

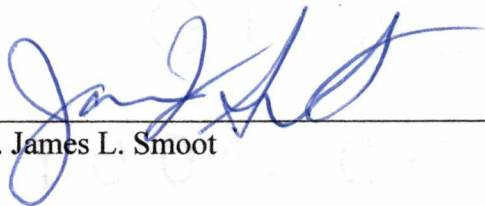
To the Graduate Council:

I am submitting herewith a thesis written by Glenn Richard Harwell entitled "Water Quality Characteristics, Temporal Trends, and Influencing Factors for Selected Streams in the Great Smoky Mountains National Park." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

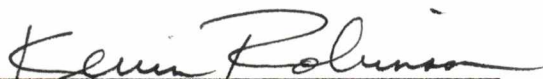


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**WATER QUALITY CHARACTERISTICS, TEMPORAL TRENDS, AND
INFLUENCING FACTORS FOR SELECTED STREAMS IN THE GREAT
SMOKY MOUNTAINS NATIONAL PARK**

A Thesis
Presented for the
Master of Science
Degree
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Glenn Richard Harwell
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information from the GIS database using software with which I was not familiar. I am especially grateful for the contributions he made and his attitude throughout the process.

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ABSTRACT

Park-wide water quality monitoring has consisted of quarterly sampling of 90 stream sites within the Great Smoky Mountains National Park (GRSM) and analyzing for pH, acid neutralizing capacity (ANC), conductivity, major cations, and major anions. The sites are distributed throughout the GRSM to include the following watersheds: Abrams Creek, Bunches Creek, Cataloochee Creek, Cosby Creek, Hazel Creek, Indian Camp Creek, East Prong Little River, Middle Prong Little River, West Prong Little River, Middle Prong Little Pigeon River, West Prong Little Pigeon River, and Oconaluftee River. Sampling sites range in elevation from 335 to 1,679 meters above mean sea level and include drainage basins with areas which have been disturbed, primarily undisturbed, underlain by different geologic formations, and covered by different vegetation types. Park-wide data collected from October 1993 to October 1998 were analyzed to describe spatial variability, temporal trends (seasonal and long-term), and influences of basin characteristics on water quality.

Multiple linear regression methods were used to explain median water quality constituent values using basin characteristics obtained from topographical maps and a GIS database. Much of the variability in water quality constituent values is explained by sample site elevation. Significant elevation trends exist ($p < 0.05$) for pH, ANC, nitrate, sodium, and potassium. Values for pH, ANC, sodium, and potassium decrease with increases in elevation. Nitrate concentrations increase with increases in elevation. Sulfate concentrations increase with elevation but the trend is not as significant ($p < 0.10$).

Seasonal trends are statistically significant for pH, ANC, conductivity, nitrate, chloride, potassium, and sodium. Values for pH, ANC, chloride, sodium, and potassium are

higher during the drier times of the year (autumn). Nitrate concentrations are the highest during the winter. Sulfate does not show seasonal differences.

Time trend analysis by linear regression modeling reveals a statistically significant decreasing trend in normalized pH over time. The time required for the upper elevation streams to become more acidic and approach critical pH values appears less than that required for lower elevation streams. If conditions remain the same and past trends continue, the model suggests that sampling sites between 1,524 and 1,676 meters above mean sea level may have pH values less than or equal to 5.50 within only four years and less than or equal to 5.00 within only 11 years. At the lower elevations, between 305 and 457 meters, sampling sites may have pH values less than or equal to 5.50 within 46 years and less than or equal to 5.00 within 67 years. The models used to predict future values of pH in sampled surface water explain an average of 12% of the variability in the data. This means that an average of 88% of the variability is unaccounted for by the models. Unexpectedly, normalized ANC does not show the same decreasing trend over time as normalized pH. Results of time trend analysis for conductivity, nitrate, and sulfate are less conclusive.

Basin characteristics explain much of the variability in water quality constituent values. The adjusted r-square values for the models range from 0.55 to 0.98. The results presented offer hope for using basin characteristics and stepwise multiple regression to predict water quality in unsampled and forested areas like the GRSM. Regression analysis demonstrates that two geologic formations, Limestone and Anakeesta, exert a significant influence on water chemistry in sampled basins. Also influential to water quality is the past disturbance history within the sampled basin, particularly the percentage of the basin which

has not been disturbed by logging or settlement prior to establishment of the GRSM.

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CHAPTER I. INTRODUCTION

Description of Study Area

The Great Smoky Mountains National Park (GRSM) is located in the Blue Ridge Physiographic Province and straddles the border of Tennessee and North Carolina. It is a truly unique area for numerous reasons. For example, it is the second largest National Park in the eastern United States, comprising more than 220,000 hectares. It is the most-visited National Park with approximately 10 million visitors each year. This number is more than twice the number of visitors to any other National Park (Moore, 2001). About 20% of the park has been classified as areas high in virgin forest attributes because of the absence of any records of land disturbance (Pyle, 1988). This makes the GRSM the largest undisturbed deciduous or coniferous forest-dominated area in the eastern United States (Delcourt and Delcourt, 1991). It is noted for its biodiversity and contains 125 species of native trees, 125 species of shrubs, 1,500 species of vascular plants, 60 ferns and fern allies, 280 mosses, 250 species of lichens, 200 species of birds, 40 reptiles, 40 amphibians, 53 species of fish, 50 mammals, and uncounted species of insects and other arthropods (Pierce, 2000). Elevation within the Park ranges from 266 meters to 2,025 meters. The highest peak, Clingmans Dome, is the second highest in the eastern United States. There are more than 3,000 kilometers of mountain streams within the GRSM. Almost half of the streams are capable of supporting trout and/or smallmouth bass (Elwood *et al.*, 1991). This is part of the highest quality cold water habitat which remains in the southeastern United States (Elwood *et al.*, 1991). The uniqueness of the area has made it an area of interest to millions of visitors and scientists from numerous backgrounds.

Development and Description of Park-Wide Water Quality Monitoring

From 1986 to 1989, scientists from around the world focused their attention on the Great Smoky Mountains National Park. During this period, a small high-elevation watershed within the GRSM (Noland Divide Watershed) was selected as one of the 17 international sites for the Integrated Forest Study (IFS). The IFS was conducted to observe and quantify atmospheric deposition and nutrient cycling in forested watersheds. This study demonstrated that the upper elevations of the GRSM receive some of the highest loading rates of acidifying nitrogen and sulphur species in North America (Johnson and Lindberg, 1992). After the IFS ended in 1989 due to a lack of funds, research was continued at the Noland Divide Watershed (NDW) to study long-term trends and relationships between atmospheric deposition and water quality. This study, which began in 1991 and continues today, is one part of the Inventory and Monitoring (I&M) program of the GRSM.

The other component of the I&M program began in October, 1993. Currently it involves quarterly sampling of stream water at 90 sites throughout the GRSM. Grab samples are analyzed for pH, acid neutralizing capacity (ANC), conductivity, nitrate, sulfate, chloride, calcium, magnesium, sodium, potassium, and ammonium. This part of the program is also interested in the impacts from acid deposition and its influence on water quality and aquatic organisms. As will be shown, the ability of sampled GRSM streams to neutralize acid is minimal. Eighty-seven of the 90 sampling sites (about 97%) are classified as either sensitive, extremely sensitive, or acidic because they have median ANC values less than or equal to 200 microequivalents per liter. Only three of the sampling sites are not classified as threatened in some way by the input of acid. In addition, about 77% of the sampled sites in

the GRSM have median pH values which have some adverse effects on aquatic organisms.

The data collected as a result of the I&M Park-wide program has provided an extensive database that can be used to answer numerous questions that are important to visitors to the GRSM, Park managers, and scientists. Some important questions include:

- With all the time and money that has been allocated to collecting this data over the years, what purpose has it served and what does the data tell us that we need to know?
- If acidic deposition continues, what will be the future impact on Park streams?
- When will the pH and acid neutralizing capacity of GRSM streams be such that aquatic organisms cannot sustain stable populations or are absent entirely?
- Are there particular areas of the GRSM that are more vulnerable to acidic deposition and its influence on water quality? If so, where are they?
- Are there particular basin characteristics that make an area more or less susceptible to having low pH and low acid neutralizing capacity? If so, what are they?
- Does water quality vary with respect to the time of the year?

The major sampled watersheds include those defined by Abrams Creek, Bunches Creek, Cataloochee Creek, Cosby Creek, Hazel Creek, Indian Camp Creek, East Prong Little River, Middle Prong Little River, West Prong Little River, Middle Prong Little Pigeon River, West Prong Little Pigeon River, and Oconaluftee River. Of the 90 sampling sites, seven sites are high elevation springs. Sampling sites within the watersheds are distributed over the entire elevation gradient. Selection of sampling sites across a wide range of elevations is intended to assess the spatial variability of water quality within the GRSM as a whole and

within a particular watershed.

Sampling sites were also selected to assess the influences of different bedrock types and disturbance histories on surface water quality. Most of the GRSM is underlain by basically inert sandstone formations which result in waters with low acid neutralizing capacity and low ionic strength (Elwood *et al.*, 1991). This makes the streams draining the GRSM particularly susceptible to acidification. Sampling sites draining areas with predominately sandstone formations were selected to assess the impacts of acidification. Other sites were chosen that drain areas underlain by the more reactive Limestone and Anakeesta Formations to monitor their influences. Past disturbance history within a drainage basin also influenced sample site selection. The past disturbance histories represented by the sampling sites include basins with little or no disturbance, those with significant disturbance from logging operations, and those with disturbances resulting from settlements prior to Park establishment.

Currently, sampling surveys are conducted during the months of March, May, August, and November. Historically, November was not a month in which samples were collected. The reasons for changing sampling from October to November are discussed in Chapter V. Sampling is performed by faculty, staff, and students from the University of Tennessee at Knoxville, National Park Service staff, and volunteers from the Little River and Great Smoky Mountain Chapters of Trout Unlimited.

From October 1993 to December 1998, chemical analyses of all samples collected in the Park-wide program were performed by personnel in the Department of Forestry, Wildlife, and Fisheries at the University of Tennessee, Knoxville. After that period, the

project was transferred to the Department of Civil and Environmental Engineering. From January 1998 to the present, all chemical analyses have been performed by staff and students in the Department of Civil and Environmental Engineering. For additional information on the protocols used for the collection and laboratory analysis of samples, refer to a summary report submitted to the National Park Service entitled 'Assessment of Stream Water Quality and Atmospheric Deposition Rates at Selected Sites in the Great Smoky Mountains National Park, 1991-1998' (Smoot *et al.*, 2000).

Analysis of calcium and magnesium is not included in this thesis due to recently resolved quality control problems. The problems associated with historical calcium and magnesium concentrations are discussed in detail in a report submitted to the National Park Service entitled 'Water Quality Analysis of Calcium and Magnesium in the Great Smoky Mountains National Park' (Robinson *et al.*, 2001).

Purpose and Scope

This thesis focuses on the analysis of stream water quality within the GRSM resulting from data collected from October 1993 to October 1998 as part of the I&M Park-wide monitoring program. Its specific objectives are as follows:

1. To show the spatial variability of water quality constituent values within the GRSM in such a way that one can easily discern which areas of the Park might be adversely impacted or not.
2. To determine statistically significant relationships between water quality constituent values and basin characteristics.
3. To determine seasonal and long-term time trends of water quality constituents

and suggest when sampled surface water and aquatic organisms will be adversely impacted.

4. To use available flow data and evaluate the flow conditions under which most samples are collected and whether they appropriately represent the range of flow conditions.
5. To suggest recommendations for future research.

CHAPTER II. REVIEW OF THE LITERATURE

Influences to Water Quality in Forested Watersheds

As water enters and flows through a forested area, numerous factors are involved in determining its chemical characteristics. Four primary factors are (a) the chemical composition of incident precipitation, (b) the abiotic materials or the biota that water contacts as it moves through a watershed, (c) the abiotic reactivity of the materials or biotic activity of the organisms contacted, and (d) the length of contact with those materials or organisms (Church, 1997). For different watersheds, the mechanisms that have the most significant impact on water quality may vary considerably. The following discussion presents some of the processes influencing surface water quality within the Great Smoky Mountains National Park (GRSM). It is certainly not a comprehensive discussion of all the processes which might be influencing water within the GRSM and particularly within smaller watersheds. Such a discussion is beyond the scope of this thesis.

Much attention has been given recently to the chemical composition of the water and the abiotic materials entering forested watersheds. The increased attention has primarily come from a concern over acid deposition and its potential detrimental influences to water quality. As a result of the combustion of fossil fuels, automobile emissions, and the smelting of nonferrous metals, many areas in North America and Europe have been documented as receiving significant amounts of atmospherically-deposited compounds, particularly sulfuric and nitric acids (Drever, 1997). These sulfur and nitrogen compounds enter as wet deposition (acid rain), cloudwater deposition, or dry deposition of particulate matter and gases (Drever, 1997). Compared to other ecosystems studied, high elevation spruce-fir

forests of the GRSM receive among the highest loadings of sulfur and nitrogen measured in North America (Johnson and Lindberg, 1992). Research of Noland Divide Watershed (NDW) in the GRSM has shown that the input of sulfur and nitrogen compounds is dominated by dry and cloudwater deposition (Nodvin *et al.*, 1995; Shubzda *et al.*, 1995). As these compounds enter a watershed, they participate in reactions that can have an impact on surface water quality. These compounds participate in reactions that increase the free hydrogen ion concentration in soil solutions and surface waters. This could have long-term impacts on the ability of surface waters to support aquatic life if processes to minimize the effects of acid deposition begin to fail.

Soil processes play a major role in the characteristics of surface water. Some soil processes occur quickly while other processes are much slower but still have an impact on long-term water quality. Cation and anion exchange and adsorption are processes that generally occur rapidly. The slower processes include litter decay, nitrification, and mineral weathering.

Cation exchange in acidic soil solutions exchanges base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Al^{3+}) for hydrogen ions in solution. Over time soils can become depleted of base cations as a result. When this occurs, charge balance is maintained by the leaching of hydrogen ions and aluminum (Cosby *et al.*, 1985). Research at NDW has shown that there is a tendency for conservation of base cations and release of acid cations like hydrogen and aluminum (Johnson and Lindberg, 1992). Significant increases in hydrogen ion and aluminum concentrations were reported during a storm event in Raven Fork, located in western North Carolina (Jones *et al.*, 1983). Aluminum solubility increases as pH decreases. This is

significant because monomeric inorganic species of aluminum, particularly Al^{3+} , are toxic to fish (Elwood *et al.*, 1991).

Anion adsorption reactions, particularly the adsorption of sulfate (SO_4^{2-}), can be very influential to surface water chemistry. As sulfate is adsorbed and removed from soil solutions, to maintain charge balance either another equivalent anion must be released into solution or protons must also be removed from solution. In acidic soil solutions, most likely protons (H^+) are removed and the net result is a decrease in acidity. Compared to watersheds in the Northeast region, watersheds in the Southern Blue Ridge Province have been shown to retain a high proportion of atmospherically derived sulfur (Church *et al.*, 1990). These reactions can become less efficient over time as the adsorptive capacities of the soils are reached. When this happens, surface water sulfate concentrations will increase to steady state conditions.

Litter decay is most significant with respect to nitrate concentrations in surface waters. As organic matter decays, inorganic species (such as nitrogen) and organic acids are brought into solution. While plants are active during the growing season, much of the nitrogen produced is taken up by the vegetation. When the plants become dormant and decay continues, nitrate can build up in the upper soil horizons and then be flushed from the system with rainfall or snow melt (Munson and Gherini, 1991).

Nitrogen can enter a watershed in the form of ammonium by deposition. Ammonium is oxidized to nitrate and hydrogen ions by bacterial reactions. The addition of these hydrogen ions to soil solutions causes a corresponding decrease in acid neutralizing capacity.

Vegetation type and forest succession are also important factors controlling surface water chemistry. Some researchers hypothesize that as ecosystems mature, the net production of biomass decreases and causes a decline in nutrient uptake by plants. This causes an increase in nutrient concentrations in surface waters which drain these ecosystems (Vitousek and Reiners, 1975). Therefore, nutrient concentrations should be higher in streams draining undisturbed and mature forests than in streams draining areas with younger forests. The nutrient budgets of the mature forests should also be nearly balanced. Research in a watershed in central New Hampshire called the Bowl does not support the hypothesis of Vitousek and Reiners. The Bowl is covered by northern hardwood forest with spruce fir at higher elevations and has never been logged or otherwise disturbed. Researchers there found that the biogeochemistry of the cations appeared to be regulated more by precipitation, soil water movement, and chemical weathering than by forest succession. Nitrate concentrations remained fairly constant with no apparent seasonal fluctuations. In a nearby 55-year-old forest, nitrate concentrations declined during the growing season. Budgets indicated a net loss of nitrate from both watersheds. However, a net accumulation of ammonium gave a net increase of total nitrogen (N) in both watersheds. Accumulation of N was greater for the Bowl than for the 55-year-old forest (Martin, 1979). Researchers in the GRSM found statistically significant elevation trends for nitrate. Nitrate concentrations increased with increases in elevation. However, they found that the regression lines for nitrate were significantly different between logged and unlogged watersheds. Streams which had at least 75% of their watersheds logged had lower nitrate concentrations than those with at most 25% of their watersheds logged (Silsbee and Larson, 1982). These results support the hypothesis

of Vitousek and Reiners.

Mineral weathering is typically a slow process and is usually associated with the addition of base cations to solutions. The geology of the GRSM is characterized by mainly metamorphosed sedimentary rock, predominately sandstones but with some limestone and dolomite. The sandstones cover about 60% of the GRSM and are composed of quartz and potassic feldspars (King *et al.*, 1968). For the most part these formations are resistant to weathering. The limestone and dolomite formations are found in the western portion of the GRSM and significantly influence water quality. Limestone consists mostly of calcite with mixtures of magnesium carbonate and other impurities. Calcite is represented by the formula CaCO_3 and dolomite by $\text{CaMg}(\text{CO}_3)_2$ (Hem, 1989). Studies in the Cades Cove area have shown that the limestone formations increased stream conductivity, total hardness, and pH (Larson *et al.*, 1986). The increased conductivity results from increased concentrations of calcium, carbonates, and bicarbonates associated with the weathering of the limestone. There is a corresponding increase in acid neutralizing capacity (ANC) and pH as a result of this process. Another formation within the GRSM that significantly affects surface water quality is the Anakeesta Formation. The influence is particularly significant if the Anakeesta has been exposed to air and water as a result of debris flows and other disturbances such as road construction. Anakeesta includes slates, phyllites, and schists composed of clay minerals and sulfides. The pyritic, iron sulfide minerals which make up Anakeesta Formations have been classified by some researchers as acid-producing materials (Byerly, 1996). These minerals oxidize in the presence of air and water to form different soluble iron sulfate compounds. The dissolution of these various sulfates produces acidity, increases

concentrations of sulfate, and consumes alkalinity.

Spatial Variability of Water Quality

There have been numerous studies of surface water and watersheds within the GRSM. Most of the studies to date were on small watersheds, were short-term, and were focused on particular problem areas or areas that appeared particularly interesting (Silsbee and Larson, 1983; Larson *et al.*, 1986; Johnson *et al.*, 1991; Cook *et al.*, 1994; Flum and Nodvin, 1995; Nodvin *et al.*, 1995; Shubzda *et al.*, 1995; Garten, 2000; McCann, 2000).

Broad synoptic studies of water quality in the GRSM include studies by Silsbee and Larson and to some extent the National Stream Survey (NSS). The study by Silsbee and Larson, results of which were published in 1982, was designed to collect baseline information on natural water conditions within the GRSM. The results of this study were to provide insight for effective long-term monitoring and future aquatic research within the GRSM. The study collected surface water quality data over a period of one year at more than 100 sites. Most sites were sampled four times over the course of the year at samples intervals of about three months. Sampling sites were selected to cover a broad elevation range and diverse basin characteristics. Sites represented surface water draining areas that were disturbed by logging and settlement prior to establishment of the GRSM and also included areas which were not significantly disturbed. The different geologic formations were also represented by the sampling strategy. Geologic formations which were represented include the Great Smoky group, Anakeesta, Walden Creek group, Snowbird group, and the Knox group. The Great Smoky group includes sandstones composed of quartz and potassic feldspar. The Anakeesta group includes slates, phyllites, and schists composed of clay

minerals and sulfides. The Walden Creek group consists of shales, siltstones, limestones, and dolomites composed of feldspars, clay minerals, and carbonates. The Snowbird group includes shales, siltstones, sandstones, and quartzites composed of feldspars, clay minerals, and quartz. The Knox group includes limestones composed of carbonates. By sampling across almost the entire elevation range of the GRSM, the different vegetation types within the GRSM were also represented.

The results of the Silsbee and Larson study provided insight into the spatial variability of water quality within the GRSM. They found significant relationships between water quality parameters and mean watershed elevation. Water quality analytes which displayed statistically significant relationships with mean watershed elevation included pH, alkalinity, nitrate, turbidity, summer temperature, sodium, potassium, and silica. Values for pH, alkalinity, turbidity, summer temperature, sodium, potassium, and silica decreased with increases in elevation. As mentioned earlier, nitrate concentrations increased with increases in elevation. They did not find significant relationships for conductivity, hardness, winter temperature, calcium, and magnesium (Silsbee and Larson, 1982).

The NSS was one component of the U.S. Environmental Protection Agency's National Surface Water Survey (NSWS). The purpose of the NSWS was to quantify the surface water chemistry in areas determined potentially susceptible to the effects of acidic deposition. The NSS survey was conducted during the spring of 1986 and focused on small to medium size streams which were managed for sport fisheries. The drainage area of the sampling sites was less than 155 square kilometers but the streams were large enough to appear as blue lines on 1:250,000 scale United States Geological Survey (USGS) topographic

maps. Samples were collected during one, two, or three visits. The specific number of samples collected from each site varied by subregion. Samples were collected at both the upstream and downstream ends of the sample reach. Flow conditions at the time of sampling were spring baseflow falling between snowmelt and leafout. No samples were collected during high flow events. One of the areas surveyed was the Southern Blue Ridge Province. Of the total area within the Southern Blue Ridge Province containing the NSS target population, only about 8% was within the boundaries of the GRSM. Therefore, the NSS was not an intensive study of surface water specifically within the GRSM like the study by Silsbee and Larson. However, approximately 64% of the area within the region sampled was completely covered by deciduous and coniferous forests. The results of the NSS found elevation trends for pH and ANC. Both pH and ANC were found to decrease with increases in elevation (Elwood *et al.*, 1991).

More recently, the USGS released its findings from sampling within the Upper Tennessee River Basin as part of the National Water Quality Assessment Program (NAWQA). This assessment took place from 1994 to 1998. The selected indicators of stream water quality in the Upper Tennessee River Basin included pesticides, phosphorus, trace elements, organo-chlorine compounds, volatile organic compounds, bacteria, and semivolatile organic compounds. The constituents included in the study for which this thesis was written include pH, ANC, conductivity, nitrate, sulfate, chloride, calcium, magnesium, sodium, potassium, and ammonium. Therefore, comparisons between the NAWQA findings and the results of this thesis are not practical.

Temporal Variability of Water Quality

Seasonal Variability

The study by Silsbee and Larson also investigated for seasonal variability of water quality constituents. They concluded that at low elevations summer (low flow) values for alkalinity, conductivity, and turbidity were higher than winter (higher flow) values. At higher elevations, the seasonal variability for these parameters was not significant. For pH, no significant difference was found at any elevation. High elevation was defined as watersheds with a mean basin elevation greater than 1,350 meters (4,430 feet) above mean sea level. Temperature and hardness showed significant differences between winter and summer values at both high and low elevations. Both temperature and hardness values were lower during the winter. They found nitrate concentrations to be the lowest in the fall and highest in the late winter and early spring.

Results from the NSS did not report seasonal variability of water quality constituents since samples were only collected during the spring.

Research at NDW revealed that values for pH and ANC were the lowest in the winter and highest in the fall. Conductivity was the lowest in the spring and highest in the winter. Nitrate concentrations were shown to reach a low in the summer months and then rise as vegetation became dormant. Sulfate concentrations were the lowest in the summer months and highest in the winter (McCann, 2000). The NDW watershed is a small (about 17.4 hectares) watershed located in the upper elevations (1,695 to 1,940 meters) of the GRSM. Therefore, the study is not a representation of seasonal differences throughout the GRSM and the results of seasonal variability might only apply to the upper elevations of the GRSM.

Despite this, comparisons between seasonal differences found in this study and the results from NDW are meaningful.

Long-term Trends

To date, no extensive analyses of long-term trends throughout the GRSM have been done. However, long-term trends have been studied at NDW within the GRSM. At NDW, results showed no significant changes in sulfate, potassium, and hydrogen ion loads and concentrations over time. Regression models did show that chloride, sodium, aluminum, and ammonium loads and concentrations have increased over time. Nitrate and silica loads and concentrations have decreased over time (McCann, 2000).

Analysis of long-term trends has been done for regions similar to the GRSM. Research in forest-covered watersheds in Virginia showed a possible decrease in future alkalinity by as much as 90 microequivalents per liter (Webb *et al.*, 1989). This prediction assumes that of the acid anions only sulfate has changed historically or will continue to change in the future as streams approach a steady state condition with atmospheric deposition. The authors estimate that the trout streams studied in Virginia would require a minimum of about 50 years to reach this steady state condition. This study provided the first quantitative assessment of acidification for the native brook trout streams in Virginia. Other results released from studies of stream water chemistry showed that sulfate, hydrogen ion, and base cation concentrations increased over an eight-year period in the White Oak Run and Deep Run watersheds in Virginia. Alkalinity decreased over the same period. The changes were attributed to increases in sulfate concentrations as sulfate retention of atmospherically deposited sulfur declined (Ryan *et al.*, 1989). Ryan and others predicted that in about 100

years steady state values of alkalinity will be reached for the White Oak Run and Deep Run watersheds. The steady state values are -28.0 microequivalents per liter and -65.0 microequivalents per liter for White Oak Run and Deep Run, respectively.

Statistical Approaches to Understanding Water Chemistry

To understand the chemistry of natural waters, Drever has identified three approaches which include thermodynamic, mass balances, and statistical (Drever, 1997). The thermodynamic approach is based upon the assumption that chemical equilibrium exists between water and the secondary minerals formed during weathering reactions. As secondary minerals are formed, it is also assumed that the products are well-defined solids and water chemistry follows predictable paths. The mass balance approach uses input and output budgets. A net difference in the budget represents contributions from various processes if positive and retention when negative. The last approach, statistical, uses tools such as correlation, multiple regression, and factor analysis to investigate for relationships between water chemistry and environmental factors. The statistical method was used in this study to investigate relationships between water quality and basin characteristics. Statistical associations do not establish cause-and-effect relationships. However, cause-and-effect relationships can frequently be deduced from the results of statistical analyses (Drever, 1997).

There are numerous examples of using statistical methods to understand relationships between water quality and environmental factors. Research by Melack and others on alpine and subalpine lakes in the Sierra Nevada Mountains included using stepwise multiple regression to try to predict alkalinity. The independent variables included lake altitude, basin

area, and lake area. They concluded that among the lakes included in their study alkalinity could not be predicted from readily available geographic data with enough certainty to be useful. They also used correlation analysis to investigate relationships between water quality and the percent areal coverage of volcanic or calcareous rocks in the basin. The concentrations of sulfate, calcium, and alkalinity were positively correlated with the percent areal coverage of these formations (Melack *et al.*, 1985). The relationship between surface water chemistry and geology in the North Branch of the Moose River was investigated by Newton and others. Using correlation analysis, they found a direct correlation between surface water alkalinity and the percentage of a watershed covered by thick glacial till. Deviations from the linear relationship allowed them to conclude which processes likely controlled the water chemistry in other basins (Newton *et al.*, 1987). Puckett and others used principle component analysis to examine regional patterns in stream chemistry and to investigate the degree to which low-order stream chemistry is controlled by bedrock geology. The study area included 69 low-order streams in the Blue Ridge and Valley and Ridge Provinces of Virginia and Maryland (Puckett *et al.*, 1992). Correlation, multiple regression, and principle component analyses were used to investigate physical and hydraulic properties of carbonate rock aquifers in central Pennsylvania. Correlation and principle component analyses were used to establish relations and associations between variables and to filter variables containing similar information. Stepwise multiple regression was then used to predict porosity and permeability with measured variables (Brown, 1993). Research in the upper Merced River watershed in the Sierra Nevada Mountains by Clow and others included performing stepwise multiple regression to predict the concentrations of weathering products

in stream water. Independent variables included basin area, percentage areal coverage of surficial material, and a "weathering index" variable. The weathering index variable described the weathering characteristics of the dominant bedrock types in the drainage area. They found that percentage areal coverage of surficial material explained the most variability in calcium, sodium, alkalinity, and silica concentrations. The amount of variability explained ranged from 37 to 54%. The weathering index variable explained an additional 22% of the variability in calcium and 24% of the variability in alkalinity (Clow *et al.*, 1996). Herlihy and others analyzed data that was collected during a stream pilot survey in 1993 by the U.S. Environmental Protection Agency in the Mid-Atlantic region. The purpose of the study was to use the data to investigate for relationships between stream chemistry and watershed land cover at the regional scale. The land cover classes included forest, agriculture, urban, wetland, and barren. Stream chemistry and land cover relationships were investigated using multiple regression with stream chemistry as the dependent variable and land cover classes as the independent variables. They concluded that the concentrations of chloride, nutrients, acid neutralizing capacity, and base cations were the constituents most strongly related to watershed land cover. Regions with predominately forested land cover had weaker relationships than areas with agriculture or urban land cover (Herlihy *et al.*, 1998). Clow and others also investigated the relationships between basin characteristics and stream chemistry in alpine/subalpine basins in Rocky Mountain National Park. The basin characteristics used in the analysis included topographic, vegetation, and geologic characteristics. They found that areas characterized by steep slopes, unvegetated terrain, and young surficial debris were negatively correlated with concentrations of base cations, silica, and alkalinity. The same

areas were positively correlated with nitrate, acidity, and runoff. These relationships were explained as the result of shorter residence times and limited soil development in these areas which limit chemical weathering and nitrogen uptake. Stepwise multiple regression was used to predict water quality constituent values using basin characteristics. Results of regression analysis included models which explained most of the variability in water quality constituent values. The r-square values ranged from 0.54 for magnesium to 0.97 for nitrate. Basin area was the best predictor for calcium, magnesium, and sulfate concentrations. The fraction of the basin area having steep slopes and old debris were the best predictors of alkalinity and nitrate concentrations. The variability of other solutes was explained by the fraction of the basin area underlain by young and old debris or a combination the two (Clow and Sueker, 2000).

The development of software and other tools to extract geographical and watershed data from GIS databases has made development of predictive models using basin characteristics much easier. However, the models developed from these types of data typically do not take into account the variations in water chemistry that occur as a result of the time of year or flow.

CHAPTER III. SPATIAL VARIABILITY OF WATER QUALITY

One goal of synoptic studies of water quality is to investigate how water quality varies spatially. The insights gained from the analysis of spatial variability in protected forests like the Great Smoky Mountains National Park (GRSM) can help researchers discover areas that are particularly important and interesting. Managers of natural resources are usually interested in these studies because "sensitive" areas are located and management decisions can be made to reduce the future impact on these areas. The following analysis utilizes the chemistry data from collected samples to describe the spatial variability of water quality at sampled sites in the GRSM. The reasons for the spatial variability are not discussed in this chapter. Chapter IV addresses the influences on water quality constituent values. Elevation trends are discussed in this chapter since elevation is a spatial descriptor and not a direct influence on water quality.

Data

The data set includes samples collected from October 1993 to October 1998. Park-wide monitoring of water quality began in October of 1993. There are 90 sites throughout the GRSM that have been included in Park-wide monitoring since the beginning and are still covered by the current sampling program. Table 3-1 lists the sampling sites along with a short description to describe location. Also included in Table 3-1 are the major watersheds in which the sampling sites are located. Figures 3-1 and 3-2 show where the sampling sites are located within the GRSM and the contributing area to each site. The contributing areas are defined by the darker lines which show basin boundaries. For formatting purposes, it was necessary to divide the Park into two parts. Figures 3-1 and 3-2 show the eastern and

Table 3-1. Sample site descriptions and locations.

Sample site	Site description	Watershed
1	Indian Camp at Old Settlers	Indian Camp Creek
3	Cosby Creek at boundary	Cosby Creek
4	Lower Rock Creek	Cosby Creek
13	Little River at boundary	EPLR
14	Little River above Y	EPLR
20	Little River at Metcalf Bottoms	EPLR
23	Lower Middle Prong Little River	MPLR
24	Lower West Prong Little River	WPLR
30	West Prong Little Pigeon at headquarters	WPLPR
34	Little River at Milsap Site	EPLR
43	Porters Creek at log bridge	MPLPR
45	Shutts Prong	MPLPR
46	Porters Creek above Shutts Prong	MPLPR
47	Lower Cannon Creek	MPLPR
49	Porters Creek at bridge to Ramsay	MPLPR
50	Middle Prong Little Pigeon below Porters	MPLPR
52	Middle Prong Little Pigeon at boundary	MPLPR
66	West Prong Little Pigeon at Chimneys picnic area	WPLPR
71	Road Prong above barrier cascade	WPLPR
73	Walker Camp Prong above Road Prong	WPLPR
74	Walker Camp Prong above Alum Cave Creek	WPLPR
103	Otter Creek	Indian Camp Creek
104	Copperhead Branch	Indian Camp Creek
106	Upper Indian Camp Prong	Indian Camp Creek
107	Indian Camp below Albright Grove	Indian Camp Creek
114	Cosby Creek at log bridge	Cosby Creek
115	Upper Cosby Creek	Cosby Creek
127	Pretty Hollow Creek above Palmer Creek	Cataloochee Creek
137	Upper Rock Creek	Cosby Creek
138	Inadu Creek	Cosby Creek
142	Beech Creek above Lost Bottom Creek	Cataloochee Creek
143	Lost Bottom Creek	Cataloochee Creek
144	Palmer Creek above Pretty Hollow Creek	Cataloochee Creek
147	Lower Cataloochee Creek	Cataloochee Creek
148	Lower Little Cataloochee Creek	Cataloochee Creek
149	Middle Cataloochee Creek at bridge	Cataloochee Creek
150	Cataloochee Creek below Caldwell Fork	Cataloochee Creek
156	Abrams Creek at ranger station	Abrams Creek
173	Mill Creek above Abrams Creek	Abrams Creek
174	Abrams Creek below Cades Cove	Abrams Creek
183	Spring at Russell Field shelter	Abrams Creek
184	Left Fork Anthony Creek at campsite 10	Abrams Creek
186	Anthony Creek above picnic area	Abrams Creek
190	Thunderhead Prong at trail crossing	MPLR

Note: Abbreviations in the table are as follows: EPLR, East Prong Little River; MPLR, Middle Prong Little River; WPLR, West Prong Little River; MPLPR, Middle Prong Little Pigeon River; WPLPR, West Prong Little Pigeon River.

Table 3-1 (continued)

Sample site	Site description	Watershed
191	Sams Creek	MPLR
192	Starkey Creek	MPLR
193	Middle Prong Little River at old trailhead	MPLR
194	Middle Prong Little River above Tremont	MPLR
195	Spring at Spence Field shelter	Eagle Creek
200	Anthony Creek above campsite 9	Abrams Creek
201	Anthony Creek below Spence Field	Abrams Creek
209	Lost Creek	EPLR
210	Little River above Fish Camp Prong	EPLR
213	Goshen Prong above Fish Camp Prong	EPLR
214	Silers Creek	EPLR
215	Ashe Camp Prong	EPLR
218	Spring at Silers Bald Shelter	EPLR
219	Double Springs Gap shelter (North Carolina side)	Forney Creek
220	Double Springs Gap shelter (Tennessee side)	EPLR
221	Hazel Creek above cascades	Hazel Creek
233	Walker Camp Prong above Alum Cave	WPLPR
234	Upper Road Prong	WPLPR
237	Walker Camp Prong at last bridge	WPLPR
251	Beech Flats above US 441 loop	Oconaluftee River
252	Beech Flats below roadcut	Oconaluftee River
253	Beech Flats above roadcut	Oconaluftee River
266	Oconaluftee River at visitors center	Oconaluftee River
268	Oconaluftee River below Smokemont	Oconaluftee River
290	Bear Branch at campsite 42	Cataloochee Creek
291	Bunches Creek above Balsam Mountain Road	Bunches Creek
293	Rough Fork at Caldwell House	Cataloochee Creek
310	Bone Valley Creek	Hazel Creek
311	Hazel Creek below Haw Gap Creek	Hazel Creek
336	Flat Creek above falls	Bunches Creek
337	Bunches Creek at Flat Creek Trail	Bunches Creek
472	Sams Creek above Thunderhead Prong	MPLR
473	West Prong Little Pigeon River across from Bearpen Prong	WPLPR
474	Little River below Husky Branch at resting bench	EPLR
475	Fish Camp Prong at angled barrier below War Branch	EPLR
479	Hazel Creek at campsite 86	Hazel Creek
480	Haw Gap Creek at bridge near campsite 84	Hazel Creek
481	Little Fork above Sugar Fork Trail	Hazel Creek
482	Sugar Fork above Little Fork	Hazel Creek
483	Sugar Fork above Haw Gap Creek	Hazel Creek
484	Hazel Creek at Cold Spring Gap Trail	Hazel Creek
485	Walker Creek above Hazel Creek Trail	Hazel Creek
488	Mill Creek at Pumphouse on Forge Creek Road	Abrams Creek
489	Abrams Creek 300 meters below trailhead bridge	Abrams Creek
492	Camel Hump Creek off Low Gap Trail	Cosby Creek
493	Palmer Creek at Davidson Branch Trail	Cataloochee Creek

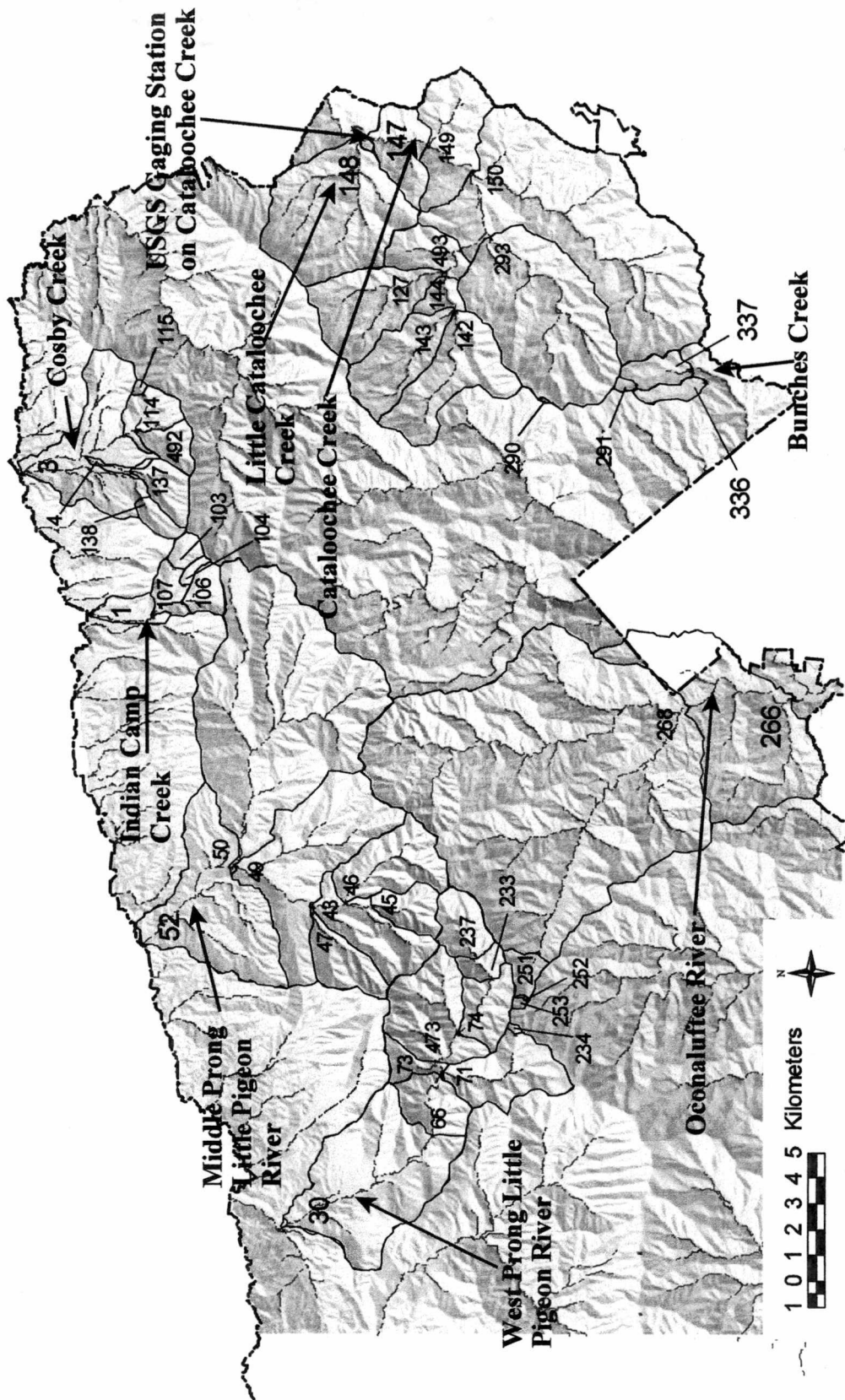


Figure 3-1. Sampled major watersheds of the eastern portion of the Great Smoky Mountains National Park.

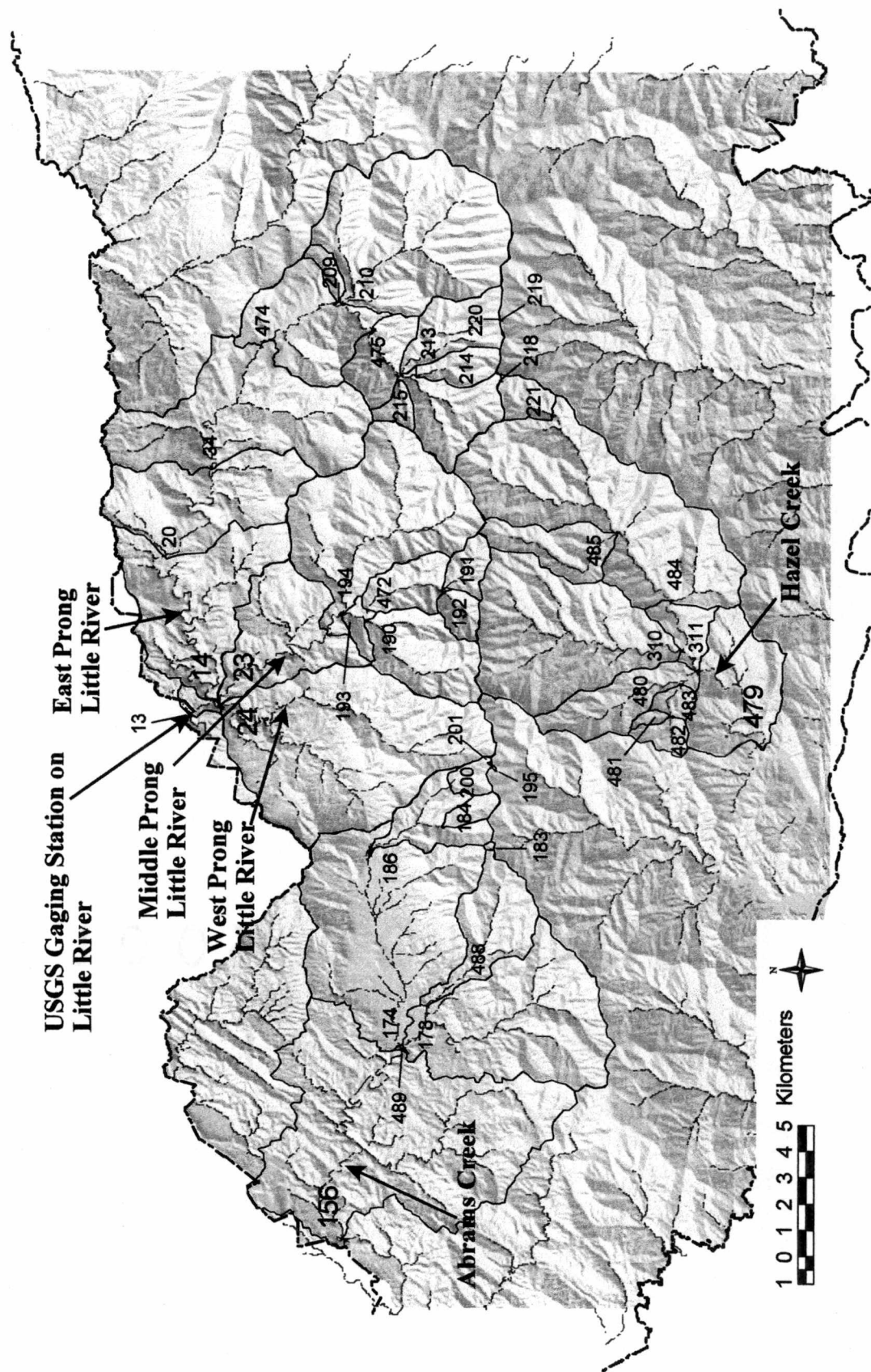


Figure 3-2. Sampled major watersheds of the western portion of the Great Smoky Mountains National Park.

western portions of the GRSM, respectively. The major watersheds are labeled in the figures for easier reference with Table 3-1. Figures 3-1 and 3-2 do not show contour lines but shading does provide an indication of land relief.

The water quality constituents included in the analysis are pH, acid neutralizing capacity (ANC), conductivity, nitrate, sulfate, chloride, sodium, potassium, and ammonium.

Methods of Analysis

Multiple techniques were used to show the spatial variability of water quality constituent values. Figures were used to show median constituent values at each of the sampling sites. Plotting intervals for each constituent were selected by looking at the range in median values and selecting those which would graphically show the variability. The interval boundaries selected for pH and ANC are often cited as "critical" values. Median values were selected to represent "true" water quality constituent values since the median is only minimally affected by the magnitude of any single observation and therefore resistant to outliers which do not reflect typical conditions (Helsel and Hirsch, 1992).

Simple linear regression was performed on median water quality constituent values with respect to sample site elevation to investigate for statistically significant trends ($p < 0.05$ for both the intercept and slope). Scatter plots were used to show the linear relationships and to show how the median constituent values deviate from linear relationships.

Box plots were also used to show the variability in constituent values at selected sites and with respect to elevation. Tukey's box plots are a useful way to convey a significant amount of information. The box portion represents the interquartile range. The lower end of the box is the 25th percentile and the upper end is the 75th percentile. The line through the

box is the median value. Fifty percent of the observed values are within the box. Fifty percent of the observed values are above the median and 50% are below the median. The lines, or whiskers, extend both above and below the box to the highest and lowest values, excluding outliers. The circles represent mild outliers and the asterisks represent extreme outliers. Outliers are considered mild if they are within 1.5 times the interquartile range away from the 25th and 75th percentile. Outliers are extreme if they are greater than three times the interquartile range away from the 25th and 75th percentile (Tukey, 1977).

Results

Figures 3-3, 3-4, 3-5, 3-6, 3-7, 3-8, 3-9, and 3-10 show the variability in median water quality constituent values at sampling sites throughout the GRSM for pH, ANC, conductivity, nitrate, sulfate, chloride, sodium, and potassium, respectively. Sample site numbers are not included in these figures because when they are, the maps appear too cluttered and difficult to read. However, sample site numbers are included in Figures 3-1 and 3-2. When Figures 3-1 and 3-2 are used in conjunction with Figures 3-3 through 3-10, the reader should be able to follow the discussions included in this chapter. Contour lines are also not included in the figures for the same reason. However, shading does provide an indication of land relief. One can also interpret elevation by inspecting the figures and realizing that the highest elevations in the GRSM are typically along the Tennessee and North Carolina border which travels through the center (from left to right) of Figure 3-3. The streams that drain the GRSM begin in the higher elevations and flow outward from the state border to Park boundaries. That is not to say that all streams flow in the north to south or south to north direction. The basins created by the sampling sites are almost equally divided

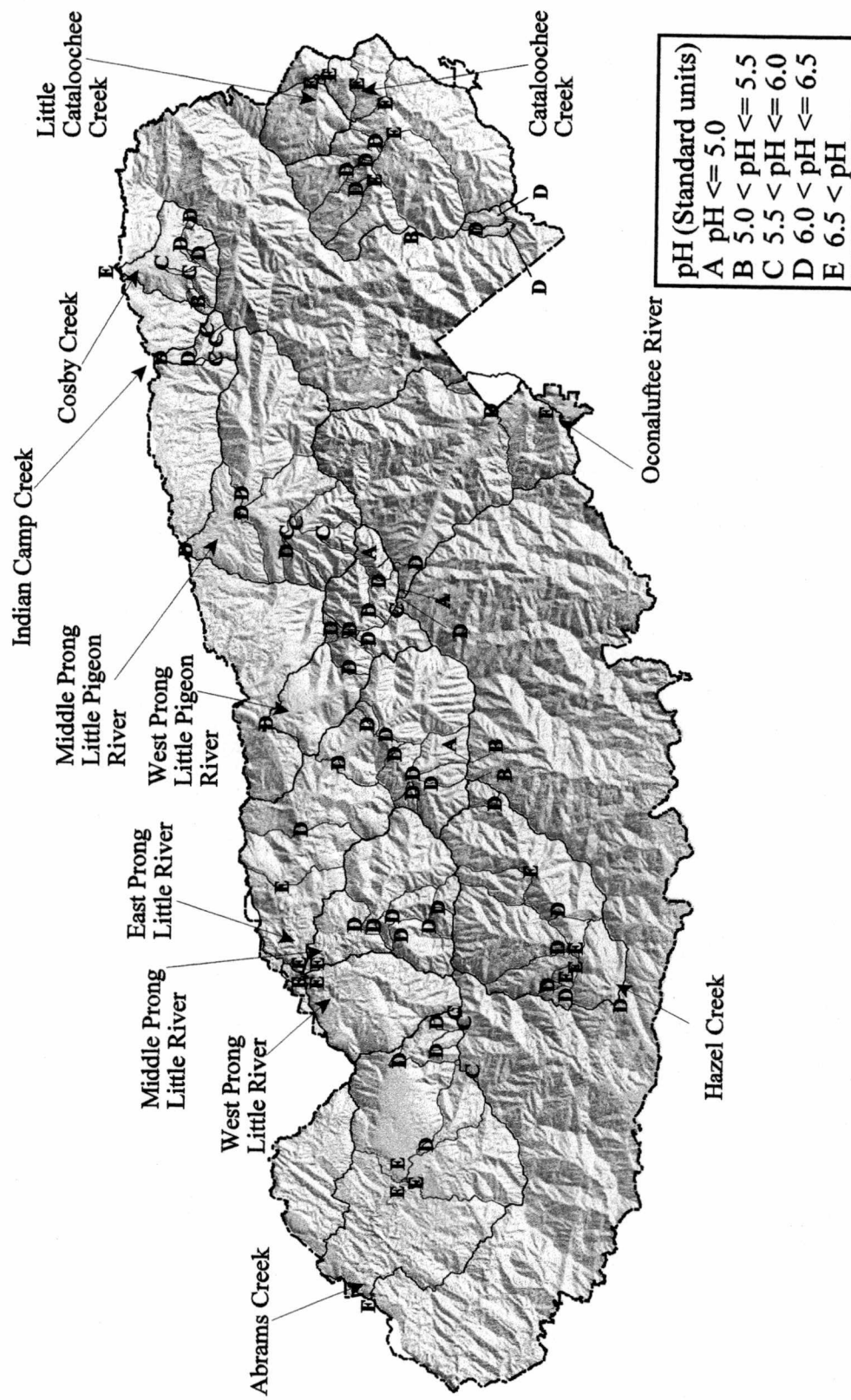


Figure 3-3. Spatial variability of pH in sampled streams of the Great Smoky Mountains National Park.

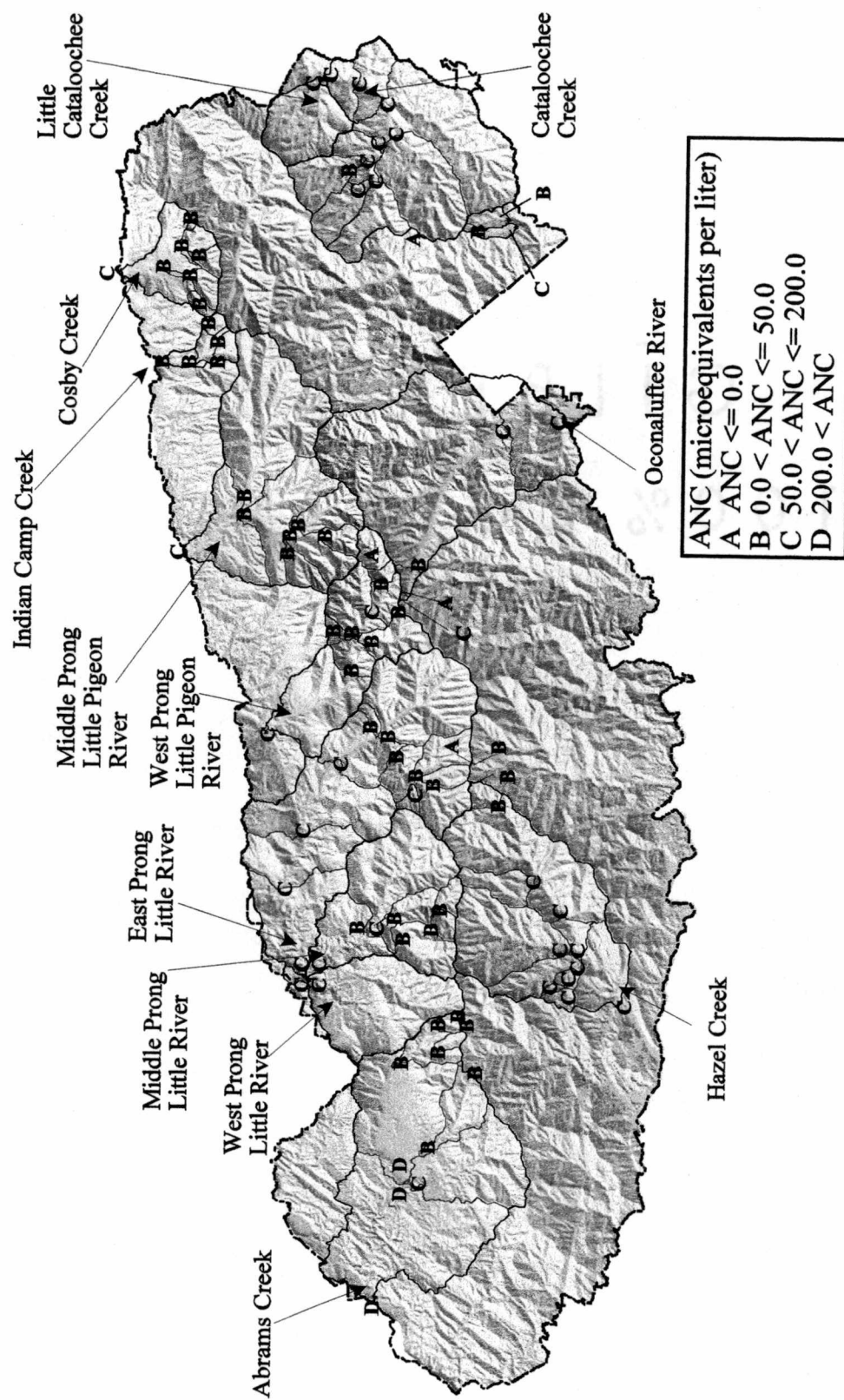


Figure 3-4. Spatial variability of acid neutralizing capacity in sampled streams of the Great Smoky Mountains National Park.

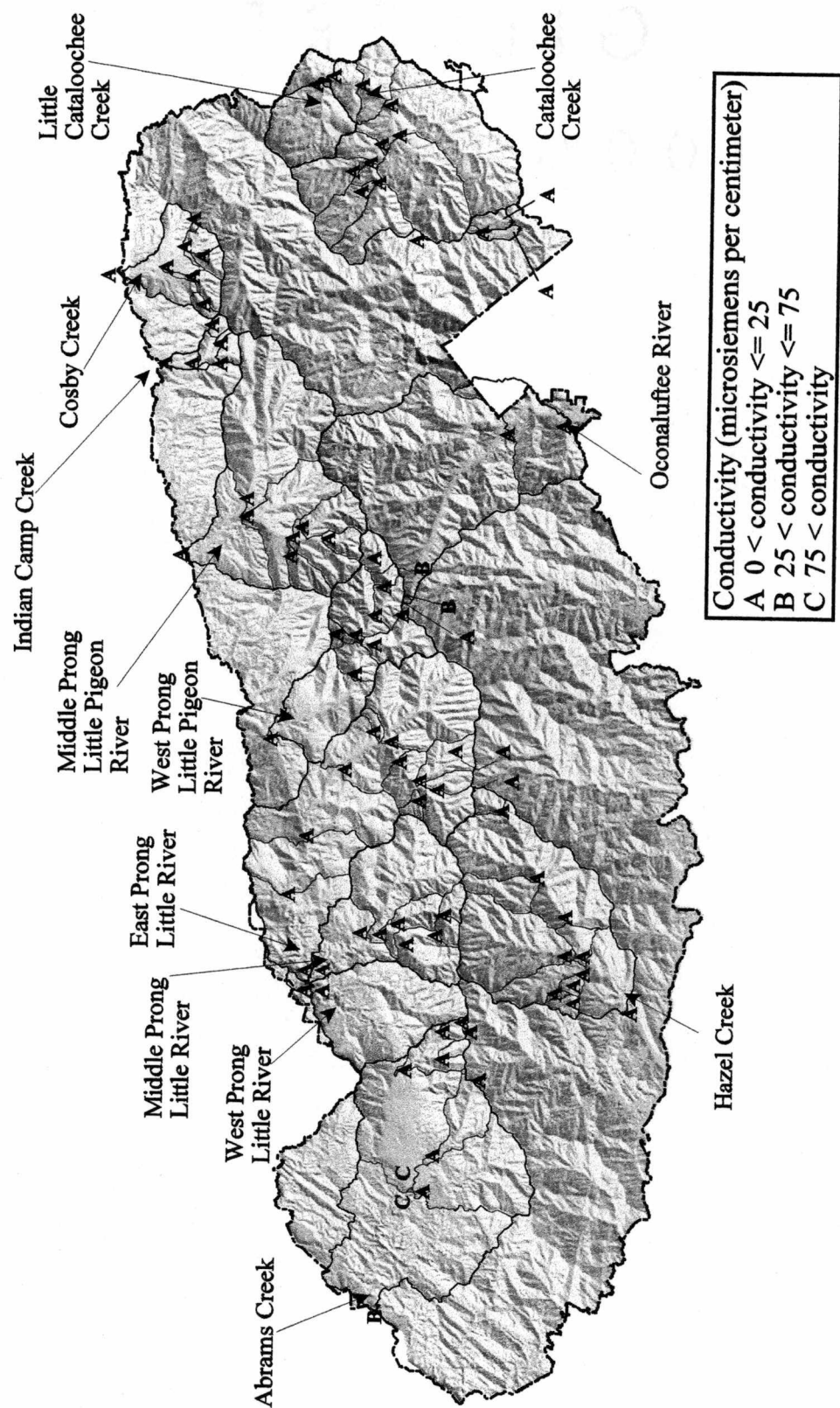


Figure 3-5. Spatial variability of conductivity in sampled streams of the Great Smoky Mountains National Park.

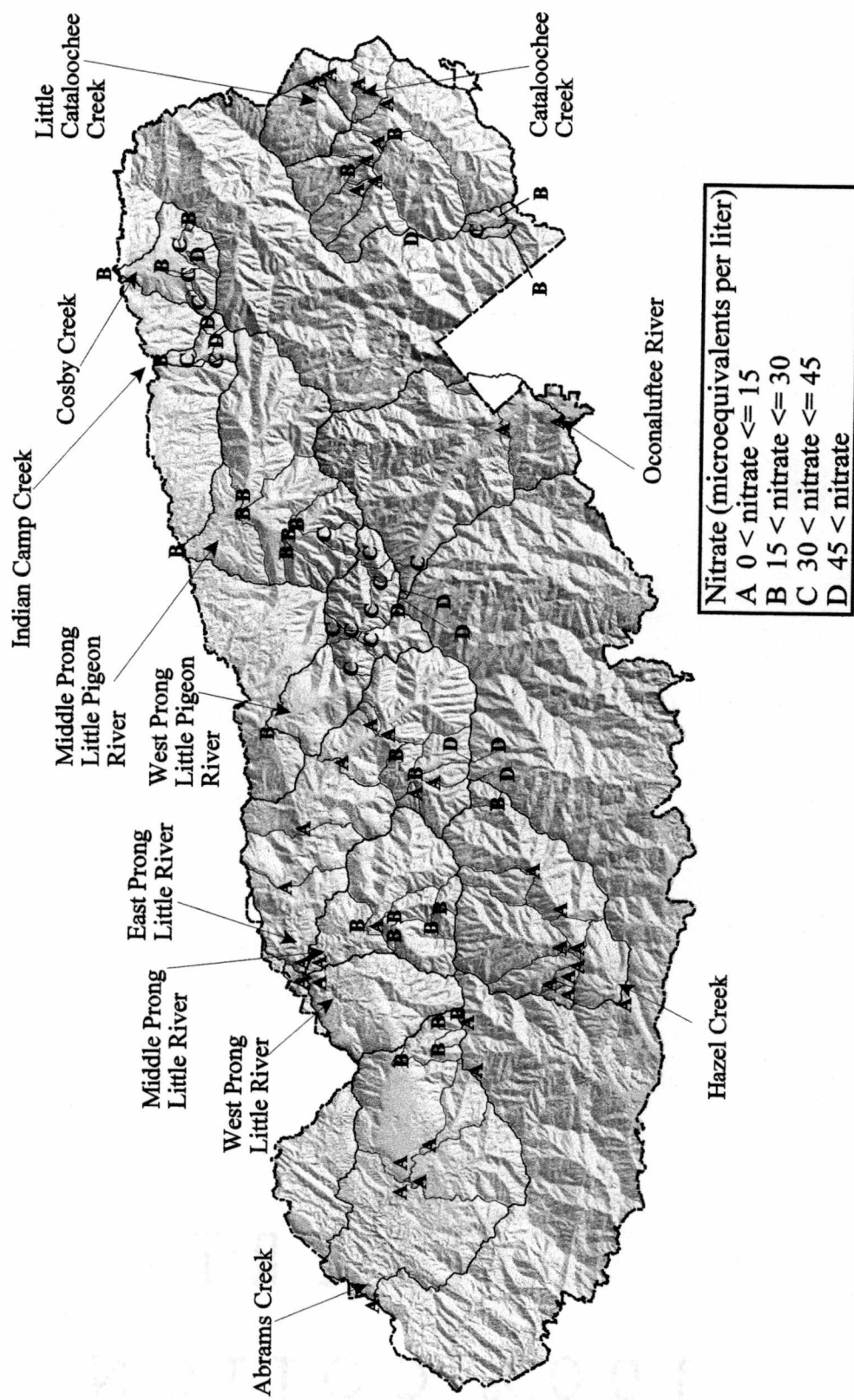


Figure 3-6. Spatial variability of nitrate in sampled streams of the Great Smoky Mountains National Park.

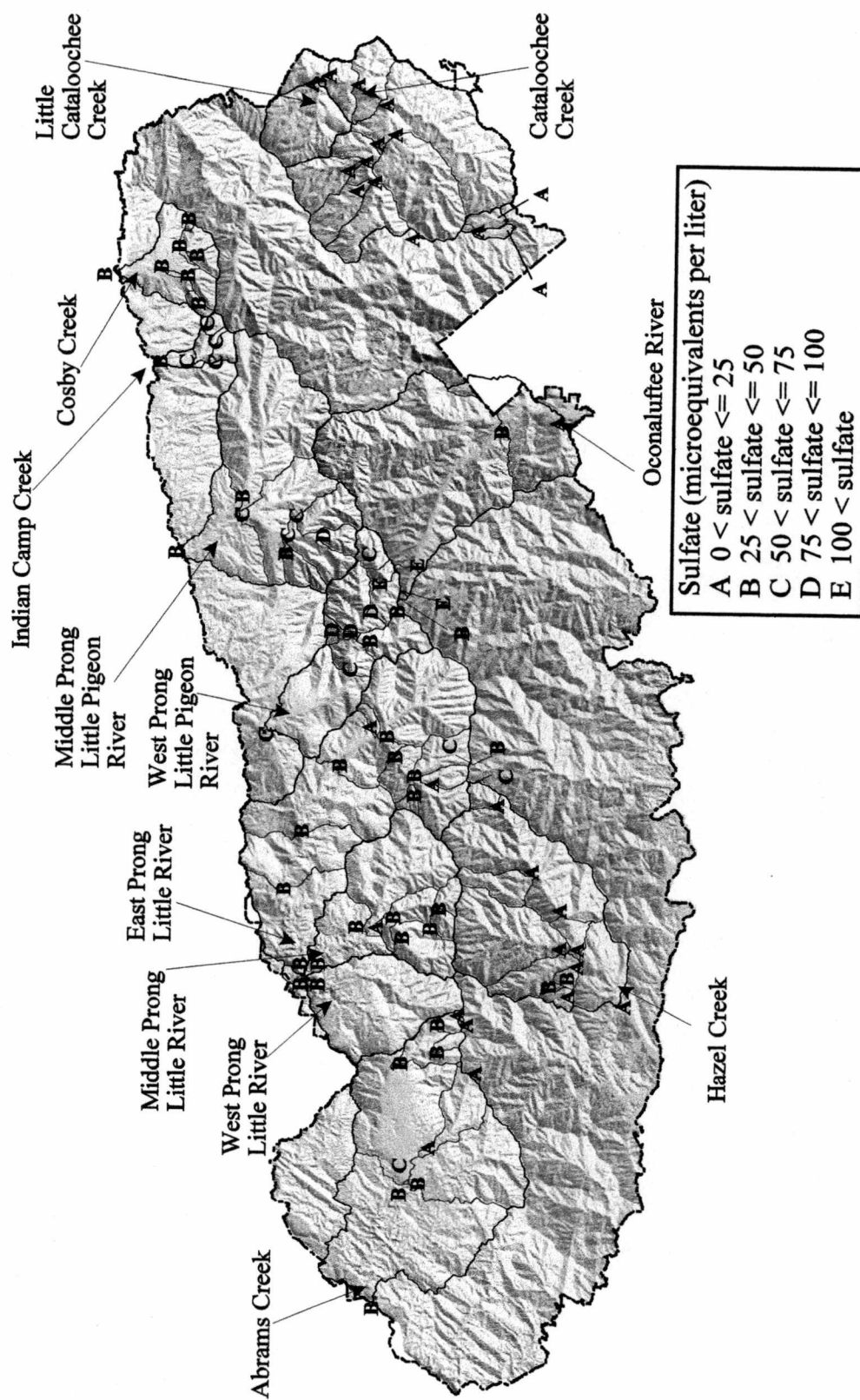


Figure 3-7. Spatial variability of sulfate in sampled streams of the Great Smoky Mountains National Park.

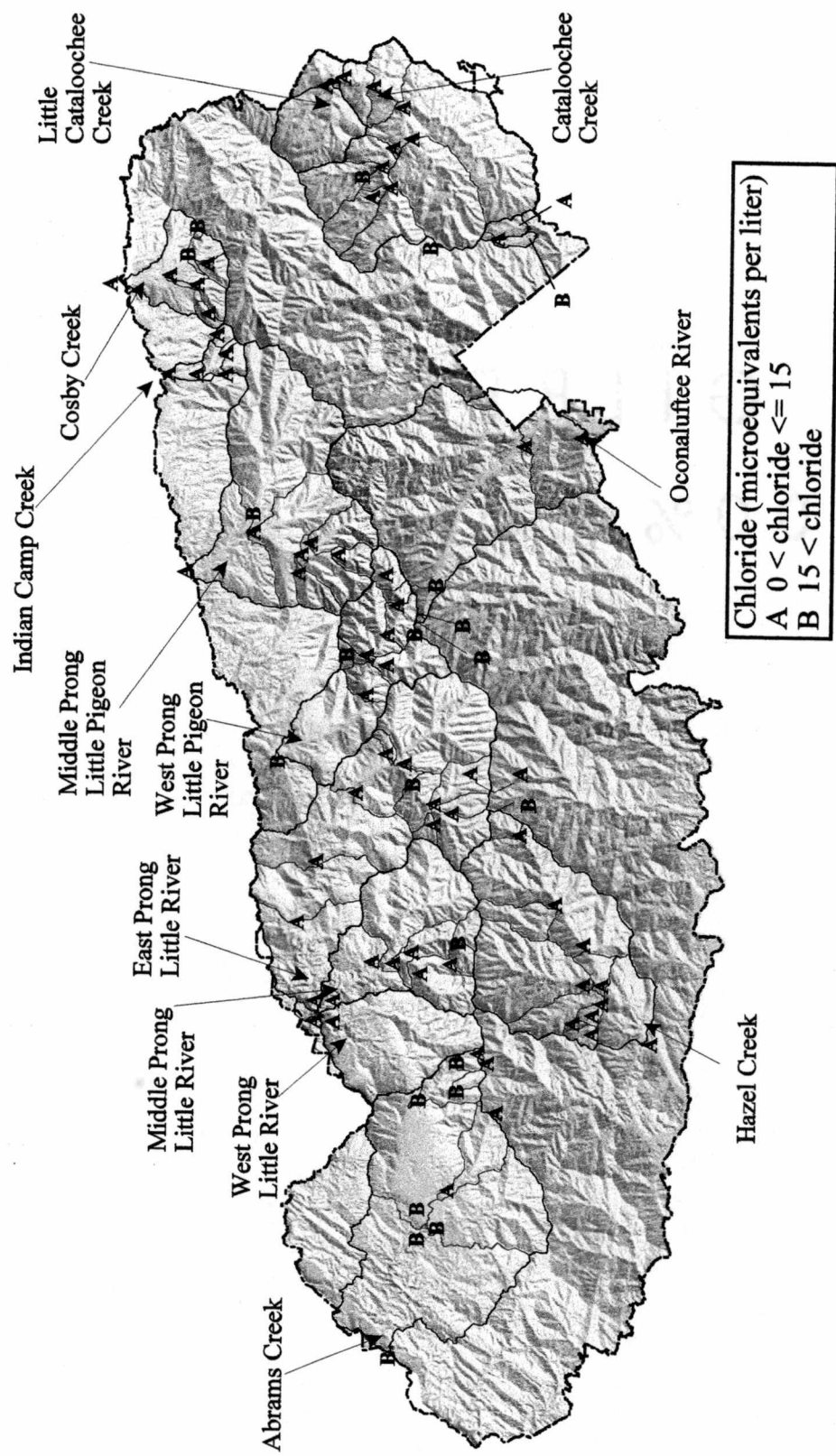


Figure 3-8. Spatial variability of chloride in sampled streams of the Great Smoky Mountains National Park.

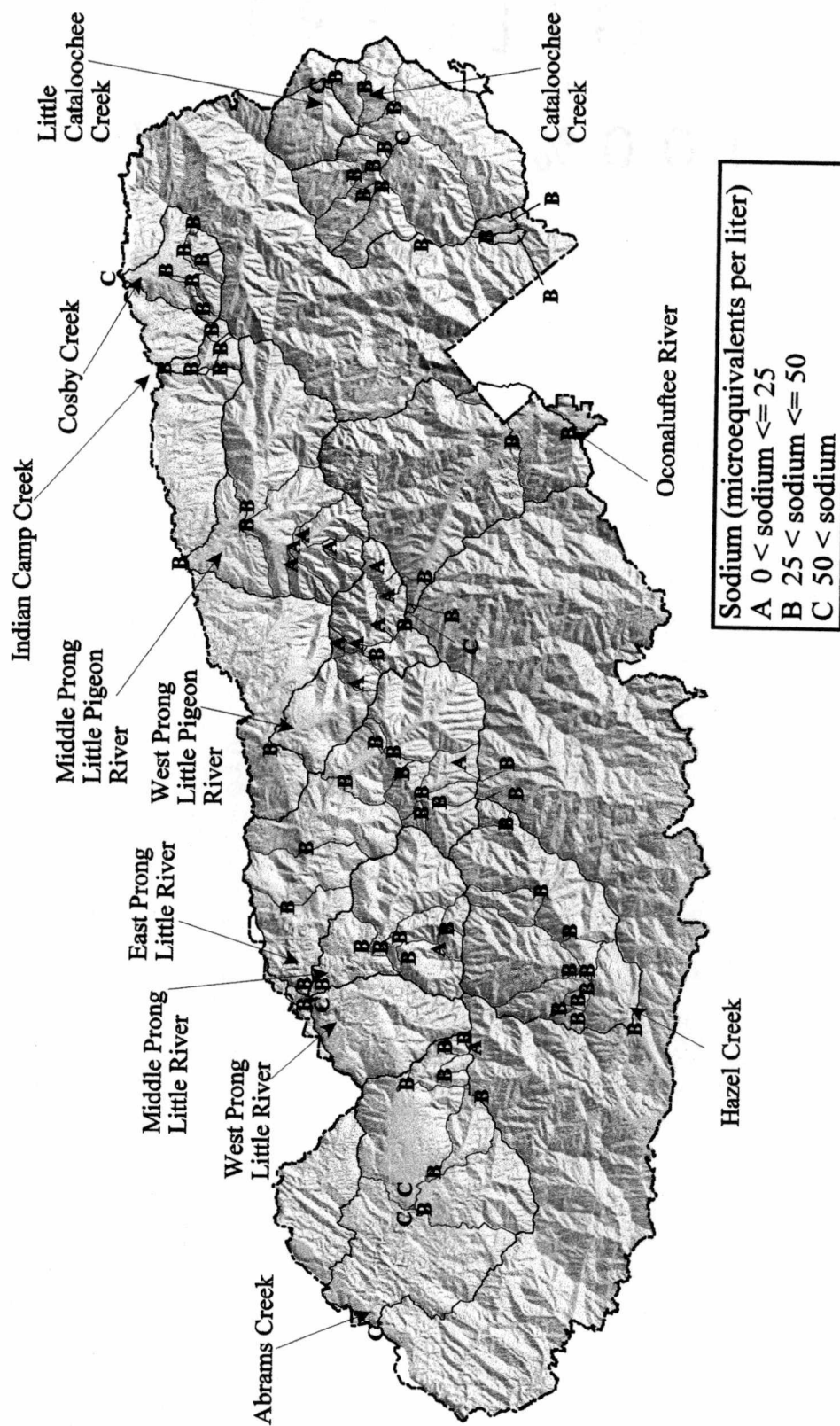


Figure 3-9. Spatial variability of sodium in sampled streams of the Great Smoky Mountains National Park.

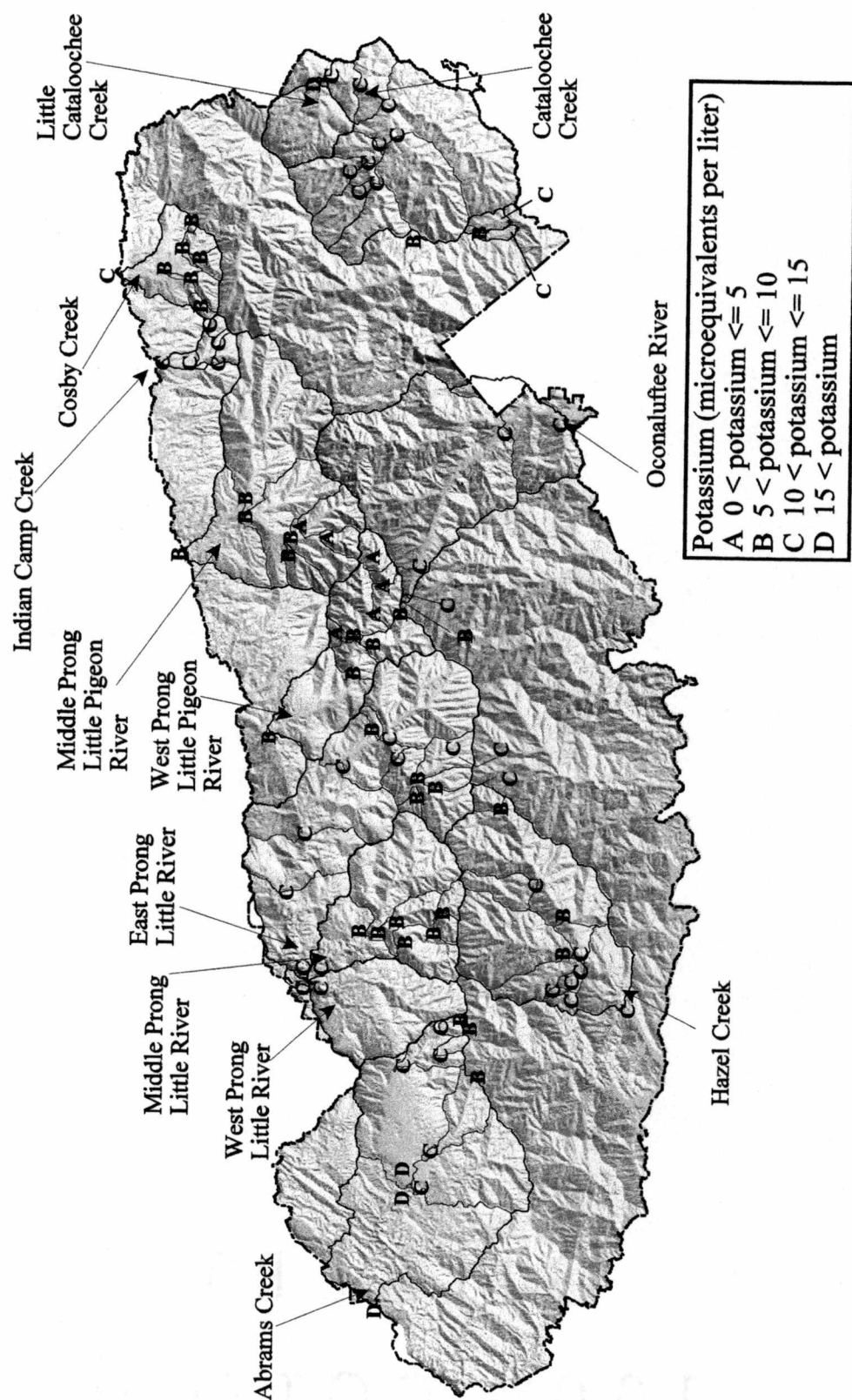


Figure 3-10. Spatial variability of potassium in sampled streams of the Great Smoky Mountains National Park.

with respect to their azimuth. Forty-seven percent of the basins are oriented between either 315 and 45 degrees or 135 and 225 degrees from true north. These orientations would correspond to a general north to south and south to north streamflow, respectively. Fifty-three percent of the basins are oriented between either 45 and 135 degrees or 225 and 315 degrees from true north. These orientations would correspond to a general east to west and west to east streamflow, respectively.

Box plots, which show the variability in water quality constituent values, are included in Figures 3-11, 3-13, 3-15, 3-17, 3-19, 3-21, 3-23, 3-25, and 3-27. These figures show the spatial variability with respect to elevation for pH, ANC, conductivity, nitrate, sulfate, chloride, sodium, potassium, and ammonium, respectively. Scatter plots of median constituent values at each sample site versus elevation are also included. These plots show the statistically significant linear trends and which sites are outliers in the relationship. They also graphically show how the median values deviate from linear relationships with elevation. Regression equations are included in these plots if elevation explains at least 25% of the variability in median constituent values. Figures 3-12, 3-14, 3-16, 3-18, 3-20, 3-22, 3-24 and 3-26 are scatter plots of sample site elevation versus median values of pH, ANC, conductivity, nitrate, sulfate, chloride, sodium, and potassium, respectively. A map showing Park-wide variability of ammonium and a scatter plot of median ammonium concentration versus elevation are not included because all sample sites have median ammonium concentrations below detection limits. The box plots of ammonium concentrations with respect to elevation are included to show outliers.

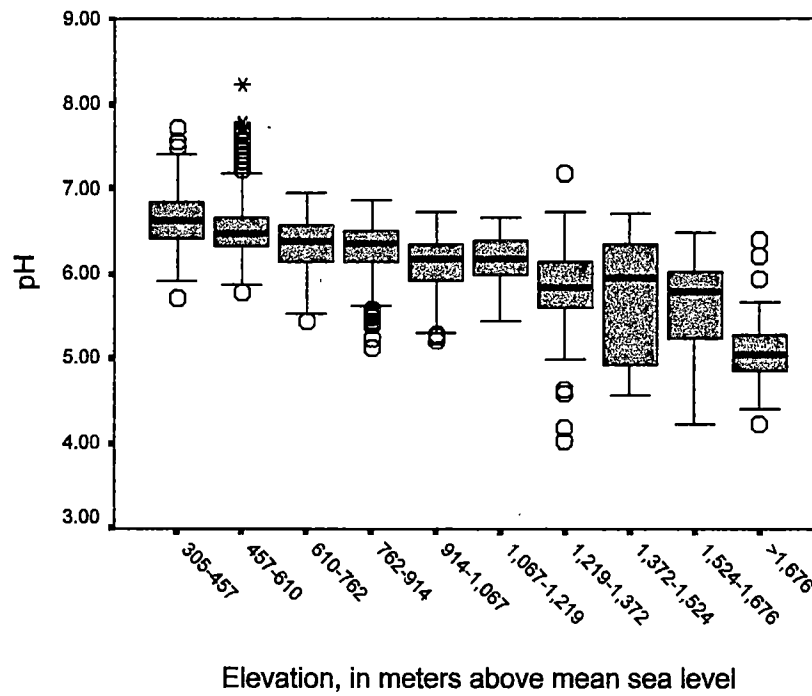


Figure 3-11. Elevation trend for pH in sampled GRSM streams.

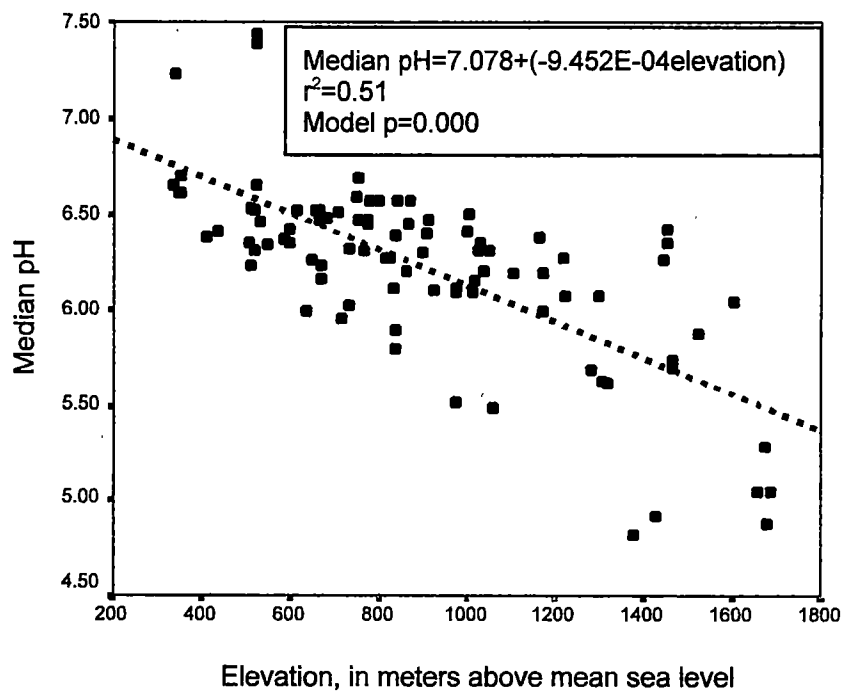


Figure 3-12. Regression analysis of median pH in sampled GRSM streams.

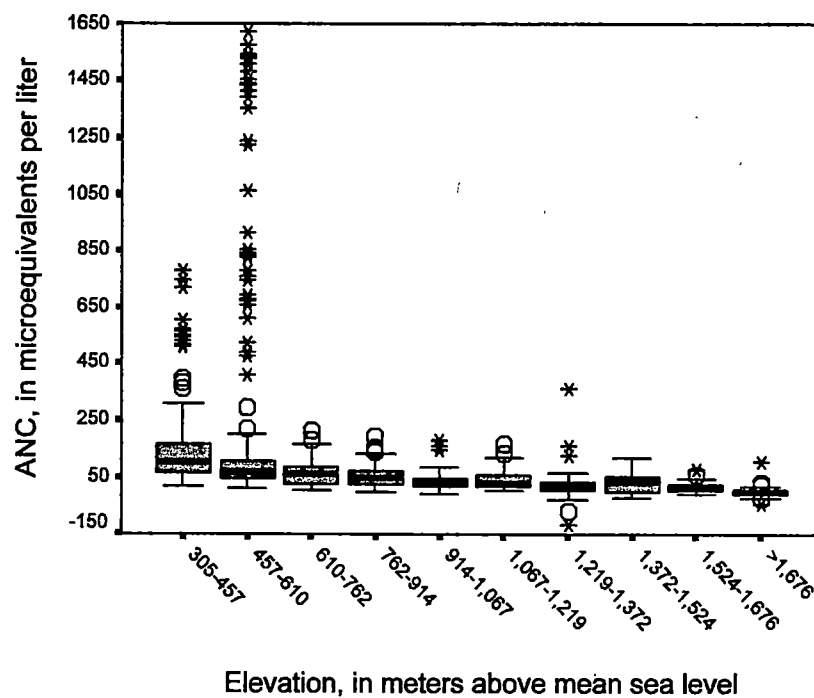


Figure 3-13. Variability of acid neutralizing capacity in sampled GRSM streams.

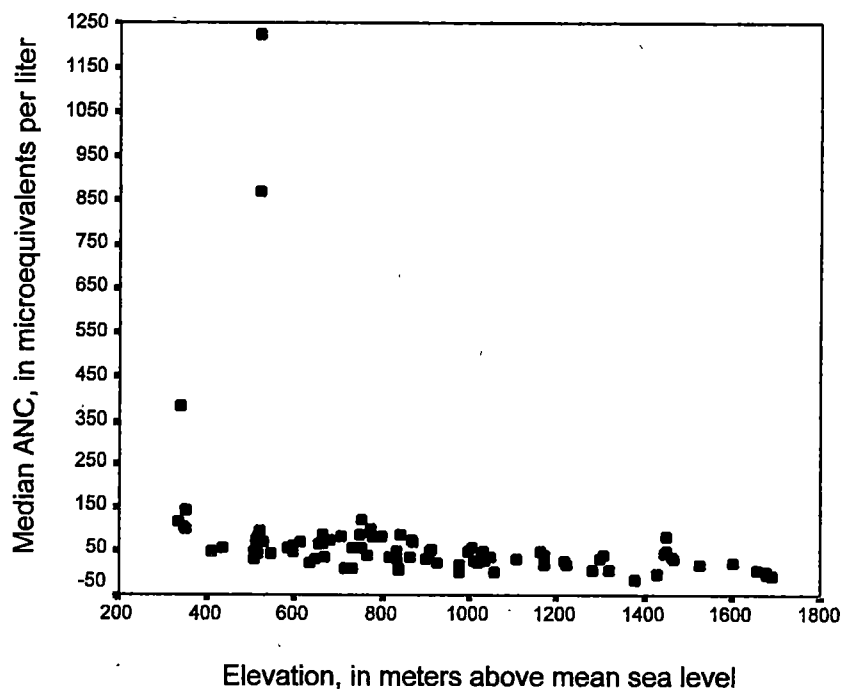


Figure 3-14. Scatter plot of median acid neutralizing capacity in sampled GRSM streams.

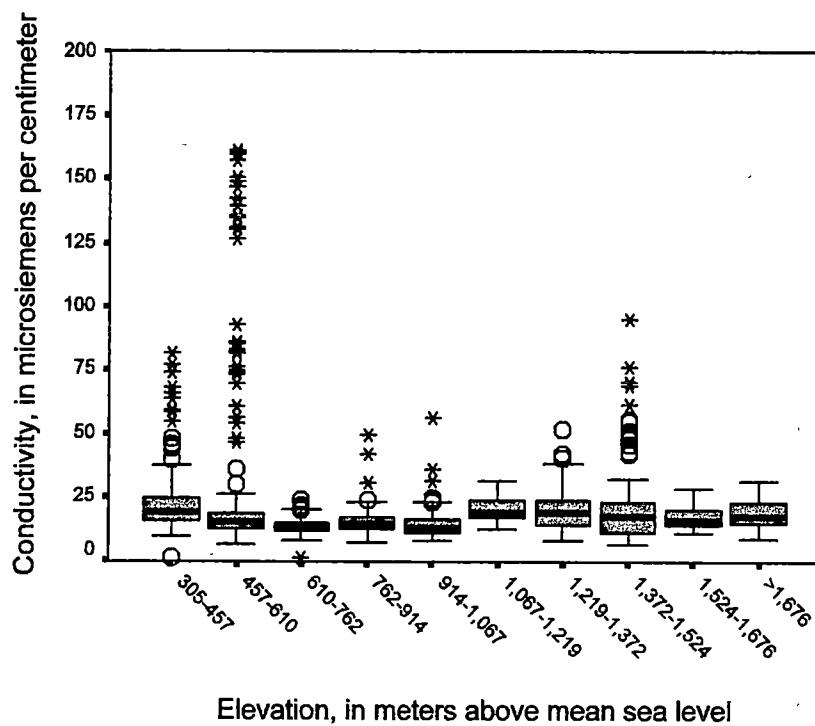


Figure 3-15. Variability of conductivity in sampled GRSM streams.

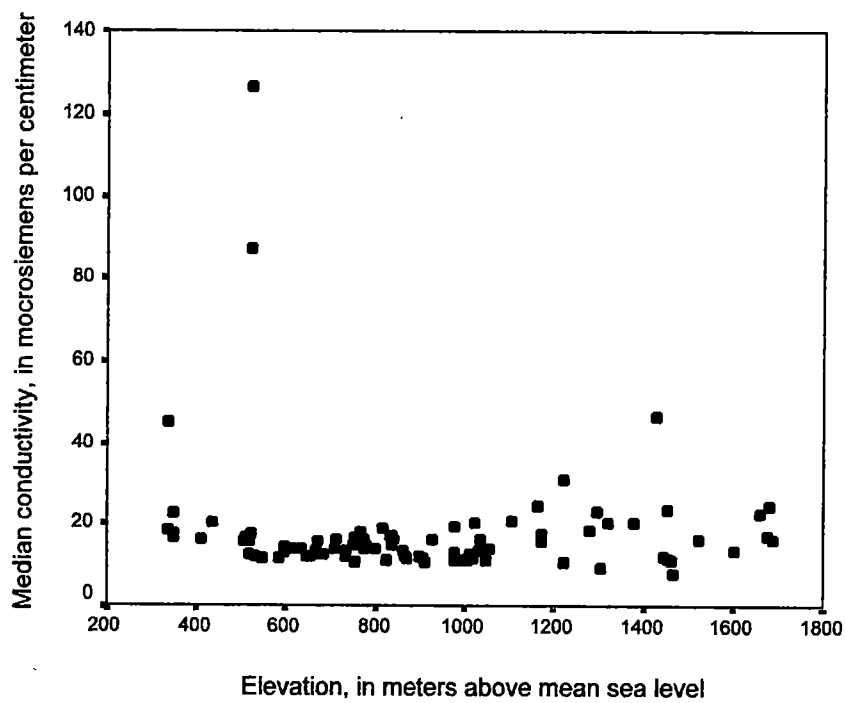


Figure 3-16. Scatter plot of median conductivity in sampled GRSM streams.

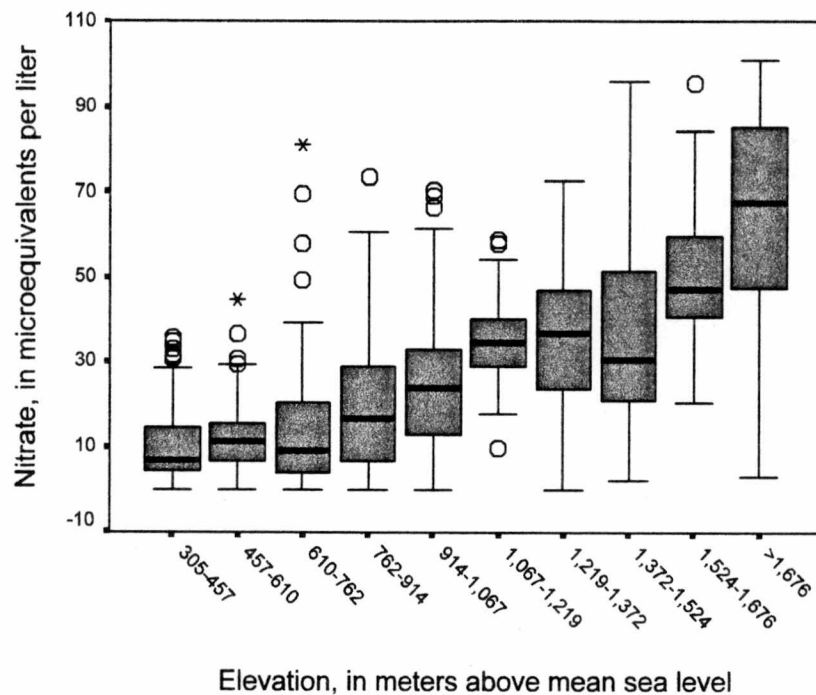


Figure 3-17. Elevation trend for nitrate in sampled GRSM streams.

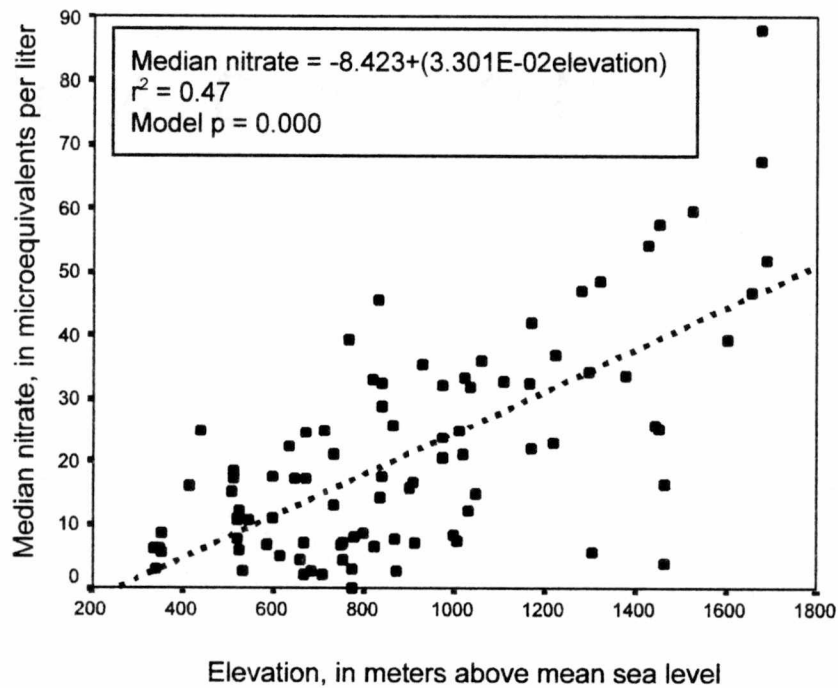


Figure 3-18. Regression analysis of median nitrate in sampled GRSM streams.

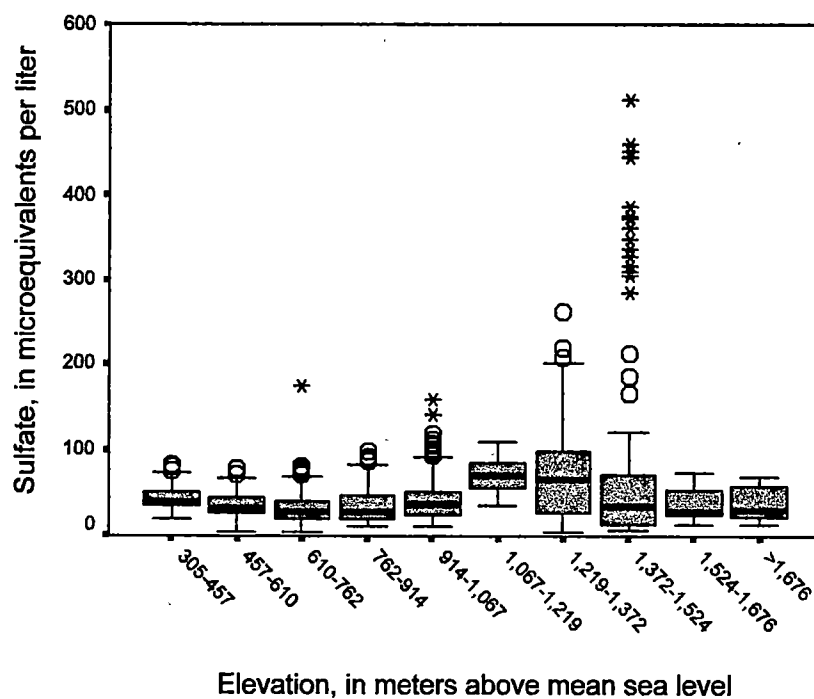


Figure 3-19. Variability of sulfate in sampled GRSM streams.

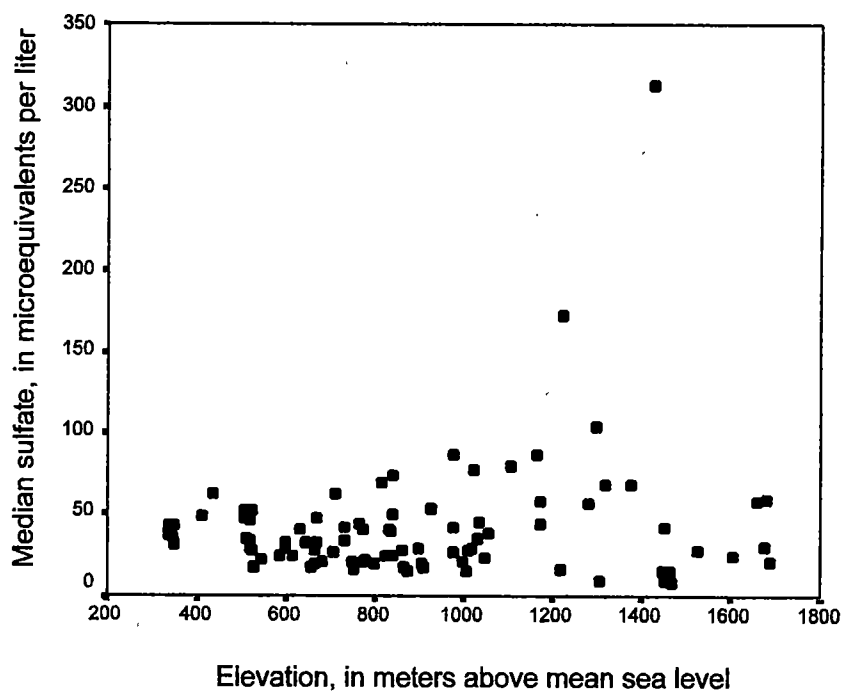


Figure 3-20. Scatter plot of median sulfate in sampled GRSM streams.

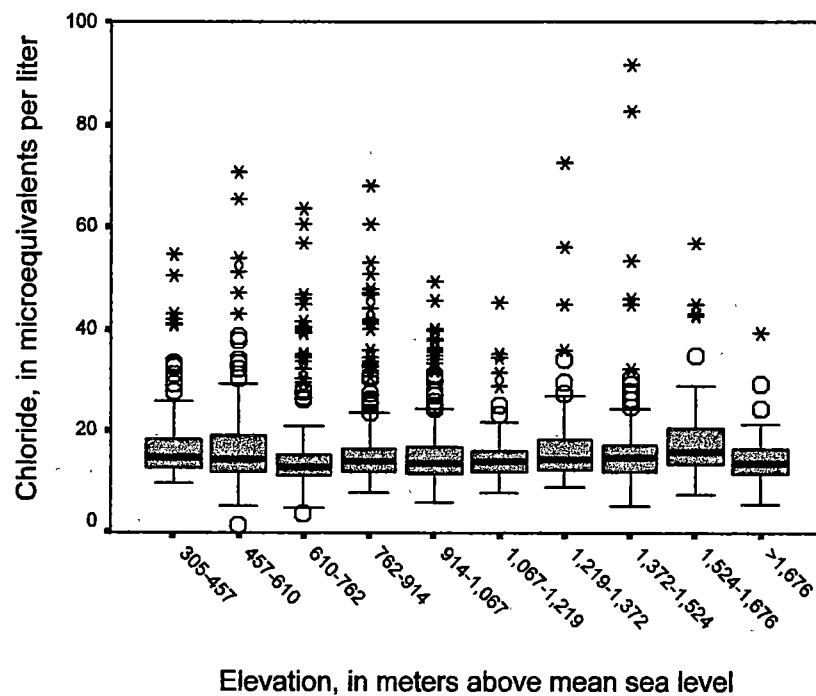


Figure 3-21. Variability of chloride in sampled GRSM streams.

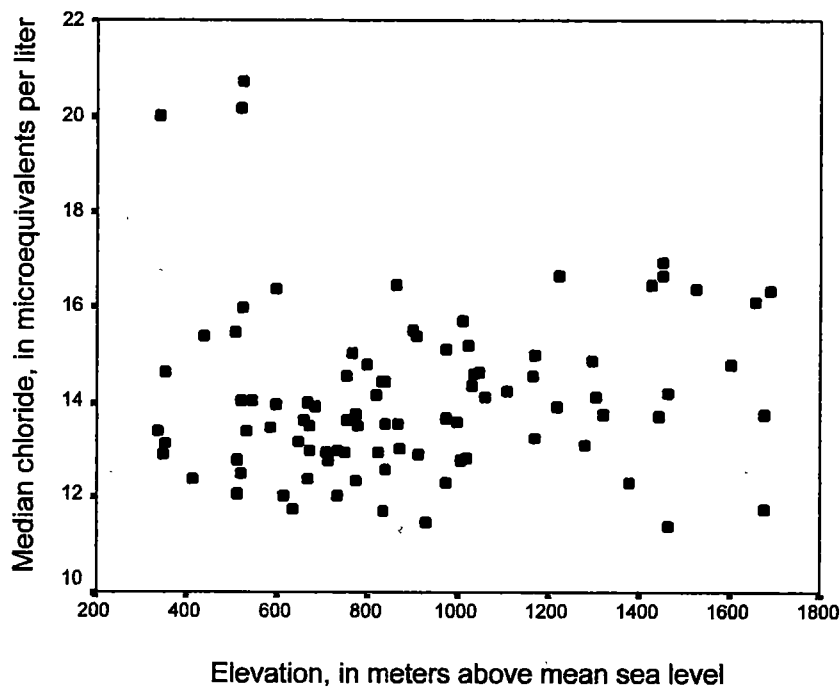


Figure 3-22. Scatter plot of median chloride in sampled GRSM streams.

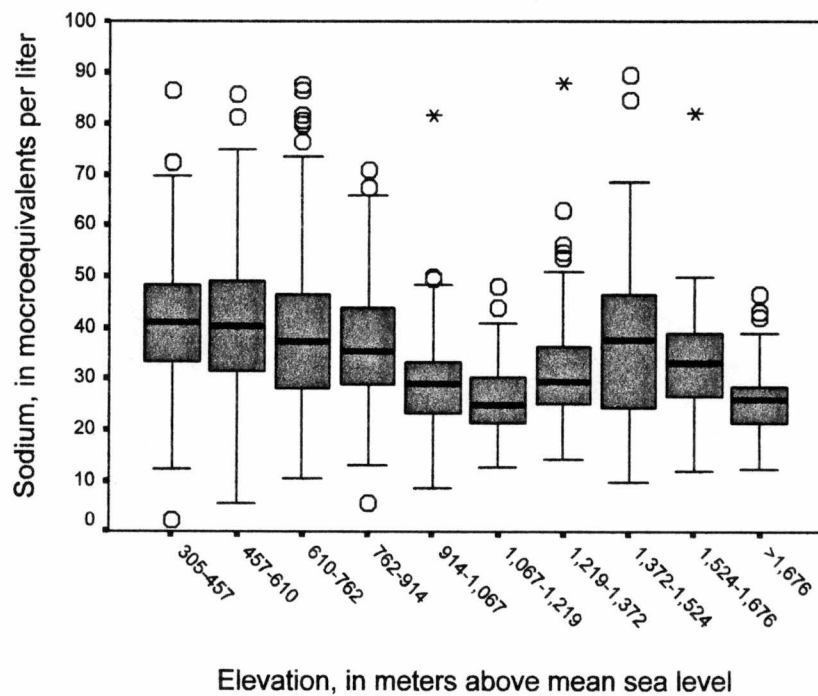


Figure 3-23. Elevation trend for sodium in sampled GRSM streams.

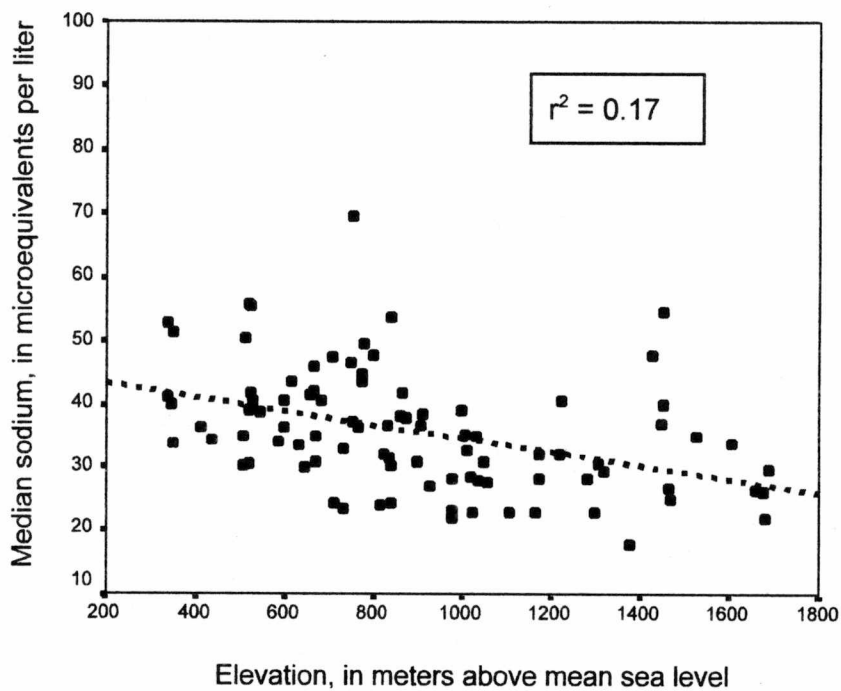


Figure 3-24. Regression analysis of median sodium in sampled GRSM streams.

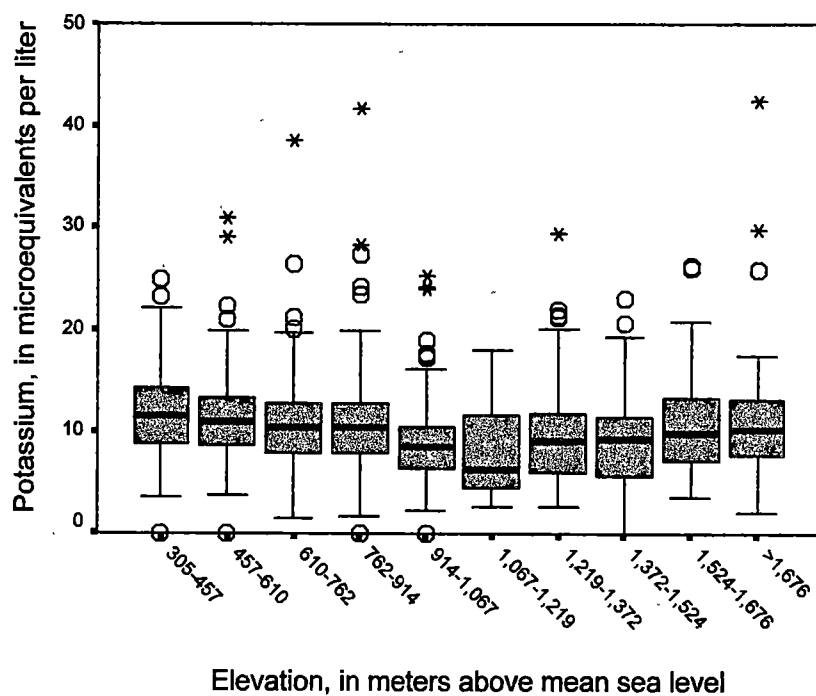


Figure 3-25. Elevation trend for potassium in sampled GRSM streams.

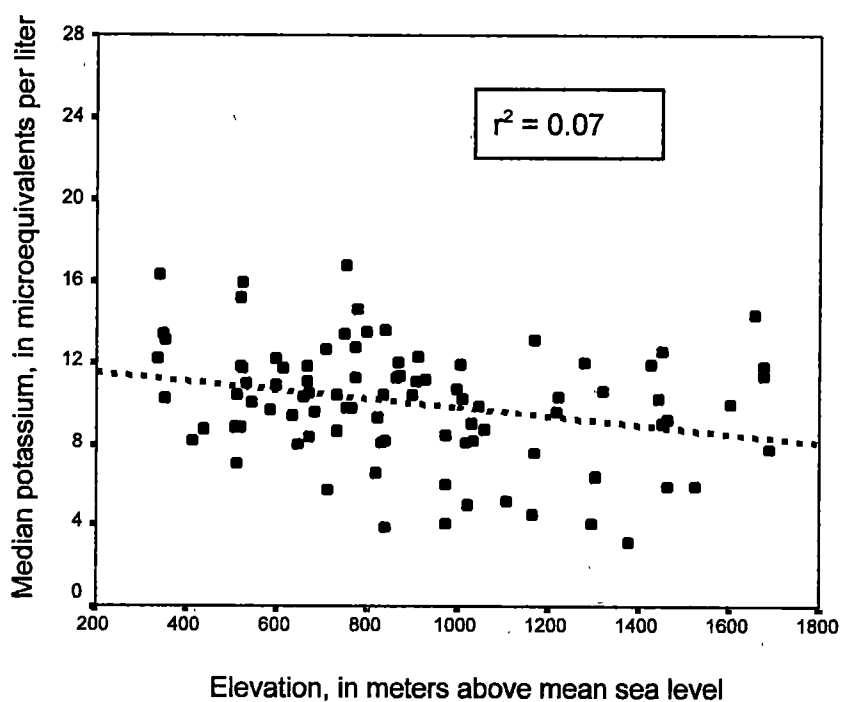


Figure 3-26. Regression analysis of median potassium in sampled GRSM streams.

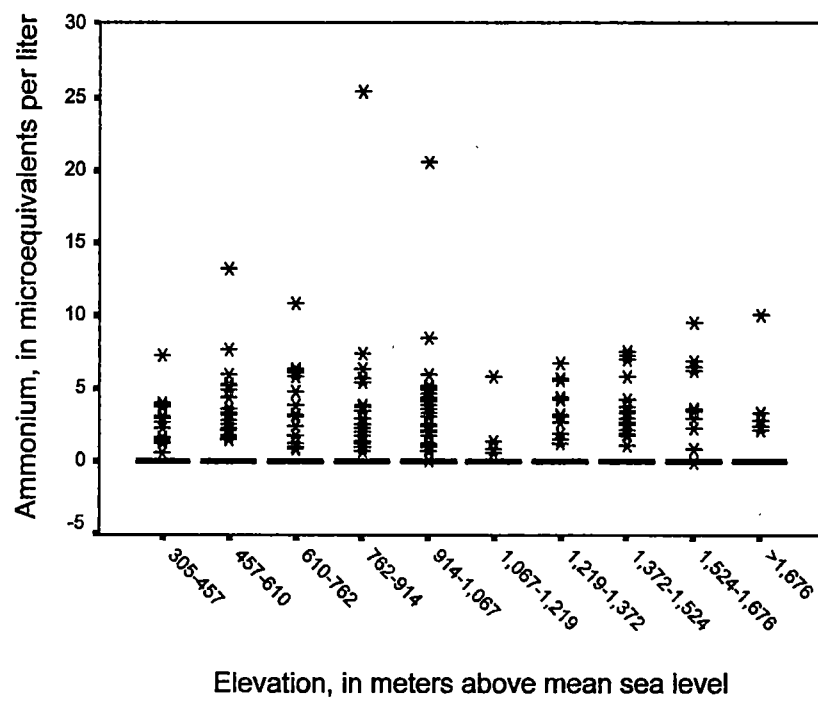


Figure 3-27. Variability of ammonium in sampled GRSM streams.

Discussion of Results

The spatial variability of each constituent is discussed in the following order: pH, ANC, conductivity, nitrate, sulfate, chloride, sodium, potassium, and ammonium.

pH

Notice in Figure 3-3 that sites located at Park boundaries (lower elevations) such as 3, 13, 156, and 266 have median pH values greater than 6.5. These sites are within the larger Cosby Creek, Little River (East, Middle, and West Prongs), Abrams Creek, and Oconaluftee River watersheds, respectively. Other sites (30, 52, and 479), which are the lowest elevation sites within the larger West Prong Little Pigeon River, Middle Prong Little Pigeon River, and Hazel Creek watersheds, have median pH values between 6.0 and 6.5. These lower elevation sites have some of the higher pH values found in the GRSM. Higher elevation sites such as 138, 218, 219, 220, 237, 252, and 290 have some of the lower median pH values. These sites have median pH values less than or equal to 5.5. The median pH at sampled sites appears to decrease with increases in elevation. Figure 3-11 shows this trend by displaying box plots of pH by different sampling site elevation ranges. Sites were grouped according to the elevation of the sampling site and placed in an elevation class, each with a range of about 152 meters (500 feet). Simple linear regression was done to see if the trend is statistically significant, and if so, how much of the variability in median pH is explained by elevation. Figure 3-12 shows a scatter plot of median pH values at each sample site versus the site elevation with the regression equation. Both the intercept and the slope are statistically significant. About half of the variability in median pH is explained by the elevation of the sampling site.

Notice the outliers in Figure 3-12 at both the lower and upper elevations. The sites at the lower elevations of the GRSM (less than 600 meters) in Figure 3-12 with median pH greater than 7.0 are all within Abrams Creeks watershed. These include sites 156, 174, and 489. Site 174 is located at the trailhead to Abrams Falls and samples are collected from Abrams Creek before it joins with Mill Creek. Site 489 is located about 300 meters downstream of where Abrams Creek and Mill Creek flow together. Site 156 is much further downstream and near the Park boundary at Abrams Creek campground and ranger station. Figure 3-3 also shows that the lower elevations of Cataloochee Creek, Little Cataloochee Creek, and Little River (East, Middle, and West Prongs) watersheds have median pH values greater than 6.5. Surface waters with pH below 6.5 can pose problems (with respect to acidity) for aquatic organisms and fish (Baker *et al.*, 1996). Table 3-2 shows the possible ecological consequences of low surface water pH and the percentage of sample sites within the ranges listed. Twenty-one of the 90 sites (23%) have median pH values above 6.5, the point at which adverse ecological effects to aquatic organisms are either nonexistent or not significant.

As mentioned, the outliers in Figure 3-12 at the upper elevations are some of the more acidic sampled waters of the GRSM. Sites 219, 237, and 252 (3% of all sampling sites) have median pH values below 5.0, the point at which ecological consequences are extremely significant. In addition to the information in Table 3-2, other researchers have given more specific "critical" pH values because they define at what pH certain species of trout have difficulty. Based on a review of the literature by some authors, the "critical" pH values for the trout found in GRSM waters are 5.5 for rainbow trout, 5.4 for brown trout, and 5.2 for

Table 3-2. Possible ecological consequences of low surface water pH.

Source: Baker, J.P., J. Van Sickle, C.J. Gagen, D.R. DeWalle, W.E. Sharpe, R.F. Carline, B.P. Baldigo, P.S. Murdoch, D.W. Bath, W.A. Krester, H.A. Simonin, and P.J. Wigington, Jr., Episodic acidification of small streams in the northeastern United States: effects on fish populations, *Ecological Applications*, 6, 422-437.

pH range	Biological effects	Percentage of sample sites with median pH within range
> 6.5	No adverse effects	23
6.0 - 6.5	Loss of sensitive benthic invertebrates	56
5.5 - 6.0	Loss of acid-sensitive fish Reduced reproduction in sensitive fish species Increase in green algae in periphyton	13
5.0 - 5.5	Loss of most fish species Green algae dominate periphyton Loss of most mayflies, stoneflies, caddisflies, and shellfish Reduced biomass and productivity	5
< 5.0	Loss of all fish species Decreased nutrient cycling rates Decline in periphyton species richness Decline in benthic invertebrates Reproductive failure of acid-sensitive amphibians	3

Note: Biological effects at pH greater than 6.5 were added by this author and were not included in the original table by the authors listed in the source above.

brook or "speckled" trout (Baker and Christensen, 1991). Therefore, at pH values below 5.5 all species of trout found in the streams of the GRSM would experience a significant population loss or would be absent entirely. Sites 138, 218, 220, and 290 (5% of all sampling sites) have median pH values between 5.0 and 5.5. Therefore, 8% of the sampling sites have median pH values less than or equal to the critical limit for all species of trout found in the GRSM. Sites 218, 219, 220, and 290 are high elevation springs. Sites 218, 219, and 220 are located closely together along the Appalachian Trail at Silers Bald and Double Springs Gap. Site 290 is a high elevation spring within Cataloochee Creek watershed. The samples from these sites are collected just as the water is exposed to the atmosphere. Other springs include sites 183, 195, and 201. They are all located closely together in the western portion of the Park. These three sites have median pH values between 5.5 and 6.0.

As mentioned, four of the seven sites with median pH below 5.5 are high elevation springs. The amount of water at these sites is probably not enough to sustain trout populations even at pH values within ideal ranges for trout. Fortunately, sampled waters do show recovery from these particularly poor conditions as the water flows to the lower elevations (see Figure 3-3). However, even as conditions improve, median pH at most sample sites (77%) is below 6.5, the point at which biological effects become significant to aquatic organisms.

Sites 138, 237, and 252 are not high elevation springs which have median pH values below 5.5. Site 138 is on Inadu Creek within Cosby Creek watershed. Site 237 is the highest elevation site along the West Prong of the Little Pigeon River where Walker Camp Prong crosses U.S. Highway 441. Site 252 is one of the highest elevation sites within the

Oconaluftee watershed. The site is located below U.S. Highway 441 along a small tributary to the Oconaluftee River called Beech Flats Creek. Figure 3-28 shows the variability in pH at all sampling sites with median pH values below 5.5.

Most sampling sites (56%) have median pH values between 6.0 and 6.5. The percentages of sample sites within the different pH ranges are listed in Table 3-2.

Acid Neutralizing Capacity

Since pH is usually positively correlated with acid neutralizing capacity, the spatial variability of ANC in sampled GRSM streams is very similar to pH. Figure 3-4 shows the Park-wide variability of ANC. By inspection of Figure 3-4, a couple of sites are particularly noticeable. The sites within Abrams Creek which have median pH values greater than 7.0 also have values of ANC greater than 200 microequivalents per liter. The other lower elevation areas of the GRSM also have higher ANC values than the upper elevations. Figure 3-13 shows the variability of ANC with respect to elevation. Sites 156, 173, 174, and 489 are all within Cades Cove. Three of these were discussed earlier with respect to pH. Site 173 is located on Mill Creek just before it joins with Abrams Creek. These sites account for the outliers in Figure 3-13 at the lower elevations (below 610 meters). Figure 3-14 shows the scatter plot of median ANC versus sample site elevation. Again, the outliers at the lower elevations are sample sites within Cades Cove. Both the intercept and the slope are statistically significant when simple linear regression is performed on the data in Figure 3-14. However, the equation does not explain much of the variability of ANC ($r\text{-square} = 0.10$). If the lower elevation sites within Cades Cove are removed from the regression analysis, the equation does a much better job of explaining the variability ($r\text{-square} = 0.30$) of ANC in

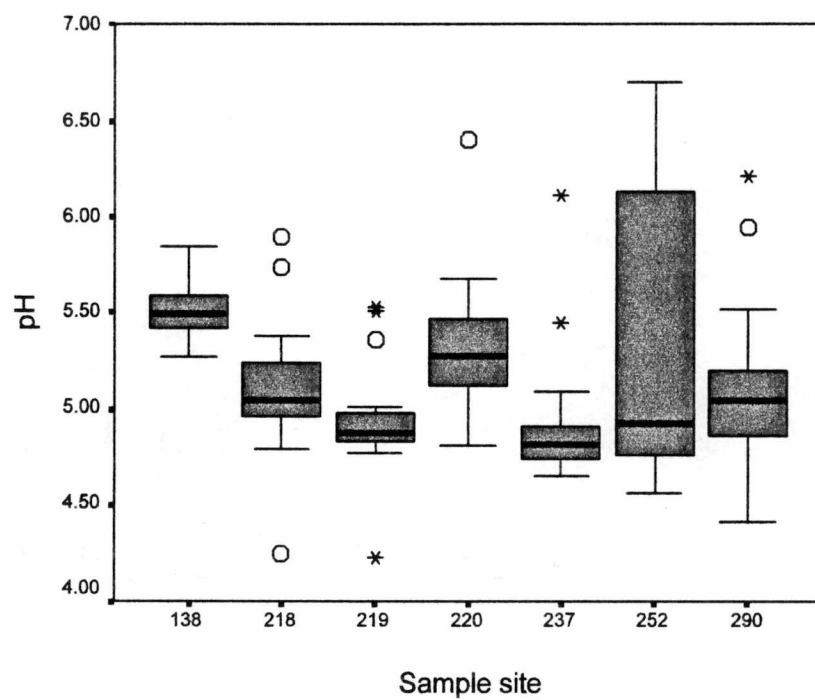


Figure 3-28. Sample sites with median pH less than or equal to 5.5.

most of the sampled GRSM streams. This is discussed in more detail in Chapter IV.

The upper elevation sites with particularly low median values for ANC (less than zero) include 219, 237, 252, and 290. The locations of these sites were discussed earlier. Figure 3-29 shows the variability of ANC at these sample sites. With median values of ANC less than or equal to zero, the water is considered acidic. Site 252 shows the greatest variability of ANC. The interquartile range (the box portion) is larger than that for the other sites. Site 252 also shows the greatest variability in pH (see Figure 3-28). As mentioned, this site is one of the highest elevation sites within the Oconaluftee watershed. The site is located below U.S. Highway 441 along a small tributary to the Oconaluftee River called Beech Flats Creek. Samples are collected as water exits a circular pipe that allows the water to flow under the roadway.

Certain ranges of ANC are commonly cited to classify the acidic level of surface water. Table 3-3 lists the range in values of ANC, its classification, and the percentage of sample sites within each range. The ranges in ANC given in Table 3-3 and their classification were used by the authors cited above the table and also by researchers for the Environmental Protection Agency during the National Surface Water Survey. By inspection of the figures and Table 3-3, one can conclude that the ability of sampled GRSM streams to neutralize acid is minimal. Eighty-seven of the 90 sampling sites (about 97%) are classified as either sensitive, extremely sensitive, or acidic. Only three of the sampling sites are not classified as threatened in some way by the input of acid. In addition, Table 3-2 shows that 77% of the sampled sites in the GRSM have median pH values which have some adverse effects on aquatic organisms.

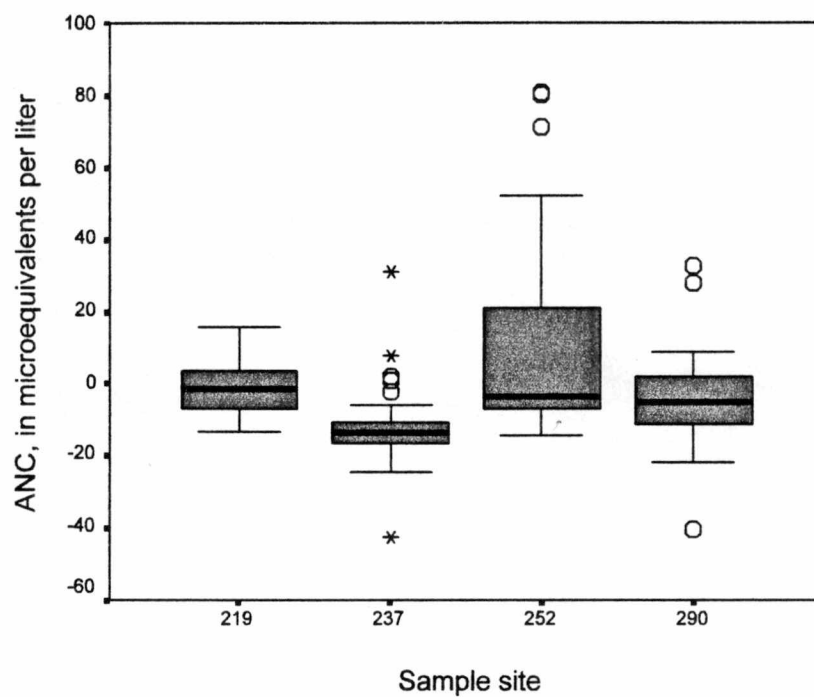


Figure 3-29. Sample sites with median acid neutralizing capacity less than or equal to zero.

Table 3-3. Summary of acidic level of water at sampled sites.

Source: Webb, J.R., B.J. Cosby, J.N. Galloway, and G.M. Hornberger, Acidification of Native Brook Trout Streams in Virginia, *Water Resources Research*, 25(6), 1,367-1,377.

ANC range ($\mu\text{eq/L}$)	Classification	Percentage of sample sites with median ANC within range
< 0	acidic	4 to 5
0 - 50	extremely sensitive	52
50 - 200	sensitive	40
> 200	not classified	3

Note: Classification of water with greater than 200 microequivalents per liter of ANC was not given by the authors listed above.

Conductivity

Figure 3-5 shows the Park-wide variability of conductivity. Eighty-five of the 90 sampling sites (about 95%) have conductivity values less than or equal to 25 microsiemens per centimeter. Three percent of the sites have conductivity values between 25 and 75 and 2% greater than 75 microsiemens per centimeter. The sites with higher ionic strength (greater than 25 microsiemens per centimeter) than most of the sites in the GRSM are located within Abrams Creek and Oconaluftee watersheds. They include sites 156, 174, 489, 251, and 252. Figure 3-15 shows box plots of the variability of conductivity with respect to elevation. The outliers in Figure 3-15 at the lower elevations result from the sites within Abrams Creek watershed. Sites 251 and 252 are responsible for the outliers between 1,372 and 1,524 meters. These sites are within the Oconaluftee River watershed on Beech Flats Creek. Site 252 was included in the discussion of the variability in pH. Site 251 is downstream of site 252. The relationship between median conductivity and elevation is not statistically significant. Figure 3-16 shows sample site median conductivity plotted with respect to sample site elevation.

Nitrate

The map which shows Park-wide variability of nitrate is included in Figure 3-6. From this figure, there appears to be an elevation trend with respect to nitrate. Most of the sampling sites with median values less than 15 microequivalents per liter appear to be located at the lower elevations of the GRSM. Those at the upper elevations, particularly in the middle and eastern portions of the GRSM, have higher concentrations of nitrate. These include the upper elevation sites within the following watersheds: East Prong Little River,

Forney Creek, West Prong Little Pigeon River, Oconaluftee River, Indian Camp Creek, Cosby Creek, and Cataloochee Creek. Nitrate concentrations appear to increase with increases in elevation.

Figures 3-17 and 3-18 also show what appears to be a significant trend in nitrate concentrations with respect to elevation. The y-axis in Figure 3-17 extends below zero because most of the whiskers extend to zero. Obviously none extend below zero to suggest negative concentrations. Nitrate concentrations appear to increase with increases in elevation. Regression analysis reveals a statistically significant trend but the intercept of the regression equation predicts negative concentrations of nitrate at elevations less than or equal to about 255 meters above sea level. The regression equation explains just less than half of the variability in median nitrate concentrations at sampled sites ($r\text{-square} = 0.47$). Since the sampling sites range in elevation from a minimum of 335 meters to a maximum of 1,689 meters above mean sea level, the regression equation is included in Figure 3-16. It is not possible to predict negative nitrate concentrations if the elevation is within the range used to model the data. Therefore, this equation should not be used to predict nitrate concentrations at elevations below 335 meters.

Notice in Figures 3-17 and 3-18 that the variability of nitrate appears to increase with increases in elevation as well. At the higher elevations the interquartile range is larger and the whiskers extend further away. In the scatter plot, the median nitrate concentrations also appear more variable at the upper elevations.

Sulfate

Park-wide variability of sulfate (Figure 3-7) appears similar to nitrate in some ways.

Sampling sites at the lower elevations appear to have lower median sulfate concentrations (less than 50 microequivalents per liter). The higher elevation sites, particularly in the middle portion of the GRSM, appear to have higher concentrations of sulfate (greater than 75 microequivalents per liter). Figures 3-19 and 3-20 show the variability of sulfate with respect to elevation. Box plots show that sulfate concentrations appear to increase with increases in elevation until about 1,372 meters and then begin to decrease and remain fairly constant with increases in elevation. A non-parametric Kruskal-Wallis H test was performed to see if there is a statistically significant difference between the higher median values found between 1,067 meters and 1,372 meters and lower values found at higher and lower elevations. The Kruskal-Wallis H test was chosen because the distribution of sulfate concentration within nine of the 10 elevation classes was not normal and the variance of sulfate within each elevation class appeared very different. Normality was determined by observation of box plots, skewness, and kurtosis. There is not a statistically significant difference ($p > 0.05$) in sulfate concentrations at sample sites between 1,067 meters and 1,372 meters. A significant difference exists ($p < 0.05$) between the high sulfate concentrations found between 1,067 meters and 1,372 meters and the lower sulfate concentrations at both higher and lower elevations.

Sulfate concentrations appear particularly high at sample sites 233, 251, and 252 (see Figure 3-7). Sample sites 233 and 251 are located at 1,297 and 1,222 meters above mean sea level, respectively. They are within the range mentioned above. Sample site 252 is located at 1,426 meters and is responsible for the outliers in Figure 3-19. The most extreme outlier in Figure 3-20 is site 252 as well.

Regression analysis did not reveal a statistically significant trend at the $p < 0.05$ level for both the intercept and the slope. The intercept was significant ($p = 0.03$) but the slope term was not ($p = 0.08$). The 95% confidence interval on the slope term included zero. The slope term was positive though, indicating that sulfate concentrations might increase with increases in elevation. The amount of variability explained by the equation was poor ($r\text{-square} = 0.04$). Obviously, elevation alone is not a good predictor of sulfate concentration in sampled GRSM streams.

Chloride

Chloride does not show much spatial variability within the GRSM. Median chloride concentrations at all sample sites are less than 21 microequivalents per liter. Figure 3-8 shows the variability of median chloride concentrations at the 90 sampling sites. The lack of significant variability of chloride in sampled GRSM streams is also evident from Figures 3-21 and 3-22. Regression analysis did not reveal a significant trend. The box plots and the scatter plot show that chloride concentrations remain fairly constant with changes in elevation. The outliers in Figure 3-22 at the lower elevations are the three sites on Abrams Creek below Cades Cove (174, 489, and 156). The outliers in Figure 3-21 appear random. Within all elevation ranges except the highest (greater than 1,676 meters), no one sample site appears to be responsible for the outliers. Site 290 in Cataloochee Creek watershed is responsible for all outliers at elevations greater than 1,676 meters.

Sodium

Park-wide variability of sodium at sampled sites is shown in Figure 3-9. Sample sites at lower elevations (except site 253) appear to have higher median sodium concentrations.

Regression analysis revealed a statistically significant trend. The results of regression analysis confirm that sodium concentrations decrease with increases in elevation. However, the equation does not explain much of the variability in the data ($r\text{-square} = 0.17$). Figures 3-23 and 3-24 show the variability and elevation trends of sodium concentrations. The box plots show that although a significant elevation trend exists, the variability of sodium among sites with similar elevations appears high.

Potassium

Park-wide variability of potassium at sampled sites is shown in Figure 3-10. The three sites on Abrams Creek and below Cades Cove and one of the lowest elevation sites in the Cataloochee watershed (148) have some of the higher median values of potassium in the GRSM. It is difficult to see a consistent trend in Figure 3-10. However, potassium and sodium show similar trends with respect to elevation. Regression analysis revealed a statistically significant trend. The slope term indicates that potassium concentrations decrease with increases in elevation. The equation does not explain much of the variability in median values ($r\text{-square} = 0.07$). Although a significant trend exists, Figures 3-25 and 3-26 show that the variability of potassium does not appear great. All sample sites have median values below 17.00 microequivalents per liter.

Ammonium

As mentioned earlier, a map showing the variability of ammonium is not included because all sample sites have median values below detection limits. For this reason, regression analysis is not included and a scatter plot is omitted as well. The box plot (see Figure 3-27) is included to show that occasionally some sample sites have ammonium

concentrations above detection limits. There does not appear to be a strong trend or "pattern" with respect to the sites which occasionally have some measurable concentration of ammonium.

Comparison with Previous Results

Other significant synoptic studies which included sampling within the Great Smoky Mountains National Park include the National Stream Survey (NSS) and the work by Silsbee and Larson. The characteristics and goals of the NSS were discussed in Chapter II. Here comparisons will be discussed between the results of the NSS and this study. All of the information from the NSS discussed in this chapter and throughout this document comes from a text which summarizes all of the findings from the NSS (Charles, 1991). The chapter of that text which discusses the results pertaining to the GRSM is entitled 'The Southern Blue Ridge Province' (Elwood *et al.*, 1991). The characteristics of the work by Silsbee and Larson were also discussed in Chapter II.

Comparisons between the results of this study and NSS are difficult. One goal of the NSS was to determine the percentage of stream lengths with pH and ANC below certain values. The values of interest used by the NSS were presented in Tables 3-2 and 3-3 and were also used in this analysis. To determine the percentage of stream lengths with pH and ANC within the different ranges researchers sampled from relatively small reaches at both the upstream and downstream ends. The NSS target population in the Southern Blue Ridge Province included 2,031 stream reaches totaling 9,036 kilometers. Therefore, the average stream reach was 0.22 kilometers. This study was not designed to obtain the same information. Sampling sites were not chosen to quantify the amount of stream reaches with

certain characteristics. The average number of stream kilometers draining to the 90 sites in this study is 54.8 kilometers. Since sampling sites do not focus on a particular small reach, the basins defined by a particular site often include numerous other streams. For example, Figure 3-1 shows that site 268 within the Oconaluftee River watershed is located on the Oconaluftee River but water at that site also includes water from Bradley Fork, which is not labeled in the figure. Bradley Fork flows in a general north to south direction and joins the Oconaluftee River just above sample site 268. The reader should be able to recognize Bradley Fork with this description. If not, refer to the figure in Appendix A1 (see Figure A1-13).

However, it is interesting to compare the percentages of stream reaches within the different ranges for pH and ANC with the percentages of sampling sites within the different ranges. The NSS found that less than 1% of the reaches had pH values less than 5.0, between 5.0 and 5.5, and between 5.5 and 6.0. Greater than 99% had pH values greater than 6.0. As shown in Table 3-2, this study found that 3% of the sampling sites have pH values less than 5.0, 5% with pH between 5.0 and 5.5, and 13% between 5.5 and 6.0. About 79% of the sampling sites have pH values greater than 6.0. The NSS also found that less 1% of the reaches had ANC values less than zero and therefore could be classified as acidic surface water. About 7.8% had ANC values between zero and 50, 70.6% between 50 and 200, and 21.6% greater than 200. All units for ANC are in microequivalents per liter for both the NSS study and this study. As shown in Table 3-3, this study found that 4% to 5% of the sample sites have ANC values less than zero. About 52% have ANC values between zero and 50 and 40% have ANC values between 50 and 200. Only 3% of the sampling sites have ANC

values greater than 200.

There are several reasons why the NSS population did not include many reaches which could be classified as acidic. The reaches which would most likely be acidic probably fell outside the boundaries and selection criteria used to define the NSS target population. A second reason might be due to the low probability of encountering them due to their low abundance (Elwood *et al.*, 1991). During the NSS study, only streams which appeared as blue lines on 1:250,000 scale United States Geological Survey (USGS) topographic maps were considered. Two of the four sites (219 and 290) which have ANC values less than zero are high elevation springs and do not appear as blue lines on these maps. Four of the seven sites with particularly low pH (less than 5.5) are also high elevation springs and do not appear as blue lines. The results of this study show that acidic surface waters do exist within the GRSM and that the NSS population describes general conditions within the larger Southern Blue Ridge Province but does not adequately describe conditions within the GRSM. The GRSM accounted for only about 8% of the total area containing the NSS target population in the Southern Blue Ridge Province.

The results of the NSS also found longitudinal, or elevation, trends for pH and ANC. The results also showed that pH and ANC decrease with increases in elevation. Upstream reaches had lower pH and ANC than downstream reaches. Upstream and downstream reaches had median pH values of 6.98 and 7.03, respectively. Upstream and downstream reaches had median ANC values of 100 and 122 microequivalents per liter, respectively. Correlation results were presented for ANC but not for pH. The log of ANC showed a significant inverse correlation with elevation ($p < 0.001$) and accounted for about 27% of the

variability in ANC. The log transform of ANC was not used in this study due to the presence of negative values for ANC. As mentioned earlier, if sites within Cades Cove are not included in the regression analysis, elevation explains about 30% of the variability in ANC.

One study by Silsbee and Larson in 1982 was designed to collect baseline information on natural water conditions within the GRSM. Studies of water prior to this were typically short-term studies and focused on particular problem areas (Silsbee and Larson, 1982). Regression analysis revealed statistically significant relationships ($p < 0.05$) with elevation for pH, alkalinity, nitrate, sodium, and potassium. Constituent values for pH, alkalinity, sodium, and potassium decreased with increases in elevation. The authors did not report how much of the variability of constituent values was explained by elevation and did not include regression equations. From the results of this study, constituent values for pH, ANC, sodium, and potassium also show statistically significant trends with elevation and the values decrease with increases in elevation. Silsbee and Larson also found that nitrate concentrations increase with increases in elevation. They too did not find a significant relationship between elevation and conductivity. The results of this analysis show a statistically significant, but very weak ($r\text{-square} = 0.04$) positive relationship between elevation and sulfate concentrations. The work by Silsbee and Larson did not analyze for sulfate. Other constituents and parameters were included in the study by Silsbee and Larson but are not discussed since comparisons cannot be made. They include calcium, magnesium, hardness, silica, temperature, fecal streptococcus, fecal coliform, and total coliform. The reason calcium and magnesium were excluded from this analysis was discussed in Chapter I.

Conclusions

From the results of the analyses presented, the following conclusions and observations were made:

1. In general, the sampled streams of the GRSM are low ionic strength waters with minimal ability to neutralize acids. Eighty-five of the 90 sampling sites (about 95%) have conductivity values less than or equal to 25 microsiemens per centimeter. Eighty-seven of the 90 sampling sites (about 97%) have ANC values less than or equal to 200 microequivalents per liter and are classified as either sensitive, extremely sensitive, or acidic. A majority of the sampling sites (52%) are classified as extremely sensitive surface waters due to median ANC values between zero and 50 microequivalents per liter.
2. About 77% of the sampling sites have median pH values less than 6.5, the point at which biological effects become significant to aquatic organisms such as sensitive benthic invertebrates. About 8% of the sampling sites have median pH values below 5.5, the point at which all species of trout found in the streams of the GRSM (rainbow, brown, and brook) would experience a significant population loss or would be absent entirely. Two of the four sites (219, 237, 252, and 290) classified as acidic surface waters (ANC less than zero microequivalents per liter) are high elevation springs. Four of the seven sites (138, 218, 219, 220, 237, 252, and 290) with median pH below the lower limits to sustain trout ($\text{pH} < 5.5$) are high elevation springs. The stream size and perhaps seasonal flow at these sites might inhibit stable trout

populations even if surface water pH was ideal. However, given the low acid neutralizing capacity of surface water throughout GRSM, the presence of these extremely poor conditions is worth noting. Twenty-three percent of the sampling sites have median pH greater than 6.5 and do not pose problems for aquatic organisms.

3. Constituent values for pH, ANC, sodium, and potassium show statistically significant trends with elevation. The values for these constituents decrease with increases in elevation. Sample site elevation explains 51% of the variability in pH. If sample sites within Cades Cove are excluded from the regression analysis, elevation explains 30% of the variability in ANC. The amount of variability in sodium and potassium concentrations explained by elevation is much less, 17% and 7%, respectively.
4. A statistically significant trend is present between elevation and nitrate concentrations. Nitrate concentrations increase with increases in elevation and 47% of the variability is explained by the relationship.
5. A statistically significant trend ($p < 0.05$ for both the intercept and the slope) does not exist between elevation and sulfate concentrations. The intercept was significant ($p = 0.03$) but the slope term was not ($p = 0.08$). The 95% confidence interval on the slope term included zero. The slope term was positive though, indicating that sulfate concentrations might increase with increases in elevation. The amount of variability explained by the equation was poor ($r\text{-square} = 0.04$). Obviously, elevation alone is not a good

predictor of sulfate concentration in sampled GRSM streams.

6. Chloride and conductivity do not show significant relationships with sample site elevation.

CHAPTER IV. WATERSHED CHARACTERISTICS, INFLUENCES ON WATER QUALITY, AND PREDICTION OF WATER QUALITY CONSTITUENT VALUES

Data

Basin characteristics were determined for each quarterly sampling site. Some of the basin characteristics determined, such as UTM (Universal Transverse Mercator) X and Y coordinates, are not particularly important with respect to water quality but are included here to provide a complete list of the information available for each of the sampling sites. Table 4-1 displays the data collected for each sampling site and its contributing area. The data were collected either from digitized United States Geological Survey (USGS) quadrangle maps with a scale of 1:24,000 or from the National Park Service GIS database. The digitized USGS maps used were manufactured by Wildflower Productions in 1999 entitled TOPO!, interactive maps on CD-ROM covering North Georgia, Great Smoky Mountains, and Atlanta. The following is a list of the data collected for each sample site along with a description of the method used.

- Elevation, in meters above mean sea level, is the elevation of the sample site. Sample sites are usually located at points along a stream where either roads or trails that appear on USGS 1:24,000 scale quadrangle maps intersect. For sampling sites that are not located at easily recognizable points on USGS quads, the sampling site location and elevation were estimated. All elevations are probably accurate to within 6.1 meters (20 feet) since contour intervals are 12.2 meters (40 feet).
- Mean elevation, in meters above mean sea level, is the average elevation of the contributing area to the sample site determined from the GIS database.
- UTM X is the easting location of a sample site, in meters, using the North American datum of 1927 (NAD 27). Digitized USGS quadrangle maps provide UTM X and UTM Y when a location is selected.
- UTM Y is the northing location of a sample site, in meters, using NAD 27 as datum. See above for explanation of method.
- Order is the stream order for the sample site using Horton's method. Any streams that appeared as blue lines on USGS 1:24,000 scale quadrangle maps were counted

Table 4-1. Basin characteristics data.

Site #	Elevation (m)	Mean elevation (m)	UTM X	UTM Y	Order	Max Channel length (km)	Basin length (km)	Azimuth
1	671	1314	294112	3959340	3	6.54	5.2	157.6
3	511	1032	299530	3961990	4	8.62	6.4	179.6
4	634	1241	300148	3959520	2	5.23	4.8	215.5
13	335	979	254281	3950270	5	42.76	19.3	126.1
14	347	1041	254908	3949370	4	41.62	18.2	125.1
20	518	1116	260417	3951334	4	28.85	15.8	143.1
23	351	1003	254675	3949105	5	19.11	11.5	116.7
24	351	748	254640	3949060	4	14.02	9.8	177.9
30	436	1221	270435	3952120	4	21.17	14.1	113.5
34	597	1176	263830	3949494	4	22.54	12.4	151.1
43	713	1306	283051	3950990	4	7.19	5.6	173.1
45	975	1366	282954	3948628	2	3.38	2.8	195.3
46	838	1291	283078	3949670	3	5.52	4.3	171.8
47	732	1329	282901	3950920	2	4.89	4.5	230.1
49	509	1186	284467	3953929	4	11.03	8.6	184.5
50	507	1245	284408	3954070	5	13.93	11.9	90.1
52	411	1145	281477	3957410	5	19.24	15.3	102.4
66	817	1460	274082	3946370	4	13.60	9.2	89.9
71	1036	1515	276295	3946000	3	6.06	5.4	182.5
73	1024	1505	276387	3946037	3	10.36	6.9	87.5
74	1164	1523	278028	3945370	2	7.91	5.3	80.1
103	1320	1614	295879	3956207	1	1.70	1.5	126.1
104	1280	1578	295238	3955875	1	1.62	1.4	136.4
106	1170	1555	294556	3955908	3	2.35	2.0	133.8
107	927	1458	294025	3957028	3	3.90	3.2	141.2
114	765	1201	301001	3958091	3	3.79	3.0	210.5
115	1170	1332	302539	3957367	1	0.63	0.6	67.5
127	908	1386	307267	3945845	3	6.46	5.3	324.1
137	838	1320	299580	3957849	2	3.35	3.2	225.3
138	1058	1435	298604	3957465	2	2.34	2.3	215.4
142	1006	1351	305727	3945447	3	6.92	5.4	285.9
143	1000	1422	305779	3945513	2	6.43	4.9	324.4
144	911	1359	307056	3945790	3	8.58	6.6	279.6
147	750	1214	312374	3948770	4	19.26	12.0	260.5
148	754	1152	312374	3949020	4	7.44	5.8	309.3
149	777	1227	312075	3946490	4	16.44	11.5	271.5
150	799	1245	311140	3944770	4	14.03	10.8	280.9
156	338	745	234153	3944350	5	31.27	19.2	105.1
173	523	918	241439	3942129	4	11.04	7.9	188.3
174	523	773	241490	3942219	4	15.35	11.5	105.6
183 ^b	1305		249188	3938782	1			

Note: Geology, vegetation, and disturbance data expressed as percent of basin area.

Shaded cells represent information that is either not available or is not applicable.

Blank cells represent a value of zero.

^aThese sites are within Hazel watershed and geology information is not available.

^bThese sites are high elevation springs and some information is not applicable.

Table 4-1 (continued)

Site #	Basin area (ha)	Stream km	Stream density (km/km ²)	Average basin slope (%)	Channel slope (%)	Basin width (km)	Basin shape
1	866	12.9	1.5	49.1	18.3	1.7	3.1
3	2664	63.6	2.4	43.3	10.5	4.1	1.5
4	378	8.4	2.2	52.5	19.7	0.8	6.2
13	27528	489.7	1.8	42.0	1.9	14.3	1.4
14	15592	284.7	1.8	41.7	2.0	8.6	2.1
20	13154	221.4	1.7	42.2	2.6	8.3	1.9
23	7152	115.1	1.6	43.7	4.8	6.2	1.8
24	4670	86.1	1.8	39.9	6.2	4.8	2.1
30	6267	84.7	1.4	49.2	5.8	4.4	3.2
34	11067	177.7	1.6	42.9	3.4	8.9	1.4
43	2564	35.1	1.4	61.7	11.2	4.6	1.2
45	377	4.8	1.3	72.1	16.5	1.4	2.1
46	867	11.7	1.4	65.3	13.1	2.0	2.1
47	506	7.1	1.4	54.1	22.4	1.1	4.0
49	4664	63.7	1.4	55.1	8.7	5.4	1.6
50	9717	134.4	1.4	50.3	11.1	8.2	1.5
52	11778	240.0	2.0	49.0	8.4	7.7	2.0
66	3770	49.4	1.3	53.5	5.7	4.1	2.2
71	893	11.6	1.3	45.4	13.9	1.7	3.2
73	2361	33.0	1.4	54.3	5.3	3.4	2.0
74	1069	14.3	1.3	51.4	6.3	2.0	2.6
103	131	1.0	0.7	52.2	31.2	0.9	1.7
104	54	1.1	2.1	50.5	35.7	0.4	3.7
106	233	4.5	1.9	54.4	33.6	1.1	1.8
107	642	10.5	1.6	53.0	25.5	2.0	1.6
114	597	9.5	1.6	56.6	18.4	2.0	1.5
115	25	0.2	0.6	55.0	49.7	0.4	1.3
127	1115	20.4	1.8	45.2	10.7	2.1	2.5
137	320	6.6	2.1	58.0	26.3	1.0	3.2
138	155	3.1	2.0	46.8	30.4	0.7	3.3
142	1149	14.6	1.3	41.6	6.9	2.1	2.6
143	847	14.6	1.7	43.5	11.7	1.7	2.8
144	2183	30.9	1.4	43.0	6.8	3.3	2.0
147	12742	199.1	1.6	41.4	3.2	10.7	1.1
148	2188	34.0	1.6	40.8	10.6	3.8	1.5
149	12156	188.9	1.6	41.4	3.9	10.5	1.1
150	11157	168.5	1.5	41.9	4.5	10.3	1.1
156	15775	277.0	1.8	33.6	1.4	8.2	2.3
173	4290	62.1	1.4	36.6	7.1	5.4	1.5
174	5056	93.7	1.9	31.2	3.7	4.4	2.6
183 ^b							

Table 4-1 (continued)

Site #	Thunderhead Sandstone	Pigeon Siltstone	Roaring Fork Sandstone	Rich Butt Sandstone	Limestone	Cades Sandstone	Metcalf Phyllite
1	81.5	4.5	7.7	6.3			
3	53.7	24.6	17.7	4.0			
4	88.2	10.1	1.7				
13	51.5				0.4	1.8	11.2
14	64.3					1.0	7.8
20	66.9						2.6
23	45.2					0.7	4.0
24	19.8				2.3	5.9	31.9
30	49.3		11.8				
34	68.2						
43	46.6						
45	3.8						
46	24.8						
47	97.1						
49	48.7		0.9				
50	67.3		0.6				
52	56.1	1.3	15.0				
66	43.4						
71	77.4						
73	22.2						
74	7.9						
103	100.0						
104	100.0						
106	100.0						
107	100.0						
114	97.0	3.0					
115	100.0						
127	98.3		1.7	0.1			
137	99.7	0.3					
138	100.0						
142	53.8		39.4				
143	98.3		1.7				
144	74.6		21.9				
147	60.3		19.4	0.5			
148	14.3		33.9	28.7			
149	63.2		19.4	0.5			
150	67.9		20.5	0.6			
156	0.2				6.9	33.2	11.1
173					0.9	17.5	11.7
174	0.7				21.0	13.5	25.5
183 ^b							

Table 4-1 (continued)

Site #	Elkmont Sandstone	Anakeesta	Unnamed sandstone	Metadiorite	Great Smoky Group	Basement complex	Longarm Quartzite
1							
3							
4							
13	15.8	14.5	3.4	0.3	0.9		
14	11.8	13.0	1.0	0.5	0.6		
20	12.6	15.4	1.2	0.6	0.7		
23	9.5	27.7	11.0	0.0	1.9		
24	39.4				0.6		
30	4.8	34.0					
34	10.6	18.3	1.5	0.7	0.9		
43		53.4					
45		96.2					
46		75.2					
47		2.9					
49	13.8	36.6					
50	9.4	22.7					
52	8.9	18.7					
66		56.5					
71		22.5		0.1			
73		77.8					
74		92.1					
103							
104							
106							
107							
114							
115							
127							
137							
138							
142						6.3	0.5
143							
144						3.3	0.3
147						1.3	17.9
148						0.4	22.3
149						1.3	14.9
150						0.7	10.2
156	34.4				0.8		
173	67.8				2.0		
174	38.5				0.8		
183 ^b							

Table 4-1 (continued)

Site #	Elkmont Sandstone	Anakeesta	Unnamed sandstone	Metadiorite	Great Smoky Group	Basement complex	Longarm Quartzite
1							
3							
4							
13	15.8	14.5	3.4	0.3	0.9		
14	11.8	13.0	1.0	0.5	0.6		
20	12.6	15.4	1.2	0.6	0.7		
23	9.5	27.7	11.0	0.0	1.9		
24	39.4				0.6		
30	4.8	34.0					
34	10.6	18.3	1.5	0.7	0.9		
43		53.4					
45		96.2					
46		75.2					
47		2.9					
49	13.8	36.6					
50	9.4	22.7					
52	8.9	18.7					
66		56.5					
71		22.5		0.1			
73		77.8					
74		92.1					
103							
104							
106							
107							
114							
115							
127							
137							
138							
142						6.3	0.5
143							
144						3.3	0.3
147						1.3	17.9
148						0.4	22.3
149						1.3	14.9
150						0.7	10.2
156	34.4				0.8		
173	67.8				2.0		
174	38.5				0.8		
183 ^b							

Table 4-1 (continued)

Site #	Spruce Fir	Northern Hardwood	Cove Hardwood	Mesic Oak	Mixed Mesic Hardwood	Tulip Poplar	Pine	Heath Bald	Xeric Oak
1	10.2	22.5	46.8	1.5	16.1	0.6	1.1	1.2	
3	0.6	13.6	36.6	4.3	22.9	3.5	11.0	1.9	4.5
4	2.1	20.6	53.3	1.3	16.3	2.8	1.9	0.9	0.4
13	1.4	7.9	38.2	4.5	12.4	7.6	12.1	1.4	12.5
14	2.5	7.9	41.4	4.9	13.0	6.2	10.4	1.5	10.5
20	3.0	9.4	47.7	5.8	12.8	6.0	5.2	1.7	7.6
23		10.6	43.1	6.0	7.5	10.3	9.1	1.7	10.5
24		4.1	20.8	1.0	17.9	8.5	21.7	0.5	22.1
30	14.0	15.7	39.7	2.4	10.0	6.5	5.4	1.8	3.5
34	3.6	11.1	52.4	6.5	10.7	5.1	2.5	2.1	5.8
43	15.5	9.7	52.1	4.9	9.4	3.5	0.3	3.2	1.0
45	22.9	9.4	54.5	3.2	5.6	1.1		2.4	
46	15.3	10.0	59.0	4.4	4.2	6.2		0.8	
47	8.6	11.7	42.8	10.7	9.7	0.8	1.0	9.2	5.2
49	10.7	9.8	50.2	4.2	11.4	6.0	1.2	2.3	3.9
50	10.6	10.9	53.3	3.6	9.4	6.6	0.8	1.4	2.9
52	8.7	9.1	46.7	3.5	13.0	7.5	4.2	1.2	5.0
66	22.8	24.3	43.1	1.6	3.0	1.9	0.2	2.5	0.2
71	21.8	38.1	35.8	0.5	2.2	0.5		1.0	0.1
73	27.1	23.4	40.4	1.0	2.3	1.6	0.2	3.2	
74	31.1	32.2	33.2	1.1	0.2	0.2	0.2	0.9	
103	13.0	37.3	48.4					1.2	
104	23.1	36.9	38.5					1.5	
106	24.8	35.7	39.5						
107	14.0	28.9	51.5	2.0	2.2	0.1		1.3	
114	0.5	22.2	56.1	5.7	12.1	0.4		3.0	
115		23.3	60.0	13.3	3.3				
127	2.0	7.0	68.4	14.3	6.8	0.1	0.1	0.3	0.9
137	2.5	22.6	60.4	1.5	9.9	1.5		1.0	0.5
138	3.1	28.0	57.5	8.8	1.0			1.6	
142	0.4	22.3	57.2	18.4	1.2			0.4	0.2
143	2.9	11.8	60.3	20.2	3.5	0.4		0.9	
144	1.4	16.3	57.2	19.1	4.3	0.3	0.3	0.5	0.5
147	1.0	9.4	45.1	9.9	27.3	0.5	4.4	0.2	1.2
148	0.1	0.7	31.4	29.7	33.3	0.2	3.9		0.6
149	1.1	9.8	46.0	10.0	26.2	0.5	4.2	0.2	1.1
150	1.2	10.6	46.7	10.6	24.7	0.4	3.7	0.2	1.1
156		3.7	12.8	2.2	14.9	3.2	28.7		26.5
173		5.6	25.1	5.9	20.9	4.2	20.1		15.4
174		5.1	12.8	1.5	14.4	3.0	23.7		21.3
183 ^b									

Table 4-1 (continued)

Site #	Pine-Oak	Grape Thicket	Treeless	Grassy Bald	Undisturbed	Light cut	Selective cut	Heavy cut	Settlement
1					68.5	3.8			27.7
3	0.9				56.9	15.7	0.1		27.2
4	0.4				89.5	7.3			3.2
13	1.5	0.4		0.1	8.5	11.9	9.9	53.1	16.6
14	1.3	0.2		0.1	9.4	16.5	12.7	51.4	9.9
20	0.6	0.1		0.1	10.7	12.1	10.0	57.1	10.1
23	0.6	0.6			8.1	2.1	4.8	47.4	37.7
24	2.8	0.5		0.1	6.1	10.0	8.5	68.5	6.8
30	0.6	0.1	0.2		70.2	9.0	1.2	4.4	15.2
34	0.2			0.1	11.9	6.7	8.4	63.6	9.3
43	0.1	0.1	0.1		93.5	0.5			6.1
45		0.2	0.9		100.0				0.0
46	0.1				87.7				12.3
47	0.2	0.2			91.4	1.5			7.1
49	0.1	0.2	0.1		80.6	4.7	0.2		14.5
50	0.2	0.2			84.5	3.3	0.1		12.1
52	0.8	0.4			71.8	9.0	0.1		19.0
66	0.1		0.4		95.9	1.8	0.1		2.2
71					99.9			0.1	
73	0.1		0.7		99.0				1.0
74	0.2		0.8		98.0				2.0
103					96.9				3.1
104					100.0				
106					100.0				
107					82.6				17.4
114					87.3	0.1		0.1	12.4
115					40.0				60.0
127					1.7	13.1	42.5	38.9	3.8
137					100.0				
138					96.9				3.1
142					0.3	6.8	54.8	23.8	14.3
143					3.9	19.3	24.1	52.7	
144		0.1			1.7	11.1	46.6	33.1	7.5
147	0.2	0.3	0.5		35.8	3.0	39.5	10.2	11.4
148	0.1				1.1		71.1	2.1	25.4
149	0.1	0.3	0.5		37.5	3.2	37.4	10.7	11.2
150	0.2	0.3	0.5		40.9	3.5	33.0	11.6	11.0
156	2.4	0.2	5.3	0.1	13.1	11.1	61.6	0.2	14.0
173	1.3	0.3	1.2	0.1	29.5	7.0	54.1		9.4
174	2.0	0.4	15.7	0.2	14.5	25.7	26.1	0.7	33.0
183 ^b									

Table 4-1 (continued)

Site #	Elevation (m)	Mean elevation (m)	UTM X	UTM Y	Order	Max Channel length (km)	Basin length (km)	Azimuth
184	863	1236	250035	3940686	1	2.60	2.4	147.9
186	599	1076	248938	3943420	3	6.66	5.8	140.7
190	646	1160	257963	3943598	3	6.66	5.4	215.2
191	975	1299	259185	3940688	2	2.99	2.4	120.7
192	975	1273	259048	3940640	2	2.49	2.0	250.7
193	585	1140	258194	3944580	4	7.69	6.0	148.2
194	518	1109	257404	3945020	5	11.79	7.5	98.9
195 ^b	1466		252227	3938660	1			
200	1012	1299	251622	3940392	2	2.09	1.8	149.2
201 ^b	1463		252500	3938900	1			
209	823	1047	270133	3944860	1	2.89	2.1	54.6
210	835	1350	270115	3944500	3	8.78	7.0	122.0
213	1018	1406	267389	3942250	3	5.98	4.3	148.8
214	1049	1332	267355	3941710	2	3.78	3.1	176.4
215	1030	1249	267168	3942380	2	2.14	1.8	298.0
218 ^b	1658		267205	3938475	1			
219 ^b	1679		269546	3938460	1			
220 ^b	1676		269544	3938500	1			
221 ^a	1219	1449	265848	3936490	2	2.99	2.7	35.9
233	1297	1596	280158	3944116	2	5.14	3.7	54.7
234	1524	1621	278028	3943220	1	0.52	0.4	93.8
237	1378	1636	281103	3944736	2	4.04	2.6	54.8
251	1222	1442	281187	3942310	2	2.71	2.3	289.4
252	1426	1550	279516	3942840	1	0.87	0.5	299.6
253	1451	1562	279409	3942860	1	0.73	0.4	304.8
266	614	1150	290926	3932586	5	22.02	15.3	358.3
268	666	1205	290659	3936607	5	16.74	11.3	359.5
290 ^b	1689		302388	3942220	1			
291	1603	1716	302974	3938635	1	0.93	0.9	346.7
293	840	1231	308549	3944140	3	10.62	7.5	233.5
310 ^a	683	1093	256885	3931580	3	10.52	8.0	18.0
311 ^a	657	1129	256106	3930916	4	16.57	13.7	54.3
336	1451	1559	303075	3935992	1	3.29	2.7	344.0
337	1445	1598	303536	3936519	2	3.45	3.1	344.8
472	671	1165	258365	3943535	3	6.52	5.0	143.9
473	1106	1506	276982	3946187	3	9.65	6.2	88.9
474	732	1267	268508	3947601	4	15.04	9.2	172.0
475	899	1305	269153	3943285	4	9.07	4.8	173.9
479 ^a	530	1089	253245	3928614	4	23.86	17.4	53.3
480 ^a	666	970	256090	3931024	3	7.59	6.4	337.4
481 ^a	774	942	254333	3931940	1	1.70	1.8	333.9
482 ^a	774	937	254311	3931919	2	2.12	1.2	306.6

Table 4-1 (continued)

Site #	Basin area (ha)	Stream km	Stream density (km/km ²)	Average basin slope (%)	Channel slope (%)	Basin width (km)	Basin shape
184	168	2.1	1.2	44.7	24.3	0.7	3.5
186	1038	15.1	1.5	44.6	12.5	1.8	3.3
190	1133	11.4	1.0	49.8	14.3	2.1	2.6
191	288	4.5	1.6	44.9	16.8	1.2	2.0
192	245	3.4	1.4	53.8	17.0	1.2	1.6
193	2358	30.3	1.3	50.4	11.2	3.9	1.5
194	5539	75.0	1.4	45.0	6.7	7.4	1.0
195 ^b							
200	183	3.2	1.8	44.8	23.1	1.0	1.8
201 ^b							
209	145	2.7	1.9	41.4	12.7	0.7	3.1
210	3536	50.4	1.4	47.9	11.8	5.1	1.4
213	735	13.7	1.9	43.5	10.8	1.7	2.6
214	342	4.8	1.4	44.7	14.0	1.1	2.8
215	169	2.7	1.6	45.1	12.6	0.9	2.0
218 ^b							
219 ^b							
220 ^b							
221 ^a	299	3.2	1.1	42.9	15.8	1.1	2.4
233	594	7.6	1.3	51.2	8.3	1.6	2.2
234	16	0.0	0.0	38.4	20.7	0.4	0.9
237	429	4.3	1.0	50.0	9.2	1.7	1.5
251	211	3.7	1.8	45.9	13.5	0.9	2.4
252	29	0.2	0.6	44.6	20.3	0.5	1.0
253	22	0.0	0.0	42.5	17.9	0.5	0.9
266	14030	228.5	1.6	49.9	2.9	9.2	1.7
268	10574	172.8	1.6	51.3	3.8	9.4	1.2
290 ^b							
291	34	0.2	0.5	34.6	24.0	0.4	2.3
293	2735	37.7	1.4	43.9	6.8	3.6	2.1
310 ^a	3088	50.1	1.6	46.6	5.1	3.9	2.1
311 ^a	10062	155.0	1.5	45.2	4.5	7.3	1.9
336	160	2.4	1.5	25.3	4.3	0.6	4.4
337	306	4.2	1.4	31.3	9.3	1.0	3.1
472	1071	15.8	1.5	51.5	11.1	2.1	2.3
473	2152	30.1	1.4	54.7	5.5	3.4	1.8
474	7930	128.1	1.6	46.0	4.9	8.6	1.1
475	2737	45.4	1.7	45.6	7.4	5.7	0.9
479 ^a	11556	182.8	1.6	44.9	3.5	6.6	2.6
480 ^a	1310	21.2	1.6	44.1	9.5	2.1	3.1
481 ^a	59	1.4	2.5	42.9	22.1	0.3	5.3
482 ^a	212	3.2	1.5	43.6	9.7	1.7	0.7

Table 4-1 (continued)

Site #	Thunderhead Sandstone	Pigeon Siltstone	Roaring Fork Sandstone	Rich Butt Sandstone	Limestone	Cades Sandstone	Metcalf Phyllite
184							
186	3.3						0.9
190	58.4						
191							
192							
193	43.3						
194	46.9						
195 ^b							
200	18.9						
201 ^b							
209	76.0						
210	81.7						
213	83.1						
214	96.6						
215							
218 ^b							
219 ^b							
220 ^b							
221 ^a							
233							
234							
237							
251	48.8						
252	31.3						
253	22.2						
266	75.2						
268	75.7						
290 ^b							
291	100.0						
293	60.5		34.4				
310 ^a							
311 ^a							
336	100.0						
337	100.0						
472	19.2						
473	16.8						
474	76.4						
475	66.8						
479 ^a							
480 ^a							
481 ^a							
482 ^a							

Table 4-1 (continued)

Site #	Elkmont Sandstone	Anakeesta	Unnamed sandstone	Metadiorite	Great Smoky Group	Basement complex	Longarm Quartzite
184	93.4				6.6		
186	92.1				3.7		
190		39.1			2.5		
191		6.4	77.2		16.4		
192		67.5	21.9		10.6		
193		40.0	12.4		4.3		
194	0.7	35.7	14.2		2.5		
195 ^b							
200	71.8				9.3		
201 ^b							
209		24.0					
210		15.5		2.1	0.8		
213		15.3			1.7		
214					3.4		
215		91.4	8.6				
218 ^b							
219 ^b							
220 ^b							
221 ^a							
233		100.0					
234		100.0					
237		100.0					
251		51.2					
252		68.8					
253		77.8					
266		16.4				4.7	
268		20.9				3.4	
290 ^b							
291							
293							
310 ^a							5.1
311 ^a							
336							
337							
472		46.8	27.2		6.8		
473		83.2			0.0		
474	0.5	18.9	2.0	0.9	1.2		
475		24.8	5.9		2.5		
479 ^a							
480 ^a							
481 ^a							
482 ^a							

Table 4-1 (continued)

Site #	Wading Branch Formation	Cochoran Formation	Nichols Shale	Nebo Quartzite	Hesse Quartzite	Wilhite Formation	Wilhite Formation Coarse
184							
186							
190							
191							
192							
193							
194							
195 ^b							
200							
201 ^b							
209							
210							
213							
214							
215							
218 ^b							
219 ^b							
220 ^b							
221 ^a							
233							
234							
237							
251							
252							
253							
266							
268							
290 ^b							
291							
293							
310 ^a							
311 ^a							
336							
337							
472							
473							
474							
475							
479 ^a							
480 ^a							
481 ^a							
482 ^a							

Table 4-1 (continued)

Site #	Spruce Fir	Northern Hardwood	Cove Hardwood	Mesic Oak	Mixed Mesic Hardwood	Tulip Poplar	Pine	Heath Bald	Xeric Oak
184		44.6	37.6		15.5	1.9	0.5		
186		18.8	35.7	4.7	19.6	5.0	10.4	0.2	4.4
190		23.0	47.7	8.6	2.0	5.0		4.4	9.0
191		35.3	53.3	7.8				3.3	
192		28.1	42.4	24.5				5.0	
193		19.4	49.0	8.5	4.3	5.8	1.3	3.4	7.8
194		13.7	52.7	7.7	5.7	8.4	1.7	2.2	7.5
195 ^b									
200		36.6	52.9	4.8	2.2	0.9		0.4	
201 ^b									
209			73.2	4.5	6.1	5.0	4.5	2.8	3.9
210	9.5	15.1	61.4	3.8	1.7	5.4		2.7	0.2
213	7.4	26.8	54.9	2.4	1.0	2.5		4.7	0.1
214	1.4	36.9	48.0	8.7	1.7	0.2		3.1	
215		1.4	64.3	23.3	0.5	3.8		5.7	1.0
218 ^b									
219 ^b									
220 ^b									
221 ^a		81.2	14.0	4.8					
233	41.2	29.3	24.6	1.4	0.3	0.3	0.3	1.4	
234	45.0	50.0	5.0						
237	49.7	26.7	20.0	0.8	0.2	0.4	0.2	1.1	
251	6.2	27.3	54.6	6.9		0.4			
252	18.8	28.1	43.8						
253	22.2	29.6	40.7						
266	2.9	13.6	45.6	16.5	13.2	0.4	0.8	0.2	1.2
268	3.7	17.1	51.0	15.6	9.8	0.5	0.4	0.3	0.8
290 ^b									
291	51.2	14.0	34.9						
293	2.3	10.7	37.4	8.3	34.9	0.6	3.0	0.3	1.2
310 ^a		10.4	40.8	21.6	17.0	0.8	0.4	0.4	8.2
311 ^a		16.0	42.7	18.1	15.4	0.6	0.7	0.2	5.9
336	2.5	58.5	27.0	11.0	0.5				
337	10.2	28.1	47.1	13.6	0.8				
472		18.5	53.4	9.5	6.2	4.6	1.7	2.8	3.1
473	27.2	23.9	40.6	1.0	1.5	1.5	0.2	3.3	0.0
474	5.0	14.8	59.3	6.2	5.0	4.6	0.3	2.7	1.7
475	2.2	22.6	55.4	8.6	3.2	2.8	0.1	4.0	1.2
479 ^a		14.0	39.7	16.6	18.3	0.5	2.3	0.2	6.6
480 ^a		0.8	24.8	18.6	36.8	1.1	2.5		13.7
481 ^a			8.5	15.5	43.7		4.2		25.4
482 ^a			21.3	16.0	42.2	0.8	2.3		12.5

Table 4-1 (continued)

Site #	Pine-Oak	Grape Thicket	Treeless	Grassy Bald	Undisturbed	Light cut	Selective cut	Heavy cut	Settlement
184					89.2	3.3	6.6		0.9
186	0.9	0.1		0.4	70.0	4.7	16.5		8.9
190		0.3			35.6	0.1	0.1	29.5	34.8
191				0.3		6.1	25.8	17.5	50.6
192					51.0	2.6	6.3	21.5	18.5
193	0.1	0.3			24.3	1.1	3.9	31.3	39.5
194	0.1	0.3			10.4	2.6	6.1	34.6	46.4
195 ^b									
200				2.2	88.1	1.3	3.5		7.0
201 ^b									
209							0.6	99.4	
210				0.2	24.9	5.6	0.3	68.0	1.2
213				0.1	31.0	1.8	3.2	63.7	0.3
214					36.6		6.5	56.6	0.2
215								100.0	
218 ^b									
219 ^b									
220 ^b									
221 ^a						94.1	2.4		3.5
233			1.4		99.0				1.0
234					100.0				
237			0.9		99.8				0.2
251			4.6		83.1	15.8			1.2
252			9.4		100.0				
253			7.4		100.0				
266	1.3		0.4		29.8	24.0	1.0	25.8	15.5
268	0.5		0.3		37.9	16.2	1.3	31.8	12.8
290 ^b									
291					2.3			97.7	
293	0.3	0.4	0.7		53.9		33.2		12.9
310 ^a	0.4				0.1	90.5			9.4
311 ^a	0.4					71.0	0.3	13.6	15.0
336			0.5				73.5	13.0	13.5
337	0.3				0.3		13.9	82.9	2.9
472	0.1	0.2		0.1	16.0	2.3	8.4	30.5	42.9
473	0.1		0.7		98.9				1.1
474	0.1			0.1	16.7	4.3	3.7	69.6	5.7
475		0.1		0.1	16.0	5.0	10.1	68.6	0.3
479 ^a	1.8					74.8	0.3	11.8	13.1
480 ^a	1.7					82.3			17.7
481 ^a	2.8					100.0			
482 ^a	4.9					100.0			

Table 4-1 (continued)

Site #	Elevation (m)	Mean elevation (m)	UTM X	UTM Y	Order	Max Channel length (km)	Basin length (km)	Azimuth
483 ^a	707	903	255541	3931564	2	3.78	2.8	314.1
484 ^a	754	1211	258786	3931903	4	13.01	11.0	50.8
485 ^a	872	1184	261409	3933962	2	7.06	5.3	357.4
488	546	1034	243151	3941241	3	7.95	6.8	109.7
489	521	839	241408	3942175	5	15.79	11.6	105.3
492	832	1260	301162	3957637	1	3.28	2.7	218.7
493	866	1332	308073	3945282	4	10.14	7.7	281.9

Table 4-1 (continued)

Site #	Basin area (ha)	Stream km	Stream density (km/km ²)	Average basin slope (%)	Channel slope (%)	Basin width (km)	Basin shape
483 ^a	430	6.4	1.5	43.2	12.6	1.5	1.8
484 ^a	5281	77.6	1.5	44.8	5.5	4.8	2.3
485 ^a	752	10.5	1.4	43.0	7.7	1.4	3.8
488	1095	15.4	1.4	38.6	11.7	1.6	4.2
489	9356	155.8	1.7	33.6	3.6	8.1	1.4
492	255	2.4	0.9	52.3	19.5	0.9	2.8
493	3756	59.1	1.6	43.4	6.2	4.9	1.6

Table 4-1 (continued)

Site #	Thunderhead Sandstone	Pigeon Siltstone	Roaring Fork Sandstone	Rich Butt Sandstone	Limestone	Cades Sandstone	Metcalf Phyllite
483 ^a							
484 ^a							
485 ^a							
488						2.3	5.0
489	0.4				11.7	13.6	18.4
492	100.0						
493	72.8		22.5	1.6			

Table 4-1 (continued)

Site #	Elkmont Sandstone	Anakeesta	Unnamed sandstone	Metadiorite	Great Smoky Group	Basement complex	Longarm Quartzite
483 ^a							
484 ^a							
485 ^a							
488	90.4				2.4		
489	54.6				1.4		
492							
493						1.9	1.1

Table 4-1 (continued)

Site #	Wading Branch Formation	Cochoran Formation	Nichols Shale	Nebo Quartzite	Hesse Quartzite	Wilhite Formation	Wilhite Formation Coarse
483 ^a							
484 ^a							
485 ^a							
488							
489							
492							
493							

Table 4-1 (continued)

Site #	Spruce Fir	Northern Hardwood	Cove Hardwood	Mesic Oak	Mixed Mesic Hardwood	Tulip Poplar	Pine	Heath Bald	Xeric Oak
483 ^a			15.7	11.5	49.2	1.5	2.1		16.2
484 ^a		24.2	49.3	16.9	7.1	0.2		0.1	2.0
485 ^a		13.0	51.8	24.3	9.9	0.4			0.4
488		12.4	36.8	7.3	19.4	3.5	14.0		5.4
489		6.1	19.8	3.7	17.2	3.5	21.3		17.5
492	0.6	20.0	57.1	7.0	9.2	0.6		5.4	
493	1.4	11.6	57.5	17.3	10.5	0.3	0.3	0.4	0.7

Table 4-1 (continued)

Site #	Pine-Oak	Grape Thicket	Treeless	Grassy Bald	Undisturbed	Light cut	Selective cut	Heavy cut	Settlement
483 ^a	3.8					100.0			
484 ^a						54.8	0.6	25.9	18.7
485 ^a	0.1					57.9		42.1	
488	0.7	0.1		0.2	36.0	7.3	49.8		6.8
489	1.6	0.3	8.9	0.1	22.1	17.2	38.5	0.4	21.9
492					99.7			0.3	
493					1.5	10.3	46.9	30.9	10.4

to determine stream order.

- Max channel length, in km, determined from the GIS database, is the distance from a sample site to the drainage divide following the longest flow path.
- Basin length, in km, is measured as the map straight line distance along a line from the sample site to the point on the drainage divide used to determine maximum channel length. Digitized USGS quadrangle maps allow a user to select these two points and determine distance.
- Azimuth is degrees from true north to the line defining basin length as determined from USGS quadrangle maps.
- Basin area, in ha, is the contributing area to the sample site determined from the GIS database.
- Stream km is the total stream kilometers contributing to the sample site. The length of any stream that appeared as a blue line on USGS 1:24,000 scale quadrangle maps was used to determine the amount of stream distance within the basin.
- Stream density is the ratio of stream kilometers to basin area in square kilometers.
- Average basin slope is the average land slope of the contributing area expressed as a percentage and determined from the GIS database.
- Channel slope, expressed as a percentage, is the slope of the channel determined by the elevation difference between points located 10 and 85 percent of the distance along the main stream channel from the sample site to the drainage basin divide, divided by 0.75 of the length of the main stream channel from the sample site to the drainage divide. This information was determined from the USGS 1:24,000 scale quadrangle maps (Choquette, 1988).
- Basin width, in km, is the basin area in square kilometers divided by basin length.
- Basin shape is the dimensionless ratio of basin length squared to the basin area.
- Geology data are expressed as the percentage of the contributing area to the sample site covered by the different geology types in the GIS database. There are 21 different geology types listed in Table 4-1. They include Thunderhead Sandstone, Pigeon Siltstone, Roaring Fork Sandstone, Rich Butt Sandstone, Limestone, Cades Sandstone, Metcalf Phyllite, Elkmont Sandstone, Anakeesta, Unnamed sandstone, Metadiorite, Great Smoky Group, Basement complex, Longarm Quartzite, Wading Branch Formation, Cochran Formation, Nichols Shale, Nebo Quartzite, Hesse Quartzite, Wilhite Formation, and Wilhite Formation Course. Geology data are available for all sites except those within Hazel Creek watershed. The geology data in the GIS database are based upon work done in 1968 (King *et al*, 1968).
- Vegetation data are expressed as the percentage of the contributing area to the sample site covered by the different vegetation types. There are 13 different vegetation types listed in Table 4-1 and include Spruce Fir, Northern Hardwood, Cove Hardwood, Mesic Oak, Mixed Mesic Hardwood, Tulip Poplar, Pine, Heath Bald, Xeric Oak, Pine-Oak, Grape Thicket, Treeless, and Grassy Bald. This information comes from the GIS database and is based upon work done in 1993 (MacKenzie, 1993).
- Disturbance history data are expressed as the percentage of the contributing area to the sample site with a certain type of historical land use. The types of disturbance

histories include undisturbed, settlement, selective cut, heavy cut, and light cut. This information comes from the GIS database and is based upon work done in 1985 and 1988 (Pyle, 1985; Pyle, 1988).

Seven of the sites are high elevation springs. At these sites, samples are collected just as the water leaves the ground and is exposed to the atmosphere. Therefore, they are not "true" surface water sites with a well-defined contributing area. Some of the physical characteristics in Table 4-1 do not apply to these sites and values are omitted. The reasonableness of GIS determined basin areas in this study were checked against values obtained by others for similar basins (Parker and Pipes, 1990). Refer to Appendix A3 for a detailed description of the methods used to retrieve information from the GIS database.

Of the geologic formations which make up the Great Smoky Mountains National Park (GRSM), most were deposited later than the Precambrian age (more than a billion years ago) but before rocks of the early to middle Paleozoic age (600 million to 300 million years ago). This means that most of the rocks which form the GRSM were formed during Precambrian time (a billion to 600 million years ago) (*King et al.*, 1968). The rocks are then subdivided into groups based upon when they were formed and other similarities. The geology data for each basin presented in Table 4-1 might be confusing with respect to some groupings. Anakeesta, Thunderhead Sandstone, Elkmont Sandstone, and Unnamed sandstone are all part of the larger class of rocks from the Great Smoky Group, yet this group exists separately in the table. This is because the geology of the GRSM is complex and formations typically do not occur completely removed from other formations. When the majority of the rocks in an area could be classified as either Anakeesta, Thunderhead Sandstone, Elkmont Sandstone, or Unnamed sandstone, then that area was described

according to the one which dominated. If the area was composed of a mix of these formations, then it was classified by the more ambiguous Great Smoky Group. This is the only case where rocks of a larger group are also listed separately.

The different vegetation, or forest, types present in the GRSM occur in specific areas and, in most cases, the species which make up each forest type are unique. Mark MacKenzie's dissertation entitled 'The Vegetation of the Great Smoky Mountains National Park: Past, Present, and Future' provided the information on which species are included in each forest type and some habitat information. Additional habitat information for the different species was obtained from *The Audubon Society Field Guide to North American Trees, Eastern Edition*, 1980 (Little, 1980). The following defines each forest type:

- Spruce Fir
The Eastern Spruce (*Picea rubens*) often grows in pure stands in the rocky, high elevation (1,372-1,981 meters) soils of the GRSM.
- Northern Hardwood
Major species in this group include the American Beech (*Fagus grandifolia*) and the Sweet Birch (*Betula lenta*). Minor species include the Red Maple (*Acer rubrum*), Sugar Maple (*Acer saccharum*), and the Northern Red Oak (*Quercus rubra*). All of these species prefer the cool and moist conditions found at higher elevations. They generally occur at elevations above 1,075 meters and often in pure stands.
- Cove Hardwood
These forests generally do not have a single dominant species that occurs in pure stands like the Spruce Fir or the Northern Hardwood forests. However, major species in this group include White Basswood (*Tilia heterophylla*), Carolina Silverbell (*Halesia carolina*), Red Maple (*Acer rubrum*), Sugar Maple (*Acer saccharum*), Yellow Buckeye (*Aesculus octandra*), American Beech (*Fagus grandifolia*), Cucumber Magnolia (*Magnolia acuminata*), Sweet Birch (*Betula lenta*), and Eastern Hemlock (*Tsuga canadensis*). Some of the species in this group are also found in the Northern Hardwood forest. However, when they occur in a Cove Hardwood forest, they are typically not pure stands. The elevation range for this type of forest is broad. Cucumber Magnolia and White Basswood trees are found in the lower elevations (about 60 meters) and other species are found at higher elevations. The Yellow

Buckeye is found at elevations as high as 1,920 meters and the Eastern Hemlock as high as 1,524 meters. The Eastern Hemlock is the only species in this group that does occur in pure stands. All of the species in the Cove Hardwood forests prefer moist soil conditions. Moist soil conditions are found at the higher elevations and at lower elevations along streams and in ravines.

- Mesic Oak

Major species in these forests include Northern Red Oak (*Quercus rubra*), Chestnut Oak (*Quercus prinus*), and White Oak (*Quercus alba*). This forest can occur throughout the GRSM at almost any elevation. It is common on ridges and south facing slopes at higher elevations and ridges and side slopes at lower elevations. The trees in this forest often grow in pure stands.

- Mixed Mesic Hardwood

This forest type has no clear dominant species. It may contain any combination of the following: Oaks (*Quercus*), Elms such as the American Elm (*Ulmus americana*), Pines (*Pinus*), Hickories such as Bitternut Hickory (*Carya cordiformis*) and Pignut Hickory (*Carya glabra*), Tulip Poplar (*Liriodendron tulipifera*), Red Maple (*Acer rubrum*), Black Walnut (*Juglans nigra*), Sweetgum (*Liquidambar styraciflua*), Sycamore (*Platanus occidentalis*), and Black Locust (*Robinia pseudoacacia*). Some of these species, such as the Sweetgum, American Sycamore and Tulip Poplar, are found in areas that have been cleared in the last 80 years as a result of farming or logging operations. These areas are usually found at the lower elevations of the GRSM. The Mixed Mesic Hardwood forests are typically found at elevations less than 750 meters. Some of these species can be found at higher elevations.

- Tulip Poplar

The Tulip Poplar, mentioned as part of the Mixed Mesic Hardwood forests, also occurs frequently enough in stands within the GRSM to be classified as a unique forest type. The Tulip Poplar is usually found in coves and valleys with moist, well-drained soils at elevations from 300 meters to as high as 1,372 meters. Most of the stands are found at lower elevations that have been logged or farmed prior to establishment of the GRSM.

- Pine

Major species in the Pine forests include Pitch Pine (*Pinus rigida*), Table Mountain Pine (*Pinus pungens*), and Shortleaf Pine (*Pinus echinata*). Minor species include Eastern White Pine (*Pinus strobus*) and Virginia Pine (*Pinus virginiana*). The Pine forests typically occur at the middle to lower elevations of the GRSM. They prefer well-drained soils such as sands and sandy loams. The Eastern White Pine can be found as high as 1,524 meters. The remainder of species in these forests is below 1,300 meters. The Virginia Pine is another species which tends to do well in areas that were farmed or logged prior to establishment of the GRSM.

- **Heath Bald**
The Heath Bald forests are dominated by evergreen ericaceous shrubs which form dense thickets in the understory of other mountain forests. Species within these forests include Mountain Laurel (*Kalmia latifolia*), Catawba Rhododendron (*Rhododendron catawbiense*), and Rosebay Rhododendron (*Rhododendron maximum*). These plants, especially the Mountain Laurel, prefer acidic soils. They are found over a broad elevation range but most are found at the middle to upper elevations (900 to 2,000 meters).
- **Xeric Oak**
Major species in this group include Scarlet Oak (*Quercus coccinea*), Chestnut Oak (*Quercus prinus*), Black Tupelo or Blackgum (*Nyssa sylvatica*), Sourwood (*Oxydendron arboreum*), and Black Locust (*Robinia pseudoacacia*). The trees in this forest can occur at high elevations in the GRSM but typically this forest occurs on ridges and slopes below 1,050 meters. These trees typically grow in mixed forests with other oaks or pines. The exception to this is the Chestnut Oak. As already mentioned, the Chestnut Oak often grows in pure stands. In this situation, it is part of what was classified as a Mesic Oak forest. The Chestnut Oak also occurs in Xeric Oak forests where it grows along with other species.
- **Pine-Oak**
This forest type contains an even mixture of pine and oak. It has the same site characteristics as the Pine forests. Species included in these forests can be any combination of the types typically found in the Pine forests or the Mesic Oak forests.
- **Grape Thicket**
These areas are composed of a number of different thicket forming *Vitis* species. They tend to occur in the low to middle elevations. Although they do represent a unique forest type within the GRSM, they are not very common. They represent only about 0.16% of the total area within the GRSM (MacKenzie, 1993).
- **Treeless**
The Treeless areas of the GRSM are those in which a major forest type does not exist, such as open fields within Cades Cove, or areas which are dominated by outcrops of rock formations, such as Anakeesta Formations found within the watersheds of the Middle Prong of the Little Pigeon River, the West Prong of the Little Pigeon River, and the upper portions of the Oconaluftee River near Beech Flats Creek. These areas only occupy about 0.68% of the GRSM (MacKenzie, 1993)
- **Grassy Bald**
These areas are found high on mountain tops above 1,525 meters. The Grassy Balds are dominated by mountain oat grass (*Danthonia compressa*) with only minor occurrences of trees. Although they represent a unique vegetation area within the GRSM, they only cover about 0.03% of the entire

area (MacKenzie, 1993).

The chemistry data set used in the following analyses includes samples collected from 83 of the 90 sampling sites and includes the period from October 1993 to October 1998. The seven sampling sites not included are the high elevation springs mentioned earlier.

Methods of Analysis

The purpose of collecting the information in Table 4-1 is to expand the database and information available for each site and then to use the more complete database to investigate relationships between basin characteristics and water quality. Stepwise multiple linear regression is then used to predict median water quality constituent values at sampled sites from basin characteristics. All statistical analyses were performed on a personal computer using SPSS statistical software, version 10.0.7 (SPSS, 1999).

Investigation of Relationships between Basin Characteristics and Constituents

To determine if linear relationships exist between basin characteristics and median water quality constituent values, correlation analysis was performed. The Kendall's tau correlation coefficient was used to test for linear relationships. It was chosen over other methods, such as Pearson's r , because it is a rank-based procedure for data which are not normally distributed and is resistant to effects of outliers. Some have noted that Kendall's tau correlation coefficients will generally be lower than values of Pearson's r for linear associations of the same strength. The lower values do not mean tau is less sensitive than r . The lower values are the result of a different scale of correlation (Helsel and Hirsch, 1992). Correlation analysis was performed on basin characteristics to investigate relationships between the characteristics and look for possible sources of multi-collinearity.

Median values for water quality constituents at each of the 83 surface water sites were tested for linear relationships with basin characteristics. The constituents analyzed include pH, acid neutralizing capacity (ANC), conductivity, nitrate, sulfate, chloride, sodium, and potassium. Although the presence of statistically significant correlations between basin characteristics and water quality constituents do not establish cause and effect relationships, they can certainly provide insight into possible and reasonable causes. Statistically significant correlations were defined as those with $p < 0.05$. For cases with missing values, they were excluded in a pairwise manner. This means that cases with missing values for one or both of a pair of variables for a correlation coefficient are excluded from the analysis. This applies only to ten sites within Hazel Creek watershed and only includes correlations with geologic data since geology data are not available for Hazel Creek.

Correlation analysis was also performed on water quality constituent values to investigate their relationships.

After performing correlation analysis, relationships between target independent variables (basin characteristics) and median water quality constituent values were observed using scatter plots.

Modeling Process

Several runs, or trials, were made with stepwise multiple regression to generate a model for each water quality constituent. The process used is explained below.

Trial one

Initially, all basin characteristics (except UTM X, UTM Y, and azimuth) were input as possible independent variables. The easting and northing coordinates of the sampling sites

were not used because they only describe location in space. The azimuth was not used for two reasons. First, correlation analysis between azimuth and median water quality constituent values did not reveal statistically significant relationships. Second, azimuth is a discontinuous variable that ranges from zero to 360 degrees. The difficulty in using azimuth as an independent variable did not seem worth the probable minimal benefits in explaining the variability of median water quality constituent values. The variables were set to enter the model if the probability of the partial F statistic was less than or equal to 0.05 and set to leave if the partial F statistic was greater than or equal to 0.10. This entry and exit criteria were used for all models.

Trial two

A second model was selected using stepwise procedures by grouping variables together which showed similar responses to a particular water quality constituent and made sense physically. The grouped variables, along with those that were left alone, were then input as possible independent variables. The purposes for grouping some variables together were to reduce the total number of possible independent variables the stepwise method had to choose from and to increase the amount of variability explained by the models. Only geology, vegetation, and disturbance history data were investigated for possibly being grouped together in some way. Variables which were not considered for grouping included elevation, mean elevation, elevation class, order, basin length, basin area, stream density, average basin slope, channel slope, maximum channel length, basin width, and basin shape. As an example, when performing regression on pH, areas classified as light cut, selective cut, heavy cut, and settlement all have positive and significant correlations with pH. Since they

all apparently have similar influences on pH, and because they are all areas of the GRSM which were disturbed in some way prior to Park establishment, these four variables were grouped together. The five disturbance history variables used in the first model were then reduced to two for the second model, disturbed and undisturbed. When modeling results are discussed later, justification for grouped variables is provided.

Model Evaluation and Selection

Models selected from trial one and trial two by stepwise procedures were evaluated with the same criteria and tests. First the overall model p values were checked for significance ($p < 0.10$) and the adjusted r-square values were checked to see how much of the variability was explained by the models. Models which explained more of the variability (higher adjusted r-square) were preferable. Next, the constant terms and the individual coefficients were checked for significance ($p < 0.10$) and their signs were compared with results from correlation analysis. Multi-collinearity was evaluated with the condition index. Models which showed an increase in the adjusted r-square over other models and condition indices less than 30 were evaluated as not having significant problems with multi-collinearity and still explaining as much of the variability as possible.

The influences of individual observations on the models selected by stepwise regression were evaluated by comparing each observation's Cook's D statistic and observation of partial regression plots. Partial regression plots are useful for detecting influential data and can reveal nonlinearity (Fox, 1997). Influence is defined as observations which have both high leverage and large outliers (Helsel and Hirsch, 1992). These observations exert a strong influence on the regression model. A set value of the Cook's D

statistic to measure influence was not used. Cook's D values for individual observations were observed and ones that appeared unreasonably large in comparison to other observations were noted. If inspection of partial regression plots showed an observation which had an unreasonably high Cook's D statistic also appeared as an outlier, then it was concluded that the observation was exerting a strong influence on the model. If removal of that observation could be well-justified, then it was considered for removal from the analysis. If its removal improved the amount of variability explained by the model and the model adhered to the assumptions of regression (discussed below), then it was removed. As will be discussed later, there was a consistent pattern to the sites which were influential and their removal was reasonable.

The models were also checked for adherence to the assumptions of regression using residual plots and partial regression plots. Curvature and heteroscedasticity were checked by plotting the model standardized residuals versus the unstandardized predicted values. Standardized residuals versus explanatory variables and partial regression plots were checked to test whether transformations were necessary and, as mentioned, to confirm observations determined as influential based on the Cook's D statistic. The plots of standardized residuals versus the explanatory variables should display a random pattern about the horizontal axis. There should also be a proportionate number of residuals above and below zero. The partial regression plots should show a linear trend. If a linear trend does not exist, then some transform of the independent variable might be required to improve the model. Finally, a box plot of the model unstandardized residuals was used to visually check for normality. Skewness and kurtosis of the unstandardized residuals were also checked for normality. If

skewness and kurtosis indices were less than one away from zero, then the distribution was considered normal.

The reasonableness of predicted median constituent values from the final model selected was checked as a last step. If the predicted range of values was reasonable, then the model was selected as the best model. Reasonable predicted values were defined as not negative. The model should not predict negative values for water quality constituents. The only exception to this would be the model to predict ANC. Values for ANC can be negative. Predicted maximum values for pH should also not exceed 14.

To check the model selection using the stepwise method, backward and forward selection procedures were also used for the regression of median pH and the results were compared. This was done only for pH since it is one of the more important water quality constituents. Stepwise regression combines the ideas of forward and backward procedures but since it does not test all possible regression models, one cannot be sure that the best model is selected (Helsel and Hirsch, 1992). Using forward selection gave exactly the same results as stepwise procedures. Backward selection produced a model with many more variables but with numerous multi-collinearity problems. Since the same results were obtained with forward selection and very poor results with backward selection, it was concluded that stepwise procedures would be adequate for model selection of pH and all other water quality constituents.

It should be noted that in cases where transformations were made on independent variables and basins were removed as observations due to their unusual influence, every attempt was made not to do so. It was viewed as preferable to have the simplest model

which explains the most variability in water quality constituent values in as many basins as possible.

Results and Discussion

Tables 4-2 and 4-3 display the results of correlation analysis. Table 4-2 displays the results of correlation analysis between basin characteristics. Table 4-3 displays the results of correlation analysis between the basin characteristics and median values of water quality constituents. Table 4-4 displays the correlation coefficients between water quality constituents. Only statistically significant correlation coefficients are reported in the tables.

Correlation Analysis

Tables 4-2 and 4-3 show that statistically significant linear relationships exist between basin characteristics and between basin characteristics and water quality constituents.

Note that not all of the geology types for which data were collected (see Table 4-1) were presented in Tables 4-2 and 4-3. Geology types in Tables 4-2 and 4-3 include Thunderhead Sandstone, Limestone, Cades Sandstone, Elkmont Sandstone, Anakeesta, Metadiorite, Great Smoky Group, and Basement complex. Other geology types were excluded from correlation and subsequent regression analysis either because they are basically inert and therefore would not influence water quality or because they are present in very small amounts within the contributing area to one sample site. Scott Southworth (employed by the USGS and working under a cooperative agreement with the National Park Service to update the earlier work done in 1968 by Philip King and others) was contacted in September 2000 to discuss which geology types could be considered inert. The geology

Table 4-2. Kendall's tau correlation coefficients for basin characteristics.

Characteristic	Elevation	Mean elevation	Elevation class	Order	Basin length	Basin area	Stream density	Average basin slope	Channel slope	Max Channel length	Basin width	Basin shape
Elevation												
Mean elevation	0.692											
Elevation class	0.929	0.714										
Order	-0.616	-0.421	-0.653									
Basin length	-0.584	-0.405	-0.624	0.764								
Basin area	-0.563	-0.385	-0.595	0.823	0.885							
Stream density	-0.251	-0.290	-0.261	0.233	0.194	0.189						
Average basin slope		0.240										
Channel slope	0.367	0.305	0.393	-0.582	-0.664	-0.679	-0.163	0.250				
Max Channel length	-0.567	-0.388	-0.603	0.772	0.921	0.905	0.192		-0.705			
Basin width	-0.517	-0.348	-0.542	0.825	0.753	0.868	0.168		-0.637	0.785		
Basin shape				-0.299		-0.211			0.160		-0.347	
Thunderhead Sandstone		0.254	0.171				0.163		0.172			
Limestone	-0.325	-0.391	-0.343	0.320	0.300	0.282	0.217	-0.347	-0.295	0.291	0.244	
Cades Sandstone	-0.408	-0.465	-0.430	0.354	0.356	0.322	0.222	-0.390	-0.326	0.345	0.265	
Elkmont Sandstone	-0.478	-0.501	-0.525	0.370	0.385	0.341		-0.282	-0.273	0.367	0.290	
Anakeesta							-0.287	0.305				-0.198
Metadiorite	-0.210		-0.231	0.240	0.327	0.308			-0.268	0.325	0.292	
Great Smoky Group	-0.254	-0.348	-0.288									
Basement complex				0.270	0.249	0.274			-0.292	0.246	0.298	-0.202
Spruce Fir	0.319	0.567	0.339				-0.176	0.282				
Northern Hardwood	0.466	0.540	0.487	-0.365	-0.359	-0.371	-0.261	0.212	0.300	-0.349	-0.350	
Cove Hardwood		0.172						0.268				
Mesic Oak		-0.229							-0.171			
Mixed Mesic Hardwood	-0.542	-0.613	-0.571	0.370	0.415	0.399	0.249	-0.183	-0.286	0.390	0.360	
Tulip Poplar	-0.588	-0.437	-0.621	0.466	0.426	0.418			-0.267	0.426	0.397	
Pine	-0.616	-0.607	-0.656	0.488	0.507	0.490	0.261	-0.306	-0.437	0.511	0.446	
Heath Bald								0.367				
Xeric Oak	-0.654	-0.721	-0.699	0.508	0.506	0.484	0.272	-0.253	-0.407	0.490	0.434	
Pine-Oak	-0.567	-0.612	-0.582	0.456	0.507	0.466	0.256	-0.220	-0.452	0.501	0.404	
Light cut	-0.406	-0.459	-0.422	0.329	0.369	0.353	0.287	-0.238	-0.323	0.353	0.314	
Undisturbed	0.203	0.382	0.226		-0.178	-0.181	-0.198	0.397	0.279	-0.182	-0.155	
Settlement	-0.396	-0.332	-0.409	0.484	0.385	0.379			-0.263	0.367	0.365	
Selective cut	-0.248	-0.256	-0.293	0.357	0.353	0.357		-0.464	-0.392	0.354	0.356	
Heavy cut				0.232	0.208	0.239		-0.262	-0.285	0.242	0.255	

Note: Blank cells indicate correlation coefficient is not significant. Normal font values are significant at the 0.01 level and bold values in shaded cells at the 0.05 level (2-tailed).

Table 4-2 (continued)

Characteristic	Thunderhead Sandstone	Limestone	Cades Sandstone	Elkmont Sandstone	Anakeesta	Metadiorite	Great Smoky Group	Basement complex	Spruce Fir
Elevation									
Mean elevation									
Elevation class									
Order									
Basin length									
Basin area									
Stream density									
Average basin slope									
Channel slope									
Max Channel length									
Basin width									
Basin shape									
Thunderhead Sandstone									
Limestone	-0.255								
Cades Sandstone	-0.288	0.798							
Elkmont Sandstone	-0.317	0.492	0.606						
Anakeesta	-0.419	-0.208							
Metadiorite				0.237					
Great Smoky Group	-0.300	0.273	0.358	0.486					
Basement complex					-0.202		-0.235		
Spruce Fir		-0.286	-0.328	-0.310	0.345		-0.467		0.265
Northern Hardwood		-0.351	-0.382	-0.314					
Cove Hardwood	0.322	-0.354	-0.369	-0.252					
Mesic Oak									
Mixed Mesic Hardwood		0.271	0.320	0.409	-0.337			0.400	-0.423
Tulip Poplar	-0.206	0.221	0.301	0.454		0.288		0.224	-0.363
Pine	-0.276	0.425	0.511	0.529			0.297	-0.190	
Heath Bald		-0.197	-0.203		0.314		0.195		-0.277
Xeric Oak	-0.207	0.420	0.495	0.504		0.207	0.294	-0.219	
Pine-Oak	-0.218	0.441	0.520	0.511					-0.413
Light cut		0.334	0.356	0.394					-0.261
Undisturbed		-0.189	-0.225		-0.195	0.198	0.219	0.225	-0.390
Settlement			0.191	0.199	0.226		-0.221	-0.216	0.510
Selective cut		0.290	0.351	0.337	-0.380		0.239		-0.307
Heavy cut						0.297	0.332	0.337	-0.325
							0.248		

Table 4-2 (continued)

Characteristic	Northern Hardwood	Cove Hardwood	Mesic Oak	Mixed Mesic Hardwood	Tulip Poplar	Pine	Heath Bald	Xeric Oak	Pine-Oak
Elevation									
Mean elevation									
Elevation class									
Order									
Basin length									
Basin area									
Stream density									
Average basin slope									
Channel slope									
Max Channel length									
Basin width									
Basin shape									
Thunderhead Sandstone									
Limestone									
Cades Sandstone									
Elkmont Sandstone									
Anakeesta									
Metadiorite									
Great Smoky Group									
Basement complex									
Spruce Fir									
Northern Hardwood									
Cove Hardwood									
Mesic Oak	-0.228	0.165							
Mixed Mesic Hardwood	-0.560	-0.195	0.215						
Tulip Poplar	-0.369			0.302	0.436				
Pine	-0.523	-0.313		0.590	0.248				
Heath Bald		0.337		-0.206					
Xeric Oak	-0.577	-0.209	0.177	0.539	0.487	0.660			
Pine-Oak	-0.509	-0.400		0.582	0.356	0.685	-0.204	0.660	
Light cut	-0.358		0.304	0.418	0.169	0.368	-0.231	0.470	0.460
Undisturbed	0.351		-0.487	-0.232		-0.216	0.180	-0.361	-0.262
Settlement			0.213	0.221	0.195	0.308		0.286	0.257
Selective cut	-0.186		0.276	0.228		0.339		0.239	0.181
Heavy cut		0.260	0.257				0.218		

Table 4-2 (continued)

Characteristic	Light cut	Undisturbed	Settlement	Selective cut
Elevation				
Mean elevation				
Elevation class				
Order				
Basin length				
Basin area				
Stream density				
Average basin slope				
Channel slope				
Max Channel length				
Basin width				
Basin shape				
Thunderhead Sandstone				
Limestone				
Cades Sandstone				
Elkmont Sandstone				
Anakeesta				
Metadiorite				
Great Smoky Group				
Basement complex				
Spruce Fir				
Northern Hardwood				
Cove Hardwood				
Mesic Oak				
Mixed Mesic Hardwood				
Tulip Poplar				
Pine				
Heath Bald				
Xeric Oak				
Pine-Oak				
Light cut				
Undisturbed	-0.481			
Settlement	0.193	-0.226		
Selective cut	0.241	-0.372	0.309	
Heavy cut		-0.427		0.357

Table 4-3. Kendall's tau correlation coefficients between basin characteristics and median values of water quality constituents.

Characteristic	pH	ANC	Conductivity	Nitrate	Sulfate	Chloride	Sodium	Potassium
Elevation	-0.424	-0.417		0.437			-0.262	-0.186
Mean elevation	-0.496	-0.516		0.577	0.164		-0.414	-0.292
Elevation class	-0.459	-0.446		0.475			-0.281	-0.211
Order	0.461	0.412		-0.390			0.211	0.199
Basin length	0.498	0.457		-0.424			0.229	0.208
Basin area	0.491	0.446		-0.426			0.217	0.209
Stream density	0.232	0.235		-0.266		-0.149	0.189	0.289
Average basin slope	-0.456	-0.450		0.320	0.397	-0.156	-0.490	-0.479
Channel slope	-0.540	-0.508		0.411	0.175		-0.275	-0.235
Max Channel length	0.497	0.458		-0.418			0.210	0.195
Basin width	0.458	0.412		-0.394			0.191	0.196
Basin shape								
Thunderhead Sandstone			-0.220			-0.191		
Limestone	0.394	0.389	0.330	-0.297		0.267	0.341	0.330
Cades Sandstone	0.425	0.415	0.273	-0.357			0.331	0.319
Elkmont Sandstone	0.339	0.349		-0.297		0.185	0.275	0.226
Anakeesta	-0.226	-0.226	0.170	0.178	0.352		-0.368	-0.510
Metadiorite								
Great Smoky Group			-0.200	-0.240	-0.213			
Basement complex	0.312	0.279	-0.211	-0.371	-0.397		0.298	0.321
Spruce Fir	-0.365	-0.366	0.326	0.503	0.407		-0.350	-0.253
Northern Hardwood	-0.448	-0.481		0.511		0.162	-0.359	-0.277
Cove Hardwood	-0.206	-0.233	-0.273				-0.209	-0.178
Mesic Oak	0.288	0.271	-0.436	-0.471	-0.518		0.223	0.164
Mixed Mesic Hardwood	0.465	0.505		-0.504	-0.194		0.469	0.337
Tulip Poplar	0.207	0.207		-0.248				
Pine	0.516	0.534	0.160	-0.441			0.381	0.316
Heath Bald	-0.218	-0.249		0.156	0.224	-0.183	-0.409	-0.339
Xeric Oak	0.514	0.530		-0.582			0.363	0.284
Pine-Oak	0.502	0.534		-0.469			0.384	0.271
Undisturbed	-0.424	-0.426	0.405	0.614	0.536		-0.316	-0.307
Light cut	0.455	0.441	-0.172	-0.559	-0.286		0.416	0.316
Selective cut	0.431	0.386	-0.251	-0.358	-0.404		0.335	0.399
Heavy cut	0.245	0.217	-0.300	-0.278	-0.318			
Settlement	0.271	0.251		-0.237				

Note: Blank cells indicate correlation coefficient is not significant. Normal font values are significant at the 0.01 level and bolded values in shaded cells at the 0.05 level (2-tailed).

Table 4-4. Kendall's tau correlation coefficients for water quality constituents.

	pH	ANC	Conductivity	Nitrate	Sulfate	Chloride	Sodium
pH							
ANC	0.863						
Conductivity							
Nitrate	-0.588	-0.581	0.259				
Sulfate	-0.309	-0.284	0.579	0.419			
Chloride			0.156	0.176			
Sodium	0.589	0.617		-0.413	-0.324		
Potassium	0.494	0.487		-0.369	-0.296		0.605

Note: Blank regions indicate correlation coefficient is not significant. Normal font values are significant at the 0.01 level and bolded values in shaded regions at the 0.05 level (2-tailed).

types determined inert include Nebo Quartzite, Hesse Quartzite, Rich Butt Sandstone, Roaring Fork Sandstone, Unnamed Sandstone, Metcalf Phyllite, Wading Branch Formation, Longarm Quartzite, and Pigeon Siltstone. Notice in Table 4-1 that some formations occur in very small amounts at sample site 156 only. They are Cochoran Formation, Nichols Shale, Nebo Quartzite, Hesse Quartzite, Wilhite Formation, and Wilhite Formation Course. Wilhite Formation Course covers only about 7.5% of the contributing area to sample site 156. Wilhite Formation covers about 3.8%. The other geology types all cover less than 1% each. Since these geology types cover only a small amount of the contributing area to one sample site, they were excluded from correlation analysis. Including them in correlation analysis would give misleading correlation coefficients of one since they are only present at one site.

Note that three of the forest types for which data were collected and presented in Table 4-1 are not reported in Tables 4-2 and 4-3. These include Grape Thicket, Treeless, and Grassy Balds. They were also excluded from regression analysis. As with some of the geology types, these three forest types are not common throughout the GRSM. They are also not well-represented by the sampled basins. When they are present within sampled basins, typically the coverage within the basin area is very small (see Table 4-1).

The following briefly presents some of the results of correlation analysis. More discussion about influences on water quality constituent values will be included in the modeling results. This discussion will not attempt to address multi-collinearity, rather the multiple linear regression will address the issue.

As expected from the results of simple linear regression in Chapter III between elevation and median water quality constituent values, Table 4-3 shows that elevation, mean

elevation, and elevation class are inversely related to both pH and ANC. This indicates that sampled surface water pH and ANC decrease with increases in elevation. Average basin slope and channel slope are also inversely related to pH and ANC. Basin length, basin area, stream density, maximum channel length, and basin width have significant positive correlations with pH and ANC. Watersheds with larger values for these characteristics have a greater portion of their area at lower elevations and are characterized by higher pH and ANC.

By inspecting other significant linear relationships in Table 4-3, one can summarize that basins located in the higher elevations of the GRSM with steep basin slopes, steep channel slopes, undisturbed areas, and Anakeesta Formations present have lower values for pH and ANC. Watersheds with a large portion of their area at lower elevations which have experienced some type of disturbance and have Limestone present have higher values for pH and ANC.

Conductivity does not have many significant linear relationships with basin characteristics. This suggests that it might be difficult to explain much of the variability of conductivity in sampled GRSM basins.

Nitrate concentrations increase with increases in elevation, mean elevation, elevation class, average basin slope, and channel slope. Nitrate concentrations also show increasing trends with forest types typically located at the higher elevations of the GRSM such as Spruce Fir, Northern Hardwood, and Heath Bald. Linear relationships with geology types are probably the result of collinearity with elevation and variables related to elevation such as elevation class and slope. There is a particularly strong relationship between the amount

of undisturbed area in a basin and nitrate concentrations. Nitrate concentrations increase as the amount of undisturbed area increases. Therefore, nitrate concentrations are highest in basins at higher elevations with steep slopes and much of their area undisturbed prior to establishment of the GRSM. Nitrate concentrations decrease with increases in stream order, basin length, basin area, stream density, maximum channel length, and basin width. Nitrate also has inverse relationships with areas that have experienced some type of past disturbance prior to establishment of the GRSM. Forest types which have inverse relationships with nitrate concentrations include Mesic Oak, Mixed Mesic Hardwood, Tulip Poplar, Pine, Xeric Oak, and Pine-Oak. All of these forest types are either concentrated at the middle to lower elevations (except Mesic Oak) of the GRSM or their presence increases with decreases in elevation. Lower nitrate concentrations are found in basins with some recent disturbance, such as logging, and with most of their area at lower elevations of the GRSM.

Sulfate concentrations do not have many strong and consistent linear relationships with the basin characteristics. Sulfate is positively correlated with mean elevation, average basin slope, and channel slope. The correlation coefficients are not very strong for mean elevation and channel slope, which are 0.164 and 0.175 respectively. The discussion in Chapter III explaining the trend in median sulfate concentrations with respect to elevation explains the lack of many strong linear relationships (see Figure 3-19). Sulfate concentrations are positively correlated with the amount of Anakeesta in a basin and the amount of undisturbed area. Discussions in Chapter III demonstrated that basins with the highest concentrations of sulfate in sampled surface water have sample site elevations between 1,067 and 1,372 meters above mean sea level (see Figure 3-19). Sulfate

concentrations increase as the amount of basin area underlain by Anakeesta Formations increases and the amount of undisturbed area increases.

Chloride has poor relationships with basin characteristics. It has the strongest relationship with the amount of basin area covered by Limestone. Research at Hubbard Brook has shown that precipitation can be a major source of chloride to a forested ecosystem (Likens *et al.*, 1977). Although elevation could possibly be a surrogate variable for precipitation in the GRSM, it does not appear to show up in the correlation results. Results from past research have shown that total precipitation does increase with increases in elevation. Within the GRSM, annual average precipitation amounts (as rainfall) ranged from 147, 177, 200, 226, and 231 centimeters at elevations of 445, 762, 1,158, 1,524, and 1,920 meters, respectively (Shanks, 1954). Chloride actually has weak, inverse relationships with two variables related to elevation, stream density and average basin elevation. The results of simple linear regression in Chapter III between sampling site elevation and median chloride concentrations showed that a statistically significant trend does not exist (see Figures 3-21 and 3-22).

Sodium, potassium, pH, and ANC have very similar relationships with basin characteristics. Since sodium, potassium, and carbonate species which contribute to alkalinity are commonly found in groundwater, it is not surprising that they show similar responses. Therefore, basins which have high ANC, mentioned earlier, also have higher concentrations of sodium and potassium. Table 4-4 also shows that these constituents have strong positive correlation coefficients with each other. The Kendall's tau correlation coefficient between pH and ANC is 0.863. The coefficients between pH and sodium and

potassium are 0.589 and 0.494, respectively. The coefficients between ANC and sodium and potassium are 0.617 and 0.487, respectively.

Modeling Results

The results of the regression analysis are summarized in Table 4-5. All coefficients and constants in the reported models are significant ($p < 0.10$). Table 4-6 summarizes some important model performance and application information. Application of the models to predict water quality constituent values in unsampled basins should be done in accordance with the restrictions listed in Table 4-6. A detailed explanation of model development is included for pH and ANC since these are two of the more important constituents with respect to impact on aquatic life and GRSM management decisions. Model characteristics to predict median water quality constituent values are discussed below.

pH

pH-Trial one

As previously discussed, in the first trial independent variables were not grouped. The possible independent variables included elevation, mean elevation, elevation class, stream order, basin length, basin area, stream density, average basin slope, channel slope, maximum channel length, basin width, basin shape, Thunderhead Sandstone, Limestone, Cades Sandstone, Elkmont Sandstone, Anakeesta, Metadiorite, Great Smoky Group, Basement complex, Spruce Fir, Northern Hardwood, Cove Hardwood, Mesic Oak, Mixed Mesic Hardwood, Tulip Poplar, Pine, Heath Bald, Xeric Oak, Pine-Oak, undisturbed, light cut, selective cut, heavy cut, and settlement (see Table 4-3). The model selected by stepwise procedures to predict pH included the variables mean elevation, basin slope, and stream

Table 4-5. Summary of stepwise multiple regression results for predicting median water quality constituent values using basin characteristics.

Constituent	Model	Adjusted r ²	Model p
pH	$7.821 + (-5.806E-04 \bullet \text{mean elevation in meters}) + (-2.203E-02 \bullet \text{basin slope in percent}) + (8.829-02 \bullet \text{stream order})$	0.74	0.000
ANC ^a	61.602•%Limestone	0.98	0.000
ANC ^b	$52.976 + (0.863 \bullet \%MMTPXPPO) + (8.603 \bullet (\text{max channel length in kilometers})^{0.5}) + (-1.089 \bullet \text{basin slope in percent})$	0.81	0.000
Conductivity ^a	12.974+(5.538•%Limestone)	0.98	0.000
Conductivity ^b	$11.914 + (4.526E-02 \bullet \% \text{undisturbed}) + (3.446E-02 \bullet \% \text{Anakeesta})$	0.55	0.000
Nitrate	$7.651 + (0.222 \bullet \% \text{undisturbed}) + (2.689 \bullet \text{elevation class}) + (-5.190 \bullet \text{stream density in kilometers per square kilometer}) + (-0.238 \bullet \% \text{MMH}) + (-5.555E-02 \bullet \% \text{Anakeesta})$	0.87	0.000
Sulfate	$21.320 + (2.997E-03 \bullet (\% \text{undisturbed})^2) + (1.922 \bullet (\% \text{Anakeesta})^{0.5})$	0.63	0.000
Chloride	$14.901 + (-1.143 \bullet \text{stream density in kilometers per square kilometer}) + (0.394 \bullet \% \text{Limestone}) + (2.156E-02 \bullet \% \text{Elkmont Sandstone}) + (2.635E-02 \bullet \% \text{Northern Hardwood})$	0.60	0.000
Sodium ^a	$44.926 + (9.377 \bullet \log(\% \text{Limestone}))$	0.88	0.003
Sodium ^b	$54.116 + (-0.508 \bullet \text{basin slope in percent}) + (0.494 \bullet \% \text{MMH})$	0.71	0.000
Potassium	$19.842 + (-0.169 \bullet \text{basin slope in percent}) + (-4.581E-02 \bullet \% \text{Anakeesta}) + (-4.266E-02 \bullet \% \text{Northern Hardwood})$	0.70	0.000

Note: All coefficients and constants reported are significant ($p < 0.10$). MMH is the percentage of the basin covered by Mixed Mesic Hardwood. MMTPXPPO is the percentage of the basin covered by Mesic Oak, Mixed Mesic Hardwood, Tulip Poplar, Pine, Xeric Oak, and Pine-Oak.

^ais the regression equation for basins which contain Limestone.

^bis the regression equation for basins which have no Limestone.

Table 4-6. Water quality constituent model application information.

Model	Predicted (min, max, median)	Observed (min, max, median)	Independent variable ranges Independent variable (min, max)	Model restrictions and applicability
pH	(5.62, 7.09, 6.36)	(5.49, 7.44, 6.36)	mean elevation (745, 1,716) basin slope (25.3, 72.1) stream order (1, 5)	Independent variables should be within ranges listed Not applicable for basins with disturbed Anakeesta
ANC ^a	(24.02, 1,295.49, 285.22)	(95.89, 1,223.05, 265.50)	Limestone (0.4, 21.0)	Independent variable should be within range listed Applicable for basins which contain Limestone and no disturbed Anakeesta
ANC ^b	(-1.25, 103.12, 43.07)	(-13.68, 124.27, 44.63)	MMMTPXPO (0.0, 72.1) max channel length (0.52, 41.62) basin slope (25.3, 72.1)	Independent variables should be within ranges listed Applicable for basins without Limestone and no disturbed Anakeesta
Conductivity ^a	(15.13, 129.43, 38.61)	(17.58, 126.40, 33.98)	Limestone (0.4, 21.0)	Independent variable should be within range listed Applicable for basins which contain Limestone and no disturbed Anakeesta
Conductivity ^b	(11.91, 19.89, 14.87)	(10.42, 24.30, 13.90)	undisturbed (0.0, 100.0) Anakeesta (0.0, 100.0)	Independent variables should be within ranges listed Applicable for basins without Limestone and no disturbed Anakeesta
Nitrate	(0.57, 51.16, 19.00)	(3.07, 59.69, 17.62)	undisturbed (0.0, 100.0) elevation class (2, 10) stream density (0.1, 2.4) MMH (0.0, 34.9) Anakeesta (0.0, 100.0)	Independent variables should be within ranges listed No other restrictions
Sulfate	(21.32, 70.51, 34.42)	(9.07, 104.88, 32.72)	undisturbed (0.0, 100.0) Anakeesta (0.0, 100.0)	Independent variables should be within ranges listed Not applicable for basins with disturbed Anakeesta
Chloride	(12.53, 22.04, 13.73)	(11.49, 20.71, 13.78)	stream density (0.1, 2.4) Limestone (0.0, 21.0) Elkmont Sandstone (0.0, 93.4) Northern Hardwood (0.0, 58.5)	Independent variables should be within ranges listed No other restrictions
Sodium ^a	(41.09, 57.33, 50.58)	(41.20, 56.02, 52.21)	Limestone (0.4, 21.0)	Independent variable should be within range listed Applicable for basins which contain Limestone and no disturbed Anakeesta
Sodium ^b	(20.22, 56.47, 33.76)	(21.96, 69.58, 35.04)	basin slope (25.3, 72.1) MMH (0.0, 49.3)	Independent variables should be within ranges listed Applicable for basins without Limestone and no disturbed Anakeesta
Potassium	(2.82, 14.35, 10.30)	(3.17, 16.78, 10.29)	basin slope (25.3, 72.1) Anakeesta (0.0, 100.0) Northern Hardwood (0.0, 58.5)	Independent variables should be within ranges listed No other restrictions

Note: Predicted column includes summary statistics for model predicted values.

Observed column includes summary statistics of dependent variable in basins used for model development.

Units for all water quality constituents are microequivalents per liter except pH (standard units) and conductivity (microsiemens per centimeter).

Units for all independent variables are the same as those reported in Table 4-1.

For explanation of abbreviated independent variables, see bottom of Table 4-5.

order.

Two sites appeared to exert a strong influence on the model. Influence was determined by the methods mentioned on pages 97 and 98. These were sites 237 and 252. The Cook's D statistics for these two sites appeared unreasonably large in comparison to other observations. The 25th, 50th, and 75th percentile values for the Cook's D statistic including all observations were 0.000577, 0.00151, and 0.00581, respectively. The Cook's D statistics for sites 237 and 252 were 0.252 and 0.248, respectively. Visual inspection of the partial regression plots showed that these two sites consistently appeared removed from other observations and deviated from apparent linear trends in these plots. Both of these sites are unique. They are both sites which have experienced significant disturbance to the Anakeesta Formations within their basins. The entire basin (100%) created by sample site 237 is underlain by Anakeesta. About 69% of the contributing area to site 252 is underlain by Anakeesta. The disturbance to the Anakeesta Formations upstream of site 237 is the result of natural exposure from debris flows. Immediately upstream of site 252, the disturbance to the Anakeesta Formations occurred when U.S. Highway 441 through the GRSM was reconstructed in 1963 and 1964. The Anakeesta was also used as roadfill material (Kucken *et al.*, 1992; Winger *et al.*, 1987). This will be discussed more when the final model selected to predict pH is discussed. These sites were removed from the analysis since they are so unique and would exert such a strong influence on the resulting model. When the model was rerun with these two sites removed, the adjusted r-square improved from 0.64 to 0.74. The normality of the unstandardized residuals improved as well. Improvement of normality was concluded by visual inspection of the box plot of the

unstandardized residuals and skewness and kurtosis. Indices of skewness and kurtosis for the model with sites 237 and 252 were -1.89 and 7.84, respectively. Indices of skewness and kurtosis without these sites were -0.15 and 2.45, respectively. A kurtosis index equal to 2.45 indicates that the distribution is somewhat more peaked than the normal distribution. This would be caused by a larger number of observations at the center of the distribution (Huck and Cormier, 1996). The model which excluded sites 237 and 252 and included the independent variables mean elevation, basin slope, and stream order appeared to predict reasonable values (greater than zero and less than 14) for median pH at sampled sites. The minimum, maximum, and median predicted pH values for this model are 5.62, 7.09, and 6.36, respectively. The actual observed minimum, maximum, and median pH values at sampled sites (excluding sites 237 and 252) are 5.49, 7.44, and 6.36, respectively. The coefficients on the independent variables mean elevation and basin slope are negative as one might expect from results of correlation analysis. The coefficient for stream order is positive indicating that as stream order increases, median pH values increase.

Visual inspection of a plot of the standardized residuals versus the unstandardized predicted values showed that the model appears to adhere to the assumptions of constant variance. The residuals appeared randomly distributed about the horizontal axis and there appeared to be a proportionate number of residuals above and below zero. The partial regression plots and plots of standardized residuals versus explanatory variables suggested that transformations of the independent variables were not necessary. The partial regression plots appeared linear. Based upon satisfactory results for all criteria (except kurtosis more than one away from zero) and minimal deviation of the unstandardized residuals from the

normal distribution, it was concluded that the model was acceptable. However, a second model which included grouped variables was tested for comparison.

pH-Trial two

A second model was selected by stepwise procedures using grouped independent variables as described earlier. Limestone, Cades Sandstone, Elkmont Sandstone, and Basement Complex (LCEB) were grouped together to create a single independent variable that represents the basin area covered by the sum of these geology types. Limestone, Cades Sandstone, and Elkmont Sandstone have statistically significant positive correlations with each other and with pH (see Tables 4-2 and 4-3). Others have noted that Cades Sandstone and Elkmont Sandstone are of similar character (King *et al.*, 1968). Limestone and Cades Sandstone are found in the Cades Cove area and Elkmont Sandstone is found in the higher elevations south and east of Cades Cove. The Basement complex is part of the foundation on which all other strata of the region have been laid (King *et al.*, 1968). Therefore, it is not surprising that these four geology types have similar affects on surface water pH and ANC. Most of the influence is probably due to the presence of Limestone within the basins. The apparently similar affect of Cades Sandstone, Elkmont Sandstone, and Basement complex on surface water pH and ANC probably results from their coexistence with the more soluble and carbonate bearing Limestone. Anakeesta was the only geology type which showed a negative correlation with pH and was therefore left alone as a possible independent variable.

Spruce Fir, Northern Hardwood, Cove Hardwood, and Heath Bald (SNCH) were grouped together to form another independent variable. They were grouped together because they all have statistically significant negative correlation coefficients with pH (see Table 4-3)

and physically it makes sense based on the information about where these forests are typically found. From the descriptions of the forest types presented earlier, one can see that Spruce Fir, Northern Hardwood, and Heath Bald are all typically found in the upper elevations of the GRSM. Cove Hardwood can be found at almost any elevation. Mesic Oak, Mixed Mesic Hardwood, Tulip Poplar, Pine, Xeric Oak, and Pine-Oak (MMMTPXPO) were grouped together as well since they have statistically significant positive linear relationships with pH and they tend to be in the middle to lower elevations of the GRSM. Disturbance history data were grouped as explained earlier. The possible independent variables for trial two included elevation, mean elevation, elevation class, stream order, basin length, basin area, stream density, average basin slope, channel slope, maximum channel length, basin width, basin shape, LCEB, Anakeesta, SNCH, MMMTPXPO, undisturbed, and disturbed.

The significant variables selected by stepwise procedures included SNCH, basin slope, and stream order. The same two sites, 237 and 252, again appeared to exert a strong influence on the model. The model was rerun with only SNCH, basin slope, and stream order as possible variables and sites 237 and 252 removed. The adjusted model r-square improved from 0.62 with sites 237 and 252 to 0.75 with the sites removed. The minimum, maximum, and median predicted pH values for the model excluding sites 237 and 252 were 5.65, 7.08, and 6.34, respectively. The results of the model from trial two appeared similar to the results from trial one, in which variables were not grouped. Model results were probably similar because the variable SNCH functions like a surrogate variable for mean elevation. Three of the forest types in the grouping SNCH are significantly correlated with mean elevation. These include Spruce Fir, Northern Hardwood, and Cove Hardwood. The

Kendall's tau correlation coefficient between the variable SNCH and mean elevation is 0.75. Heath Bald is probably not correlated with mean elevation because it only occurs at the higher elevations so there are no observations at the lower elevations. It is interesting to note that some of the species included in this grouping, particularly Heath Bald and Spruce Fir, prefer the acidic soils of the higher elevations. The coefficient on the independent variable SNCH indicated that pH decreases as coverage of this grouping increases.

The final model chosen and reported in Table 4-5 includes mean elevation, basin slope, and stream order. This model is chosen over the similar second model (from trial two) because mean elevation is a variable which is easier to determine. There are ways to determine mean basin elevation using topographical maps and grid paper. Although it is tedious to determine mean elevation from topographical maps compared to extracting the data from GIS databases, someone without knowledge of using GIS could obtain the necessary input information. The other two variables, basin slope and stream order, are included in both models. Basin slope can also be determined with a good topographical map, grid paper, and diligence. The model explains almost 75% of the variability in median pH in sampled basins of the GRSM. Application of the model would not be appropriate when trying to predict pH in basins draining areas with disturbed Anakeesta Formations since sites with this characteristic were removed from the regression analysis. The model should also not be used for basins which have characteristics outside the range of those used to create the model. The ranges (minimum, maximum) for the independent variables are as follows: mean elevation (745 meters, 1,716 meters); basin slope (25.3%, 72.1%); and stream order (1,5). Figure 4-1 is a plot of predicted pH versus median pH. The gridlines are included in the

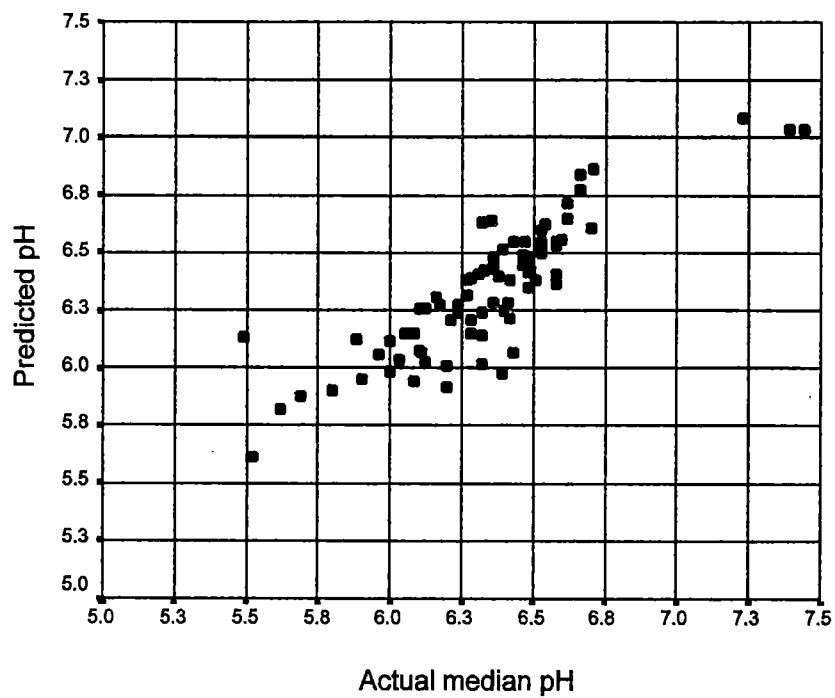


Figure 4-1. Predicted versus actual pH from regression model to predict pH in sampled GRSM basins.

figure to facilitate comparison between the values. Notice the major intervals are the same for the predicted values and the actual values. One would expect an intercept of zero and a slope equal to one for the best-fit line through the data points in Figure 4-1. Simple linear regression was performed on the predicted values and the actual values to compare the intercept and slope terms with what one would expect. The intercept and the slope terms were statistically significant ($p < 0.05$) and equal to 1.610 and 0.746, respectively. The model appears to predict lower than actual values for sites with particularly high pH (greater than 7.0) and predict higher than actual values for sites with low pH (less than 5.5).

As discussed in Chapter III, the sites with median pH greater than 7.0 are within the Abrams Creek watershed and below Cades Cove. These include sites 156, 174, and 489. The contributing areas to these sites contain Limestone and the amount of Limestone in each basin is 7.0, 21.0, and 11.7%, respectively. Sites further upstream and above the Cades Cove area include 184, 186, and 200 (see Figure 3-2). The median pH values at these sites are 6.2, 6.4, and 6.1, respectively. The water at these slightly acidic (pH less than 7.0) upstream sites is buffered by the presence of soluble Limestone within the Cades Cove area. The presence of Limestone within the GRSM is not typical. Most of the GRSM is underlain by basically inert sandstone formations which result in waters with low acid neutralizing capacity and low ionic strength (Elwood *et al.*, 1991). Surface waters which are high in acid neutralizing species such as carbonate and bicarbonate are typically less acidic and have higher pH values compared to waters low in acid neutralizing species. The Limestone present in these basins and the acid neutralizing species which it contributes to the water is responsible for the higher than usual pH values.

Also discussed in Chapter III were the sites with median pH less than or equal to 5.5. Two of the sites, 237 and 252, exerted such a strong influence on the modeling results that they were removed from the analysis. The Anakeesta Formations within these basins has been disturbed. The pyritic, iron sulfide minerals which make up Anakeesta Formations have been classified by some researchers as acid-producing materials (Byerly, 1996). These minerals oxidize in the presence of air and water to form different soluble iron sulfate compounds. The dissolution of these various sulfates produces acidity, increases concentrations of sulfate, and consumes alkalinity. The low pH at sites 237 and 252 results from this acidifying effect of disturbed Anakeesta Formations. Other areas (drainage basins) identified as having significant debris flows of Anakeesta Formations include Porters Creek, Eagle Rocks Prong, Breedlove Branch, Gulf Prong of Bradley Fork, and Left Fork of Deep Creek (personal communication, Scott Southworth).

As mentioned, the model to explain the variability in pH includes three independent variables (mean elevation, basin slope, and stream order) related to elevation. The coefficients on the independent variables indicate that pH in sampled basins of the GRSM decreases with increases in elevation. Research at high elevations in the GRSM (greater than 1,720 meters) has shown an elevation gradient to deposition of acidifying species such as sulfate in throughfall. Researchers found that sulfate fluxes increased by about a factor of two due to higher cloudwater interception at 1,940 meters versus 1,720 meters (Shubzda *et al.*, 1995). This elevation gradient to deposition of acidifying species is one explanation to the variability in pH with respect to elevation. Other possible influences which explain the trend include the presence of Anakeesta Formations and undisturbed areas at the upper

elevations of the GRSM. The influences of Anakeesta have already been discussed. The amount of undisturbed area and nitrate concentrations are positively correlated with each other (see Table 4-3). In soils low in base cations or with a tendency to conserve base cations, charge balance can be maintained by the leaching of hydrogen ions and aluminum (Cosby *et al.*, 1985). It is possible that hydrogen ions are the principal cations maintaining charge balance in surface waters draining basins with undisturbed areas. Sodium and potassium are negatively correlated with the amount of undisturbed area (see Table 4-3). Therefore, they are probably not the principal cations maintaining charge balance. Calcium and magnesium could also be important cations but analysis of calcium and magnesium was not included due to reasons discussed in Chapter I.

Acid Neutralizing Capacity

From the results of simple linear regression analysis discussed in Chapter III and initial attempts to predict median ANC using multiple regression, it was apparent that two different models might be necessary. The basins which contain Limestone heavily influenced any attempts to explain the variability in ANC. There are six sampled basins in which Limestone is present. They are sites 13, 24, 156, 173, 174, and 489. The amount of Limestone in each basin is 0.4, 2.3, 7.0, 1.0, 21.0, and 11.7% respectively. Three of these sites, as already discussed, are within Cades Cove and part of the Abrams Creek watershed. One site, 173, is located on Mill Creek just before it joins with Abrams Creek (see Figure 3-2). The other two sites, 13 and 24, are part of the Little River watershed (see Figure 3-2). The decision was made to model separately basins which contain Limestone and basins which have no Limestone present.

For basins which contain Limestone, simple linear regression was used to predict median ANC based on the amount of watershed area covered by Limestone. A plot of median ANC versus Limestone coverage is shown in Figure 4-2. Regression results in which the line was not forced through the origin gave a slope term which was statistically significant ($p < 0.05$) but a constant term which was not significant ($p = 0.326$). The 95% confidence interval for the constant term included zero. A second line was fit to the data but forced the intercept through the origin. Since the 95% confidence interval of the constant term in the model which did not force the intercept through the origin included zero, forcing a line through the origin seemed reasonable. The regression results are reported in Table 4-5. The model selected for predicting median ANC in basins with Limestone was compared with the one which did not force the intercept through the origin. For all values of percent coverage by Limestone, the difference between the predicted median ANC values at the sample site was not more than 10%. The model predicts that as the amount of Limestone in a basin increases, the amounts of acid neutralizing species also increase.

The model in Table 4-5 should not be used for predicting ANC in basins with more than 21% of their area covered by Limestone. It should also not be used if disturbed Anakeesta Formations are present in the basin. The minimum, maximum, and median predicted ANC values are 24.02, 1,295.59, and 285.22 microequivalents per liter, respectively. The observed minimum, maximum, and median ANC values in sampled basins with Limestone are 95.89, 1,223.05, and 265.50.

To predict ANC in basins without Limestone, the same methods were used as for development of the model to predict pH. The first trial did not group independent variables.

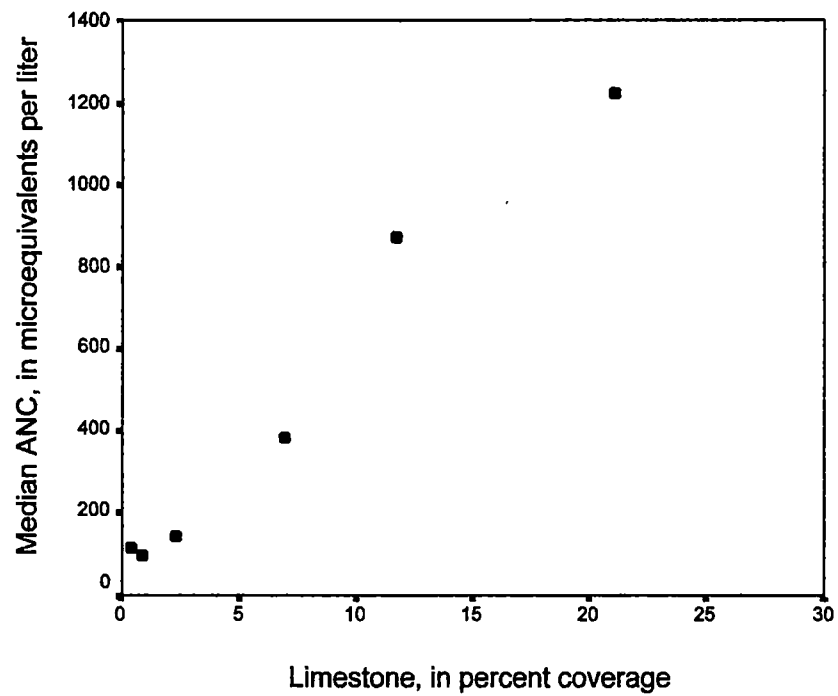


Figure 4-2. Relationship between median acid neutralizing capacity and percent coverage of limestone in sampled GRSM basins.

The actual model which was selected and reported in Table 4-5 resulted from grouping some independent variables together (trial two). This will be discussed later. The discussion below explains the model selected by stepwise procedures on ungrouped variables and why it was not selected.

Acid Neutralizing Capacity-Trial one

For basins which do not have Limestone, the possible independent variables in trial one included elevation, mean elevation, elevation class, stream order, basin length, basin area, stream density, average basin slope, channel slope, maximum channel length, basin width, basin shape, Thunderhead Sandstone, Limestone, Cades Sandstone, Elkmont Sandstone, Anakeesta, Metadiorite, Great Smoky Group, Basement complex, Spruce Fir, Northern Hardwood, Cove Hardwood, Mesic Oak, Mixed Mesic Hardwood, Tulip Poplar, Pine, Heath Bald, Xeric Oak, Pine-Oak, undisturbed, light cut, selective cut, heavy cut, and settlement. Variables in the model selected by stepwise procedures included Mixed Mesic Hardwood, maximum flow length, Mesic Oak, and basin slope.

Site 253 appeared to exert a strong influence on the model. The Cook's D statistic for this site appeared unreasonably large in comparison to other observations. The 25th, 50th, and 75th percentile values for the Cook's D statistic including all observations were 0.000512, 0.00233, and 0.00738, respectively. The Cook's D statistic for site 253 was 0.260. Visual inspection of the partial regression plots showed that site 253 was far removed from other observations and deviated from apparent linear trends in these plots. This site is located immediately upstream of site 252 (one of the sites which exerted a strong influence on the model for median pH) and above the roadcut on Beech Flats Creek within the larger

Oconaluftee watershed. Site 253 was removed from analysis because the variability of water quality constituent values in sampled surface waters which are close to roads with basins containing disturbed Anakeesta Formations is unusual. These sites do not represent "typical" conditions within the GRSM. These atypical conditions strongly influence resulting models and reduce the likelihood of producing stronger models that might work well to predict the more typical conditions found throughout the GRSM. Removal of site 253 improved the adjusted r-square from 0.76 to 0.83.

The coefficients and the constant term appeared reasonable with respect to magnitude and sign. The coefficients for Mixed Mesic Hardwood, Mesic Oak, and maximum channel length were all positive, indicating that ANC would increase as values for these variables increased. Correlation analysis revealed strong positive relationships between Mixed Mesic Hardwood, Mesic Oak, and maximum channel length. Kendall's tau correlation coefficients were 0.505, 0.271, and 0.458, respectively. The coefficient for basin slope was negative, indicating that with increases in basin slope (increases in elevation) ANC would decrease. The Kendall's tau correlation coefficient between basin slope and ANC was -0.450.

All condition indices were below twenty-one. This satisfied the criteria that condition indices should be below 30, the point at which there could be significant problems with multi-collinearity.

However, there were numerous problems with the model that could not be resolved well. Visual inspection of the box plot of the unstandardized residuals did not appear normal due to the presence of numerous outliers. The partial regression plots of maximum channel length, basin slope, and Mesic Oak did not appear linear and residual plots revealed problems

with heteroscedasticity. Attempts at transformations did not improve results. Scatter plots of median ANC versus these three variables suggested that transformations going “down” the ladder of powers would be most appropriate. Transformations going down the ladder of powers include taking the base 10 log, the reciprocal, the square root, the cube root, and so on (Helsel and Hirsch, 1992). Transformations which were tried included taking the base 10 log, the reciprocal, and the square root of the independent variables maximum channel length, basin slope, and Mesic Oak. The transformations did not significantly improve problems with heteroscedasticity or normality of unstandardized residuals.

Acid Neutralizing Capacity-Trial two

The second model selected by stepwise procedures chose from grouped variables. The groupings were the same as those used for predicting median pH. These groupings were explained and justified in the discussion of the model selected by stepwise procedures for pH-trial two. It was reasonable to use the same groupings because pH and ANC have almost identical relationships with basin characteristics (see Table 4-3). Therefore, the possible independent variables included elevation, mean elevation, elevation class, stream order, basin length, basin area, stream density, average basin slope, channel slope, maximum channel length, basin width, basin shape, LCEB, Anakeesta, SNCH, MMMTPXPO, undisturbed, and disturbed. The significant variables selected by stepwise procedures included MMMTPXPO, maximum channel length, and basin slope.

Site 253 again appeared as a strong influence on the model. The 25th, 50th, and 75th percentile values for the Cook's D statistic including all observations were 0.000984, 0.00273, and 0.0101, respectively. The Cook's D statistic for site 253 was 0.340. Visual

inspection of the partial regression plots showed that site 253 was far removed from other observations and deviated from apparent linear trends in these plots. Notice in Figure 4-3 that site 253 appears in the top portion of the plot removed from the other observations. Since site 253 exerted such a strong influence on the modeling results and the site represents atypical conditions, it was removed from the analysis. Removal of site 253 improved the adjusted r-square from 0.74 to 0.81.

A review of the modeling results indicated that maximum channel length and basin slope might require transformations to improve problems with heteroscedasticity. Figure 4-4 displays the residuals plotted against maximum channel length for the model in which maximum channel length was not transformed. Visually, the variance appears to increase for basins located at higher elevations (shorter channel lengths). To reduce problems with heteroscedasticity, several transformations were tried. Those going down the ladder of powers appeared most appropriate based on visual inspection of scatter plots of median ANC versus maximum channel length and basin length. Transformations which were tried included taking the base 10 log, the reciprocal, and the square root of the independent variables maximum channel and basin slope. Taking the square root of the maximum channel length improved problems with heteroscedasticity. Figure 4-5 displays the residuals plotted against the square root of maximum channel length. There appears to be a significant improvement in adherence to the assumptions of constant variance by transforming the variable. The observations appear more randomly distributed about the horizontal axis. There also appears to be a proportionate number of residuals above and below zero. Figure 4-6 displays the partial regression plot of median ANC and the transformed maximum

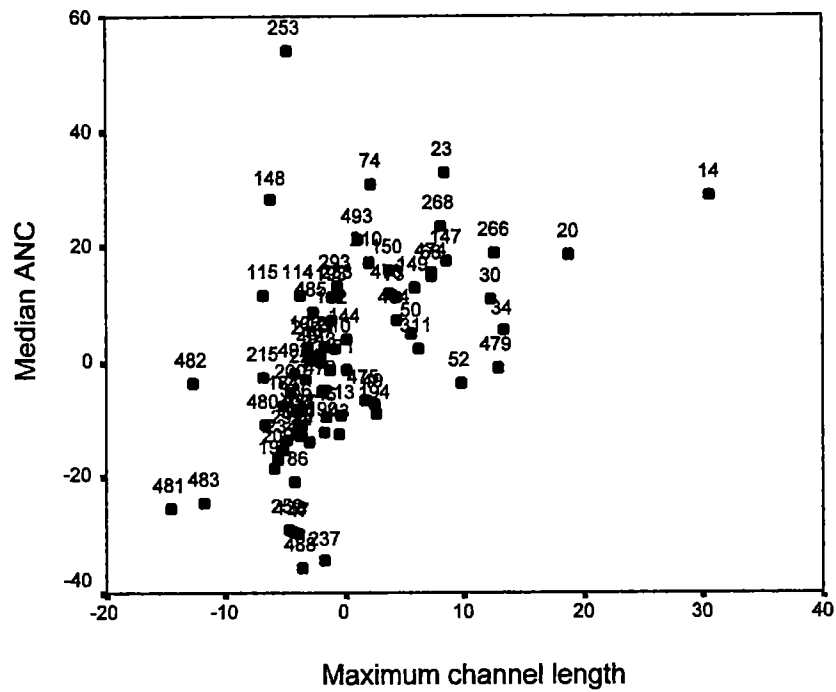


Figure 4-3. Partial regression plot of median ANC and maximum channel length with influential site 253.

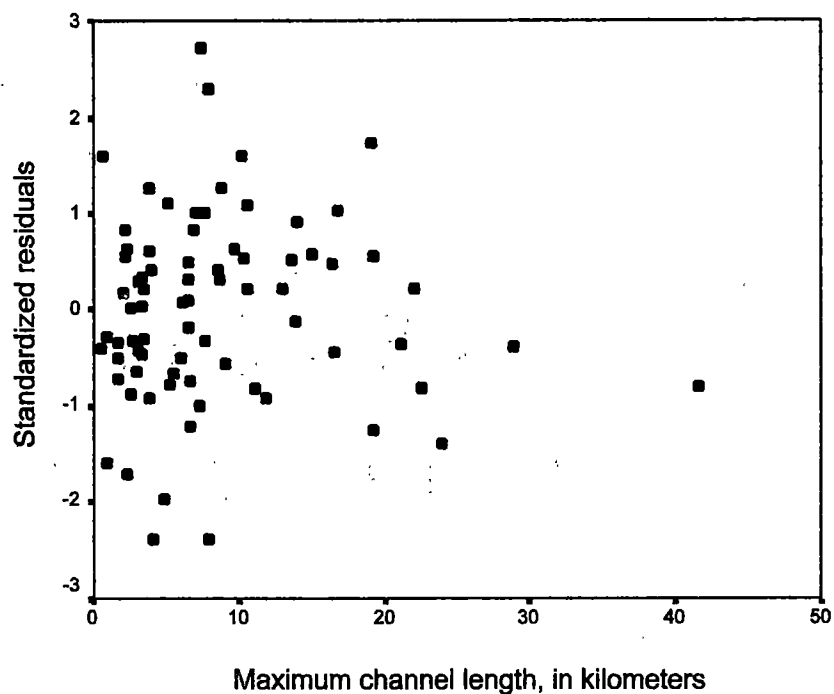


Figure 4-4. Residuals plot for ANC regression model with untransformed maximum channel length.

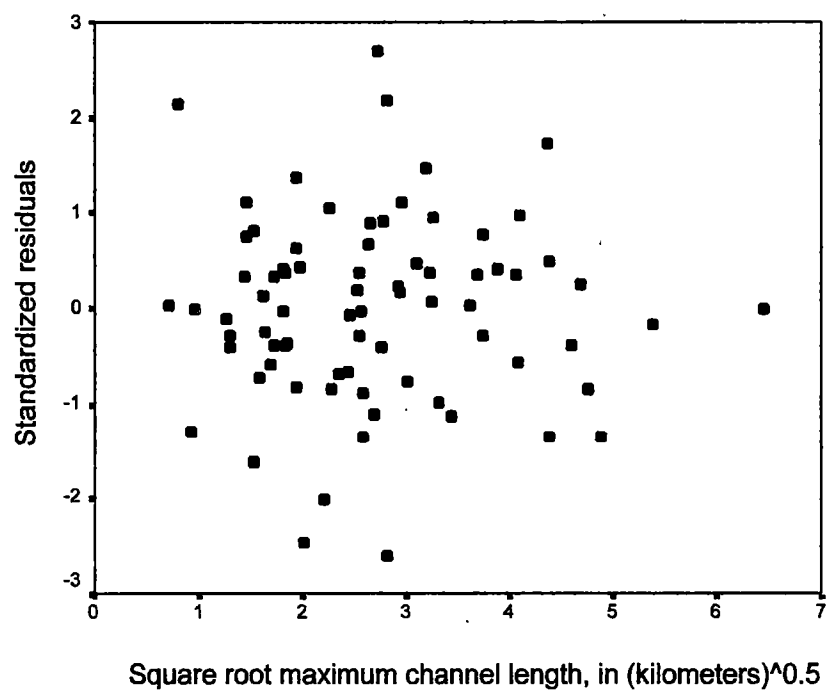


Figure 4-5. Residuals plot for ANC regression model with transformed maximum channel length.

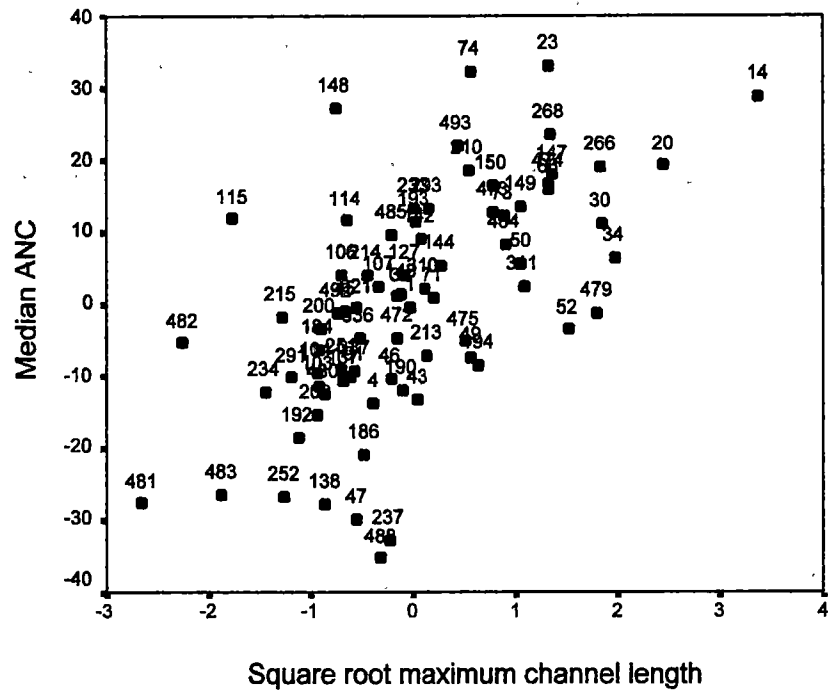


Figure 4-6. Partial regression plot of median ANC and transformed maximum channel length with site 253 removed from regression.

channel length with site 253 removed from the regression. It is certainly not a perfectly straight line, but notice that the linear trend in Figure 4-6 appears better than the one in Figure 4-3. The relationship between median ANC and maximum channel length was apparently made more linear by the transformation and removal of site 253.

Improvements by transformation of basin slope appeared minimal. Heteroscedasticity could not be significantly reduced with transformations. Figure 4-7 displays the plot of the standardized residuals versus basin slope, which shows some signs of nonconstant variance. This was judged acceptable because other model criteria were satisfied and, more important, because most of the sampled basins have basin slopes that are within the range in which the clustering in Figure 4-7 occurs. Of the basins used to generate the model, 84% have an average basin slope between 40 and 50%. Based on this, some clustering of data points could be expected. Therefore, basin slope was left in the model because of its contribution to explaining some of the variability in median ANC without significant deviation from the assumptions of linear regression. The model adjusted r-square without basin slope was 0.75. Including basin slope in the model improved the adjusted r-square to 0.81.

The box plot of the unstandardized residuals appeared normal and skewness and kurtosis indices were no more than one away from zero. The minimum, maximum, and median predicted ANC values are -1.25, 103.12, and 43.07 microequivalents per liter, respectively. The actual observed minimum, maximum, and median ANC values in sampled basins included in the model are -13.68, 124.27, and 44.63 microequivalents per liter, respectively. The final model is reported in Table 4-5. This model, like the one for predicting pH, is not recommended for predicting ANC with disturbed Anakeesta

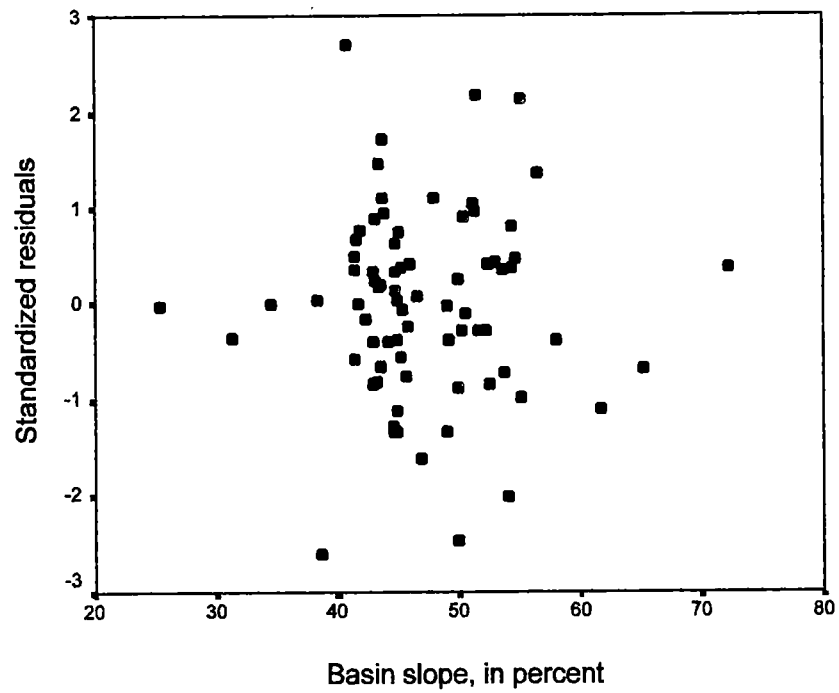


Figure 4-7. Residuals plot for basin slope in ANC regression model with transformed maximum channel length.

Formations. As already mentioned, this model is also not appropriate for basins with Limestone. The model should also not be used for basins which have characteristics outside the range of those used to create the model. The ranges (minimum, maximum) for the independent variables are as follows: MMMTPXPO (0.0%, 91.6%); maximum channel length (0.52 kilometers, 41.62 kilometers); and basin slope (25.3%, 72.1%). Figure 4-8 is a plot of predicted ANC versus the actual ANC. One would expect an intercept of zero and a slope equal to one for the best-fit line through the data points in Figure 4-8. Simple linear regression was performed on the predicted values and the actual values to compare the intercept and slope terms with what one would expect. The intercept and the slope terms were statistically significant ($p < 0.05$) and equal to 8.497 and 0.817, respectively.

The variables in the model to predict ANC in basins without Limestone are related to elevation. The forest types which make up the grouping MMMTPXPO are typically found at the middle to lower elevations of the GRSM. The coefficient on MMMTPXPO indicates that as the percent coverage of this forest type increases ANC increases. The coefficients on the other two variables, maximum channel length and basin slope, indicate that as elevation increases ANC decreases. The reasons that were cited in the discussion beginning on page 121 to explain trends in pH are also applicable to trends in acid neutralizing capacity.

Refer to Appendix A4 for the complete SPSS output that was used to evaluate the model (resulting from trial two) to predict ANC in basins without Limestone. It was selected as a "model" representation of the process used for all other constituents for several reasons. Acid neutralizing capacity is considered one of the more important constituents. To resolve problems and satisfy assumptions of multiple linear regression, one of the independent

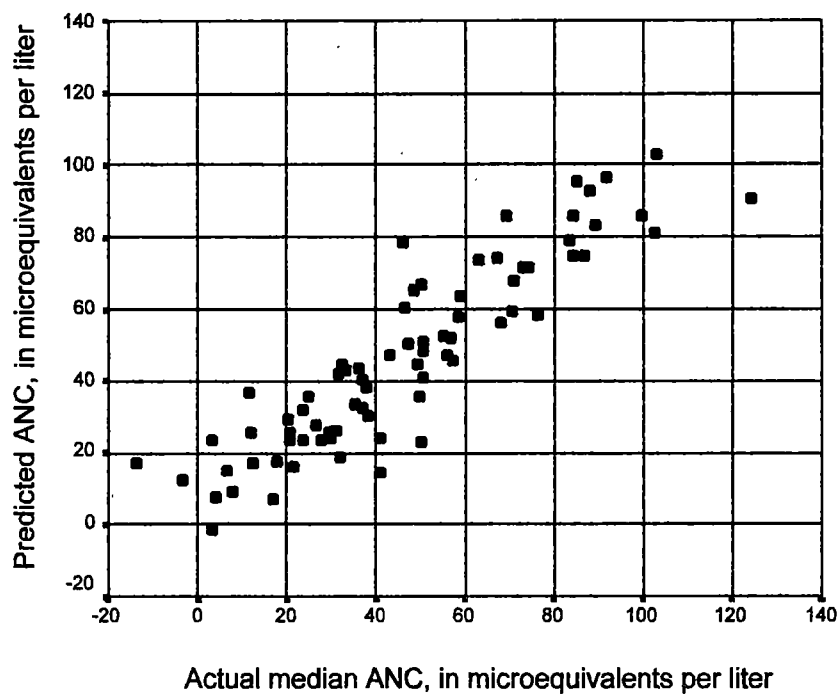


Figure 4-8. Predicted versus actual ANC from regression model to predict ANC in sampled GRSM basins.

variables, maximum channel length, was transformed. One site exerted a strong influence on the model and was removed from the regression. The residuals for one of the independent variables, basin slope, showed some problems with nonconstant variance, but for reasons that were determined explainable and acceptable. With the fairly detailed explanation of model development for pH and ANC, the reader should have an understanding of the process used for all other models. Therefore, model results for all other constituents will be less detailed but discuss important points.

Conductivity

Based on initial attempts to predict median conductivity using multiple regression, it was apparent that two different models would be necessary. As with ANC, the decision was made to model separately basins which contain Limestone and basins which have no Limestone present. However, the model for predicting median conductivity in basins without Limestone did have different independent variables than the model for predicting median ANC in basins without Limestone.

The relationship between median conductivity and the amount of Limestone in a basin is shown in Figure 4-9. As the amount of Limestone in a basin increases, conductivity also increases. Conductivity increases due to increases in concentrations of acid neutralizing species such as carbonate and bicarbonate. Table 4-5 displays the results of simple linear regression. The slope term and the constant were both significant ($p < 0.05$). The minimum, maximum, and median predicted conductivity values are 15.13, 129.43, and 38.61 microsiemens per centimeter, respectively. The observed minimum, maximum, and median conductivity values in sampled basins with Limestone are 17.58, 126.40, and 33.98

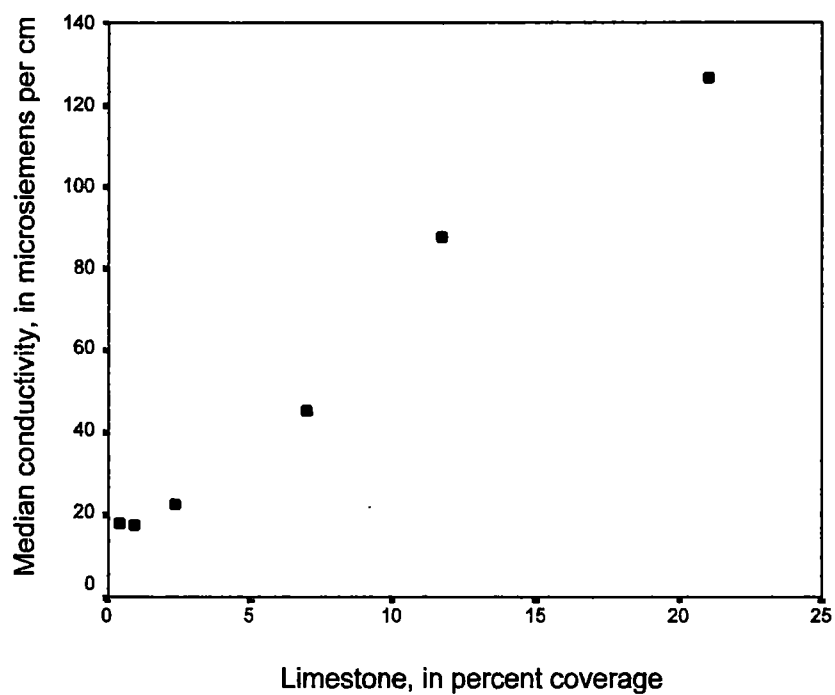


Figure 4-9. Relationship between median conductivity and percent coverage of limestone in sampled GRSM basins.

microsiemens per centimeter, respectively. The model in Table 4-5 should not be used for predicting conductivity in basins with more than 21% of their area covered by Limestone. It should also not be used if disturbed Anakeesta Formations are present.

For basins which do not have Limestone, significant variables in the final model selected by stepwise procedures and reported in Table 4-5 include the amount of undisturbed area and the percentage of the basin area covered by Anakeesta. The coefficients on the independent variables are both positive. As the amount of undisturbed area and area with Anakeesta increases, the concentrations of nitrate and sulfate increase. This will be discussed more in the discussion of nitrate and sulfate models. As the concentrations of these anions increase, the concentration of neutralizing cations (probably hydrogen ions) increases as well and there is a corresponding increase in ionic strength. Kendall's tau correlation coefficients between pH and the amount of undisturbed area and Anakeesta are -0.424 and -0.226, respectively. Since pH is negatively correlated with the amount of undisturbed area and Anakeesta coverage, then hydrogen ion concentrations increase. Sodium and potassium are both negatively correlated with undisturbed area and Anakeesta (see Table 4-3). Therefore, the cations which maintain neutrality are probably not sodium or potassium. Calcium and magnesium could also be important cations but analysis of calcium and magnesium was not included due to reasons discussed in Chapter I.

The ranges on the independent variables indicate that the model reported in Table 4-5 could be used for all basins within the GRSM, except those with disturbed Anakeesta upstream and Limestone present. Two sites with disturbed Anakeesta upstream were removed from the analysis because they exerted a large influence on the resulting model.

These included sites 251 and 252. The ranges, minimum and maximum, for both independent variables are 0% and 100%, respectively. The minimum, maximum, and median predicted conductivity values are 11.91, 19.89, and 14.87 microsiemens per centimeter, respectively. The observed minimum, maximum, and median conductivity values in sampled basins used to model the data are 10.42, 24.30, and 13.90 microsiemens per centimeter, respectively.

Nitrate

The model reported in Table 4-5 for predicting median nitrate concentrations is applicable for all sampled basins. No single basin was particularly more influential than any other and therefore basins were not excluded from the regression analysis. Transformations of variables did not appear necessary. The model explains a large portion of the variability of nitrate ($r\text{-square} = 0.87$). The model also contains more independent variables than any of the other models. The independent variables include percent undisturbed, elevation class, percent Mixed Mesic Hardwood, stream density, and percent Anakeesta.

The amount of undisturbed area in a basin explains 61% of the variability in median nitrate concentrations. The coefficient on this variable indicates that as the amount of undisturbed area increases, nitrate concentrations increase. The large undisturbed areas of the GRSM tend to be located in the middle to upper elevations. The amount of undisturbed area is positively correlated with elevation and mean elevation (see Table 4-2). The upper elevations were not accessible to early style loggers and the areas were not as useful to settlers as the lower elevation coves and valleys. Nitrate levels have been found by others to be significantly different between streams which had at least 75% of their watersheds

logged and those with no more than 25% of their watersheds logged. Streams draining watersheds with older-growth forests where logging was minimal or nonexistent had higher nitrate concentrations than younger forests (Silsbee and Larson, 1982). Figure 4-10 displays box plots of the percentage of anions as nitrate in basins with different amounts of undisturbed area. For basins with more than 50% of undisturbed area, the 25th, 50th, and 75th percentile values for percentage of anions as nitrate are 22.66, 28.52, and 35.20 microequivalents per liter, respectively. For basins with less than 50% of undisturbed area, the 25th, 50th, and 75th percentile values for percentage of anions as nitrate are 9.72, 16.44, and 23.62 microequivalents per liter, respectively. The percentages of anions as nitrate (median values) were compared using the Kruskal-Wallis (KW) H test. There is a statistically significant difference (KW significance < 0.05) between the percentage of anions as nitrate in these two types of basins. Based on the mean ranks of the Kruskal-Wallis test, basins with a majority of undisturbed area have a greater percentage of anions as nitrate. Two variables in the model are related to elevation, elevation class and stream density. Stream density is negatively correlated with sample site elevation and mean basin elevation (see Table 4-2). The coefficients on elevation class and stream density indicate that as elevation increases, nitrate concentrations increase. These results agree with the results of simple linear regression presented in Chapter I. Mixed Mesic Hardwood forests are located at the lower elevations (below 750 meters) in areas that have been settled or logged. The coefficient on Mixed Mesic Hardwood is consistent with other variables. The negative coefficient suggests that as elevation decreases and the amount of disturbed area increases, nitrate concentrations in surface water decrease as well. The coefficient on the independent

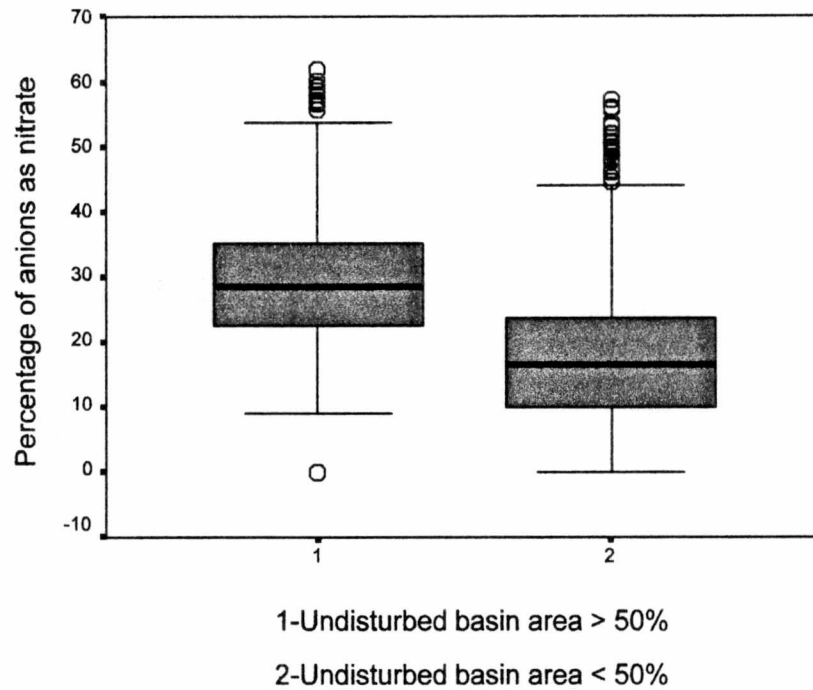


Figure 4-10. The percentage of anions as nitrate in sampled GRSM basins with different amounts of undisturbed area.

variable Anakeesta indicates that as the amount of basin area covered by these formations increases, nitrate concentrations decrease. The major anion in sampled surface water in basins with a majority of their watershed covered by Anakeesta (greater than 50%) is sulfate. Figure 4-11 displays box plots of the percentage of anions as sulfate in basins with a majority of the area covered by Anakeesta Formations and those with less than 50% coverage. For basins with more than 50% coverage, the 25th, 50th, and 75th percentile values for percentage of anions as sulfate are 55.18, 61.44, and 66.81 microequivalents per liter, respectively. For basins with less than 50% coverage of Anakeesta, the 25th, 50th, and 75th percentile values for percentage of anions as sulfate are 44.36, 52.00, and 58.90 microequivalents per liter, respectively. The percentages of anions as sulfate (median values) were compared using the Kruskal-Wallis H test. There is a statistically significant difference (KW significance < 0.05) between the percentage of anions as sulfate in these two types of basins. Based on the mean ranks of the Kruskal-Wallis test, basins with a majority of Anakeesta coverage have a greater percentage of anions as sulfate.

The ranges (minimum, maximum) for the independent variables are as follows: undisturbed (0.0%, 100.0%); elevation class (2, 10); stream density (0.1, 2.4 kilometers per square kilometer); Mixed Mesic Hardwood (0.0%, 34.9%); and Anakeesta (0.0%, 100.0%). The minimum, maximum, and median predicted nitrate concentrations are 0.57, 51.16, and 19.00 microequivalents per liter, respectively. The observed minimum, maximum, and median nitrate concentrations in sampled basins used to create the model are 3.07, 59.69, and 17.62 microequivalents per liter, respectively. Figure 4-12 is a plot of predicted nitrate versus actual nitrate concentrations. One would expect an intercept of zero and a slope equal

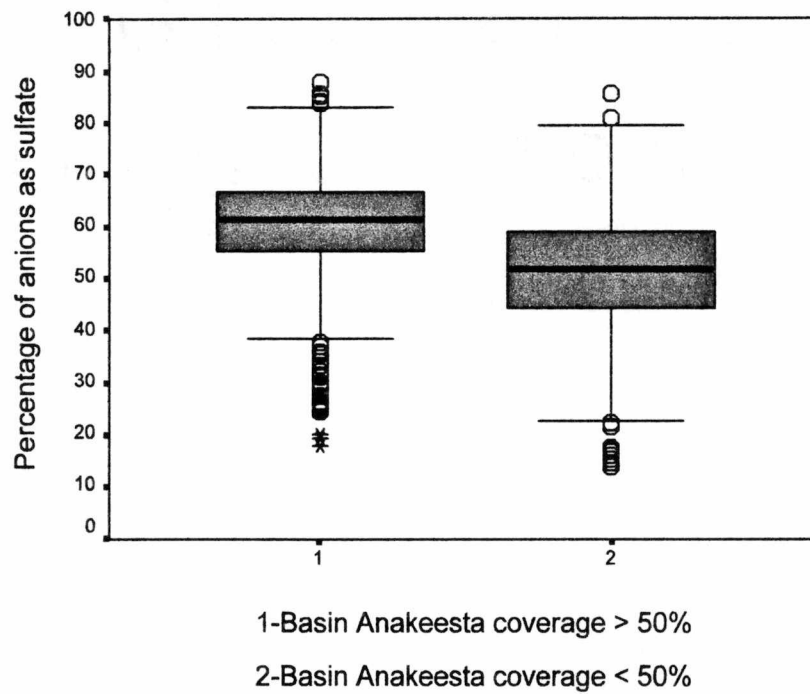


Figure 4-11. The percentage of anions as sulfate in sampled GRSM basins with different amounts of Anakeesta.

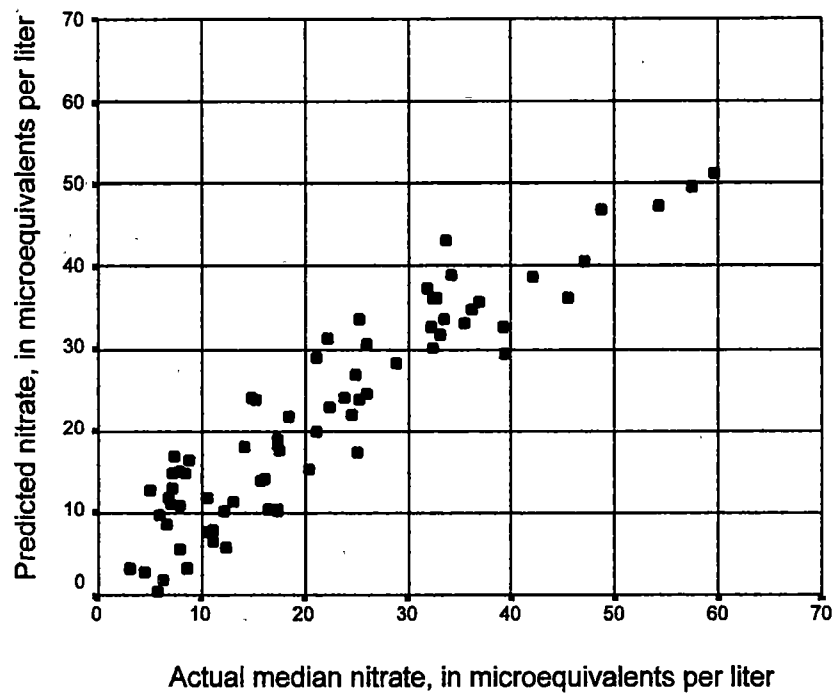


Figure 4-12. Predicted versus actual nitrate concentration from regression model to predict nitrate in sampled GRSM basins.

to one for the best-fit line through the data points in Figure 4-12. Simple linear regression was performed on the predicted values and the actual values to compare the intercept and slope terms with what one would expect. The intercept and the slope terms were statistically significant ($p < 0.05$) and equal to 5.204 and 0.839, respectively. Based on visual inspection of Figure 4-12, the model appears to underestimate nitrate concentrations in basins with median concentrations greater than about 40 microequivalents per liter.

Sulfate

The model to predict sulfate concentrations explains 63% of the variability in sulfate. The significant variables are the percentage of the basin which has not been disturbed prior to establishment of the GRSM and the percentage of the basin with Anakeesta Formations. Both of the independent variables were transformed to satisfy assumptions of regression. The amount of undisturbed area was transformed by squaring the values and the percent coverage of Anakeesta was transformed by taking the square root. The coefficients indicate that sulfate concentrations increase as the percent coverage in both undisturbed area and Anakeesta increases. It is interesting to compare the magnitudes of the coefficients on the amount of undisturbed area for the nitrate model and the sulfate model. The model to predict nitrate also included the percentage of undisturbed area as an independent variable. Its sign suggested that as the amount of undisturbed area increases, nitrate concentrations increase. Figure 4-10 and the earlier discussion demonstrated that undisturbed areas have a greater percentage of anions as nitrate. Notice that the magnitude of the coefficient on the amount of undisturbed area in the model to predict sulfate (0.002997) is much smaller than the coefficient in the model to predict nitrate (0.222). The difference between these two

coefficients is about 195 percent. This suggests that as the amount of undisturbed area in a basin increases, both sulfate and nitrate concentrations increase. However, the increase in nitrate is greater than that for sulfate. As was shown earlier with Figure 4-11 and the discussion, basins with a majority of Anakeesta coverage have a greater percentage of anions as sulfate. Notice the positive sign on the independent variable for percent coverage of Anakeesta in the model to predict sulfate concentrations.

The model should not be used when predicting sulfate concentrations at sites close to and immediately downstream of disturbed Anakeesta Formations. Two sites with disturbed Anakeesta upstream were removed from the analysis because they exerted a large influence on the resulting model. These included sites 251 and 252. The percentage of the basin that is undisturbed refers to the percent of the basin that was not logged or settled in a manner that "disturbed" conditions of the watershed. Disturbed Anakeesta Formations refer to areas where the geology was altered due to road construction or debris flows. The presence of percent coverage of Anakeesta in models for predicting conductivity and sulfate in basins with predominantly undisturbed Anakeesta upstream suggests that Anakeesta Formations which have not been disturbed do increase surface water sulfate concentrations and, correspondingly, conductivity.

The ranges, minimum and maximum, for both independent variables are 0% and 100%, respectively. The minimum, maximum, and median predicted sulfate concentrations are 21.32, 70.51, and 34.42 microequivalents per liter, respectively. The observed minimum, maximum, and median sulfate concentrations in sampled basins used to create the model are 9.07, 104.88, and 32.72 microequivalents per liter, respectively. Figure 4-13 is a plot of

predicted sulfate versus actual sulfate concentrations. Simple linear regression was performed on the predicted values and the actual values to compare the intercept and slope terms with what one would expect. The intercept and the slope terms were statistically significant ($p < 0.05$) and equal to 15.543 and 0.627, respectively. Figure 4-13 and the lower adjusted r-square compared to models for pH, ANC, and nitrate, indicate that the sulfate model does not perform as well.

A model which includes flow as an independent variable would probably explain more of the variability in sulfate. As mentioned in Chapter I, flow is not recorded when samples are collected. Other variables related to flow, such as stage, are also not recorded. Flow might be particularly important in explaining the variability of sulfate for a couple of reasons. The weathering of Anakeesta Formations is probably greater during periods with greater amounts of precipitation. Since foliar leaching and uptake of sulfate is minimal, it is a relatively “conservative” anion when compared to other anions such as nitrate. Research at Noland Divide Watershed in the GRSM during a storm event showed that sulfate concentrations were significantly higher on the rising and falling limbs of the hydrograph than in baseflow. There also did not appear to be dilution effects (McCann, 2000).

Chloride

The model for predicting median chloride concentrations in sampled GRSM basins is applicable for all regions of the Park. It was not necessary to exclude basins from model development due to influence. The significant variables in the final model include Limestone, Elkmont Sandstone, Northern Hardwood, and stream density. Limestone and Elkmont Sandstone occur primarily in Abrams Creek watershed and some portions of the

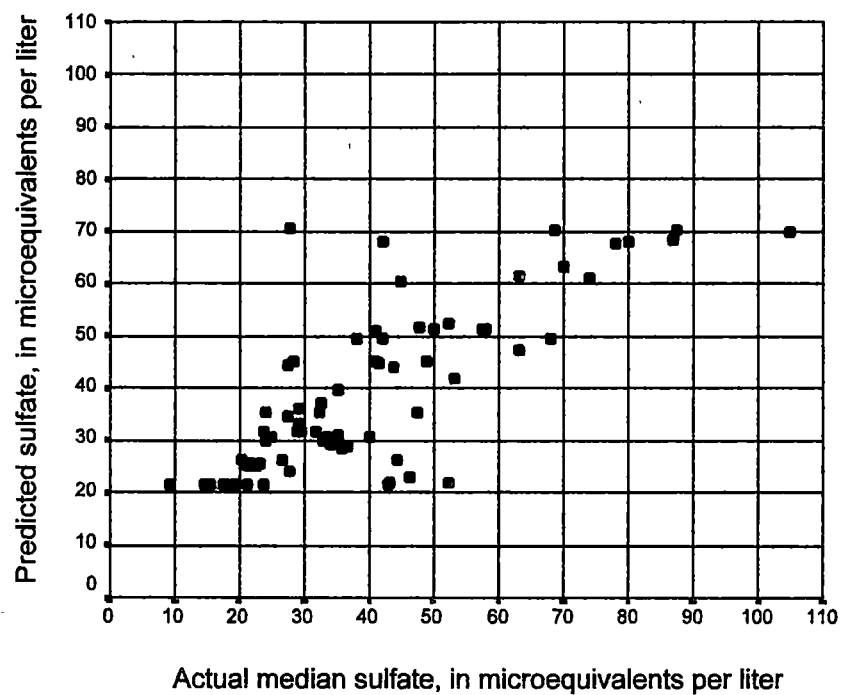


Figure 4-13. Predicted versus actual sulfate concentration from regression model to predict sulfate in sampled GRSM basins.

Little River watershed, respectively. The signs on both of the coefficients suggest that chloride concentrations increase as the percentage of basin area covered by Limestone and Elkmont Sandstone increases. The sign on the coefficient for stream density indicates that chloride concentrations decrease as stream density increases. The sampled basins with higher stream densities are located in the lower elevations of the GRSM based on results from correlation analysis presented in Table 4-2. The sign on Northern Hardwood indicates that as the percent coverage increases, chloride concentrations increase. The percentage of Northern Hardwood within a basin is positively correlated with elevation and mean elevation (see Table 4-2). Research at Hubbard Brook showed that throughfall and stemflow accounted for about 26% of the total annual flux of chloride from undisturbed forests studied (Likens *et al.*, 1977). The species which are included in the Northern Hardwood forests (see page 91) are described as large trees in *The Audubon Society Field Guide to North American Trees, Eastern Region* (Little, 1980). All species in the group can reach heights of 24 meters with diameters of 0.8 meters. Some species, like Sugar Maples, grow larger and reach heights of 30 meters with diameters of 0.9 meters. The surface area of the leaves on these large trees might capture a significant amount of the chloride input as both wet and dry deposition.

The ranges (minimum and maximum) for the independent variables in the model are as follows: Limestone (0.0%, 21.0%); Elkmont Sandstone (0.0%, 93.4%); Northern Hardwood (0.0%, 58.5%); stream density (0.1, 2.39 kilometers per square kilometer). The minimum, maximum, and median predicted chloride concentrations are 12.53, 22.04, and 13.73 microequivalents per liter, respectively. The observed minimum, maximum, and

median chloride concentrations in sampled basins used to create the model are 11.49, 20.71, and 13.78 microequivalents per liter, respectively.

Sodium

Sodium is another constituent which required two models to explain the variability in surface water concentrations and adhere to assumptions of multiple linear regression. As with the models to predict ANC and conductivity, one model is for basins that contain Limestone and the other is for basins with no Limestone present. Neither model should be used to predict sodium concentrations close to and downstream of sites where Anakeesta Formations have been significantly disturbed.

The model for basins with Limestone required transforming the single independent variable. The base 10 log of the percentage of the watershed covered with Limestone explained more of the variability. The adjusted r-square of the model using the base 10 log of Limestone is 0.88. Other transformations included the reciprocal and the square root. When these transformations were used, the adjusted r-square values of the resulting models were 0.74 and 0.72, respectively. As the amount of Limestone in a basin increases, sodium concentrations increase as well. In the Cades Cove area, surface water infiltrates into subsurface and permeable conduits composed of Limestone (Larson, 1986). As water flows through those conduits, there could be significant contributions from groundwater flow through the permeable Limestone rocks. Sodium is a common component of groundwater flow. This would explain the increase in sodium concentrations as percent coverage of Limestone increases.

The minimum, maximum, and median predicted sodium concentrations are 41.09,

57.33, and 50.58 microequivalents per liter, respectively. The observed minimum, maximum, and median sodium concentrations in sampled basins with Limestone are 41.20, 56.02, and 52.21 microequivalents per liter, respectively. The model in Table 4-5 should not be used for predicting sodium concentrations in basins with more than 21% of their area covered by Limestone.

The signs of the coefficients for the model to predict median sodium concentrations in basins with no Limestone present indicate that sodium concentrations decrease with increases in elevation. These results agree with the results of simple linear regression presented in Chapter I. The significant independent variables include the percent of the basin covered by Mixed Mesic Hardwood and the average basin slope. Mixed Mesic Hardwood forests are typically found in the lower elevations of the GRSM in areas that were logged prior to Park establishment. The forest type might be a surrogate variable for elevation influences and not be the cause of increased sodium concentrations in these sampled basins. The model to predict ANC in basins without Limestone predicts higher ANC at lower elevations. The results of this model and the one for ANC, again support the conclusion that sodium concentrations are closely related to groundwater flow. Similar conclusions were made from investigations at NDW where higher median sodium concentrations were found in stream water than in soil solutions at varying depths (McCann, 2000).

The ranges (minimum and maximum) for the independent variables in the model are as follows: Mixed Mesic Hardwood (0.0%, 49.3%); basin slope (25.3%, 72.1%). The minimum, maximum, and median predicted sodium concentrations are 20.22, 56.47, and 33.76 microequivalents per liter, respectively. The observed minimum, maximum, and

median sodium concentrations in sampled basins used to create the model are 21.96, 69.58, and 35.04 microequivalents per liter, respectively. Sample sites 251, 252, 253, and 237 were removed from the regression analysis due to their influence on the model results.

Potassium

The model reported in Table 4-5 to predict median concentrations of potassium is applicable to all sampled basins. It was not necessary to exclude any basins due to justifiable and strong influence. The significant independent variables are the percentage of basin area covered by Anakeesta Formations, basin slope, and the percentage of basin area with Northern Hardwood forests. The coefficients for all three variables are negative. As basin slope increases (basins at higher elevations), potassium concentrations decrease. The presence of Northern Hardwood forests is positively correlated with elevation and probably serves as a surrogate variable. The presence of Anakeesta might also be a surrogate variable for elevation. Higher potassium concentrations at lower elevations are consistent with results of sodium and ANC. All three of these water quality constituents have higher values at lower elevations of the GRSM and they are all common components of groundwater.

The ranges (minimum and maximum) for the independent variables in the model are as follows: basin slope (25.3%, 72.1%); Anakeesta (0.0%, 100.0%); and Northern Hardwood (0.0, 58.5). The minimum, maximum, and median predicted potassium concentrations are 2.82, 14.35, and 10.30 microequivalents per liter, respectively. The observed minimum, maximum, and median potassium concentrations in sampled basins used to create the model are 3.17, 16.78, and 10.29 microequivalents per liter, respectively. The model should only be used to predict potassium concentrations in basins with independent variables within the

ranges for model development.

Disturbed Anakeesta Sites

Due to the unique water chemistry close to and downstream of sites with disturbed Anakeesta, an attempt was made to predict important water quality constituent values such as pH, ANC, and sulfate when these conditions are present. However, the variability in the data could not be explained with the basin characteristics. This is due to the lack of a significant number of sites close to and downstream of disturbed Anakeesta Formations and because there is variability between the sites that exist in the sampling program. Some sites are immediately downstream of the disturbance and others vary with respect to the downstream distance between the sampling site and the disturbance.

Conclusions

From the results of the analyses presented, the following conclusions and observations were made:

1. Basin characteristics obtained from topographical maps and GIS databases can explain much of the variability in water quality constituent values of sampled basins in the GRSM. The adjusted r-square values for the models presented range from 0.55 for conductivity in basins without Limestone to 0.98 for ANC and conductivity in basins which contain Limestone. The results presented offer hope for using basin characteristics and stepwise multiple regression to predict water quality constituent values in unsampled and forested areas like the Great Smoky Mountains National Park. The results could also aid in selecting sites which might be important for

sampling in regional-scale assessments of water quality.

2. Although correlation analysis and the models presented do not simulate watershed processes, they can provide some insight into what might be controlling water quality. The conclusions which follow discuss the influences.
3. Two geologic formations, Limestone and Anakeesta, exert a significant influence on water chemistry in sampled basins. The application of only three models (nitrate, chloride, and potassium) is not restricted to basins which have either Limestone or Anakeesta Formations present. The influence of Anakeesta Formations is more profound if it has been disturbed by the construction of roads or by natural debris flows and the rocks are exposed to weathering. Models to predict pH, ANC, conductivity, sulfate, and sodium were heavily influenced by basins with disturbed Anakeesta Formations. The models to predict these constituents should not be used in basins with disturbed Anakeesta Formations. The presence of Limestone strongly influenced the models for ANC, conductivity, and sodium. Separate models were used to predict these constituents in basins with Limestone.
4. Limestone and Anakeesta have very different influences on water quality. The water draining from basins with Limestone is less acidic, has higher buffering capacity against acid input, and has elevated conductivity resulting from carbonate species. Basins with disturbed Anakeesta Formations are more acidic, have less acid neutralizing species, and elevated conductivity

due to increased concentrations of sulfate and neutralizing cations (probably hydrogen ions).

5. All three independent variables in the model to predict pH in sampled GRSM streams are related to elevation. They include mean basin elevation, basin slope, and stream order. The model explains 74% of the variability in pH. The signs on the independent variables indicate that pH decreases as elevation increases. There are numerous explanations for this trend. Limestone is present in basins located in the lower elevations (less than 523 meters above mean sea level) of the GRSM. The presence of Anakeesta Formations is positively correlated with elevation. Research at high elevations in the GRSM (greater than 1,720 meters) has shown an elevation gradient to deposition of acidifying species such as sulfate in throughfall. Researchers found that sulfate fluxes increased by about a factor of two due to higher cloudwater interception at 1,940 meters versus 1,720 meters (Shubzda *et al.*, 1995). This elevation gradient to deposition of acidifying species is another explanation to the variability in pH with respect to elevation. Another possible influence which explains the trend includes the presence of undisturbed areas at the upper elevations of the GRSM. The amount of undisturbed area and nitrate concentrations are positively correlated with each other (see Table 4-3). The percentage of undisturbed area is negatively correlated with pH. In soils low in base cations or with a tendency to conserve base cations, charge balance can be maintained by the

leaching of hydrogen ions and aluminum (Cosby *et al.*, 1985). It is possible that hydrogen ions are the principal cations maintaining charge balance in surface waters draining basins with undisturbed areas. Sodium and potassium are negatively correlated with the amount of undisturbed area. Therefore, they are probably not the principal cations maintaining charge balance. Calcium and magnesium could also be important cations.

6. Two models were required to predict the variability of ANC in sampled basins. One model predicts ANC in basins which contain Limestone and it explains 98% of the variability in ANC. The only independent variable in the model is the percentage of the basin underlain by Limestone. As the amount of Limestone in a basin increases, ANC also increases due to increases in concentrations of acid neutralizing species such as carbonate and bicarbonate. The other model is for basins which do not have Limestone present. This model explains 81% of the variability in ANC and includes independent variables directly and indirectly related to elevation. The signs on the independent variables indicate that ANC decreases with increases in elevation. The reasons given to explain the trends in decreasing pH with respect to elevation also explain the variability in ANC.
7. Two models were also required to predict the variability of conductivity in sampled basins. One model predicts conductivity in basins which contain Limestone and it explains 98% of the variability. The only independent variable in the model is the percentage of the basin underlain by Limestone.

As the amount of Limestone in a basin increases, conductivity also increases due to increases in concentrations of acid neutralizing species such as carbonate and bicarbonate. The other model is for basins which do not have Limestone present. This model explains 55% of the variability in conductivity. The independent variables are the percentage of the basin underlain by Anakeesta Formations and the percentage of the basin which has not been disturbed by logging and settlement prior to establishment of the GRSM. As the amount of undisturbed area and area with Anakeesta increases, the concentrations of nitrate and sulfate increase, respectively. As the concentrations of these anions increase, the concentration of neutralizing cations (probably hydrogen ions) increases as well and there is a corresponding increase in ionic strength.

8. The independent variables in the model to predict nitrate include percent undisturbed, elevation class, stream density, percent Mixed Mesic Hardwood, and percent Anakeesta. This model explains 87% of the variability of nitrate in sampled basins. Basins with a majority of undisturbed area have a greater percentage of anions as nitrate. The model predicts that nitrate concentrations increase as the percentage of undisturbed area increases. The coefficients on elevation class and stream density indicate that as elevation increases, nitrate concentrations increase. Mixed Mesic Hardwood forests are located at the lower elevations (below 750 meters) in areas that have been settled or logged. The coefficient on Mixed Mesic Hardwood is consistent

with other variables. The negative coefficient suggests that as elevation decreases and the amount of disturbed area increases, nitrate concentrations in surface water decrease as well. The coefficient on the independent variable Anakeesta indicates that as the amount of basin area covered by these formations increases, nitrate concentrations decrease. The major anion in sampled surface water in basins with a majority of their watershed underlain by Anakeesta (greater than 50%) is sulfate.

9. The model to predict sulfate concentrations explains 63% of the variability in sulfate. The significant variables are the percentage of the basin which has not been disturbed prior to establishment of the GRSM and the percentage of the basin with Anakeesta Formations. The magnitude of the coefficient on the amount of undisturbed area in the model to predict sulfate (0.002997) is much smaller than the coefficient in the model to predict nitrate (0.222). The difference between these two coefficients is about 195 percent. This suggests that as the amount of undisturbed area in a basin increases, both sulfate and nitrate concentrations increase. However, the increase in nitrate is greater than that for sulfate. As mentioned, basins with a majority of Anakeesta coverage have a greater percentage of anions as sulfate. As the percentage of basin area underlain by Anakeesta increases, sulfate concentrations increase as well.
10. The presence of percent coverage of Anakeesta in models for predicting conductivity and sulfate in basins with predominantly undisturbed Anakeesta

upstream suggests that Anakeesta Formations which have not been disturbed do increase surface water sulfate concentrations and, correspondingly, conductivity. However, pH does not appear to be significantly influenced.

11. The significant variables in the final model to predict chloride concentrations include Limestone, Elkmont Sandstone, Northern Hardwood, and stream density. The model explains 60% of the variability in chloride. The signs on the independent variables did not reveal an elevation trend and it is unclear as to what might be controlling chloride concentrations in sampled GRSM streams.
12. Sodium is another constituent which required two models to explain the variability in surface water concentrations and adhere to assumptions of multiple linear regression. As with the models to predict ANC and conductivity, one model is for basins that contain Limestone and the other is for basins with no Limestone present. The relationship between sodium and percent Limestone is logarithmic and the model explains 88% of the variability in sodium. As the amount of Limestone in a basin increases, sodium concentrations increase as well. In the Cades Cove area, surface water infiltrates into subsurface and permeable conduits composed of Limestone (Larson, 1986). As water flows through those conduits, there could be significant contributions from groundwater flow through the permeable Limestone rocks. Sodium is a common component of groundwater flow. This would explain the increase in sodium concentrations

as percent coverage of Limestone increases. For basins which do not contain Limestone, the significant independent variables include the percent of the basin covered by Mixed Mesic Hardwood and the average basin slope. The signs of the coefficients predict that sodium concentrations decrease with increases in elevation. Mixed Mesic Hardwood forests are typically found in the lower elevations of the GRSM in areas that were logged prior to Park establishment. The forest type might be a surrogate variable for elevation influences and not be the cause of increased sodium concentrations in these sampled basins. The model to predict ANC in basins without Limestone predicts higher ANC at lower elevations. The results of this model and the one for ANC, again support the conclusion that sodium concentrations are closely related to groundwater flow. Similar conclusions were made from investigations at NDW where higher median sodium concentrations were found in stream water than in soil solutions at varying depths (McCann, 2000).

13. The model to predict potassium concentrations explains 70% of the variability. The independent variables include basin slope, Anakeesta, and Northern Hardwood. The coefficients for all three variables are negative. As basin slope increases (basins at higher elevations), potassium concentrations decrease. The presence of Northern Hardwood forests is positively correlated with elevation and probably serves as a surrogate variable. The presence of Anakeesta might also be a surrogate variable for elevation. Higher potassium

concentrations at lower elevations are consistent with results of sodium and ANC. All three of these water quality constituents have higher values at lower elevations of the GRSM and they are all common components of groundwater.

14. It was not possible to model water quality in basins with disturbed Anakeesta Formation. This is due to the lack of a significant number of sites close to and downstream of disturbed Anakeesta Formations and because there is variability between the sites that exist in the sampling program. Some sites are immediately downstream of the disturbance and others vary with respect to the downstream distance between the sampling site and the disturbance.

CHAPTER V. TEMPORAL VARIABILITY OF WATER QUALITY

Seasonal Variability

Data

Samples collected from the 90 sites which are still covered in the quarterly sampling program were analyzed for differences between sampling periods. The data set includes samples collected from October 1993 to October 1998. Samples collected in October 1993 were the first samples collected in the Park-wide water quality monitoring effort. The constituents analyzed for seasonal variability include pH, acid neutralizing capacity (ANC), conductivity, nitrate, sulfate, chloride, sodium, and potassium. Table 5-1 shows that about 77% of the samples were collected during the months of March, May, August, and October. Table 5-1 also shows which months are included in each sampling period. These sampling times are intended to represent winter, spring, summer, and autumn, respectively. The rationale for these seasonal groupings is discussed below.

Useful data also included historical flow information from the United States Geological Survey (USGS) gaging station located at the boundary of the Great Smoky Mountains National Park (GRSM) in Townsend, TN on the Little River. This data set included historical daily mean flow rates from January 1993 to October 1998.

Methods of Analysis

To assess seasonal variability, each month was assigned to a season based on the activity of plant life and precipitation (flow) amounts so that similar months were grouped together. Sampling period one includes months when plants become active after a dormant winter period and flow rates are similar. Figure 5-1 shows the variability of flow by month

Table 5-1. Distribution of samples collected with respect to time of year.

Month	Sampling period	Percentage of samples
1	4	1.9
2	4	5.5
3	4	19.9
4	4	3.1
5	1	19.0
6	1	1.6
7	2	3.3
8	2	18.0
9	2	3.2
10	3	20.4
11	3	0.5
12	4	3.6

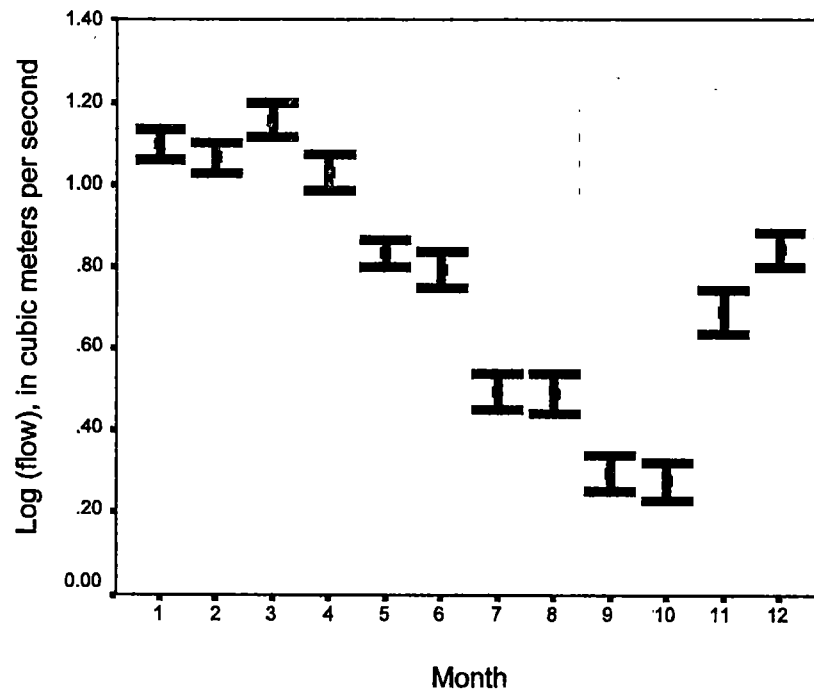


Figure 5-1. Confidence intervals (95%) of historical monthly mean flow from USGS gage on the Little River.

on the Little River. Daily mean flow rates were used to construct the 95% confidence interval for each month to give historical monthly mean flow rates. The log of flow was used to generate the 95% confidence intervals since the distribution of log (flow) approximates the normal distribution better for such a parametric analysis. As can be seen in Figure 5-1, May and June have similar flows and constitute sampling period one. Sampling period two includes months when precipitation and flow are decreasing and foliage on plants is at a maximum. Sampling period three includes months when the growing season is ending and many plants begin to lose their foliage. Almost all of the samples in sampling period three were collected in October (see Table 5-1). Figure 5-1 shows that October is typically the driest month of the year. Sampling period four, including the months of December through April, is characterized by higher precipitation and flow and inactive plants.

These sampling periods were compared and tested for differences in water quality and flow rates using the non-parametric Kruskal-Wallis (KW) H test since the distributions of most analytes and flow rates with respect to sampling periods were not normal. Normality testing was done by inspection of box plots, skewness, and kurtosis. The distributions were considered non normal if skewness and kurtosis indices were more than one away from zero. Initially, the Kruskal-Wallis H test was done by checking to see if at least one sampling period was different from the others. If this step indicated at least one was different, then each sampling period was compared to determine which sampling periods differ.

Results and Discussion

Seasonal differences determined by the Kruskal-Wallis H test are summarized in Table 5-2. Summary statistics of the actual constituent values for each sampling period are

Table 5-2. Summary of sampling period differences.

Constituent	Sampling periods compared							Mean rank from highest to lowest	Percent differences between sampling period median values ^c
	1-2	1-3	1-4	2-3	2-4	3-4	All ^e		
pH								3>(2&1)>4	1.24;2.06
ANC ^a								3>2>1>4	29.90;48.90;68.56
ANC ^b								3>2>1>4	32.37;51.21;76.21
ANC ^c								(3&2)>(1&4)	69.97
Conductivity ^a								(3&2)>1>4	9.60;12.79
Conductivity ^b								(3&2)>1>4	9.31;12.97
Conductivity ^c								(3&2)>(1&4)	57.17
Nitrate								4>(2&1)>3	21.95;86.11
Sulfate								no differences	no differences
Chloride								3>(4&1&2)	18.09
Potassium								3>(2&4)>1	25.79;32.07
Sodium								3>2>1>4	8.78;23.94;30.04
Flow ^d								4>1>2>3	54.57;125.85;139.97

Shaded regions are significantly different (KW significance <0.05).

^aIncludes all sampled watersheds.

^bIncludes all sampled watersheds except Abrams.

^cIncludes only sites 156, 174, and 489 within Abrams.

^dTaken from historical monthly mean flow rates on the Little River.

^ePercent difference between median constituent value of sampling period with highest mean rank to all other sampling periods.

*Shaded if at least one sampling period initially was determined to be different from the others.

provided in Tables 5-3 through 5-6 for reference and comparison. Figures 5-2 through 5-12 show box plots of the distributions of the constituents by sampling period. See Chapter III, pages 26 and 27, for explanation of the information contained in the box plots. To clarify Table 5-2 and how it should be interpreted, consider pH. The column which shows the mean ranks indicates that pH is the highest during sampling period three. Sampling periods two and one are grouped together in a parenthesis since a significant difference was not found to exist. Sampling period four had the lowest pH values. The last column shows the percent difference between median constituent values of the sampling period with highest mean rank to all other sampling periods. For example, there is a 1.24% difference between the higher median pH values during sampling period three to median pH values during sampling periods two and one. There is a 2.06% difference between median pH values during sampling period three to median pH values during sampling period four. Although statistically significant differences exist between sampling periods with respect to pH values, the percent differences between sampling periods are less than five percent.

By inspection of Table 5-2, a consistent trend is apparent. As noted earlier, almost all of the samples in sampling period three were collected during October. October is characterized by low surface water flow resulting from typically dry summers and low precipitation amounts during October. Table 5-2 shows that sampling period three has the lowest flow based on the mean rank from the results of Kruskal-Wallis H test. November was not included in the analysis since only 0.5% of all the samples were collected in November. Therefore, surface flow during October results from base flow. The streams have higher concentrations of constituents commonly found in groundwater such as

Table 5-3. Summary statistics for sampling period one.

Constituent	Mean	Median	Standard deviation	Minimum-maximum
pH	6.20	6.32	0.51	4.77-7.77
ANC ^a	62.08	38.70	129.85	-19.13-1,392.16
ANC ^b	41.89	37.44	32.38	-19.13-158.38
ANC ^c	684.49	663.27	355.78	254.58-1,392.16
Conductivity ^a	17.79	14.58	13.55	1.35-134.80
Conductivity ^b	16.36	14.70	7.90	1.35-94.81
Conductivity ^c	72.56	74.05	32.67	29.80-134.80
Nitrate	23.13	18.95	18.12	0.00-97.71
Sulfate	43.91	34.48	41.13	3.91-452.19
Chloride	14.68	13.39	4.75	1.66-46.65
Potassium	9.63	8.98	8.82	1.44-153.53
Sodium	32.90	31.58	10.91	5.45-69.81
Flow ^d	8.06	6.05	7.00	2.01-79.29

Note: All units are microequivalents per liter except conductivity (microsiemens per centimeter) and flow (cubic meters per second). Zeroes denote below detection limit.

^aIncludes all sampled watersheds.

^bIncludes all sampled watersheds except Abrams.

^cIncludes only sites 156, 174, and 489 within Abrams.

^dTaken from historical monthly mean flow rates on the Little River.

Table 5-4. Summary statistics for sampling period two.

Constituent	Mean	Median	Standard deviation	Minimum-maximum
pH	6.21	6.30	0.54	4.03-7.73
ANC ^a	86.80	47.17	191.24	-113.12-1,542.61
ANC ^b	53.96	45.60	45.23	-17.75-225.18
ANC ^c	928.61	778.35	447.99	124.30-1,542.61
Conductivity ^a	19.85	16.06	17.86	1.17-161.10
Conductivity ^b	17.27	16.13	6.03	1.17-55.40
Conductivity ^c	96.82	79.85	46.20	16.81-161.10
Nitrate	22.32	19.62	16.06	0.00-96.31
Sulfate	44.81	35.41	38.41	5.39-374.05
Chloride	14.44	13.31	5.40	3.74-54.52
Potassium	9.79	9.39	4.21	0.00-29.04
Sodium	38.02	36.79	12.53	5.72-81.81
Flow ^d	3.85	2.41	5.57	0.62-88.35

Note: All units are microequivalents per liter except conductivity (microsiemens per centimeter) and flow (cubic meters per second). Zeroes denote below detection limit.

^aIncludes all sampled watersheds.

^bIncludes all sampled watersheds except Abrams.

^cIncludes only sites 156, 174, and 489 within Abrams.

^dTaken from historical monthly mean flow rates on the Little River.

Table 5-5. Summary statistics for sampling period three.

Constituent	Mean	Median	Standard deviation	Minimum-maximum
pH	6.31	6.37	0.48	4.23-8.24
ANC ^a	104.82	63.75	216.18	-40.51-1,624.49
ANC ^b	70.41	63.21	49.04	-40.51-248.53
ANC ^c	1,216.27	1,449.81	450.64	531.80-1,624.49
Conductivity ^a	20.88	16.04	22.96	7.02-252.00
Conductivity ^b	18.07	16.14	13.99	7.02-252.00
Conductivity ^c	117.96	137.20	41.88	47.60-160.30
Nitrate	15.94	9.57	18.88	0.00-97.96
Sulfate	44.23	34.85	38.38	6.62-445.74
Chloride	20.47	16.14	11.79	7.31-91.67
Potassium	12.62	12.41	4.56	0.00-30.94
Sodium	41.83	40.17	13.20	2.30-87.91
Flow ^d	2.74	1.87	4.34	0.71-45.87

Note: All units are microequivalents per liter except conductivity (microsiemens per centimeter) and flow (cubic meters per second). Zeroes denote below detection limit.

^aIncludes all sampled watersheds.

^bIncludes all sampled watersheds except Abrams.

^cIncludes only sites 156, 174, and 489 within Abrams.

^dTaken from historical monthly mean flow rates on the Little River.

Table 5-6. Summary statistics for sampling period four.

Constituent	Mean	Median	Standard deviation	Minimum-maximum
pH	6.12	6.24	0.52	4.56-7.66
ANC ^a	48.32	31.20	98.33	-30.56-1,239.26
ANC ^b	33.40	28.33	31.63	-24.64-360.95
ANC ^c	488.09	409.96	284.82	183.61-1,239.26
Conductivity ^a	16.48	14.12	10.83	6.60-131.20
Conductivity ^b	15.40	14.17	6.98	6.73-76.40
Conductivity ^c	55.16	46.50	27.11	24.40-131.20
Nitrate	26.73	24.04	19.26	0.00-101.22
Sulfate	45.65	36.88	43.32	6.21-511.48
Chloride	15.90	13.69	7.34	7.76-68.02
Potassium	9.74	9.76	4.26	0.00-42.54
Sodium	31.15	29.68	11.14	8.59-89.51
Flow ^d	14.57	10.59	17.42	2.15-254.85

Note: All units are microequivalents per liter except conductivity (microsiemens per centimeter) and flow (cubic meters per second). Zeroes denote below detection limit.

^aIncludes all sampled watersheds.

^bIncludes all sampled watersheds except Abrams.

^cIncludes only sites 156, 174, and 489 within Abrams.

^dTaken from historical monthly mean flow rates on the Little River.

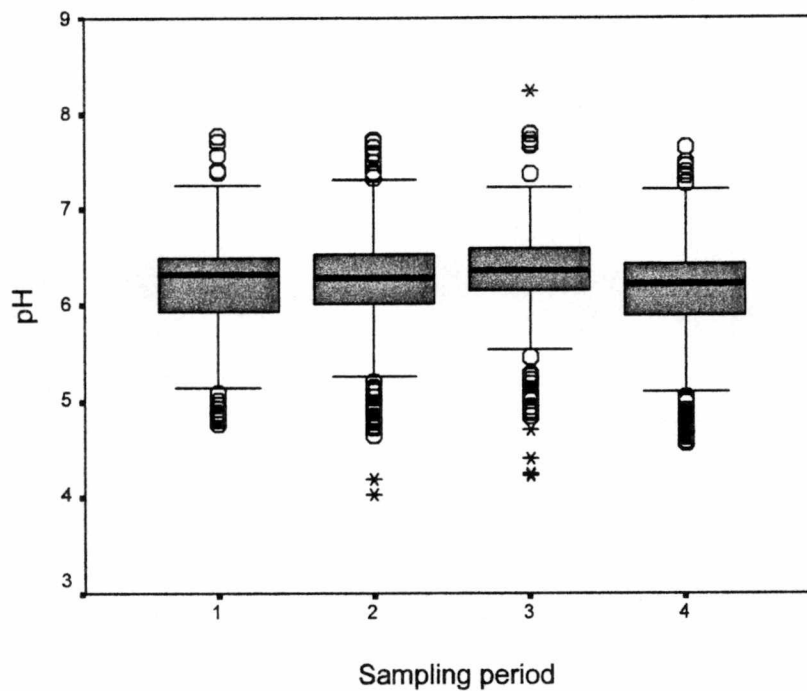


Figure 5-2. Distribution of pH with respect to sampling period.

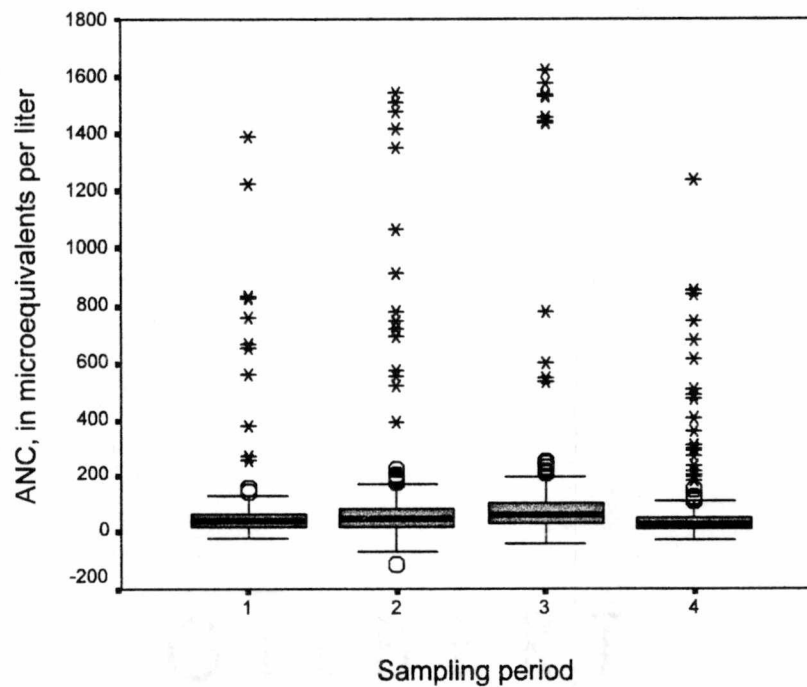
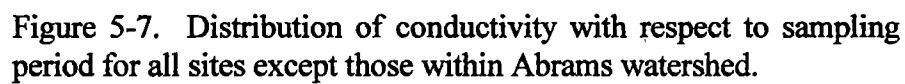
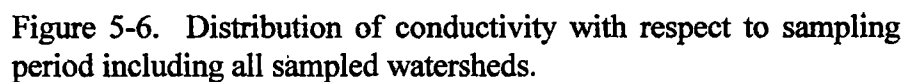


Figure 5-3. Distribution of acid neutralizing capacity with respect to sampling period including all sampled watersheds.



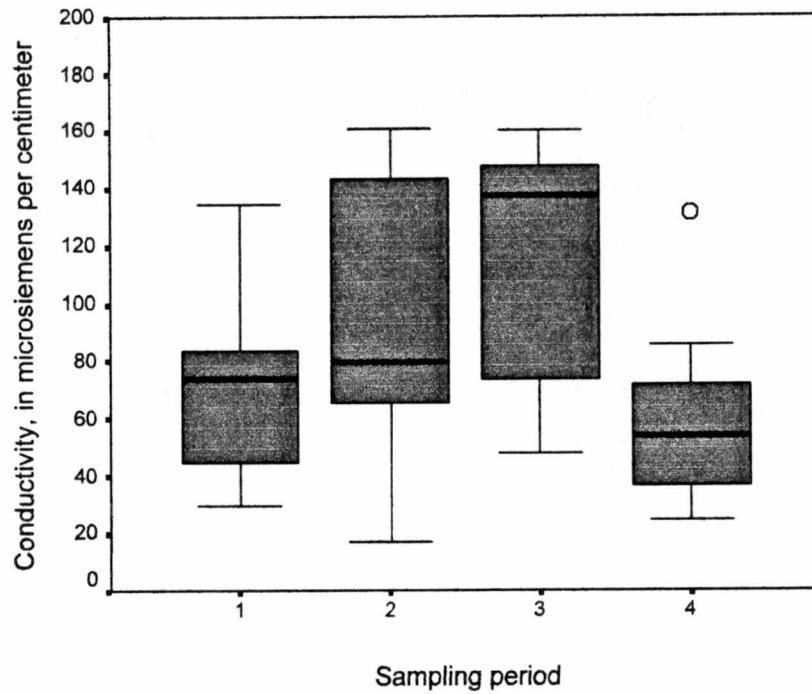


Figure 5-8. Distribution of conductivity with respect to sampling period for sites 156, 174, and 489 within Abrams watershed.

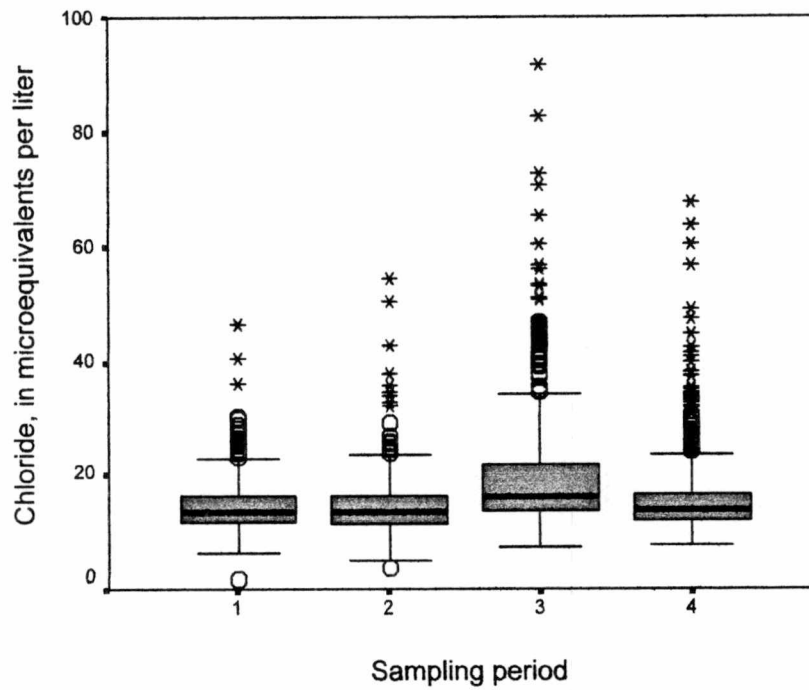


Figure 5-9. Distribution of chloride with respect to sampling period.

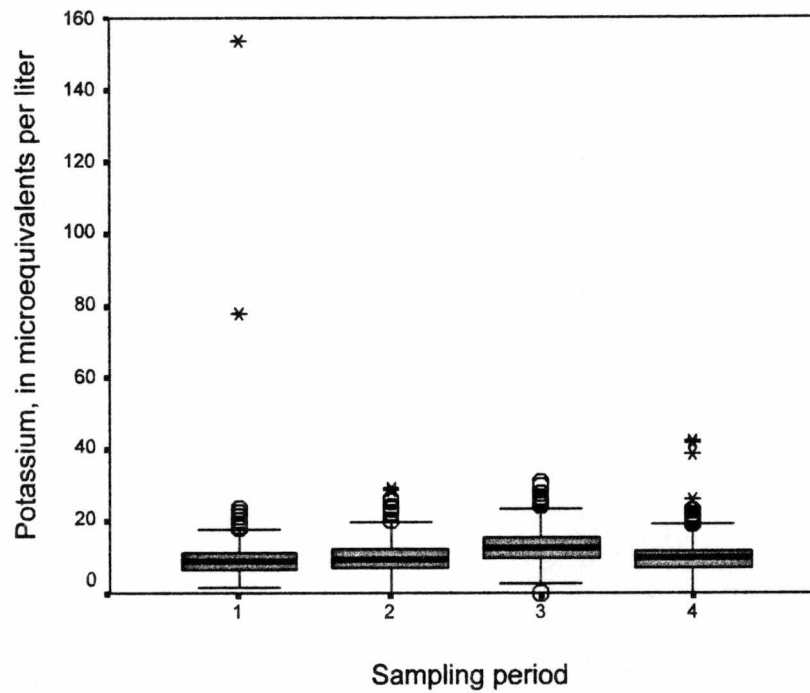


Figure 5-10. Distribution of potassium with respect to sampling period.

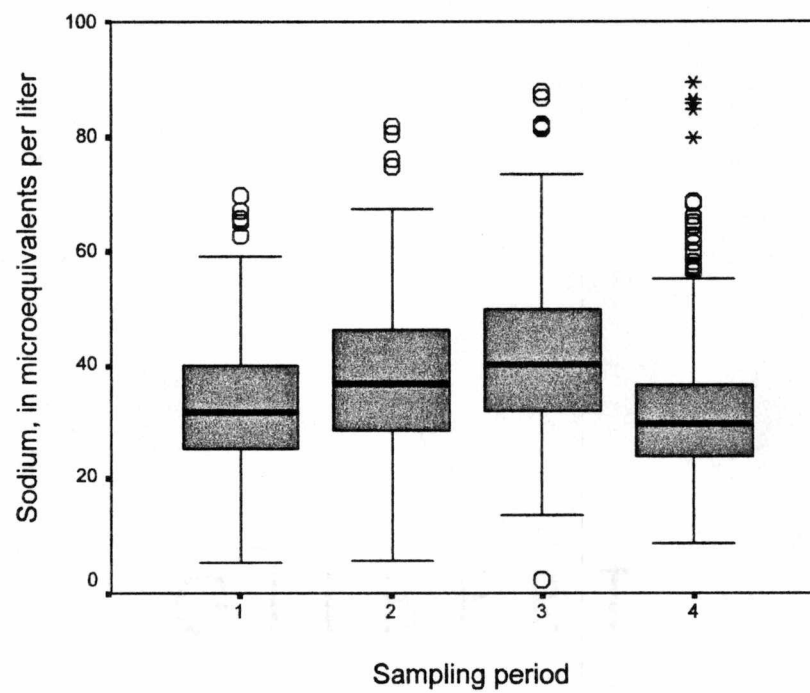


Figure 5-11. Distribution of sodium with respect to sampling period.

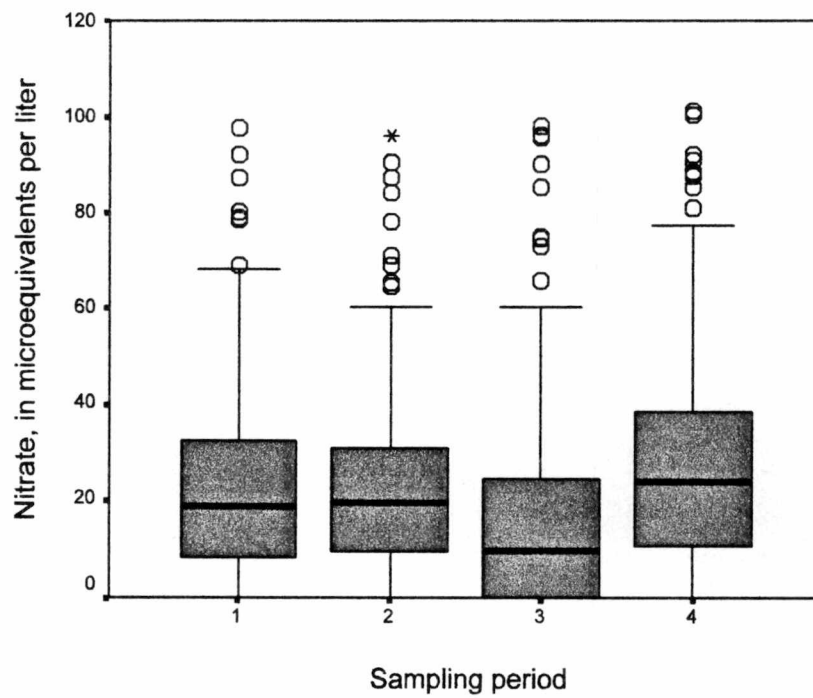


Figure 5-12. Distribution of nitrate with respect to sampling period.

potassium, sodium, chloride, and carbonate species. Carbonate species contribute to acid neutralizing capacity and tend to correlate with higher pH. The presence of these anions and cations in greater concentrations explains the high conductivity during sampling period three. The percent differences between median constituent values during sampling period three to median values during sampling periods with higher surface water flow (four, one, and two), show that for most cases the percent differences are greater than 10 percent. In many cases the percent differences are much greater than 10 percent. Acid neutralizing capacity not only shows statistically significant differences between sampling periods, but the percent differences between median values during sampling period three and median values during sampling periods with higher surface water flow are all greater than 29% and are as high as about 76 percent. There is an 18% difference between median chloride concentrations during sampling period three to median chloride concentrations during sampling periods four, one, and two. There is a 26% difference between median potassium concentrations during sampling period three to median concentrations during sampling periods two and four. The percent difference between median potassium concentrations during sampling period three to median values during sampling period one is 32 percent. There is only an 8% difference between median sodium concentrations during sampling period three to median values during sampling period two. The percent differences between median sodium concentrations during sampling period three to sampling periods one and four are 24% and 30%, respectively.

Figures 5-2 through 5-11 show box plots of the distributions of these constituents across sampling periods. Figures 5-3 through 5-8 are box plots of acid neutralizing capacity

and conductivity with respect to sampling period for different watersheds and sites. As discussed in Chapters III and IV, Abrams Creek watershed is unique because some of the lower elevation sites in the Cades Cove area are underlain by limestone, particularly sites 156, 174, and 489. Most of the GRSM is underlain by sandstone formations which result in water with low acid neutralizing capacity and low ionic strength (Elwood *et al.*, 1991). However, similar seasonal trends exist between sites not within Abrams Creek watershed and those within Abrams Creek watershed and underlain by limestone. One might expect that sites underlain by primarily sandstones and inert geologic formations would not show the same trends as sites underlain by more soluble limestone formations which contribute to changes in water quality. As expected though, they do differ with respect to the concentrations of acid neutralizing species and conductance. The sites underlain by limestone in Abrams watershed show higher ANC (70% difference between periods with most and least surface water flow) and higher conductivity (57% difference between periods with most and least surface water flow) in the drier times of the year. The sites not within Abrams do show much lower acid neutralizing capacity and conductance (see Tables 5-3 through 5-6). Sites not within Abrams watershed have median ANC values of 37.44, 45.60, 63.21, and 28.33 during sampling periods one, two, three, and four, respectively. Sites within Abrams have median ANC values of 663.27, 778.35, 1,449.81, and 409.96 during sampling periods one, two, three, and four, respectively. Therefore, the percent differences between median ANC values for sites within Abrams watershed and sites not within Abrams with respect to sampling periods are all greater than 174 percent. The percent differences between median conductivity values for sites within Abrams watershed and sites not within

Abrams with respect to sampling periods are all greater than 106 percent.

Nitrate concentrations are the highest during sampling period four. Table 5-2 shows that the percent differences between median nitrate concentrations during sampling period four and other sampling periods are 22% (sampling periods two and one) and 86% (sampling period three). The decaying organic matter, high in total nitrogen, probably contributes to the increased concentrations found in surface water. Sampling period three, perhaps unexpectedly, shows the lowest concentrations of nitrate. During sampling period three, foliage begins to fall and decay. As mentioned, most of the samples are collected in October. By this time the leaves have changed color but most of the leaves probably fall in November. Sampling in November might show higher nitrate concentrations in sampling period three. With the current sampling scheme they are the lowest during sampling period three perhaps because foliage remains on the plants and because sampling in October comes toward the end of the growing season and the plants have consumed much of the nitrogen in the soil. Figure 5-12 shows the distribution of nitrate across sampling periods.

Interestingly, sulfate concentrations did not show any statistically significant seasonal differences.

Some of Figures 5-2 through 5-12 might lead one to conclude that there are not significant differences between the different sampling periods that Table 5-2 shows exist. However, the sample population must be considered. Increases in the sample population increase the confidence one can have in measures of location such as the median. Therefore, when statistically significant differences are found between median values of two large sample populations, the difference is probably a "real" difference rather than one resulting

from not having enough observations to adequately reflect reality. For example, compare Figures 5-3 and 5-5. Figure 5-3 was generated by including all sampled watersheds. Assuming no samples were missed and laboratory results were obtained from all samples, then 450 is the sample population (90 sites over five years) for each box plot in Figure 5-3. Figure 5-5 was generated from data for only three sites. Therefore, 15 is the sample population for each box plot. Notice that the boxes in Figure 5-3 are very small and show the decreased variability about the median from such a large sample population. The boxes in Figure 5-5 are much larger due to the greater variability about the median from a smaller sample population.

Comparison with Previous Results

Others have found some similar seasonal trends, with a few exceptions, in the Great Smoky Mountains National Park. At low elevations, research has shown higher values for alkalinity, conductivity, and turbidity during drier times of the year. At higher elevations, the seasonal variability for these parameters was not significant. For pH, no significant difference was found at any elevation (Silsbee and Larson, 1982). High elevation was defined as watersheds with a mean basin elevation greater than 1,350 meters (4,430 feet) above mean sea level. Research at Noland Divide Watershed (NDW), a watershed with an elevation range of 1,695 to 1,940 meters (5,560-6,365 feet), has shown lower pH and higher conductivity during months with more rainfall. During drier months, higher pH and lower conductivity values were found (McCann, 2000). In this study about 63% of the sampling sites have a mean basin elevation less than or equal to 1,350 meters. Due to the predominance of sampling sites at lower elevations, the results in this study agree with those

by Silsbee and Larson with respect to higher conductivity and the greater presence of species which contribute to alkalinity during drier times of the year. Trends in pH are probably revealed in this study due to the extended period of time that samples have been collected and analyzed. The Silsbee and Larson study was conducted from October 1977 to September 1978. This study comprises five years and therefore the chances of detecting seasonal differences in pH and other constituent values is much greater. The reasons higher conductivity values were observed at NDW during months with more rainfall are not clear. It is possible that rainfall at higher elevations has more ionic species in solution from acid deposition of sulfate and nitrate.

Seasonal variability of nitrate concentrations found in this study are also similar to those found by Silsbee and Larson and McCann. Silsbee and Larson found nitrate concentrations to be the lowest in the fall (sampling period three) and highest in the winter (sampling period four). Work at NDW shows nitrate concentrations to be the lowest in the summer and highest during the winter and early spring. As mentioned earlier, samples were collected in October for this study. During October the growing season is over but significant decomposition has probably not occurred. Therefore, results at NDW and this study agree because nitrate concentrations are the lowest toward the end of the growing season but before foliage decays. Nitrate concentrations are the highest after foliage has had time to decay and before the plants become highly active.

The work by Silsbee and Larson did not analyze for sulfate, so comparisons between their results and the results of this study cannot be made. Sulfate concentrations were found to be seasonally different in the NDW. Sulfate concentrations were higher during periods

of more rainfall, generally in the winter. This is probably due to the presence of higher concentrations of sulfate in the rainfall itself (McCann, 2000). Seasonal differences are probably not detected in this study due to the predominance of sites at lower elevations, which receive less precipitation, and dilution of the water deposited at higher elevations as it moves downstream.

The results of this analysis provide some insight for managers of natural resources within the Great Smoky Mountains National Park. Since pH and ANC are the highest during the drier times of the year, then these times of the year might be the best times to take any actions which might affect the trout populations or the populations of organisms which trouts depend on for food. Trout and some of the organisms which they depend on are sensitive to depressions in pH. Research has shown that at pH values between 6.0 and 6.5 the water becomes uninhabitable for sensitive benthic invertebrates. When pH is between 5.5 and 6.0 there is a loss of acid sensitive fish and reduced reproduction (Baker *et al.*, 1996). Based on a review of the literature by some authors, the critical pH values for the trout found in GRSM waters are 5.5 for rainbow trout, 5.4 for brown trout, and 5.2 for brook or "speckled" trout (Baker and Christensen, 1991).

Temporal Variability

Data

The same water quality data set that was used to investigate seasonal variability was used in the following analyses for long-term trends. The data set was organized by elevation class to include sites with similar elevations. Table 5-7 shows the elevation classes, the

Table 5-7. Elevation classes defined for data analysis.

Elevation class	Range of elevation, in meters above mean sea level	Number of sampling sites
1	less than 305	0
2	305-457	7
3	457-610	13
4	610-762	16
5	762-914	18
6	914-1,067	13
7	1,067-1,219	4
8	1,219-1,372	6
9	1,372-1,524	7
10	1,524-1,676	3
11	greater than 1,676	3

range of elevation included in each, and the number of sample sites in each elevation class.

Methods of Analysis

Analyses of pH, ANC, conductivity, nitrate, and sulfate data were done to identify trends over time within the different elevation classes. It was necessary to perform trend analysis on sites with similar elevations since much of the variability in constituent concentrations and values can be explained by elevation. This was discussed in Chapters III and IV. The days when samples were collected were identified by the Julian day. Then, to be consistent with other time trends performed on data at NDW, January 1, 1991 was designated as day number one and each sample was assigned a cumulative Julian day. This corresponds to the number of days after January 1, 1991 that the sample was collected and defines the independent variable. To account for seasonal fluctuations that might be present in the trends over time, the sine and cosine functions were used to model seasonal oscillations. This required transforming the time variable. Transforming the time variable was accomplished by determining the fractional portion of a year that had elapsed when the sample was collected. This fractional portion of the year was then multiplied by 2π so that one year would represent one complete period of the sine and cosine functions. The constituent values, such as pH, were normalized by dividing the measured value for a particular sampling site by the calculated median value for that site. Normalizing the data was necessary because of the variability in constituent values between sites within the same elevation class. The equation used in regressions to model the data and identify time trends is as follows:

$$\text{normalized pH} = a + b \cdot \cos\theta + c \cdot \sin\theta + d \cdot t$$

where normalized pH = predicted normalized pH
 $\theta = 2\pi \cdot (\text{fraction of a year})$
 $t = \text{cumulative Julian days}$

To perform the regressions, the following procedure was used for each constituent and for each elevation class. First, all three independent variables were entered into the model. If all were determined to be significant ($p < 0.10$), then the process was stopped. If one was not significant, then the following was done. If the time variable, t , was not significant, then the model was rerun with time removed. The seasonal variables ($\cos\theta$ and $\sin\theta$) were then reexamined for significance. If they were significant, then the process was stopped again and the new coefficients were reported. If the first run showed only one of the seasonal variables was insignificant but time was significant, then both seasonal variables were kept and the coefficients were reported. If both seasonal variables were determined insignificant after the first run, then they were removed. The model was rerun with only the time variable and the new coefficient reported. When only one seasonal variable was insignificant, both were kept in the model because the absence of one affects the phase shift of the function (Helsel and Hirsch, 1992).

Time trend analyses were performed only for pH, ANC, conductivity, nitrate, and sulfate because they are more important with respect to effects on biological communities than other constituents such as sodium and potassium.

Results

The results of the time trend analyses are summarized in Tables 5-8 through 5-13. With respect to the constant and the time variable, if the coefficients are reported in the

Table 5-8. Time trend analysis of normalized pH.

Elevation class	Model	r ²	Model p
2	normalized pH=1.017+(-1.899E-02)•cosθ+(-1.262E-02)•sinθ+(-1.008E-05)•t	0.214	0.000
3	normalized pH=1.032+(-1.167E-02)•cosθ+(-6.695E-03)•sinθ+(-1.580E-05)•t	0.099	0.000
4	normalized pH=1.025+(-1.210E-05)•t	0.044	0.000
5	normalized pH=1.024+(-8.517E-03)•cosθ+(-7.697E-03)•sinθ+(-1.385E-05)•t	0.103	0.000
6	normalized pH=1.036+(-9.153E-03)•cosθ+(-1.498E-02)•sinθ+(-2.016E-05)t	0.232	0.000
7	normalized pH=0.996+(-8.964E-03)•cosθ+(-2.321E-02)•sinθ	0.262	0.000
8		0.032	0.225
9	normalized pH=1.014+(-2.020E-02)•cosθ+(-8.178E-03)•sinθ	0.030	0.105
10	normalized pH=1.071+(-3.561E-05)•t	0.132	0.002
11		0.041	0.487

Note: Shaded regions denote all independent variables were insignificant (p>0.10).

Table 5-9. Time trend analysis of normalized hydrogen ion concentration.

Elevation class	Model	r ²	Model p
2	normalized $H^+ = 1.211 + (0.306) \cdot \cos\theta + (0.155) \cdot \sin\theta$	0.060	0.005
3	normalized $H^+ = 0.756 + (0.238) \cdot \cos\theta + (5.873E-02) \cdot \sin\theta + (2.102E-04) \cdot t$	0.032	0.034
4	normalized $H^+ = 0.631 + (8.796E-02) \cdot \cos\theta + (4.686E-02) \cdot \sin\theta + (2.260E-04) \cdot t$	0.071	0.000
5	normalized $H^+ = 0.702 + (0.176) \cdot \cos\theta + (0.118) \cdot \sin\theta + (2.295E-04) \cdot t$	0.069	0.000
6	normalized $H^+ = 0.401 + (0.193) \cdot \cos\theta + (0.257) \cdot \sin\theta + (3.968E-04) \cdot t$	0.182	0.000
7	normalized $H^+ = 1.297 + (0.188) \cdot \cos\theta + (0.536) \cdot \sin\theta$	0.150	0.003
8		0.007	0.801
9	normalized $H^+ = 0.669 + (0.195) \cdot \cos\theta + (-1.251E-02) \cdot \sin\theta + (2.070E-04) \cdot t$	0.070	0.015
10		0.065	0.235
11	normalized $H^+ = 1.293 + (0.405) \cdot \cos\theta + (-0.176) \cdot \sin\theta$	0.086	0.070

Note: Shaded regions denote all independent variables were insignificant ($p > 0.10$).

Table 5-10. Time trend analysis of normalized ANC.

Elevation class	Model	r ²	Model p
2	normalized ANC=1.049+(-0.210)•cosθ+(-0.374)•sinθ	0.551	0.000
3	normalized ANC=1.122+(-7.078E-02)•cosθ+(-0.343)•sinθ	0.150	0.000
4	normalized ANC=1.249+(-0.114)•cosθ+(-0.349)•sinθ	0.075	0.000
5	normalized ANC=1.087+(-1.520E-02)•cosθ+(-0.341)•sinθ	0.096	0.000
6	normalized ANC=1.156+(-4.608E-02)•cosθ+(-0.470)•sinθ	0.173	0.000
7	normalized ANC=1.177+(-0.150)•cosθ+(-0.625)•sinθ	0.379	0.000
8		0.017	0.515
9		0.027	0.259
10	normalized ANC=1.112+(-0.146)•cosθ+(-0.435)•sinθ	0.126	0.014
11		0.025	0.693

Note: Shaded regions denote all independent variables were insignificant (p>0.10).

Table 5-11. Time trend analysis of normalized conductivity.

Elevation class	Model	r ²	Model p
2	normalized conductivity=1.024+(-0.109)•cosθ+(-0.199)•sinθ	0.445	0.000
3	normalized conductivity=1.025+(-6.654E-02)•cosθ+(-0.123)•sinθ	0.109	0.000
4	normalized conductivity=1.001+(-1.492E-02)•cosθ+(-7.292E-02)•sinθ	0.156	0.000
5	normalized conductivity=1.134+(-7.202E-02)•cosθ+(-7.501E-02)•sinθ+(-6.002E-05)•t	0.099	0.000
6	normalized conductivity=1.012+(-8.508E-02)•cosθ+(-3.816E-02)•sinθ	0.057	0.000
7	normalized conductivity=1.008+(-5.301E-02)•cosθ+(-7.951E-02)•sinθ	0.262	0.000
8		0.032	0.236
9		0.012	0.623
10	normalized conductivity=0.993+(-3.270E-03)•cosθ+(-6.896E-02)•sinθ	0.177	0.002
11		0.099	0.113

Note: Shaded regions denote all independent variables were insignificant (p>0.10).

Table 5-12. Time trend analysis of normalized nitrate.

Elevation class	Model	r ²	Model p
2	normalized nitrate=1.011+(9.702E-02)•cosθ+(0.418)•sinθ	0.224	0.000
3	normalized nitrate=0.983+(-4.033E-02)•cosθ+(0.273)•sinθ	0.170	0.000
4	normalized nitrate=0.996+(-7.091E-02)•cosθ+(0.370)•sinθ	0.112	0.000
5	normalized nitrate=0.964+(-6.683E-02)•cosθ+(0.236)•sinθ	0.159	0.000
6	normalized nitrate=1.133+(2.251E-02)•cosθ+(0.207)•sinθ+(-7.142E-05)•t	0.205	0.000
7	normalized nitrate=0.790+(0.148)•cosθ+(9.153E-02)•sinθ+(1.400E-04)•t	0.125	0.026
8	normalized nitrate=0.819+(0.246)•cosθ+(0.118)•sinθ+(1.239E-04)•t	0.152	0.000
9	normalized nitrate=1.036+(0.143)•cosθ+(7.273E-02)•sinθ	0.155	0.000
10		0.037	0.492
11	normalized nitrate=1.465+(0.120)•cosθ+(0.122)•sinθ+(-2.681E-04)•t	0.464	0.000

Note: Shaded region denotes all independent variables were insignificant (p>0.10).

Table 5-13. Time trend analysis of normalized sulfate.

Elevation class	Model	r ²	Model p
2	normalized sulfate=1.036+(7.639E-02)•cosθ+(-1.489E-02)•sinθ	0.048	0.015
3	normalized sulfate=1.132+(8.872E-02)•cosθ+(-1.656E-02)•sinθ+(-4.829E-05)•t	0.066	0.000
4	normalized sulfate=1.025+(7.068E-02)•cosθ+(-8.026E-04)•sinθ	0.014	0.150
5	normalized sulfate=1.045+(8.769E-02)•cosθ+(1.965E-02)•sinθ	0.061	0.000
6		0.010	0.331
7		0.027	0.587
8		0.033	0.222
9		0.007	0.790
10	normalized sulfate=1.054+(9.605E-02)•cosθ+(-0.109)•sinθ	0.129	0.012
11	normalized sulfate=1.153+(0.199)•cosθ+(-0.156)•sinθ	0.117	0.025

Note: Shaded regions denote all independent variables were insignificant (p>0.10).

model, then they are statistically significant ($p < 0.10$). If the coefficients are reported for the seasonal variables, then at least one of them is statistically significant ($p < 0.10$). In Tables 5-8 through 5-13, the model r-square and the overall model p are also reported. Table 5-14 shows summary statistics for each elevation class and constituent for reference and comparison.

Table 5-8 shows the results of the analysis for normalized pH. The coefficients of the slope are negative for six elevation classes, suggesting a decreasing trend in normalized pH of sampled streams over time.

A similar analysis was performed on normalized hydrogen ion concentrations. Table 5-9 shows the results of the analysis. As expected, the trends are similar to the results for normalized pH. Within five of the elevation classes, the coefficients of the slope are positive, suggesting an increasing trend in normalized hydrogen ion concentrations over time.

Table 5-10 shows the results of the time trend analysis on normalized ANC. Unexpectedly, normalized ANC did not show the same decreasing trend as normalized pH. Normalized ANC showed no trends over time, increasing or decreasing. This is probably due to greater variability in normalized ANC from one site to another within the elevation classes. Table 5-14 shows the standard deviation in ANC values within the elevation classes. Compared to the dispersion in pH between elevation classes, ANC dispersion is much greater.

Normalized conductivity showed a decreasing trend over time within one elevation class (see Table 5-11). Since the trend was only significant for one elevation class, whether

Table 5-14. Summary statistics for different elevation classes.

Class	pH			ANC			Conductivity			Nitrate			Sulfate		
	Mean	Median	σ	Mean	Mean	σ	Mean	Median	σ	Mean	Median	σ	Mean	Median	σ
2	6.66	6.64	0.32	145.78	102.80	140.73	23.16	19.20	12.91	10.51	7.05	9.37	44.18	40.43	12.14
3	6.57	6.47	0.40	200.95	67.08	370.11	26.94	15.10	34.33	11.50	11.26	7.56	35.63	32.78	12.86
4	6.34	6.39	0.30	59.63	59.71	38.20	13.67	13.39	2.57	12.80	8.99	11.98	32.84	28.66	17.58
5	6.30	6.35	0.30	51.62	45.77	32.30	14.82	14.36	4.13	18.79	16.64	14.60	36.77	28.75	20.19
6	6.12	6.17	0.34	30.97	26.69	23.35	14.30	13.20	4.53	23.88	23.77	13.05	42.94	36.79	24.53
7	6.18	6.17	0.28	41.47	27.27	34.82	20.41	19.15	4.57	35.23	34.85	9.99	71.19	70.67	19.49
8	5.85	5.85	0.46	22.32	17.63	40.18	20.05	19.03	8.48	34.69	36.94	17.09	74.80	65.83	55.44
9	5.74	5.95	0.68	31.62	33.99	34.23	20.84	17.35	15.20	34.58	30.52	19.96	72.80	35.69	108.9
10	5.66	5.80	0.49	18.10	18.05	15.10	17.32	16.14	4.42	49.91	47.34	13.81	37.70	28.63	17.72
11	5.11	5.05	0.38	2.14	0.34	18.22	22.85	17.65	30.24	64.31	67.41	22.52	38.04	30.57	17.92

Note: All units are microequivalents per liter except conductivity (microsiemens per centimeter).

or not a trend really exists cannot be determined from this analysis with confidence.

Normalized nitrate showed different trends (see Table 5-12). Within two of the elevation classes normalized nitrate shows an increasing trend over time. However, within two elevation classes concentrations appear to be decreasing over time.

Normalized sulfate (see Table 5-13) showed a decreasing trend over time within only one elevation class. Since the trend was only significant for one of the elevation classes, whether or not a trend really exists cannot be determined from this analysis with confidence.

Discussion of Results

Time trend analysis aims to answer two important questions. One is "Are things getting better or worse?" The next question is more quantitative. If things are found to be getting worse, one next wants to know by how much and how quickly. Answering these questions requires an extensive data set over time. The analyses presented here comprise data collected over five years and attempts to explain the variability over time with sine and cosine functions for seasonal variation. It is possible that other variables, such as flow, might explain much of the variability as well and should therefore be included in the model. Flow information is not available for the analysis. Samples are collected consistently at the same locations throughout the GRSM, but flow measurements are not made at the time of collection. The results of these analyses attempt to answer both questions whenever possible.

Figure 5-13 was generated from the data and the model for elevation class six. The slope suggests that within elevation class six, normalized pH has decreased 0.74% per year. This value was obtained by multiplying the coefficient of the time variable by 365 to get 0.0074. Since the constituent values were normalized by division with the median, then pH

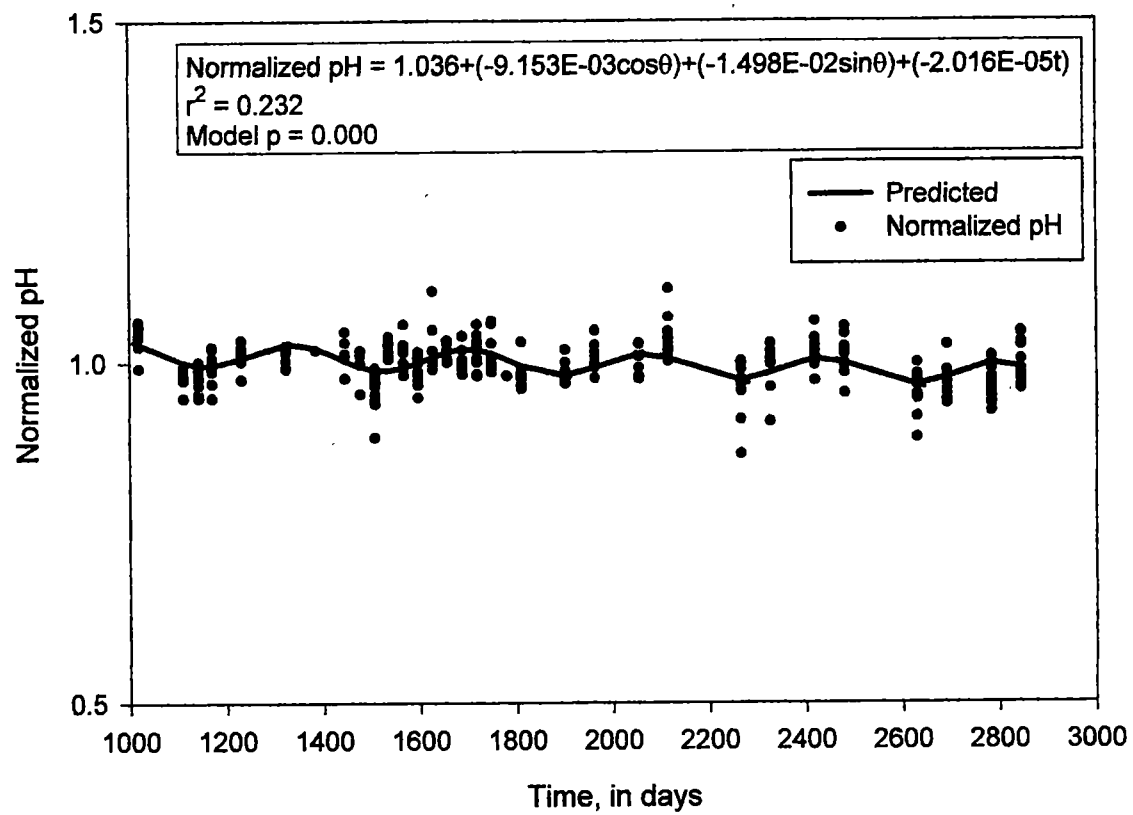


Figure 5-13. Time trend for pH within elevation class six (914-1,067 meters).

has decreased from the median by 0.74% per year. The low r-square value (0.232) indicates that seasonal and time factors explain only 23% of the statistical variance of normalized pH. The remaining 77% of the variance is due to factors unaccounted for in the model. However, the analysis suggests a significant decreasing trend in normalized pH over time, especially at lower elevations.

The annual percent decrease in normalized pH from the time trend analysis can be used to estimate when sampled GRSM streams might reach critical pH values mentioned in earlier chapters (see Table 3-2) and in the analysis of seasonal variability. Table 5-15 summarizes those estimations. Notice that the time required for pH to reach critical pH values appears to increase with decreases in elevation. Sampling sites between 1,524 meters and 1,676 meters (5,000 feet to 5,500 feet) above mean sea level might have pH values less than or equal to 5.50 within four years and less than or equal to 5.00 within 11 years. At the lower elevations, between 305 meters and 457 meters (1,000 feet and 1,500 feet), sampling sites might have pH values less than or equal to 5.50 within 46 years and less than or equal to 5.00 within 67 years. When pH is between 5.5 and 6.0 there is a loss of acid sensitive fish and reduced reproduction (Baker *et al.*, 1996). At 5.0, the pH will be below the critical pH for all species of trout found in GRSM streams. Table 5-15 shows that within 26 years sampled GRSM streams at the lower elevations (305 meters to 457 meters) might have pH values near 6.00. The time required for sampling sites at higher elevations (914 meters to 1,067 meters) to reach 6.00 appears to be only four years. Research has shown that at pH values between 6.0 and 6.5 the water becomes uninhabitable for sensitive benthic invertebrates (Baker *et al.*, 1996).

Table 5-15. Summary of time to critical pH values within the elevation classes.

Class	Median pH	% annual decrease in normalized pH	t to 6.50	t to 6.00	t to 5.50	t to 5.00
2	6.64	0.37	6	26	46	67
3	6.47	0.58		13	26	39
4	6.39	0.44		14	32	50
5	6.35	0.51		11	26	42
6	6.17	0.74		4	15	26
7	6.17					
8	5.85					
9	5.95					
10	5.80	1.30			4	11
11	5.05					

Note: Time (t) to critical pH values is in years. Shaded regions indicate no significant trend.

The lower elevations probably respond slower due to the presence of geologic formations at lower elevations which buffer against changes in pH. However, further research is required to verify this. Elevation gradients in the flux of sulfates in throughfall might explain why shorter times to critical pH values are predicted for higher elevations. Research at high elevations in the GRSM (greater than 1,720 meters) has shown an elevation gradient to deposition of acidifying species such as sulfate in throughfall. Researchers found that sulfate fluxes increased by about a factor of two due to higher cloudwater interception at 1,940 meters versus 1,720 meters (Shubzda *et al.*, 1995).

The results of time trends for normalized hydrogen ion concentrations are consistent with those found for normalized pH. Figure 5-14 shows the results of the analysis within elevation class six. The NDW monitoring site lies in elevation class eleven. Tables 5-8 and 5-9 show no statistically significant long-term time trends for elevation class eleven. This is consistent with the research at NDW, which showed no significant changes in pH over time (McCann, 2000).

The lack of significant slope terms for normalized ANC and normalized conductivity suggest that values are not changing over time. However, it is possible that significant trends exist but are not revealed by the analysis presented here. Research by others in Virginia showed a possible decrease in future alkalinity by as much as 90 microequivalents per liter (Webb *et al.*, 1989). This prediction assumes that of the acid anions only sulfate has changed historically or will continue to change in the future as streams approach a steady state condition with atmospheric deposition. The authors estimate that the trout streams studied in Virginia would require a minimum of about 50 years to reach this steady state condition.

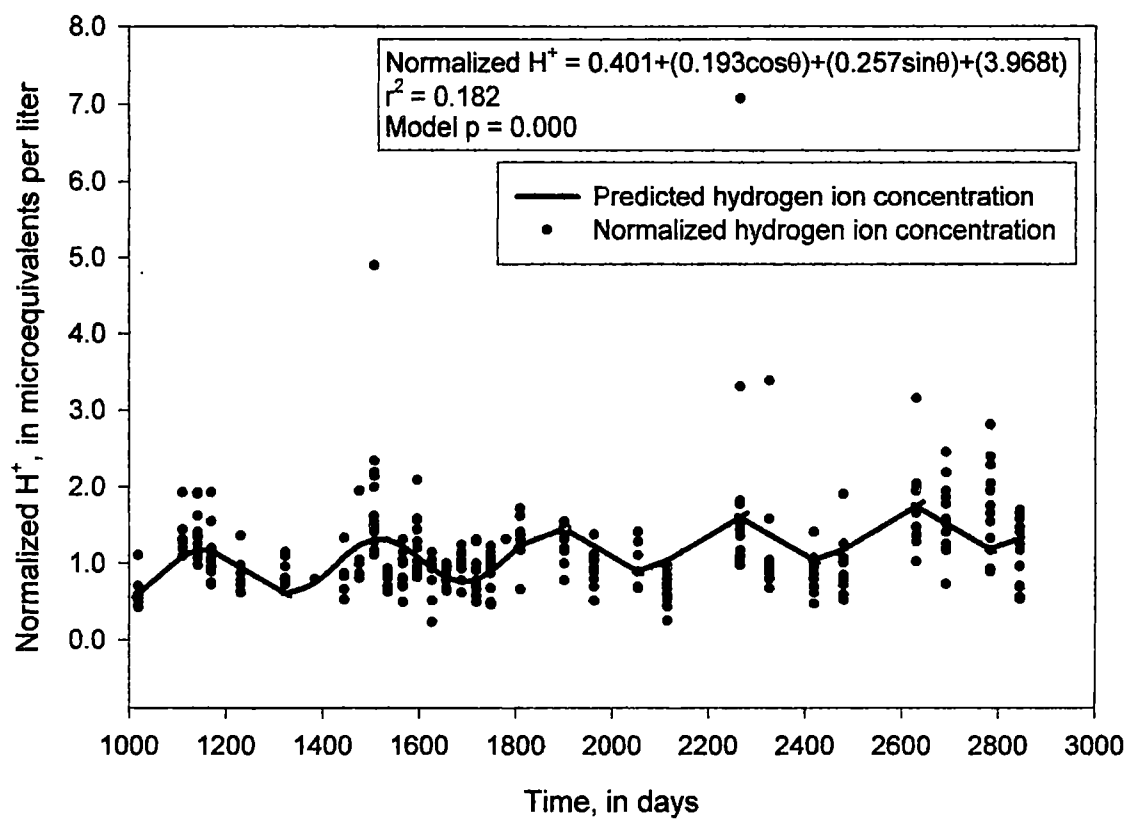


Figure 5-14. Time trend for hydrogen ion concentration within elevation class six (914-1,067 meters).

Normalized nitrate concentrations showed different trends within different elevation classes. Research at NDW showed that nitrate concentrations and loads have significantly decreased over time (McCann, 2000). The author suggests that the decreasing trend in nitrate concentration is explained by changes in the watershed due to infestation of Frasier firs by the balsam woody adelgid. The death of many trees in this high elevation watershed resulted in a drastic reduction of canopy cover. This allowed for increased growth in the understory and many young Frasier firs were able to grow well because the woody adelgid was unable to land on the smooth bark. During this period of rapid forest growth, nitrate was taken up rapidly as well (McCann, 2000). The results of this analysis are consistent with results found at Noland. Within elevation class 11, normalized nitrate concentrations show a decreasing trend over time. The model for this elevation class also has the highest r-square value (0.464).

Results from this analysis showed a decreasing trend over time for normalized sulfate concentrations within one of the lower elevation classes. The lack of a consistent trend within multiple elevation classes leads one to conclude that either a trend does not exist or it is not revealed by the data and analysis. The research at NDW supports the conclusion that a trend does not exist. Regression models on NDW data showed no significant long-term trend in sulfate loads or concentrations (McCann, 2000). Research on throughfall deposition at NDW has shown that sulfate concentrations are decreasing over time but loads are not changing (Shubzda *et al.*, 1995; Nodvin *et al.*, 1995).

Based on the lack of significant trends over time or the lack of consistent trends, it is not possible to give estimations like those presented for pH for future constituent values

of ANC, conductivity, nitrate, and sulfate.

Conclusions

From the results of the analyses of seasonal variability and long-term trends, the following conclusions and observations were made:

1. Seasonal trends were found to be statistically significant for pH, ANC, conductivity, nitrate, chloride, potassium, and sodium. Values for pH and ANC were higher during sampling periods three and two, which are typically drier than other times of the year. Although statistically significant differences exist between sampling periods with respect to pH values, the percent differences between sampling periods are less than five percent. Acid neutralizing capacity not only shows statistically significant differences between sampling periods, but the percent differences between median values during sampling period three and median values during sampling periods with higher surface water flow are all greater than 29% and are as high as about 76 percent. Concentrations of chloride, potassium, and sodium were also higher during the drier sampling periods. There is an 18% difference between median chloride concentrations during sampling period three to median chloride concentrations during sampling periods four, one, and two. There is a 26% difference between median potassium concentrations during sampling period three to median concentrations during sampling periods two and four. The percent difference between median potassium concentrations during sampling period three to median values during sampling period one

is 32 percent. There is only an 8% difference between median sodium concentrations during sampling period three to median values during sampling period two. The percent differences between median sodium concentrations during sampling period three to sampling periods one and four are 24% and 30%, respectively. Groundwater flow during these dry periods probably explains the higher concentrations and higher values for pH and ANC.

2. With respect to ANC and conductivity, similar seasonal trends were found between sites with contributing areas underlain by predominately unreactive geologic formations and those with more reactive geologic formations, such as limestone and dolomite, located in Cades Cove. As expected, the sites within Cades Cove did show much higher values of conductivity and greater acid neutralizing capacity than other areas of the GRSM. The sites underlain by limestone in Abrams watershed show higher ANC (70% difference between periods with most and least surface water flow) and higher conductivity (57% difference between periods with most and least surface water flow) in the drier times of the year. The percent differences between median ANC values for sites within Abrams watershed and sites not within Abrams with respect to sampling periods are all greater than 174 percent. The percent differences between median conductivity values for sites within Abrams watershed and sites not within Abrams with respect to sampling periods are all greater than 106 percent.

3. Nitrate concentrations were highest during sampling period four. The percent differences between median nitrate concentrations during sampling period four and other sampling periods are 22% (sampling periods two and one) and 86% (sampling period three). Sampling during November instead of October might show higher concentrations of nitrate during sampling period three.
4. Sulfate concentrations did not show seasonal differences.
5. Time trend analysis revealed a statistically significant decreasing trend in normalized pH over time. The time required for pH to reach critical values appears to increase with decreases in elevation. Sampling sites between 1,524 meters and 1,676 meters (5,000 feet to 5,500 feet) above mean sea level might have pH values less than or equal to 5.50 within only four years and less than or equal to 5.00 within only 11 years. At the lower elevations, between 305 meters and 457 meters (1,000 feet and 1,500 feet), sampling sites might have pH values less than or equal to 5.50 within 46 years and less than or equal to 5.00 within 67 years. At pH values between 5.5 and 6.0, there is a significant loss of acid sensitive fish and reduced reproduction (Baker *et al.*, 1996). At 5.0, the pH will be just below the critical pH for all species of trout found in GRSM streams. Within 26 years sampled GRSM streams at the lower elevations (305 meters to 457 meters) might have pH values near 6.00. The time required for sampling sites at higher elevations (914 meters to 1,067 meters) to reach 6.00 appears to be only four years. Research has shown that at pH values between 6.0 and 6.5 the water becomes

uninhabitable for sensitive benthic invertebrates (Baker *et al.*, 1996).

6. Unexpectedly, normalized ANC did not show the same decreasing trend over time as normalized pH. Normalized ANC showed no trends over time, increasing or decreasing. This is probably due to greater variability in ANC from one site to another within the elevation classes.
7. Results of time trend analyses for normalized values of conductivity, nitrate, and sulfate are less conclusive. Normalized conductivity showed a decreasing trend over time within only one elevation class. Whether or not any trends exist cannot be determined with confidence from these analyses. Normalized nitrate showed conflicting trends, increasing concentrations within two elevation classes and decreasing within two. Research at NDW, within elevation class 11, showed that nitrate concentrations and loads have significantly decreased over time. From the results of this analysis, normalized nitrate concentrations show a decreasing trend over time within elevation class 11. The model for this elevation class also had the highest r-square value (0.464). Decreasing nitrate concentrations and loads at NDW have been attributed to forest regrowth. Normalized sulfate concentrations showed a decreasing trend over time within only one of the lower elevation classes. The lack of a consistent trend within multiple elevation classes leads one to conclude that either a trend does not exist or it is not revealed by the data and analysis. Research at NDW supports the conclusion that a trend does not exist.

CHAPTER VI. ANALYSIS OF FLOW DATA

Data

Flow information from two United States Geological Survey (USGS) gaging stations located within the boundaries of the Great Smoky Mountains National Park (GRSM) was collected to investigate how well the past and current quarterly sampling program represents the different flow conditions that have occurred over the years. Quarterly sampling periods were discussed in Chapter V. The gaging stations which provided the data for the following analysis include Cataloochee Creek near Cataloochee, North Carolina (USGS#03460000) and Little River above Townsend (USGS#03497300). The Cataloochee station is located about five kilometers upstream from the boundary of the GRSM near Waterville Lake (see Figure 3-1). Sampling site 147 is located on the opposite stream bank of the gaging station. The drainage area to the station is 12,742 hectares. The Little River gaging station is about 0.6 kilometers upstream from the Park boundary along State Road 73 (see Figure 3-2). The drainage area to the station is 27,454 hectares. The map straight-line distance between the two stations is about 61.5 kilometers. Data retrieved from these two stations include the daily mean flow rates for the period of October 1993 to October 1998, the annual mean flow rates (calendar years 1964 to 1998), and the annual peak flow rates (water years 1963 to 1998). The Little River at Townsend station began reporting these values in water year 1963. Data from the Cataloochee station goes back much further, but water year 1963 was selected due to the lack of data for the Little River.

Methods of Analysis

The daily mean flow rates from the two gaging stations were assumed to represent

flow conditions throughout the Park from October 1993 to 1998. All analyses of water quality constituents in this report have included this time period. Frequency distributions were generated using the Weibull plotting position formula. It has been used by others for plotting flow-duration and flood frequency curves (Helsel and Hirsch, 1992). The Weibull formula used to determine the probability of exceedance is as follows:

$$\text{Probability of exceedance} = m/(n+1)$$

where

m = rank of flow values

n = total number of observations

To generate the probability plots, the daily mean flow rates are sorted from highest to lowest and ranked. The formula above determines the probability of exceedance for the corresponding mean daily flow. The daily mean flow rates are then plotted against the exceedance probability on log-probability paper. Eight probability plots were generated to analyze the data since there are four sampling periods and data from two gaging stations. Separate frequency distributions were generated by using the mean daily flow rates for the days in which samples were collected. The two distributions, daily mean flow and sampled flow, were plotted on the same graph and the distributions compared. If the sampled flow represents the range of flow from the historical records well, then the two distributions should appear very similar. This also enables one to see what flow rates are not represented well. As discussed in Chapter V, most samples (77%) were collected during the months of March, May, August, and October (see Table 5-1). When constructing the probability plots,

only these months were used. Including other months would place too much weight on mean daily flow rates for months when much fewer samples were collected.

The assumption that the daily mean flow rates from the two gaging stations represent conditions throughout the GRSM was evaluated by comparing the historical annual mean flow rates and the historical annual peak discharges between the two stations. If these two stations are to represent general flow conditions throughout the Park, then they themselves should show similarities.

Results and Discussion

The frequency distributions discussed are shown in Figures 6-1 through 6-8. Figures 6-1 and 6-2 are for samples collected during sampling period one. Figures 6-3 and 6-4 are for samples collected during sampling period two. Figures 6-5 and 6-6 are for samples collected during sampling period three and 6-7 and 6-8 for sampling period four. The figures show that samples are usually collected during "average" flow conditions. The exceedance probabilities appear to be between 0.05 and 0.95 for all sampling periods. This means that when samples are collected, the percentage of the time that the flow is higher than the flow at the time of collection is 5% and 95%. These are high flow conditions and low flow conditions, respectively. The exceedance probabilities are a function of the number of sampling data points. Sampling periods one, two, and four have 12 sampling data points. The Weibull plotting method will automatically give 7.7% (1/13) and 92.3% (12/13) probabilities. As the number of sampling data points increases, the range of flows represented increases. The figures do show that the higher flow conditions (storm flows) are not represented by the current sampling strategy. Notice in Figures 6-1 through 6-8 that the

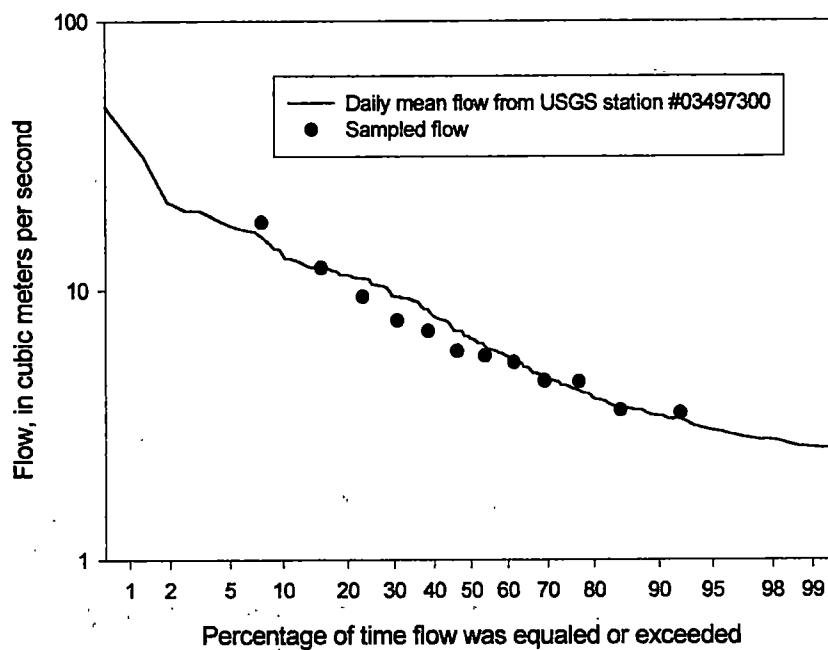


Figure 6-1. Frequency distributions during sampling period one for the Little River.

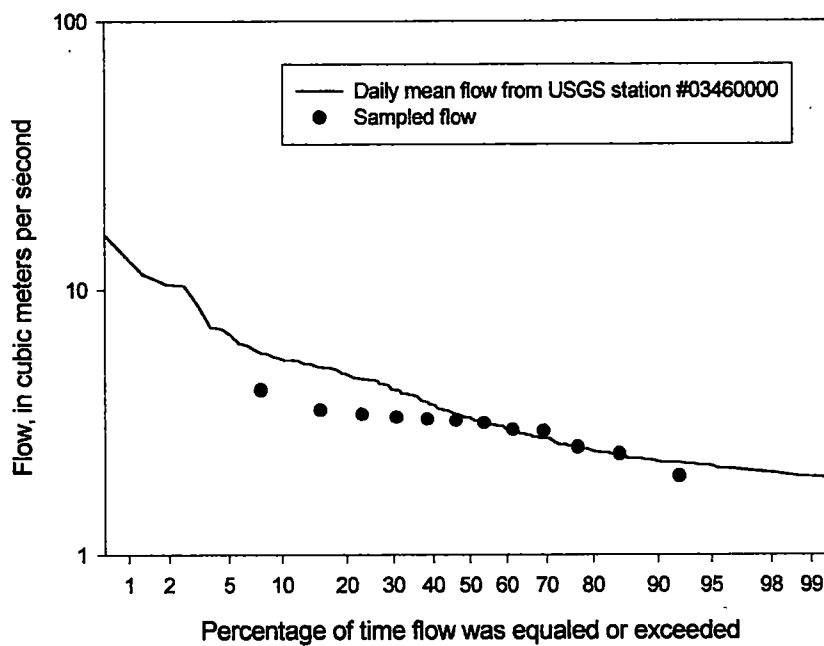


Figure 6-2. Frequency distributions during sampling period one for Cataloochee Creek.

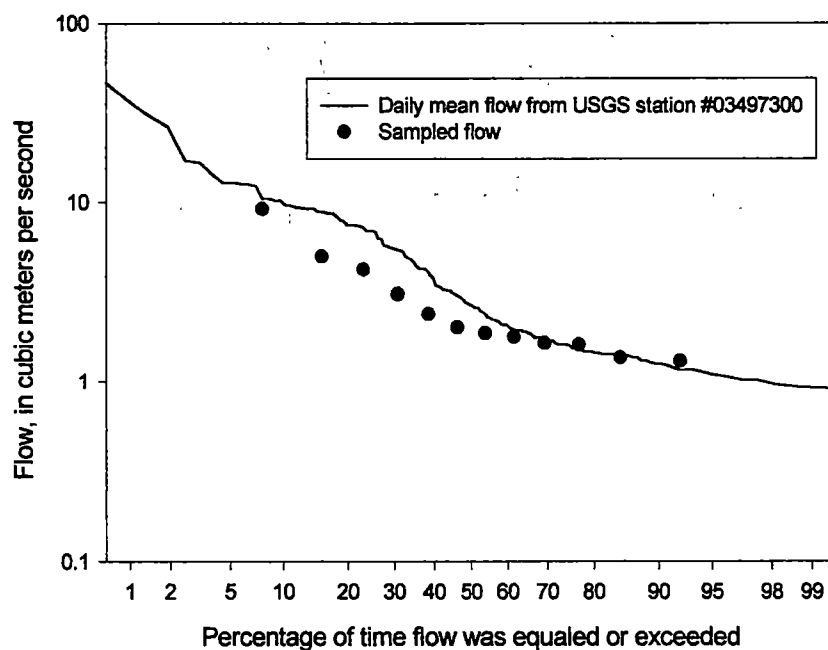


Figure 6-3. Frequency distributions during sampling period two for the Little River.

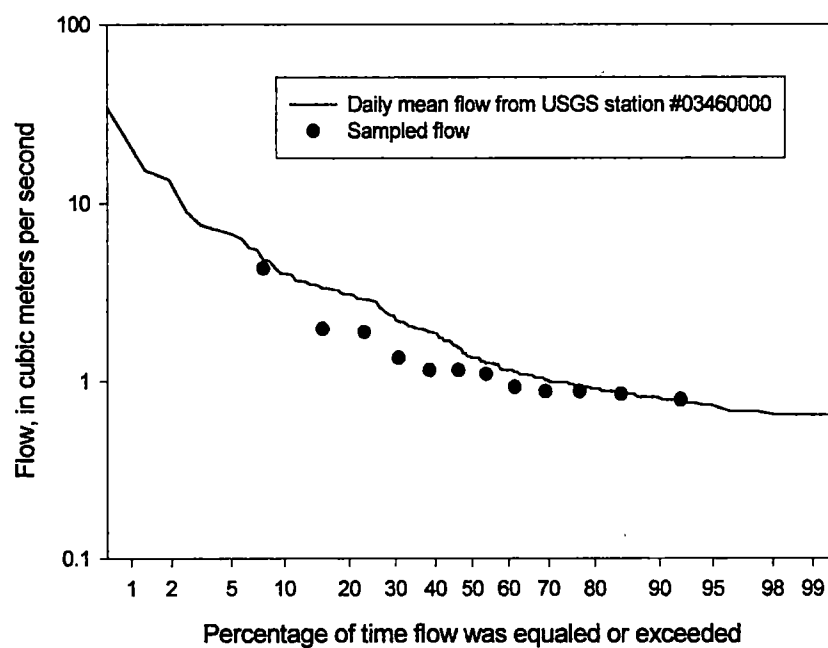


Figure 6-4. Frequency distributions during sampling period two for Cataloochee Creek.

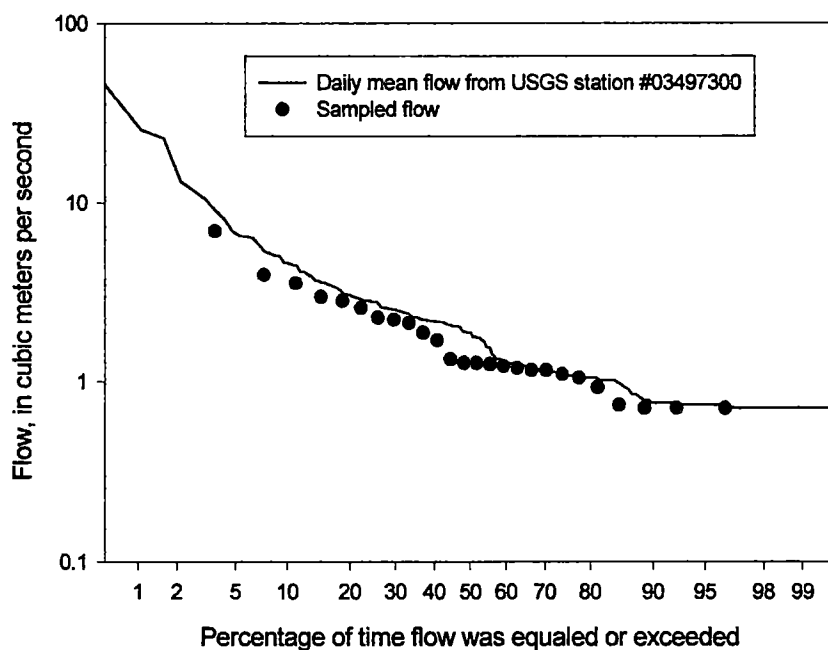


Figure 6-5. Frequency distributions during sampling period three for the Little River.

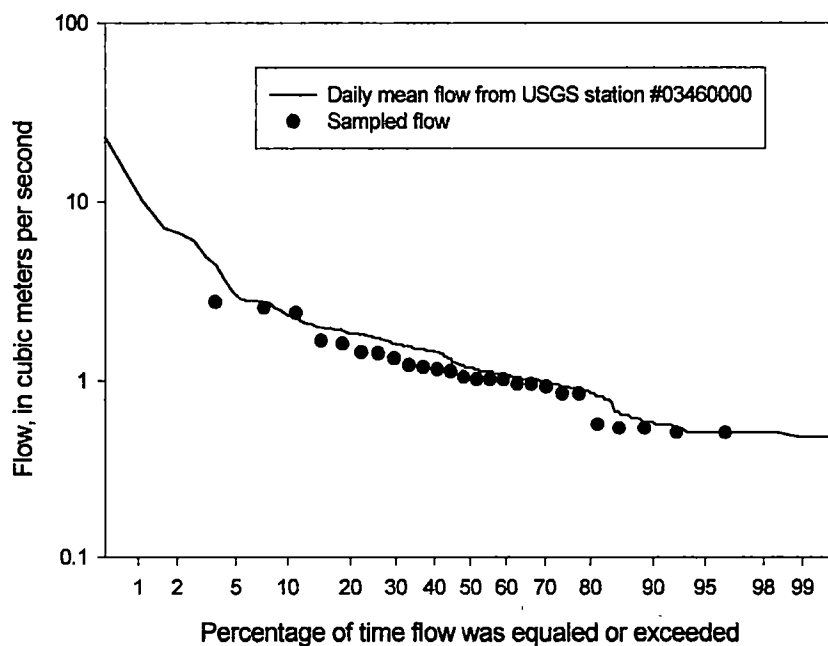


Figure 6-6. Frequency distributions during sampling period three for Cataloochee Creek.

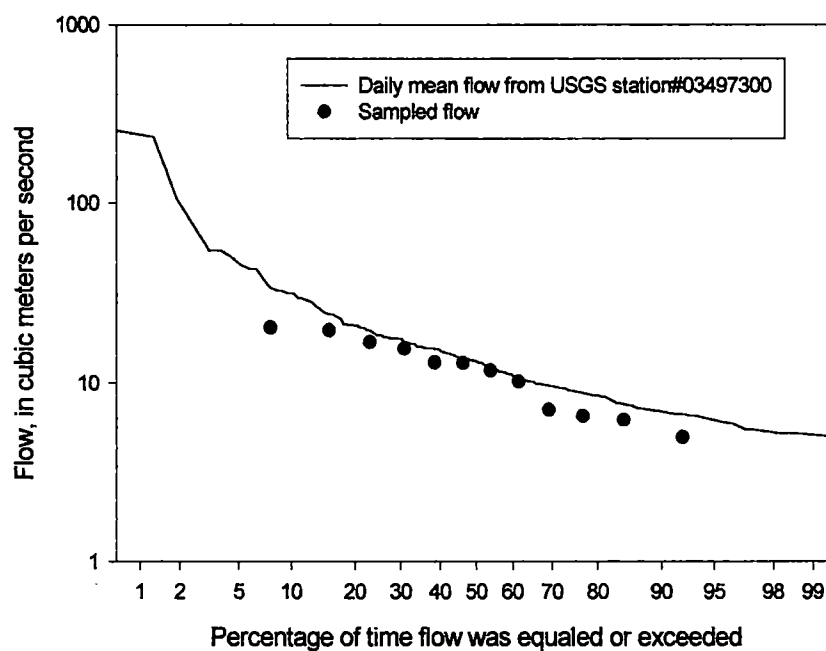


Figure 6-7. Frequency distributions during sampling period four for the Little River.

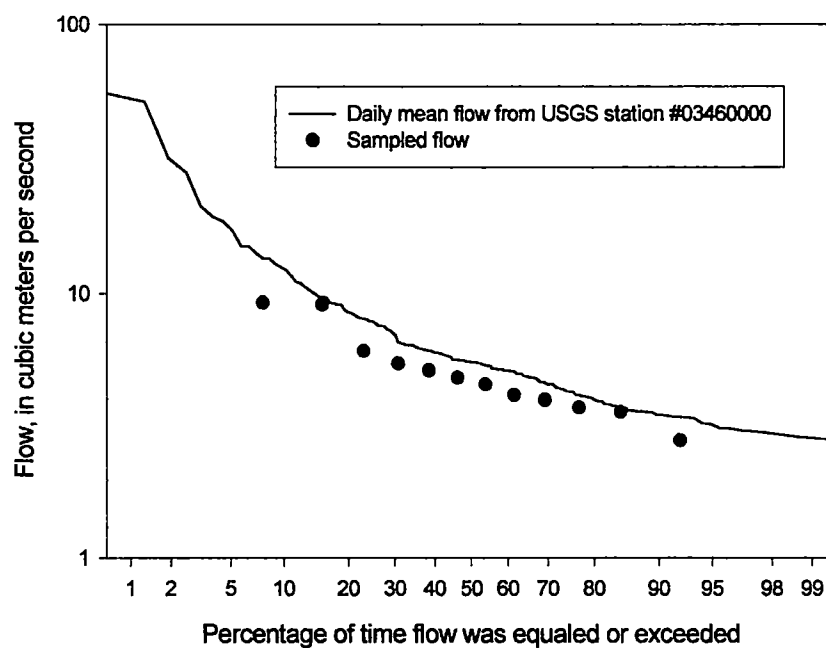


Figure 6-8. Frequency distributions during sampling period four for Cataloochee Creek.

highest daily mean flows are much greater than the highest daily mean flows when samples were collected. For example, Figure 6-1 shows that the highest daily mean flow is 48.14 cubic meters per second and the highest daily mean flow when samples were collected is 17.81 cubic meters per second. Therefore, the highest daily mean flow is 2.70 times higher than the highest daily mean flow when samples were collected during sampling period one on the Little River. For all sampling periods on the Little River, the highest daily mean flows average 6.73 times larger than the highest daily mean flows when samples were collected. For all sampling periods on Cataloochee Creek, the highest daily mean flows average 6.50 times larger than the highest daily mean flows when samples were collected. The figures also show that the extremely low flow conditions do not differ that much from samples collected during low flow conditions. For all sampling periods on the Little River, the lowest daily mean flows average 1.20 times smaller than the lowest daily mean flows when samples were collected. For all sampling periods on Cataloochee Creek, the lowest daily mean flows average 1.08 times smaller than the lowest daily mean flows when samples were collected.

Storm flows occur less frequently and therefore the chance of being in the field collecting a sample during these times is small. It is during these high flow conditions that stream chemistry could change significantly with respect to the concentration of a particular constituent and its total flux from the watershed. For example, data from Noland Divide Watershed (NDW) shows that storm events might account for much of the total flux of sulfate and nitrate from the watershed (McCann *et al.*, 2000). It is during these high flow conditions that pH can drop significantly. In soils low in base cations or with a tendency to conserve base cations, charge balance can be maintained by the leaching of hydrogen ions

and aluminum (Cosby *et al.*, 1985). This could have significant impacts on aquatic life. Hydrogen ion concentrations could increase during storm events and drop pH to levels which are harmful to fish and aquatic organisms (see Table 3-2). Elevated concentrations of aqueous aluminum are potentially harmful to aquatic organisms. The harmful effects of aluminum are related to its speciation (McAvoy, 1989). When quarterly Park-wide sampling began in 1993, aluminum was one of the constituents for which analysis was done. That was stopped for several reasons. The main reason for discontinuing analysis for aluminum was because most sites were below detection limits for aluminum. The costs associated with analyzing for aluminum were not worth the benefits since most of the time aluminum was either not present or present in very low concentrations. However, this further proves that the past and current sampling strategy misses the higher storm flow events. This is when the presence of aluminum in measurable, and sometimes high, concentrations are most likely to occur. During a storm event at NDW, aluminum concentrations increased 22.0 micromoles per liter and reached a maximum of 25.9 micromoles per liter (McCann, 2000).

Figures 6-9 and 6-10 show the historical annual mean flow rates for the Little River and Cataloochee Creek, respectively. The two watersheds are different with respect to discharge values. The contributing area to the Little River gaging station is more than twice the size of the contributing area to the Cataloochee station. However, notice in these two figures that the "trends" are very similar for the two watersheds. Moving from left to right across the x-axis (calendar years) in both figures there is a pattern with respect to increases and decreases in annual mean flow rates for both watersheds. If annual mean flow for the Little River increases from one year to the next, then Cataloochee Creek shows an increase

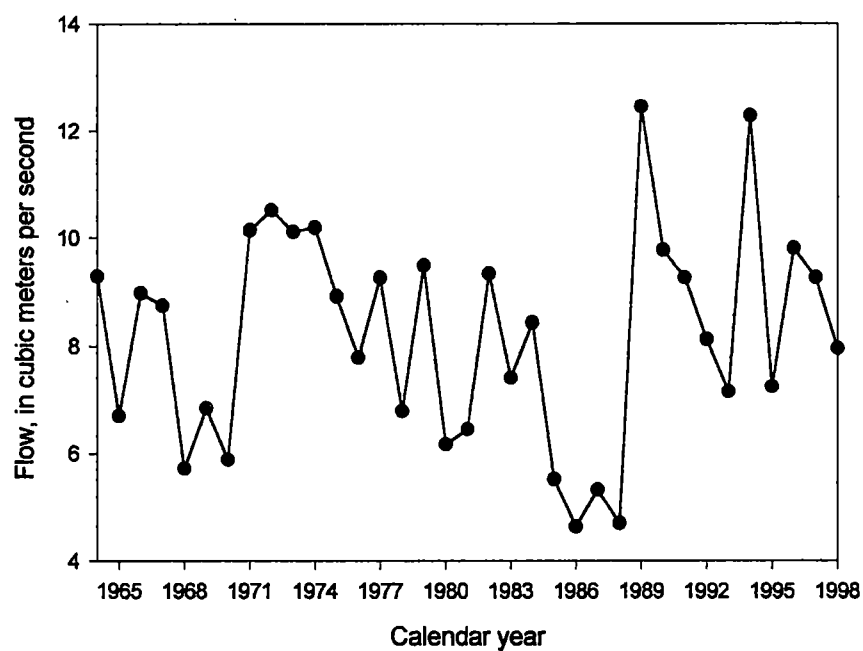


Figure 6-9. Historical annual mean flow rates for the Little River (1964-1998).

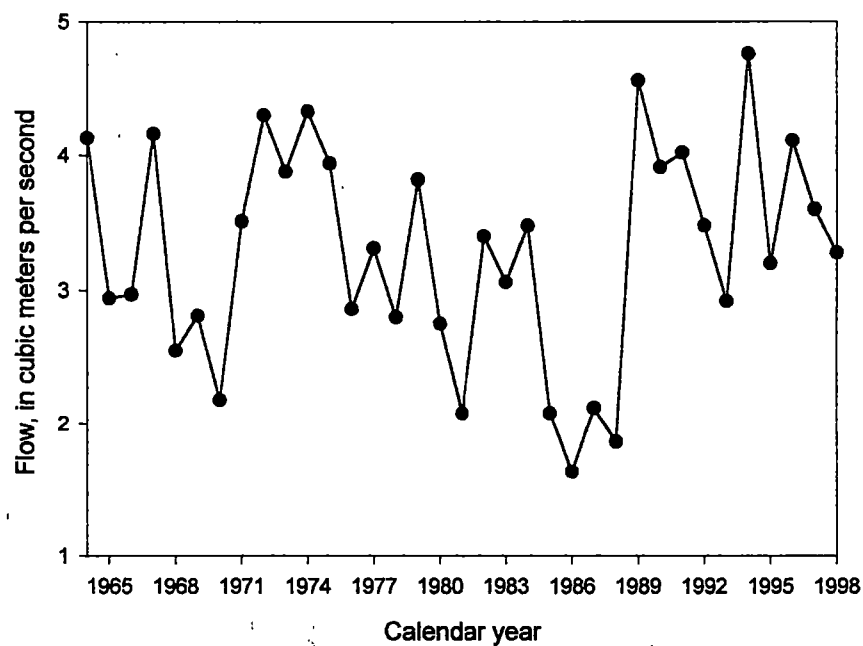


Figure 6-10. Historical annual mean flow rates for Cataloochee Creek (1964-1998).

as well for the same years. The same is true for decreases in annual mean flow rates from one year to the next.

Figures 6-11 and 6-12 show the historical annual peak flow rates for the Little River and Cataloochee. The annual peak flow rates are the highest recorded flow rates at the stations by water year. The gray bars represent years when the Little River and Cataloochee Creek had similar peak days. Similar peak days were defined as when peaks occurred either on the same day or within two days. The black bars represent years when the two watersheds recorded peak flow rates at very different times of the water year. Notice that for the 35 years shown in the figures (water years 1963 to 1998), only ten years are different. This means that 71% of the time the Little River and Cataloochee Creek recorded peak flows either on the same day or within two days of each other. Most of the time they recorded peak flows on the same day. Of the years when peak flow rates were recorded within two days of each other, only five years were not on exactly the same day. This means that 57% of the time the Little River and Cataloochee Creek recorded peak flows on the same day for the period analyzed.

Since these two streams, separated by 61.5 kilometers and on opposite sides of the GRSM, are very similar with respect to flow conditions, then conclusions about sampling conditions in other areas of the GRSM based on these two streams are probably reasonable. The analyses presented do not mean to say that precipitation and flow do not vary spatially in the GRSM. They certainly do. However, the two stations are probably similar enough for the purpose of trying to understand what flow conditions are represented by the quarterly sampling strategy.

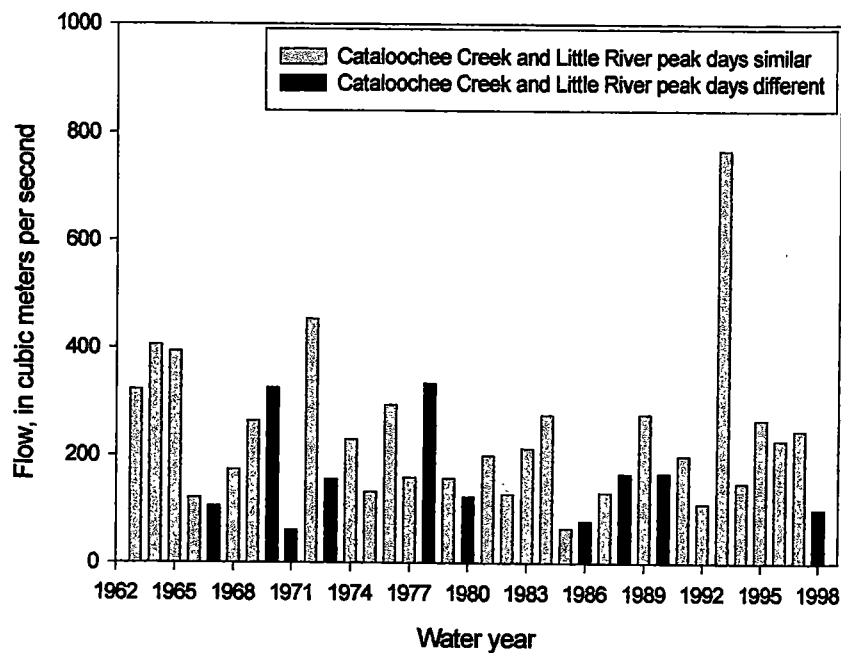


Figure 6-11. Historical annual peak flow rates for the Little River by water year (1963-1998).

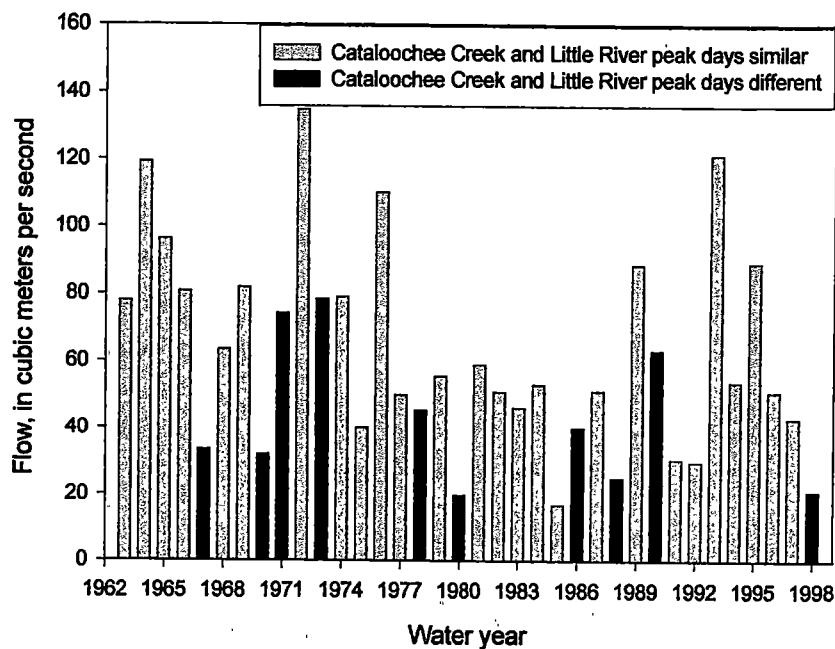


Figure 6-12. Historical annual peak flow rates for Cataloochee Creek by water year (1963-1998).

Conclusions

Based on the results of the analyses presented, the following conclusions and observations were made:

1. The Little River and Cataloochee Creek gaging stations are adequate to generally describe flow conditions in other areas of the GRSM. The Little River and Cataloochee Creek show similar "trends" with respect to historical annual mean flow rates. From 1963 to 1998, the Little River and Cataloochee Creek recorded peak flows either on the same day or within two days of each other 71% of the time. Most of the time they recorded peak flows on the same day. Of the years when peak flow rates were recorded within two days of each other, only five years were not on exactly the same day. This means that 57% of the time the Little River and Cataloochee Creek recorded peak flows on the same day for the period analyzed.
2. Frequency distributions of daily mean flow rates when samples were collected demonstrate that the current sampling strategy misses the higher flow conditions. For all sampling periods on the Little River, the highest daily mean flows average 6.73 times larger than the highest daily mean flows when samples were collected. For all sampling periods on Cataloochee Creek, the highest daily mean flows average 6.50 times larger than the highest daily mean flows when samples were collected. It is during the storm flow conditions that stream chemistry is particularly important with respect to influences on aquatic life in GRSM streams.

3. Frequency distributions of daily mean flow rates when samples were collected demonstrate that the current sampling strategy does a good job of capturing common flow conditions and even low flow conditions. For all sampling periods on the Little River, the lowest daily mean flows average 1.20 times smaller than the lowest daily mean flows when samples were collected. For all sampling periods on Cataloochee Creek, the lowest daily mean flows average 1.08 times smaller than the lowest daily mean flows when samples were collected.

CHAPTER VII. IMPLICATIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The objective of this chapter is to take the results of data analyses presented in previous chapters and summarize important implications while making recommendations for future research. They are as follows:

1. Time trend analysis revealed a statistically significant decreasing trend in normalized pH over time. The time required for pH to reach critical values appears to increase with decreases in elevation. If conditions and trend continue sampling sites between 1,524 meters and 1,676 meters (5,000 feet to 5,500 feet) above mean sea level might have pH values less than or equal to 5.50 within only four years and less than or equal to 5.00 within only 11 years. At the lower elevations, between 305 meters and 457 meters (1,000 feet and 1,500 feet), sampling sites might have pH values less than or equal to 5.50 within 46 years and less than or equal to 5.00 within 67 years. At pH values between 5.5 and 6.0, there is a significant loss of acid sensitive fish and reduced reproduction (Baker *et al.*, 1996). At 5.0, the pH will be just below the critical pH for all species of trout found in GRSM streams. Within 26 years sampled GRSM streams at the lower elevations (305 meters to 457 meters) might have pH values near 6.00. The time required for sampling sites at higher elevations (914 meters to 1,067 meters) to reach 6.00 appears to be only four years. Research has shown that at pH values between 6.0 and 6.5 the water becomes uninhabitable for sensitive benthic invertebrates

(Baker *et al.*, 1996). The models used to predict future values of pH in sampled surface water explain an average of 12% of the variability in the data. This means that an average of 88% of the variability is unaccounted for by the models. However, this in no way negates the statistical validity of the trends found from regression. The use of these models to predict future values of pH assumes that the factors which are unaccounted for by the models will not change over time and remain the same as what was observed during the period which was modeled. Some of the factors which are unaccounted for include stream flow, precipitation, and deposition rates. Although it is far from certain that such serious pH declines will occur, stream pH warrants serious concern and continued monitoring.

2. The analysis of spatial variability and the investigation for relationships between water quality and a newly developed data base of basin characteristics will help to guide future selection of sampling sites and analytes within the Great Smoky Mountains National Park (GRSM). Sampling sites which are similar with respect to water quality and basin characteristics such as elevation, geology, vegetation, and disturbance history might provide redundant information. As a result, it might be possible to reduce the number of sampling sites in the future.
3. Sampling during high flow is not represented well. Storm sampling should be performed for important constituents such as nitrates, sulfates, hydrogen ions, monomeric aluminum and other species of concern which are flushed

from the watersheds. Concentrations and fluxes during storm events can have significant impacts on water quality and adversely affect aquatic organisms. Storm sampling from areas affected by Anakeesta debris flows might be especially interesting.

4. Regression analysis revealed that Anakeesta Formations can exert a significant influence on water chemistry, particularly decreased pH. The influence of Anakeesta Formations is stronger if it has been disturbed and exposed to weathering by the construction of roads or by natural debris flows. This reinforces the need to use proper construction methods during road construction and repair to control acid generation when Anakeesta Formations are disturbed. Water quality monitoring in areas of human disturbance of Anakeesta is recommended. Undisturbed Anakeesta Formations do not appear to be strongly associated with decreased pH.
5. Regression analysis also revealed that the percentage of limestone in a drainage basin is a good predictor of alkalinity and conductivity. The water draining from basins with limestone is less acidic, has higher buffering capacity against acid input, and has elevated conductivity resulting from carbonate species. These areas of the Park are expected to be less sensitive to pH and alkalinity problems. These areas include portions of the Abrams Creek watershed within and downstream of Cades Cove and lower elevations of the Little River watershed.
6. In 1995, monthly sampling was conducted at 160 sites throughout the GRSM.

The models presented in Chapter IV to predict median water quality constituent values used the 90 sites which have been sampled since the beginning and are still active sites. Ancillary data (geology, vegetation, and disturbance) was not collected for the other sites which are currently not included in the sampling network. Future work should include collecting ancillary data for discontinued sites and using the data to validate the models presented in Chapter IV.

7. Other data should be added as it becomes available. For example, soils data is currently being collected for the GRSM. Soils types might explain some of the variability in water quality constituent values.
8. Fish and benthic data is also collected within the GRSM by other researches. Multivariate techniques, such as principle component analysis and cluster analysis, could be used to investigate for relationships between surface water quality and aquatic organisms. Table 7-1 summarizes the types of data available for each sample site.
9. In the past, pH has been recorded in the laboratory. As of August 2001, field pH was also recorded at the time of sample collection. Measurements of laboratory pH should continue along with field pH measurements to understand this relationship and provide insight into how that relationship affects long-term trends presented in Chapter V.

Table 7-1. Matrix summarizing available data for sample sites.

Sample site	Basin physical properties	Geology	Vegetation	Disturbance history	Fish site	Benthic site
1	X	X	X	X		X
3	X	X	X	X		
4	X	X	X	X		X
13	X	X	X	X		
14	X	X	X	X		
20	X	X	X	X		X
23	X	X	X	X		
24	X	X	X	X		
30	X	X	X	X		X
34	X	X	X	X		
43	X	X	X	X		
45	X	X	X	X		X
46	X	X	X	X		
47	X	X	X	X		
49	X	X	X	X		
50	X	X	X	X		
52	X	X	X	X		
66	X	X	X	X		
71	X	X	X	X		X
73	X	X	X	X		
74	X	X	X	X		
103	X	X	X	X		
104	X	X	X	X		
106	X	X	X	X		
107	X	X	X	X		X
114	X	X	X	X		
115	X	X	X	X		
127	X	X	X	X		
137	X	X	X	X		X
138	X	X	X	X		
142	X	X	X	X		X
143	X	X	X	X		X
144	X	X	X	X		
147	X	X	X	X		X
148	X	X	X	X		X
149	X	X	X	X		
150	X	X	X	X		
156	X	X	X	X		X
173	X	X	X	X		
174	X	X	X	X		
183						
184	X	X	X	X		
186	X	X	X	X		
190	X	X	X	X		X

X denotes that data is available

Table 7-1 (continued)

Sample site	Basin physical properties	Geology	Vegetation	Disturbance history	Fish site	Benthic site
191	X	X	X	X		X
192	X	X	X	X		X
193	X	X	X	X		
194	X	X	X	X		
195						
200	X	X	X	X		
201						
209	X	X	X	X		
210	X	X	X	X		
213	X	X	X	X		
214	X	X	X	X		X
215	X	X	X	X		X
218						
219						
220						
221	X		X	X		
233	X	X	X	X		
234	X	X	X	X		
237	X	X	X	X		
251	X	X	X	X		
252	X	X	X	X		X
253	X	X	X	X		X
266	X	X	X	X		
268	X	X	X	X		
290						
291	X	X	X	X		
293	X	X	X	X		
310	X		X	X		
311	X		X	X		
336	X	X	X	X		X
337	X	X	X	X		X
472	X	X	X	X	X	
473	X	X	X	X		
474	X	X	X	X	X	X
475	X	X	X	X	X	
479	X		X	X		X
480	X		X	X		
481	X		X	X		X
482	X		X	X		
483	X		X	X		X
484	X		X	X	X	X
485	X		X	X	X	
488	X	X	X	X	X	
489	X	X	X	X	X	X
492	X	X	X	X	X	X
493	X	X	X	X	X	X

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APPENDICES

APPENDIX A1. MAPS OF MAJOR SAMPLED WATERSHEDS

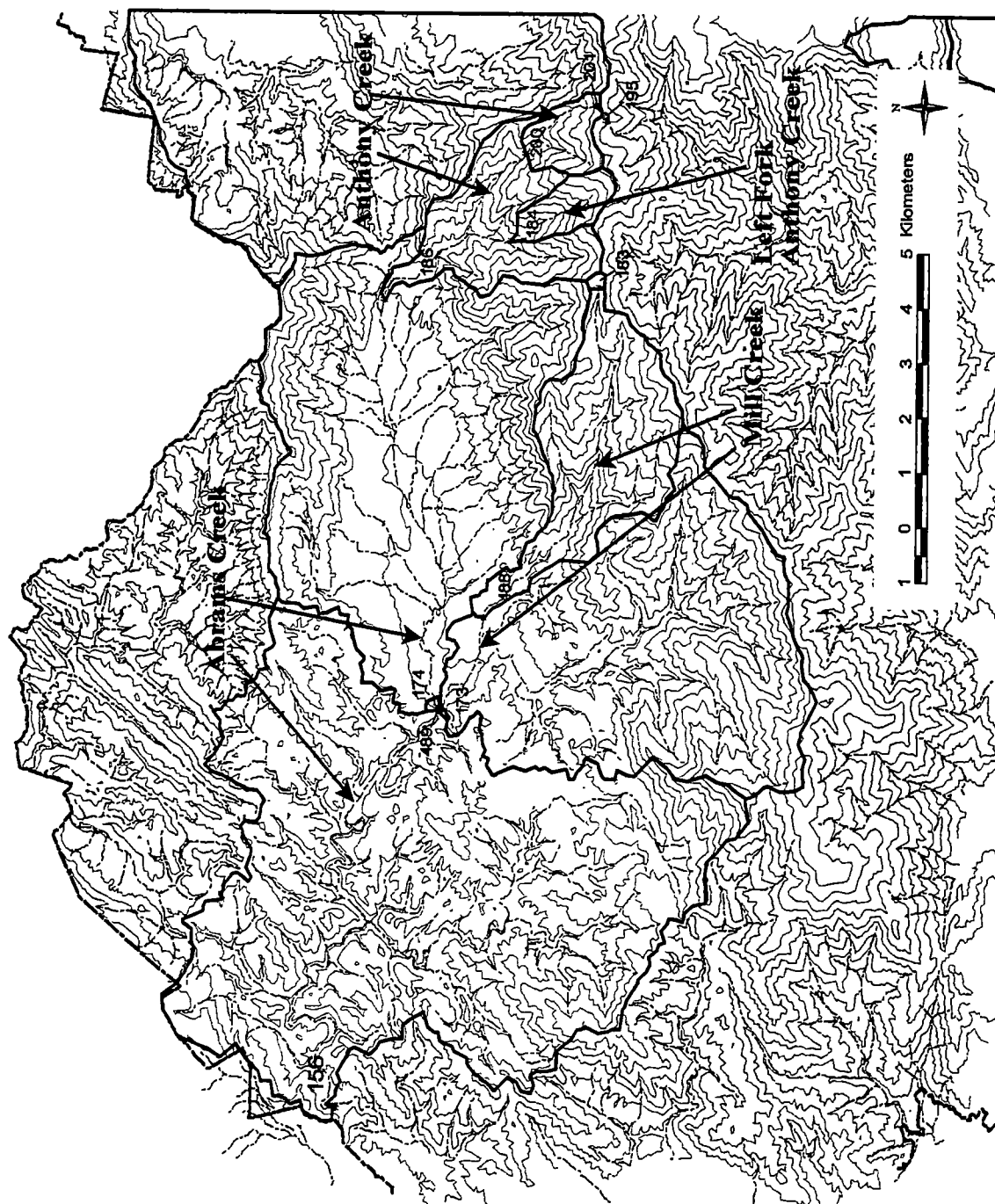


Figure A1-1. Abrams Creek watershed.

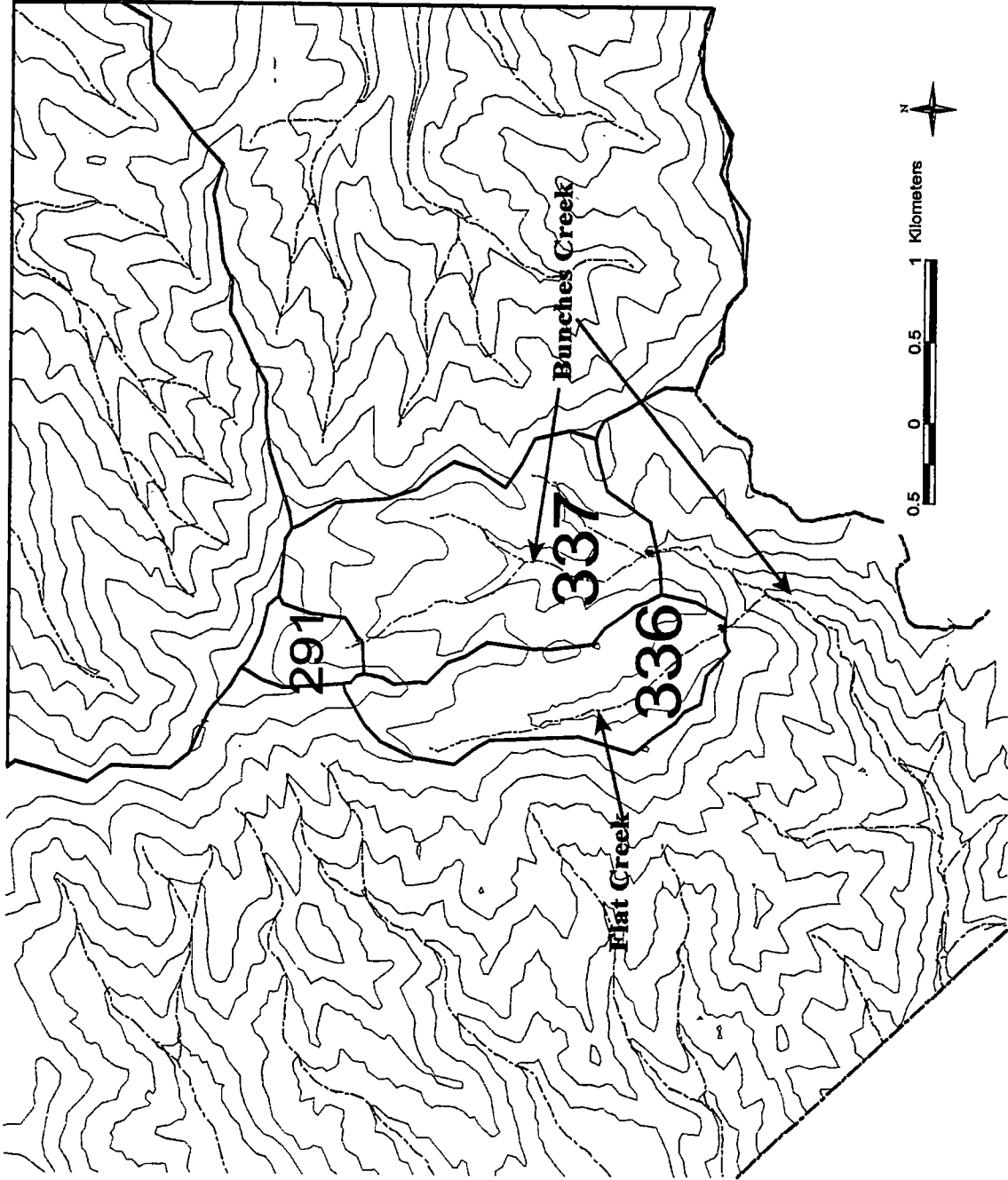


Figure A1-2. Bunches Creek watershed.

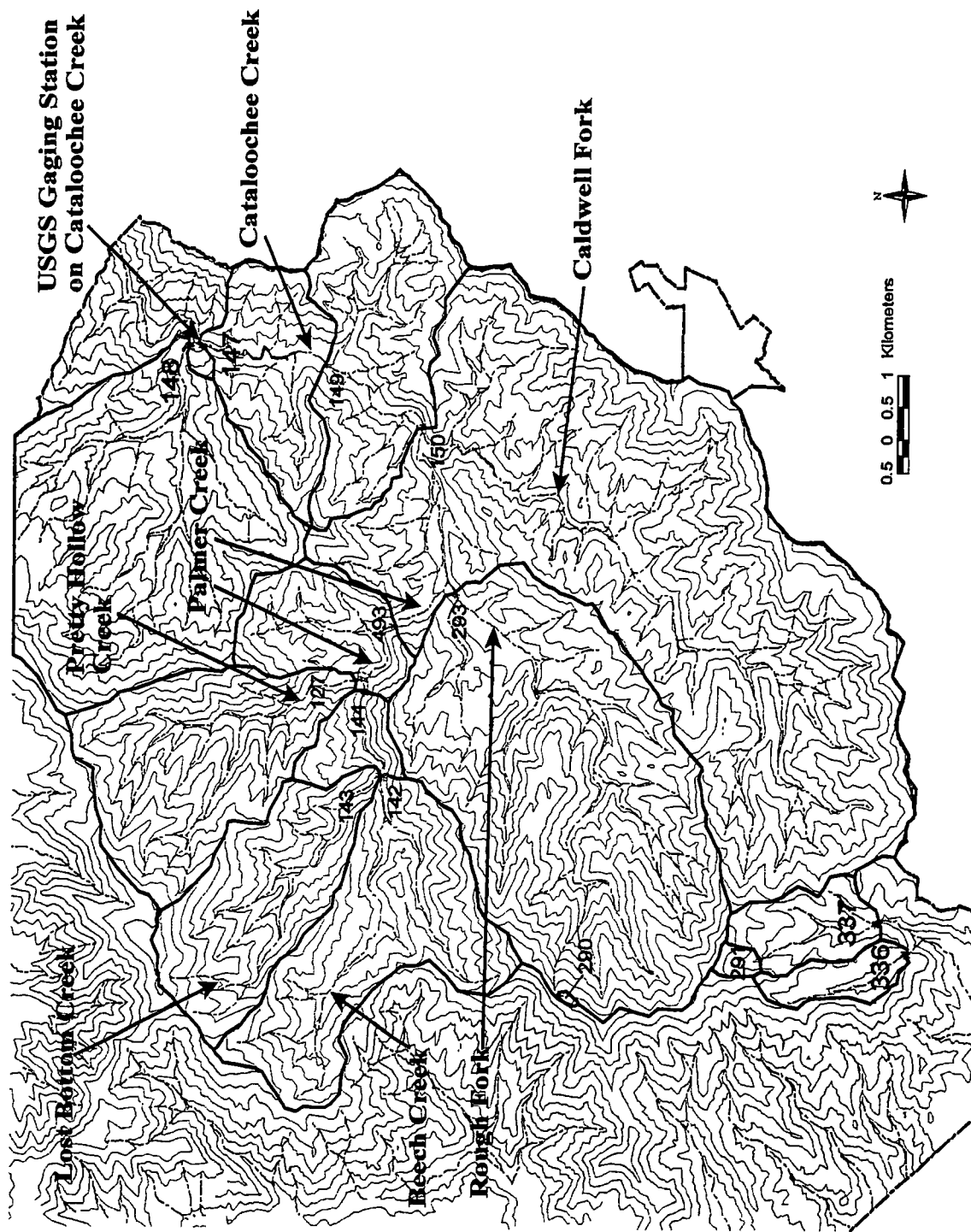


Figure A1-3. Cataloochee Creek watershed.

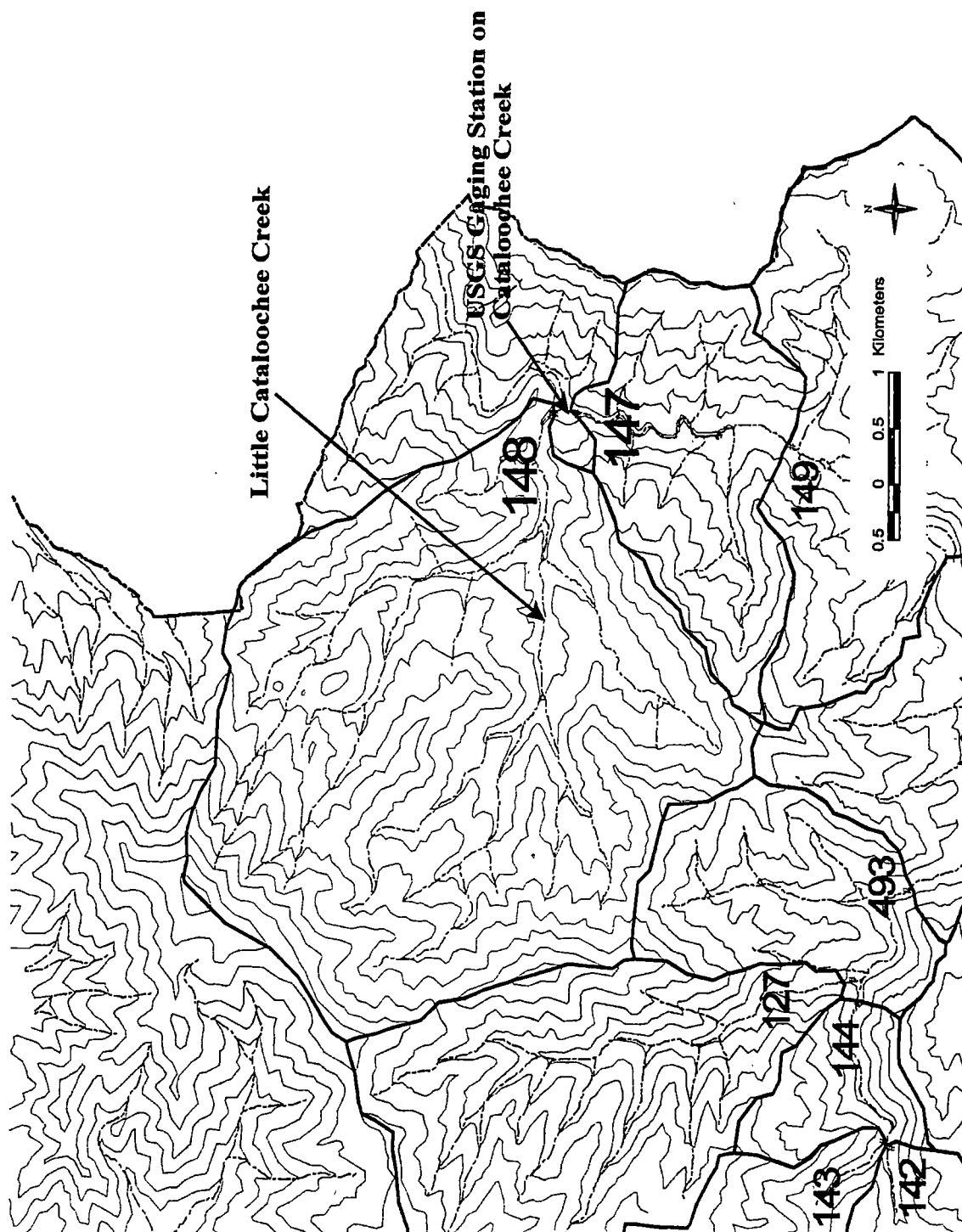


Figure A1-4. Little Cataloochee Creek watershed.

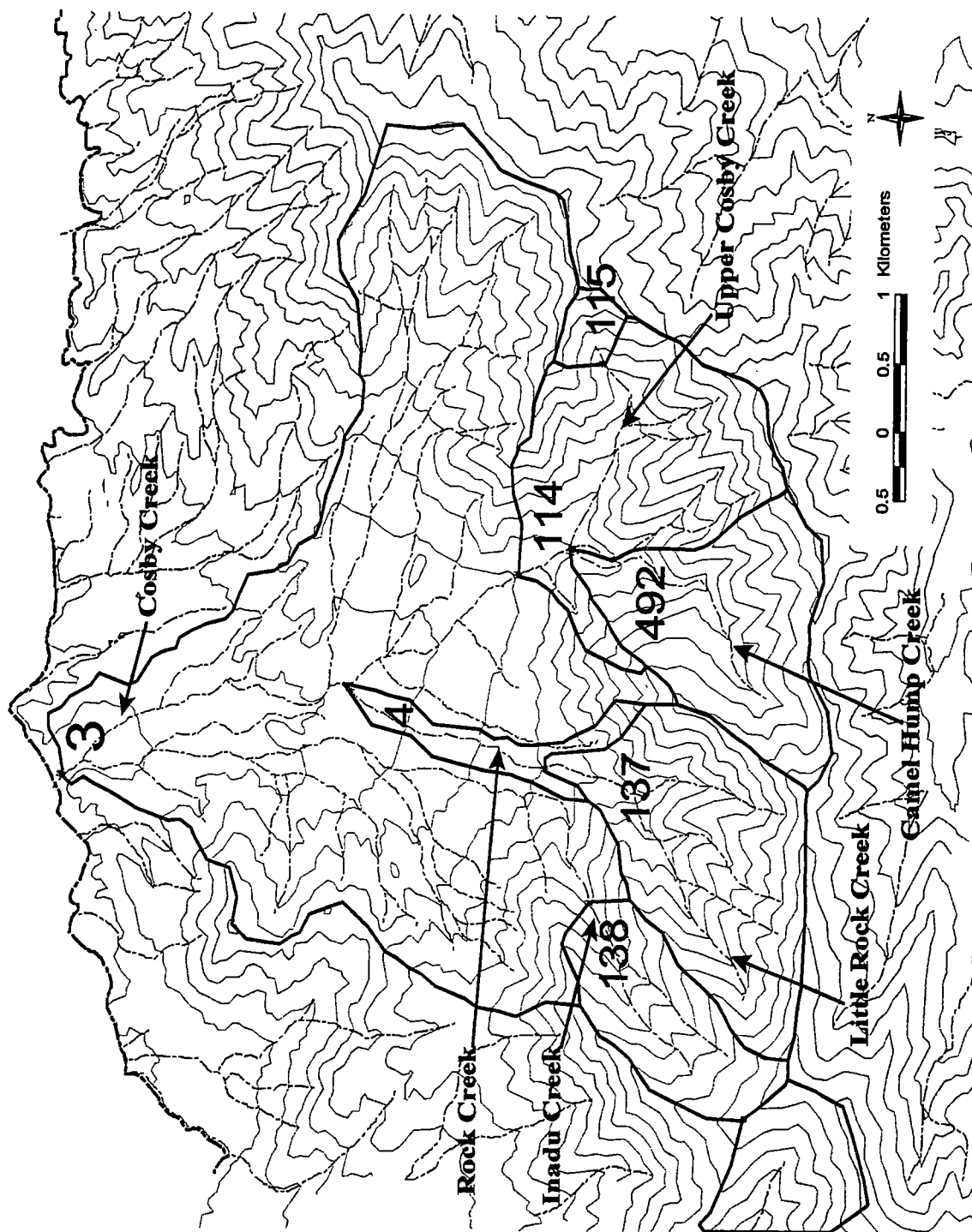


Figure A1-5. Cosby Creek watershed.

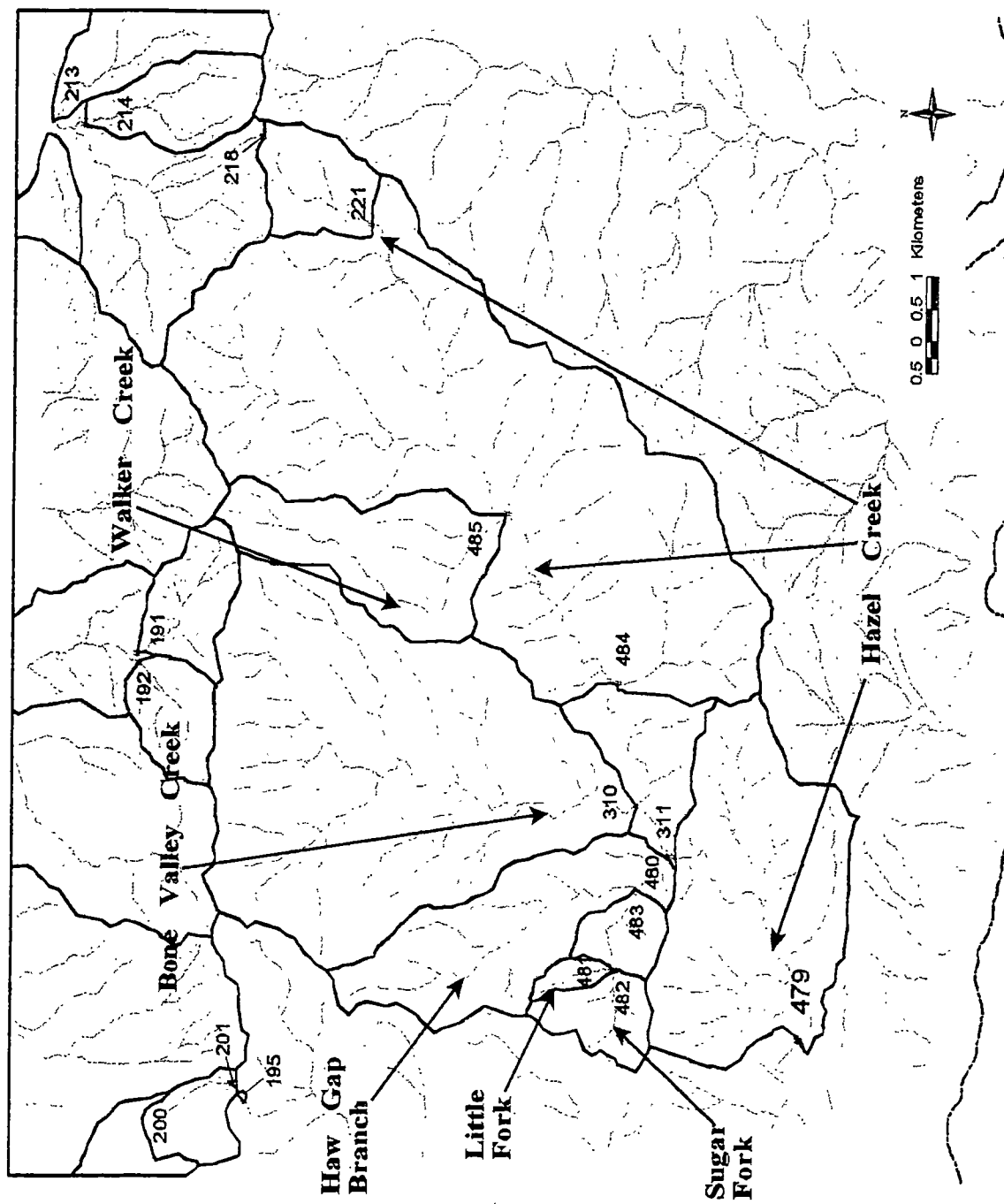


Figure A1-6. Hazel Creek watershed.

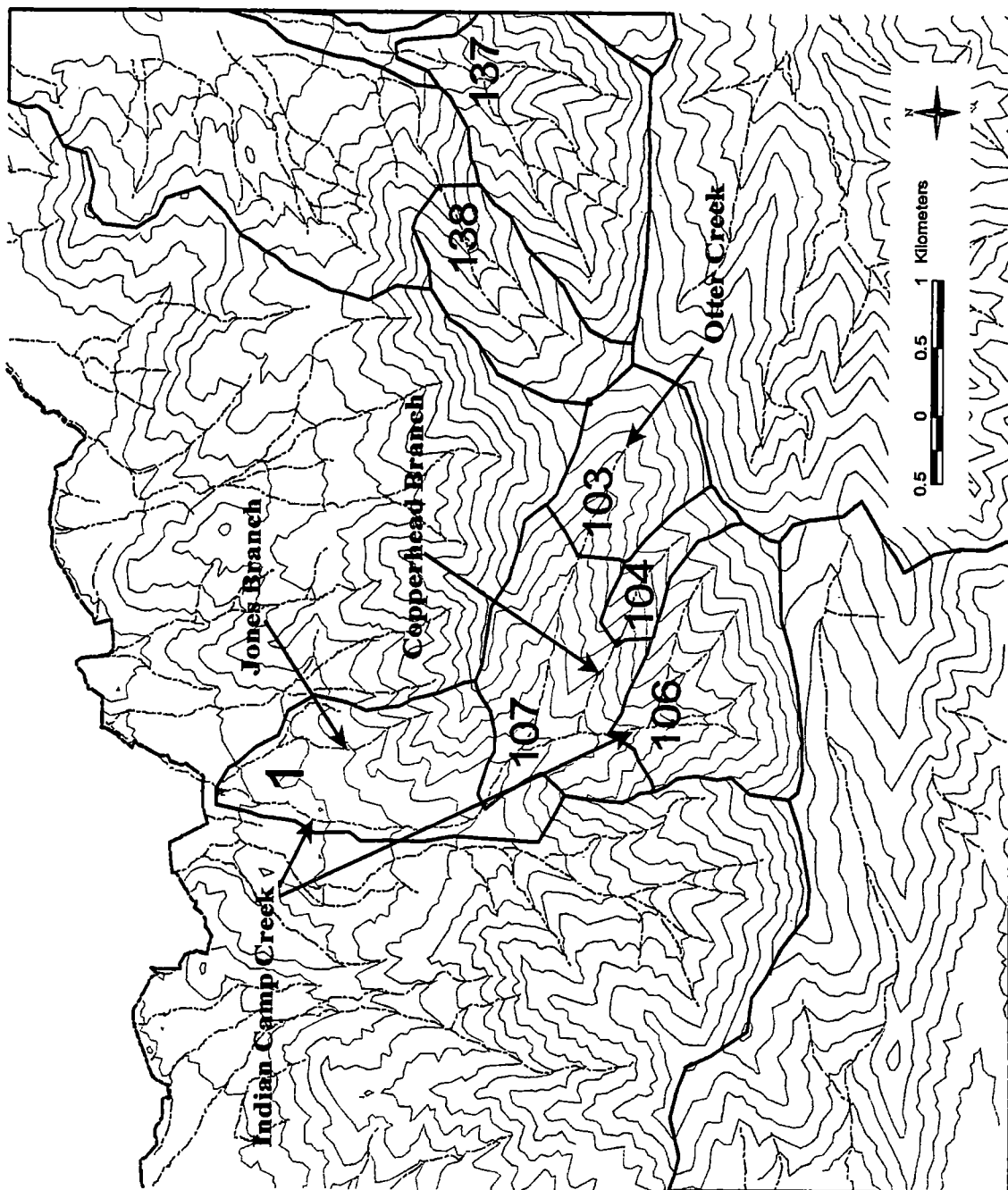


Figure A1-7. Indian Camp Creek watershed.

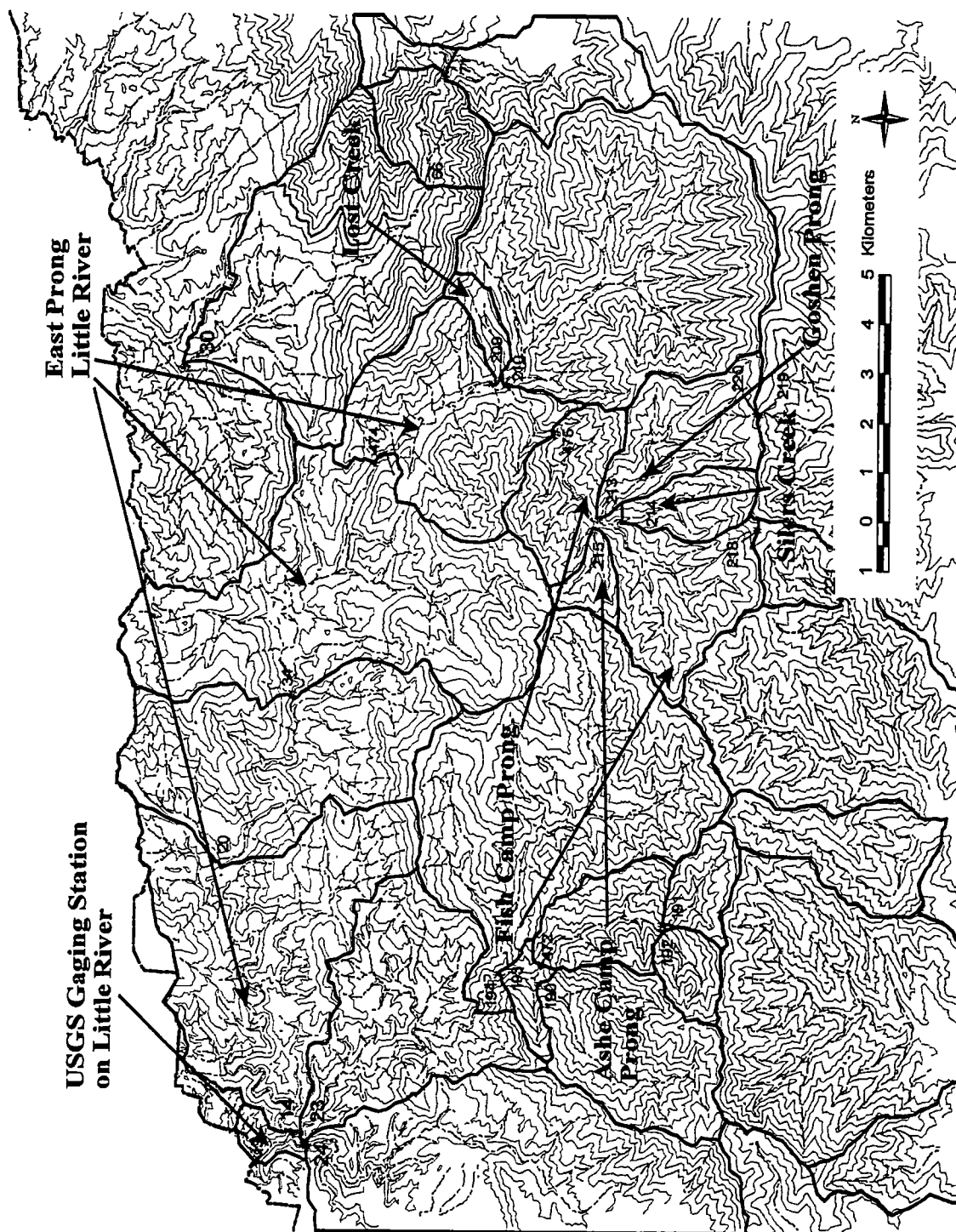


Figure A1-8. East Prong Little River watershed.

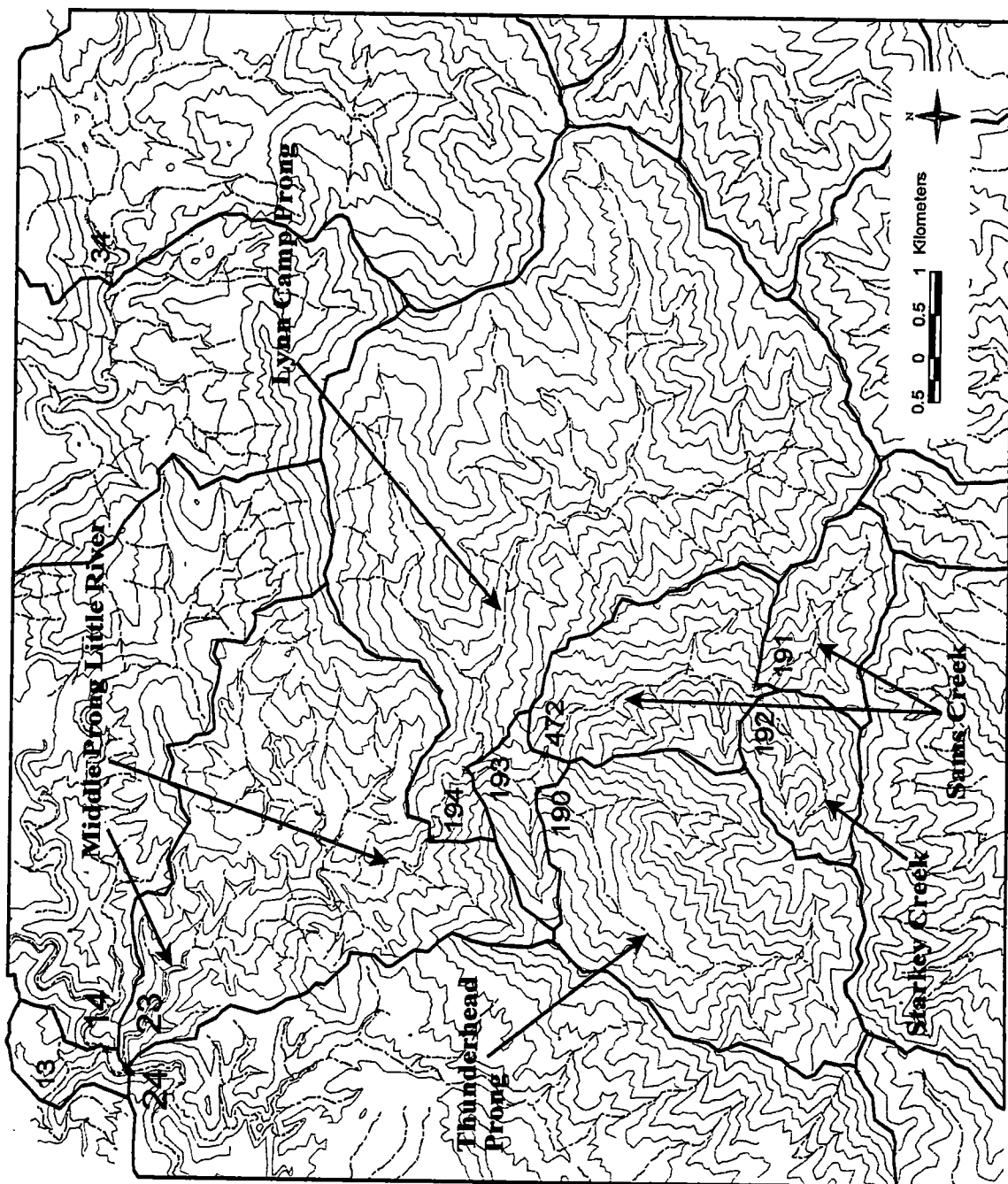


Figure A1-9. Middle Prong Little River watershed.

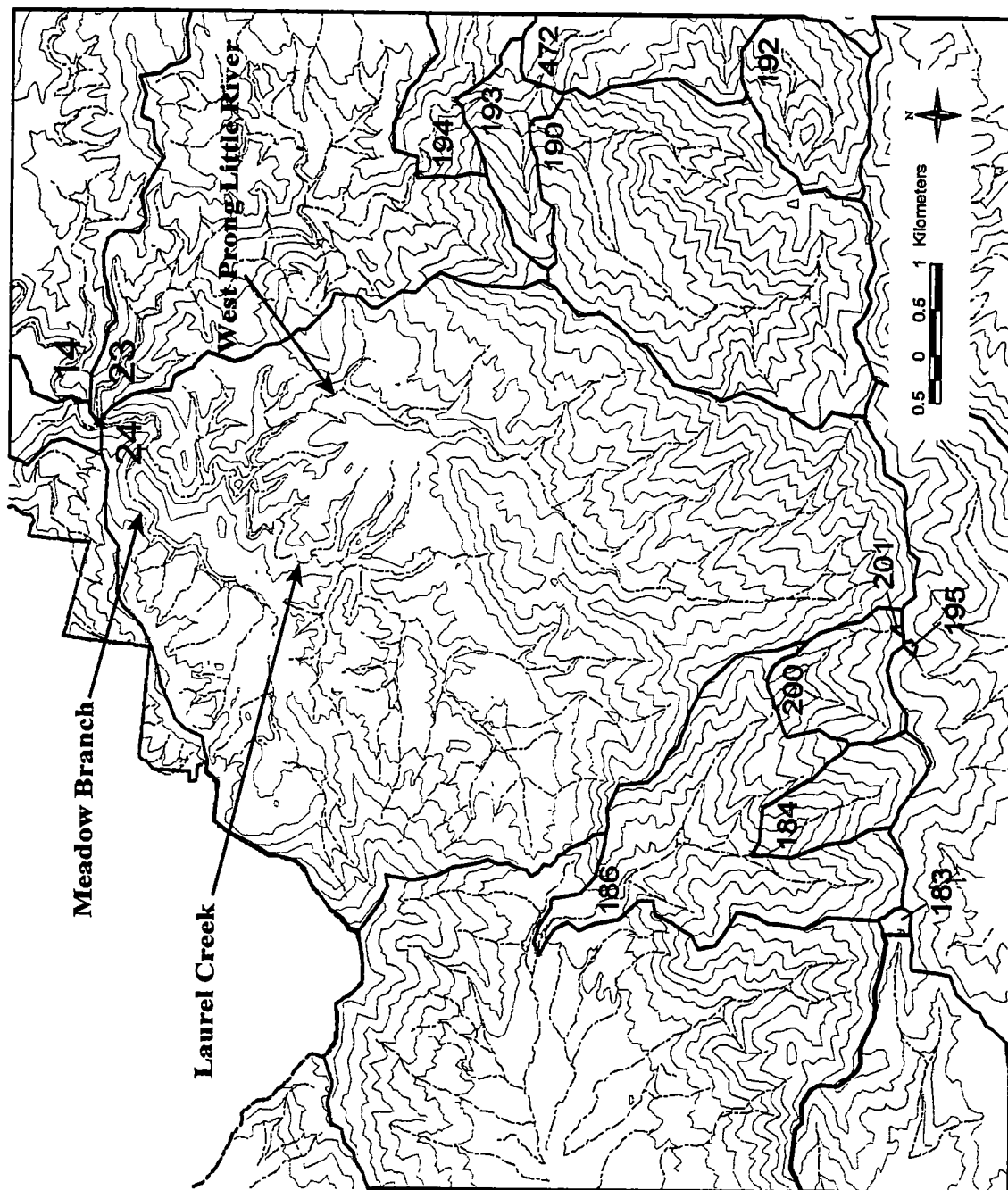


Figure A1-10. West Prong Little River watershed.

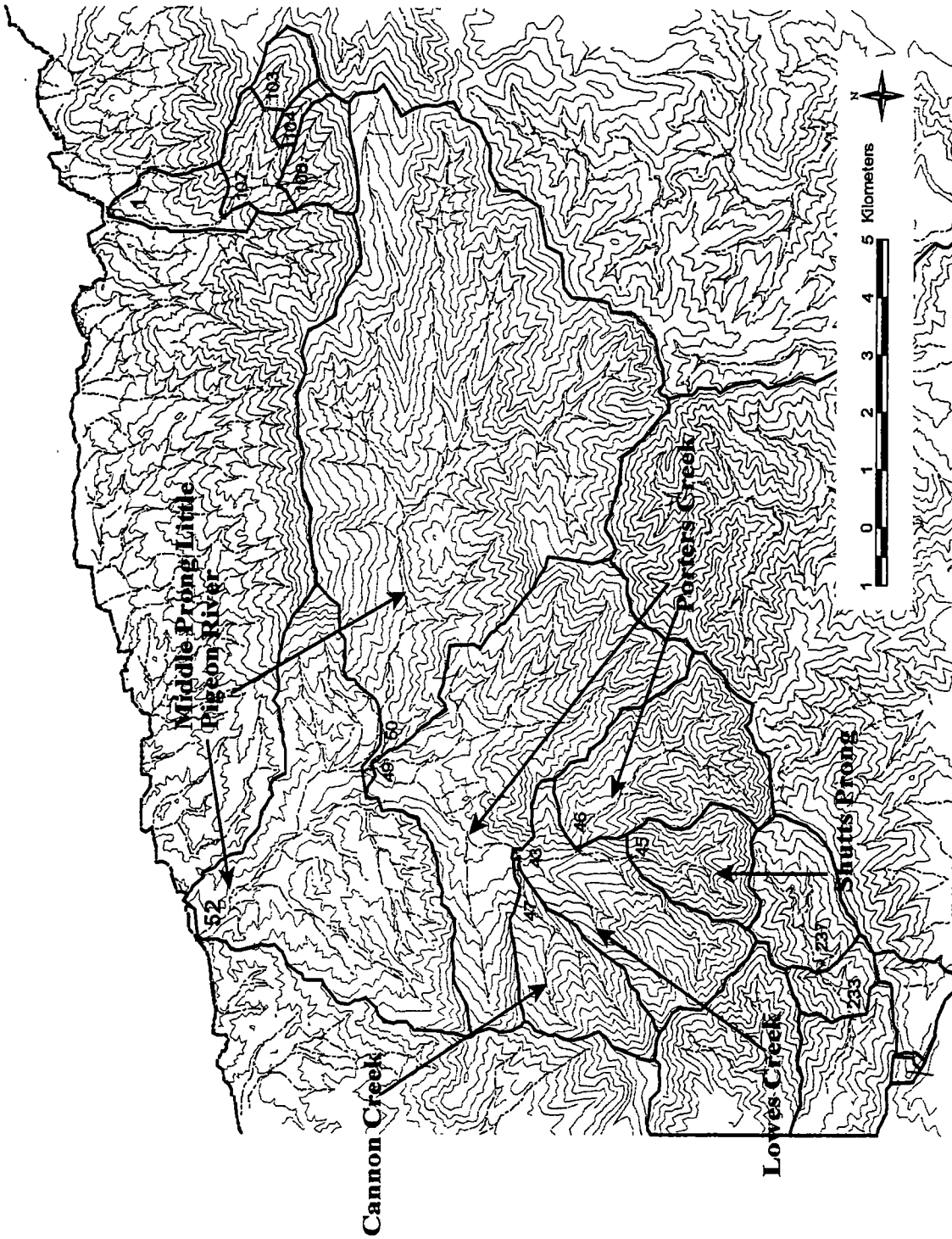


Figure A1-11. Middle Prong Little Pigeon River watershed.

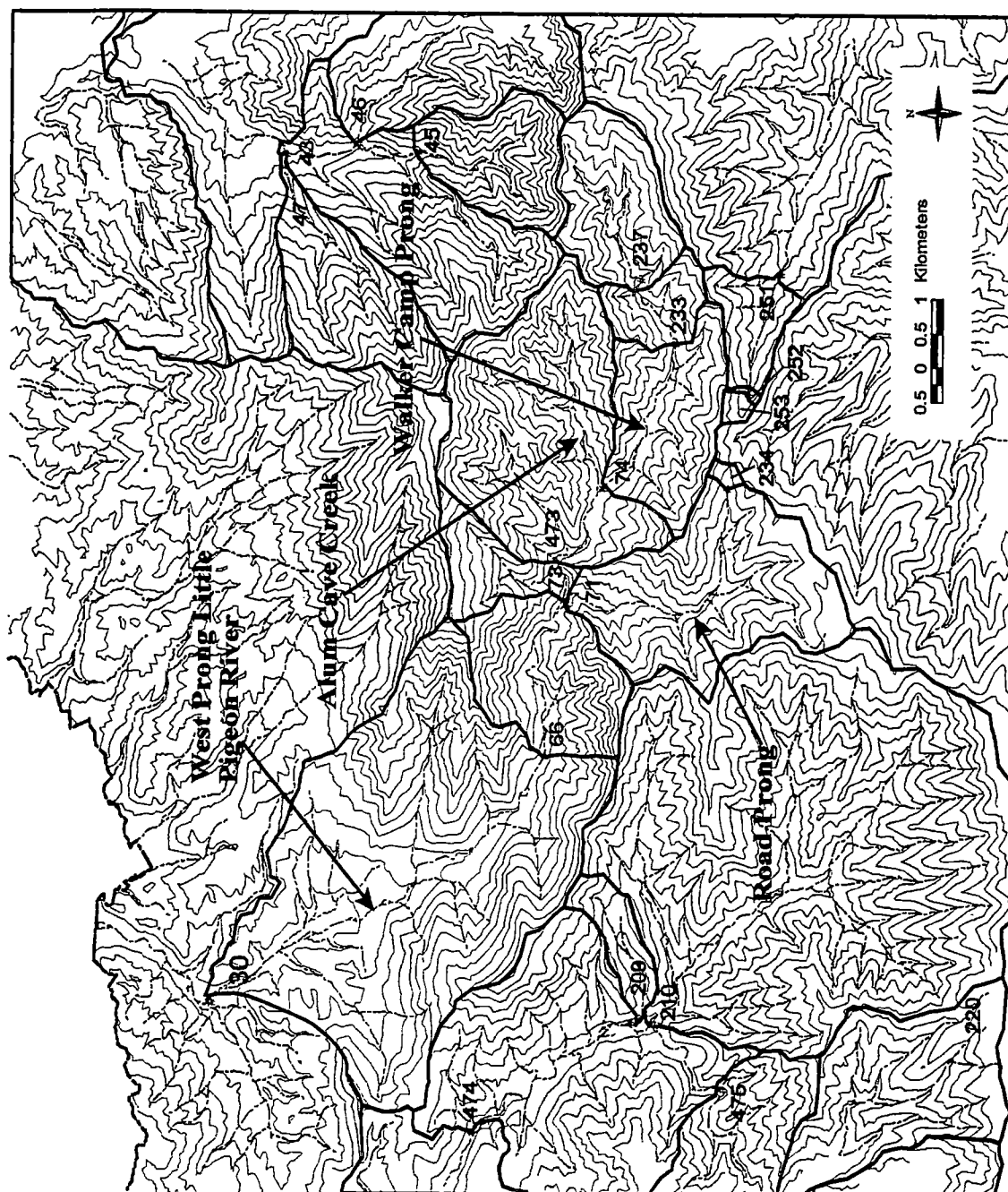


Figure A1-12. West Prong Little Pigeon River watershed.

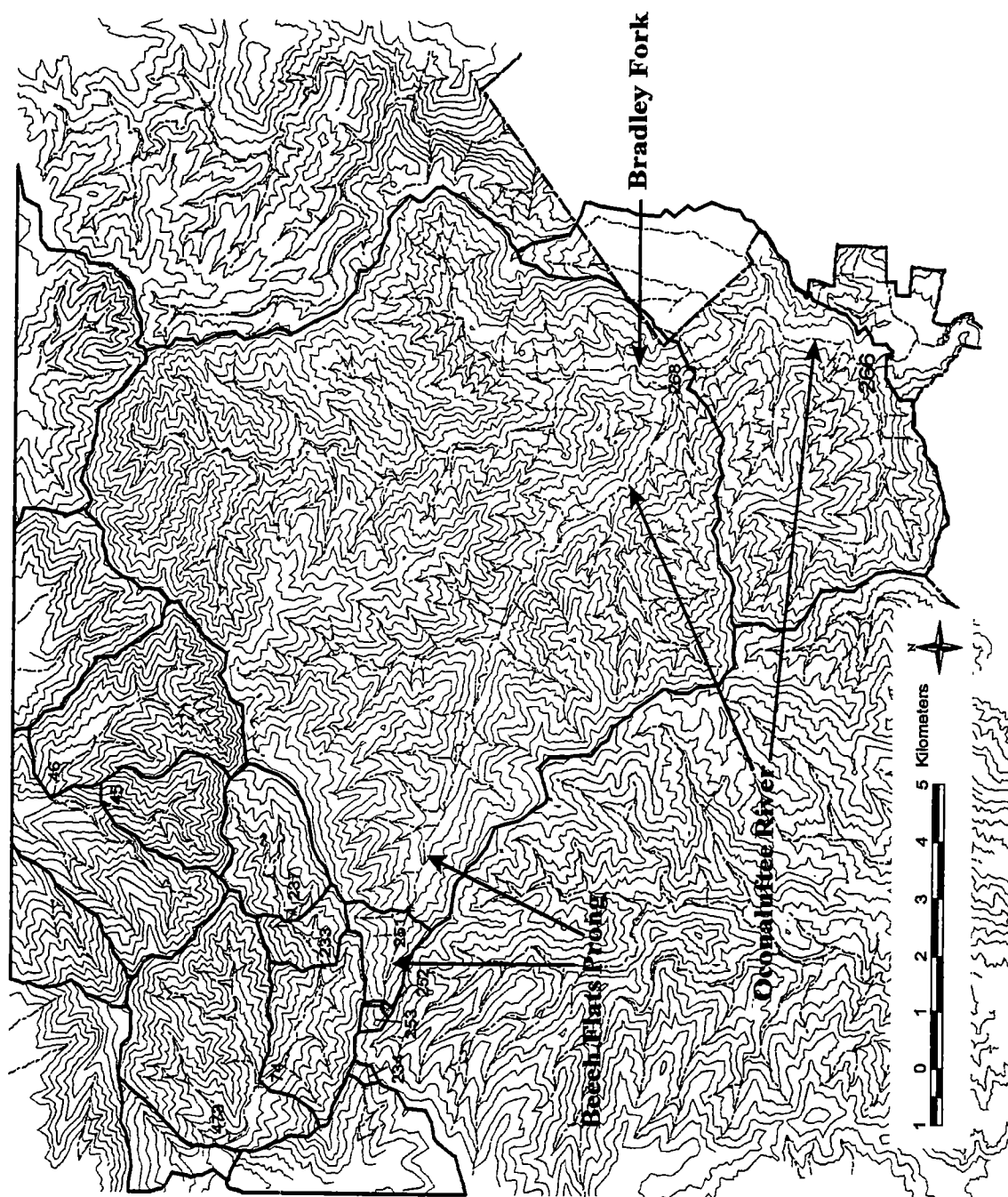


Figure A1-13. Oconalufee River watershed.

APPENDIX A2. CONSTITUENT SUMMARY STATISTICS

Table A2-1. Summary statistics for pH within the watersheds sampled. Missing values due to small sample size.

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Abrams Creek	156	7.16	6.77	6.85	7.23	7.37	7.57
	173	6.68	6.45	6.50	6.66	6.80	7.01
	174	7.38	6.81	7.13	7.39	7.69	7.77
	183	5.64	4.23	5.58	5.63	6.11	6.33
	184	6.23	6.01	6.12	6.21	6.35	6.47
	186	6.38	6.11	6.25	6.36	6.50	6.67
	200	6.09	5.79	5.98	6.10	6.24	6.33
	201	5.73	5.43	5.56	5.70	5.97	6.20
	488	6.35	5.97	6.29	6.35	6.52	6.65
	489	7.37	6.80	7.09	7.44	7.66	7.78
Bunches Creek	291	6.02	5.71	5.80	6.05	6.18	6.28
	336	6.38	6.16	6.25	6.36	6.53	6.60
	337	6.23	5.96	6.10	6.27	6.36	6.40
Cataloochee Creek	127	6.38	6.11	6.26	6.41	6.48	6.57
	142	6.48	6.24	6.39	6.51	6.57	6.67
	143	6.42	6.27	6.32	6.42	6.52	6.58
	144	6.46	6.30	6.37	6.48	6.53	6.60
	147	6.60	6.38	6.53	6.60	6.70	6.77
	148	6.70	6.56	6.59	6.70	6.79	6.87
	149	6.55	6.39	6.44	6.58	6.63	6.69
	150	6.56	6.34	6.43	6.58	6.69	6.80
	290	5.08	4.64	4.79	5.05	5.21	5.87
	293	6.55	6.34	6.48	6.58	6.64	6.69
Cosby Creek	493	6.46	6.11	6.37	6.46	6.61	
	3	6.50	6.34	6.40	6.54	6.58	6.68
	4	6.15	5.76	5.94	6.00	6.53	6.63
	114	6.24	5.89	6.18	6.32	6.35	6.48
	115	6.20	6.02	6.10	6.20	6.26	6.47
	137	5.88	5.61	5.75	5.90	5.94	6.21
	138	5.52	5.30	5.40	5.49	5.62	5.81
Hazel Creek	492	6.14	5.81	6.04	6.12	6.32	6.39
	221	6.22	5.89	6.07	6.28	6.34	6.48
	310	6.52	6.29	6.39	6.49	6.62	6.82
	311	6.50	6.28	6.39	6.53	6.57	6.70
	479	6.53	6.32	6.41	6.47	6.67	6.85
	480	6.56	6.38	6.46	6.53	6.63	6.81
	481	6.53	6.25	6.40	6.48	6.67	6.86
	482	6.45	6.20	6.31	6.46	6.55	6.77
	483	6.54	6.28	6.45	6.52	6.67	6.82
	484	6.46	6.20	6.30	6.48	6.57	6.76
Indian Camp Creek	485	6.55	6.27	6.43	6.58	6.70	6.80
	1	6.23	5.93	6.10	6.24	6.38	6.47
	103	5.58	5.30	5.42	5.62	5.75	5.81
	104	5.72	5.08	5.50	5.69	5.88	6.19
	106	6.01	5.78	5.93	6.00	6.12	6.21
	107	6.07	5.85	5.97	6.11	6.17	6.24

Table A2-1 (continued)

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Middle Prong Little Pigeon River	43	5.94	5.66	5.79	5.96	6.06	6.25
	45	5.55	5.23	5.39	5.52	5.70	5.84
	46	5.76	5.36	5.53	5.80	5.97	6.08
	47	5.95	5.68	5.86	6.03	6.08	6.11
	49	6.25	5.98	6.10	6.24	6.40	6.49
	50	6.36	6.05	6.16	6.36	6.53	6.72
	52	6.43	6.20	6.30	6.39	6.60	6.73
West Prong Little Pigeon River	30	6.42	6.20	6.27	6.42	6.53	6.70
	66	6.24	5.82	6.11	6.28	6.38	6.60
	71	6.19	5.82	6.09	6.21	6.37	6.45
	73	6.23	5.63	6.14	6.32	6.39	6.54
	74	6.34	5.94	6.26	6.39	6.49	6.65
	233	5.99	5.20	5.83	6.08	6.35	6.55
	234	5.89	5.48	5.74	5.88	6.06	6.25
	237	4.89	4.69	4.75	4.82	4.91	5.08
	473	6.13	5.48	5.68	6.20	6.47	6.59
Oconaluftee River	251	6.03	5.68	5.86	6.08	6.19	6.32
	252	5.34	4.67	4.76	4.92	6.15	6.56
	253	6.39	6.08	6.35	6.43	6.49	6.58
	266	6.53	6.30	6.42	6.53	6.62	6.82
	268	6.48	6.24	6.39	6.48	6.58	6.67
East Prong Little River	13	6.66	6.43	6.55	6.66	6.82	6.92
	14	6.64	6.35	6.47	6.62	6.83	6.86
	20	6.55	6.25	6.41	6.53	6.76	6.82
	34	6.42	6.26	6.32	6.43	6.49	6.62
	209	6.24	5.88	6.19	6.28	6.34	6.40
	210	6.38	6.14	6.28	6.40	6.50	6.55
	213	6.11	5.82	5.92	6.16	6.23	6.35
	214	6.29	6.10	6.16	6.32	6.39	6.49
	215	6.39	6.15	6.30	6.36	6.47	6.64
	218	5.10	4.84	4.96	5.05	5.25	5.60
	220	5.32	4.92	5.12	5.28	5.52	5.68
	474	6.36	6.18	6.23	6.33	6.46	6.64
	475	6.31	6.03	6.22	6.31	6.45	6.52
Middle Prong Little River	23	6.58	6.34	6.40	6.62	6.78	6.86
	190	6.25	6.04	6.16	6.27	6.36	6.40
	191	6.11	5.85	5.99	6.12	6.22	6.38
	192	6.11	5.88	5.95	6.10	6.22	6.32
	193	6.40	6.27	6.29	6.38	6.49	6.64
	194	6.38	6.20	6.24	6.32	6.53	6.60
	472	6.17	5.89	6.13	6.17	6.24	6.39
West Prong Little River	24	6.74	6.46	6.60	6.71	6.93	7.01
Other Springs	195	5.74	5.53	5.65	5.74	5.87	5.97
	219	4.93	4.78	4.82	4.88	4.99	5.48

Table A2-2. Summary statistics for acid neutralizing capacity within the watersheds sampled. All units are microequivalents per liter. Missing values due to small sample size.

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Abrams Creek	156	420.30	193.37	261.63	385.43	558.65	729.70
	173	135.17	52.16	72.68	95.89	151.83	243.99
	174	1100.66	484.95	752.79	1223.05	1492.46	1555.78
	183	28.12	-68.78	33.95	39.25	45.56	56.13
	184	36.31	24.45	27.08	35.27	41.38	55.05
	186	58.67	35.90	36.98	48.65	69.12	89.30
	200	29.14	17.02	20.30	27.80	34.64	48.79
	201	35.88	20.67	32.14	34.02	39.37	50.97
	488	50.65	31.94	39.95	46.18	61.22	83.20
	489	984.51	333.55	672.49	870.48	1441.74	1526.74
Bunches Creek	291	24.88	5.66	13.84	23.70	32.08	44.16
	336	53.62	40.17	44.60	50.67	55.01	67.00
	337	42.11	27.04	32.38	43.07	47.77	58.52
Cataloochee Creek	127	48.49	30.75	34.71	49.48	56.94	76.33
	142	62.43	37.69	48.51	55.96	72.87	86.14
	143	52.00	32.42	42.45	50.62	62.67	69.03
	144	56.55	29.02	44.05	55.38	69.06	79.79
	147	87.03	56.70	68.82	89.40	106.76	114.12
	148	121.96	68.20	88.44	124.27	144.11	180.78
	149	82.73	55.80	65.38	83.55	101.46	111.85
	150	83.81	53.33	67.69	84.31	105.18	112.44
	290	-4.04	-21.70	-11.88	-5.27	2.75	24.23
	293	88.31	69.38	77.16	86.77	100.87	111.66
Cosby Creek	493	69.06	30.55	52.23	76.62	85.03	
	3	79.94	47.05	63.41	74.22	105.10	116.52
	4	44.67	9.35	13.99	25.04	75.67	118.00
	114	39.37	21.32	33.27	41.02	48.73	53.43
	115	39.34	16.44	21.98	41.25	55.28	61.27
	137	13.08	7.59	10.53	12.40	16.63	19.19
	138	4.60	-1.59	-0.19	3.41	7.81	11.41
Hazel Creek	492	33.91	17.33	21.99	31.30	45.20	56.01
	221	31.55	24.17	25.84	29.45	35.23	44.75
	310	77.55	52.44	67.75	73.01	86.47	103.88
	311	75.09	49.75	60.52	67.30	85.82	111.92
	479	71.26	45.10	60.17	69.25	85.15	97.14
	480	87.60	67.51	76.51	87.90	101.28	105.88
	481	97.38	65.61	78.99	91.59	111.88	148.03
	482	102.46	71.89	76.80	99.89	117.26	155.43
	483	94.10	64.94	74.42	85.16	105.27	152.01
	484	64.31	42.48	50.49	58.38	69.68	125.91
Indian Camp Creek	485	78.19	53.93	61.50	70.65	91.49	124.93
	1	39.02	21.22	27.57	37.97	44.91	55.26
	103	4.04	-2.34	0.51	3.90	7.24	12.12
	104	28.40	-3.89	2.59	7.72	14.70	91.47
	106	18.33	8.02	12.30	17.01	21.10	26.55
	107	22.49	12.99	17.61	21.42	24.57	28.34

Table A2-2 (continued)

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Middle Prong Little Pigeon River	43	18.16	3.87	7.22	11.86	20.55	39.74
	45	5.20	-2.29	0.08	3.48	8.91	18.06
	46	10.67	-0.85	2.03	6.43	12.63	19.71
	47	21.30	7.98	9.18	11.65	18.64	66.92
	49	45.17	14.36	21.31	32.30	52.70	103.00
	50	55.57	15.51	26.26	47.15	74.46	128.46
	52	54.76	26.30	35.98	50.04	74.82	86.05
West Prong Little Pigeon River	30	65.86	30.64	47.15	58.89	92.76	100.34
	66	40.25	10.40	27.33	36.88	52.20	63.90
	71	35.37	12.80	19.76	26.70	42.00	54.58
	73	34.65	4.90	18.86	30.78	53.44	62.56
	74	60.08	11.44	30.31	50.15	94.81	115.96
	233	27.67	-7.63	13.49	31.82	41.64	54.21
	234	21.17	8.10	14.59	17.81	20.85	47.72
	237	-12.73	-19.04	-17.01	-13.68	-10.80	-2.44
Oconaluftee River	473	44.13	4.92	8.60	29.90	64.00	137.20
	251	19.79	3.31	11.42	20.57	26.47	33.00
	252	10.89	-9.64	-7.39	-3.43	23.58	74.07
	253	79.73	64.57	72.79	82.08	89.25	95.07
	266	79.76	47.63	56.87	71.16	101.14	122.47
East Prong Little River	268	70.89	40.31	53.76	68.21	81.92	101.41
	13	116.62	55.72	77.16	116.40	157.08	189.68
	14	109.35	48.14	75.53	103.07	131.77	187.88
	20	86.00	47.09	62.83	84.13	109.89	121.38
	34	70.46	40.13	43.45	63.18	93.22	122.36
	209	35.95	23.34	31.38	36.06	41.55	47.18
	210	54.89	32.27	42.06	49.75	59.68	67.07
	213	23.51	12.50	16.45	23.64	29.46	33.75
	214	39.61	22.76	30.86	38.06	50.25	54.10
	215	53.91	33.30	37.38	50.50	58.47	68.09
	218	8.69	-4.41	-0.95	7.51	20.19	26.48
	220	11.21	-1.45	0.38	3.44	13.93	25.31
	474	57.54	28.06	43.31	57.08	66.18	91.94
	475	39.98	22.77	26.83	33.27	51.00	66.35
Middle Prong Little River	23	104.46	37.75	56.11	102.54	150.72	188.72
	190	33.51	18.50	22.44	31.34	38.54	40.63
	191	21.13	11.40	13.76	20.85	27.15	30.29
	192	22.22	8.16	14.11	20.22	31.28	38.27
	193	55.71	28.82	36.78	57.29	70.77	87.78
	194	50.64	25.02	32.73	46.54	64.85	77.57
	472	39.02	18.60	25.64	37.03	53.17	67.18
West Prong Little River	24	151.31	79.59	105.59	145.56	201.01	225.44
Other Springs	195	30.11	21.88	27.05	30.69	33.28	36.52
	219	-0.45	-9.53	-7.22	-1.20	3.90	14.03

Table A2-3. Summary statistics for conductivity within the watersheds sampled. All units are microsiemens per centimeter. Missing values due to small sample size.

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Abrams Creek	156	49.26	29.25	36.35	45.45	62.23	75.75
	173	19.49	12.88	15.01	17.58	22.80	25.62
	174	108.53	50.88	74.90	126.40	149.55	160.12
	183	12.94	8.01	8.23	9.11	12.89	31.50
	184	13.73	11.50	12.14	13.47	15.08	16.45
	186	14.09	11.42	12.30	13.08	15.67	19.11
	200	12.42	10.56	11.00	12.49	13.29	14.92
	201	11.21	9.18	10.02	11.22	12.61	13.54
	488	11.73	9.16	10.69	11.73	12.76	13.83
	489	98.79	39.99	73.95	87.45	136.65	141.90
Bunches Creek	291	13.70	11.58	12.06	13.55	15.05	16.69
	336	11.90	10.54	11.10	11.77	12.34	14.14
	337	12.07	8.15	10.84	11.85	13.12	15.41
Cataloochee Creek	127	11.50	9.38	10.56	11.60	12.63	13.38
	142	10.95	8.99	9.89	10.96	12.17	12.91
	143	11.08	9.00	9.85	11.22	12.31	13.06
	144	11.14	9.33	9.61	10.78	12.78	13.37
	147	14.51	11.58	12.54	14.63	16.50	17.04
	148	17.21	13.29	14.13	16.86	20.03	21.71
	149	14.47	12.36	12.80	14.61	16.08	16.90
	150	14.38	11.98	12.61	13.90	15.86	17.15
	290	16.58	13.01	13.97	16.15	17.27	22.62
	293	16.49	13.72	15.14	16.20	18.35	18.95
Cosby Creek	493	12.21	9.60	11.27	11.82	13.82	
	3	16.93	14.10	14.97	16.49	18.23	21.30
	4	13.63	11.55	12.64	13.90	15.21	16.62
	114	18.81	14.81	16.88	18.00	19.82	25.70
	115	16.00	12.84	14.16	15.48	18.27	20.42
	137	15.05	12.69	13.85	15.20	16.30	17.41
	138	13.73	11.73	12.91	13.79	14.47	15.60
Hazel Creek	492	17.39	14.53	16.27	17.03	18.70	21.11
	221	10.63	9.14	9.59	10.42	11.29	12.75
	310	12.81	10.02	10.90	12.62	14.66	15.41
	311	11.78	9.27	10.16	12.05	13.43	13.86
	479	11.70	7.99	10.71	12.03	12.68	14.38
	480	13.46	10.54	12.12	13.54	14.98	15.74
	481	16.78	14.41	15.52	16.32	17.89	20.64
	482	13.73	11.28	12.48	13.94	14.89	15.79
	483	14.08	11.71	13.17	13.83	15.42	16.44
	484	10.70	9.02	9.97	10.66	11.78	12.25
Indian Camp Creek	485	11.47	9.40	10.25	11.61	12.97	13.62
	1	15.03	11.76	13.87	15.77	16.22	17.79
	103	19.91	16.41	18.15	20.45	21.83	22.83
	104	20.03	15.74	17.38	18.36	20.75	23.56
	106	17.72	15.40	16.73	17.72	18.23	20.32
	107	16.29	14.33	14.82	16.10	17.22	19.11

Table A2-3 (continued)

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Middle Prong Little Pigeon River	43	15.54	12.61	13.66	16.06	16.75	17.66
	45	19.37	15.40	17.27	19.33	20.85	22.20
	46	17.01	13.55	15.46	16.94	18.52	19.93
	47	12.49	10.35	11.31	12.13	12.81	15.39
	49	16.18	12.29	13.82	15.67	17.24	22.55
	50	16.12	13.00	14.19	15.80	18.06	20.20
	52	16.21	13.15	14.83	15.99	17.71	19.21
West Prong Little Pigeon River	30	20.47	17.55	18.95	20.40	22.15	24.00
	66	19.58	16.89	18.58	19.07	21.00	22.60
	71	16.04	14.00	15.09	16.10	16.94	17.25
	73	20.59	17.27	18.52	20.50	22.90	24.02
	74	24.44	19.11	21.38	24.30	28.90	30.41
	233	23.13	17.43	20.93	22.95	25.50	28.55
	234	16.05	14.86	15.40	16.11	16.81	17.32
	237	19.78	17.35	17.84	20.10	21.20	22.44
Oconaluftee River	473	21.03	17.85	18.13	20.65	24.15	25.02
	251	29.34	11.42	28.23	30.90	34.28	37.85
	252	44.54	20.70	29.20	46.80	55.20	69.65
	253	26.25	19.49	21.70	23.50	25.30	29.02
	266	13.85	10.73	12.22	13.82	15.62	16.88
East Prong Little River	268	13.68	11.14	12.35	13.04	14.69	16.76
	13	18.62	13.69	14.75	18.30	22.10	25.34
	14	18.72	14.01	15.03	17.78	22.75	26.04
	20	15.61	11.50	13.40	15.53	17.43	19.91
	34	14.53	10.01	11.85	14.43	16.55	20.34
	209	11.58	8.28	9.30	10.87	11.40	12.86
	210	15.73	12.54	13.27	14.68	15.52	16.19
	213	11.58	10.07	10.29	11.36	12.08	13.44
	214	12.16	9.65	10.14	11.16	12.10	13.93
	215	15.33	10.54	12.46	13.40	15.50	17.22
	218	21.99	14.92	20.10	22.70	24.70	27.46
	220	17.81	13.57	16.01	17.29	19.71	21.58
	474	13.05	11.35	11.93	13.31	13.86	14.44
Middle Prong Little River	475	11.71	10.07	10.46	12.20	12.66	13.40
	23	16.85	11.04	12.77	16.44	21.00	26.04
	190	12.15	10.30	11.28	11.95	12.93	13.49
	191	10.87	9.47	10.08	10.90	11.48	12.56
	192	13.33	10.97	12.05	12.93	14.78	15.62
	193	12.10	9.36	9.90	11.60	14.24	16.01
	194	14.14	9.93	10.76	12.40	15.12	17.82
West Prong Little River	472	12.32	10.64	11.23	12.35	13.35	14.03
	24	22.94	15.96	17.73	22.50	26.78	32.05
Other Springs	195	8.43	6.82	7.43	7.98	9.19	11.22
	219	34.49	12.70	23.10	24.50	26.50	28.02

Table A2-4. Summary statistics for nitrate within the watersheds sampled. All units are micro-equivalents per liter. Zeroes denote below detection limit. Missing values due to small sample size.

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Abrams Creek	156	2.97	0.00	0.00	3.07	4.63	7.17
	173	5.53	0.00	1.84	5.95	8.48	11.16
	174	12.05	9.44	11.09	12.30	13.28	15.95
	183	6.57	0.00	3.50	5.75	7.19	16.35
	184	25.63	17.29	21.34	25.94	29.12	33.79
	186	17.23	5.64	14.59	17.45	20.44	26.46
	200	25.46	12.64	20.57	25.16	29.99	35.30
	201	16.42	9.63	12.42	16.41	17.94	30.10
	488	10.31	2.11	5.63	10.62	12.97	23.36
	489	11.39	9.63	10.65	11.14	11.88	13.97
Bunches Creek	291	39.35	31.68	34.80	39.27	41.69	46.96
	336	26.38	19.63	23.85	25.28	28.89	34.73
	337	24.92	17.39	22.10	25.99	29.30	31.67
Cataloochee Creek	127	15.13	2.62	11.10	16.55	19.63	24.21
	142	6.88	0.41	4.84	7.40	9.47	12.40
	143	7.86	0.70	6.44	8.48	11.09	13.13
	144	7.05	0.42	4.53	7.13	10.16	11.96
	147	6.77	0.00	2.92	6.81	11.02	12.85
	148	3.43	0.00	0.00	4.41	5.83	6.53
	149	6.98	0.00	0.87	7.90	10.39	14.10
	150	7.47	0.00	0.00	8.72	10.58	16.56
	290	50.57	33.90	43.07	51.77	60.54	68.77
	293	17.04	7.69	13.53	17.62	20.74	25.56
Cosby Creek	493	6.57	0.00	1.19	7.80	10.69	
	3	17.36	5.23	12.70	17.31	22.02	27.29
	4	19.42	1.09	4.86	22.39	29.53	37.78
	114	39.16	23.81	36.88	39.35	44.32	49.34
	115	29.21	12.32	19.06	22.16	39.71	54.28
	137	35.47	26.43	28.76	32.35	40.32	53.14
	138	37.82	25.39	31.04	36.09	42.06	57.32
	492	48.04	42.23	45.14	45.53	51.51	59.26
Hazel Creek	221	23.08	14.65	17.65	22.94	26.81	31.95
	310	3.47	0.00	0.00	2.81	6.12	8.41
	311	3.76	0.00	0.37	4.43	5.73	7.09
	479	2.59	0.00	0.42	2.81	4.48	4.67
	480	1.51	0.00	0.00	2.15	2.69	3.09
	481	0.75	0.00	0.00	0.00	1.65	2.50
	482	2.77	0.00	0.00	2.92	4.62	6.27
	483	1.54	0.00	0.00	2.05	2.77	3.52
	484	5.84	0.00	0.00	7.16	8.63	12.42
	485	2.32	0.00	0.00	2.70	3.94	4.89
Indian Camp Creek	1	24.49	7.56	17.72	24.59	32.40	34.94
	103	50.15	38.51	42.77	48.72	57.74	63.45
	104	44.87	26.08	38.11	47.02	53.53	58.47
	106	42.54	32.64	34.02	42.14	50.13	53.71
	107	35.23	27.40	29.48	35.53	41.03	43.13

Table A2-4 (continued)

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Middle Prong Little Pigeon River	43	24.46	13.48	21.97	24.92	29.63	33.01
	45	32.55	21.24	28.85	32.17	34.94	42.00
	46	28.20	18.48	24.63	28.90	32.78	34.54
	47	24.07	12.66	16.84	21.05	28.15	32.39
	49	18.11	9.24	15.32	18.43	22.50	26.84
	50	17.60	4.59	11.48	15.16	25.49	33.28
	52	16.97	7.28	12.91	16.20	24.01	27.03
West Prong Little Pigeon River	30	25.43	13.44	20.90	25.06	31.18	35.66
	66	34.20	23.24	29.12	33.08	37.26	43.47
	71	32.62	22.81	27.75	31.91	37.11	42.12
	73	34.58	23.47	30.13	33.40	38.41	43.22
	74	32.85	23.39	28.99	32.35	38.21	40.31
	233	36.59	25.55	29.17	34.15	43.81	51.29
	234	57.87	49.75	55.73	59.69	63.00	66.21
	237	34.76	24.28	27.75	33.73	39.27	46.87
	473	33.20	20.92	27.96	32.79	38.23	46.46
Oconaluftee River	251	36.69	18.46	35.61	36.96	39.59	49.86
	252	55.72	43.01	48.02	54.24	58.81	78.13
	253	59.24	49.94	53.13	57.54	60.18	73.91
	266	6.44	0.00	0.68	5.03	9.62	17.42
	268	11.38	1.89	5.72	7.24	11.94	21.51
East Prong Little River	13	7.15	0.00	4.19	6.33	11.32	13.06
	14	8.07	0.00	4.62	6.28	12.02	15.60
	20	9.46	0.00	5.32	7.87	13.02	17.38
	34	8.86	0.00	1.75	11.03	13.05	15.58
	209	6.87	0.00	3.48	6.58	9.68	12.53
	210	14.63	3.47	11.65	14.18	18.27	23.45
	213	20.49	7.50	17.89	21.19	25.90	31.48
	214	14.58	2.99	11.53	14.81	19.39	22.84
	215	12.78	3.84	11.25	12.26	15.66	18.77
	218	52.39	34.43	45.61	46.66	56.68	80.74
	220	62.48	37.74	48.71	67.41	74.49	87.14
	474	11.58	0.00	4.91	13.03	16.15	21.21
	475	13.14	0.36	3.70	15.75	18.73	22.30
Middle Prong Little River	23	8.12	0.00	5.91	8.62	11.45	13.30
	190	16.56	4.64	15.32	17.31	20.49	23.07
	191	21.63	8.04	11.91	20.43	25.42	38.27
	192	23.95	13.41	18.71	23.76	28.66	34.90
	193	6.24	0.00	5.33	7.00	9.03	9.62
	194	9.92	0.00	9.12	10.60	13.36	15.50
	472	15.70	5.52	13.27	17.28	19.24	21.14
West Prong Little River	24	4.41	0.00	2.19	5.69	6.46	6.92
Other Springs	195	3.87	2.66	3.38	3.93	4.27	5.08
	219	79.79	33.56	72.53	88.04	94.22	100.08

Table A2-5. Summary statistics for sulfate within the watersheds sampled. All units are micro-equivalents per liter. Missing values due to small sample size.

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Abrams Creek	156	43.38	37.46	39.53	43.02	45.98	50.74
	173	29.90	20.89	23.34	27.85	30.59	44.43
	174	50.20	44.17	45.70	52.32	55.03	61.78
	183	17.72	6.14	7.20	9.06	25.29	53.11
	184	28.88	20.76	26.14	28.31	30.67	41.02
	186	30.74	24.25	26.64	29.07	31.46	43.62
	200	27.52	19.25	25.12	27.36	29.77	36.45
	201	15.54	12.07	13.31	14.72	17.16	19.15
	488	22.04	14.21	20.27	22.53	25.06	26.46
	489	46.37	38.37	42.55	46.36	49.21	58.11
Bunches Creek	291	25.99	18.42	20.15	23.76	28.32	44.09
	336	10.60	6.87	7.76	9.07	10.60	18.05
	337	16.91	11.05	13.41	14.53	18.28	25.79
Cataloochee Creek	127	20.31	16.21	18.26	19.43	21.46	27.64
	142	17.14	12.75	13.61	15.46	19.34	23.37
	143	21.07	13.56	17.75	21.20	22.26	31.91
	144	18.67	14.64	15.30	17.36	20.37	28.05
	147	20.33	9.64	18.46	21.09	22.01	29.20
	148	21.16	14.40	17.13	19.19	22.49	35.25
	149	22.59	17.89	18.95	21.66	25.91	29.72
	150	21.13	17.08	17.96	20.25	22.19	29.73
	290	24.84	13.77	15.75	20.97	28.32	52.13
	293	23.64	18.08	21.61	23.86	24.65	28.46
Cosby Creek	493	18.24	14.71	15.93	17.64	19.24	
	3	35.28	25.58	30.63	35.01	40.63	45.37
	4	36.10	17.10	20.16	40.91	47.86	50.51
	114	44.21	36.22	41.98	43.79	47.07	51.48
	115	48.45	35.94	40.31	44.16	55.32	77.55
	137	53.41	44.63	46.73	49.86	56.14	71.40
	138	39.73	34.42	35.91	37.96	40.09	51.17
Hazel Creek	492	39.97	34.87	37.70	40.81	42.48	46.06
	221	16.90	12.58	14.74	16.74	19.70	21.96
	310	21.30	16.86	18.18	21.04	23.37	28.33
	311	18.07	14.59	16.53	17.49	19.44	22.94
	479	16.77	9.62	16.32	17.75	18.40	19.75
	480	20.62	17.37	18.71	19.97	21.80	26.98
	481	44.26	30.63	37.53	41.01	54.81	61.17
	482	20.43	18.40	19.45	20.56	21.51	22.11
	483	26.68	20.03	24.04	26.80	30.39	31.39
	484	17.00	14.15	15.75	16.52	17.99	21.30
Indian Camp Creek	485	15.92	12.74	13.88	14.84	17.06	22.85
	1	45.50	30.21	37.83	47.53	49.83	55.58
	103	68.39	64.12	65.97	67.99	71.60	74.90
	104	59.98	51.47	55.08	57.31	61.07	81.92
	106	58.74	51.57	54.81	57.86	61.11	68.07
	107	52.80	47.23	50.45	53.07	55.27	57.90

Table A2-5 (continued)

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Middle Prong Little Pigeon River	43	62.85	47.97	54.84	63.04	75.68	78.88
	45	89.90	71.33	77.19	87.39	100.77	111.30
	46	74.74	57.55	62.25	73.87	90.58	93.03
	47	47.37	32.59	36.88	41.87	48.55	51.50
	49	53.17	41.05	45.53	52.20	60.61	65.71
	50	48.71	37.07	41.20	47.63	54.58	62.59
	52	49.42	37.98	43.30	48.92	54.57	58.55
West Prong Little Pigeon River	30	62.23	53.16	59.12	63.02	67.17	71.19
	66	69.76	61.18	64.41	70.03	74.79	81.89
	71	49.73	38.70	42.82	44.85	49.62	52.23
	73	78.49	61.06	68.63	77.91	82.84	92.79
	74	86.77	68.81	76.95	86.99	96.78	106.84
	233	103.83	83.08	91.95	104.88	115.13	121.00
	234	27.44	18.86	25.07	27.83	28.95	31.28
	237	69.69	58.79	63.60	68.45	76.30	85.61
Oconaluftee River	473	81.72	68.23	71.49	80.02	92.57	96.90
	251	155.52	37.37	143.01	172.74	194.21	215.37
	252	281.82	88.39	132.22	313.23	374.47	456.40
	253	41.97	34.49	36.13	42.12	44.70	52.52
	266	23.79	17.62	21.01	23.82	26.69	29.29
East Prong Little River	268	30.36	20.80	23.20	27.29	32.26	49.91
	13	38.17	29.74	33.65	36.56	38.64	52.87
	14	37.31	29.90	32.06	35.73	41.38	49.55
	20	35.55	25.49	31.97	33.92	36.70	48.07
	34	33.13	24.57	30.76	32.72	36.23	41.51
	209	26.97	20.48	22.62	24.76	28.25	32.16
	210	41.25	36.63	38.50	39.95	42.41	51.66
	213	30.20	25.85	27.58	29.49	31.37	34.69
	214	24.67	18.41	20.75	23.02	25.12	32.55
	215	36.49	25.74	31.74	35.24	38.17	48.28
	218	58.71	47.43	54.14	58.05	66.10	71.71
	220	33.62	22.47	25.67	29.62	33.27	61.96
	474	34.46	29.81	32.29	33.30	36.64	43.04
Middle Prong Little River	475	29.43	24.71	25.83	28.76	31.98	38.05
	23	34.24	26.33	29.84	31.64	35.13	42.49
	190	32.93	26.51	29.19	32.44	34.60	39.88
	191	30.86	20.92	23.52	26.49	30.38	40.28
	192	42.54	33.63	38.91	41.48	44.86	53.51
	193	25.59	19.63	22.87	24.11	27.88	34.55
	194	30.42	25.74	27.40	29.00	33.07	39.30
West Prong Little River	472	32.28	27.97	29.63	32.39	35.34	36.53
	24	43.72	36.83	39.28	42.94	46.42	54.38
Other Springs	195	8.01	6.58	7.62	8.10	8.53	9.12
	219	55.45	32.32	52.19	58.59	62.21	66.37

Table A2-6. Summary statistics for chloride within the watersheds sampled. All units are micro-equivalents per liter. Missing values due to small sample size.

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Abrams Creek	156	22.31	15.53	17.39	20.00	25.42	37.46
	173	19.53	12.34	13.81	15.99	19.54	40.29
	174	23.20	17.00	19.33	20.71	24.41	30.35
	183	16.65	9.54	12.18	14.13	18.58	21.33
	184	18.65	13.69	14.49	16.48	22.54	26.17
	186	16.70	12.31	14.03	16.38	19.23	21.69
	200	17.57	10.69	13.82	15.72	20.05	24.62
	201	12.05	9.63	10.06	11.39	13.77	15.84
	488	17.69	12.35	12.84	14.05	17.87	42.19
	489	24.97	16.38	18.03	20.16	24.51	61.58
Bunches Creek	291	16.43	10.35	12.34	14.82	17.43	24.43
	336	17.60	10.38	14.00	16.67	17.35	30.48
	337	15.74	10.17	11.30	13.74	16.37	26.56
Cataloochee Creek	127	18.72	10.97	12.81	15.42	18.16	41.77
	142	15.65	9.93	11.42	12.79	15.40	33.62
	143	14.86	10.76	12.57	13.62	17.23	19.67
	144	16.77	10.49	11.42	12.91	15.61	31.03
	147	13.86	9.82	11.12	12.93	15.71	18.37
	148	16.31	10.04	11.00	13.66	16.63	36.67
	149	15.25	10.73	11.86	13.53	17.95	23.88
	150	15.52	9.94	11.52	14.80	16.18	24.33
	290	16.77	11.42	13.64	16.34	18.77	23.87
	293	16.49	10.94	12.22	14.46	17.08	27.66
Cosby Creek	493	18.21	9.31	11.39	13.58	24.32	
	3	14.24	9.31	10.60	12.08	15.23	24.07
	4	12.90	8.98	10.32	11.75	14.15	15.49
	114	20.07	10.71	11.40	15.06	24.59	44.17
	115	19.17	10.23	11.07	15.02	23.99	42.23
	137	16.00	10.13	11.67	13.59	16.77	20.42
	138	16.81	10.46	11.93	14.13	20.70	27.43
Hazel Creek	492	16.64	10.75	11.70	14.45	16.70	37.72
	221	17.09	11.11	11.33	13.93	19.20	30.46
	310	16.62	10.23	11.62	13.94	17.08	28.26
	311	18.24	11.33	11.82	13.67	16.23	47.33
	479	16.68	7.10	11.82	13.42	15.50	41.30
	480	15.15	10.24	10.99	12.37	16.19	33.79
	481	15.99	10.37	10.84	12.36	15.80	39.34
	482	16.38	9.86	11.60	13.79	16.05	41.29
	483	14.63	11.00	11.46	12.94	15.30	26.87
	484	16.90	10.77	11.78	14.55	17.11	40.30
Indian Camp Creek	485	15.86	10.32	11.32	13.03	17.41	33.03
	1	13.18	9.74	10.80	12.98	15.20	16.82
	103	15.55	10.03	12.25	13.78	18.27	24.64
	104	15.23	11.14	11.73	13.08	15.04	26.65
	106	13.58	8.99	10.55	13.25	15.77	20.07
	107	12.47	9.09	10.81	11.49	12.26	17.26

Table A2-6 (continued)

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Middle Prong Little Pigeon River	43	13.96	10.03	10.68	12.80	14.70	18.76
	45	15.87	10.43	11.18	13.69	17.07	26.84
	46	14.52	10.13	11.23	12.57	17.61	24.17
	47	15.01	8.55	9.83	12.01	15.30	29.93
	49	14.24	10.21	11.36	12.77	14.03	24.77
	50	16.95	9.94	12.01	15.49	19.43	29.96
	52	16.47	10.37	11.05	12.39	18.16	30.50
West Prong Little Pigeon River	30	17.21	12.33	13.09	15.40	18.23	25.36
	66	15.64	11.78	12.74	14.17	15.99	23.21
	71	17.21	10.62	11.61	14.62	18.88	31.10
	73	16.18	12.47	13.46	15.21	17.01	20.89
	74	15.89	12.04	12.60	14.55	15.90	23.52
	233	16.93	12.22	13.67	14.87	17.45	26.48
	234	18.01	12.75	13.61	16.38	20.03	26.15
	237	13.74	9.79	10.48	12.29	14.24	26.52
Oconaluftee River	473	15.85	11.15	12.93	14.27	16.76	26.54
	251	18.70	9.74	14.79	16.68	18.68	22.92
	252	20.10	14.33	15.29	16.48	20.58	23.93
	253	23.19	14.60	15.69	16.94	23.19	42.82
	266	16.08	9.64	10.64	12.02	16.29	38.42
East Prong Little River	268	17.99	9.61	11.30	14.00	18.09	36.05
	13	15.25	11.10	12.53	13.41	16.91	22.84
	14	14.44	10.91	11.45	12.90	15.81	24.19
	20	14.75	9.72	11.55	12.52	15.54	23.10
	34	18.23	10.94	11.92	13.97	20.67	37.87
	209	14.80	10.36	11.77	12.94	15.22	27.72
	210	13.69	9.56	10.75	11.69	14.59	23.28
	213	14.05	10.95	11.88	12.83	14.02	18.57
	214	16.35	10.95	12.04	14.65	17.39	26.84
	215	15.97	11.03	11.82	14.36	17.84	25.24
	218	20.83	10.63	13.37	16.11	26.10	40.87
	220	12.91	9.41	10.65	11.73	12.37	15.40
	474	16.51	11.31	12.61	12.98	17.00	32.77
	475	17.86	12.06	13.85	15.53	17.00	33.73
Middle Prong Little River	23	17.16	11.54	12.59	13.14	16.88	34.55
	190	14.12	10.16	12.36	13.17	15.17	17.93
	191	15.50	10.47	11.15	15.11	17.15	23.65
	192	13.68	9.00	10.38	12.31	13.98	23.15
	193	14.28	9.70	11.84	13.51	16.85	17.24
	194	14.82	10.74	11.41	14.06	16.31	21.14
	472	16.30	10.89	11.16	13.55	19.06	30.39
West Prong Little River	24	15.58	11.49	12.83	14.66	16.07	20.08
Other Springs	195	14.97	11.09	11.60	14.20	16.75	23.56
	219	13.85	10.05	12.57	13.76	15.78	17.71

Table A2-7. Summary statistics for sodium within the watersheds sampled. All units are micro-equivalents per liter. Missing values due to small sample size.

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Abrams Creek	156	52.72	35.12	45.96	53.03	60.11	67.97
	173	44.92	28.91	36.51	41.99	54.63	60.08
	174	55.34	44.59	49.02	55.45	64.12	65.52
	183	32.63	20.22	27.67	30.66	36.96	42.42
	184	39.53	24.89	31.01	38.39	48.61	53.97
	186	39.85	17.99	31.64	40.77	45.10	57.36
	200	33.11	20.73	28.35	32.56	39.15	45.88
	201	26.56	19.87	24.02	26.76	28.70	32.34
	488	38.93	27.70	35.72	38.96	42.30	49.18
	489	55.58	45.41	50.14	56.02	59.68	66.33
Bunches Creek	291	34.15	25.64	30.39	33.75	39.87	42.74
	336	40.52	32.79	37.72	40.15	41.89	46.52
	337	35.91	25.74	32.36	37.23	39.42	42.36
Cataloochee Creek	127	37.33	25.66	31.44	36.89	44.37	49.65
	142	36.74	30.32	31.75	35.39	44.24	46.59
	143	37.19	26.76	30.11	39.33	43.48	47.16
	144	38.52	28.32	32.19	38.68	45.88	49.62
	147	47.10	25.34	38.92	46.63	59.83	64.98
	148	67.04	38.92	56.77	69.58	80.47	87.11
	149	48.57	30.13	43.50	49.62	58.45	62.88
	150	47.79	30.22	41.44	47.93	57.45	61.80
	290	30.58	20.69	25.60	29.60	36.26	42.81
	293	52.33	34.28	47.32	53.86	61.53	66.55
Cosby Creek	493	43.08	31.79	34.19	41.78	52.85	
	3	52.10	38.99	43.50	50.61	59.29	67.66
	4	39.09	25.63	28.17	33.43	48.45	64.43
	114	35.48	23.14	33.70	36.61	38.95	41.97
	115	33.55	21.51	29.96	31.95	39.76	46.73
	137	31.81	26.14	27.38	30.19	36.62	39.69
	138	27.83	18.64	25.19	27.66	31.09	36.93
Hazel Creek	492	36.32	28.47	29.68	36.77	42.23	45.16
	221	33.81	24.66	29.84	32.17	38.66	44.20
	310	39.77	24.76	31.82	40.80	46.49	52.83
	311	40.56	27.74	34.13	41.70	45.48	51.38
	479	39.57	14.54	36.32	40.81	47.17	52.68
	480	45.92	34.13	41.36	46.17	50.54	56.38
	481	44.39	35.98	39.61	43.78	49.86	53.37
	482	45.96	39.44	42.24	44.96	50.50	53.04
	483	47.74	38.85	42.83	47.65	53.65	58.74
	484	37.88	30.92	34.35	37.37	40.68	47.18
Indian Camp Creek	485	39.54	24.18	36.40	37.97	47.71	49.16
	1	35.57	26.14	29.83	35.08	38.81	46.37
	103	30.29	23.88	25.71	29.51	32.40	40.81
	104	30.90	20.77	24.73	28.09	31.25	45.16
	106	27.26	20.92	22.39	28.16	31.24	34.59
	107	26.87	20.70	24.29	26.85	30.50	32.24

Table A2-7 (continued)

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Middle Prong Little Pigeon River	43	25.06	18.10	21.94	24.21	30.43	31.84
	45	22.81	16.65	18.82	21.96	27.13	31.12
	46	26.28	21.25	22.62	24.17	31.55	34.03
	47	24.32	17.63	21.15	23.40	28.00	31.17
	49	32.03	24.78	25.87	30.35	37.66	41.81
	50	35.42	24.03	28.53	35.17	42.38	47.20
	52	36.45	27.33	30.82	36.60	42.91	47.93
West Prong Little Pigeon River	30	32.96	14.82	27.80	34.48	39.84	45.62
	66	23.75	15.78	19.46	24.00	27.02	29.33
	71	27.83	21.86	22.62	27.76	31.89	33.05
	73	23.17	17.92	19.31	22.73	26.68	28.00
	74	23.48	14.27	19.64	22.76	28.56	30.83
	233	23.04	16.97	20.18	22.88	25.68	28.93
	234	33.57	21.36	29.80	35.04	38.05	42.90
	237	17.29	12.43	15.25	17.60	19.21	22.82
	473	22.17	17.22	18.87	22.96	24.62	26.77
Oconaluftee River	251	39.02	24.56	32.08	40.62	46.42	50.37
	252	51.72	40.60	44.57	47.83	59.23	67.28
	253	54.62	38.98	48.93	54.63	60.74	65.83
	266	44.27	29.39	37.74	43.58	54.25	58.37
	268	39.77	25.95	33.33	42.08	46.75	50.21
East Prong Little River	13	42.03	30.73	34.06	41.20	46.34	55.57
	14	40.44	29.20	32.87	40.17	50.40	52.15
	20	38.14	27.26	31.47	39.32	43.61	50.03
	34	36.91	23.83	29.39	36.41	44.95	53.01
	209	32.38	25.03	29.47	32.01	37.02	39.25
	210	30.75	24.81	27.05	31.33	34.57	35.97
	213	27.72	20.89	24.27	28.39	31.48	33.49
	214	31.49	14.46	27.34	30.93	37.64	41.94
	215	33.94	17.11	31.73	35.09	40.18	42.74
	218	31.94	17.45	21.87	26.44	39.23	47.53
	220	24.58	14.88	23.05	26.13	26.66	29.69
	474	32.33	17.58	27.22	33.03	37.45	42.83
	475	29.97	9.60	26.70	30.82	35.05	40.85
Middle Prong Little River	23	36.39	23.57	29.63	33.98	45.34	49.31
	190	32.20	24.79	26.63	30.00	39.76	42.95
	191	29.21	18.51	22.96	28.13	31.78	33.95
	192	24.31	16.78	20.86	23.13	29.27	31.46
	193	33.62	21.69	27.27	34.10	41.24	44.02
	194	33.50	20.27	26.23	30.66	41.16	49.01
	472	33.39	11.66	26.39	30.86	41.01	61.02
West Prong Little River	24	52.61	38.81	45.55	51.38	59.12	66.15
Other Springs	195	24.44	17.75	22.07	24.90	26.15	31.25
	219	23.05	14.28	18.91	21.83	27.30	29.77

Table A2-8. Summary statistics for potassium within the watersheds sampled. All units are micro-equivalents per liter. Missing values due to small sample size.

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Abrams Creek	156	16.67	10.05	14.43	16.32	19.09	22.72
	173	13.58	9.71	10.17	11.79	16.85	20.84
	174	18.44	11.96	13.24	15.99	18.25	24.19
	183	7.44	3.83	5.00	6.42	9.25	12.18
	184	11.88	6.83	9.38	11.27	12.70	18.91
	186	10.97	7.09	10.52	10.96	12.44	13.57
	200	10.56	6.86	8.18	10.29	12.34	14.68
	201	8.86	4.75	6.84	9.25	10.69	11.63
	488	9.98	7.35	9.31	10.09	10.99	11.80
	489	15.20	11.87	13.04	15.19	17.29	18.71
Bunches Creek	291	9.96	6.23	8.88	10.00	10.81	14.04
	336	13.31	9.98	11.13	12.62	15.14	18.15
	337	10.34	6.70	9.25	10.26	12.14	13.79
Cataloochee Creek	127	11.32	6.83	9.15	11.11	14.20	15.52
	142	11.67	7.93	10.24	11.97	13.11	14.82
	143	11.54	9.02	9.36	10.76	13.33	16.43
	144	12.87	9.72	10.60	12.31	14.31	17.68
	147	13.07	4.94	11.92	13.46	16.60	17.40
	148	15.67	7.95	13.13	16.78	18.87	20.46
	149	14.57	9.01	13.26	14.66	17.52	18.40
	150	14.56	8.29	11.71	13.55	16.49	22.82
	290	7.84	4.57	6.00	7.76	9.55	11.67
	293	14.31	9.18	12.00	13.66	15.08	17.83
Cosby Creek	493	11.99	8.91	9.75	12.01	14.03	
	3	10.48	7.65	8.17	10.49	12.52	14.82
	4	9.79	5.32	7.13	9.47	12.43	13.69
	114	10.25	5.74	7.78	9.85	11.29	16.67
	115	7.70	4.00	5.76	7.60	9.84	11.63
	137	8.48	4.91	6.19	8.26	10.32	12.62
	138	8.60	5.23	6.36	8.77	10.72	12.39
Hazel Creek	492	8.92	7.74	7.83	8.16	9.27	12.98
	221	11.07	7.05	7.71	9.68	12.88	18.85
	310	9.80	5.40	8.09	9.61	11.90	14.07
	311	10.96	7.07	9.80	10.43	13.03	15.17
	479	11.04	2.38	9.92	11.00	13.38	16.26
	480	12.19	8.90	11.36	11.83	13.66	15.55
	481	13.21	11.08	12.25	12.78	14.55	16.56
	482	11.44	9.00	10.21	11.29	12.37	14.81
	483	14.17	11.36	12.01	12.66	16.35	19.10
	484	10.48	7.50	8.88	9.86	12.52	14.95
Indian Camp Creek	485	11.30	6.88	9.87	11.41	12.70	16.25
	1	12.57	7.66	9.45	10.53	11.94	23.35
	103	11.27	5.92	8.95	10.62	12.71	16.94
	104	12.70	7.80	8.86	12.02	15.97	19.31
	106	13.10	11.02	11.65	13.12	14.73	15.67
	107	11.81	7.78	9.86	11.19	12.72	17.13

Table A2-8 (continued)

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Middle Prong Little Pigeon River	43	6.12	4.10	4.82	5.79	6.68	9.42
	45	4.80	2.81	3.19	4.08	6.16	8.41
	46	4.15	2.41	3.36	3.91	4.76	6.53
	47	8.92	5.75	7.91	8.67	10.70	11.69
	49	7.56	5.23	6.12	7.08	8.50	10.27
	50	10.09	6.74	8.02	8.90	10.79	17.75
	52	13.77	5.99	7.14	8.28	9.26	10.94
West Prong Little Pigeon River	30	8.71	5.00	7.91	8.78	10.47	11.83
	66	6.55	4.12	6.08	6.58	7.59	8.29
	71	8.50	6.74	7.87	8.21	9.02	10.81
	73	5.16	3.64	4.17	4.99	5.91	8.08
	74	5.08	3.18	3.70	4.58	5.73	8.02
	233	4.45	2.72	3.71	4.10	5.24	7.03
	234	6.41	4.79	5.30	5.90	7.46	8.28
	237	3.76	2.28	2.49	3.17	4.44	6.53
Oconaluftee River	473	5.39	4.11	4.29	5.22	6.42	7.52
	251	9.97	6.49	9.04	10.42	11.17	12.64
	252	12.90	9.16	10.56	12.00	16.27	18.00
	253	9.11	5.63	7.20	9.06	10.21	12.51
	266	12.02	8.27	10.33	11.78	13.80	16.24
East Prong Little River	268	10.59	6.28	9.26	11.13	12.41	13.56
	13	12.70	9.15	11.16	12.26	13.94	16.11
	14	13.88	10.46	11.63	13.46	16.11	18.20
	20	12.02	7.03	10.45	11.90	14.42	15.82
	34	13.29	9.86	10.58	12.24	16.70	18.10
	209	9.79	7.71	8.83	9.41	10.96	13.16
	210	10.39	7.42	9.04	10.50	11.58	13.40
	213	8.77	6.09	7.69	8.17	9.58	12.55
	214	9.54	6.26	7.85	9.94	10.99	13.12
	215	8.97	6.49	7.70	9.09	10.29	10.76
	218	14.92	8.84	11.04	14.33	18.02	23.91
	220	12.54	7.66	10.53	11.91	14.17	15.10
Middle Prong Little River	474	11.10	6.20	9.61	10.51	12.25	17.77
	475	11.94	8.83	8.89	10.45	12.77	21.66
	23	10.62	6.99	8.36	10.30	12.33	14.13
	190	8.06	5.60	6.55	8.09	9.26	10.56
	191	9.11	5.81	7.46	8.52	9.37	11.53
	192	6.16	4.01	4.98	6.00	7.43	8.76
	193	9.60	4.90	7.92	9.74	10.69	13.99
West Prong Little River	194	9.48	6.00	7.57	8.93	11.21	14.79
	472	9.02	3.40	6.66	8.43	11.20	17.03
Other Springs	24	13.21	8.16	11.07	13.16	15.12	18.50
	195	5.89	4.43	5.50	5.89	6.44	7.07
	219	13.22	6.43	9.25	11.38	14.50	24.23

Table A2-9. Summary statistics for ammonium within the watersheds sampled. All units are micro-equivalents per liter. Zeroes denote below detection limit.

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Abrams Creek	156	0.81	0.00	0.00	0.00	0.75	3.85
	173	0.00	0.00	0.00	0.00	0.00	0.00
	174	0.51	0.00	0.00	0.00	0.00	3.39
	183	0.16	0.00	0.00	0.00	0.00	0.00
	184	0.71	0.00	0.00	0.00	0.00	3.30
	186	0.20	0.00	0.00	0.00	0.00	0.00
	200	0.16	0.00	0.00	0.00	0.00	0.68
	201	0.65	0.00	0.00	0.00	0.00	4.65
	488	0.20	0.00	0.00	0.00	0.00	1.65
	489	0.00	0.00	0.00	0.00	0.00	0.00
Bunches Creek	291	0.00	0.00	0.00	0.00	0.00	0.00
	336	1.15	0.00	0.00	0.00	0.00	7.01
	337	0.27	0.00	0.00	0.00	0.00	2.27
Cataloochee Creek	127	0.55	0.00	0.00	0.00	0.00	2.19
	142	0.00	0.00	0.00	0.00	0.00	0.00
	143	1.74	0.00	0.00	0.00	0.00	6.84
	144	0.06	0.00	0.00	0.00	0.00	0.00
	147	0.00	0.00	0.00	0.00	0.00	0.00
	148	0.00	0.00	0.00	0.00	0.00	0.00
	149	0.00	0.00	0.00	0.00	0.00	0.00
	150	0.39	0.00	0.00	0.00	0.00	2.32
	290	0.26	0.00	0.00	0.00	0.00	1.72
	293	0.00	0.00	0.00	0.00	0.00	0.00
	493	0.00	0.00	0.00	0.00	0.00	0.00
Cosby Creek	3	0.32	0.00	0.00	0.00	0.00	1.62
	4	0.08	0.00	0.00	0.00	0.00	0.00
	114	0.24	0.00	0.00	0.00	0.00	1.13
	115	0.00	0.00	0.00	0.00	0.00	0.00
	137	0.23	0.00	0.00	0.00	0.00	0.00
	138	0.50	0.00	0.00	0.00	0.00	3.29
	492	0.58	0.00	0.00	0.00	0.00	5.12
Hazel Creek	221	0.55	0.00	0.00	0.00	0.00	3.40
	310	0.37	0.00	0.00	0.00	0.00	1.27
	311	0.30	0.00	0.00	0.00	0.00	1.62
	479	0.00	0.00	0.00	0.00	0.00	0.00
	480	0.00	0.00	0.00	0.00	0.00	0.00
	481	0.00	0.00	0.00	0.00	0.00	0.00
	482	0.00	0.00	0.00	0.00	0.00	0.00
	483	0.00	0.00	0.00	0.00	0.00	0.00
	484	0.00	0.00	0.00	0.00	0.00	0.00
	485	0.00	0.00	0.00	0.00	0.00	0.00
Indian Camp Creek	1	0.26	0.00	0.00	0.00	0.00	0.00
	103	0.30	0.00	0.00	0.00	0.00	1.66
	104	0.41	0.00	0.00	0.00	0.00	2.02
	106	0.07	0.00	0.00	0.00	0.00	0.42
	107	0.14	0.00	0.00	0.00	0.00	0.40

Table A2-9 (continued)

Watershed	Sample site	Mean	Percentiles				
			10	25	50	75	90
Middle Prong Little Pigeon River	43	0.24	0.00	0.00	0.00	0.00	0.00
	45	0.31	0.00	0.00	0.00	0.00	0.00
	46	0.24	0.00	0.00	0.00	0.00	0.00
	47	1.09	0.00	0.00	0.00	0.00	5.51
	49	0.00	0.00	0.00	0.00	0.00	0.00
	50	0.59	0.00	0.00	0.00	0.00	4.11
	52	0.00	0.00	0.00	0.00	0.00	0.00
West Prong Little Pigeon River	30	0.13	0.00	0.00	0.00	0.00	0.80
	66	0.17	0.00	0.00	0.00	0.00	0.00
	71	0.33	0.00	0.00	0.00	0.00	1.21
	73	0.14	0.00	0.00	0.00	0.00	0.26
	74	0.27	0.00	0.00	0.00	0.00	0.29
	233	0.18	0.00	0.00	0.00	0.00	0.00
	234	0.31	0.00	0.00	0.00	0.00	2.40
	237	0.54	0.00	0.00	0.00	0.00	3.00
	473	0.00	0.00	0.00	0.00	0.00	0.00
Oconaluftee River	251	0.33	0.00	0.00	0.00	0.00	1.09
	252	0.18	0.00	0.00	0.00	0.00	0.74
	253	0.00	0.00	0.00	0.00	0.00	0.00
	266	0.19	0.00	0.00	0.00	0.00	0.93
	268	0.25	0.00	0.00	0.00	0.00	0.00
East Prong Little River	13	0.07	0.00	0.00	0.00	0.00	0.00
	14	0.57	0.00	0.00	0.00	0.00	2.61
	20	0.46	0.00	0.00	0.00	0.00	1.79
	34	3.28	0.00	0.00	0.00	1.69	10.09
	209	0.11	0.00	0.00	0.00	0.00	0.00
	210	0.00	0.00	0.00	0.00	0.00	0.00
	213	0.08	0.00	0.00	0.00	0.00	0.00
	214	0.76	0.00	0.00	0.00	0.00	4.16
	215	0.18	0.00	0.00	0.00	0.00	0.00
	218	1.57	0.00	0.00	0.00	2.30	6.79
	220	0.77	0.00	0.00	0.00	0.00	2.86
	474	0.32	0.00	0.00	0.00	0.00	2.69
	475	2.81	0.00	0.00	0.00	0.00	21.40
Middle Prong Little River	23	0.09	0.00	0.00	0.00	0.00	0.00
	190	0.04	0.00	0.00	0.00	0.00	0.00
	191	0.28	0.00	0.00	0.00	0.00	1.94
	192	0.21	0.00	0.00	0.00	0.00	0.88
	193	0.55	0.00	0.00	0.00	0.00	0.00
	194	0.15	0.00	0.00	0.00	0.00	0.00
	472	0.00	0.00	0.00	0.00	0.00	0.00
West Prong Little River	24	0.21	0.00	0.00	0.00	0.00	0.27
Other Springs	195	0.00	0.00	0.00	0.00	0.00	0.00
	219	0.00	0.00	0.00	0.00	0.00	0.00

APPENDIX A3. EXPLANATION OF GIS METHODS

The following explains the software and procedures used to extract basin physical characteristics from the National Park Service GIS database. The information presented here was contributed by Richard R. Schulz, GIS specialist for the Great Smoky Mountains National Park. Richard was responsible for extracting the information presented in this thesis. Also explained are problems encountered and how they were handled.

Software

- ArcView 3.1
- ArcView Spatial Analyst 1.1
- Hydrologic Modeling Sample Extension v1.1 which comes with ArcView
- ArcInfo 7.2.1 GRID module

Procedures

Digital Elevation Model (DEM) preparation was done with ArcInfo GRID. The DEM data came from 30 meter square pixels using USGS 1:24,000 topographical maps. This data was mosaiced to cover the entire Great Smoky Mountains National Park. All sinks were filled using the GRID FILL command. A flow direction grid was created using the GRID FLOWDIRECTION command. To create the contributing area polygons to each of the sampling sites, the sampling sites were first imported from an Excel file into ArcInfo using the UTM X and UTM Y coordinates of the sampling sites to create an event theme shapefile. The shapefile of the sampling site locations was then converted into a grid. The GRID WATERSHED command was used to create a grid of all 90 contributing areas. The resulting grid was converted into a polygon shapefile and examined in ArcView. If any polygons did not reasonably portray the known contributing areas, the corresponding sampling site was moved or manually edited in ArcView and the process explained above

was repeated. How sites were moved or manually edited is discussed later. Because the contributing area for downstream sites included all upstream polygons for which subsequent procedures could not work with overlapping polygons, a single polygon shapefile was created for each contributing area. All contributing polygons were merged into one contributing area polygon using ArcView GeoProcessing Wizard's Dissolve operation.

The mosaiced and filled elevation grid and the individual contributing area polygon shapefiles were used with the Hydrologic Modeling Sample Extension v1.1 to calculate the following watershed characteristics for all 90 sites: basin area, maximum channel length, mean elevation, and average basin slope. This procedure attached the resulting characteristics to the contributing area shapefiles.

The Spatial Analyst's Tabulate Areas procedure was used to cross-tabulate the individual contributing area polygon shapefiles with three other existing GIS data layers. These layers included geology, vegetation, and disturbance history. An Avenue script was created to batch process the cross-tabulation of the 90 contributing area shapefiles with each of the three other data layers. Each of the three were run separately because the procedure would not work with a shapefile of overlapping polygons. The resulting tables were exported into Excel spreadsheets. The spreadsheets were examined and any obvious errors were corrected (see Problems Encountered below).

Problems Encountered and Resolutions

Many sampling site point locations had to be moved so they coincided with the DEM's perceived stream locations since some streams had not been burned into the DEM's. Moving sampling sites from their known locations was minimized but had to be done for the

GRID WATERSHED command to select the correct contributing area. Some sampling site movement involved moving sites further up or downstream. A few contributing area polygons had to be manually edited in ArcView to reflect the known contributing area. Some sites produced either blank tables or clearly incorrect areas. For the sites which this occurred, it was expected. They were all high elevation springs for which many of the contributing area characteristics do not apply.

**APPENDIX A4. SPSS STATISTICAL OUTPUT FOR STEPWISE REGRESSION
TO PREDICT ACID NEUTRALIZING CAPACITY**

Variables Entered/Removed^a

Model	Variables Entered	Variables Removed	Method
1	mesic,mixed mesic, tulip, pine,xeric, pineoak (MMMPXPO)		Stepwise (Criteria: Probability-of-F-to-enter <= .050, Probability-of-F-to-remove >= .100).
2	square root max channel length		Stepwise (Criteria: Probability-of-F-to-enter <= .050, Probability-of-F-to-remove >= .100).
3	basin slope		Stepwise (Criteria: Probability-of-F-to-enter <= .050, Probability-of-F-to-remove >= .100).

a. Dependent Variable: median ANC

Model Summary^d

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.806 ^a	.649	.645	17.0917
2	.867 ^b	.752	.746	14.4570
3	.904 ^c	.817	.809	12.5241

a. Predictors: (Constant), mesic,mixed mesic, tulip, pine,xeric, pineoak

b. Predictors: (Constant), mesic,mixed mesic, tulip, pine,xeric, pineoak, square root max channel length

c. Predictors: (Constant), mesic,mixed mesic, tulip, pine,xeric, pineoak, square root max channel length, basin slope

d. Dependent Variable: median ANC

ANOVA^d

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	40012.625	1	40012.625	136.971	.000 ^a
	Residual	21617.234	74	292.125		
	Total	61629.859	75			
2	Regression	46372.443	2	23186.221	110.936	.000 ^b
	Residual	15257.416	73	209.006		
	Total	61629.859	75			
3	Regression	50336.351	3	16778.784	106.971	.000 ^c
	Residual	11293.508	72	156.854		
	Total	61629.859	75			

a. Predictors: (Constant), mesic,mixed mesic, tulip, pine,xeric, pineoak

b. Predictors: (Constant), mesic,mixed mesic, tulip, pine,xeric, pineoak, square root max channel length

c. Predictors: (Constant), mesic,mixed mesic, tulip, pine,xeric, pineoak, square root max channel length, basin slope

d. Dependent Variable: median ANC

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	18.240	3.102		5.881	.000
	mesic,mixed mesic, tulip, pine,xeric, pineoak	1.125	.096	.806	11.703	.000
2	(Constant)	-.449	4.285		-.105	.917
	mesic,mixed mesic, tulip, pine,xeric, pineoak	.965	.086	.691	11.188	.000
	square root max channel length	8.437	1.529	.341	5.516	.000
3	(Constant)	52.976	11.257		4.706	.000
	mesic,mixed mesic, tulip, pine,xeric, pineoak	.863	.077	.618	11.144	.000
	square root max channel length	8.603	1.325	.348	6.491	.000
	basin slope	-1.089	.217	-.263	-5.027	.000

Coefficients^a

Model		95% Confidence Interval for B	
		Lower Bound	Upper Bound
1	(Constant)	12.060	24.421
	mesic,mixed mesic, tulip, pine,xeric, pineoak	.933	1.316
2	(Constant)	-8.989	8.091
	mesic,mixed mesic, tulip, pine,xeric, pineoak	.793	1.137
	square root max channel length	5.389	11.485
3	(Constant)	30.535	75.416
	mesic,mixed mesic, tulip, pine,xeric, pineoak	.709	1.018
	square root max channel length	5.961	11.245
	basin slope	-1.520	-.657

a. Dependent Variable: median ANC

Collinearity Diagnostics^a

Model	Dimension	Eigenvalue	Condition Index
1	1	1.775	1.000
	2	.225	2.808
2	1	2.662	1.000
	2	.259	3.209
	3	7.984E-02	5.774
3	1	3.570	1.000
	2	.317	3.357
	3	.104	5.866
	4	9.074E-03	19.836

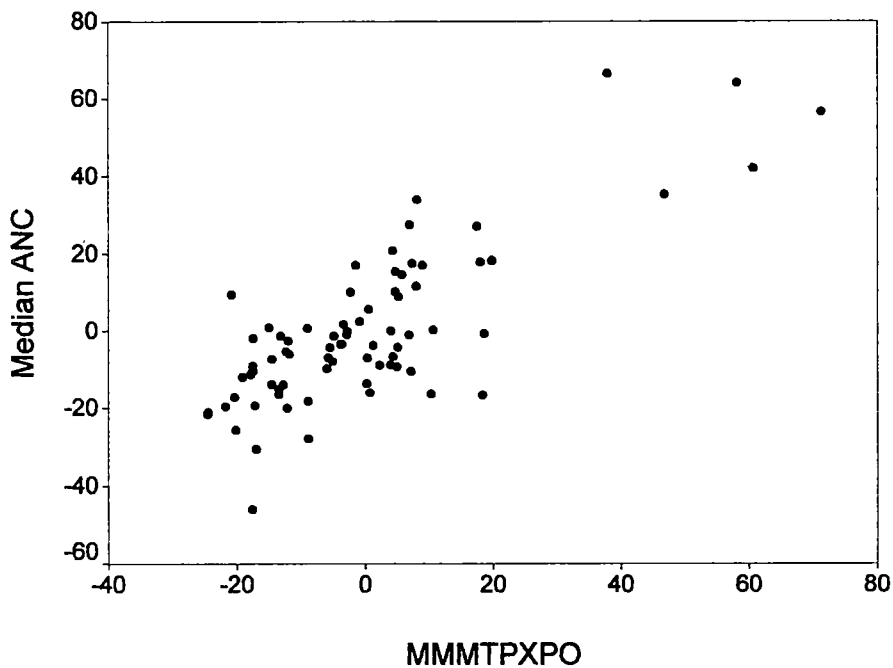
a. Dependent Variable: median ANC

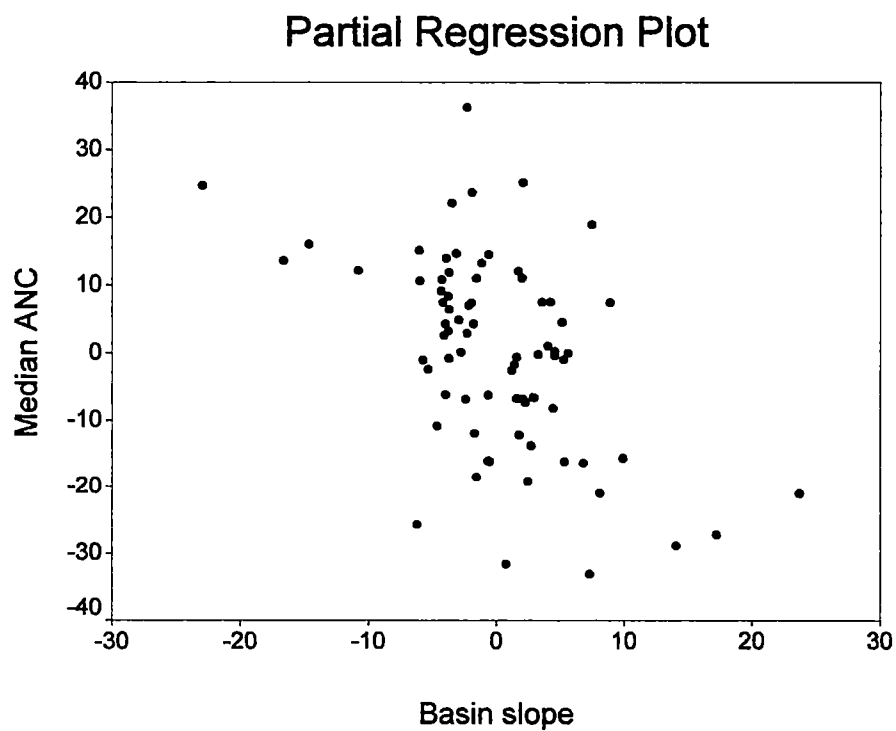
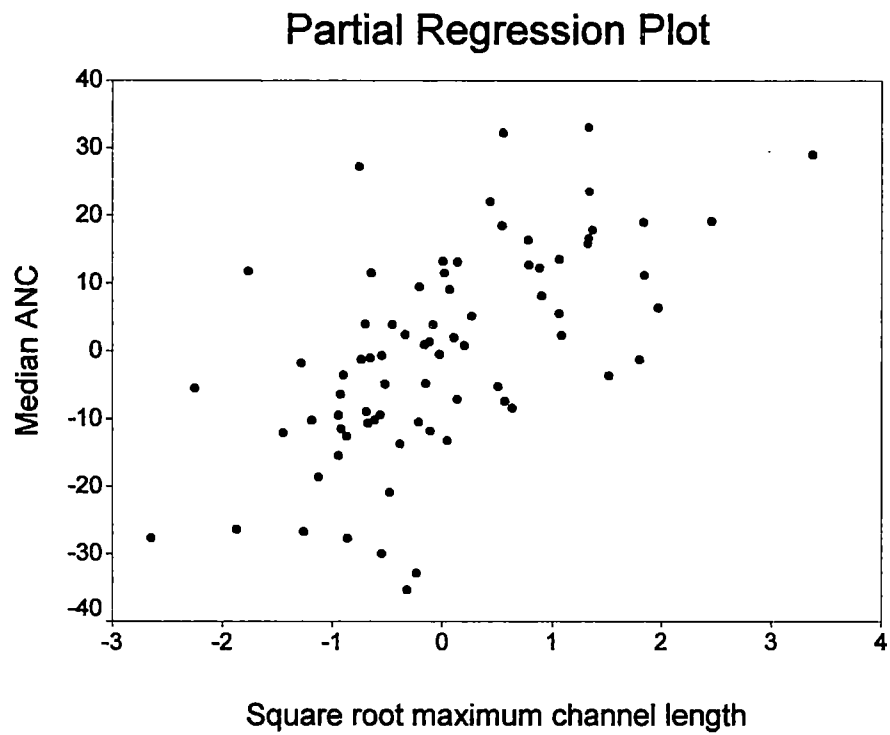
Residuals Statistics^a

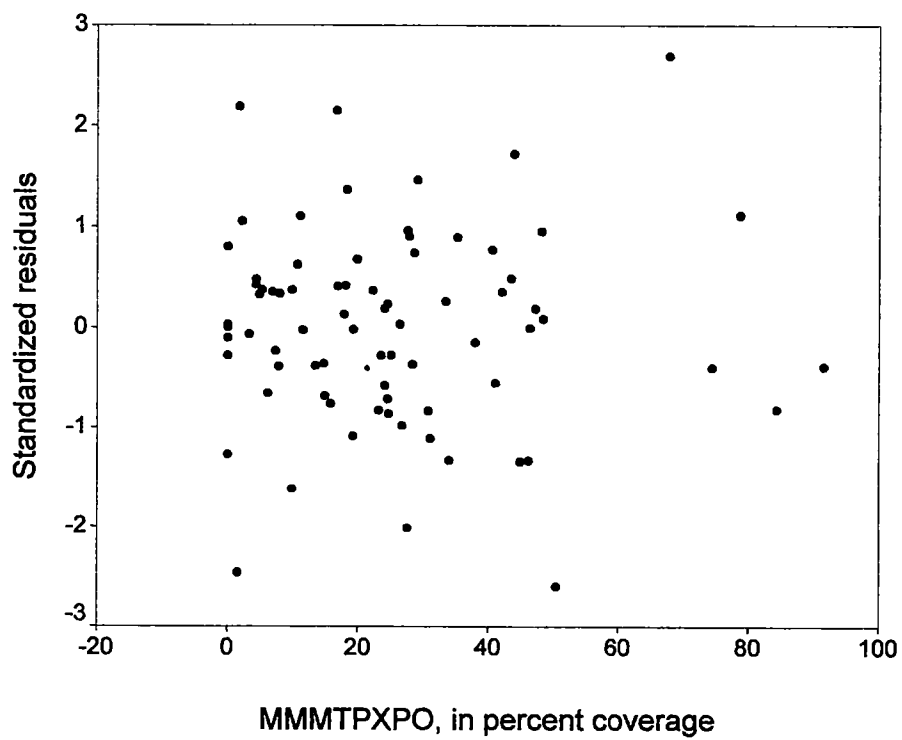
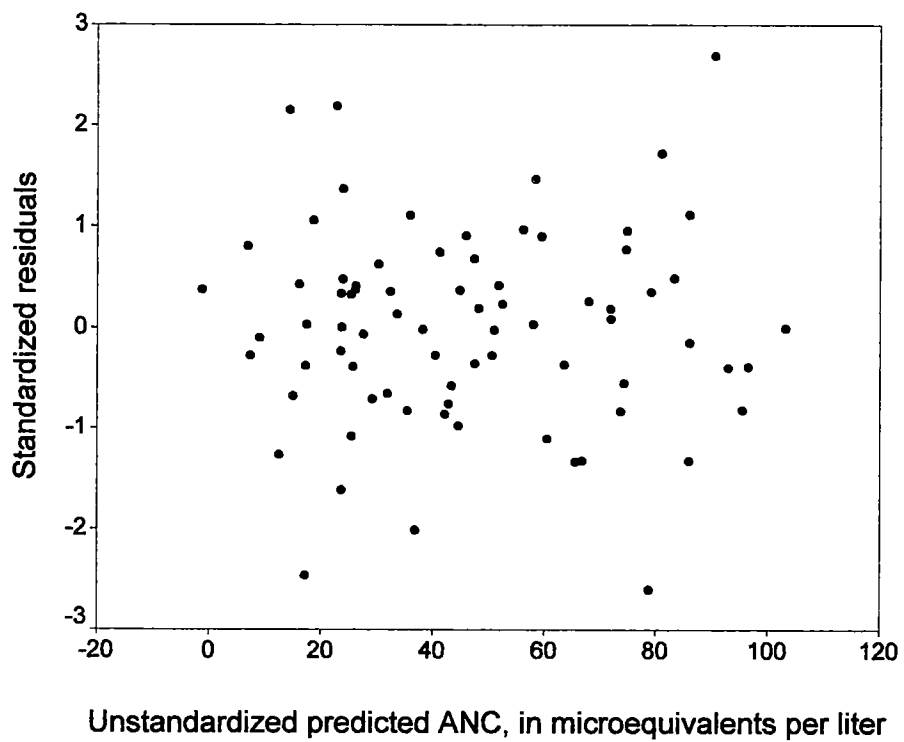
	Minimum	Maximum	Mean	Std. Deviation	N
Predicted Value	-1.2489	103.1152	46.3705	25.9066	76
Std. Predicted Value	-1.838	2.190	.000	1.000	76
Standard Error of Predicted Value	1.5236	6.0430	2.6977	.9955	76
Adjusted Predicted Value	-2.3729	103.1237	46.3796	25.9607	76
Residual	-32.5683	33.7621	-2.2E-14	12.2711	76
Std. Residual	-2.600	2.696	.000	.980	76
Stud. Residual	-2.663	2.809	.000	1.005	76
Deleted Residual	-34.1538	36.6674	-9.1E-03	12.9069	76
Stud. Deleted Residual	-2.785	2.957	.000	1.025	76

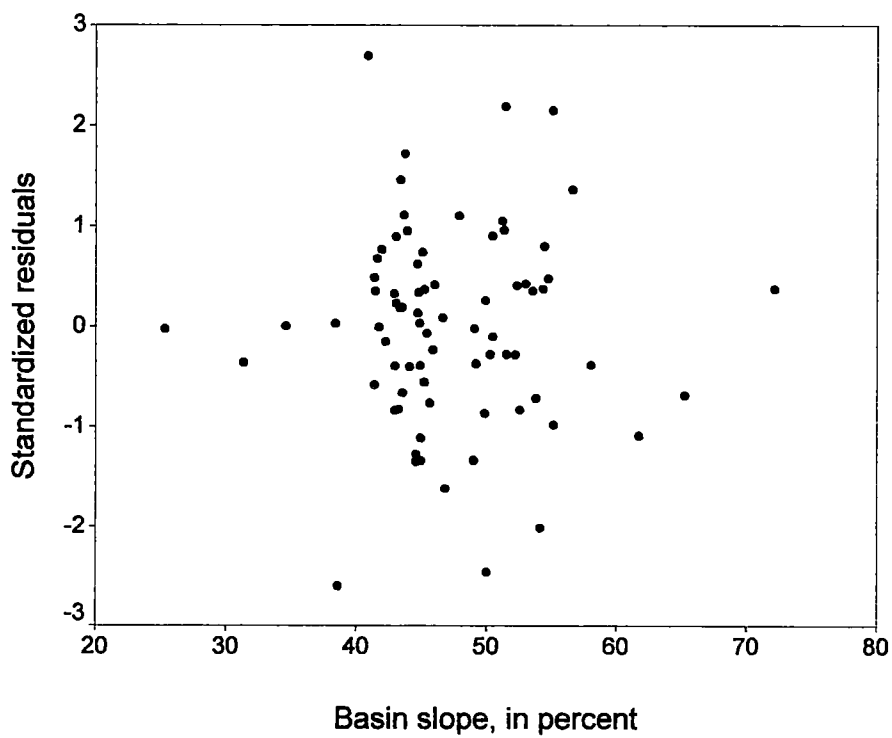
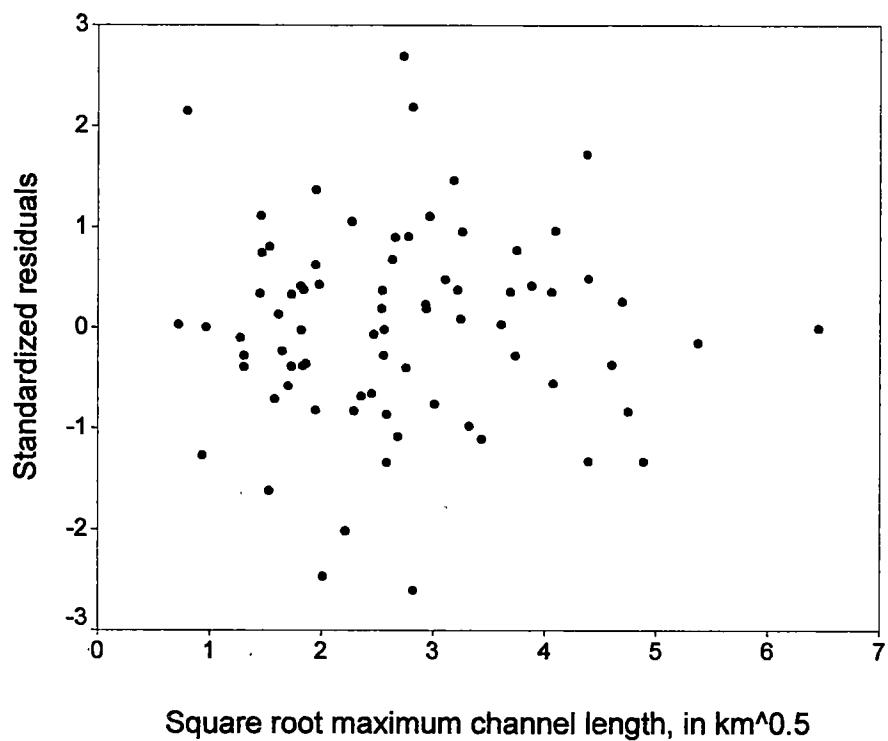
a. Dependent Variable: median ANC

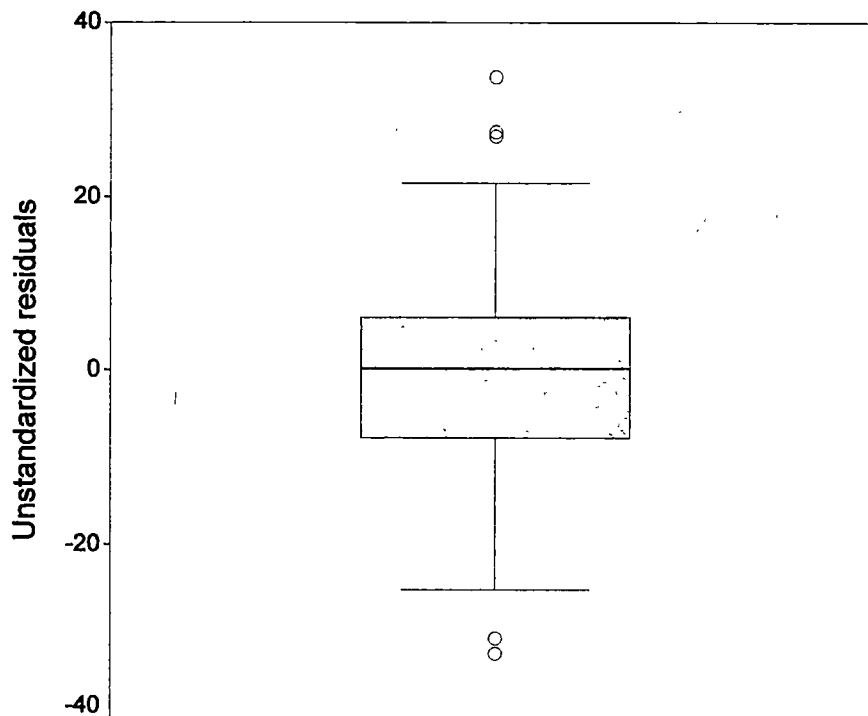
Partial Regression Plot











Descriptives

			Statistic	Std. Error
Unstandardized residuals	Mean		-2.28E-14	1.407593
	95% Confidence Interval for Mean	Lower Bound	-2.8040684	
		Upper Bound	2.8040684	
	5% Trimmed Mean		-9.13E-03	
	Median		.2211685	
	Variance		150.580	
	Std. Deviation		12.271109	
	Minimum		-32.56833	
	Maximum		33.76209	
	Range		66.33042	
	Interquartile Range		14.103262	
	Skewness		-.019	.276
	Kurtosis		.772	.545

VITA

Glenn R. Harwell was born in Mobile, Alabama on January 19, 1970. Shortly thereafter, he and his family moved to Chattanooga, Tennessee where he resided until graduation from Hixson High School. He entered the University of Tennessee at Knoxville to study Civil Engineering in August 1995. In spring of 1999 he graduated with a Bachelor of Science degree. During this time as an undergraduate he was made a member of Chi Epsilon, the National Civil Engineering Honor Society. Upon graduation, he accepted an offer to pursue a graduate degree in Environmental Engineering as a research assistant and began the summer of 1999. He completed the requirements for the degree of Master of Science, with a major in Environmental Engineering, in August 2001. He currently lives in Fort Worth, Texas and is employed by the United States Geological Survey.