitat alterations. Stream habitats can become filled in with sediment or be completely washed away as “flashy” runoff during peak discharges surmounts normal condition thresholds. Roads within a certain distance of streams can also serve as an indicator of development and anthropogenic impacts. This indicator is useful because vehicle-related chemicals (e.g., oil and grease, antifreeze), in addition to road salt and sediment, are often washed via runoff during precipitation events. Streams occurring near roads will often receive such runoff directly (Ebert and Wade 2004).

2.3 Non-Point Source Water Pollution

NPS pollution is important and difficult to address. Multiple causes (e.g., stormwater runoff, seasonal variations, anthropogenic activities) and multiple effects (e.g., degraded drinking-water supplies, increased water treatment costs, impairment of aquatic and terrestrial ecosystems) create management complexity (Randhir et al. 2001). Unlike point-source pollution, NPS pollution is characterized by pollutants that cannot be traced to a single source (e.g., a pipe) but instead are dispersed over large geographic areas. Agricultural and urban areas are important contributors of NPS pollution (Turner et al. 2001). Sources of NPS pollution include mining, construction, timber harvesting, erosion, and landslides. Seasonal and climate-dependent factors such as runoff and atmospheric deposition can also cause NPS pollution (Basnyat et al. 2000; Randhir et al. 2001). Two common forms of NPS pollution include sediment and nutrients (e.g., nitrogen and phosphorus), two of the most frequently cited causes of impairments in the state of Tennessee (USEPA 2008b).

Natural processes can contribute to, exacerbate, and further complicate NPS loading and concentrations. In-stream flow levels and precipitation events can determine the magnitude of a pollutant's effect. The loading of NPS pollutants into water bodies can vary greatly as loading patterns may not consistently coincide with discharge levels (Gordon et al. 2004). The rising stage of a hydrograph will typically have higher concentrations than the same discharge on the falling limb of a hydrograph. The “first flush” effect of a rainfall event occurs when runoff initially picks up higher concentrations of available pollutants. As the supply is exhausted, concentrations will drop. In the case of sediment, coarser sediment particles deposit out quickly after discharge begins to reduce during the falling limb. Goonetilleke et al. (2005) discuss some of the management and economic implications of the first flush effect in urban water quality scenarios.

Anthropogenic factors can contribute to and exacerbate NPS pollutant loading in streams. Changes from natural land cover (e.g., forest) to modified land cover (e.g., urban) creates conditions that promote NPS pollution. Seasonal activities such as crop planting schedules result in variations in the timing and concentrations of such NPS pollutants as nitrogen, phosphorus, and sediment. Precipitation in urban areas can result in chemicals and sediment being washed into streams as a result of stormwater runoff.

Early studies of NPS pollution and water quality focused on the effects of agricultural land runoff as a significant contributor of nutrients and sediment (e.g., Omernik 1976; Omernik 1977; Omernik et al. 1981; McCool et al. 1987). More current studies have extended such work using new methods (Jones et al. 1997; O'Neill et al. 1997; Harding et al. 1998; Basnyat et al. 2000; Tong and Chen 2002; TVA 2003; Wickham et al. 2003; Tang et al. 2005) and by examining other factors such as impervious surface cover (Arnold and Gibbons 1996). Various landscape metrics (e.g., Riitters et al. 1995) and characteristics of suburbanized lands (e.g., “suburban sprawl”) have gained attention as well (Robbins et al. 2001; Robbins and Birkenholtz 2003). Programs such as the US Environmental Protection Agency Regional Environmental Vulnerability

Assessment Program continue to study the connections between ecosystem health and landscape change (e.g., Tran et al. 2004) using new methods and approaches.

2.4 Indicators of Water Quality

Ammonia Nitrogen as N (NH_3), as part of the “nitrates” category of indicators, is connected to the decomposition of nitrogenous matter and can serve as an indicator of contamination from sewage and septic systems, fertilizers, wastewater treatment plants, and runoff from agriculture and livestock operations (USEPA 2006b). Nitrite and Nitrate ($\text{NO}_2 + \text{NO}_3$) represent the sum of nitrate and nitrite concentrations in water. Total kjeldahl nitrogen (total KN) represents the sum of NH_3 , organic nitrogen, and inorganic nitrogen (NH_4 also known as ammonium). Nitrates in excessive amounts can cause eutrophication. Eutrophication is the increase in an ecosystem's primary productivity associated with excessive plant growth (e.g., algal blooms) and subsequent plant decay. This, in turn, results in increased oxygen demand or hypoxia, which is a lowered level of dissolved oxygen (USEPA 2008d).

NH_3 is a key component of the first part of the nitrification process (USEPA 2002b). Nitrification is the process by which nitrogen compounds are converted to nitrite and nitrate. The nitrification process is influenced by NH_3 concentrations, temperature, pH, light, and available oxygen levels. Nitrite, or NO_2 , is the product of the first step of nitrification. Oxygen and ammonia-oxidizing bacteria are necessary ingredients for this process to occur, which is one reason increased nitrification can stress dissolved oxygen (DO) levels in streams. DO is also necessary, along with nitrite-oxidizing bacteria, for the second step of the nitrification process, which results in NO_3 . Both steps of the nitrification process can result in lowered alkalinity, pH, DO, and increased bacterial growth (USEPA 2002b). Alkalinity and pH are also important in conjunction with NH_3 and NO_2 and NO_3 for monitoring the nitrogen cycle (Scott 2008).

DO is oxygen in its dissolved form in water. DO levels are important for supporting aquatic life respiration and DO is a general indicator of stream health (USEPA 2006e). The breakdown of organic materials via decomposition (e.g., nitrification), stormwater runoff, feedlots, and failing septic systems can lower DO levels. Water temperatures also affect DO, as warmer water holds less oxygen than cooler water.

Temperature determines the rates of biological and chemical processes (e.g., nitrification) in addition to influencing DO levels. Temperature can affect plant photosynthesis rates and the ability of certain plants and animals to survive as many species have optimal environment temperature ranges. Water temperatures can be driven outside normal ranges by, for example, urban storm water runoff, weather, or alteration of riparian vegetation. These deviations can stress biota and natural stream processes.

Total phosphorus (total P) is another important nutrient, in addition to nitrogen. Total P includes orthophosphate, condensed phosphate, and organic phosphate, and enters surface waters through rainwater, plant residue, absorption into sediment, runoff from fertilized lawns and cropland, animal waste, soil and rocks, wastewater treatment plants, failing septic systems, and commercial cleaning preparations (USEPA 2006c). Phosphorus, like nitrogen, is necessary for both plants and animals. Concentrations are normally low in fresh water; however, so even a slight increase in concentration can serve as an impetus for accelerated plant growth via eutrophication.

Specific conductance can serve as a useful indicator of stream behavior and condition relative to the surrounding landscape. Conductivity measures how well water can pass an electrical current and is influenced by the amount of dissolved solids in a stream. The presence of inorganic dissolved solids includes anions (ions that carry a negative charge) such as nitrate, phosphate, and sulfate and cations (ions that carry a positive charge) such as sodium,

magnesium, and calcium (USEPA 2006a). Conductivity is greatly influenced by the geology and soil of the surrounding landscape. High levels of conductivity in a forested watershed might indicate the presence of effluent streams receiving water, from, for example, a karst geological environment.

Land cover and land use in a watershed can also affect conductivity. Failing sewage systems can also raise conductivity because of the presence of chloride, phosphate, and nitrate (USEPA 2006a). Dissolved materials and pollutants transported via urban runoff, mining activities, and land-cover/land-use change can result in increased conductivity levels. Water temperature also influences the ability of water to conduct electricity in that warmer temperatures promote higher conductivity. Consequently, the standard temperature for reporting conductivity is 25 degrees Celsius.

Total hardness primarily represents the concentrations of calcium and magnesium (Ca^{2+} and Mg^{2+}) ions in water. Municipal water supplies known for having “hard” water have water with higher levels of calcium and magnesium. The primary sources of calcium are calcium carbonate (CaCO_3) from drainage of calcareous sediments, such as limestone and chalk, or calcium sulfate (CaSO_4) (Murphy 2007). Magnesium comes primarily from dolomite ($\text{CaMg}(\text{CO}_3)_2$). It is estimated that 89.3 percent of US homes have hard water; Tennessee is noted as having moderately hard waters in many rivers (Briggs and Ficke 1977). Hard water is likely to exhibit higher levels of conductivity as calcium and magnesium are both cations.

Sediment, including total suspended solids (TSS), is one of Tennessee’s primary forms of nonpoint source pollution (TDEC 2002a; TDEC 2004a; TDEC 2006b; TDEC 2008). TSS consists of particulate matter that can be removed via filter from a water sample. TSS can include both organic materials (e.g., plant debris and decaying plant matter) and mineral particles (e.g., clay and silt) and can impact overall stream health, stream biota, and the ability to process and use water resources. Sources of TSS can be both human (anthropogenic) and natural. Natural geologic erosion can influence particle size and the levels of solids in a stream (both dissolved and suspended). Natural debris slides and hill slope failures can also contribute sediment due to natural phenomena such as the freeze/thaw action of rock and soil during the cold months of the year. Stream bank erosion can contribute to TSS during high-flow events resulting from, for example, “flashy” urban runoff, and can be influenced by such characteristics as stream channel shape, bank vegetation cover, and bank composition (e.g., alluvial vs. bedrock).

Anthropogenic changes can have serious consequences and long-term effects on sediment loading in streams. Broad-scale land cover change, including the clearing of forests for residential/urban development or for agriculture, can result in sediment inputs into local streams. Vegetation naturally protects soil from the impacts of raindrops through interception and from runoff-transported sediment through the stability added by root systems. When vegetation is removed, soil infiltration of rainfall is likely to decrease due to the packing down of exposed soil from rain drops. Overland flow resulting from impervious and compacted surfaces serves as a transport mechanism for sediment. Sediment transported by runoff also serves as a transport mechanism for nutrients (e.g., phosphorus and nitrates resulting from agriculture) and toxic substances (e.g., heavy metals, polychlorinated biphenyls).

Increased levels of TSS can result in aggradation. This is the deposit of sediment and subsequent building up of the stream bed. Aggradation of a stream occurs when the streams capacity for transporting higher TSS levels is exceeded (Gordon et al. 2004). Higher TSS levels can also impact the organisms in a stream by adding particulate matter, or “fines,” to stream beds. This can affect small organisms by suffocating them and/or burying them and trapping their eggs and young (Gordon et al. 2004).

Turbidity is usually but not always associated with high levels of TSS (USEPA 1999b; Lewis et al. 2001). Turbidity can affect temperature, gas exchange, decomposition rates, and photosynthetic processes (Hart 2006; USEPA 2006d). Turbidity is a measure of the degree to

which light can penetrate water. Organisms, particularly plants, are affected by turbidity via their ability to carry out activities such as photosynthesis. High levels of TSS and turbidity can impact water temperatures because suspended particles hold more heat. Higher levels of turbidity resulting from higher levels of TSS can also impact the ability of fish to see in water and find food.

2.5 Water Quality and Total Maximum Daily Loads (TMDLs)

The United States Clean Water Act (CWA) was passed in 1972 with the purpose of protecting surface water quality in the US. The act requires that states identify and report polluted waters that do not comply with established usage criteria (US Congress 2002). The CWA was amended in 1987 to include the requirement for states to address nonpoint source pollution (USEPA 2008a). Section 319 of the CWA mandates that water quality be managed at the state, territory, and tribal level for mitigation and accountability purposes. Section 303(d) established the Total Maximum Daily Load (TMDL) program as a standardized framework for water quality management (US Congress 2002). All states must establish water quality standards, designated uses for waterbodies, and develop a list of threatened and impaired water bodies as per section 303(d) of the CWA. These are known as “303(d) lists” or the “Threatened and Impaired List.” State water quality standards require EPA approval every three years. The CWA also specifies that states are to produce a summary report every two years that describes water quality issues and water bodies that are currently polluted as per section 305(b). This is known as the 305(b) report. EPA uses state 305(b) reports to compile the National Water Quality Inventory Report to Congress.

A TMDL is “the sum of the individual wasteload allocations for point sources and load allocations for nonpoint sources and natural background with a margin of safety” (USEPA 1999a). In other words, a TMDL establishes the maximum amount of a specific pollutant that a waterbody can receive and still meet the water quality standards associated with its designated use. A margin of safety is included for the purpose of accounting for uncertainty about the relationship between pollutant loads and receiving water quality. Several factors must be considered during TMDL development for pollutants. These factors include point source (wasteload) allocations, nonpoint sources (load) allocations, background levels pertaining to the pollutant for a stream segment, and both existing and future pollutant loadings (TDEC 2006b). Additional TMDL considerations include temporal (seasonal or interannual) variations and the combined effects of pollutants (USEPA 1999a; USEPA 1999b).

2.6 Relevant Local and Regional Studies

Hart (2006) studied sediment loading in the LR watershed after storm events as well as the effects of adjacent land use on TSS measurements. Water quality samples were collected after storm events in the LR to quantify the relationship between TSS and turbidity. Hart also examined long-term trends in turbidity data from a Blount County water treatment plant. Results of the study concluded that land use (and subsequently land cover) is a major factor of influence on both sources and quantities of sediment in the LR. Higher levels of TSS were found in both agriculture and urban land use areas. Hart found significant positive correlations, at a 95 percent probability, for TSS and percent imperviousness, for TSS and percent urban land use, and for TSS and percent agriculture, and a negative correlation between percent forest and TSS. She also found positive correlations between TSS and rainfall, and noted that TSS and turbidity levels in the LR are highly correlated at a 99 percent significance level.

Sutherland (2004) examined the effects of excess sediment and nutrients on aquatic organisms in the Nails and Ellejoy Creek subwatersheds in the LR. The primary objective was to assess the impact of sediment loading on aquatic organisms in the aforementioned watersheds. Sutherland focused on NPS pollutants, including total phosphorus, nitrates and nitrites, total

kjeldahl nitrogen, TSS, turbidity, and ammonia nitrogen. Benthic macroinvertebrate data were also collected in addition to physical habitat data. Sutherland found that nitrates were associated with low species diversity in both watersheds. Agricultural lands were found to be a significant contributor of sediment and nutrients, accounting for over 70 percent of inputs in the LR. In addition, Sutherland found that poor bank conditions and poor benthic habitats were correlated, which indicates that aquatic life is influenced by land use in the LR.

Moniodes (2004) looked at the appropriateness of broad-scale land-cover data and a broad-scale hydrologic model for assessing county-scale areas for nutrient export potential, prioritization, and decision making. Various land cover data sets at different resolutions were used to determine if they were appropriate. In addition, the study examined whether excessive nutrient exports were more likely to occur in the riparian zone or at farther distances from the stream. Land-cover data resolutions evaluated were 10 m, 30 m (NLCD data), and 1 km. An export coefficient model was used to assess the LR watershed for areas of high level nutrient export potential. Results of the study found that broad-scale land cover data, such as the NLCD 30m data set, could be used for prioritizing subwatershed-size areas for nutrient flux remediation at the county mapping scale. The study also found that LR nutrient flux areas were primarily in non-riparian areas of the watershed.

The Tennessee Valley Authority (TVA) Integrated Pollutant Source Identification (IPSI) study was an in-depth assessment of Blount County/Little River land use for the purpose of estimating pollutant loads based on sources and location (TVA 2003). High resolution photography was used to derive watershed features as well as likely NPS pollutant source features. Land use projections were applied to current landscape proportions and pollutant loading models were devised using EPA methods and the Universal Soil Loss Equation (USLE). The results suggest that considerable land-use change will occur across the watershed between the years 2000 and 2020, with the developed/residential land-use type increasing the most. Agriculture was predicted to decrease slightly across the watershed, likely as a result of conversion to urban land uses. Urban land uses would become the primary source of nutrients (total phosphorus and total nitrogen) along with zinc.

Climate change is an important consideration for water resource managers and is already showing impacts in the United States (Miller and Yates 2005). Mulholland et al. (1997) discuss the implications of climate change for the southeastern United States and the Gulf Coast of Mexico. Regional climate model results suggest that changes in atmospheric composition may result in an increase of temperature and a subsequent increase in precipitation, but an even greater increase in evapotranspiration in the Southeast. Storm intensities are anticipated to increase, resulting in larger peak flows but, overall, lower base flows and periods of drought will occur. Mulholland et al. (1997) discuss several anticipated ecological impacts and also note that climate changes are expected to exacerbate current anthropogenic stresses. Areas of research recommended, given the anticipated changes, include long-term monitoring of key hydrological and chemical properties as well as a thorough assessment of the effects of current water management activities on organisms and ecosystems.

This study will contribute to and build on the aforementioned literature. Compiling data from various sources allowed the breadth of existing data to be evaluated for usability (e.g. formatting, parameters, sampling consistency, etc.); it is uncertain as to whether such an undertaking had been done for the LR. Quantitative information is now available on associations among water quality parameters as well as similarities and differences of both water quality and land cover proportions across the watershed. This information can be used to prioritize what to monitor and where. In addition, quantitative information is available on land-cover change in the LR, which can be used as an indicator of potential future water quality risk.

2.7 Quantitative Methods for Studies of Water Quality

Multivariate statistical techniques are both appropriate and useful for studies of water quality. Numerous studies have demonstrated the utility of such methods in water quality assessment and management (e.g., Helsel and Hirsch 1992; Vega et al. 1998; Haag and Westrich 2002; Reghunath et al. 2002; Simeonov et al. 2003; Shrestha and Kazama 2007). Methods exist for confirming statistically significant differences, determining underlying relationships among variables, elucidating relationships between cases for classification, and predicting group membership based on key variables. Understanding how water quality varies both spatially and temporally, as well as which indicators best represent variance, is critical for monitoring protocol design and making decisions.

Water quality vary over space and time. Nonparametric analysis of variance (ANOVA), also known as Kruskal-Wallis ANOVA, is a quantitative method for determining whether differences between sample times or between sample sites are greater than those within sample groups. St-Hilaire et al. (2004) used nonparametric ANOVA, to test for the existence of significant differences between samples from multiple sites in Canada. Tong and Chen (2002) used a similar approach but with land-use type proportions in a study of land use relationships with water quality in Ohio. Vega et al. (1998) used ANOVA tests to verify the existence of seasonal and spatial differences in the Duero River Basin of North-Central Spain. Use of nonparametric ANOVA could also be extended to physical stream characteristics (e.g., flow) as well as geomorphological and habitat metrics.

Large and complex water quality data sets with many variables require robust tools for extracting information for decision making. Principal Component Analysis (PCA) is an exploratory multivariate statistical technique that has been widely applied to water quality research (Vega et al. 1998; Wunderlin et al. 2001; Singh et al. 2004; Goonetilleke et al. 2005). PCA is useful in studies of water quality as it highlights underlying relationships between variables. In addition, PCA works to determine the variance contributed to a data set by parameters. Parameters can then be prioritized for monitoring based on their interrelationships and their overall influence on the water quality data.

Simeonov et al. (2003) successfully applied PCA to a study of water quality in northern Greece and were able to account for 90 percent of the data set variance. Water quality parameters were then apportioned to their respective contributing sources based on underlying parameter relationships. Haag and Westrich (2002) used PCA to determine whether or not underlying watershed processes were active at individual sampling sites in the River Neckar Region of Germany. In addition, they successfully used PCA to determine changes in underlying processes based on a comparison of PCA results on historical data and recent data. Santos-Roman, Warner, and Scatena (2003) used PCA to successfully identify parameters that represented water quality in a Puerto Rican watershed. The number of parameters needed to represent water quality conditions in their study watershed was reduced by 66 percent from 18 to 6 as a result of their study.

Geographic analysis of water quality can be complex without methods for elucidating similarities and differences between sample locations and between sample periods. Cluster analysis (CA) is a common pattern-recognition analysis that has been widely used in studies of surface water quality (Vega et al. 1998; Reghunath et al. 2002; Singh et al. 2004; Shrestha and Kazama 2007). The most common form of CA applied to studies of water quality works to maximize the similarities of cases within groups and maximize differences of cases between groups. Singh et al. (2004) applied CA to water quality data from the Gomti River region of India and were successful in reducing the number of sampling sites in their monitoring network as a result of the site classifications. Simeonov et al. (2003) discussed the use of results from a CA of water quality data for developing a rapid water quality assessment protocol. St.-Hilaire et al.

(2004) incorporated results of a PCA of water quality into a CA by only clustering water quality variables that exhibited a large influence on their data set. As a result, combined use of PCA and CA allowed them to prioritize processes influencing water quality as well as the regions in their study area where water quality was not optimal for aquatic biota.

Additional methods exist for spatiotemporal pattern recognition and water quality parameter prioritization. Discriminant Analysis (DA) has been successfully applied to water-quality studies for data reduction and pattern recognition (Wunderlin et al. 2001; Singh et al. 2004; Shrestha and Kazama 2007). Interestingly, Wunderlin et al. (2001) noted that DA had not been applied to water-quality analysis nearly as frequently as CA and FA/PCA in previous studies. However, Wunderlin et al. (2001), Singh et al. (2004), and Shrestha and Kazama (2007) all found that DA gave as good if not better results for spatiotemporal pattern recognition and reduction of data set parameters.

DA is useful for studies of water quality because it works to determine which predictor variables differentiate best between two or more known groups. DA devises a predictive equation for classifying cases into predefined groups. Interpretation of the predictive equation coefficients provides a better understanding of predictor variable relationships. Wunderlin et al. (2001) used a DA of water quality data to determine which subset of parameters significantly contribute to predefined seasonal and spatial groups in the Suquia River Basin in Argentina. Santos-Roman, Warner, and Scatena (2003) incorporated results of a CA of physical watershed attributes into a DA to determine which attributes best distinguished each group. Shrestha and Kazama (2007) also found that DA gave results useful for identifying a reduced number of key water quality parameters responsible for a large proportion of data set variation in a study of the Fuji River Basin in Japan.

Chapter 3 Study Area

The proposed watershed for this study is the HUC-10 (HUC 0601020101) LR watershed, an EPA Targeted Watershed for 2005 (USEPA 2005). Located primarily in Blount County, the LR is the main source for the county's drinking water and also supports several state and federally listed plant and animal species (USEPA 2005; Little River Big Future 2006). Nonpoint source pollution from urban development and agriculture are the prominent pollution types in the LR watershed (Little River Big Future 2006). The LR watershed has two EPA-approved TMDLs: one for pathogens such as *E. coli* (TDEC 2005) and one for habitat alteration/siltation (TDEC 2006a). Habitat alteration, siltation, and pathogens such as *E. coli* are the top three cited causes of water-quality impairment in Tennessee (TDEC 2006a). Other problems, such as contaminated sediment from polychlorinated biphenyls (PCBs), a documented decline in biodiversity, and nitrates, also have been identified in the LR watershed (TDEC 2006b). Factors influencing the decline in biodiversity have yet to be identified.

3.1 Physiography, Geology, and Soils

The LR itself originates in the Great Smoky Mountains National Park (GSMNP); the portion of the river in the Park is considered a reference stream and is classified as Outstanding Natural Resource Waters (TDEC 2006a). The river is perennial and flows northwestward from the Park into the Tennessee River. The LR basin, located in the Upper Tennessee River Basin, drains 98,018 hectares in Knox, Blount, and Sevier counties, with most of the basin (70,192 hectares) in Blount County. Elevations range from approximately 400 m at the mouth of the river to above 2000 m at the highest headwaters. Most of the watershed lies in the Blue Ridge level 3 ecoregion, while the northwest portion lies in the Ridge and Valley level 3 ecoregion and physiographic province. The climate is primarily temperate, and temperature and precipitation are largely dependent on local elevation. Average annual precipitation can range from 102 centimeters in the lower lying Valley and Ridge areas to upwards of 229 centimeters in high elevation areas of the GSMNP (Hampson et al. 2000).

The portion of the LR basin found in the Valley and Ridge physiographic province/level 3 ecoregions is also known as the Tennessee Valley. This area consists of linear ridges and valleys which create a rolling to hilly landscape that varies from level flat areas to steep relief. The prominence of limestone bedrock in the Valley and Ridge physiographic region creates a landscape replete with karst topography and caves. Karst settings are noted as being more vulnerable to ground water contamination as a result of disappearing streams, caves, and sinkholes that provide direct pathways for contaminants into ground water (Johnson 2002).

Bedrock in the area is primarily metamorphosed sedimentary rocks of the late Precambrian age, with the dominant geologic units consisting of the Elkmont and Thunderhead Sandstones. Intense folding and faulting has resulted in areas of bedrock inclined at high angles or entirely overturned. The massive feldspathic sandstones of the LR are composed of quartz, potassium feldspar, plagioclase, and metamorphic biotite, muscovite, and chlorite (Mast and Turk 1999). Ridges in the Tennessee Valley are underlain by low-grade dolomites, sandstones, and shales, while limestones and interbedded limestones and shales underlie the valleys between ridges (Robins et al. 1979). The Anakeesta Formation, found in the southeastern portion of the LR basin in the GSMNP, consists of frequently outcropped rocks with levels of iron sulfide. This pyritic carbonaceous phyllite occurs at higher elevations and is prone to mass wasting as a result of weathered conditions and steep slopes. The Anakeesta Formation is also known to have a significant influence on the pH of water in the GSMNP. Water in contact with the iron sulfide pyrite of Anakeesta Formation rocks and sediments releases sulfuric acid (Barnett 2003).

Soils in the LR basin consist of Inceptisols which are generally deep, well-drained soils (USDA 1959). Soils in the southeast area of the LR in Blount County in HUC-060102010103 are primarily from the Ramsey soil series. This series, found with rocky outcrops of slate or quartzite, consists of silt loams on steep to moderate slopes and loamy fine sands on river bottoms (USDA 1959). Soils in the central area of HUC-060102010105 are mainly of the Dandridge Whitesburg Hamblen series and consist of shaley silt loams and alluvial silt loams occurring on eroded, moderately steep slopes and gentle slopes, as well as on river bottoms (USDA 1959). Soils in the southern portion of HUC-060102010107 are of the Sequoia Litz Hamblen series and consist of severely eroded silty clays, silty clay loams, shaley silty clay loams, and silt loams, found on moderate and gentle slopes and on river bottoms (USDA 1959). Soils found in the central portion of HUC-060102010107 are in the Dunmore Pace Greendale and Sequoia Litz Hamblen series. These are composed of silt loam, silty clay, silty clay loam, and shaley silty clay loams, on steep, moderate, and gentle slopes (USDA 1959).

3.2 Land Cover and Vegetation

Land cover in the LR watershed consists of 60 percent forest (25 percent of which is the GSMNP), 25 percent agriculture (pasture, cropland, livestock, dairy and horse farms), 4 percent commercial/industrial, and 10 percent residential, according to the TVA IPSI study (TVA 2003). Development has increased as a result of tourism outside of the GSMNP and urbanization near the cities of Maryville and Alcoa (Ezzell et al. 2005). Vegetation found in the LR basin is primarily hardwood-hemlock forests, including hemlock, dogwood, yellow poplar, red maple, white maple, black oak, sweet birch, white pine, short leaf pine, pitch pine, and sumac (USDA 1959).

Chapter 4 Data and Analytical Methods

4.1 Water Quality Data

Water quality data used in the study were from EPA STORET—both Legacy (pre-1998) and Modern (post-1998) systems as well as from the USGS National Water Information System (NWIS). Because the study area is at the HUC-10 level and the STORET systems only query up to a HUC-8 level, additional processing with GIS tools was carried out to identify sampling locations that fell within the HUC-10 watershed boundaries. Additional water quality data were obtained from the Tennessee Department of Environment and Conservation (TDEC) (contact person: Linda Cartwright at the TDEC office in Nashville, Tennessee).

As data standardization is important for any statistical analysis, water quality data used in the study were reformatted and standardized prior to analysis (St-Hilaire et al. 2004). The data reformatting and standardization to combine data from EPA STORET, the TDEC Access database, and the USGS NWIS system were carried out automatically via several Visual Basic macros run in Microsoft Excel to assure consistency throughout the process. Several data source-related issues emerged during the process. For example, there were mismatches between IDs obtained from STORET and the data in the TDEC Access database. No metadata or data dictionary was provided with the TDEC Access database. Sampling site ID name changes also had to be addressed. Parameter names had to be standardized for all data from both STORET systems, the TDEC Access database, and the USGS NWIS system. Limited or non-existent documentation greatly increased the complexity of this task. Parameters and associated data were cross-walked from the three systems to the best of the ability given time, resources, and information available.

Further complexity resulted from the fact that neither of the data sets in the two STORET systems nor the data set in the TDEC Access database contained all data available for the LR. For example, the TDEC Access database contained data primarily after 1998 for the two study areas, but also included some data before 1998. In many instances, TDEC and other agency records in the STORET systems, particularly the Legacy STORET system, were not in the TDEC Access database, and data several years back in the TDEC Access database (both sampling site IDs and data records) were not in the STORET system. There were also general data quality/data entry error issues with the TDEC Access database that had to be addressed during assessment (e.g., activity dates such as 9-31-05; September does not have 31 days). It was also unclear why site IDs in the TDEC Access database had no data associated with them either in the STORET system or in any additional legacy dBase files obtained with assistance from Linda Cartwright at the TDEC office in Nashville.

4.2 Determining Sampling Sites and Water Quality Indicators

Individual sampling sites selected for the analysis are shown in Figure 4.1. However, due to the sample sizes, data from sites within the LR HUC-12 subwatersheds were grouped together to form a larger sample. Figure 4.2 shows the resulting combined sites. In this case, the grouped sample represents a combined site of the individual sites. The purpose of this was to increase the length of the records. To create a combined site, the grouped data points were tested with non-parametric ANOVA tests to determine whether data points could be considered to be from the same population (St-Hilaire et al. 2004).

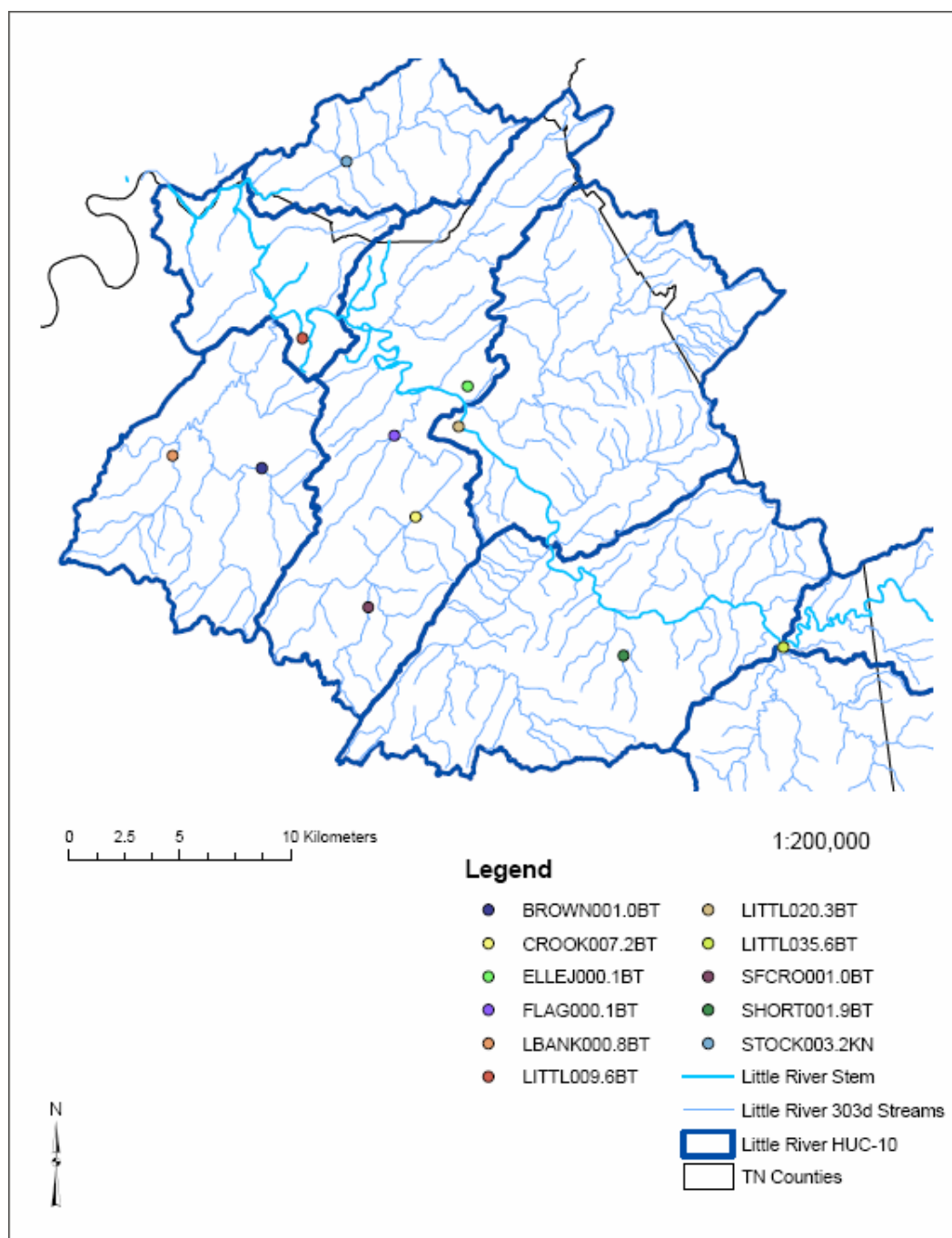


Figure 4.1. Individual Sampling Sites in the Little River Watershed Used for Nonparametric ANOVA Tests of Water Quality Variability

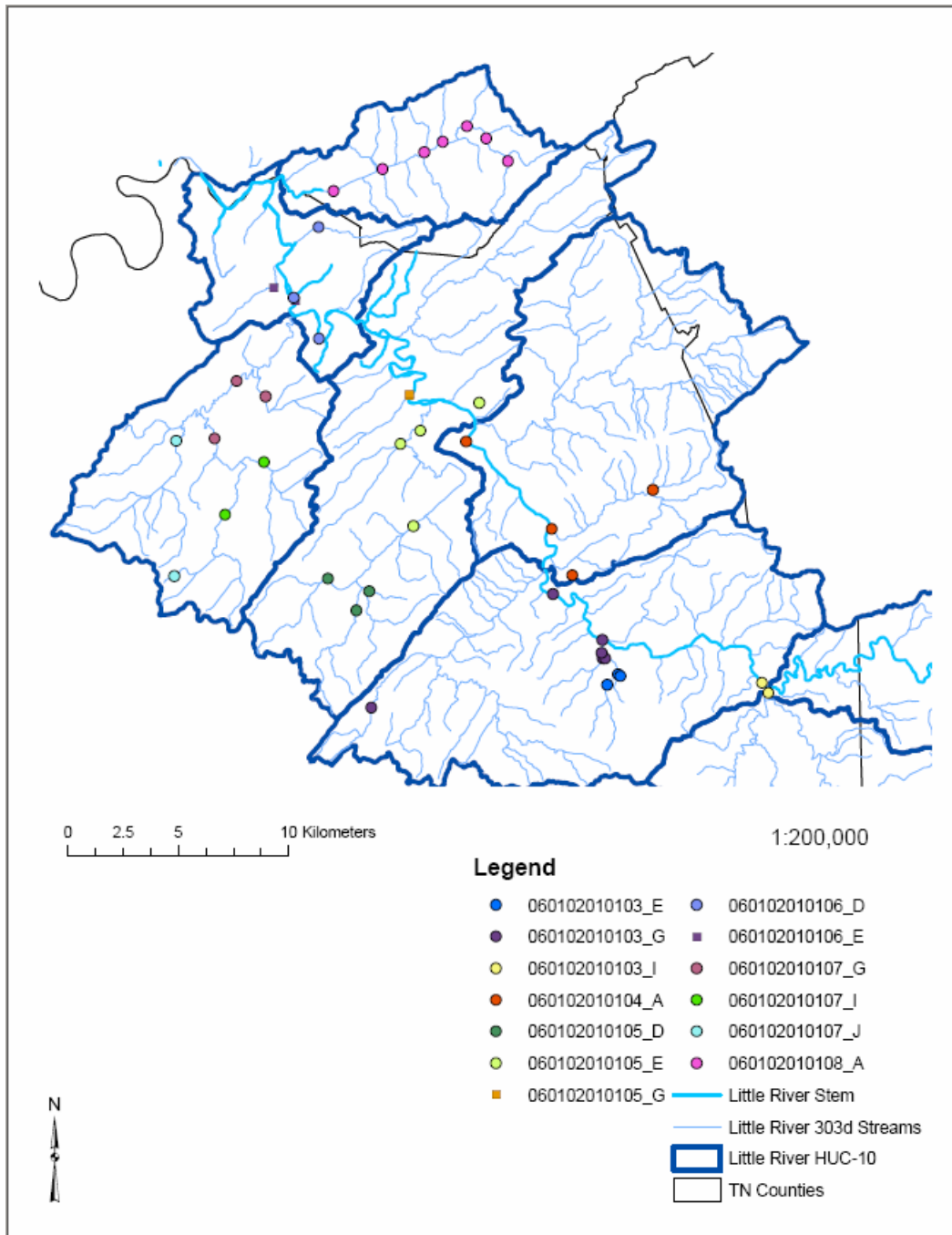


Figure 4.2. Combined Sites in the Little River Watershed

Note: circles represent temporally more recent data; squares denote locations with older data used in combined site “temporal” analyses.

If the ANOVA test was failed, those individual sites would not be grouped together. Tests were iteratively carried out on parameters common to all sites. Sampling sites were iteratively added to or removed from potential groups based on the significance of the ANOVA tests. Sample sites were grouped where ANOVA tests of water quality parameters were not significant. Combined site IDs were assigned based on the HUC-12 in which the combined site is located. The respective letters appended to the end of each combined site ID are a result of the iterative analysis process described above as a means of keeping track of the multi-site test results.

Taking into account the differences in sampling periods at individual sites and the inconsistency of water quality parameters sampled, a suite of key parameters were identified as common to approximately all sampling sites. They included Ammonia Nitrogen (NH₃), Dissolved Oxygen (DO), Temperature, Total Kjeldahl Nitrogen (total KN), Total Phosphorus (total P), Total Suspended Solids (TSS), and Turbidity. These are parameters that are noted as being relevant to studies of land cover, NPS pollution, and the water quality issues in the study area (Arnold and Gibbons 1996; O'Neill et al. 1997; Jones et al. 2001; Turner et al. 2001; TVA 2003; TDEC 2005; TDEC 2006a; TDEC 2006b). Phosphorus and nitrogen are noted as being important to a watershed's water quality (Hagerman 2007). Additional parameters included in the individual site data sets because of data availability were specific conductance, nitrate and nitrite (NO₂ + NO₃), and total hardness (Ca + Mg).

Known point sources in the LR were accounted for by using the EPA Toxic Release Inventory/National Pollutant Discharge Elimination System Permits (TRI/NPDES) data set (USEPA 2007a). The data set includes the source (e.g., a specific manufacturer), the types of pollutants, geographic location, discharge levels (historic and current), permit information, and contact information. The only TRI sites occurring in the LR watershed are in the Pistol Creek area. However, the locations of the sources had minimal discharges and were also downstream of all sites used in this study. Point source pollution is noted as not being a significant issue in the LR (Hagerman 2007).

4.3 Land Cover Data

The Multi-Resolution Land Characteristics Consortium (MRLC) National Land Cover Data (NLCD) Set 1992-2001 Retrofit Change Product for was used for characterizing land cover and land-cover change (MRLC 2007). The NLCD Change Product data set is a fairly new and robust land-cover classification data set resulting from over 15 years of landscape characterization expertise and an overarching need for compatibility of the two original NLCD data sets. The NLCD Change Product was made publicly available via the MRLC web site approximately mid-November 2007 (Vandersnick 2008). The NLCD classification system consists of 21 categories of land cover information at a 30m resolution. The original NLCD land cover data set consists of Landsat 5 imagery from 1992 to 1995 classified based on a modified level 2 version of the Anderson land-use and land-cover classification system (Anderson et al. 1976). The second NLCD data set for 2001 consists of Landsat 5 and Landsat 7 imagery from 1999 through 2001 also classified on a modified Anderson level 2.

The impetus for development of the NLCD Change Product was several inherent differences between the NLCD 1992 and NLCD 2001 data sets, including source image seasonality and georegistration, mapping methods, and classification types and accuracies (MRLC 2008). Any direct comparison of the two data sets for the purpose of determining land-cover change locations, extents, and types of change would result in unavoidable error and uncertainty. To solve this problem, the MRLC devised a methodology for making the two data sets comparable by reclassifying both data sets using a decision tree classifier at Anderson Level 1, the coarsest resolution of land cover/land use detail. An Anderson Level 1 classification was used so that incompatible differences between the original data sets at an Anderson Level 2

classification would be eliminated (MRLC 2008). Though land-cover/land-use detail was lost, considerable information was gained by being able to determine “from-to” changes and the types of changes that occurred (e.g., forest land cover converted to urban land cover). The 9-year imagery interval (in this case 1992–2001) is sufficient for detecting land-cover changes (Coppin et al. 2004).

Table 4.1 shows the differences between the NLCD 1992 and NLCD 2001 data sets. Figure 4.3 shows the Anderson Level 1 classified land cover for the LR watershed, and Figure 4.4 shows NPS pollutant-contributing land-cover change in the LR. The types of change that constituted NPS pollutant-contributing land-cover change are specifically identified in Section 4.6.

Table 4.1. NLCD1992-2001 Anderson Level I Cross-walk Table (adapted from MRLC 2008)

NLCD 1992 Class Code	NLCD 1992 Description	NLCD 2001 Class Code	NLCD 2001 Description	Modified Anderson Level 1
11	Open Water	11	Open Water	1
12	Perennial Ice, Snow	12	Perennial Ice, Snow	8
85	Urban, Recreational Grasses	21	Developed, Open Space	2
21	Low Intensity Residential	22	Developed, Low Intensity	2
22	High Intensity Residential	23	Developed, Medium Intensity	2
23	Commercial, Industrial	24	Developed, High Intensity	2
31	Bare Rock, Sand	31	Barren Land, Rock, Sand	3
		32	Unconsolidated Shore	3
32	Quarry, Strip Mine, Gravel Pit	31	Barren Land, Rock, Sand	3
33	Transitional Barren	31	Barren Land, Rock, Sand	3
33	Transitional Barren	31	Barren Land, Rock, Sand	3
41	Deciduous Forest	41	Deciduous Forest	4
42	Evergreen Forest	42	Evergreen Forest	4
43	Mixed Forest	43	Mixed Forest	4
		51	Dwarf Scrub	8
51	Shrubland	52	Shrub, Scrub	5
61	Orchards, Vineyards, Other			6
71	Grasslands, Herbaceous	71	Grassland, Herbaceous	5
		72	Sedge, Herbaceous	8
		73	Lichens	8
		74	Moss	8
81	Pasture, Hay	81	Pasture, Hay	6
82	Row Crops	82	Cultivated Crops	6
83	Small Grains	82	Cultivated Crops	6
84	Fallow	82	Cultivated Crops	6
85	Urban, Recreational Grasses	21	Developed, Open Space	2
91	Woody Wetlands	90	Woody Wetlands	7
82	Emergent, Herbaceous Wetland	95	Emergent Herbaceous Wetlands	7
		91	Palustrine Forested Wetland	7
		92	Palustrine Scrub Wetland	7
		93	Palustrine Forested Wetland	7
		94	Estuarine Scrub Wetland	7
		96	Palestine Emergent Wetland	7
		97	Estuarine Emergent Wetland	7
		98	Palustrine Aquatic Bed	7
		99	Estuarine Aquatic Bed	7

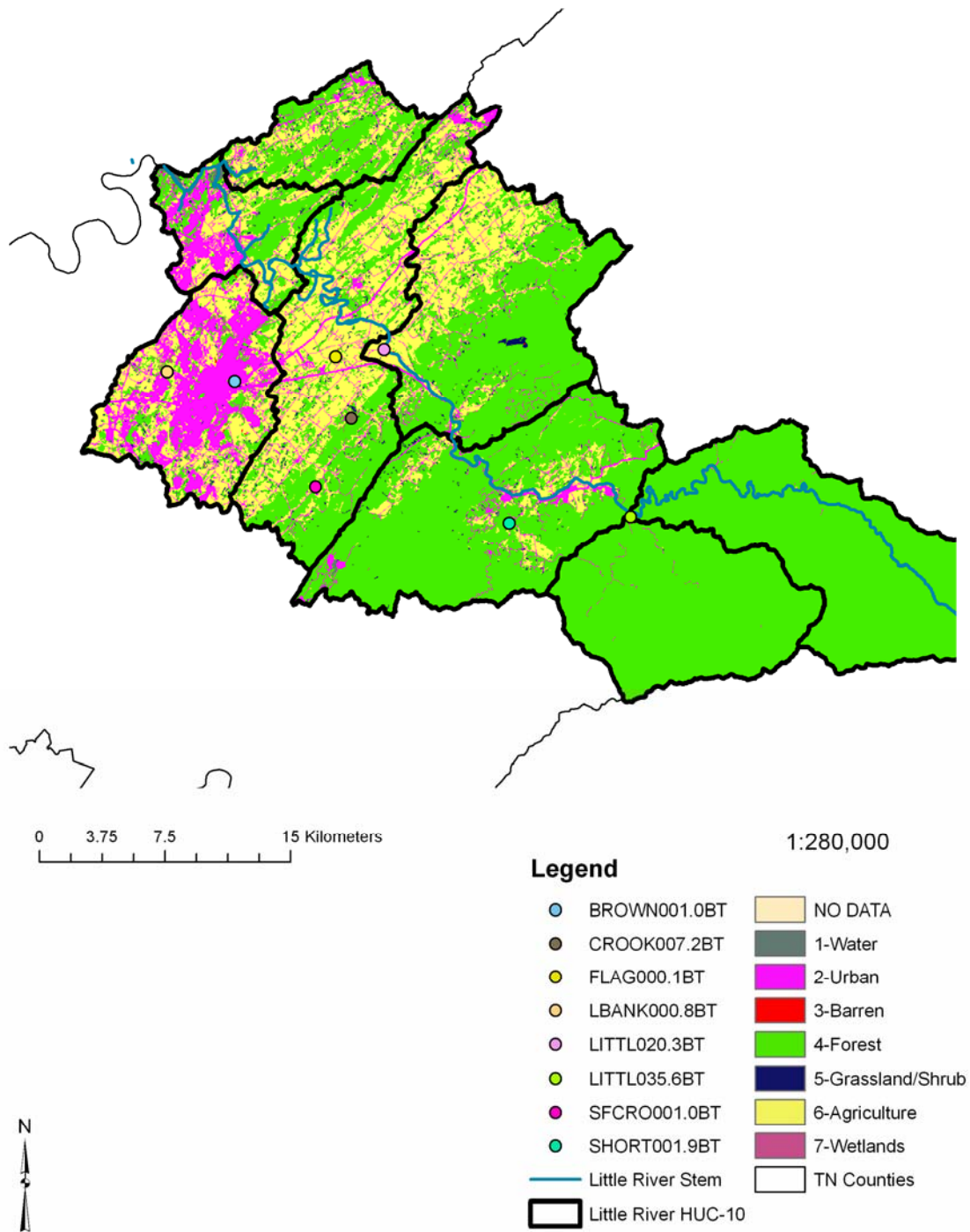


Figure 4.3. NLCD Change Product Re-Classed as Anderson Level I 2001 Land Cover

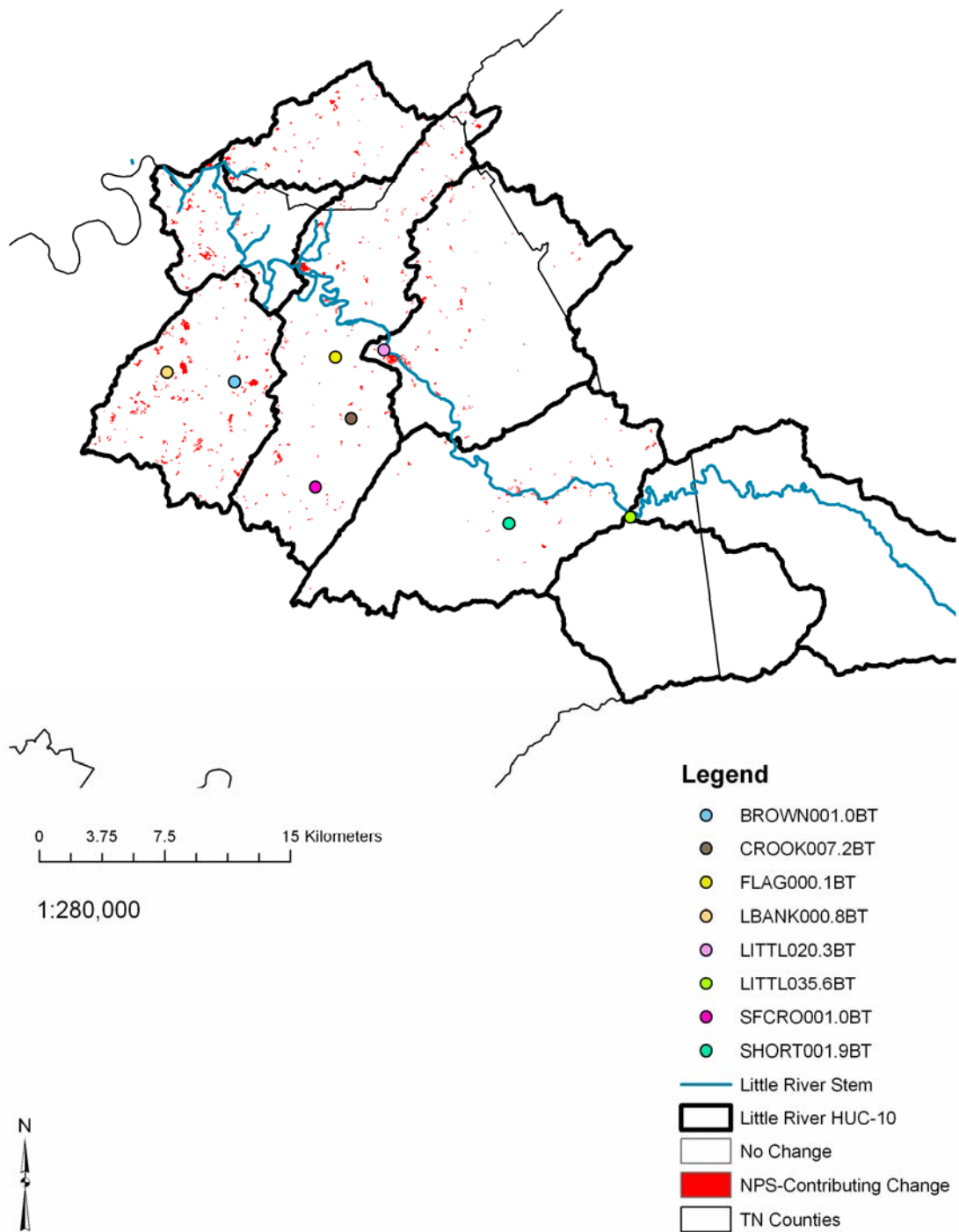


Figure 4.4. NLCD Change Product Main NPS Pollutant Contributing Land Cover Change (1992-2001)

4.4 Statistical and Multivariate Methods

Summary statistics were calculated for both individual site parameters (Tables A.1 through A.10 in Appendix) and combined site parameters (Tables A.11 through A.17 in Appendix). Nonparametric analysis of variance (ANOVA) tests were conducted to determine if there are statistically significant spatial and seasonal differences between sites and between sample time periods (Vega et al. 1998). Nonparametric ANOVA tests the null hypothesis that two or more independent samples come from distributions with the same median. Rejection of the null hypothesis indicates a significant difference between sites at a given statistical significance level. Median parameter values were used to assess which of the sites compared had higher measurements.

Non-parametric tests were used because the data were not normally distributed and were usually positively skewed, often containing extreme observations (Hirsch and Slack 1984). Parameters tested included NH_3 , DO, total KN, total P, TSS, and turbidity (Tables A.18 and A.19 in Appendix). Change over time was also analyzed where sufficient data were available. With the latter analyses, combined sites with longer records were broken into two parts based on a natural break in the data as is the case with combined site 060102010104_A. In other cases, combined site data sets were divided into two approximately equal proportions, as is the case with 060102010103_I. Data sets associated with individual sites did not have sufficient temporal lengths for performing a change-over-time analysis. Tables A.20 and A.21 (Appendix) show the individual and combined sites used in the multivariate analyses. Table A.22 (Appendix) gives the descriptions of the individual site names, and Table A.23 (Appendix) shows which individual sites comprise the combined sites.

A time-series analysis was carried out to determine if any cyclical patterns existed in LR flow data. A spectral analysis was used as it is a common method for identifying periodic behavior in time series data. Monthly flow averages for the 30-year period of 1976-2005 were used from the LR USGS hydrological flow site at Maryville (USGS Site ID # 03498500). The analysis was carried out on trend-removed data by calculating the long-term individual monthly averages for the site and then subtracting the long-term averages from each respective month's flow average to determine the "residue." The trend equation for the plotted residue was then determined and the equation used to remove the long-term trend of the original raw monthly averages by plugging the raw data into the x variable of the equation. The resulting trend-removed data were then subjected to a time-series analysis to determine if any cyclical patterns existed.

Monthly flow averages were calculated for the same 30-year flow period to determine if any seasonal flow patterns exist. Based on these results (discussed further in Chapter 5) the sample records were classified by "flow season" as either high-flow season data (October – March) or low-flow season data (April – September). This coincides with the USGS-defined water year (USGS 2007a) of October 1st through September 30th. This is also the standard water year for the United States (Gordon et al. 2004). The use of a generalized high flow/low flow season classification was more appropriate than a more detailed seasonal breakdown (e.g., spring, summer, winter fall) for this study because irregular sampling had resulted in intermittent data.

4.4.1 Principal Component Analysis

PCA was used to elucidate relationships between water quality parameters and to determine parameter influence on data set variance. PCA involves the calculation of eigenvalues and their corresponding eigenvectors (PCs) of the data set correlation (or covariance) matrix. Each PC is orthogonal to the PCs before it. The calculated eigenvalues, which represent the sum

of a PC's squared loadings, represent the importance of the associated PC. A high loading of a variable on a PC (i.e., the correlation of each original variable with a PC), whether positive or negative, means that the variable is highly involved in that PC (Haag and Westrich 2002). The PCs are rotated to maximize or minimize the variable loadings. This creates new PCs where medium-range correlations have been minimized between the components and original variables. This helps to enable interpretation of the underlying data set processes (Mazlum et al.1999).

PCA data sets were composed of pooled, log-transformed, standardized data from individual sites as shown in Figure 4.5. Eight individual sites that had ten parameters including NH_3 , DO, specific conductance, $\text{NO}_2 + \text{NO}_3$, temperature, total hardness, total KN, total P, TSS, and turbidity, were analyzed (Table A.20 in Appendix). A binary flow season variable was included in the PCA data sets. PCA was also carried out on individual combined sites (Figure 4.2) in an attempt to determine whether processes from the LR pooled data analysis could be found at individual sites (Haag and Westrich 2002). The individual site data sets (Figure 4.5) were not of adequate length for this purpose.

The correlation matrix was used (as opposed to the covariance matrix) for PCA based on the decision that all included parameters are equally important (Chatfield and Collins 1980). PCs with eigenvalues greater than one were selected for interpretation. Varimax rotation was applied to the PC loadings to maximize or minimize the loadings of variables on each PC which helps to enhance interpretability (Chatfield and Collins 1980; Vega et al. 1998; Santos-Roman et al. 2003).

Outputs from PCA were assessed using several metrics. The Kaiser-Meyer-Olkin (KMO) statistic was used which is a common metric for the evaluation of the adequacy of a PCA. The KMO value of 0.5 was used as the cutoff for determining if the PC solution representing the relations between parameters should be considered useful and statistically acceptable (Parinet et al. 2004; Statistics Canada 2007). Communality values were also examined to determine the proportion of variance represented by the PCs for each parameter. PC loadings were interpreted based on the guidelines suggested by Comrey and Lee (1992) as cited in Santos-Roman et al. (2003) where 0.71 and higher is considered excellent, 0.63 very good, 0.55 good, 0.45 fair, and 0.32 poor.

4.4.2 Cluster Analysis

CA was used to determine similarities among sites across the watershed. Hierarchical CA is an unsupervised pattern-recognition technique that organizes a dataset into classes, or clusters, based on similarity between cases and/or variables. The most common form of hierarchical CA, the agglomerative approach, works from the bottom up by determining the most similar pair of components, or, in the case of this study, sampling sites. The method then works upward, grouping similar clusters until a single cluster containing all samples is obtained (Vega et al. 1998). The other type of CA, called non-hierarchical CA, clusters a dataset based on a predefined number of clusters (Wunderlin et al. 2001). An example of this type of CA is K-means cluster analysis. With this approach, subsequent clustering does not depend on previously found clusters.

Hierarchical CA is the more commonly used of the two approaches, probably because it allows for the underlying structure and behavior between samples and/or variables to be learned without assumptions about the data (Vega et al. 1998; Singh et al. 2004; Shrestha and Kazama 2007). In this study, I wanted to determine whether the grouping of several individual sites into a combined site was valid or not. For those reasons, Hierarchical CA was used in this study to study the spatial and temporal patterns/clusters of water quality data.

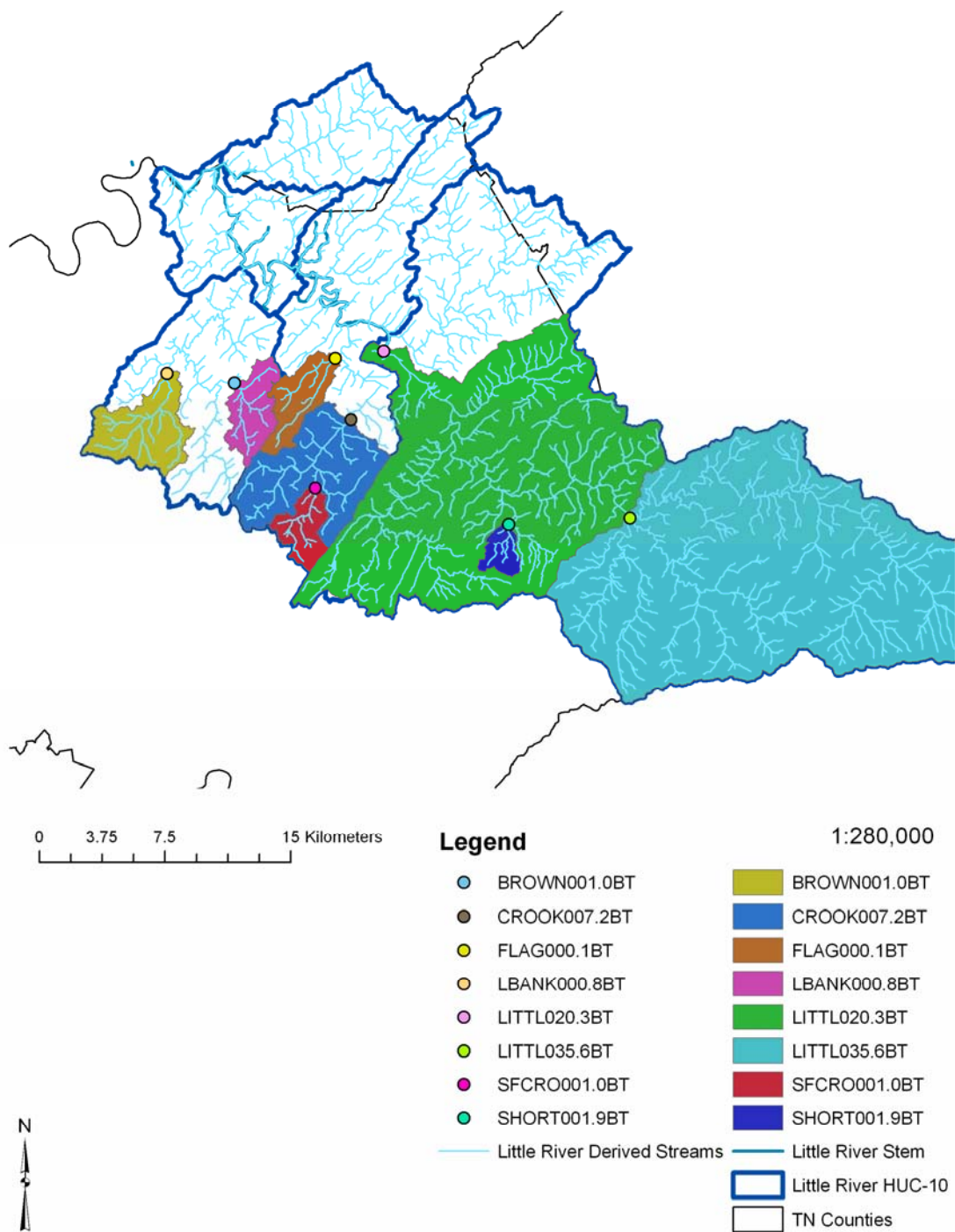


Figure 4.5. Little River Individual Sampling Sites and Contributing Subwatersheds

The same data sets used for PCA were used for CA. Ward's CA method along with the Squared Euclidean distance measure was the chosen analysis approach (Wunderlin et al. 2001; St-Hilaire et al. 2004). The number of sites and their geographic distribution were inadequate for using any other predetermined spatial framework (e.g., ecoregions).

4.4.3 Discriminant Analysis

DA was used to determine which water quality parameters differentiate best between groups in the LR watershed. DA, unlike CA, is a supervised pattern-recognition technique that depends on prior knowledge of association of data with particular groups (Wunderlin et al. 2001; Singh et al. 2004). DA is performed on raw data. Resulting discriminant functions, which are essentially weighted averages of the independent variables, can then be used to predict a record's membership in one or more predetermined groups. Somewhat like ANOVA, DA uses the F-statistic to determine whether or not the discriminant function(s) differentiates between the groups significantly better than pure chance. Examples of such pre-known groups may be a temporal group of a particular monitoring time period such as a particular season, a spatial group consisting of a series of monitoring sites, or clusters derived from CA.

DA has two common forms: standard and stepwise. In standard DA, all variables are included. With stepwise DA, variables are iteratively entered into the analysis. The best predictor variables in the context of the predefined groups are selected based on a predetermined cutoff significance level for adding a variable. Both standard and stepwise DA were used in this study. It should be noted that stepwise DA has an element of "chance" in that the analysis picks and chooses the variables to be included. Because of this, cross-validation or even a separate unselected data set should be used to validate the accuracy and utility of the discriminant functions (Garson 2008).

DA was carried out on the same data sets used for the PCA and CA analyses. The CA results were used as the predefined site groups (Shrestha and Kazama 2007). A two-cluster solution was used as the classifying variable for DA. The DA results were evaluated using the Wilk's Lambda statistic and the Wilk's Lambda table (Santos-Roman et al. 2003). The Wilk's Lambda statistic shows how well a variable discriminates between groups while the table measures how well the discriminant function separates the cases into the predetermined groups. In both cases, a lower statistic equates to better discriminating ability. Wilk's Lambda is measured on a 0 to 1 scale, with values closer to 0 being better. The significance value indicates how well the function does as compared with pure chance. The discriminant function canonical correlation value was used to evaluate how well the discriminant scores correlated with the grouping variable.

In addition, the standardized canonical discriminant function coefficients were used to assess the importance of each parameter's contribution to the discriminant function. Coefficients with large absolute values correspond to the variables with greater discriminating ability. The standardized coefficients allow variables measured on different scales to be compared directly in terms of their importance. Finally, cross-validation was used to assess the accuracy of the DA classifications. As an extra validation procedure, the pooled data sets were divided based on their CA cluster membership and then those cluster groups were each split in half. One half of each group was used in the DA while the other half was used for discriminant function validation.

4.5 Delineation of Watersheds and Stream Networks

To determine the contributing land surface of each individual sampling site, the contributing subwatershed area for each site had to be delineated. One-third arc-second DEM data were used for this study. The data were obtained from the US Geological Survey Seamless Data Viewer as individual tiles (USGS 2007). The individual tiles had to be mosaicked before they could be worked with. Because USGS DEM data are provided in decimal degrees in the geographic coordinate system North American Datum 1983, the data were then projected to the project coordinate system of USA Contiguous Albers Equal Area Conic. An equal area projection was chosen for the project geodatabase as it is important to use a projection that accurately represents the Earth's surface for hydrologic modeling (Kopp and Noman 2006). This is also important for calculating percent slope, as the horizontal and vertical units must be the same (Ebert and Wade 2004). The projected and mosaicked data set was then clipped to the LR HUC-10 watershed boundary using ArcGIS version 9.2 software (ESRI 2007).

The freeware ArchHydro extension for ArcGIS (ESRI 2007a) was used to delineate the study area. Using ArchHydro, hydrologic attributes such as flow direction, flow accumulation, derived streams, catchments and catchment drainage points, and subwatersheds can be automatically derived. The tools, where appropriate, also allow the user to enter user-defined parameters that determine how hydrologic features are derived from the original DEM data and subsequent derived layers.

4.6 Calculating Landscape Metrics

The EPA Analytical Tools Interface for Landscape Assessment (ATtILA) extension for ESRI ArcView GIS 3.2 was used to calculate the landscape metrics for the LR (ESRI 1999; USEPA 2004). ATtILA is a free package that can be used to calculate many common landscape metrics, such as riparian characteristics, human stressors, and physical characteristics. The TVA IPSI road data layer (TVA 2003, further described below), the NLCD Change Product data, the streams derived from the stream network delineation, and the USGS DEM data were used as input data in ATtILA.

The differences between the NLCD Change Product and original NLCD 2001 data set had to be reconciled. These differences, a result of the Anderson classification level used for each, are shown in Table 4.1. A new 2001 land-cover data set for the LR was created for compatibility because the NLCD Change Product is an Anderson Level I classification, while the actual NLCD 2001 data set was an Anderson Level II classification. The LR Change Product areas were reclassified based on the land-cover "to" changes (e.g., urban to agriculture, where agriculture is the "to" change) to create a consistent 2001 Anderson Level I land-cover data set. Figure 4.3 shows the NLCD Change Product reclassified to an Anderson Level I classification of 2001 land cover.

Several key landscape composition metrics were calculated that are acknowledged indicators of water quality in a watershed. They include proportions of urban, forest, agriculture (cropland and pasture combined), barren land, impervious surface (threshold of 10 percent), and impervious surface (threshold 10 percent) (Arnold and Gibbons 1996) on steep slopes (threshold 9 percent) (McCool et al. 1987; Smith et al. 2001). The NLCD 2001 impervious surface cover data set was used for the impervious surface metrics. The raster cell values are classified based on their proportion of impervious surface occurring on the ground in each 30 m (900m²) cell. Proportions of watershed with agriculture on steep slopes using a slope threshold of 9 percent or greater, proportion of stream length with adjacent riparian agriculture, forest, and urban land

cover, watershed road density, proportion of streams having roads within 30 m (Jones et al. 1997), proportion of NPS-contributing land cover change, and proportion of NPS-contributing land cover change on steep slopes (9 percent) were calculated for the LR subwatersheds.

The metric abbreviations are included in parentheses as follows (hereafter the landscape metrics shall be referred to by their ATtILA abbreviations given below)

- Urban (PURB)
- Forest (PFOR)
- Agriculture (cropland and pasture) (PAGT)
- Barren land (both man-made and natural) (PNBAR)
- Impervious surface (threshold of 10 percent) (PIMPER)
- Impervious surface (threshold of 10 percent) on steep slopes (threshold of 9 percent) (PIMPSL9)
- Watersheds with agriculture on steep slopes (threshold of 9 percent) (AGTSL9)
- Stream length with adjacent riparian agriculture (RAGT30)
- Stream length with adjacent riparian forest (RFOR30)
- Stream length with adjacent riparian urban (RURB30) land cover
- Watershed road density (RDDENS)
- Streams having roads within 30m (RNS30)
- NPS-contributing land cover change (PUSER)
- NPS-contributing land cover change on steep slopes (threshold of 9 percent) (USERSL9).

The TVA IPSI roads layer provided roads data for the LR ATtILA calculations. This data set consists of road features derived from 1:24,000 topographic maps and updated with approximately 2001 high resolution aerial imagery (TVA 2003). The TVA IPSI roads layer was particularly useful for this study as attention was paid to road features that might not be considered important in other contexts (e.g., gravel or dirt haul roads) but which can be extremely important to NPS contributions (Huntman 2008). The TVA IPSI roads data set was also useful for calculating the proportion of streams having roads nearby.

The NLCD change product data set was extremely useful for determining land-cover changes (both extent and types) between the first and second dates of products (1992 and 2001, respectively). Anywhere from two to six years or more is noted as being an adequate time interval between images for detecting land cover changes (Coppin et al. 2004). As previously mentioned, this was not possible with the original NLCD data sets. Changes that are associated with NPS pollution in the context of an Anderson Level I classification (hereto after referred to as NPS-contributing land-cover change) were the most relevant to this study. These include:

- Urban to agriculture
- Barren to urban
- Barren to agriculture
- Forest to urban
- Forest to barren
- Forest to agriculture
- Agriculture to urban
- Agriculture to barren

These land-cover change types were lumped together and considered collectively as NPS-pollutant-contributing land-cover change. Figure 4.4 shows the primary NPS contributing land-cover change locations in the LR.

Chapter 5 Results and Discussion

5.1 Results

5.1.1 Spatial and Temporal Variations

The results of the time-series analysis on stream flow at USGS gaging site 03498500 are shown in Figure 5.1. The presence of an annual pattern can be seen by the spike at approximately 0.083 (or 1/12). Except for the clear annual return interval, the time-series analysis did not detect any other temporal cycle in the data. The length of the discharge data set is likely not long enough to detect any longer-term cyclical patterns; 30 years is the standard minimum length for climatic-influenced data sets and 60 years of data were not available at this site (NCDC 2008). The results of the graphed 30-year monthly averages (Figure 5.2) also show the annual return interval cycle along with information on periods of high flow and low flow. The highest average flows occur in March and flows decline until the lowest average in September. Greater ranges of flows characterize the high-flow season, while an increased number of outliers and extremes occur during the dry season.

Table 5.1 shows the results of the nonparametric ANOVA tests for individual sites. The results and median values show that there are significant differences between parameter concentrations in the upper and lower parts of the watershed. Tests of measurements of NH_3 , TSS, and turbidity show some significant results, with higher median values at sites in the lower part of the watershed. Median values of NH_3 are the highest at Pistol Creek sites compared with middle part and upper part sites. Tests on measurements of DO, total KN, and total P also show higher median values at upper part sites than at middle part sites.

The nonparametric ANOVA tests on DO (Table 5.2) show a significant difference between concentrations based on flow-defined season. A similar pattern is observed with total P. The combined site analyses based on flow season also show significant results for TSS and turbidity.

5.1.2 Multivariate Analyses – PCA Results

PCA was used to elucidate the underlying relationships among water quality parameters. Table 5.3 (PCA 1) shows the PC loadings and communalities for individual LR sites. The first three PCs explain 63.1 percent of the data set variance. PC 1 of PCA 1 is highly associated with specific conductance, $\text{NO}_2 + \text{NO}_3$, total hardness, and is moderately associated with turbidity. Loading of these parameters on the first PC represents inorganic dissolved solids (anions and cations) and ground water ionic contributions to the stream (Hem 1985). The presence and erosion of dolomites (composed of calcium magnesium carbonates), limestones, shales, and sandstones as are found in the LR watershed is associated with PC 1. The loading of turbidity is likely associated with the conditions necessary for higher levels of conductivity.

Seasonality, temperature, TSS, and turbidity load highly on PC 2 of PCA 1. The loading of these parameters along with the seasonal variable represents the seasonal influence on both temperature and sediment at the LR sites. Total P loads moderately on this component. PC 3 is associated with NH_3 , total KN, and total P, and is negatively associated with DO. PC 3 represents nutrients in the LR and suggests a negative impact on DO levels as a likely result of nutrient-driven processes such as eutrophication.

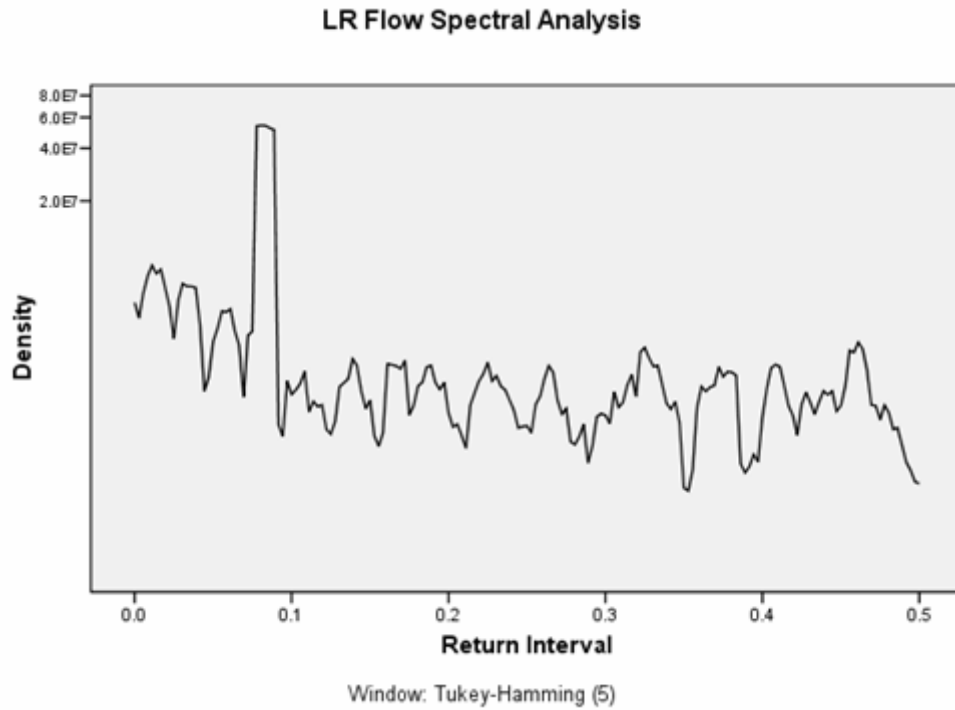


Figure 5.1. Time-Series Analysis of Discharge Data (1976-2005) from the USGS Little River Near Maryville (03498500) Gaging Site.

Note: the peak at .083 (1/12) represents the annual return interval in the data set; period and frequency are reciprocals of each other.

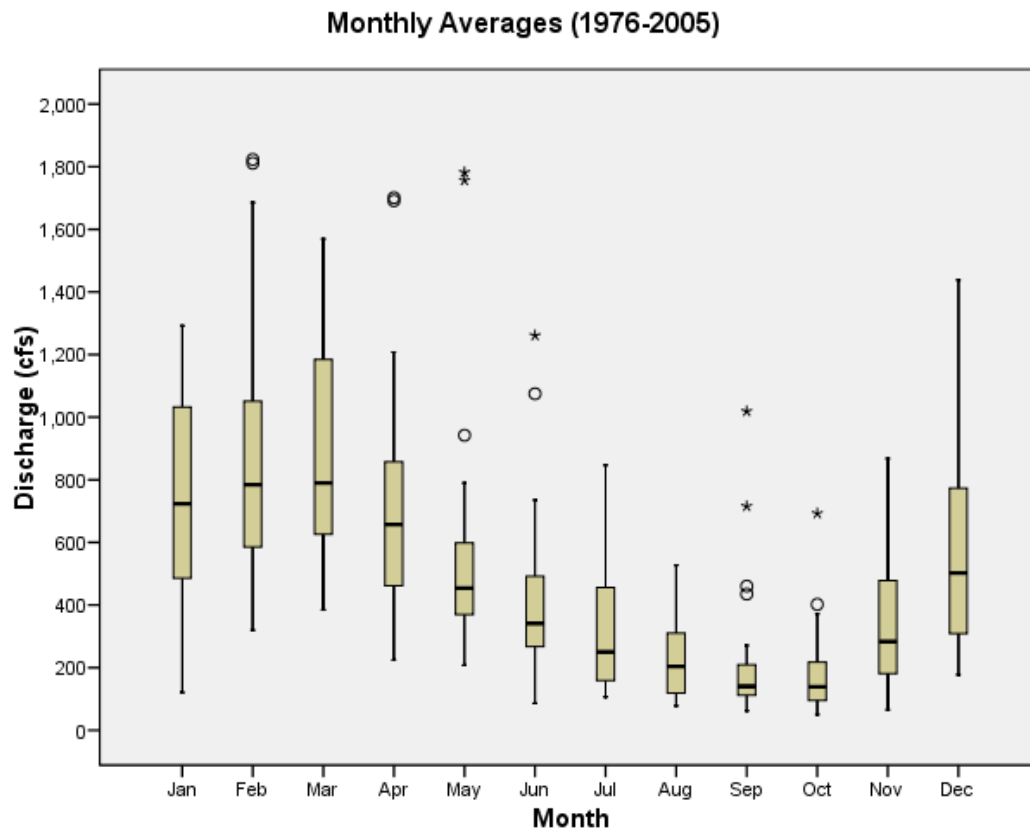


Figure 5.2. Monthly Averages (1976-2005) of Stream Flow for the USGS Little River Near Maryville Gaging Site (03498500).

Note: Circles represent outliers; stars represent extremes.

Table 5.1. Individual Site Nonparametric ANOVA Tests of Water Quality Variation

Sites Compared	Ammonia Nitrogen (mg/l)	DO (mg/l)	Total KN (ug/l)	Total Phosphorus (mg/l)	TSS (mg/l)	Turbidity (NTU)
LITTL035.6BT	0.020	10.250	0.100	0.010**	4.000	0.800
LITTL020.3BT	0.020	10.580	0.100	0.008**	3.000	2.050
LITTL020.3BT	0.020	10.580**	0.100	0.008	3.000**	2.050**
LITTL009.6BT	0.020	7.005**	0.100	0.009	10.000**	12.900**
ELLEJ000.1BT	0.020	X	0.100	0.010	10.000	10.900
STOCK003.2KN	0.020		0.100	0.019	10.000	8.000
SHORT001.9BT	0.020*	9.255	0.100	0.020	10.000	5.450
FLAG000.1BT	0.020*	10.560	0.100	0.008	10.000	5.450
SHORT001.9BT	0.020**	9.255	0.100**	0.020	10.000	5.450
CROOK007.2BT	0.020**	10.545	0.100**	0.017	10.000	6.500
CROOK007.2BT	0.020	10.545	0.100	0.017	10.000	6.500**
SFCRO001.0BT	0.020	10.925	0.100	0.018	10.000	3.900**
LBANK000.8BT	0.030	6.920	0.150	0.020	10.000	6.900**
BROWN001.0BT	0.030	8.890	0.150	0.020	10.000	3.600**

Note: Time period of data sets given in Table A.19. Values in rows adjacent to site names are median values for each parameter. A dark line separating rows in the table denotes separate analyses. Significantly different values are boldface. * significant at 90 percent confidence, ** significant at 95 percent confidence.

Table 5.2. Individual Site Nonparametric ANOVA Tests of Water Quality Variation Based on Flow Season

Sites Compared	Ammonia Nitrogen (mg/l)	DO (mg/l)	Total KN (ug/l)	Total Phosphorus (mg/l)	TSS (mg/l)	Turbidity (NTU)
FLAG000.1BT - HF	0.02	11.88**	0.10	0.004*	10	3.9
FLAG000.1BT - LF	0.02	9.06**	0.10	0.0395*	10	4.1
SFCRO001.0BT - HF	0.02	11.88**	0.10	0.004	10	3.9
SFCRO001.0BT - LF	0.02	9.72**	0.10	0.024	10	4

Note: Time period of data sets given in Table A.19. Values in rows adjacent to site names are median values for each parameter. A dark line separating rows in the table denotes separate analyses. Significantly different values are boldface. * significant at 90 percent confidence, ** significant at 95 percent confidence. HF = High Flow LF = Low Flow

Table 5.3. PCA 1 – Extracted Rotated PC Loadings for Little River Individual Sites

Parameter	PC 1	PC 2	PC 3	Communality
Season	-0.311	0.799	-0.032	0.736
Ammonia Nitrogen	0.176	0.158	0.763	0.638
DO	0.096	-0.003	-0.618	0.391
Conductance	0.873	0.015	0.206	0.805
Nitrate + Nitrite	0.680	-0.014	-0.111	0.475
Temperature	-0.224	0.759	0.247	0.687
Hardness	0.827	-0.068	0.323	0.793
Total KN	0.191	-0.008	0.777	0.640
Total Phosphorus	0.151	0.438	0.493	0.458
TSS	0.176	0.676	0.003	0.488
Turbidity	0.561	0.706	0.068	0.818
Percent Variance	29.1	21	13	63.1

Note: Highest loading of each parameter bolded. Time period of data sets given in Table A.20.

PC variable loadings associated with the PCA of combined sites showed some differences compared with PCA 1 (Tables 5.4, 5.5, and 5.6 show PCAs 2, 3, and 4 respectively). Data sets from remaining combined sites were inadequate for PCA. The different loadings are a likely result of the use of watershed-wide data in PCA 1 versus data from smaller areas of the watershed. This is a matter of geographic scale and context. For example, the results shown in Table 5.5 are from data collected in an area having high agricultural activity. Sediments, DO, and total P load highly with seasonality which likely represents the influence of seasonal agricultural land use. The combined site associated with the results in Table 5.6 shows a seasonal influence on TSS and turbidity as per PC 1. NH_3 and total KN represent more data set variance compared with the other PCA results. Total P loads highly with DO on the third PC. This likely represents the influence of phosphorus on DO as a result of urban contributing sources (storm water, fertilizer, etc.) and processes such as eutrophication.

The PCA results show that relationships exist among water quality parameters. In addition, the flow season (high-flow or low-flow) influences DO, nutrients, temperature, TSS, and turbidity in streams across the watershed. The single combined site PCA results show different parameter relationships as compared with the whole watershed PCA results. Influences such as adjacent seasonal agricultural land use and developed lands are likely influencing factors for particular combined sites.

5.1.3 Multivariate Analyses – Cluster Analysis Results

CA was used to analyze multivariate similarities among individual site data records. Figure 5.3 shows the resulting dendrogram and a two-cluster solution. Table 5.7 shows the parameter median values for data associated with clusters 1 and 2 respectively. Sample records in cluster 1 are associated with sites primarily in the upper part and middle part areas, while sample records in cluster 2 are associated with some middle part sites, but primarily lower part sites. Nonparametric t-tests show that the two clusters are significantly different in terms of NH_3 , DO, specific conductance, $\text{NO}_2 + \text{NO}_3$, temperature, hardness, total KN, total P, TSS, and turbidity. Cluster 2 is associated with higher median concentrations of the aforementioned parameters. Differences in the groups can be attributed to upper part and lower part influences of land cover and associated runoff.

Similar to a study by Singh et al. (2004), an additional CA was carried out using the median value of each indicator at each individual site (Figure 5.4). Sites grouped in the same cluster are close to each other geographically (see Figure 4.5). The lower part Pistol Creek sites clearly separate from the other LR sites. LR main stem sites grouped in a second cluster, and all other LR tributary sites clustered together in a third group. Table 5.8 shows the results of a nonparametric ANOVA test on the three-cluster solution; significant results are associated with NH_3 , specific conductance, $\text{NO}_2 + \text{NO}_3$, temperature, hardness, total KN, and total P. The possible two-cluster solution shown in Figure 5.4 serves to demonstrate the difference of the Pistol Creek sites compared with the rest of the individual sites. A CA of the mean value of site parameters gave similar results.

In general the results of the CA are in harmony with the nonparametric ANOVA tests. The T-tests and the nonparametric ANOVA tests of cluster parameter values show statistically significant differences in water quality measurements when comparing upper part, and lower part

Table 5.4. PCA 2 – Extracted Rotated PC Loadings for Combined Site 05_D

Parameter	PC 1	PC 2	PC 3	Communality
Season	0.908	0.121	-0.116	0.853
Ammonia Nitrogen	0.498	-0.513	0.546	0.810
DO	-0.817	-0.456	-0.110	0.888
Temperature	0.849	0.295	-0.011	0.808
Total KN	-0.110	0.089	0.935	0.894
Total Phosphorus	0.689	0.275	0.480	0.780
TSS	0.257	0.814	0.058	0.732
Turbidity	0.415	0.853	0.062	0.903
Percent Variance	50.6	19.1	13.6	83.3

Note: Highest loading of each parameter bolded. Time period of data sets given in Table A.20.

Table 5.5. PCA 3 – Extracted Rotated PC Loadings for Combined Site 05_E

Parameter	PC 1	PC 2	Communality
Season	0.893	0.073	0.803
Ammonia Nitrogen	0.058	0.845	0.717
DO	-0.955	-0.223	0.961
Temperature	0.919	0.087	0.853
Total KN	0.248	0.820	0.734
Total Phosphorus	0.639	0.517	0.675
TSS	0.655	0.406	0.594
Turbidity	0.866	0.300	0.840
Percent Variance	61.7	15.8	77.5

Note: Highest loading of each parameter bolded. Time period of data sets given in Table A.20.

Table 5.6. PCA 4 – Extracted Rotated PC Loadings for Combined Site 07_I

Parameter	PC 1	PC 2	PC 3	Communality
Season	0.781	0.337	-0.056	0.726
Ammonia Nitrogen	0.044	0.922	0.003	0.852
DO	-0.258	0.230	-0.801	0.761
Temperature	0.874	0.210	0.262	0.876
Total KN	0.064	0.942	0.031	0.893
Total Phosphorus	-0.147	0.232	0.818	0.745
TSS	0.668	-0.195	-0.157	0.509
Turbidity	0.924	-0.060	0.132	0.876
Percent Variance	36.5	24.5	17	78

Note: Highest loading of each parameter bolded. Time period of data sets given in Table A.20.

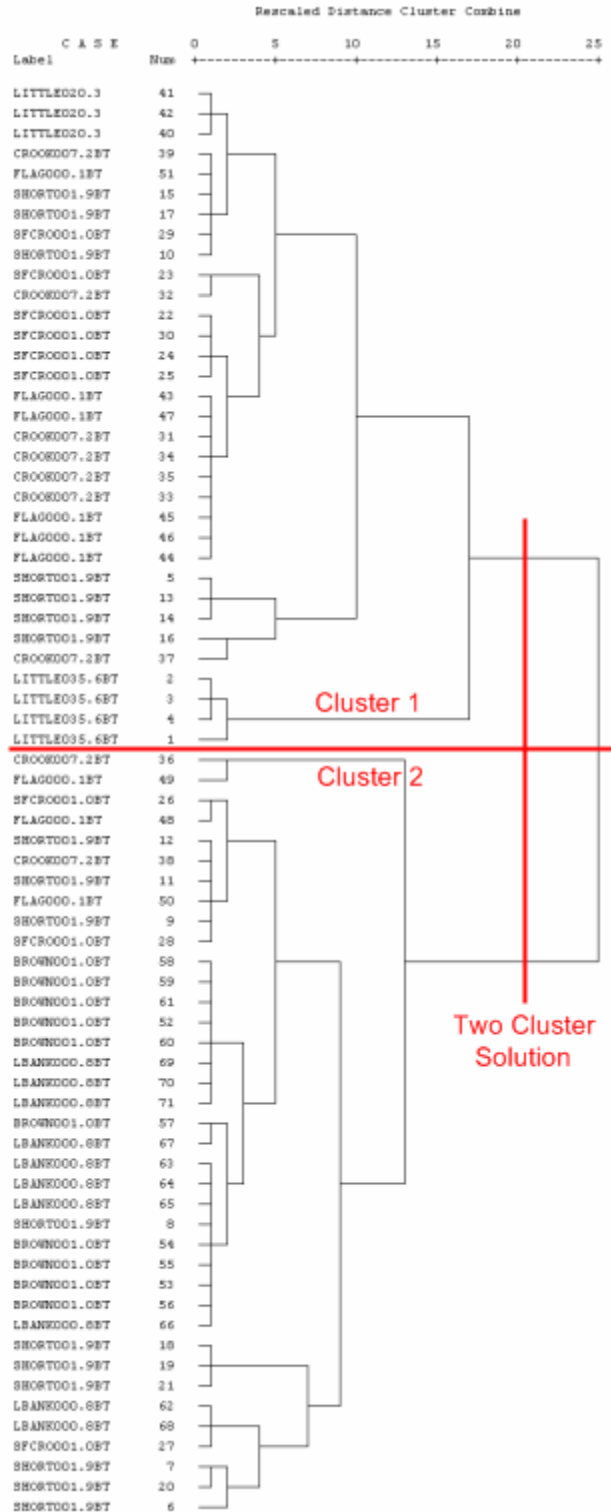


Figure 5.3. Dendrogram of Cluster Analysis of Individual Site Data

Note: Dendrogram case labels are individual site names (Figure 4.5); each instance represents a water quality sample record for that site. Data set time periods shown in Table A.20.

Table 5.7. CA of Individual Sites – Two Cluster Solution T-test Results

Cluster	Ammonia Nitrogen (mg/l)	DO (mg/l)	Conductance (uMHO)	Nitrate + Nitrite (mg/l)	Temperature (C)
Cluster 1	0.02**	11.08**	272**	0.18**	11.94**
Cluster 2	0.03**	8.32**	339**	0.43**	17.62**

Cluster	Hardness (mg/l)	Total KN (ug/l)	Total Phosphorus (mg/l)	TSS (mg/l)	Turbidity (NTU)
Cluster 1	128**	0.1**	0.004**	10**	3.9**
Cluster 2	184.5**	0.15**	0.02**	10**	6.1**

Note: Time period of data sets given in Table A.20. Values in rows adjacent to site names are median values for each parameter per cluster. Significantly different values are boldface. * significant at 90 percent confidence, ** significant at 95 percent confidence

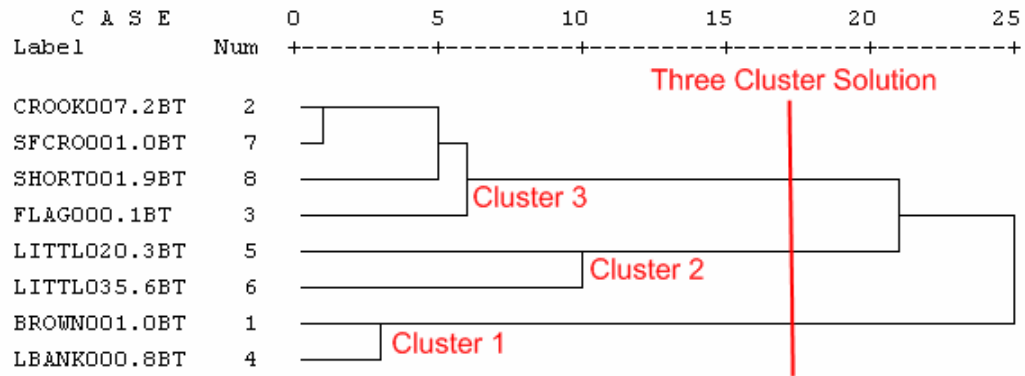


Figure 5.4. Dendrogram of Cluster Analysis of the Median Value for Each Respective Parameter at Sampling Sites

Note: Time period of data sets given in Table A.20.

**Table 5.8. CA of Individual Site Parameter Median Values – Three Cluster Solution
Nonparametric ANOVA Test Results**

Cluster	Ammonia Nitrogen (mg/l)	DO (mg/l)	Conductance (uMHO)	Nitrate + Nitrite (mg/l)	Temperature (C)
Cluster 1	0.03*	7.905	420.25**	0.54*	17.318*
Cluster 2	0.02*	10.553	287**	0.27*	11.563*
Cluster 3	0.02*	10.015	44.75**	0.095*	14.478*

Cluster	Hardness (mg/l)	Total KN (ug/l)	Total Phosphorus (mg/l)	TSS (mg/l)	Turbidity (NTU)
Cluster 1	215**	0.15*	0.02*	10	5.25
Cluster 2	146.25**	0.1*	0.017*	10	5.45
Cluster 3	24.025**	0.1*	0.007*	6.5	1.35

Note: Time period of data sets given in Table A.20. Values in rows adjacent to site names are median values for each parameter per cluster. Significantly different values are boldface. * significant at 90 percent confidence, ** significant at 95 percent confidence

samples. The groupings determined through use of CA also differentiate geographically between upper part and lower part sites. The sites in the Pistol Creek subwatershed, representing the watershed lower part sites in this study, are differentiated from the other study sites (Figure 5.4).

5.1.4 Multivariate Analyses – Discriminant Analysis Results

DA was used to determine which parameters differentiate between the CA-derived clusters. The CA solutions (Figures 5.3 and 5.4) were used as the classifying variable. Both standard and stepwise DA results are presented here.

Tables 5.9 through 5.12 show the results of the DA of individual site data. The standard DA results using all parameters are good, with most having acceptable classification accuracies above 80 percent (Wunderlin et al. 2001; Shrestha and Kazama 2007). In general the Wilk's Lambda values were highly significant for all analyses and the canonical correlations were high. On the other hand, the stepwise DA of the same data sets resulted in not only a reduction of needed parameters, but, in most cases, better correct classification percentages as compared with standard DA.

The stepwise DA results (Table 5.9) show that specific conductance, DO, and total P are significantly related to the CA site clusters. NH₃ and TSS are significantly related to the median value site groups (Table 5.11). The discriminating power of nutrient concentrations along with levels of DO suggests the influence of land-cover types such as agriculture and urban, stormwater runoff, in-stream flow levels, and the breakdown of organic matter. Sites in the LR midwatershed area are adjacent to considerable agricultural land cover. Lower part sites in the Pistol Creek area are surrounded by residential and industrial lands. In addition, Table 5.3 further illustrates the association between total P and DO along with total KN and NH₃.

5.1.5 Land-Cover Pattern Analysis Results

Land-cover metrics were calculated for delineated subwatersheds whose outlets are the individual LR sampling sites. Figures A.1 through A.14 (Appendix) show the landscape metric results visualized in rendered maps. Table 5.13 shows the raw results of the landscape metric calculations.

A general trend of increasing modified land cover in the lower part of the watershed can be seen by comparing the HUC 060102010107 (Pistol Creek) subwatershed metrics versus upper part subwatershed metrics. A general decrease in forest land cover proportions from the upper part to the lower part can be seen in Figures A.4 and A.8 moving away from the GSMNP.

Site LITTL035.6BT proved to be a sort-of "reference" subwatershed for low proportions of modified land-cover types and high proportions of unmodified land cover types. This is due to being composed of protected lands contained in the GSMNP. Both of the Pistol Creek sites had higher proportions of several problematic land-cover types. Those subwatersheds also have experienced the highest proportions of NPS-contributing land-cover change.

A CA of the landscape metric proportions was conducted to assess subwatershed similarities. Figure 5.5 shows the results of the landscape metric proportion CA. LITTL035.6BT is an anomaly compared to the other site subwatersheds as can be seen by its singular cluster membership. This is because that subwatershed's lands consist of protected lands in the GSMNP

Table 5.9. Standardized Canonical Discriminant Function Coefficients for Individual Site DA

DA Analysis	Ammonia Nitrogen	DO	Conductance	Nitrate + Nitrite	Temperature	Hardness	Total KN	Total Phosphorus	TSS	Turbidity
Individual Site Standard	0.0455	-0.8570	0.7249	-0.3522	-0.3369	-0.3937	0.1678	1.0435	-0.1621	0.5751
Individual Site Stepwise	X	-0.8161	0.7499	X	X	X	X	0.9702	X	X

Note: Time period of data sets given in Table A.20.

Table 5.10. DA Summary Statistics

DA Analysis	Cross-Validation % Correct Classification	Unselected Cases % Correct Classification	Canonical Correlation	Wilk's Lambda	% Data Reduction vs. Standard DA of Same Data
Individual Site Standard DA	85.70	80.60	0.906	.180***	X
Individual Site Stepwise DA	88.60	88.30	0.884	.218***	70%
Individual Site Standard Seasonal DA	85.30	83.80	0.901	.187***	X
Individual Site Stepwise Seasonal DA	88.20	83.80	0.793	.371***	80%

Note: * significant at 90 percent confidence, ** significant at 95 percent confidence, *** significant at 99 percent confidence. A dark line separating rows in the table denotes separate analyses.

Table 5.11. Standardized Canonical Discriminant Function Coefficients for Individual Site DA Using the CA Median Site Parameter Three Cluster Solution As the Classifying Variable

DA Function	Ammonia Nitrogen	DO	Conductance	Nitrate + Nitrite	Temperature	Hardness	Total KN	Total Phosphorus	TSS	Turbidity
Standard DA Function 1	0.2427	0.0056	0.7878	0.1726	-0.5619	-0.2005	-0.0109	0.4040	-0.6770	0.8919
Standard DA Function 2	-1.1400	0.2361	0.6820	-0.0110	0.2419	-0.0639	-0.1169	0.1742	1.6880	-1.1916
Stepwise DA Function 1	0.0465	X	1.0027	X	X	X	X	X	0.1685	X
Stepwise DA Function 2	1.1849	X	-0.2052	X	X	X	X	X	-0.7795	X

Note: Time period of data sets given in Table A.20. A dark line separating rows in the table denotes separate analyses.

Table 5.12. DA Summary Statistics for Individual Site DA Using the CA Median Site Parameter Three Cluster Solution As the Classifying Variable

DA Analysis	Cross-Validation % Correct Classification	Unselected % Correct Classification	Canonical Correlation – Function 1	Canonical Correlation – Function 2	Wilk's Lambda Function 1	Wilk's Lambda Function 2	% Data Reduction vs. Standard DA of Same Data
Standard DA	97.20	0.657	0.932	0.854	.036*	.271*	X
Stepwise DA	97.20	0.771	0.905	0.805	.064*	.352*	70%

Note: * significant at 99 percent confidence

Table 5.13. Calculated Landscape Metrics for Littler River Individual Site Contributing Subwatersheds

NAME	PUSER	USERSL9	PIMPER	PIMPSL9	PFOR	PNBAR	PURB
BROWN001.0BT	3.53	1.11	29.13	8.34	17.31	0.07	43.58
CROOK007.2BT	0.77	0.45	1.63	0.71	60.91	0.02	5.62
FLAG000.1BT	0.51	0.16	7.73	2.00	19.78	0.07	13.85
LBANK000.8BT	3.37	1.29	21.71	4.99	20.41	0.17	34.29
LITTL020.3BT	0.60	0.24	1.47	0.76	84.27	0.02	5.76
LITTL035.6BT	0.00	0.00	0.00	0.00	99.51	0.00	0.36
SFCRO001.0BT	0.36	0.27	0.70	0.42	82.71	0.00	4.02
SHORT001.9BT	0.15	0.15	0.27	0.19	87.67	0.00	5.17

NAME	PAGT	AGTSL9	RFOR30	RURB30	RAGT30	RNS30	RDDENS
BROWN001.0BT	36.47	12.16	31.75	33.78	28.03	0.22	5.77
CROOK007.2BT	31.48	14.39	52.70	6.58	37.77	0.26	3.22
FLAG000.1BT	63.90	16.80	34.25	8.09	54.07	0.11	4.26
LBANK000.8BT	43.08	8.41	24.43	21.33	50.39	0.26	6.41
LITTL020.3BT	8.53	3.47	74.03	10.20	13.41	0.34	2.75
LITTL035.6BT	0.00	0.00	97.83	1.44	0.01	0.16	0.90
SFCRO001.0BT	12.00	6.73	64.06	11.98	21.98	0.34	2.57
SHORT001.9BT	6.29	2.94	80.06	5.29	12.48	0.28	3.95

Note: Calculated values are percentages (proportions) of total subwatershed area in square meters. Landscape metric acronyms are defined in Section 4.6.

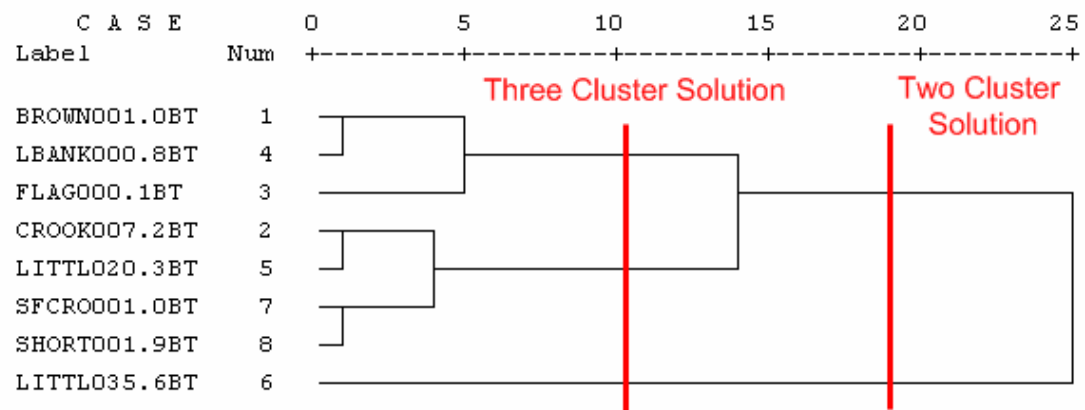


Figure 5.5. Dendrogram Showing Results of CA of Landscape Metric Proportions

and are over 99.5 percent forested (Table 5.13). Figure 5.6 illustrates the similarities between the water quality median CA results and the land cover proportion CA results. This clustering reflects the geographic arrangement of land-cover types and subsequent subwatershed land-cover proportions. The land use associated with land ownership of different parts of the watershed (e.g., the GSMNP versus the city of Maryville in Pistol Creek) are an influencing factor. A general trend of lower part sites and subwatersheds clustering together, LR tributary sites and subwatersheds clustering together, and LR stem sites and subwatersheds clustering together can be seen.

5.1.6 Relating Land Cover and Water Quality

Table 5.14 shows the results of a nonparametric correlation analysis of water quality and land cover. Median values of water quality indicators at individual sites were used along with the calculated proportions of landscape metrics. NH_3 , specific conductance, $\text{NO}_2 + \text{NO}_3$, total hardness, and total KN all have several significant positive correlations with metrics including PUSER, PIMPER, PURB, RAGT30, and RDDENS. Negative correlations exist for the aforementioned parameters with PFOR and RFOR30. RDDENS has the most significant correlations out of all metrics included which suggests the overall importance of all road types (both paved and unpaved) for water quality in the LR. As previously mentioned, the IPSI road layer was unique as it was designed to represent NPS pollution sources by including both paved roads and unpaved roads (TVA 2003). The higher quality and resolution of the roads data as compared with the 30-m NLCD imagery may also be a contributing factor in the high correlations. In general, these results suggest that proportions of certain land-cover types relate to levels of certain water quality indicators.

Available precipitation data are not adequate for analysis with flow data because the finest temporal resolution available is daily precipitation quantities. This is too coarse a resolution for studying the influence of historic precipitation events on river and stream flow and any associated impacts on water quality indicator concentrations. Furthermore, only two USGS gages exist in the LR, and the finest resolution of data available for those is daily flow measurements.

Linear regression could not be performed due to the inadequacy of sites relative to the number of landscape metrics examined. There should be about 20 times more cases (water quality sites in this study) than independent variables (landscape metrics in this study) in order to conduct reliable linear regression analyses (Ho 2006). That is, if a study incorporates five independent variables, there should be close to 100 cases. In the case of this study, even if only two landscape metrics were used, approximately 30-40 sample sites would be needed for reliable linear regression results.

Additional nonparametric ANOVA tests of the sample site parameter median values using the CA results of landscape metric proportions as the grouping variable were carried out (Figure 5.5). The results were significant for specific conductance, $\text{NO}_2 + \text{NO}_3$, and hardness. The nonparametric correlation analysis identified positive correlations between these parameters and landscape metrics associated with anthropogenic land-cover types, which occur in greater proportions in the lower part of the watershed. These results, in addition to the overall nonparametric correlation analysis, the nonparametric ANOVA tests and t-tests, and the multivariate analysis results, suggest that variations of select water quality indicators are likely a result of the types and proportions of land cover and flow season influences.

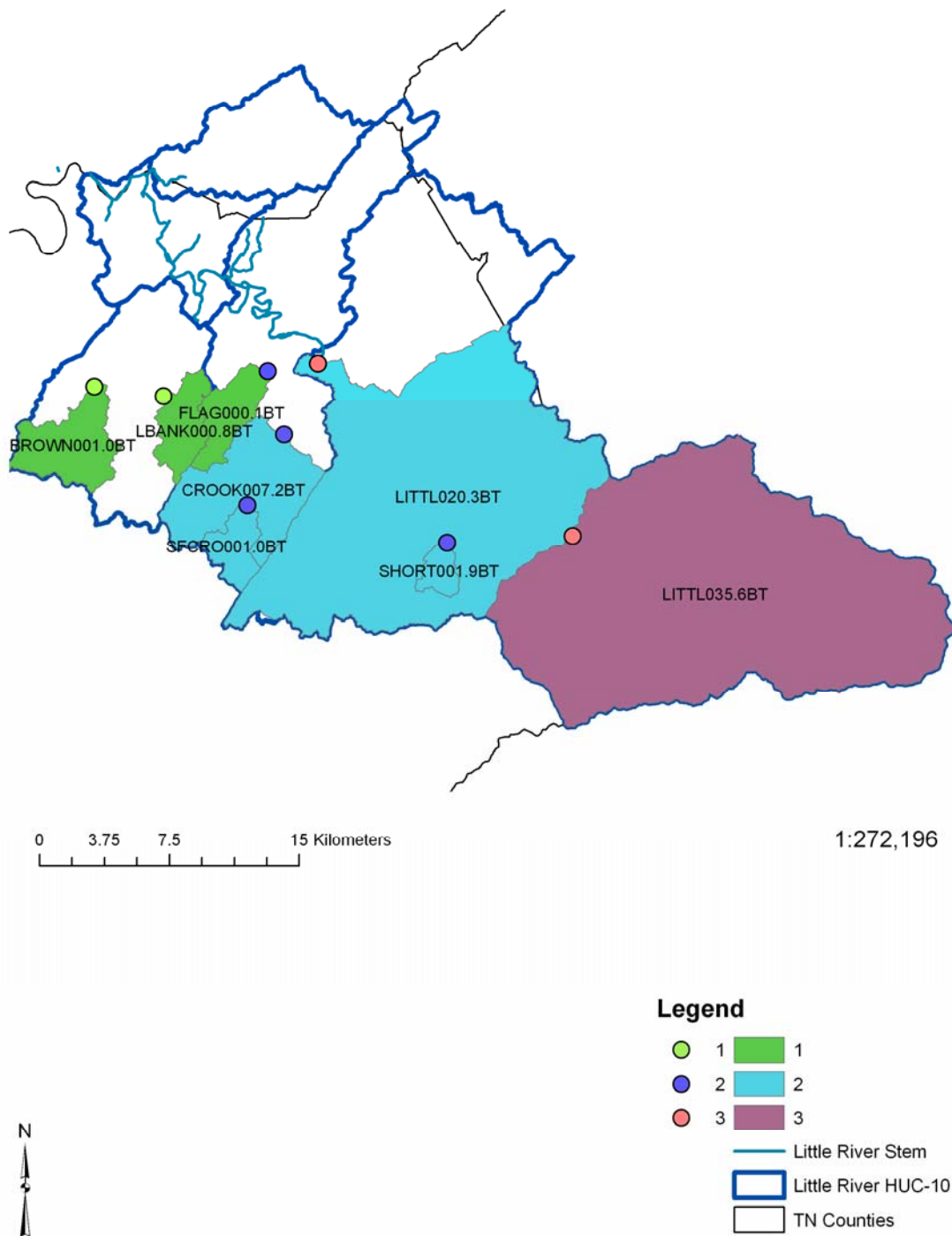


Figure 5.6. CA Three Cluster Solution of Water Quality Site Median Parameter Values Displayed with Three Cluster Solution of Landscape Metrics

Table 5.14. Nonparametric Correlation Analysis of Little River Landscape Metrics and Individual Site Parameter Median Values

Landscape Metric	Ammonia Nitrogen	DO	Conductance	Nitrate + Nitrite	Temperature	Correlation and Significance
PUSER	0.756	-0.595	0.333	0.214	0.690	Correlation Coefficient
	0.030	0.120	0.420	0.610	0.058	Sig. (2-tailed)
USERSL9	0.756	-0.548	0.262	0.095	0.548	Correlation Coefficient
	0.030	0.160	0.531	0.823	0.160	Sig. (2-tailed)
PIMPER	0.756	-0.381	0.833	0.833	0.333	Correlation Coefficient
	0.030	0.352	0.010	0.010	0.420	Sig. (2-tailed)
PIMPSL9	0.756	-0.333	0.786	0.762	0.381	Correlation Coefficient
	0.030	0.420	0.021	0.028	0.352	Sig. (2-tailed)
PFOR	-0.630	0.238	-0.833	-0.905	-0.167	Correlation Coefficient
	0.094	0.570	0.010	0.002	0.693	Sig. (2-tailed)
PNBAR	-0.129	-0.073	-0.195	-0.342	0.073	Correlation Coefficient
	0.761	0.863	0.643	0.408	0.863	Sig. (2-tailed)
PURB	0.756	-0.452	0.833	0.786	0.476	Correlation Coefficient
	0.030	0.260	0.010	0.021	0.233	Sig. (2-tailed)
PAGT	0.504	-0.167	0.762	0.905	0.024	Correlation Coefficient
	0.203	0.693	0.028	0.002	0.955	Sig. (2-tailed)
AGTSL9	0.252	0.024	0.619	0.857	-0.214	Correlation Coefficient
	0.547	0.955	0.102	0.007	0.610	Sig. (2-tailed)
RFOR30	-0.756	0.381	-0.833	-0.833	-0.238	Correlation Coefficient
	0.030	0.352	0.010	0.010	0.570	Sig. (2-tailed)
RURB30	0.756	-0.167	0.619	0.476	0.262	Correlation Coefficient
	0.030	0.693	0.102	0.233	0.531	Sig. (2-tailed)
RAGT30	0.378	-0.095	0.667	0.857	-0.119	Correlation Coefficient
	0.356	0.823	0.071	0.007	0.779	Sig. (2-tailed)
RNS30	-0.252	0.429	-0.333	-0.476	-0.452	Correlation Coefficient
	0.547	0.289	0.420	0.233	0.260	Sig. (2-tailed)
RDDENS	0.756	-0.667	0.952	0.857	0.500	Correlation Coefficient
	0.030	0.071	0.000	0.007	0.207	Sig. (2-tailed)

Table 5.14. Continued.

Landscape Metric	Hardness	Total KN	Total Phosphorus	TSS	Turbidity	Correlation and Significance
PUSER	0.333	0.756	0.098	0.082	-0.072	Correlation Coefficient
	0.420	0.030	0.818	0.846	0.866	Sig. (2-tailed)
USERSL9	0.262	0.756	0.220	0.247	0.060	Correlation Coefficient
	0.531	0.030	0.601	0.555	0.888	Sig. (2-tailed)
PIMPER	0.833	0.756	0.415	0.082	0.431	Correlation Coefficient
	0.010	0.030	0.307	0.846	0.286	Sig. (2-tailed)
PIMPSL9	0.786	0.756	0.390	-0.082	0.311	Correlation Coefficient
	0.021	0.030	0.339	0.846	0.453	Sig. (2-tailed)
PFOR	-0.833	-0.630	-0.342	-0.247	-0.419	Correlation Coefficient
	0.010	0.094	0.408	0.555	0.301	Sig. (2-tailed)
PNBAR	-0.195	-0.129	0.075	0.423	-0.160	Correlation Coefficient
	0.643	0.761	0.860	0.297	0.706	Sig. (2-tailed)
PURB	0.833	0.756	0.439	-0.082	0.347	Correlation Coefficient
	0.010	0.030	0.276	0.846	0.399	Sig. (2-tailed)
PAGT	0.762	0.504	0.220	0.247	0.599	Correlation Coefficient
	0.028	0.203	0.601	0.555	0.117	Sig. (2-tailed)
AGTSL9	0.619	0.252	0.073	0.247	0.551	Correlation Coefficient
	0.102	0.547	0.863	0.555	0.157	Sig. (2-tailed)
RFOR30	-0.833	-0.756	-0.464	-0.247	-0.599	Correlation Coefficient
	0.010	0.030	0.247	0.555	0.117	Sig. (2-tailed)
RURB30	0.619	0.756	0.561	-0.082	0.168	Correlation Coefficient
	0.102	0.030	0.148	0.846	0.691	Sig. (2-tailed)
RAGT30	0.667	0.378	0.146	0.247	0.695	Correlation Coefficient
	0.071	0.356	0.729	0.555	0.056	Sig. (2-tailed)
RNS30	-0.333	-0.252	0.342	-0.412	0.012	Correlation Coefficient
	0.420	0.547	0.408	0.310	0.978	Sig. (2-tailed)
RDDENS	0.952	0.756	0.634	0.247	0.635	Correlation Coefficient
	0.000	0.030	0.091	0.555	0.091	Sig. (2-tailed)

Note: Significant results are in boldface

5.2 Discussion

Land-use and land-cover legacies are relevant to future water quality (Gergal et al. 2002; Strayer et al. 2003). For example, impacts from the conversion of forested lands to impervious surfaces will be felt in the hydrologic cycle as long as the impervious surface cover remains. There is a 2–3 year gap between water quality records and those of land cover. Although any additional conversions during the time period after 2001 (NLCD change product recent date) are unknown, they are not likely to be of a type to nullify the patterns and relationships discovered via this study. In addition, Harding et al. (1998) found that historic land use and land cover may be a more useful indicator in an ecological context than present land use and land cover in a study of the Little Tennessee and French Broad River watersheds in western North Carolina. Their study found that high-impact historic anthropogenic disturbances such as, for example, agriculture, have a much longer temporal impact than short-term catastrophic disturbances like floods. The combination of a lag effect and the magnitude of the impact were the primary factors driving the importance of historic land use and land cover.

The results of multivariate analyses are reflective of the nature and quality of the data (Santos-Roman et al. 2003). Mazlum et al. (1999) also note the importance of systematically observed data that allow for representative multivariate results. Existing LR water quality data in general seem to have been collected on a need/case-by-case basis. Water quality samples typically exist only for a portion of a calendar year at most sites. This presents some difficulty for water quality assessment in terms of accounting for seasonal and spatial variations (USEPA 1999a; USEPA 1999b; USEPA 2002a).

The water quality analyses provide information related to my first research question regarding spatiotemporal patterns of water quality in the LR watershed. This study confirms variations in water quality among upper part, middle part, and lower part areas. The summary statistics in Tables A.1 through A.17 show higher mean and median water quality values occurring at the lower part sites for NH_3 , specific conductance, $\text{NO}_2 + \text{NO}_3$, hardness, total KN, total P, and turbidity.

The results of the nonparametric ANOVA tests show some significant spatial and temporal water quality differences. The significant differences of NH_3 can be seen by examining the summary statistics (Table A.1) which show a considerably higher mean at the Short Creek site compared with the Crooked Creek site. Toxicity of ammonia measurements is dependent on pH and temperature, but, in general, can be toxic to freshwater organisms at concentrations ranging from 0.083 mg/l to 4.6 mg/l (USEPA 1986). The median values are the same, however, which suggests that some Short Creek measurements may have been associated with, for example, runoff events.

The nonparametric ANOVA DO results showed one instance of a significant difference with higher levels occurring near the middle part of the LR watershed on the main stem as compared with the lower part. The lower area has considerably more developed lands and likely experiences increased pollutant loading which can negatively affect DO levels. DO levels are important for fish and aquatic life and criteria vary from a minimum of 5.0 mg/l as the minimum to 8.0 mg/l as the minimum in trout streams supporting naturally producing populations (USEPA 2008c)

Nonparametric ANOVA total P results showed one instance of a significant difference from comparing two LR main stem sites. The upper-most site actually had the higher median value. Higher loadings at the upper part site may likely from natural sources including soil, rocks, and plant residue. The criteria for total P in Tennessee are fairly general and do not specify thresholds because nutrients can cause problems at varying levels. Concentrations of total P are

normally low in fresh water so even a slight increase in concentrations given other factors (e.g., temperature) can trigger problems (USEPA 2006c).

TSS and turbidity nonparametric ANOVA analyses both had significant results, with higher median values occurring in the lower part of the watershed or downstream of the two sample sites compared. This makes sense as developed areas will likely experience higher sediment loading. Similar to total P, sediment criteria are somewhat general for the state and are more specific in local TMDLs. The criteria for Tennessee state that “There shall be no total suspended solids, turbidity, or color in such amounts or character that will result in any objectionable appearance to the water, considering the nature and location of the water” (TDEC 2007). The median values for the sites compared are, in most cases, above the USEPA recommended 25th percentile for all seasons (USEPA 2000b).

The PCA results show underlying associations that make sense in the context of chemical and physical water quality parameters. Conductance, turbidity, and NH₃ best represent the watershed processes associated with their respective PCs given their loadings shown in Tables 5.3 through 5.6. These could be used as proxy parameters for variations of other common water quality indicators (Table 5.3). The CA results differentiate between upper part and lower part sample records, with middle part records representing a transitional area for water quality. The clear spatial pattern shown in Figure 5.4 makes sense in the context of LR land-cover patterns as higher proportions of anthropogenic developed land cover occur around cluster 1. DA integrated the approaches of PCA and CA by determining which variables best represent the spatial groups identified through CA. DO, total P, NH₃, and TSS significantly relate to the CA groups and best differentiate between the upper part and lower part groups.

The landscape metric results provide answers to my second research question regarding the patterns of land cover in the LR watershed. Land ownership differences (e.g., public and private) and associated land cover development patterns can be seen moving from the upper part to the lower part of the watershed. Protected lands occur in the uppermost areas, agriculture is prominent in the middle part, and developed/urban lands have the highest proportions in the lower part of the watershed. Consequently, the middle and lower part LR subwatersheds have higher proportions of anthropogenic land-cover types, which are known to impact water quality (Figures 4.3 and 4.4). The Pistol Creek area has a higher risk due to relatively higher proportions of NPS pollution-contributing land cover.

Length of water quality records at sites were inadequate to fully compare water quality after the first date of the NLCD data (1992) with water quality after the second date of the NLCD data (2001). As a result, a “before-and-after” comparison in the context of land cover and associated land cover change was not possible. The derived NPS-contributing data (Figure 4.4) instead can be used to indicate areas that might become degraded in the future as a result of, for example, a change from forest to urban. Such information could be used to prioritize monitoring for assessing attainment status. Further exploration of the potential for using land-cover change information at different scales in studies of water quality should be pursued.

The correlation analysis provides information relevant to my third research question regarding the relationship between land cover patterns and water quality. Several parameters including NH₃, specific conductance, NO₂ + NO₃, total hardness, and total KN all have significant positive correlations with anthropogenic land cover proportions and significant negative correlations with natural land cover types. In addition, a synthesis of the landscape metric and water quality data analyses shows that water quality patterns generally differentiate between upper part and lower part sites. As water flows towards the LR main stem through tributaries and down through the main stem to the lower part of the watershed, increased NPS pollutant loading occurs as a result of the anthropogenic land cover. In addition, water quality often declines as water flows away from its origin due to inflowing runoff. This coincides with the pattern of

anthropogenic land cover. These results are in harmony with the findings of other land cover/water quality connection studies (e.g. Johnson et al. 1997; O'Neill et al. 1997; Hampson et al. 2000; Wickham et al. 2000; USEPA 2001) and the information presented in the literature (e.g., Turner et al. 2001). This supports my second hypothesis of a connection between spatiotemporal patterns of water quality and land cover.

Seasonal influences play a role in water quality in the LR watershed. The PCA results and nonparametric ANOVA results show that parameters including DO, sediments, and in some cases nutrients are driven by flow-season differences. Figures 5.1 and 5.2 demonstrate the annual flow patterns which highly influence parameter concentrations. This supports my first hypothesis of a relationship between patterns of water quality and seasonal variations given the data that were available for the study. Unfortunately, available data were inadequate for examining the validity of my third hypothesis regarding runoff from developed areas and a connection between precipitation events and water quality.

Existing studies have focused on the connections between sediments and season. The analytical results confirm the presence of a seasonal influence even at a coarse scale (high flow/low flow seasons) on temperature, TSS, and turbidity (Tables 5.3). Both Hart (2006) and Riedal et al. (2004) discuss the influence of season on sediment loading in Southern Appalachian streams; both also demonstrate the importance of flow data for understanding sediment processes in streams. In addition to sediment, the PCA of single combined sites (Tables 5.4, 5.5, and 5.6) show a high-flow/low-flow seasonal influence on DO and total P in addition to TSS and turbidity in subwatershed areas.

This study supplements existing state, Federal, and academic assessments of water quality in the LR. For example, the TVA IPSI study found that, based on TVA's modeling results and projections, forest land cover has a low impact on water quality, while agricultural and urban land covers have high impacts on water quality (TVA 2003). The results herein show that landscape proportions of agriculture and urban are highest in the middle part and lower part areas (e.g., Figures A.1, and A.11, respectively). The correlation analysis results show both positive and negative connections between land cover and water quality. Also, the analysis of land-cover change provides important information on anthropogenic impacts and can serve as an indicator for water quality risk; such analysis has previously not yet been done for the LR. NPS-contributing land cover change has primarily occurred in the lower part of the watershed. Those areas will likely be at greater risk in the future.

Parameter relationships are often site specific. This study provides additional information on the underlying associations between key parameters as well as spatial similarities and differences across the LR watershed. For example, Lewis et al. (2001) found that similar turbidity values from two different tributary watersheds in California could indicate appreciably different TSS values. The nonparametric correlation analysis confirms relationships between several parameters and land-cover proportions. There were no significant correlations with TSS median values, however. Turbidity did show a slight correlation with proportion of agriculture in this study. The PCA analyses show consistent associations between TSS and turbidity based on PC loadings for the whole watershed and for single combined sites. Hart (2006) found significant correlations with sediment levels and land cover in the LR. The study done by Hart (2006) was specifically geared towards examining the effects of storm events and adjacent land use on TSS. By collecting samples in close temporal proximity to storm events, she was likely able to get a better picture of the effects of land cover on TSS and turbidity levels than was represented in TDEC and EPA STORET data.

Examination of the raw LR data revealed instances of "spikes" in TSS measurements likely associated with rain events. The influence of these spikes is evident in both individual site and combined site summary statistics (Tables A.9, A.10, A.16, and A.17) by comparing mean

values with median values. The overall lack of flow data with water quality samples as well as the effect of hysteresis as a “first flush” mechanism create difficulty in fully understanding sediment processes without a sampling approach geared towards sediment monitoring.

5.3 Relevance to TMDL Development

The application of nonparametric ANOVA to TMDL development could be useful for pollution source assessments (USEPA 1999a; USEPA 1999b). For example, LR water quality data show significant differences between upper part, middle part, and lower part sites and between flow seasons. Such information might be useful in various aspects, for example, to answer the question of whether high total P measurements are associated with inputs from adjacent farmlands in the middle part area or an adjacent development near Maryville, Tennessee. Accounting for spatial and temporal variability is important for establishing a link between water quality targets and sources (USEPA 1999a). Similar applications could involve regular change monitoring between key sites. Even though, in this study, the median values of parameters were not in extreme violation of state or national criteria, tests such as nonparametric ANOVA are still sensitive enough to detect even small significant differences between sampling locations. This is particularly useful in cases of, for example, TSS or turbidity measurements where management goals include achieving as minimal levels of sediment as possible.

Methods such as PCA can be used with existing data to determine the association among various water quality indicators. It is important to consider the combined effects of pollutants in the development of a TMDL (USEPA 1999b). Identified relationships between parameters can help to determine common processes or factors driving variance in those parameters. This information could then be used to guide future sampling. For example, results presented in Tables 5.3 and 5.5 suggest negative associations between DO and season, temperature, nutrients, and sediment. The increase of certain land-cover types in the associated areas of the LR watershed may likely result in increased loading of nutrients and sediment. This, in turn, may negatively impact DO levels to the point where those streams would not be in attainment.

Options exist for monitoring efficiency in the LR through use of multivariate techniques. The identification of water quality indicators and target values component of a TMDL could benefit from such information (USEPA 1999b). Santos-Roman et al. (2004) took the approach of selecting the parameter most associated with extracted PCs for representing and further analyzing the water quality of their study area. Singh et al. (2004) applied PCA results to a monitoring design by considering the likely parameter association influences (e.g., anthropogenic, seasonal, mineral, runoff). The source assessment portion of a TMDL could benefit from such information (USEPA 1999b). For example, the results of the PCA analyses of this study show strong relationships between TSS and turbidity in the LR. Turbidity data could be used as a substitute for regular sampling of TSS data in the Pistol Creek area. Water treatment plants in the cities of Alcoa and Maryville, both in the Pistol Creek watershed, have turbidity data sets that exist through the early 1990s. Those consistently collected data could be used as an important change-monitoring tool in the developed Pistol Creek watershed. Hart (2006) conducted a change over time analysis for the Maryville Water Treatment Plant data and found that recent data from 2002-2004 had higher proportions of days exceeding a benchmark of 50 Nephelometric Turbidity Units (NTU) during high flows compared with data from 1990 through 2001.

CA as demonstrated herein provides useful information for creating monitoring efficiency. For example, samples from a key site in each cluster shown in Figure 5.4 could serve as a rapid assessment of water quality for sites in the same cluster. Wunderlin et al. (2001) and Simeonov et al. (2004) were successful in a similar application of CA results to monitoring network design. In addition to cost savings, a potential reduction in needed field samples might allow for more

regular sampling of those sites determined to be representative of the cluster group with which they are associated. The follow-up monitoring and evaluation component of a TMDL could certainly benefit from such efficiency (USEPA 1999a).

DA could be useful for TMDL development because of its ability to identify parameters that significantly relate to differences between known groups. This is important for the identification of water quality indicators component of a TMDL as it can help to reduce sampling costs and increase overall efficiency (USEPA 1999b). Monitoring overall water quality variations can be optimized if the most efficient differentiating parameters are collected. DA might also help identify important indicators that may not initially be determined as relevant during the problem definition stage of a TMDL. For example, the results of this study show that DA was able to differentiate between LR site clusters based on total P, total KN, and specific conductance. Changes in specific conductance levels at a particular site might suggest the need for more frequent monitoring to determine if variations exist for other water quality indicators. It should be noted that specific conductance is one of the few parameters sampled consistently at the USGS gage sites in the LR. In addition, nitrogen and P are both important nutrient indicators which can drive the water quality picture of a whole watershed (Hagerman 2007) and, as demonstrated herein, could serve as potential change monitoring indicators for the LR sites used in this study.

The problem identification and source assessment components of a TMDL can benefit from the addition of relevant geographic information (USEPA 1999a). Proportions of land cover and common landscape metrics are useful for assessing water quality risk and for prioritizing monitoring in times of limited resources (Wickham et al. 2000). The methods and results of this study could be used in an application similar to a recent TMDL developed for Eagleville Brook, Mansfield, Connecticut (SCDEP 2007). A Stressor Identification (SI) study (USEPA 2000a) was carried out to determine the likely cause of impaired aquatic communities. Impervious surface cover was determined to be a probable factor partially causing or contributing to the impairment. The Connecticut TMDL identified a strong correlation between pollutant loads, stormwater flows, and impervious surface runoff as is often the case in many urbanized areas (USEPA 1993). Nonpoint source pollution from urban development is a well known issue in the LR watershed (Little River Big Future 2006). NPS pollutants transported via stormwater, similar to those examined in this study, were determined to be the primary cause of impairment. Proportion of impervious surface cover was used as a surrogate for the typical mix of NPS pollutants which occur as a result of runoff. The Wasteload Allocation (WLA) and Load Allocation (LA) of the TMDL were both expressed in terms of percent imperviousness (SCDEP 2007).

The use of landscape metrics in cases of absent water quality data or complex NPS stressors should be considered for TMDL development. Based on the results of this study, impervious surface and road density are highly correlated with the parameters studied. Proportion of impervious surface, arguably, is one of the most important and will likely become a common metric for assessing risk and allocating wasteloads and loads in TMDLs. This approach could benefit TMDL development by helping to determine the linkages between possible causes and impacts (USEPA 2000a). A recent EPA report documents 17 example TMDLs from around the nation that focus on stormwater as a primary impairment mechanism (USEPA 2007b). Several of the TMDLs outlined therein, including the aforementioned Connecticut (SCDEP 2007) impervious surface TMDL, utilize land cover information in their TMDL process and associated load, wasteload, and margin of safety calculations. In addition, Federal regulations support the use of surrogate measures for TMDL establishment. For example, 40 CFR §130.7 (c)(1)(i) of the Code of Federal Regulations Title 40: Protection of Environment states that "TMDLs may be established using a pollutant-by-pollutant or biomonitoring approach....Site-specific information should be used wherever possible." In addition, 40 CFR §130.2-(i) states that "TMDLs can be expressed in terms of either mass per time, toxicity, or other appropriate measure" (US Congress 1998).

Chapter 6 Conclusions and Recommendations

The results of this study provide helpful information for future monitoring and research in the LR. The statistical and multivariate analyses revealed associations among water quality parameters and spatiotemporal patterns of water quality parameters across the watershed. Significant differences exist between upper part and lower part water quality, between high-flow and low-flow season water quality samples, and between upper part and lower part land cover. The overall results show a clear connection between land cover and water quality in the LR. In particular, the Pistol Creek area of the watershed shows evidence of higher levels of problem-causing water quality indicators.

The multivariate techniques presented herein can be useful to TDEC for TMDL development in the LR. PCA, CA, and DA complement each other for analyses of existing water quality data. PCA, which operates on data variables, determined that specific conductance, turbidity, and NH_3 could be used as proxy parameters for variations of other common water quality indicators (Table 5.3). An increased sampling frequency of TSS, turbidity, and total P would be beneficial for understanding seasonal variations and for TMDL MOS definitions, as illustrated by the associations of these parameters with flow season (Tables 5.3, 5.4, 5.5, and 5.6). CA, which operates on data records/samples, identified similarities between sample records and associated sites, which could be selectively sampled for rapid assessments (Figure 5.4). DA integrates the approaches of PCA and CA by determining which variables best represent the spatial groups identified through CA. DO, total P, NH_3 , and TSS significantly relate to the CA groups and best differentiate between the upper part and lower part groups.

GIS complements multivariate techniques by enabling spatial data integration and visualization. This study serves as a prototype for the analysis of the types and locations of anthropogenic land-cover change occurring in Tennessee watersheds. The information gained from a land-cover change analysis is useful for assessing future risk. Further analysis should be explored by examining the full HUC-10 LR watershed and/or the whole state of Tennessee. In addition, change analysis at different scales should be considered as patterns and processes are frequently influenced by processes at other scales (Peters 2007). In addition, the use of ATtILA on data of a finer scale (e.g., classified 10m SPOT imagery) may provide even more useful information on land cover proportions relevant to water quality.

Figures A.1 through A.14 show the trends of NPS pollution-contributing land-cover types. A CA of land cover proportions was visualized with water quality CA results to determine spatial similarities (Figure 5.6). Sampling sites that grouped in the same cluster are close to each other geographically. In addition, their associated contributing subwatersheds grouped in a similar pattern. Further correlation analysis confirmed relationships between the water quality parameters NH_3 , specific conductance, $\text{NO}_2 + \text{NO}_3$, hardness, total KN, total P, and turbidity and land-cover types associated with NPS pollution. TDEC should focus sampling efforts in the lower part of the LR watershed, given the increased risk of water quality impairment associated with the predominant land-cover types there.

Additional work is warranted in the LR watershed. The collection of flow data along with water quality measurements should be considered since flow levels determine pollutant loads. Flow measurements at the time of water quality sampling in the LR were sparse. The prioritization of sample locations via methods such as CA could potentially enable the sampling of fewer locations more frequently versus more locations less frequently (Wunderlin et al. 2001; Simeonov et al. 2003). As was demonstrated in this study, a decision had to be made between more sample sites and considerably fewer water quality indicators or more water quality indicators and considerably fewer sampling sites. An increased number of samples at fewer sites would provide greater statistical confidence with larger sample sizes. Even sampling at a 2 or 3 month interval

consistently over a longer period of time could provide more useful information on likely sources and seasonal influences.

Additional work could also entail further reconciliation of data for a study of larger watersheds (e.g., HUC-8). A more comprehensive analysis of parameter compatibility for cross-walking different systems (e.g., USGS NWIS, EPA STORET, Army Corps of Engineers, TDEC in-house) and for overall standardization should also be explored. The forthcoming 2006 NLCD land-cover data set will serve as an additional freely available tool for examining land-cover change from 1992 through 2006. The development of an ArcGIS 9.x compatible version of the EPA ATtILA software package, in addition to the currently available ArcView 3.2 version, will also extend analytical capabilities for calculating landscape metrics (Yankee 2008). This will be a significant tool as the ATtILA analytical capabilities will be more closely integrated with commonly available GIS software versions and other tools such as the ArchHydro data model and tool suite.

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Appendix

Tables

Table A.1. Summary Statistics for Ammonia Nitrogen Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	0.0194	0.0655	0.0229	0.0227
Median	0.02	0.02	0.02	0.02
Standard Deviation	0.0024	0.1381	0.0145	0.0090
Range	0.01	0.62	0.08	0.03
Minimum	0.01	0.02	0.01	0.02
Maximum	0.02	0.64	0.09	0.05
Count	17	20	24	11

Statistic	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT	CROOK007.2BT
Mean	0.021	0.0358	0.0358	0.02
Median	0.02	0.03	0.03	0.02
Standard Deviation	0.0031	0.0202	0.0202	3.6387E-18
Range	0.01	0.07	0.07	0
Minimum	0.02	0.03	0.03	0.02
Maximum	0.03	0.1	0.1	0.02
Count	10	12	12	11

Note: Ammonia nitrogen measurement units are mg/l

Table A.2. Summary Statistics for DO Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	10.289	28.6333	10.2947	10.198
Median	10.25	9.255	10.58	10.56
Standard Deviation	1.4555	39.8433	1.433	1.5825
Range	5.5	112.55	4.7	5.26
Minimum	7.8	2.75	8	7.47
Maximum	13.3	115.3	12.7	12.73
Count	20	18	17	10

Statistic	CROOK007.2BT	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT
Mean	10.207	10.648	7.71	9.0491
Median	10.545	10.925	6.92	8.89
Standard Deviation	1.8057	1.6237	1.9298	1.5663
Range	6.09	5.43	6.31	5.54
Minimum	7.01	8	4.73	6.18
Maximum	13.1	13.43	11.04	11.72
Count	10	10	11	12

Note: DO measurement units are mg/l

Table A.3. Summary Statistics for Conductance Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	18.1631	314.3333	68.6	322.25
Median	17.3	318	68	321.5
Standard Deviation	4.2689	39.0875	17.5083	43.3508
Range	16	130	57	124
Minimum	12	254	40	251
Maximum	28	384	97	375
Count	19	21	15	12

Statistic	CROOK007.2BT	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT
Mean	247	168.6666	343	426.5833
Median	256	171	358	482.5
Standard Deviation	45.4592	34.8146	58.1807	97.6212
Range	145	123	153	293
Minimum	166	94	262	234
Maximum	311	217	415	527
Count	12	12	11	12

Note: Conductance measurement units are uMHO

Table A.4. Summary Statistics for Nitrate+Nitrite Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	0.12882	0.2294	0.12857	0.8515
Median	0.15	0.21	0.12	0.85
Standard Deviation	0.0668	0.2095	0.0663	0.24538
Range	0.22	0.994	0.23	1.01
Minimum	0.01	0.006	0.04	0.39
Maximum	0.23	1	0.27	1.4
Count	17	20	14	12

Statistic	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT	CROOK007.2BT
Mean	0.14575	1.0466	1.26	0.307
Median	0.1495	0.425	0.655	0.33
Standard Deviation	0.0486	2.0707	1.9480	0.1151
Range	0.15	7.31	7	0.37
Minimum	0.07	0.3	0.38	0.09
Maximum	0.22	7.61	7.38	0.46
Count	12	12	12	12

Note: Nitrate+Nitrite measurement units are mg/l

Table A.5. Summary Statistics for Temperature Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	13.0684	16.2628	14.4586	12.5766
Median	13	16.94	11.97	11.84
Standard Deviation	6.3831	2.9083	6.9683	4.46915
Range	20	9.72	21	15.03
Minimum	4	10.52	5	5.89
Maximum	24	20.24	26	20.92
Count	19	21	15	12

Statistic	CROOK007.2BT	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT
Mean	11.9860	11.2225	16.1481	16.4433
Median	11.285	10.905	17.18	17.455
Standard Deviation	5.2887	5.1535	5.0354	4.6975
Range	17.29	17.37	13.74	13.25
Minimum	4.36	3.19	9.53	9.95
Maximum	21.65	20.56	23.27	23.2
Count	12	12	11	12

Note: Temperature measurement units are in C

Table A.6. Summary Statistics for Total Hardness Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	13.91	156.805	38.725	174.5454
Median	12	164	37	175
Standard Deviation	7.3979	36.9361	12.0447	8.3948
Range	36	179.9	46	26
Minimum	1	7.1	24	164
Maximum	37	187	70	190
Count	20	20	16	11

Statistic	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT	CROOK007.2BT
Mean	89.6666	187.5	242.1	115.825
Median	94	185	245	128.5
Standard Deviation	14.0798	10.9772	20.8297	37.0174
Range	57	34	79	140.1
Minimum	55	169	191	7.9
Maximum	112	203	270	148
Count	12	10	10	12

Note: Hardness measurement units are in mg/l

Table A.7. Summary Statistics for Total KN Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	0.1	0.1395	0.1014	0.1241
Median	0.1	0.1	0.1	0.1
Standard Deviation	0	0.1038	0.0053	0.0588
Range	0	0.47	0.02	0.21
Minimum	0.1	0.1	0.1	0.08
Maximum	0.1	0.57	0.12	0.29
Count	5	20	14	12

Statistic	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT	CROOK007.2BT
Mean	0.1241	0.3241	0.3708	0.095
Median	0.1	0.15	0.15	0.1
Standard Deviation	0.0689	0.3969	0.7649	0.0271
Range	0.24	1.35	2.65	0.12
Minimum	0.1	0.15	0.15	0.03
Maximum	0.34	1.5	2.8	0.15
Count	12	12	12	12

Note: Total KN measurement units are in ug/l

Table A.8. Summary Statistics for Total Phosphorus Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	0.02	0.0362	0.0092	0.0311
Median	0.01	0.02	0.008	0.0075
Standard Deviation	0.0281	0.0385	0.0114	0.0417
Range	0.106	0.096	0.056	0.138
Minimum	0.004	0.004	0.004	0.004
Maximum	0.11	0.1	0.06	0.142
Count	16	20	23	12

Statistic	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT	CROOK007.2BT
Mean	0.0473	0.0308	0.0191	0.03925
Median	0.0175	0.02	0.02	0.0165
Standard Deviation	0.0642	0.0284	0.0066	0.0462
Range	0.195	0.09	0.02	0.147
Minimum	0.004	0.01	0.01	0.004
Maximum	0.199	0.1	0.03	0.151
Count	12	12	12	12

Note: Total P measurement units are in mg/l

Table A.9. Summary Statistics for TSS Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	5.3157	10.65	4.2941	13.6666
Median	4	10	3	10
Standard Deviation	3.8593	1.2258	3.5313	10.9489
Range	9	4	9	38
Minimum	1	10	1	10
Maximum	10	14	10	48
Count	19	20	17	12

Statistic	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT	CROOK007.2BT
Mean	10.5833	10.4166	10.4166	18.8333
Median	10	10	10	10
Standard Deviation	2.0207	0.9962	1.1645	24.6201
Range	7	3	4	86
Minimum	10	10	10	10
Maximum	17	13	14	96
Count	12	12	12	12

Note: TSS measurement units are in mg/l

Table A.10. Summary Statistics for Turbidity Samples at Individual Little River Sites

Statistic	LITTL035.6BT	SHORT001.9BT	LITTL020.3BT	FLAG000.1BT
Mean	0.7166	5.995	1.95	9.6333
Median	0.8	5.45	2.05	5.45
Standard Deviation	0.3970	2.3279	1.0148	8.7929
Range	1.2	9.9	2.3	27.2
Minimum	0.1	2.3	0.7	2.7
Maximum	1.3	12.2	3	29.9
Count	6	20	4	12

Statistic	SFCRO001.0BT	LBANK000.8BT	BROWN001.0BT	CROOK007.2BT
Mean	5.9272	9.2	4.6333	24.85
Median	3.9	6.9	3.6	6.5
Standard Deviation	6.5268	5.1858	4.0207	49.7602
Range	22.7	15.4	15	176
Minimum	1.9	2.9	1.4	3
Maximum	24.6	18.3	16.4	179
Count	11	12	12	12

Note: Turbidity measurement units are in NTU

Table A.11. Summary Statistics for Ammonia Nitrogen Samples at Combined Little River Sites

Statistic	060102010103_E	060102010103_G	060102010103_I	060102010104_A	060102010105_D	060102010105_E
Mean	0.0430	0.0366	0.0201	0.0217	0.0215	0.0248
Median	0.02	0.02	0.02	0.02	0.02	0.02
Standard Deviation	0.0878	0.0385	0.0155	0.0114	0.0072	0.0153
Range	0.62	0.21	0.11	0.08	0.04	0.09
Minimum	0.02	0.01	0.01	0.01	0.02	0.02
Maximum	0.64	0.22	0.12	0.09	0.06	0.11
Count	53	57	61	39	32	56

Statistic	060102010106_D	060102010107_G	060102010107_I	060102010107_J	060102010108_A
Mean	0.0204	0.03285	0.0329	0.0329	0.0388
Median	0.02	0.03	0.03	0.03	0.02
Standard Deviation	0.002	0.0127	0.0142	0.0142	0.0709
Range	0.01	0.07	0.07	0.07	0.55
Minimum	0.02	0.03	0.03	0.03	0.02
Maximum	0.03	0.1	0.1	0.1	0.57
Count	25	35	24	24	79

Note: Ammonia nitrogen measurement units are in mg/l

Table A.12. Summary Statistics for DO Samples at Combined Little River Sites

Statistic	060102010103_E	060102010103_G	060102010103_I	060102010104_A	060102010105_D
Mean	29.318	26.6993	10.5535	10.1878	10.285
Median	9.88	10.14	10.6	10.1	10.17
Standard Deviation	39.4351	37.9765	1.5088	1.4294	1.8170
Range	119.85	132.852	6.5	4.7	7.71
Minimum	2.75	0.148	7.8	8	6.71
Maximum	122.6	133	14.3	12.7	14.42
Count	45	49	80	23	30

Statistic	060102010105_E	060102010106_E	060102010106_D	060102010107_I	060102010107_J
Mean	9.848	8.3864	7.62875	8.7229	8.3378
Median	10.17	8.1	7.085	8.735	8.65
Standard Deviation	1.8781	1.6110	1.3336	1.4537	1.7006
Range	6.64	8.6	3.59	6.04	6.31
Minimum	6.46	5.6	6.33	5.68	4.73
Maximum	13.1	14.2	9.92	11.72	11.04
Count	35	59	8	24	23

Note: DO measurement units are in mg/l

Table A.13. Summary Statistics for Temperature Samples at Combined Little River Sites

Statistic	060102010103_I	060102010104_A	060102010105_D	060102010105_E
Mean	12.8631	14.0557	11.7502	12.7315
Median	12.5	13.3	11.48	12.39
Standard Deviation	5.813121611	6.790331046	4.987908017	5.104772748
Range	23	22.23	19.61	17.42
Minimum	1	3.77	1.89	4.36
Maximum	24	26	21.5	21.78
Count	114	21	35	41

Statistic	060102010106_D	060102010107_G	060102010107_I	060102010107_J
Mean	18.876	17.6471	15.985	15.6034
Median	21.875	18.11	16.69	16.29
Standard Deviation	6.9267	4.0475	3.7879	3.8367
Range	17.64	14.02	13.25	13.74
Minimum	8.86	11.44	9.95	9.53
Maximum	26.5	25.46	23.2	23.27
Count	10	35	24	23

Note: Temperature measurement units are in C

Table A.14. Summary Statistics for Total KN Samples at Combined Little River Sites

Statistic	060102010103_E	060102010103_G	060102010104_A	060102010105_D	060102010105_E
Mean	0.1234	0.1211	0.1007	0.1127	0.1363
Median	0.1	0.1	0.1	0.1	0.1
Standard Deviation	0.0669	0.0324	0.0039	0.0501	0.0898
Range	0.47	0.13	0.02	0.33	0.53
Minimum	0.1	0.1	0.1	0.01	0.03
Maximum	0.57	0.23	0.12	0.34	0.56
Count	52	51	26	36	58

Statistic	060102010106_D	060102010107_G	060102010107_I	060102010107_J	060102010108_A
Mean	0.1143	0.246	0.2895	0.3379	0.1364
Median	0.1	0.15	0.15	0.15	0.1
Standard Deviation	0.0514	0.3853	0.5534	0.3995	0.0922
Range	0.24	2.15	2.65	1.35	0.5
Minimum	0.1	0.15	0.15	0.15	0.1
Maximum	0.34	2.3	2.8	1.5	0.6
Count	23	35	24	24	79

Note: Total KN measurement units are in ug/l

Table A.15. Summary Statistics for Total Phosphorus Samples at Combined Little River Sites

Statistic	060102010103_E	060102010103_G	060102010103_I	060102010104_A
Mean	0.0404	0.0233	0.0162	0.0153
Median	0.02	0.007	0.01	0.0055
Standard Deviation	0.0649	0.0326	0.0151	0.0391
Range	0.414	0.116	0.106	0.236
Minimum	0.004	0.004	0.004	0.004
Maximum	0.418	0.12	0.11	0.24
Count	53	57	77	38

Statistic	060102010106_D	060102010106_E	060102010107_G	060102010107_I
Mean	0.0477	0.0737	0.026	0.0170
Median	0.017	0.05542	0.02	0.02
Standard Deviation	0.1148	0.0597	0.0272	0.0062
Range	0.556	0.25102	0.13	0.02
Minimum	0.004	0.00326	0.01	0.01
Maximum	0.56	0.25428	0.14	0.03
Count	25	59	35	24

Statistic	060102010105_D	060102010105_E	060102010105_G
Mean	0.0392	0.0563	0.0913
Median	0.007	0.019	0.05
Standard Deviation	0.0519	0.1555	0.1712
Range	0.195	1.096	0.84
Minimum	0.004	0.004	0.02
Maximum	0.199	1.1	0.86
Count	36	51	23

Statistic	060102010107_J	060102010108_A
Mean	0.0283	0.0642
Median	0.02	0.02
Standard Deviation	0.0242	0.2095
Range	0.09	1.82
Minimum	0.01	0
Maximum	0.1	1.82
Count	24	79

Note: Total P measurement units are in mg/l

Table A.16. Summary Statistics for TSS Samples at Combined Little River Sites

Statistic	060102010103_E	060102010103_G	060102010105_D
Mean	10.5576	13.3181	11.1111
Median	10	10	10
Standard Deviation	2.3298	9.3305	4.0410
Range	16	50	22
Minimum	10	10	10
Maximum	26	60	32
Count	52	44	36

Statistic	060102010106_E	060102010107_G	060102010107_I
Mean	13.0208	10	10.2083
Median	8	10	10
Standard Deviation	12.8683	0	0.8329
Range	56	0	4
Minimum	1	10	10
Maximum	57	10	14
Count	48	35	24

Statistic	060102010105_E	060102010105_G	060102010106_D
Mean	24.3829	17.6613	10.9230
Median	10	14	10
Standard Deviation	44.1674	13.9372	1.9348
Range	263	47.9	6
Minimum	10	1.1	10
Maximum	273	49	16
Count	47	44	13

Statistic	060102010107_J	060102010108_A
Mean	12.8260	10.2820
Median	10	10
Standard Deviation	9.8056	1.8649
Range	46	15
Minimum	10	10
Maximum	56	25
Count	23	78

Note: TSS measurement units are in mg/l

Table A.17. Summary Statistics for Turbidity Samples at Combined Little River Sites

Statistic	060102010103_I	060102010105_D	060102010105_E	060102010105_G	060102010106_D
Mean	0.8224	7.6771	32.4319	7.5208	22.82
Median	0.6	4.9	7.9	6.7	7.8
Standard Deviation	1.3632	11.8836	90.1793	5.2254	36.6627
Range	10.9	68.8	589.4	17.75	131.2
Minimum	0.1	1	2.7	0.25	2.8
Maximum	11	69.8	592.1	18	134
Count	69	35	47	23	15

Statistic	060102010106_E	060102010107_G	060102010107_I	060102010107_J	060102010108_A
Mean	15.7686	4.4142	4.9833	11.9	9.0589
Median	10	3.6	4.25	8.35	6.6
Standard Deviation	15.8784	2.6860	3.5169	10.0740	8.0975
Range	70.2	11.7	15	41.1	50.7
Minimum	1.8	1.6	1.4	2.9	1.5
Maximum	72	13.3	16.4	44	52.2
Count	51	35	24	24	78

Note: Turbidity measurement units are in NTU

Table A.18. Individual Site IDs with Temporal Period Coverage and Included Parameters Used in Nonparametric ANOVA Analyses

Site ID	# Records	Temporal Coverage	Ammonia Nitrogen	DO	Total KN	Total Phosphorus	TSS	Turbidity
SFCRO001.0BT	12	4/12/2004 – 5/9/2005	X	X	X	X	X	X
LBANK000.8BT	12	9/14/2005 – 11/28/2006	X	X	X	X	X	X
CROOK007.2BT	12	4/12/2004 – 4/11/2005	X	X	X	X	X	X
BROWN001.0BT	12	9/14/2005 – 11/28/2006	X	X	X	X	X	X
FLAG000.1BT	12	4/12/2004 – 4/11/2005	X	X	X	X	X	X
LITTL009.6BT	15	6/23/1998 – 11/24/2003	X	X	X	X	X	X
LITTL020.3BT	28	4/29/1992 – 11/24/2003	X	X	X	X	X	X
LITTL035.6BT	21	4/29/1992 – 12/15/1998	X	X	X	X	X	X
STOCK003.2KN	27	6/23/1998 – 2/19/2004	X		X	X	X	X
ELLEJ000.1BT	15	6/23/1998 – 2/19/2004	X	X	X	X	X	X
SHORT001.9BT	21	4/6/2004 – 11/3/2005	X	X	X	X	X	X

Table A.19. Nonparametric ANOVA Tests Combined Site IDs with Temporal Period Coverage and Parameters

Combined Site ID	# Records	Temporal Coverage	Ammonia Nitrogen	DO	Total KN	Total Phosphorus	TSS	Turbidity
060102010103_E	54	4/04 – 11/05	X	X	X	X	X	
060102010103_G	72	6/98 – 12/98; 7/03 – 11/05	X	X	X	X	X	
060102010103_I	116	10/85 – 8/05	X	X		X		X
060102010104_A	43	4/92 – 9/04	X	X	X	X		
060102010105_D	36	1/04 – 5/05	X	X	X	X	X	X
060102010105_E	59	6/98 – 4/05	X	X	X	X	X	X
060102010105_G	58	8/79 – 1/85				X	X	X
060102010106_D	25	6/98 – 12/03	X	X	X	X	X	X
060102010106_E	59	1/71 – 12/71; 3/79 – 9/82		X		X	X	X
060102010107_G	35	9/05 – 11/05; 6/06 – 11/06	X	X	X	X	X	X
060102010107_I	24	9/05 – 11/05; 6/06 – 11/06	X	X	X	X	X	X
060102010107_J	24	9/05 – 11/05; 6/06 – 11/06	X	X	X	X	X	X
060102010108_A	79	6-98 – 9-98; 4/03 – 2/04	X		X	X	X	X

Table A.20. Multivariate Analyses Individual Sites and Parameters Used

Site ID	# Records	Temporal Coverage	Ammonia Nitrogen	DO	Conductance	Nitrate + Nitrite	Temperature
SFCRO001.0BT	12	4/2004 – 5/2005	X	X	X	X	X
LBANK000.8BT	12	9/14/2005 – 11/2006	X	X	X	X	X
CROOK007.2BT	12	4/2004 – 4/2005	X	X	X	X	X
BROWN001.0BT	12	9/2005 – 11/2006	X	X	X	X	X
FLAG000.1BT	12	4/2004 – 4/2005	X	X	X	X	X
LITTL020.3BT	28	4/1992 – 11/2003	X	X	X	X	X
LITTL035.6BT	21	4/1992 – 12/1998	X	X	X	X	X
SHORT001.9BT	21	4/2004 – 1/2005	X	X	X	X	X

Site ID	# Records	Temporal Coverage	Hardness	Total KN	Total Phosphorus	TSS	Turbidity
SFCRO001.0BT	12	4/2004 – 5/2005	X	X	X	X	X
LBANK000.8BT	12	9/14/2005 – 11/2006	X	X	X	X	X
CROOK007.2BT	12	4/2004 – 4/2005	X	X	X	X	X
BROWN001.0BT	12	9/2005 – 11/2006	X	X	X	X	X
FLAG000.1BT	12	4/2004 – 4/2005	X	X	X	X	X
LITTL020.3BT	28	4/1992 – 11/2003	X	X	X	X	X
LITTL035.6BT	21	4/1992 – 12/1998	X	X	X	X	X
SHORT001.9BT	21	4/2004 – 1/2005	X	X	X	X	X

Table A.21. Multivariate Analyses Combined Sites and Parameters Used

Combined Site ID	# Records	Temporal Coverage	Ammonia Nitrogen	DO	Temperature	Total KN	Total Phosphorus	TSS	Turbidity
060102010105_D	36	1/04 – 5/05	X	X	X	X	X	X	X
060102010105_E	59	6/98 – 4/05	X	X	X	X	X	X	X
060102010106_D	25	6/98 – 12/03	X	X	X	X	X	X	X
060102010107_G	35	9/05 – 11/05; 6/06 – 11/06	X	X	X	X	X	X	X
060102010107_I	24	9/05 – 11/05; 6/06 – 11/06	X	X	X	X	X	X	X
060102010107_J	24	9/05 – 11/05; 6/06 – 11/06	X	X	X	X	X	X	X

Table A.22. Descriptive Definitions of Individual Sampling Site Names

Site ID	Description
SFCRO001.0BT	South Fork of Crooked Creek, River Mile 1, Butler Mill Road
LBANK000.8BT	Laurel Bank Branch, River Mile 0.8, 50 yards upstream from Middle Settlement Road
CROOK007.2BT	Crooked Creek, River Mile 7.2, 1st private drive off Friendship Way
BROWN001.0BT	Brown Creek, River Mile 1, Highway 411 Bridge
FLAG000.1BT	Flag Branch, River Mile 0.1, 45 yards upstream from Centennial Road
LITTL020.3BT	Little River Stem, River Mile 20.3, Coulters Bridge behind Heritage High School
LITTL035.6BT	Little River Stem, River Mile 35.6, Smoky Mountain Parkway above confluence with Middle Prong
SHORT001.9BT	Short Creek, River Mile 1, private drive crossing off Old Cades Cove Road (Rich Mt. Gap Road)

Table A.23. Individual Site Membership in Combined Sites

Combined Site ID	060102010103_E	060102010103_G	060102010103_I	060102010104_A
Individual Sites Comprising Combined Site	SHORT001.9BT	TIPTO000.1BT	LITTLE035.6	LITTLE020.3BT
	SHORT001.4BT	SHORT000.0	USGS_3497300	ECO66E17
	DSPRI000.2BT	SHORT000.5BT		REED000.1BT
		SHORT000.7BT		HESSE000.2BT
		LITTLE027.0BT		
		FLAT002.4BT		

Combined Site ID	060102010105_D	060102010105_E	060102010105_G	060102010106_D
Individual Sites Comprising Combined Site	SFCRO001.0BT	CROOK001.1BT	1715	LITTLE009.6BT
	MOOK000.3BT	CROOK007.2BT	USGS_3498500	LITTLE007.6BT
	NFCRO000.3BT	FLAG000.1BT		RODDY000.6BT
		ELLEJOY000.1BT		

Combined Site ID	060102010106_E	060102010107_G	060102010107_I	060102010107_J
Individual Sites Comprising Combined Site	475177	PISTO004.3BT	BROWN001.0BT	CULTO001.5BT
	475296	SPRIN000.7BT	PISTO011.1BT	LBANK000.8BT
		PISTO007.6BT		

Combined Site ID	060102010108_A
Individual Sites Comprising Combined Site	STOCK002.0KN
	STOCK003.2KN
	STOCK004.6KN
	STOCK005.3KN
	STOCK006.5KN
	STOCK007.3KN
	STOCK008.4KN

Figures

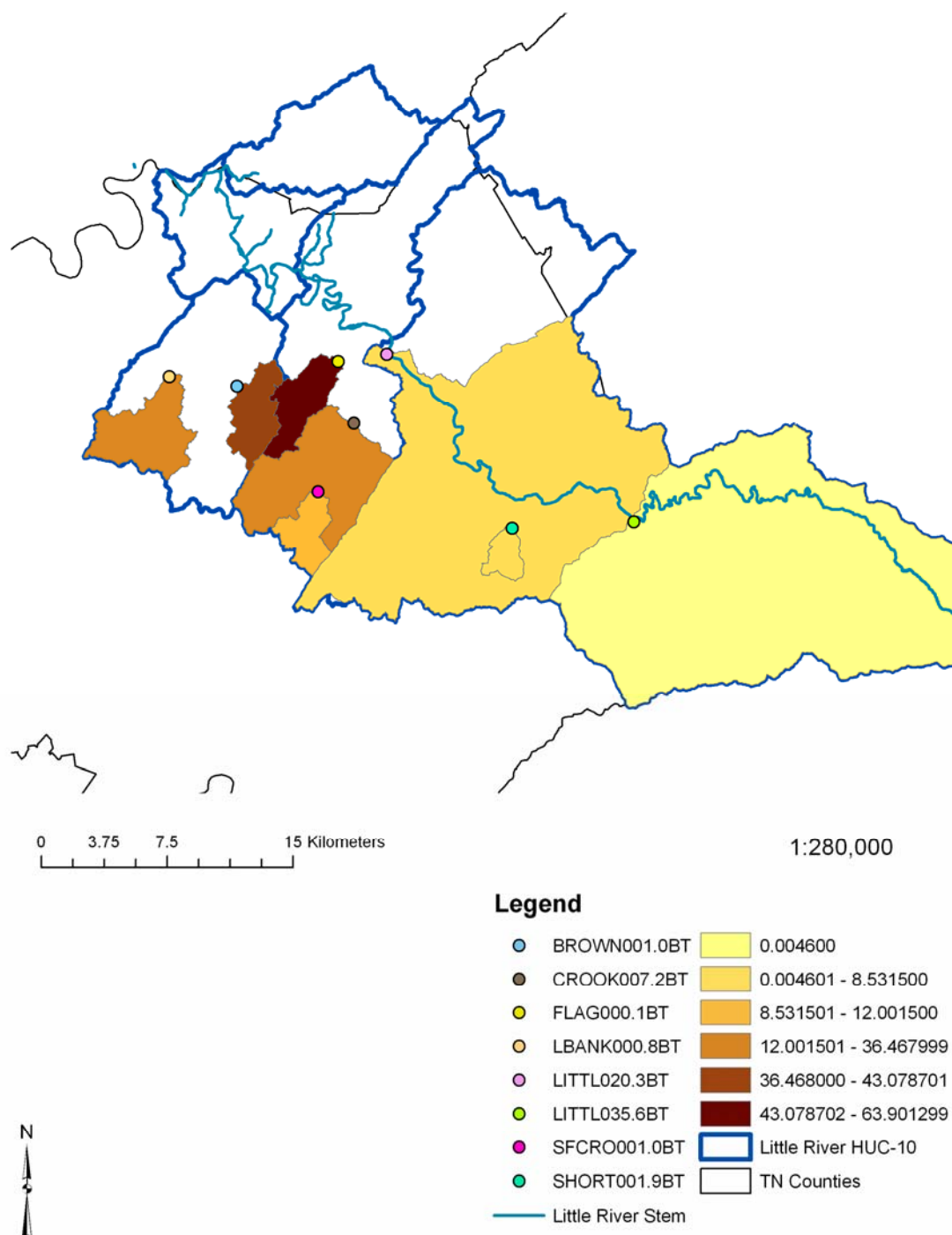


Figure A.1. Proportion of Little River Analysis Sampling Site Subwatershed Agricultural Land Cover - 2001

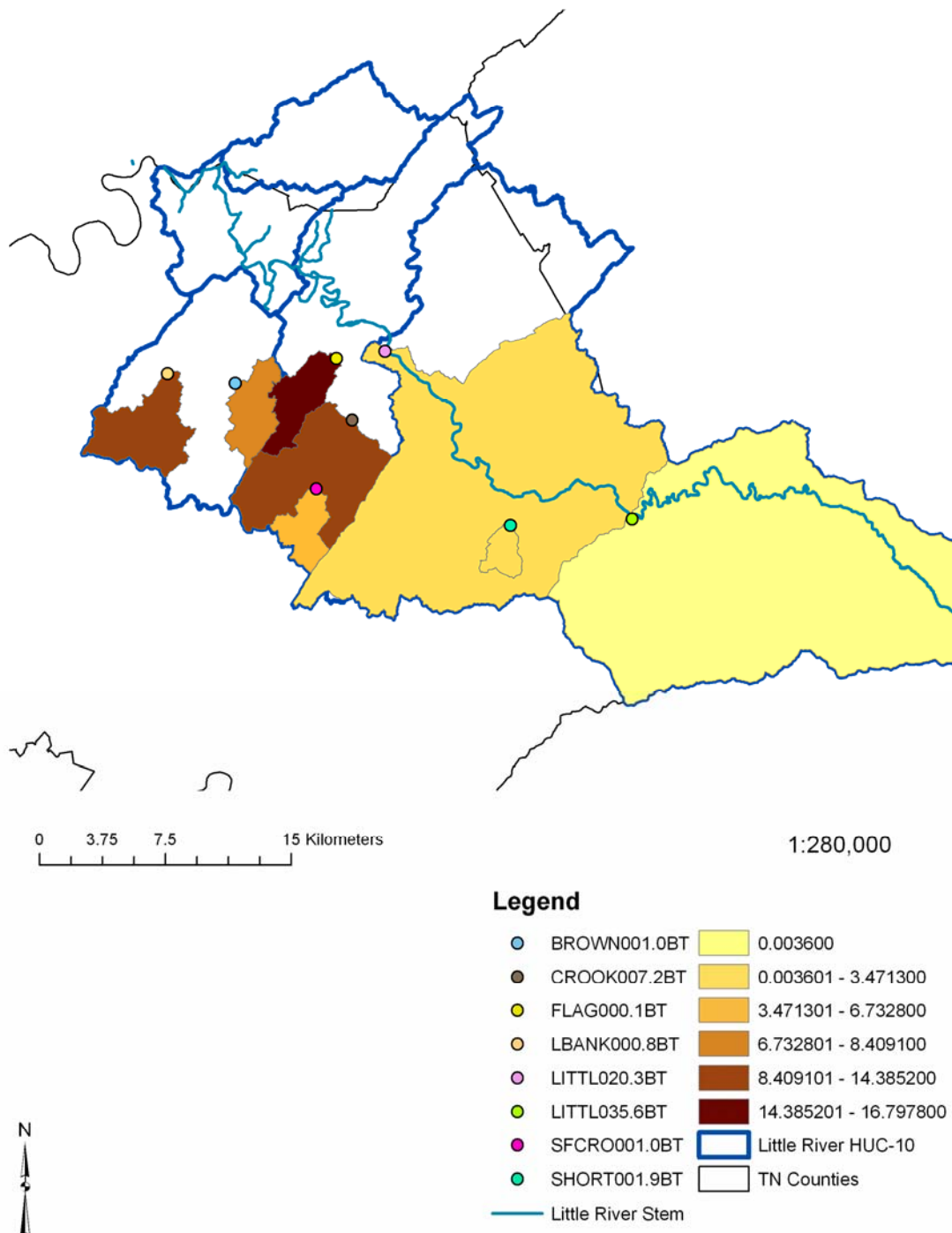


Figure A.2. Proportion of Little River Analysis Sampling Site Subwatershed Agriculture on Steep Slopes (9 percent threshold) – 2001

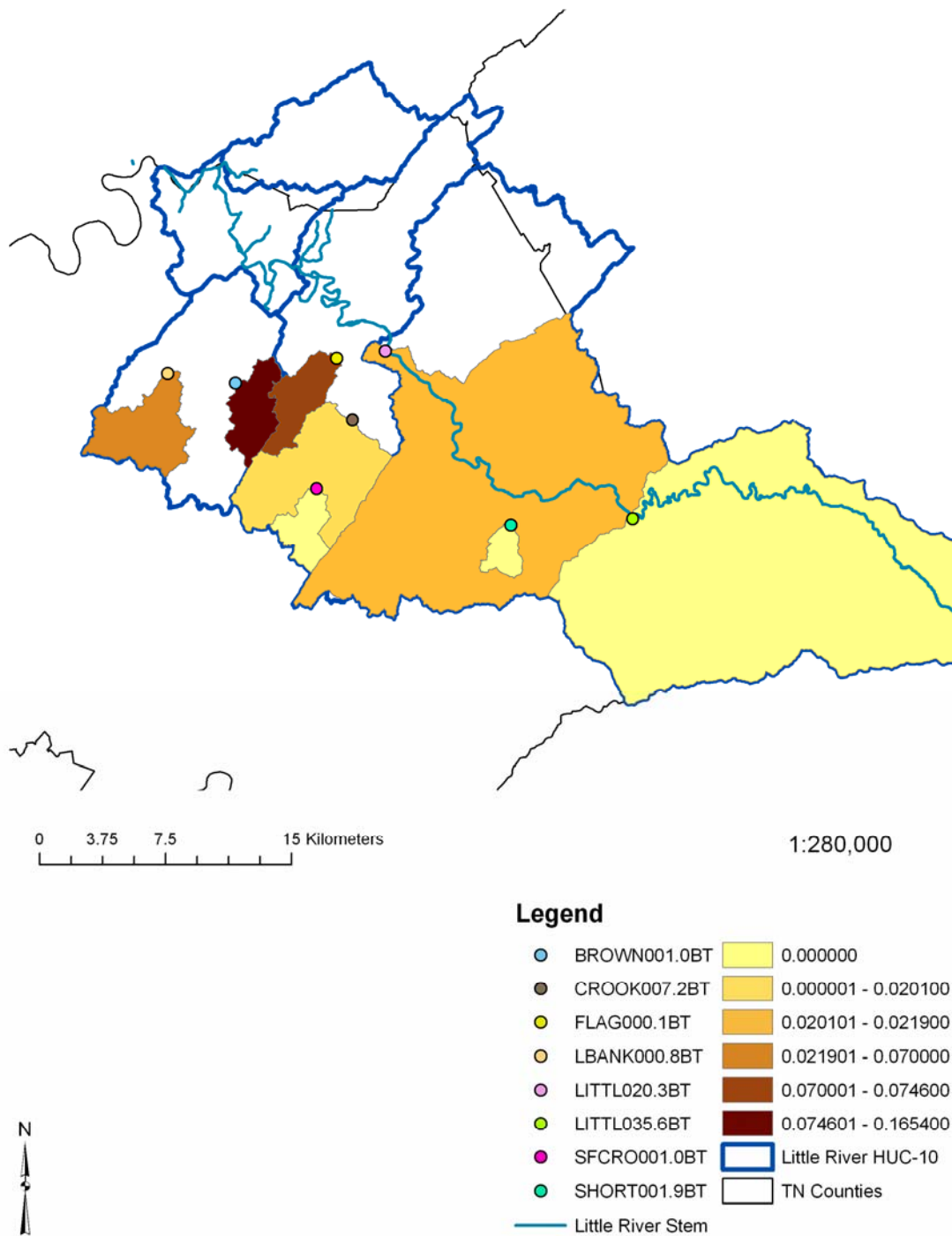


Figure A.3. Proportion of Little River Analysis Sampling Site Subwatershed Barren Land Cover - 2001

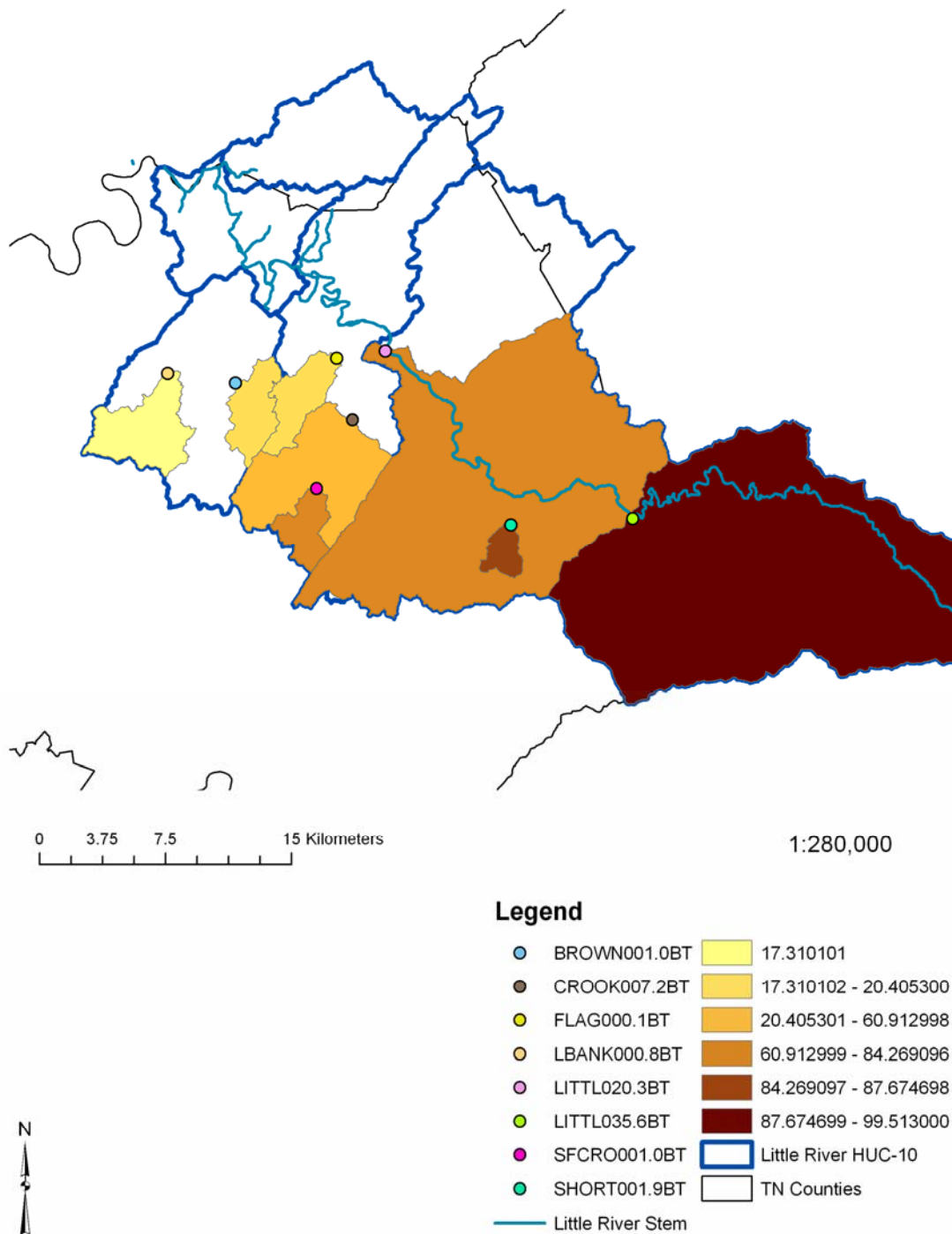


Figure A.4. Proportion of Little River Analysis Sampling Site Subwatershed Forest Land Cover – 2001

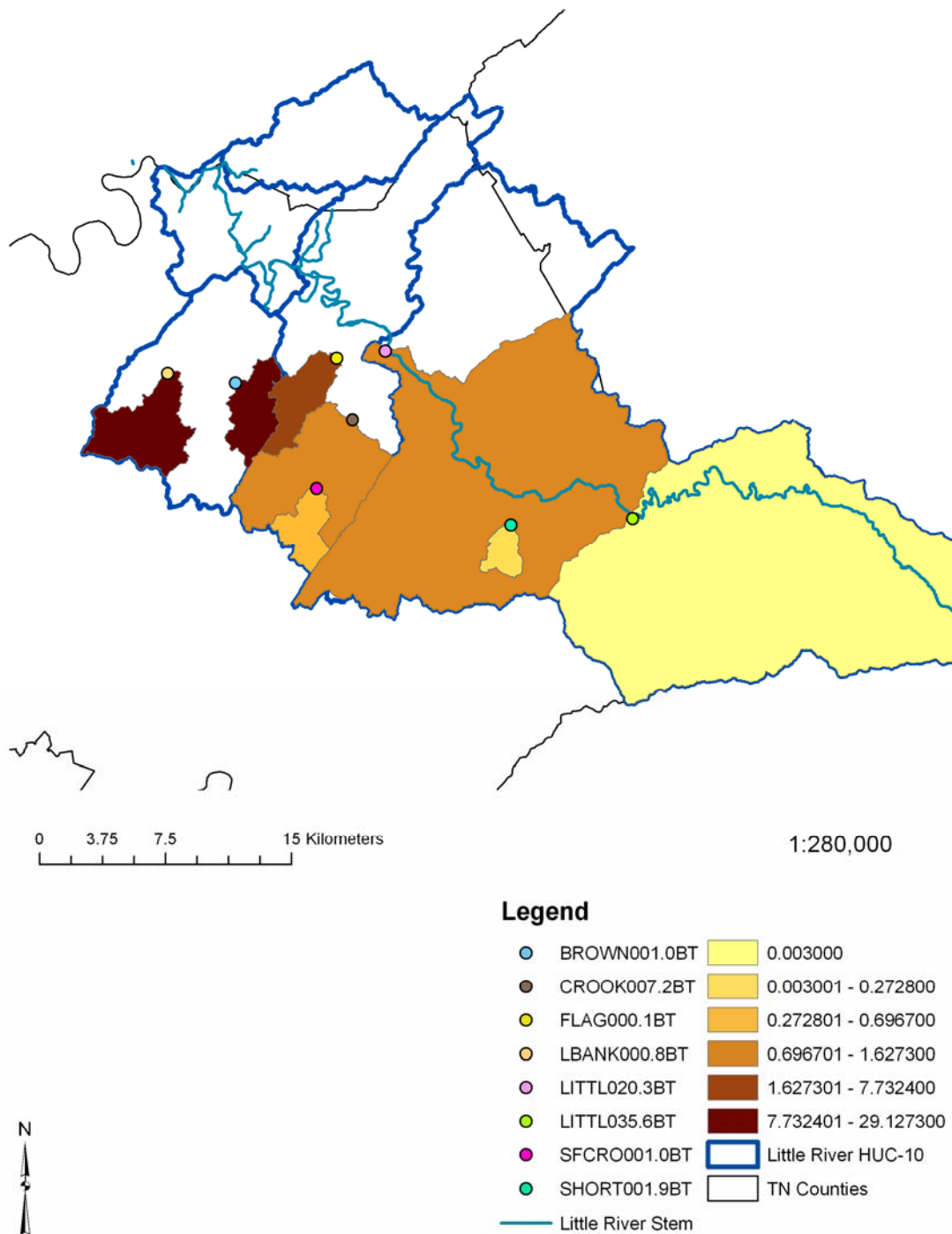


Figure A.5. Proportion of Little River Analysis Sampling Site Subwatershed Impervious Surface Land Cover Equal To or Greater Than 10 percent – 2001

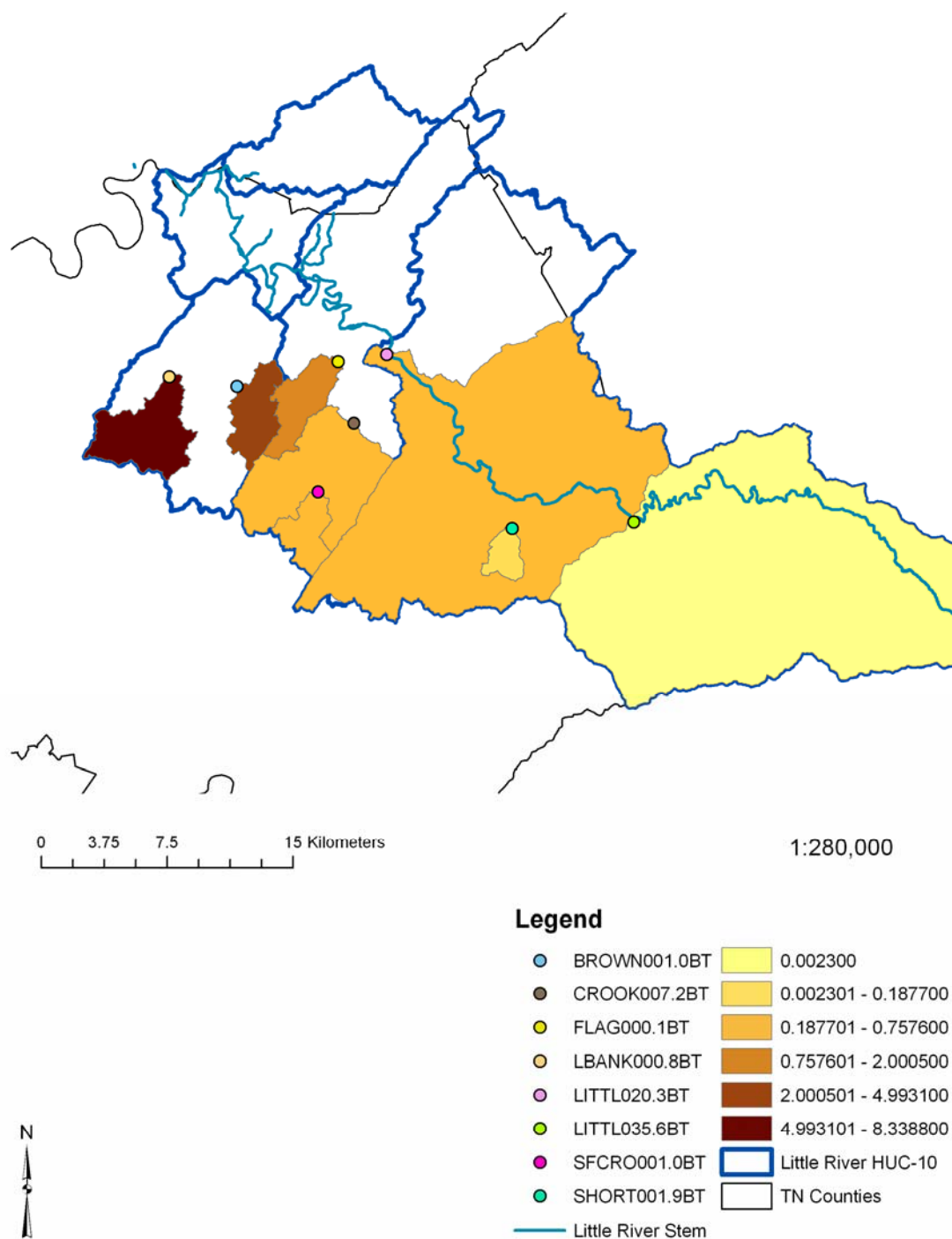


Figure A.6. Proportion of Little River Analysis Sampling Site Subwatershed Impervious Surface Land Cover Equal To or Greater Than 10 percent on Steep Slopes (9 percent threshold) – 2001

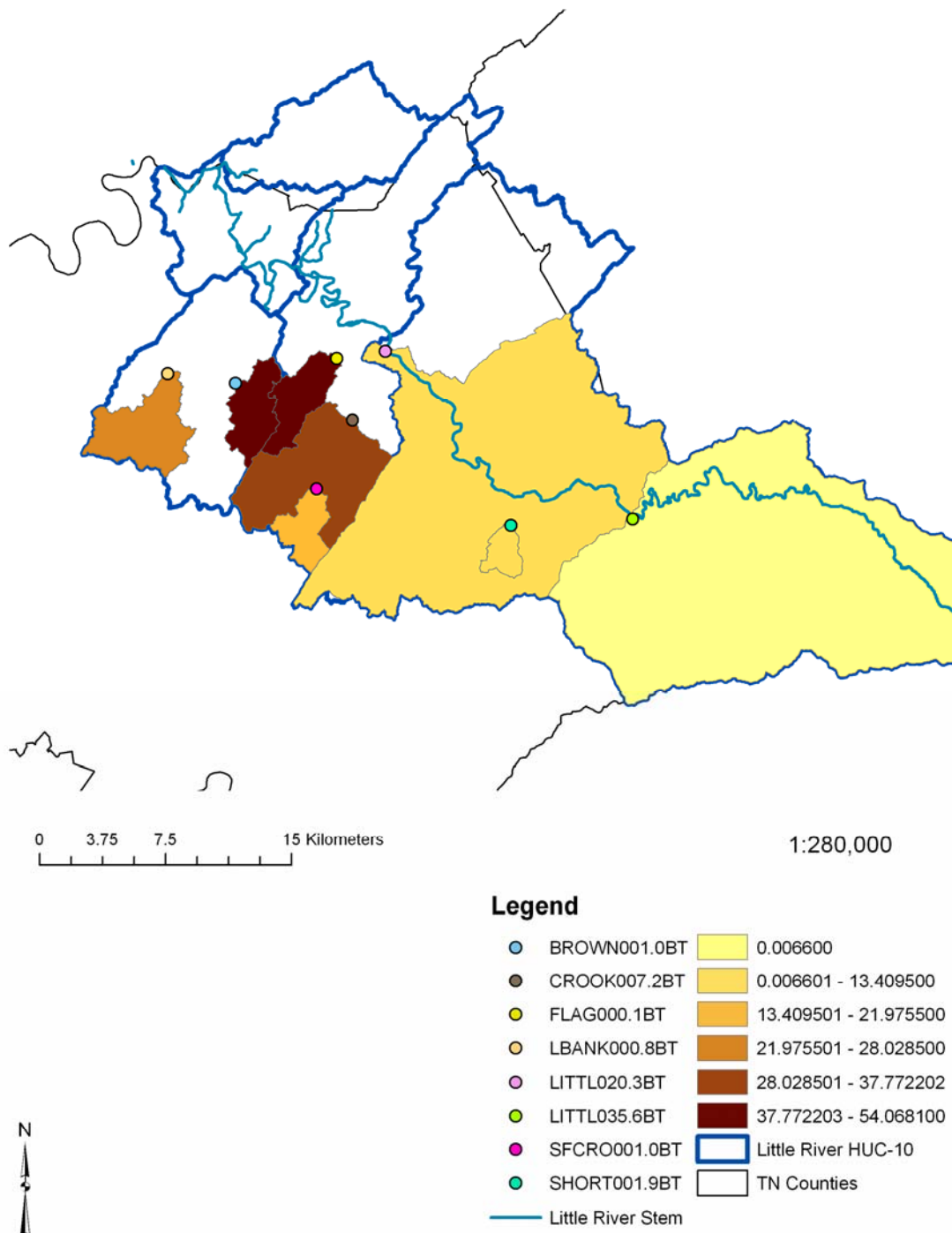


Figure A.7. Proportion of Little River Analysis Sampling Site Subwatershed Stream Length Riparian Agriculture Land Cover - 2001

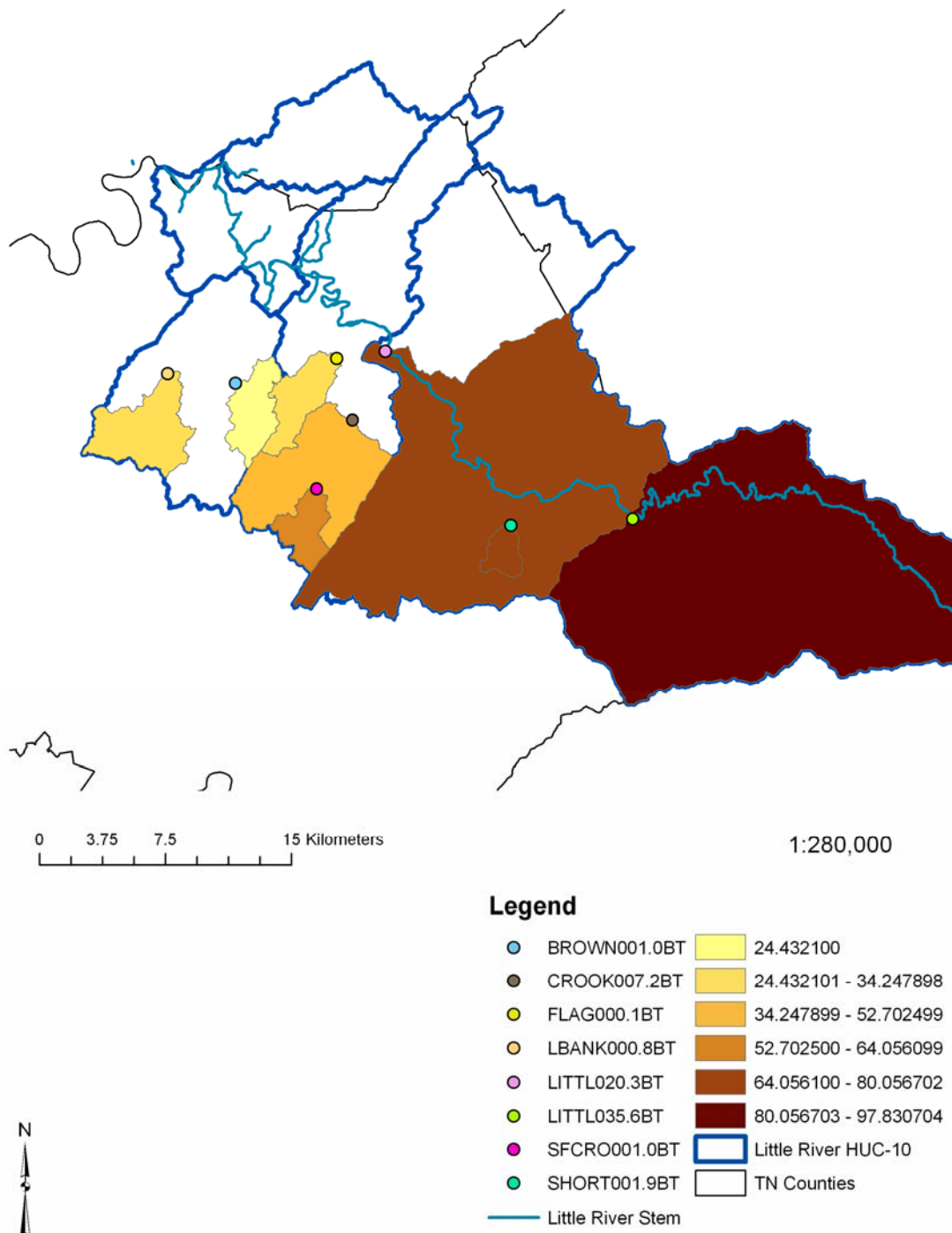


Figure A.8. Proportion of Little River Analysis Sampling Site Subwatershed Stream Length Riparian Forest Land Cover - 2001

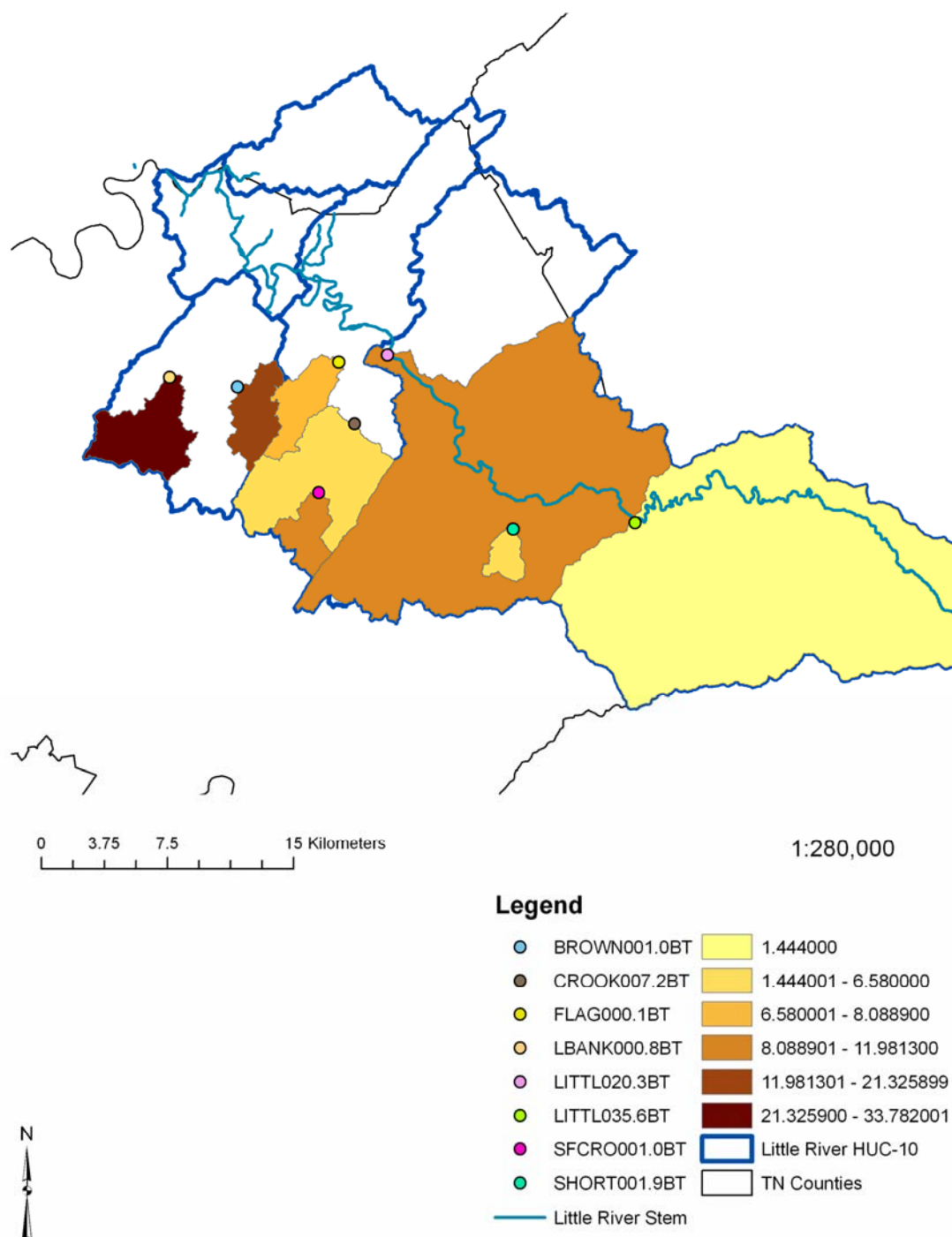


Figure A.9. Proportion of Little River Analysis Sampling Site Subwatershed Stream Length Riparian Urban Land Cover - 2001

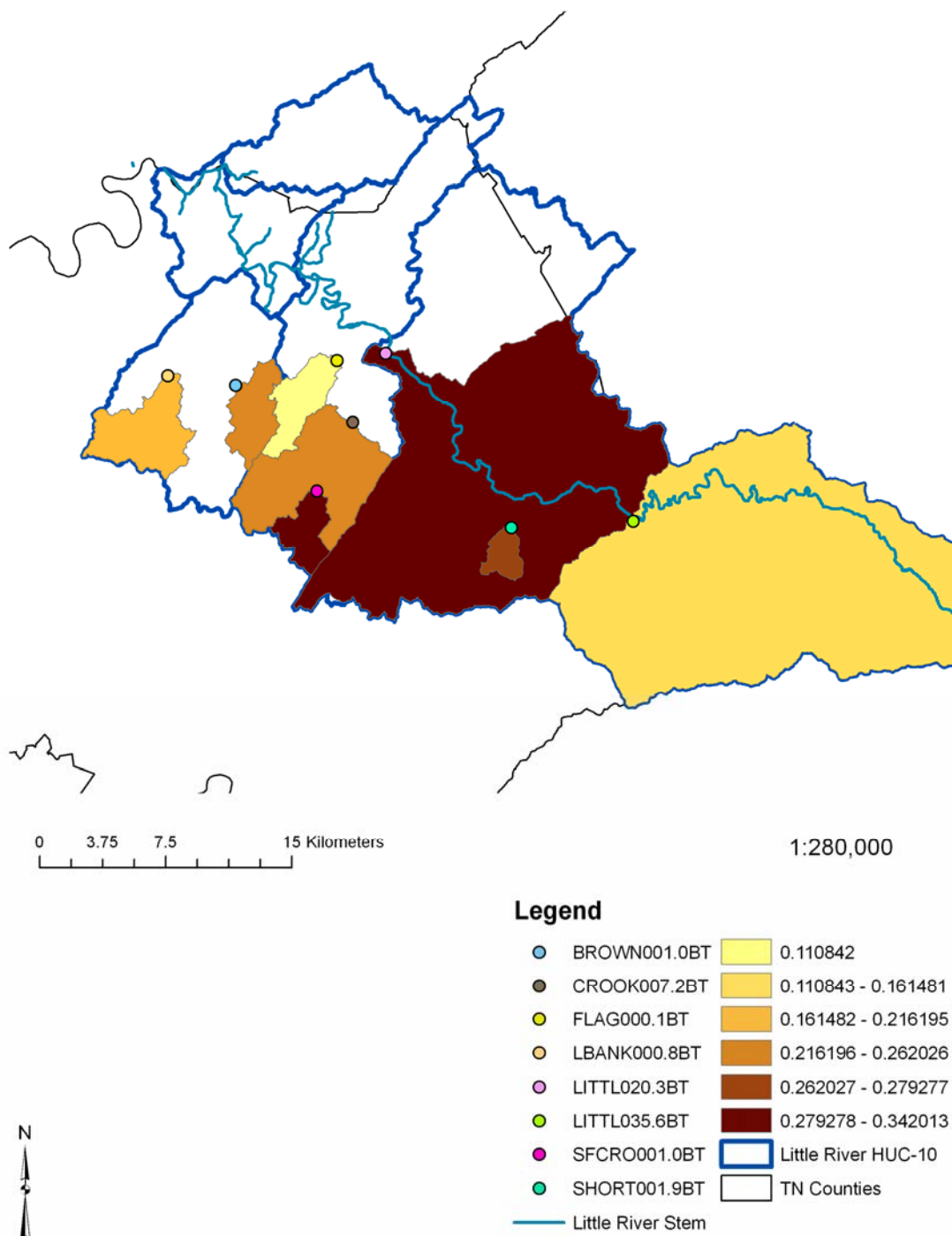


Figure A.10. Proportion of Little River Analysis Sampling Site Subwatershed Streams Within 30 m of a Road - 2001

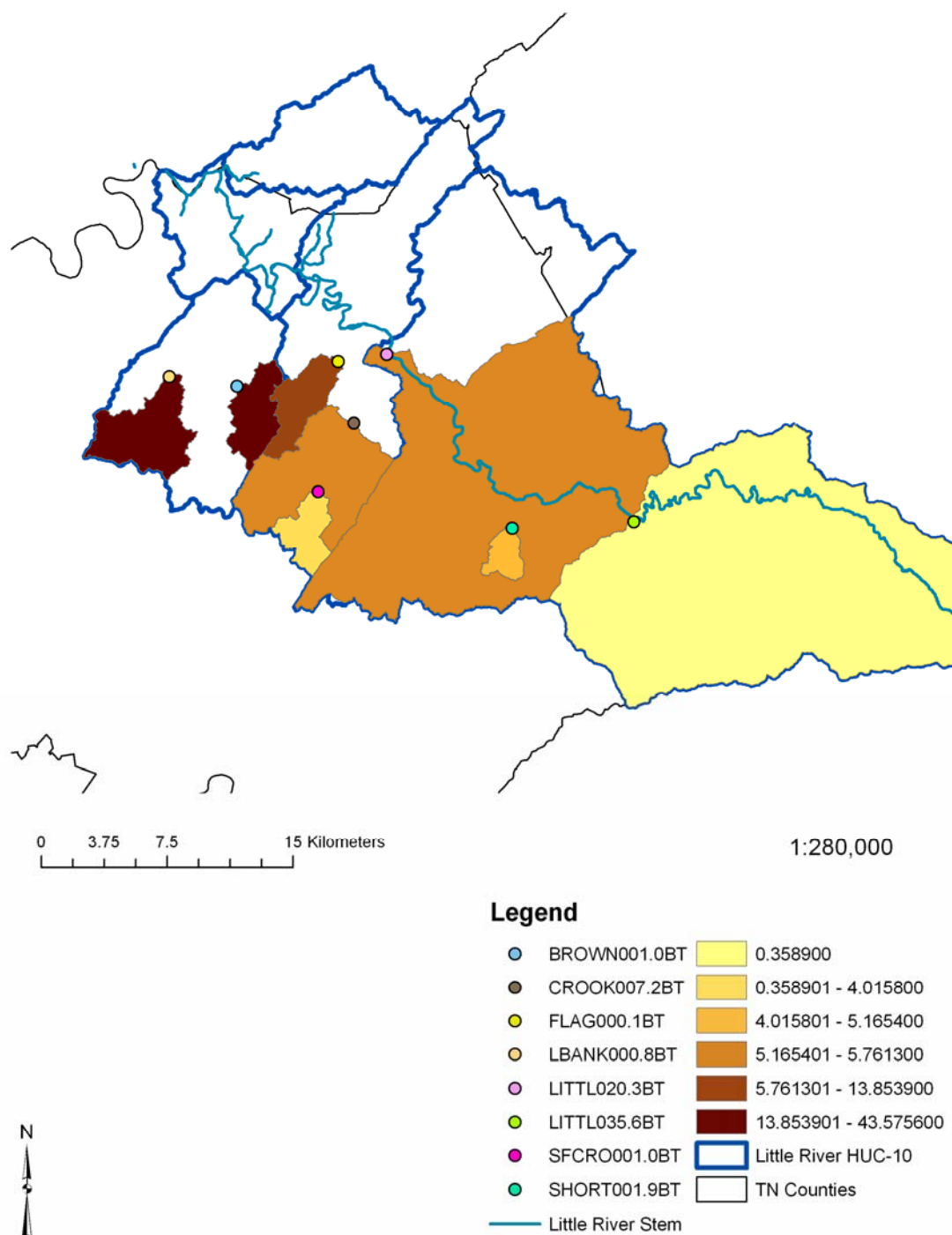


Figure A.11. Proportion of Little River Analysis Sampling Site Subwatershed Urban Land Cover – 2001

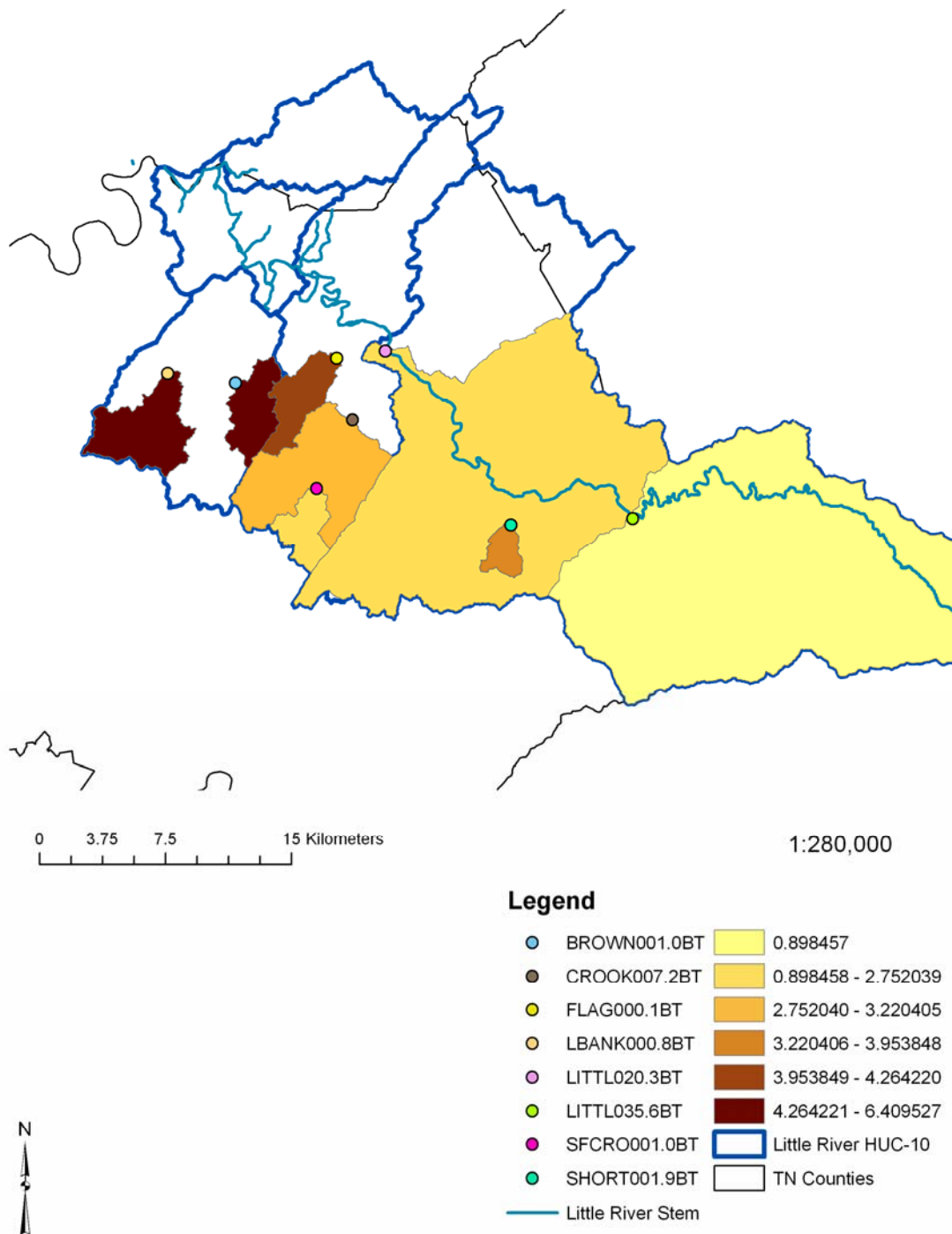


Figure A.12. Proportion of Little River Analysis Sampling Site Subwatershed Road Density in km² – 2001

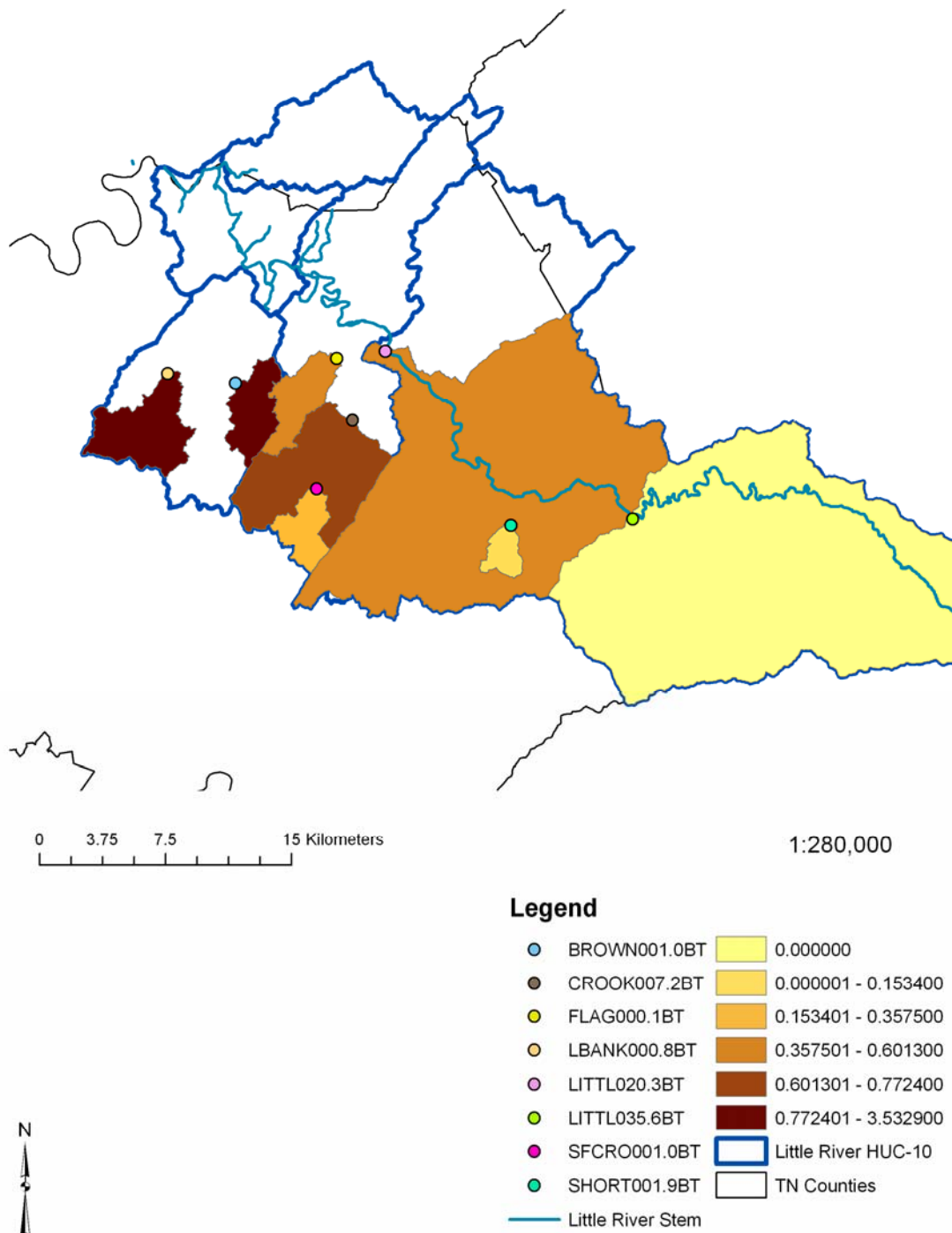


Figure A.13. Proportion of Little River Analysis Sampling Site Subwatershed NPS-Contributing Land Cover Change – 1992–2001

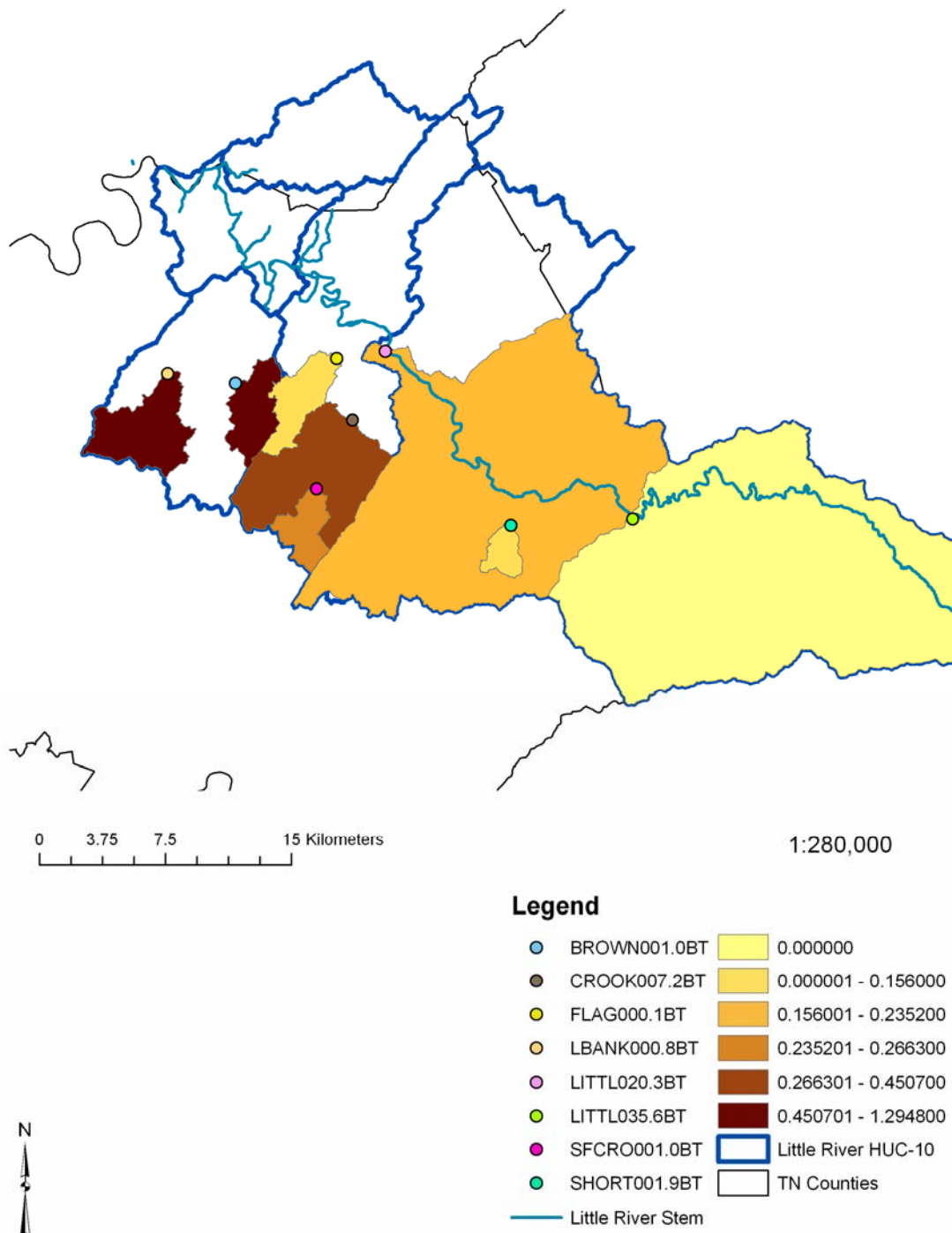


Figure A.14. Proportion of Little River Analysis Sampling Site Subwatershed NPS-Contributing Land Cover Change on Steep Slopes (9 percent threshold) – 1992- 2001

Vita

Thomas Edward Burley was born and spent the first 11 years of his life outside of Akron, Ohio, and then moved to Nashville, Tennessee in 1992. He graduated *Cum laude* with a Bachelor of Science degree in Business Administration and a Bachelor of Arts degree in Geography from the University of Tennessee in December of 2004. He immediately began working full time as a Research Associate with the Joint Institute for Energy and Environment (JIEE), which became the Institute for a Secure and Sustainable Environment (ISSE) at the University of Tennessee and where he still works at the time of the publication of this thesis. He returned to school in the Fall of 2005 to begin graduate classes and enrolled in the Department of Geography graduate program in Fall of 2006. He graduated in December of 2008 with a Master of Science degree in Geography and plans to continue to conduct research on environmental science issues and geospatial applications.