

Preliminary Assessment of Water Quality in the Great Smoky Mountains National Park

Outline of results from July 1991 to August 1996

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Preface

This report has been prepared by the scientific staff of the Southern Appalachian Field Laboratory at the University of Tennessee for the Resource Management and Inventory and Monitoring Program of the Great Smoky Mountains National Park. It is designed to provide an overview of the type of data and information that can be provided to the Park by an integrated water quality monitoring program. We believe the landscape approach developed here can be a powerful, comprehensive, and well integrated monitoring program for the Great Smoky Mountains National Park. The entire report is designed to show the utility of water quality data for analysis of both terrestrial and aquatic processes over the full spectrum of spatial and temporal scales associated with the Park.

Executive Summary

The Great Smoky Mountains are known to receive some of the highest rates of deposition of acidic atmospheric pollutants among forested ecosystems in North America. The Inventory and Monitoring (I&M) program of the Great Smoky Mountains National Park (GRSM) includes a component to monitor water quality in the face of such high levels of atmospheric deposition. This report describes the basic design of the water quality monitoring program and briefly describes some of the major findings since 1991.

Design of the Monitoring Program

The water quality component of the GRSM I&M program is designed to incorporate a hierarchy of sampling intensities. One level of the sampling hierarchy involves the intensive monitoring of a single high elevation watershed near the center of the Park. This level of the sampling hierarchy utilizes a small watershed approach. The small watershed approach is based on monitoring precipitation and deposition of atmospheric pollutants to determine rates of inputs for key nutrient elements to the watershed while stream discharge and water chemistry are monitored to estimate rates of output for the key elements from the watershed. Sampling is conducted on a fifteen minute interval for stream discharge, pH, conductivity, and temperature while basic water chemistry variables are measured weekly for precipitation samples, throughfall samples, and streamwater samples. The data collected with this approach allows calculation of input-output budgets for many of the major nutrient elements in the watershed so that interactions between atmospheric deposition, terrestrial processes, and surface water quality can be examined.

Another level of the sampling hierarchy involved monthly sampling of stream water at about 160 sites in 14 of the major stream systems of the GRSM. This intensity of sampling provided information on the seasonal variation in water quality over the entire elevational gradient

for the streams that were sampled. The last level of the sampling hierarchy provided a more complete picture of spatial variation across the entire GRSM by sampling over 360 sites for streamwater quality on a biannual basis. This level of sampling provided enough data points across the Park to utilize geostatistical tools to assess the spatial patterns of water quality across the GRSM landscape.

Results

The results obtained from monitoring at Noland Divide Watershed since 1991 support the findings of earlier studies in the GRSM that atmospheric inputs of sulfur and nitrogen are as high as any forested ecosystem in North America. Differences between inputs of acidic nitrogen and sulfur compounds from throughfall and wet precipitation indicate that dry and cloud forms of deposition are very important. Input-output balances from the watershed indicate that water inputs approximately balance streamwater outflow while much of the sulfur input to the system is retained by adsorption within the soil. A very high proportion of the nitrogen deposited to the watershed from the atmosphere is lost to the streams. This, coupled with relatively high concentrations of nitrate in streamwater year round, indicate that the Noland Divide Watershed has reached an advanced stage of nitrogen saturation. The high concentrations of nitrate along with some sulfate in the stream, coupled to low availability of base cations in the soil, provide conditions sufficient for stream acidification to occur. The pH of Noland Creek currently ranges between 5.5-5.7, however the stream pH can drop by one pH unit during storm events.

Park-wide water quality monitoring indicates that water quality at Noland Divide is typical of water quality at high elevations throughout the GRSM. Although stream acidification is occurring at high elevation, water quality is generally good below about 3000 ft. All water quality variables have a distinct elevational gradient. Patterns of seasonal variation in stream nitrate

concentrations indicate that nitrogen saturation has reached advanced stages primarily along the main ridge of the Park from Double Springs Gap across Clingmans Dome east to Newfound Gap and Mt. LeConte. Other areas of advanced nitrogen saturation occur in the Chiltoes Mountain area in the Cataloochee Creek system and in the Raven Fork basin. Much of the high elevation area in the central and eastern portions of the Park are beginning to show evidence of early stages of nitrogen saturation.

Implications for Aquatic Ecosystems

Deposition of large quantities of acidic nitrogen and sulfur compounds has negatively impacted water quality in the GRSM. Analysis of Acid Neutralizing Capacity (ANC) variation across the GRSM show that more than 90% of the Park area is moderately susceptible to acidification. Over 30% of the area has minimum stream pH below 6.0 which is low enough to affect some benthic invertebrates and fish species. Analysis of water chemistry in three streams that have lost all fish populations during this century suggest that a pH of 5.5 may be the lower limit for fish survival in the GRSM. If this endpoint is accurate, then streams in over 10% of the Park area maybe impacted by acidification. Most of the streams with pH currently below 5.5 occur where weathering of naturally acidic bedrock contributes substantially to the acidification problem. Some of the headwater streams not affected by acidic bedrock may not support fish anyway. Regardless of these precautionary statements however, the available data suggest that an additional 19% of the Park area has minimum pH between 5.5 and 6.0 and may be impacted if acidification continues to progress.

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Introduction

The National Park Service (NPS) is entrusted with preserving certain natural and historical resources of the United States within the borders of the National Parks. This is difficult to achieve since National Parks are not isolated from or immune to impacts from outside the park. Exposure of watersheds to atmospheric pollutants affects vegetation and processes occurring in terrestrial ecosystems (Smith, 1990). Changes in terrestrial ecosystem processes brought about by atmospheric pollutants can also lead to impacts on surface water quality (Church *et al.*, 1990; Baker *et al.*, 1991; Herlihy *et al.*, 1991; Munson and Gherini, 1991; Johnson and Lindberg, 1992). Recent reports from long-term studies suggest that impacts of atmospheric deposition on terrestrial and aquatic systems are often not fully realized for decades (*e.g.* Peterjohn *et al.*, 1996). An understanding of long term effects from external stressors such as air pollutants or invasions by exotic organisms are therefore essential to proper management of park resources.

In partial response to the need for monitoring data, the NPS established the Inventory and Monitoring (I&M) program in the early 1990s. The purpose of the I&M program was to produce an inventory of natural resources in national parks and institute protocols for assessing long-term changes in the status of those resources. The Great Smoky Mountains National Park (GRSM) was selected as 1 of 4 prototype parks in the I&M program. Within the I&M program at GRSM, two components provide both intensive and extensive monitoring data on the impacts of atmospheric pollutants to water quality in the park. The Noland Divide Watershed (NDW) project provides an integrated view of the interactions between the atmosphere, terrestrial ecosystem, and aquatic ecosystem through intensive monitoring of a small, high elevation watershed. A more extensive view of impacts of atmospheric pollutants, and other factors influencing water quality, is

provided by a periodically conducted park-wide stream survey. This report briefly summarizes some of the major findings of these two projects since 1991.

Background

The GRSM is the second largest National Park in the eastern U.S. and the most visited of all the National Parks with over 9.3 million visitors in 1992 (Peine *et al.*, 1995). Despite heavy visitation and intense boundary encroachment, particularly on the Tennessee and southeastern North Carolina sides of the park, human influences within the Park are primarily limited to automobile traffic, trail use, and air pollution. Due to its extensive elevational range (268 m to 2025 m), geographical location, and history relative to past ice ages, the GRSM is a center of biodiversity (Delcourt and Delcourt, 1991). The Park contains approximately 1,200 species of native vascular plants, over 300 lichen species, over 800 species of moths and butterflies, over 2,200 species of macro fungi, 60 species of mammals, 53 species of fish, 30 species of salamanders, over 325 confirmed species of aquatic insects in the major orders as well as numerous species of birds that frequent the Park during the spring and autumn when the Great Smokes form part of the corridor of the eastern migratory flyway. The total amount of land that has not been disturbed by massive logging operations or human settlement exceeds that of any other deciduous or coniferous forest-dominated landscape in the Eastern United States. The uniqueness of GRSM natural and cultural resources was an important factor in the selection of the park as an International Biosphere Reserve and a World Heritage Site.

Description of the Study Area

The Great Smoky Mountains are located along the border of Tennessee and North Carolina on the western edge of the Blue Ridge Physiographic Province (Figure 1). The Park straddles a ridge line of the Appalachian Mountain chain and is bounded on the east and northeast by the Pigeon River Gorge, on the south by the Little Tennessee River Gorge, and on the



Figure 1. Location of the Great Smoky Mountains on the Western Edge of the Blue Ridge Physiographic Province.

northwest by the Great Valley of the Tennessee River. The main ridge of the range traverses the landscape from west to east and includes 16 peaks over 1820 m (6000 ft.) in elevation including the second highest peak in the Eastern U.S., Clingmans Dome, at 2025 m (6642 ft.). Streams mainly drain away from the central ridge toward the Park boundaries through deeply eroded catchments that are oriented primarily northwestward on the Tennessee side and southeastward on the North Carolina side. There are 28 streams reaching fourth order or greater before exiting the Park and several smaller stream systems draining lower ridges along the periphery. The Little Tennessee River is dammed just below the confluence of Eagle Creek at the southwest corner of the GRSM. This dam creates Fontana Lake which forms most of the southern boundary on the

western half of the park. Several of the lower reaches of the large streams on the North Carolina side are affected by this impoundment.

Important Features of the Geology and Soil

Bedrock geology is an important factor influencing water quality in the GRSM (Flum and Nodvin, 1995). The geology of the Smoky Mountains is dominated by sandstone formations of the Great Smokies Group of the Ocoee Series that have undergone various degrees of metamorphism and are composed mainly of quartz and potassium feldspar (Hadley and Goldsmith, 1963; King, 1964; Neumann and Nelson, 1965). The main block of metasandstone rock was thrown over younger limestone and dolomite of the Knox Group along the Great Smoky thrust fault. Erosion of the overlying rocks of the mountains have exposed the underlying limestone and dolomite in some areas of the western part of the GRSM (King *et al.*, 1968). Limestone and dolomite weathering greatly increases the concentration of calcium and magnesium which in turn increases pH and acid neutralizing capacity (ANC) in these streams (Mathews, 1978; Burge *et al.*, 1979; Silsbee and Larson, 1982; Flum and Nodvin, 1995).

One of the most important rock strata in terms of water quality is a dark phyllite containing a high pyrite (FeS) content called the Anakeesta Formation (King *et al.*, 1968). Due to the tilting and folding of the rocks, this formation appears in scattered locations even at low elevations, particularly on the North Carolina side of the GRSM (Keith, 1907). Oxidation of pyrite following exposure to the atmosphere, which can occur through landslides or road cuts, results in the production of sulfuric acid (Stumm and Morgan, 1981). Release of substantial amounts of sulfuric acid by bedrock weathering greatly increases the potential for chronic stream acidification in areas underlain by Anakeesta (Huckabee *et al.*, 1975; Kucken *et al.*, 1992; Cook *et al.*, 1994; Flum and Nodvin, 1995).

Aside from the Knox Group and Anakeesta formations, the bedrock of the GRSM is primarily metasandstone which is highly resistant to chemical and mechanical weathering. This bedrock, coupled with steep and highly erodible slopes, leads to soils that are thin, rocky, and deeply weathered. Although a detailed soils map for the GRSM is not available, the soils on high ridges have been generally classified as Inceptisols (*e.g.* Harrison *et al.* 1989) while soils at lower elevations grade to Ultisols (Eilers and Selle, 1991). Base saturation and cation exchange capacity are very low, and aluminum is the dominant exchangeable cation appearing in soil solutions (Johnson *et al.*, 1991; Elwood, 1991). Little of this aluminum is transported to surface waters because stream pH is often above the minimum pH for aluminum solubility (Elwood, 1991). The low number of other potential solutes from the terrestrial system results in highly dilute waters that are typical of mountain streams (*e.g.* Messer *et al.*, 1986; Kaufman *et al.*, 1988; Sale *et al.*, 1988; Elwood *et al.*, 1991; Cosby *et al.*, 1991; Melack and Stoddard, 1991; Williams *et al.*, 1993). Streams throughout the Park generally have very low concentrations of base cations (with the exception of areas around Cades Cove) resulting in streams that are highly susceptible to acidification.

Air Pollution Concerns

The most important atmospheric pollutants contributing to acidification of surface waters across the world are various forms of nitrogen and sulfur. In North America, oxides of nitrogen and sulfur (nitrate and sulfate) produced by combustion of fossil fuels are the most important, because they are potentially mobile in soil solutions. As a result of this mobility, it is the movement of anions that dictates the potential acidification of soil and surface waters (Johnson and Cole, 1980). As the mobile anions move through the soil in response to hydrologic gradients, cations are carried with them to maintain electrical neutrality. Where the availability of base

cations is low, such as in the GRSM, the requirement for positive charge to balance the mobile nitrate and sulfate anions moving through the soil, is met by mobilizing the acidic hydrogen ion (H^+). Thus, atmospheric deposition of nitrogen and sulfur pollutants can lead to acidification of stream waters.

Development of the Noland Divide Watershed Project

The concept of examining surface water chemistry to monitor the status of both terrestrial and aquatic systems has a long history but is based on the findings from small watershed studies such as those at Coweeta Hydrologic Lab and Hubbard Brook Experimental Forest (Likens *et al.*, 1977). The small watershed approach is the standard used today for critical ecosystem evaluation (*e.g.* Swank and Johnson, 1994) and has already been applied at other National Parks including Shenandoah National Park (Ryan *et al.*, 1989) and Denali National Park (Stottlemeyer, 1992). Using this approach, ecosystem function is evaluated by estimating input-output budgets for various elements with year-round collection of wet precipitation and throughfall, weekly stream water chemistry sampling, and continuous measurement of stream pH, conductivity, and discharge (Nodvin *et al.*, in revision).

In the GRSM, a small watershed study (The Noland Divide Watershed) was set-up within the same watershed as the retired Integrated Forest Study (IFS) ST site (Johnson and Lindberg, 1992), to examine the long-term relationship between deposition and stream water quality. The Noland Divide Watershed (NDW) was selected for intensive monitoring activities for a number of reasons including: documented high rates of atmospheric deposition, availability of historical data (collected during the IFS), extending the data set with respect to deposition monitoring activities, and low environmental impacts with respect to installation of stream monitoring equipment.

Development of the Park-Wide Stream Survey Project

The most comprehensive of the surface water monitoring programs initiated in the U.S. was the National Surface Water Survey conducted during the 1980s (Messer *et al.*, 1986). This program lead to the National Stream Survey which had a substantial component in the mid-Atlantic and southeastern regions of the U.S. (Kaufmann *et al.*, 1988; Sale *et al.*, 1988). The results from these regional surveys indicated that streams in the Blue Ridge Physiographic Province during the 1980s were not acidic despite relatively high levels of atmospheric deposition due mainly to adsorption of acidic sulfur and nitrogen compounds within the soil (Elwood, 1991; Elwood *et al.*, 1991). Nevertheless, sulfate levels in streams were observed to increase by about 1 $\mu\text{eq/L}$ per year over the 10 year span of the survey, indicating that mobilization of base cations was not sufficient to compensate for increasing levels of atmospheric deposition (Elwood *et al.*, 1991).

To examine changes in water quality from historical data, sites from previous studies were selected for monitoring in the I&M program. This list of sites included about 100 sites from Silsbee and Larson (1982a, 1982b) and several sites from Winger *et al.* (1987), Olem *et al.* (1988), Kucken *et al.* (1992) and Cook *et al.* (1994). Several sites overlap with a much older survey conducted by Powers (1929). In addition, sites were selected in areas where restoration projects involving brook trout have been conducted or are planned in the future.

Sites were also selected to assess the effect of bedrock geology on water quality by sampling streams draining different bedrock types (King *et al.*, 1968). Earlier surveys in the southern Blue Ridge Physiographic province suggested particular susceptibility of streams draining metasandstones (which dominate in the GRSM) to acidification (Kaufmann *et al.*, 1988; Webb *et al.*, 1989a, 1989b; Elwood, 1991; Elwood *et al.*, 1991, Morgan and Janicki, 1991).

Emphasis was also placed on monitoring streams draining catchments underlain by the pyretic Anakeesta formation. The effects of past land use including settlement disturbance and logging history (Pyle, 1988) on water quality was also taken into account in selecting sites. More emphasis was placed on assessing the effect of forest stand age on water quality than forest cover type (McKenzie, 1991). The vegetation of the GRSM is so complex that most watersheds have a combination of forest cover types. This makes assessing the role of forest cover types on water quality difficult to determine.

Examining the longitudinal gradient in water quality in major streams serves several purposes. The major streams are where most of the fish are found. The longitudinal gradients also show the cumulative effects of watershed and in-stream processes over the elevational gradient. The role of in-stream processes is probably greater as stream size increases. Sampling smaller streams along the elevational gradient provides a better view of how watershed processes change with elevation. With some care regarding the details of each watershed, the relative roles of terrestrial and in-stream processes on water quality can be estimated. Such understanding would greatly improve our ability to model water quality in the Park.

Approach

The water quality monitoring component of the I&M program is based on a hierarchical sampling design. The broadest level of the hierarchical design included the sampling of stream water chemistry at 360 sites on a biannual basis. This level of effort provided sufficient coverage of the Park area to allow spatial patterns in water quality to be analyzed in relatively good detail. Sampling was conducted in March when water levels are expected to be highest (and water quality poorest) and October when water levels are low (and water quality was expected to be at its best) (McMaster and Hubbard, 1970). Over the long term, this biannual stream survey should elucidate the full range of spatial and temporal variation in water quality present in the GRSM. To provide even greater detail in the analysis of temporal patterns of water quality change in certain watersheds, the biannual stream surveys were extended to include monthly sampling at a subset of 160 of the sites. This level of the sampling hierarchy ensured closer examination of seasonal patterns that can provide key insights into underlying processes controlling water quality as discussed in greater detail below.

The most intensive part of the water quality monitoring program is based on work being conducted at the Noland Divide Watershed (NDW). Samples are collected once per week at NDW to provide the data necessary to determine the input and output of important nutrient elements from this small, high elevation watershed. Such intensive sampling provides the details necessary to understand how atmospheric deposition is influencing nutrient cycling in the terrestrial system and thereby altering the chemistry of soil solutions and surface waters. By including all three levels of sampling intensity, a more complete picture of water quality and the factors that influence it are obtained.

The Noland Divide Watershed

The NDW is equipped to collect samples of various nutrient elements from their input as atmospheric deposition through the terrestrial system as soil solution to export from the watershed as streamflow. Sample collection sites consist of one functioning atmospheric deposition monitoring station at 1740 m (a second higher elevation monitoring station, at 1920 m was sampled from August 93 to July 96), one soil solution station, and one stream gauging station. The atmospheric deposition station consists of two monitoring facilities, one in which wet-only precipitation is collected, and one throughfall site. The soil solution station is located within the deposition monitoring station and consists of 12 lysimeters placed at three different depths, four below the Oi, A, and Bw horizons. The stream monitoring station consists of two H-flumes (which measure discharge), one hydrolab (which records continuous measurements for pH, conductivity, and temperature), and one datalogger (a device which stores all the data).

Collections are made on a weekly basis for the deposition and stream stations, and monthly for the soil station. Weekly stream discharge and deposition volume measurements are coupled with their corresponding chemistries to produce weekly flux or watershed nutrient budget data. All weekly flux measurements are combined by month, and monthly estimates are combined to form a water year. A water year is defined as all the collections made from August 1st to July 31st in any given year. Soil solution data are organized by simple monthly measurements and pooled to yield yearly estimates. The annual sums of atmospheric deposition inputs and streamflow outputs amount to input-output budgets for the watershed and provide essential information on the mechanisms by which atmospheric deposition influences the chemistry of the soil solution and surface water.

The Park-Wide Stream Survey

It is not feasible to attempt to monitor input-output budgets for the entire GRSM. Nevertheless, the patterns and processes examined at NDW can be used to infer possible processes occurring across the GRSM based on stream water quality data alone. Thus, water quality data is useful not only for its own sake but for what it can be used to infer about processes occurring across the GRSM. Park-wide patterns of water quality were monitored at two levels of sampling intensity. The most comprehensive level of sampling effort included biannual sample collection at 367 sites from all 28 of the major and many of the smaller stream systems within the GRSM (Figure 2). Sampling sites were located over the entire elevational gradient of the GRSM and in all stream orders. Catchments with different bedrock and vegetation types as well as different disturbance histories were included to provide as broad a range of factors that might influence water quality in the GRSM as possible.

The biannual stream surveys were designed to provide the data needed for assessment of the spatial patterns of water quality at the landscape scale. The approach developed here to examine spatial patterns utilized the natural gradients within the GRSM and can be contrasted to approaches taken in other surveys designed to examine water quality patterns at the regional scale (Kaufmann *et al.*, 1988; Sale *et al.*, 1988). Many of the earlier regional scale stream surveys intentionally avoided sampling the same stream at more than one location along the elevational gradient. This was done to prevent violating the assumption of sampling independence associated with many standard statistical techniques employed for the analysis of data. Sampling at more than one site on a stream can lead to violation of sampling independence because water quality at any site on a stream is probably related to the water quality at a site upstream. This statistical problem is avoided by utilizing geostatistical techniques in the analysis of the data rather

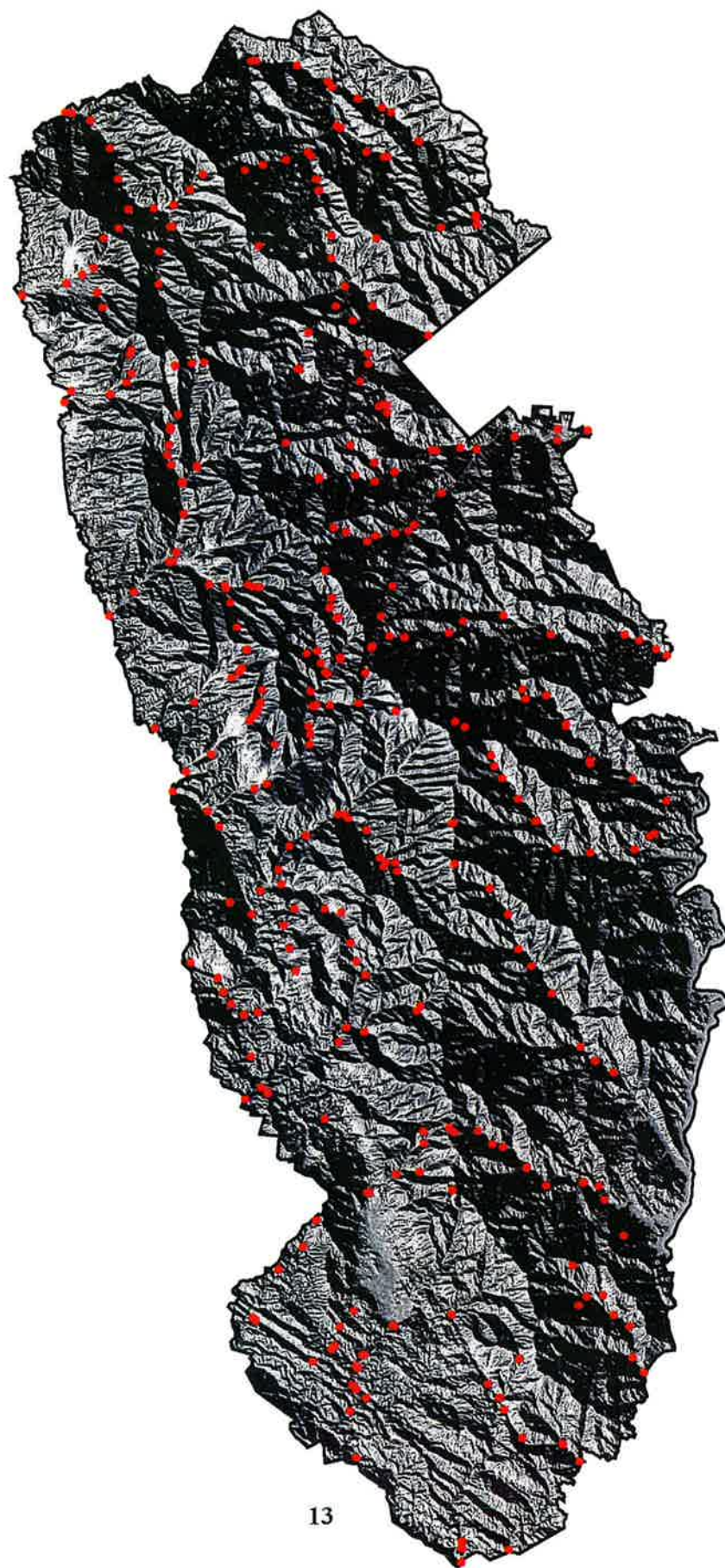


Figure 2. Biannual sampling sites for the Park-wide stream survey.

• Sample Site Location:

than standard statistical approaches. Geostatistical approaches are designed to take advantage of spatial trends in data sets so that estimates of conditions between sampling points can be developed. Interpolation of conditions between sampling points allows maps of conditions over entire areas to be produced. Thus, while surveys designed to utilize standard statistical approaches can provide useful information on the proportion of streams in an area with certain water quality characteristics, utilization of the geostatistical approach can provide information, even if hypothetical, about the water quality in any stream within an area regardless of whether the stream was actually sampled or not. The ability to provide information about any selected stream in an area is a great advantage to resource management and is the primary reason why the geostatistical approach was adopted instead of a more standard stream survey design.

The biannual stream surveys were extended to monthly sampling at about 160 sites in 1995 (Figure 2). Monthly sampling was also attempted in 1994 but was interrupted by the effects of devastating flooding that destroyed roads and influenced most park activities. Of the 28 major stream systems in the GRSM, a subset of 14 were selected for this level of monitoring. Monthly sampling at sites provided data on the seasonal variation in water quality at each site. Although biannual surveys would eventually provide data on the range of water quality conditions in the GRSM, monthly sampling produces data and elucidates temporal patterns more quickly. Examination of seasonal patterns is especially useful in examining specific mechanisms influencing water quality such as the effect of uptake of nutrient elements by vegetation during the growing season.

Collection of the large number of samples required for monthly and biannual surveys in a timely manner required the recruitment and training of volunteers. Volunteers for the sampling efforts came primarily from the membership of two local chapters of Trout Unlimited (the Little

River Chapter and the Great Smokies Chapter) and students from the University of Tennessee. The volunteers were trained in the proper technique for collection of water quality grab samples as described in the protocols document for the project (Nodvin *et al.*, 1995). Volunteers were organized into groups and provided with maps with the locations of sampling sites and written site description giving landmarks and other information needed to locate sites. Most sites were located at easily identified locations such as trail crossings, bridges, campsites, or stream confluences. Volunteers were debriefed upon completion of their collections to ensure any problems that may have arisen were clarified immediately.

Results

Noland Divide Watershed

For the past 5 years the amount of inorganic nitrogen entering the NDW as throughfall (TF) averaged 1100 Eq/ha/yr (15.5 kg N/ha/yr) (Figure 3) and appears to be slowly increasing. The apparent increase in nitrogen influx during this period can be attributed to relatively high rainfall during both the 93-94 and 95-96 water years (Figure 4) and therefore may not represent a true trend. The average rainfall amount collected as TF during the study period was 249 cm (Table 1), 36 cm higher than the 3 year average reported during the IFS at the same location during the late 1980's. The five year average nitrogen deposition coming in as wet only precipitation was 480 Eq/ha/yr (7 kg N/ha/yr) (Table 1). Higher water volumes and chemical

Table 1. The five year average throughfall and precipitation deposition of SO_4^{2-} , NO_3^- , and NH_4^+ , to the Noland Divide Watershed expressed as Eq/ha/yr.

	Volume (cm)	pH	Sulfate	Nitrate	Ammonium
Precipitation	244	4.63	620	253	226
Throughfall	249	4.09	2100	893	209

concentrations in throughfall compared to wet-only precipitation can be attributed to the effects of both dry and cloud deposition collecting on vegetation surfaces. However, nitrogen (N) species are very reactive within the canopy structure, so TF measurements of N are very poor indicators of the total deposition rates (*e.g.* Shubzda *et al.*, 1995). The IFS estimated that approximately 850 Eq/ha/yr (12 kg N/ha/yr) of inorganic nitrogen is retained within the canopy based on the net-canopy exchange [$\text{NCE} = \text{throughfall} - \text{total deposition}$ (where total deposition is

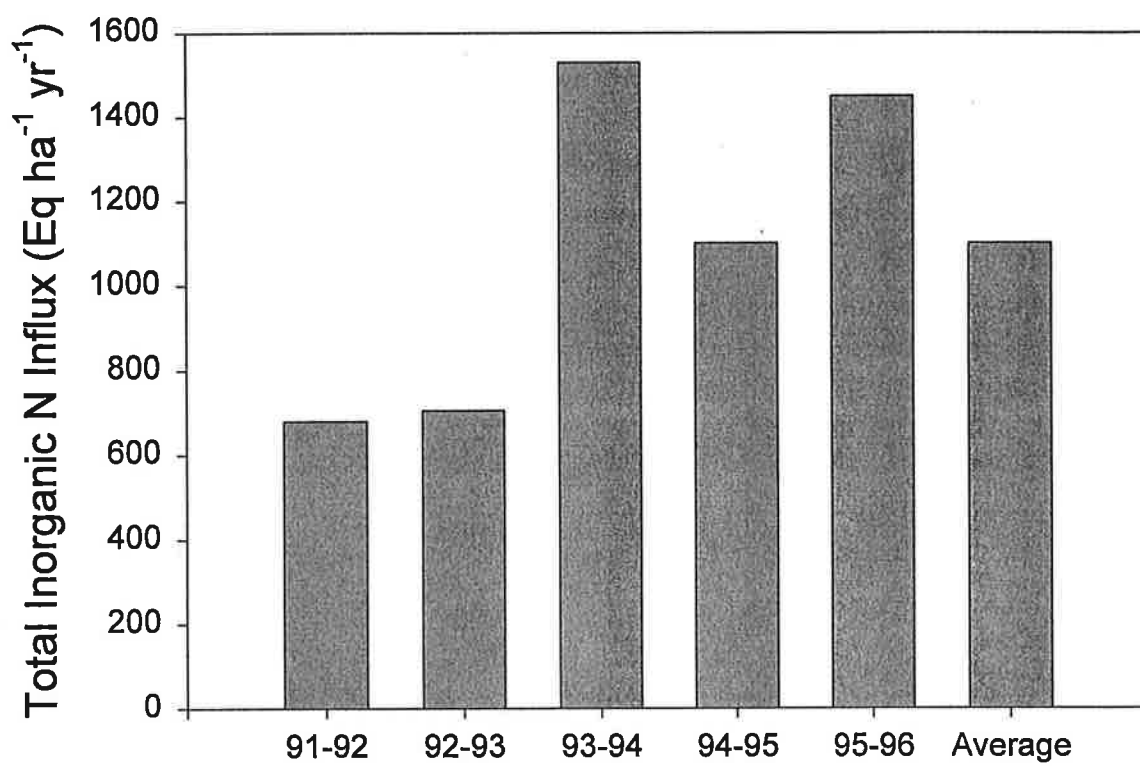


Figure 3. Total throughfall deposition of inorganic nitrogen at Noland Divide Watershed.

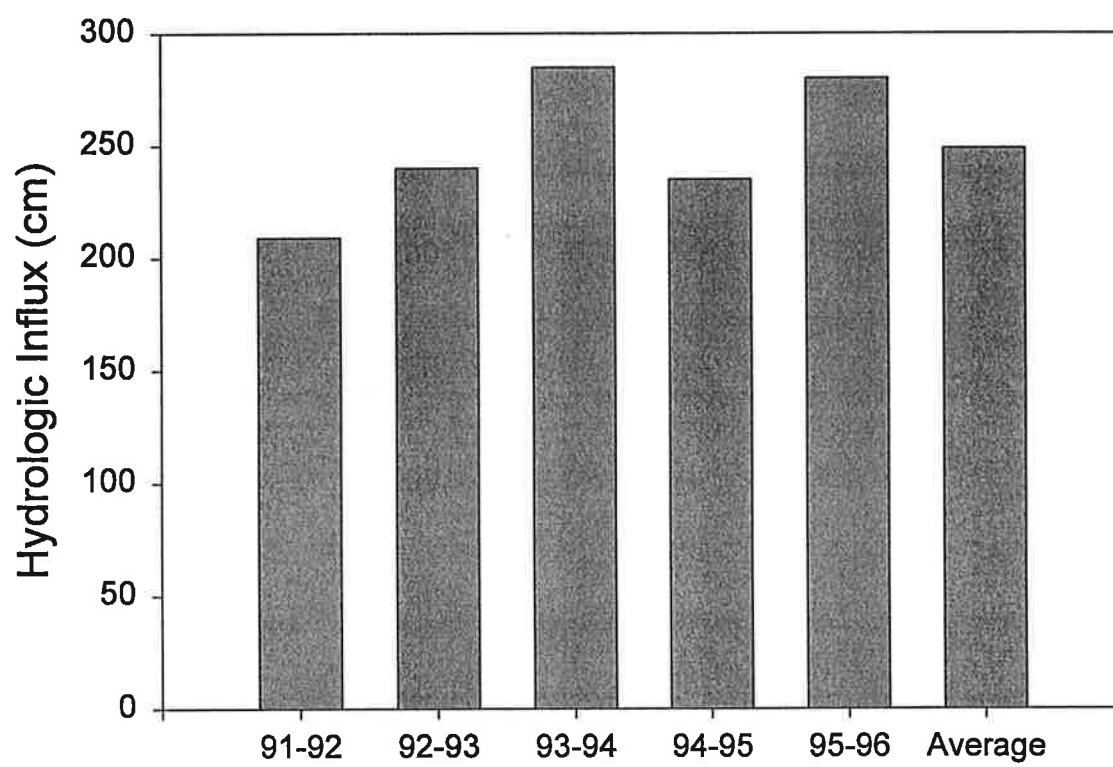


Figure 4. Hydrologic flux as throughfall at Noland Divide Watershed.

the sum of wet-only, dry, and cloud deposition)] (Johnson and Lindberg, 1992). By combining the NCE measurements made during the IFS with throughfall measurements made at the NDW for the past five years, the total deposition of inorganic nitrogen at NDW can be estimated to be approximately 1950 Eq/ha/yr (27 kg N/ha/yr).

Sulfate fluxes measured as TF during the study period are approximately 2100 Eq/ha/yr (100 kg SO_4^{2-} /ha/yr) (Figure 5). This flux is comparable to the sulfate deposition levels measured during the IFS at NDW during the late 1980's (Johnson and Lindberg, 1992). The sulfate flux in precipitation was much smaller than that in throughfall and averaged 620 Eq/ha/yr (30 kg SO_4^{2-} /ha/yr) (Table 1). The difference between precipitation inputs and TF inputs represents a very good estimate of the combined dry and cloudwater inputs to these systems since, unlike nitrogen, sulfur is virtually unreactive in the forest canopy (Garten *et al.*, 1988; Lindberg and Garten, 1988; Shubzda *et al.*, 1995).

Elevational Differences in Deposition

Generally, total atmospheric deposition increases with increasing elevation because of a higher frequency of cloud water contact at higher elevations and higher wind speeds that bring a larger volume of polluted air into contact with the vegetation (Lovett and Kinsman, 1990). To examine the elevational gradient at NDW, a second deposition monitoring station was established at 1920 m in the summer of 1993. Sulfate deposition was about 37% higher at the new upper site (2900 Eq/ha/yr, or 140 kg SO_4^{2-} /ha/yr) but the inorganic N in TF was lower at the upper site by about 34% (Figure 6). In fact, all the major ions in TF increased by 10-50% with increasing elevation, except nitrate and ammonium (Figure 6 & 7). Throughfall deposition at NDW varies considerably over short distances along the elevational gradient of the watershed (Lindberg and Owens, 1993; Shubzda *et al.*, 1995).

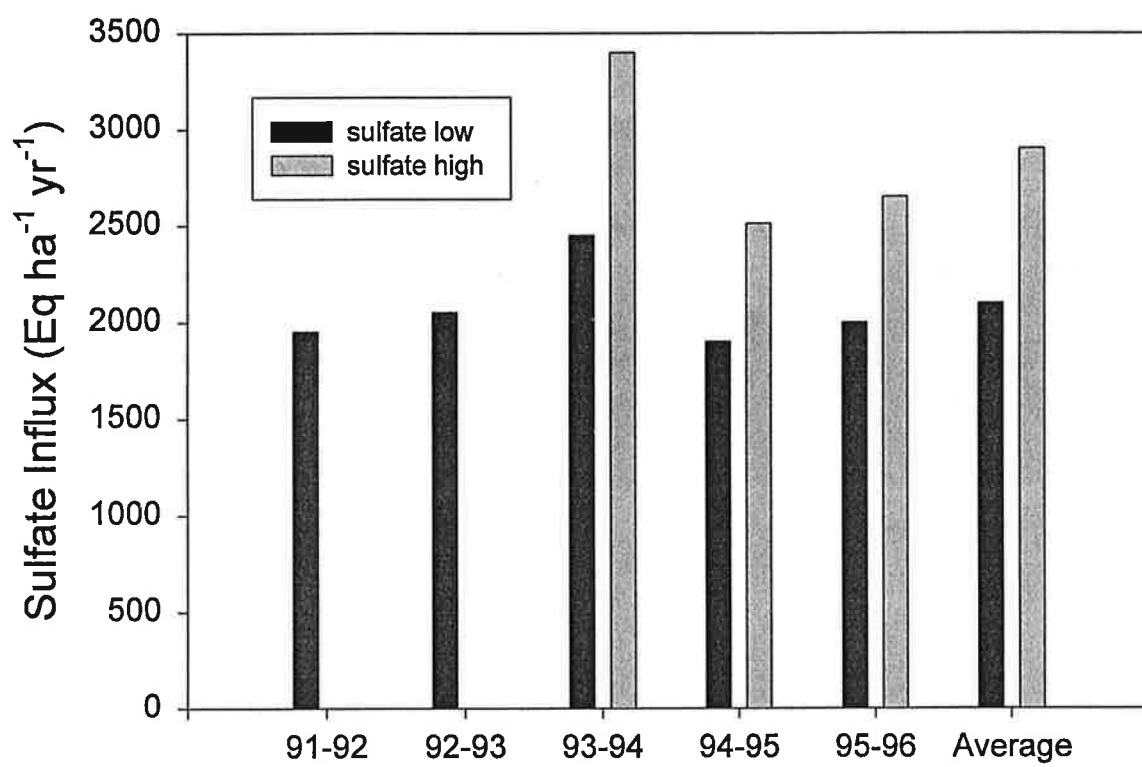


Figure 5. Influx of sulfate as throughfall to Noland Divide watershed.

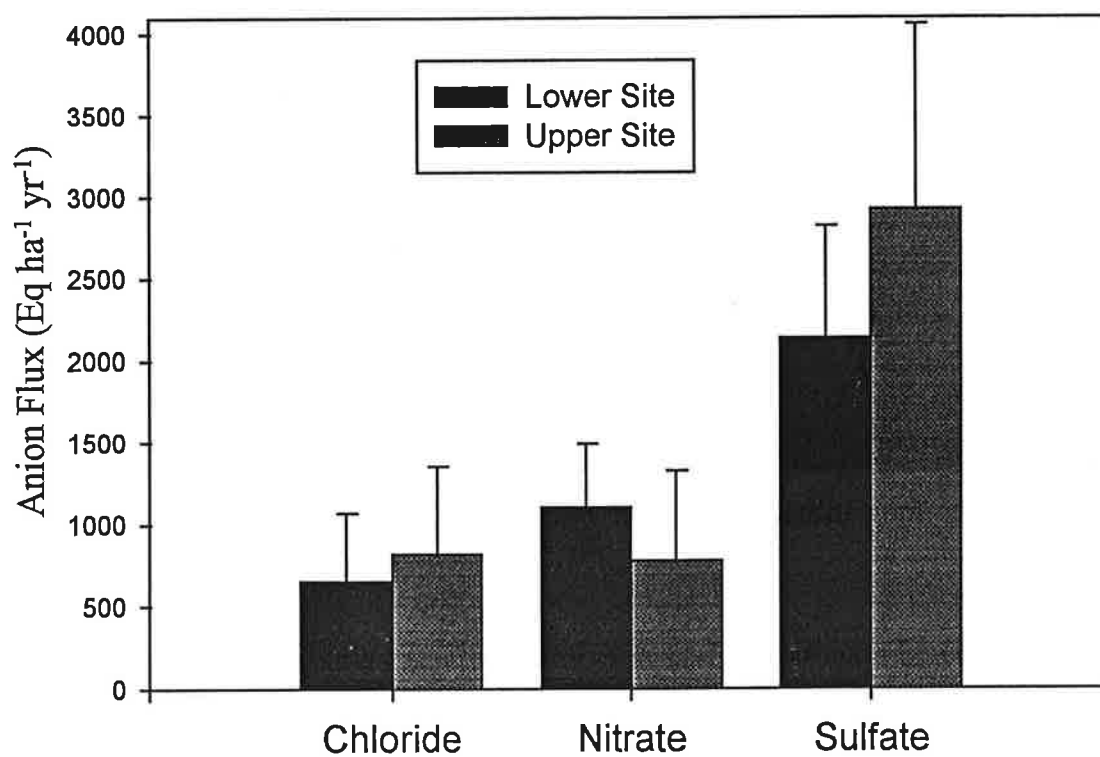


Figure 6. Three Year Average Anion Fluxes Entering the Noland Divide Watershed as Throughfall (Collections were made from 8-93 to 7-96). Error Bars are 95% CI of the mean (N=3).

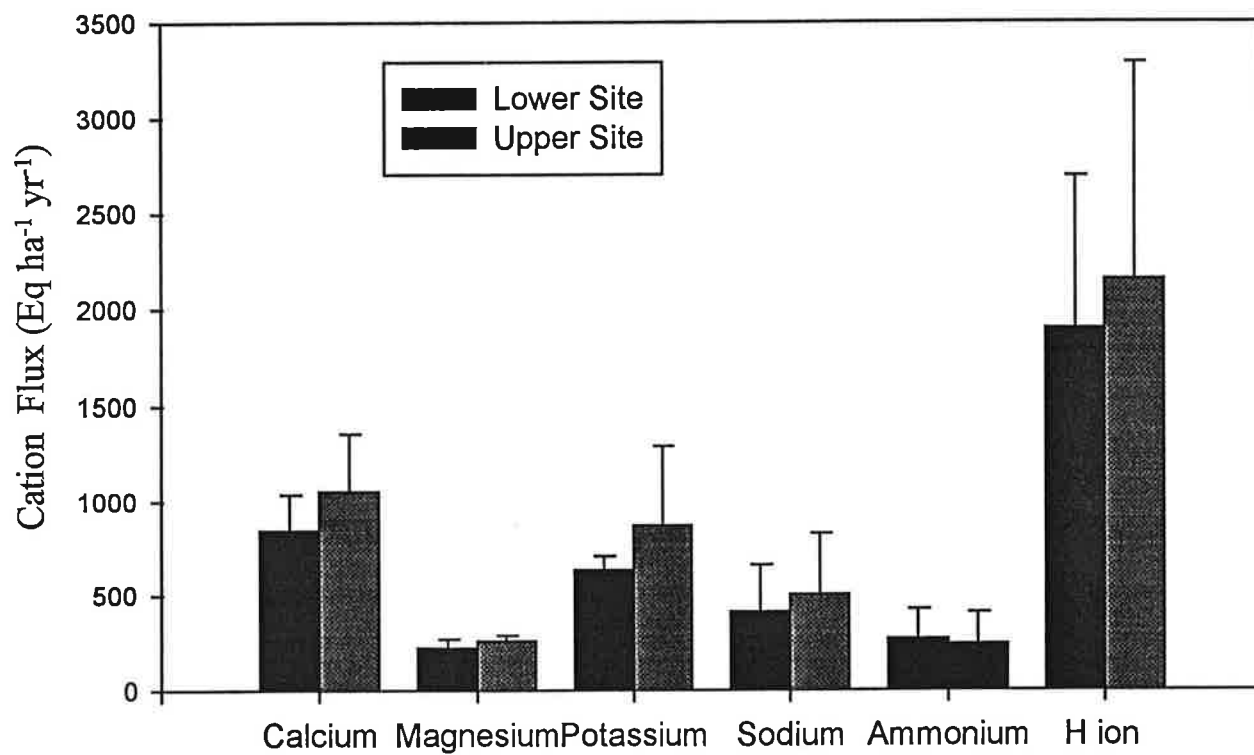


Figure 7. Three Year Average Cation Fluxes Entering the Noland Divide Watershed as Throughfall (Collections were made from 8-93 to 7-96). Error Bars are 95% CI of the mean (N=3).

There are two possible reasons why inorganic N in throughfall declines with increasing elevation: 1) dry deposition of N is actually much higher at the lower site, and/or 2) the canopy uptake rates of N is much higher at the upper site. If anything, the dry deposition rates should increase with increasing elevation, because higher wind speeds near the top of the ridge force more air through the canopy where deposition occurs. Since there were no significant differences in the amount of anions or cations in precipitation at the two sites (Figure 8 & 9), the higher throughfall fluxes at the upper site must be attributed to higher rates of either cloud or dry deposition or both. The lower throughfall flux of nitrate and ammonium at the upper site must therefore be a result of higher foliar uptake rates at the upper site (Shubzda *et al.*, in prep). These findings further emphasize the fact that nitrogen found in TF is a poor indicator of the total deposition entering a watershed (Shubzda *et al.*, 1995).

Cloud or occult deposition is a very important process that occurs within this watershed and throughout the entire Park above cloudbase, which is ~1800 m (5500 ft.) (Lindberg and Owens, 1993). The exceedingly high sulfate deposition can be attributed to the high amounts of cloud water entering the watershed. Cloud water represents up to 50% or more of the total sulfate loading (Shubzda *et al.*, 1995). We estimate that the lower and upper sites annually receive ~40 and 70 cm of cloudwater, respectively (Figure 10). These estimates are based on previous work done during the IFS, for a complete description of these estimates refer to Lovett (1986).

The rates of nitrogen and sulfur deposition at NDW are very high with respect to other locations around the world where acid deposition is a problem (Table 2). The sites shown in Table 2 are ranked in order of descending sulfate deposition and NDW falls in the middle of this list. The sites with higher throughfall rates than NDW are all in Europe where regulation of

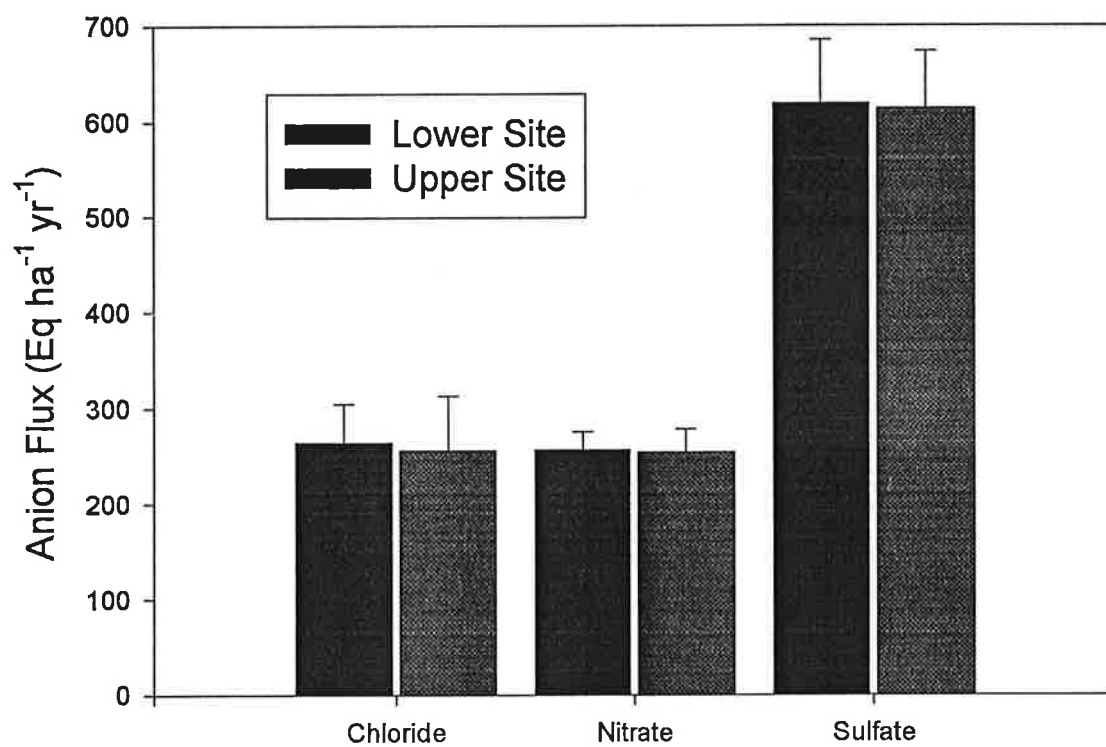


Figure 8. Three Year Average Anion Fluxes Entering the Noland Divide Watershed as Precipitation (Collections were made from 8-93 to 7-96). Error Bars are 95% CI of the mean (N=3).

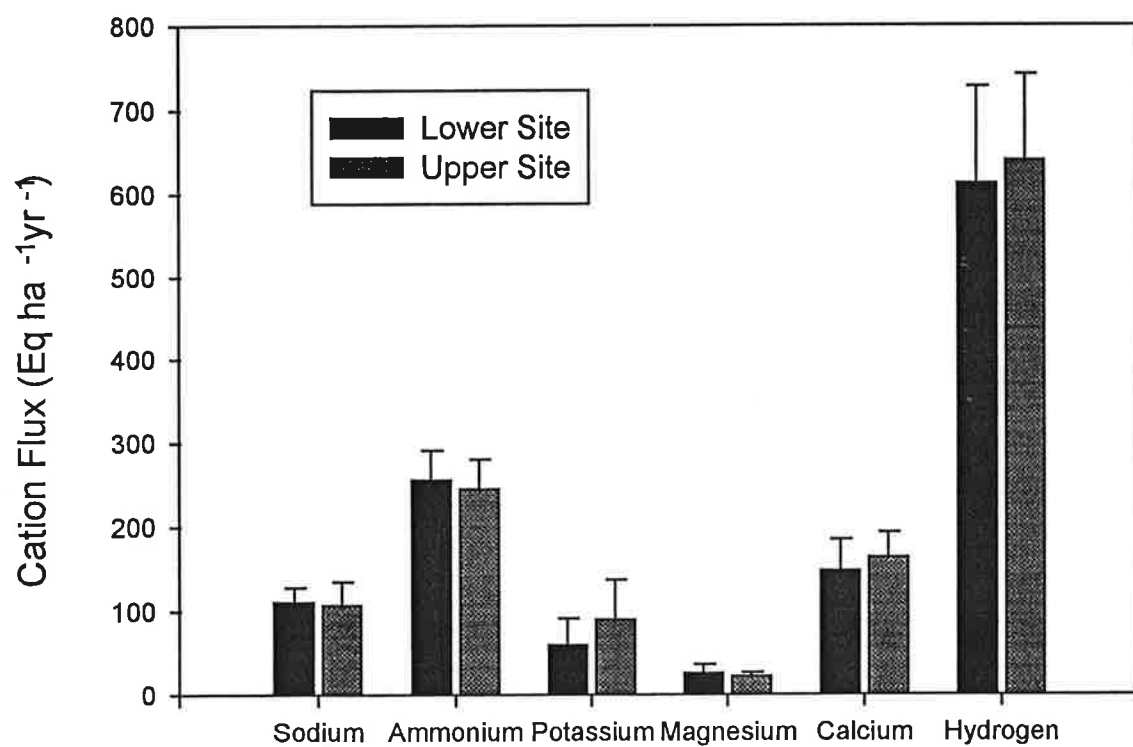


Figure 9. Three Year Average Cation Fluxes Entering the Noland Divide Watershed as Precipitation (Collections were made from 8-93 to 7-96). Error Bars are 95% CI of the mean (N=3).

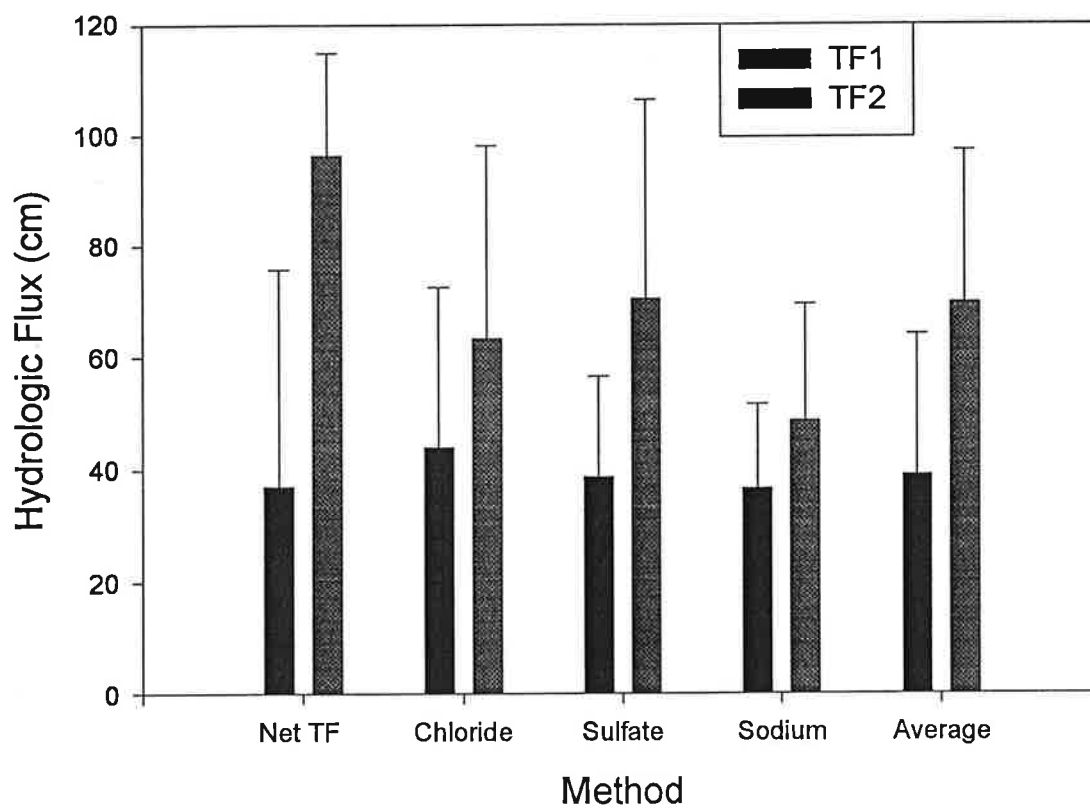


Figure 10. Cloudwater Volume Estimates for the Noland Divide Watershed (Collections were made from 8-93 to 7-96). Error Bars are 95% CI of the mean (N=3).

Table 2. Comparison of Atmospheric Deposition Rates based on Throughfall Measurements for Various Sites Around the World where Acid Deposition is Suspected of being a Problem.

Watershed (Reference)	Location	Elevation (m)	NO ₃ ⁻ (Eq/ha/yr)	NH ₄ ⁺ (Eq/ha/yr)	SO ₄ ²⁻ (Eq/ha/yr)	Forest Condition
Uhlirska (1)	Czechoslovakia	830	1282	710	4408	20 yr Spruce
Lunteren (2)	Netherlands	-	998	5063	4114	Douglas Fir
Amerongen (2)	Netherlands	-	691	3047	2604	Douglas Fir
Nacetin (1)	Czechoslovakia	780	1009	687	2478	Spruce, >30% defoliated
Noland Divide Watershed	Great Smoky Mountains, USA	1740	893	209	2100	Virgin Spruce-Fir
Whiteface Mtn. (3, 4)	New York, USA	1025	321	164	1800	Spruce-Fir
Oberbarenburg (1)	Germany	735	226	721	1666	40 yr Spruce
Hardewijk (2)	Netherlands	-	932	1744	1284	Douglas Fir
Fredriksborg (5)	Denmark	-	642	678	998	Mixed Deciduous Forest
Ulborg (5)	Denmark	-	635	857	905	Mixed Deciduous Forest
Duke Forest (4)	North Carolina, USA	213	590	410	840	Loblolly Pine
Coweeta (4)	North Carolina, USA	725	330	180	600	White Pine
Thompson Forest (4)	Washington, USA	220	240	110	400	Douglas Fir
Alberta (6)	Canada	-	9.1	55.4	-	White Spruce

¹Cerny and Paces, 1995

²Erisman, 1993

³Lovett and Lindberg, 1993

⁴Johnson and Lindberg, 1992

⁵Hovmand and Andersen, 1995

⁶Blew *et al.*, 1993

emissions has been relatively slow. At some of the European sites the deposition of ammonium is higher than for nitrate which is usually not the case in North America. The high ammonium deposition rates in Europe are the result of the agricultural practices of that region. Although NDW has the highest rates of N or S throughfall deposition we could find in North America (*cf.* Johnson and Lindberg, 1992), several sites have been shown to have higher total deposition (wet + dry + cloud deposition) of N and S including Madonna Mountain in Vermont, Mt. Moosilauke in New Hampshire (Lovett and Kinsman, 1990). These sites were not included here because throughfall was not measured. One site in West Virginia may have comparable levels of N deposition as throughfall but data were not clearly reported (Peterjohn *et al.*, 1996). Regardless of the actual ranking of deposition rates, NDW certainly receives some of the highest rates of N and S deposition as throughfall in North America.

Streamwater Chemistry

There are two streams that drain NDW and both are gauged for measurement of discharge and monitored for water chemistry. There is considerable variability between the two streams due to differences in flowpaths for water draining to each stream. Gauging experiments conducted with scientists from Oak Ridge National Laboratory indicate that the two streams are interconnected within the upper reaches of the watershed and the NE streamlet has a large hyperheric zone located approximately 50 m upstream from the flume. During baseflow conditions and smaller storm events the SW streamlet generally receives the higher proportion of flow. However, during periods of high flow and particularly in the winter when the stage height in the flume exceeds 0.5 feet, the NE streamlet receives the larger proportion of flow. The differences in stream flow between the two streams result in differences in water chemistry as well.

The predominant strong acid anion in the streams draining NDW during the study period was nitrate (Nodvin *et al.*, 1995, Figure 11). The order of average stream water concentration of acid anions expressed as equivalents was:



Nitrate is not expected to be the dominant anion in forest ecosystems because biological uptake generally exceeds inputs from internal and external sources (Likens *et al.*, 1977; Likens and Bormann, 1995). For this reason forest ecosystems are generally nitrogen limited and very little leaches out of the rooting zone and into streams as either nitrate or ammonium. This is not the case at NDW however, as nitrate concentrations within the two streams ranged from 40-80 $\mu\text{eq/L}$ (Figure 11, Table 3) with very distinct seasonal patterns of concentration change (Figure 12).

Table 3. Summary of the Last Five Years of Stream Water Chemistry Collected at the Noland Divide Watershed. All values are expressed as $\mu\text{eq/L}$, except pH which is expressed as standard units.

	SW			NE		
	Minimum	Average	Maximum	Minimum	Average	Maximum
pH	5.13	5.86	6.28	4.73	5.65	6.26
ANC^a	-6.40	12.94	42.41	-9.65	4.34	24.91
Cl⁻	6.65	13.02	54.43	7.89	15.29	61.94
NO₃⁻	24.36	44.16	65.72	20.01	50.57	74.09
SO₄²⁻	20.79	29.76	57.35	26.97	41.83	73.60
Na⁺	13.91	25.24	45.58	13.29	24.26	43.35
NH₄⁺	0	0.84	23.96	0	0.87	15.73
K⁺	2.28	7.54	25.86	4.07	10.29	42.73
Mg²⁺	11.68	20.41	33.64	14.57	22.28	31.80
Ca²⁺	37.08	58.27	82.86	40.32	62.66	88.31

^aAcid Neutralizing Capacity, Gran-Titration method.

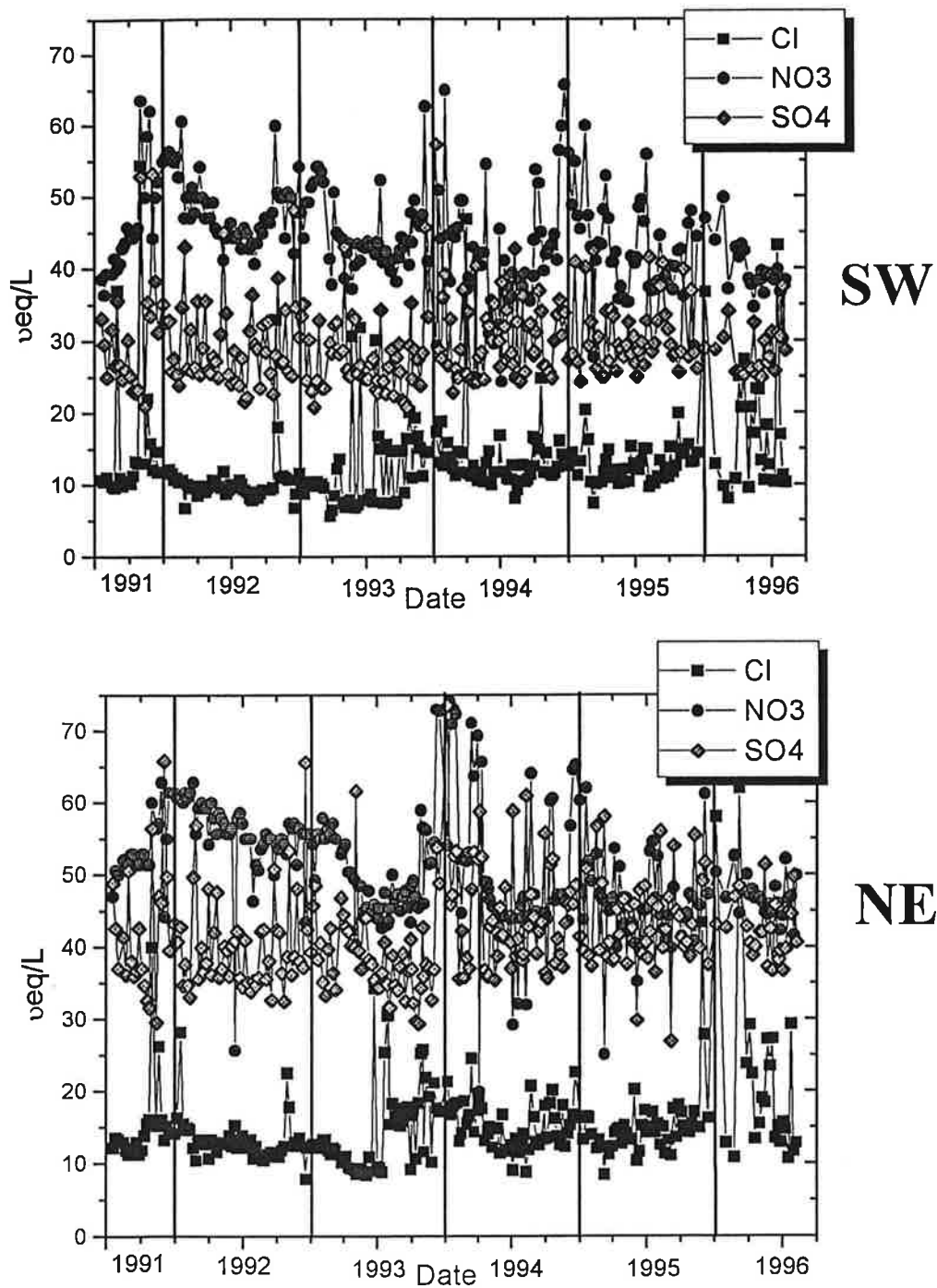


Figure 11. Streamwater Anion Concentrations Draining the Noland Divide Watershed.

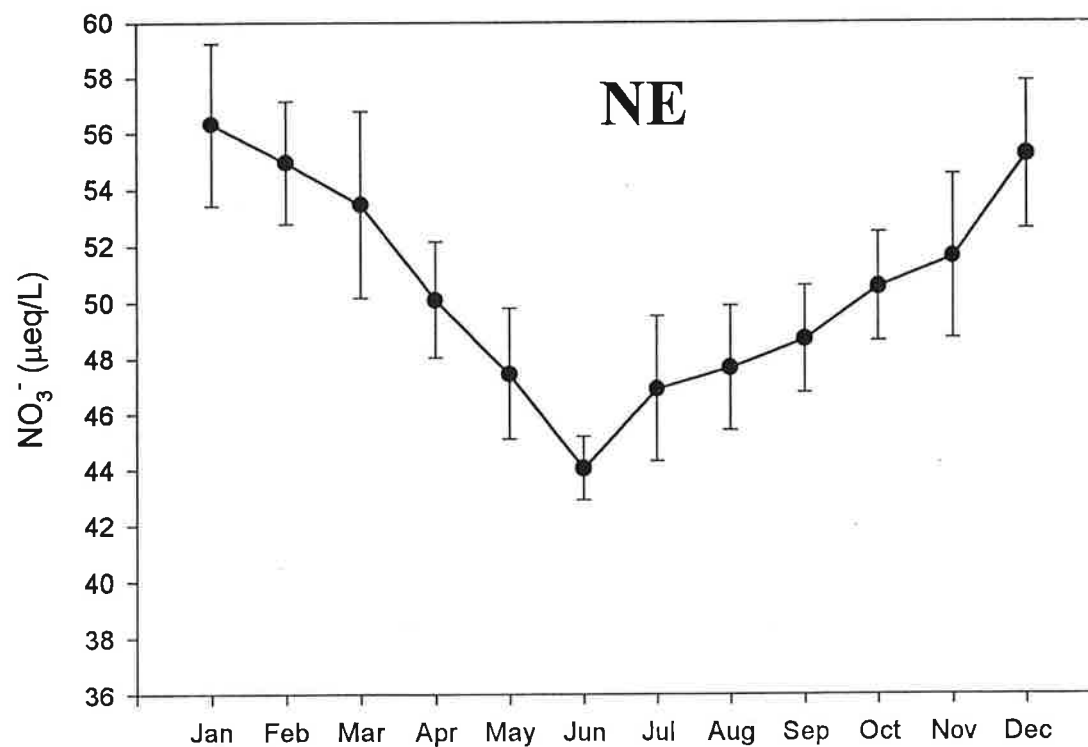
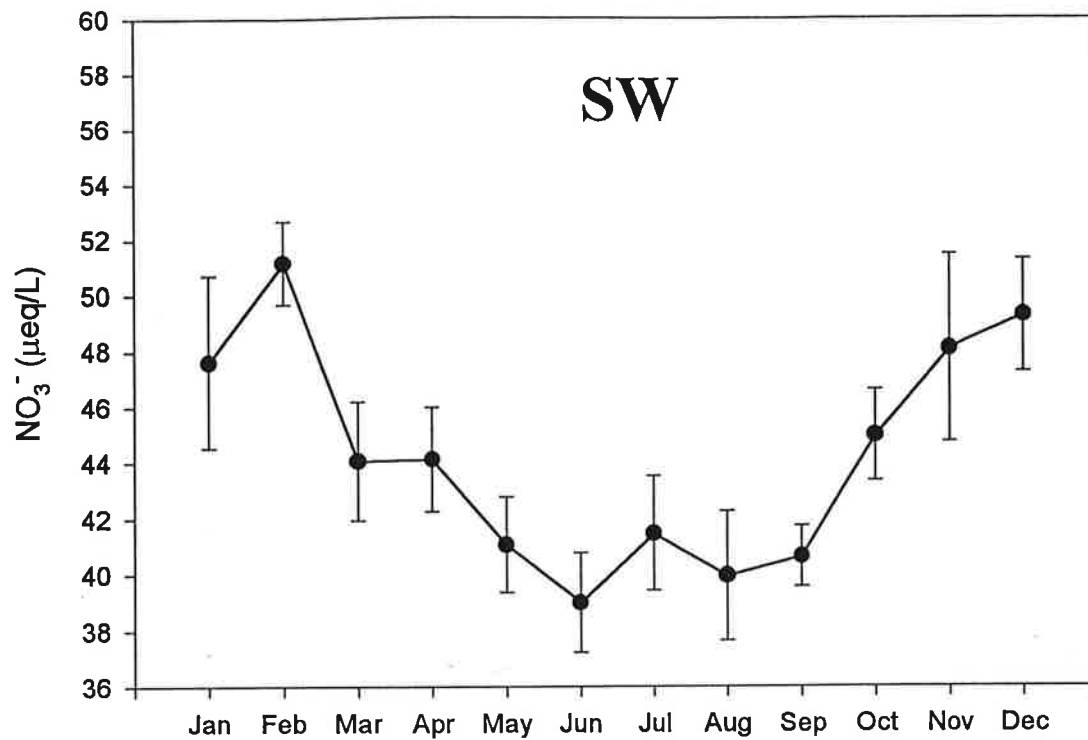
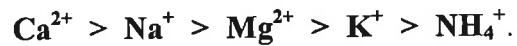


Figure 12. Five Year Monthly Weighted Mean Nitrate Concentrations Draining the Noland Divide Watershed. Error Bars are S.E.. of the mean.

The sulfate levels generally ranged between 20-75 µeq/L (Figure 13, Table 3) with the highest recorded values occurring during winter when flow is generally highest (Figure 13). The predominant cation within these systems is calcium (Figure 14). The rank order of cation concentration expressed as equivalents is:



This is a common order of cation concentration in stream water anywhere although magnesium may exceed sodium concentration even in some streams within the GRSM.

Although the rank order of cations is typical of stream water anywhere, the actual concentrations are extremely low (Table 4). The average concentration of sulfate at NDW is low relative to streams in the northeastern US that receive comparable or even lower levels of sulfur deposition (Table 4). This suggests that sulfate adsorption within the NDW watershed is high (*cf.* Harrison *et al.*, 1989; Elwood, 1991). Average nitrate concentrations in the streams of NDW are lower than many other sites that receive high nitrogen inputs from either atmospheric deposition or agricultural fertilizers as in Europe and Minnesota (Table 4). Nitrate concentrations at NDW are comparable to many streams that receive high agricultural inputs and are higher than most streams in the northeastern US. The real problem for NDW however, is the low levels of base cations such as calcium (Table 4). The low concentration of base cations means that anions moving through the soil and into the stream will be balanced by H^{+} or potentially toxic aluminum ions. The effects of both nitrate and sulfate (and chloride) reaching the streams are sufficiently high to create chronically low pH (Figure 15) and ANC (Figure 16).

Watershed Flux Balances

The input-output budgets for various nutrient elements and water were calculated by comparing inputs based on TF and streamwater exports calculated as the product of stream

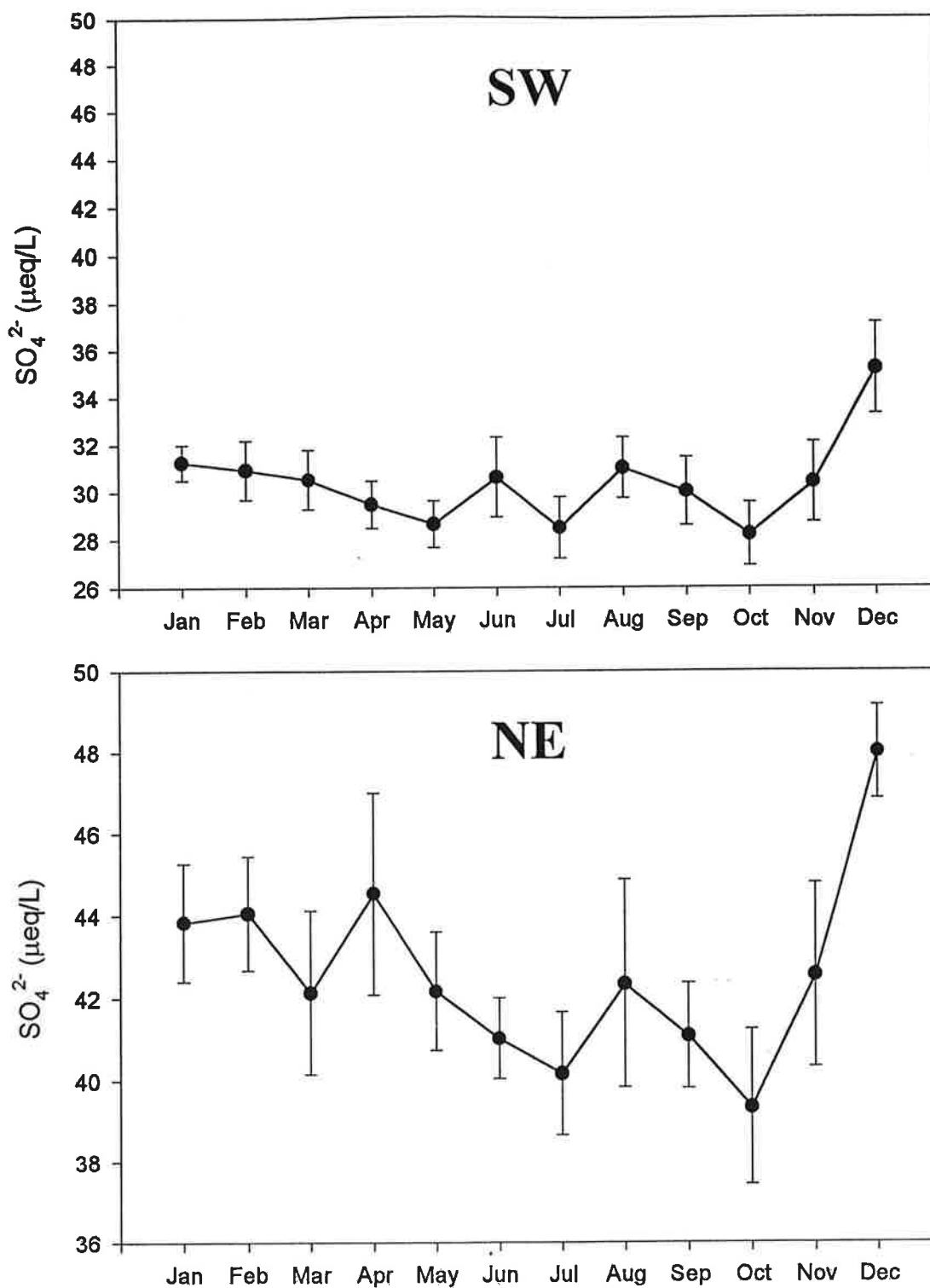


Figure 13. Five Year Average Monthly Weighted Mean Sulfate Concentrations Draining the Noland Divide Watershed. Error Bars are S.E. of the mean.

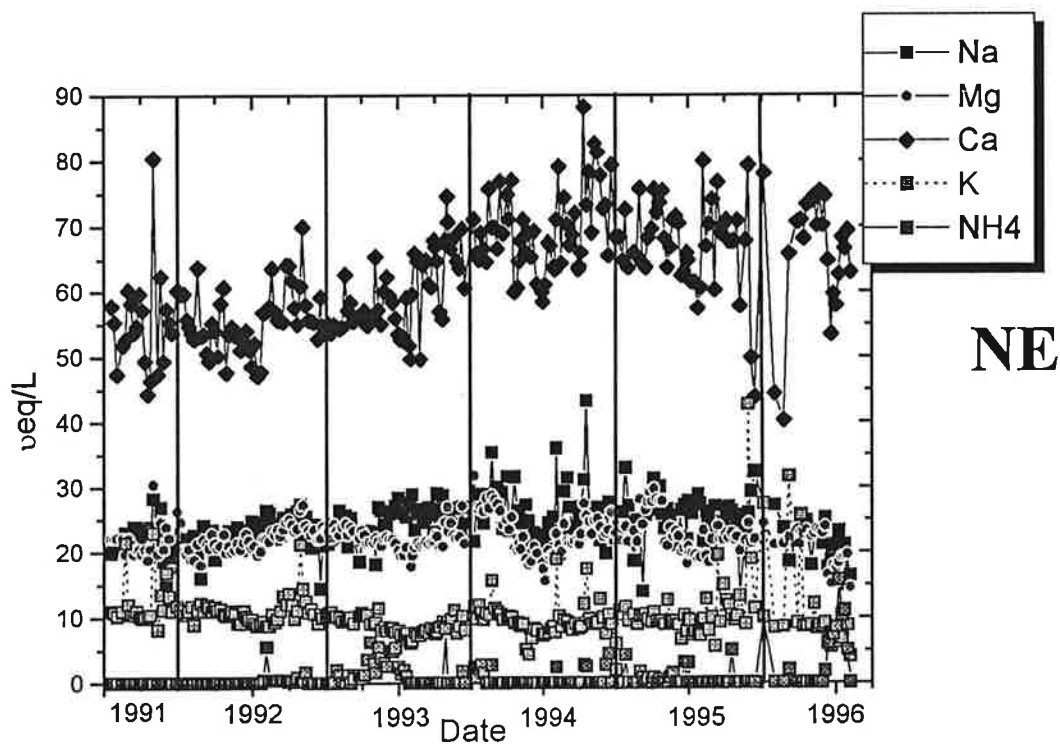
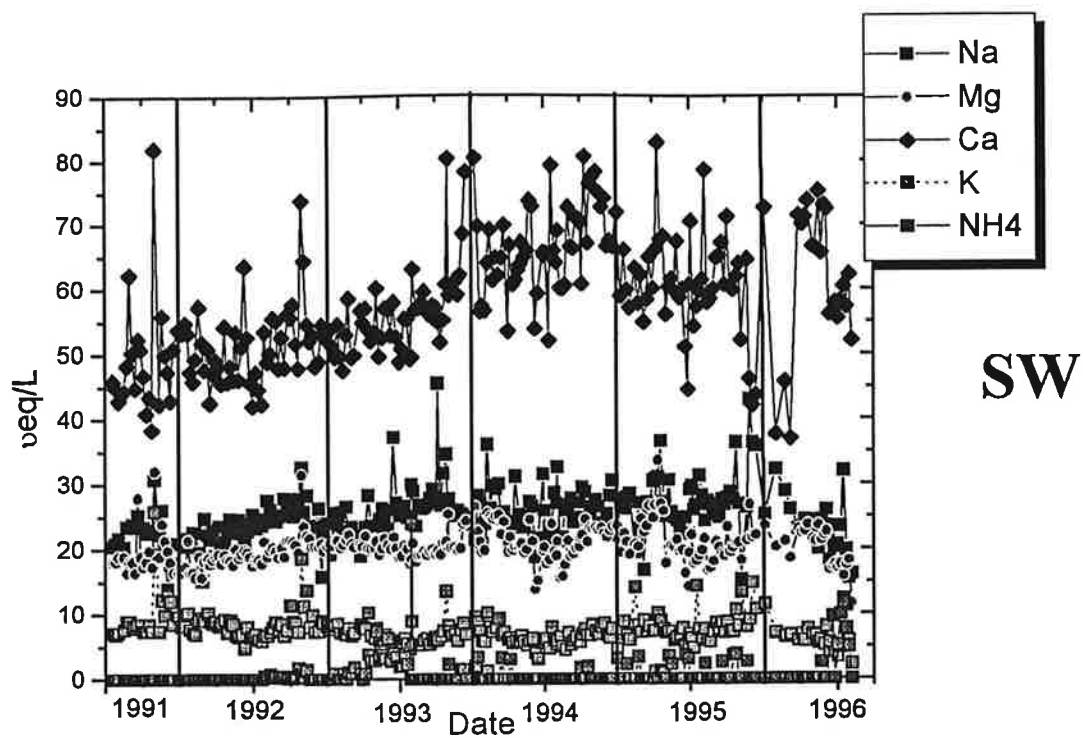


Figure 14. Streamwater Cation Concentrations Draining the Noland Divide Watershed.

Table 4. Comparison of average chemical composition for select streams ranked in order of descending nitrate concentration. Czech streams receive acid deposition, Minnesota streams receive agricultural inputs, northeastern US streams have higher sulfate levels than NDW, and Colorado stream receive little deposition.

Watershed (Reference)	Location	Elevation (m)	Nitrate ($\mu\text{eq/L}$)	Sulfate ($\mu\text{eq/L}$)	Calcium ($\mu\text{eq/L}$)	pH
Jezeri Brook 1978-1994 (1)	Czechoslovakia	475	Declined from 220 to about 90	Declined from 1550 to about 1175	748	-
Blue Earth River (2)	Minnesota, USA	250	113 (564max)	470	780	7.32
Jizerka 1984 - 1995 (1)	Czechoslovakia	870	Declined from 90 to about 65	Declined from 240 to about 120	-	Increased from 4.0 to 5.5
Uhlirka (1)	Czechoslovakia	780	81.8	170	142	5.45
Watershed 4 stream -1990 (3)	Fernow Experimental Forest, West Virginia, USA	?	69.6	-	-	-
Noland Divide Watershed	North Carolina, USA	1550	50.6	41.8	62.7	5.65
Cottonwood River (2)	Minnesota, USA	260	48.4 (161 max.)	450	790	7.10
Beddgeler (4)t	Wales, UK	-	45.0	-	-	-
Biscuit Brook (5)	New York, USA	-	~40	~130	-	~5.5
Watershed 6 Hubbard Brook (6)	New Hampshire, USA	500	~10	~110	~55	~5.0
E. St. Louis Creek (7)	Fraser Experimental Forest, Colorado, USA	2880	2.1	41	297	6.70
Fool Creek (7)	Fraser Experimental Forest, Colorado, USA	3180	1.0	28	151	6.77

¹Cerny and Paces, 1995

²Payne, 1992

³Peterjohn *et al.*, 1996

⁴Emmett *et al.*, 1993

⁵Murdoch and Stoddard, 1992

⁶Likens and Bormann, 1995

⁷Stottlemeyer and Troendle, 1992

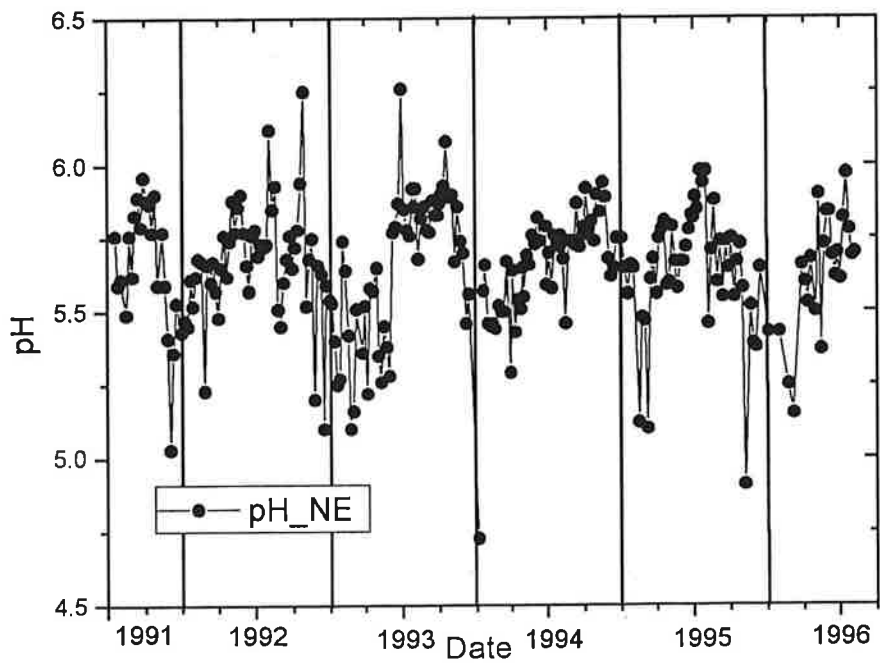
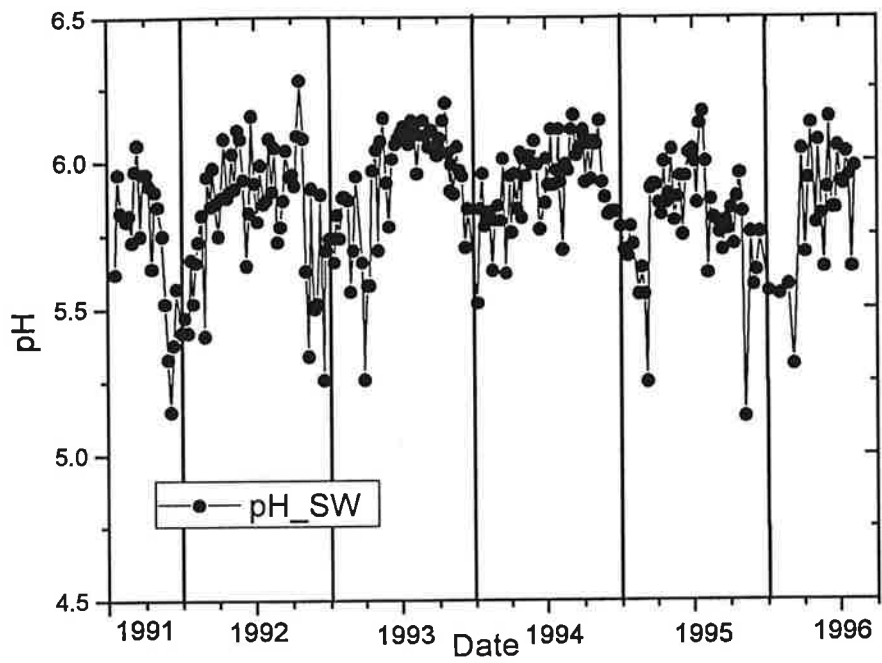


Figure 15. Five Year pH Values Draining the Noland Divide Watershed.

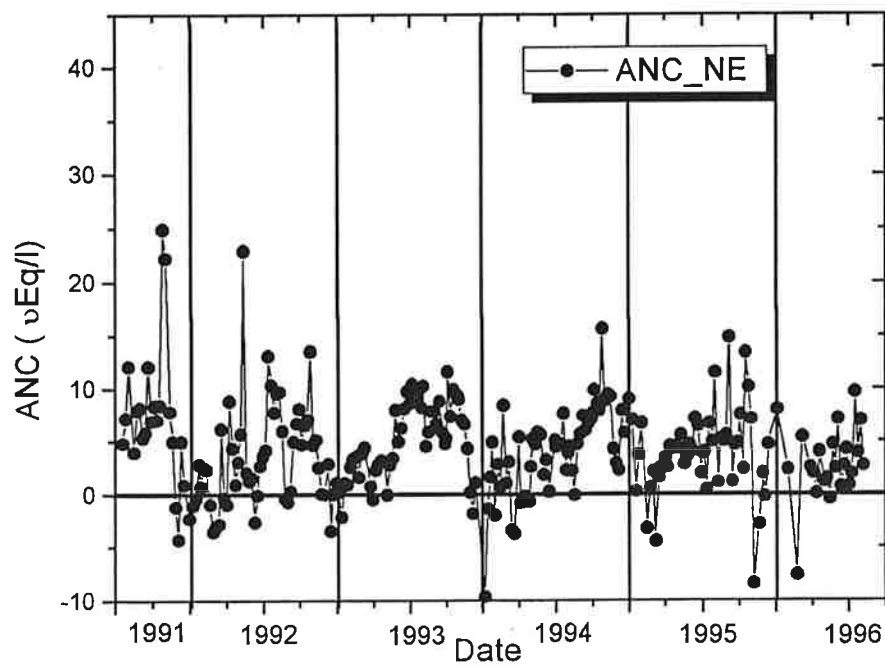
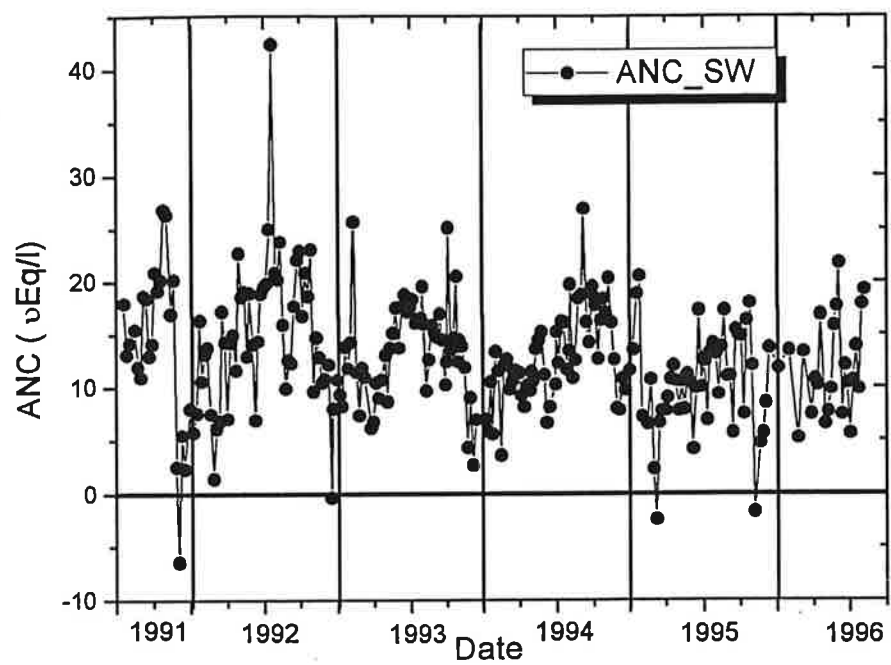


Figure 16. Five Year ANC Values Draining the Noland Divide Watershed.

concentration and flow expressed on a per unit area basis for NDW (*e.g.* Nodvin *et al.*, 1995). The hydrologic balance for the NDW shows that throughfall inputs are similar to or slightly greater than streamflow outputs (Figure 17). Differences between hydrologic throughfall inputs and stream flow volume are probably the result of evapotranspiration which was estimated by the IFS to be about 19%. (Johnson and Lindberg, 1992).

The input of hydrogen ions in throughfall greatly exceeds the output in streamwater (Figure 18). This indicates that most of the hydrogen ion entering the watershed is retained within the terrestrial ecosystem. Some of the hydrogen ion may be exchanged for base cations such as calcium on ion exchange sites in the soil. The ability to maintain base cations within the soil complex is a function of how rapidly base cations are released by parent rocks in weathering reactions and the rate of leaching out of the system. The metasandstone rock underlying the GRSM is highly resistant to weathering and thus do not yield large quantities of base cations. Leaching rates are thus the key to understanding the loss of base cations, soil acidification and ultimately streamwater acidification in the GRSM.

Leaching rates are ultimately controlled by the movement of anions through the soil (Johnson and Cole, 1982). The principle anions regulating the mobility of soil solutes are also the strong acid anions chloride, nitrate, and sulfate. Chloride inputs to NDW are not unusually high. The average sulfate inputs to NDW over five years of 2100 Eq/ha/yr is relatively high but exceeds the average exports of 860 Eq/ha/yr (Figure 19). This indicates that the watershed has a net retention of about 59% of the deposited sulfate or that only about 41% leaches out of the system in streamflow. This level of sulfate adsorption is similar to estimates made by other workers for the GRSM and southern Appalachians (Harrison *et al.*, 1989; Elwood, 1991). High retention of sulfate within these systems limits the potential export of base cations by sulfate leaching

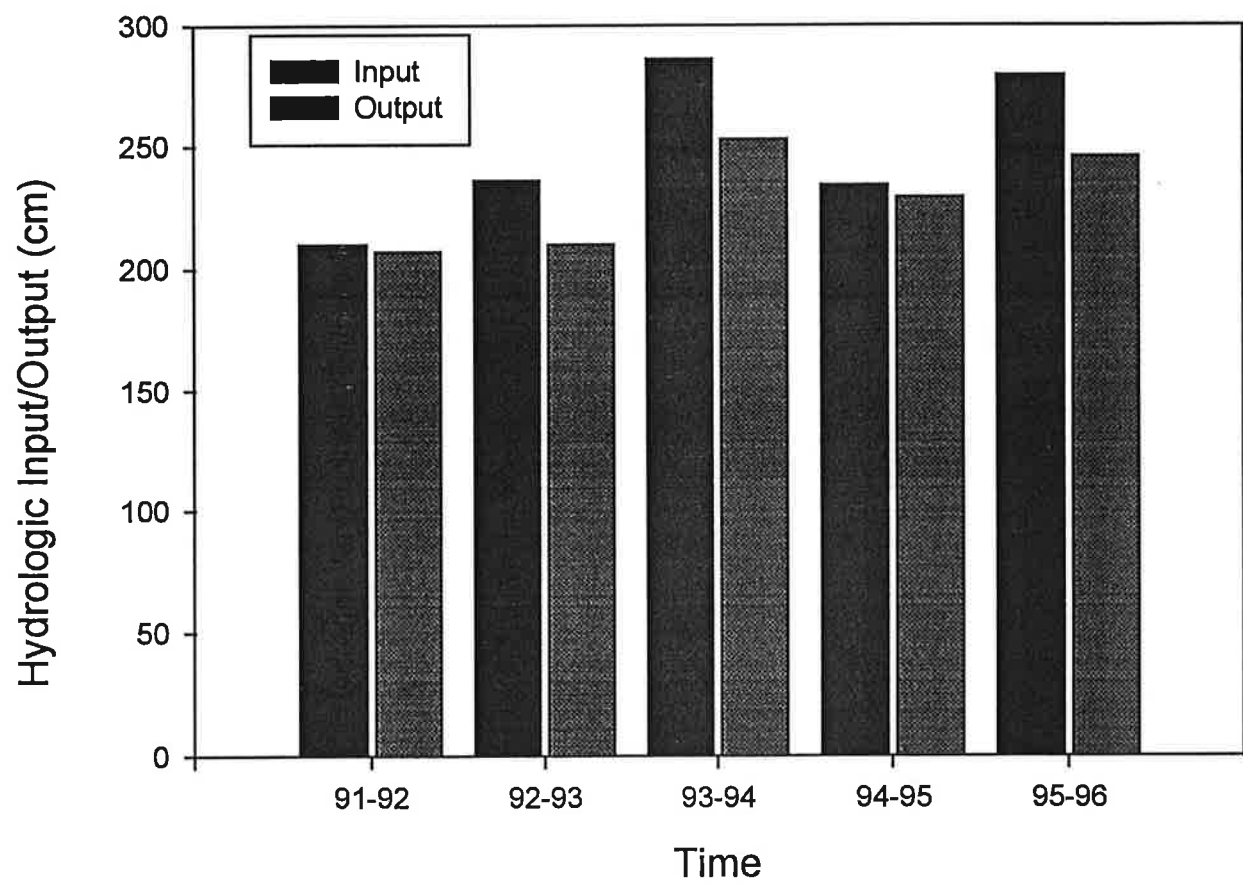


Figure 17. Five Year Annual Hydrological Budgets for the Noland Divide Watershed.

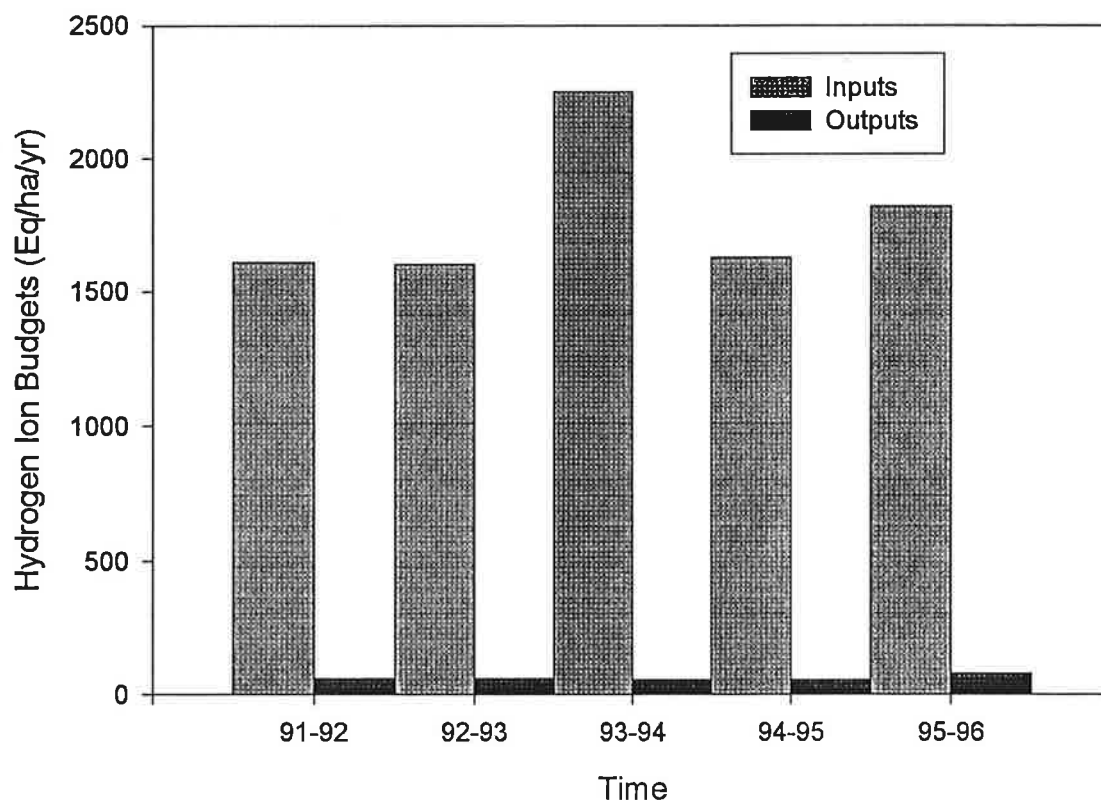


Figure 18. Hydrogen Ion Budgets for the Noland Divide Watershed.

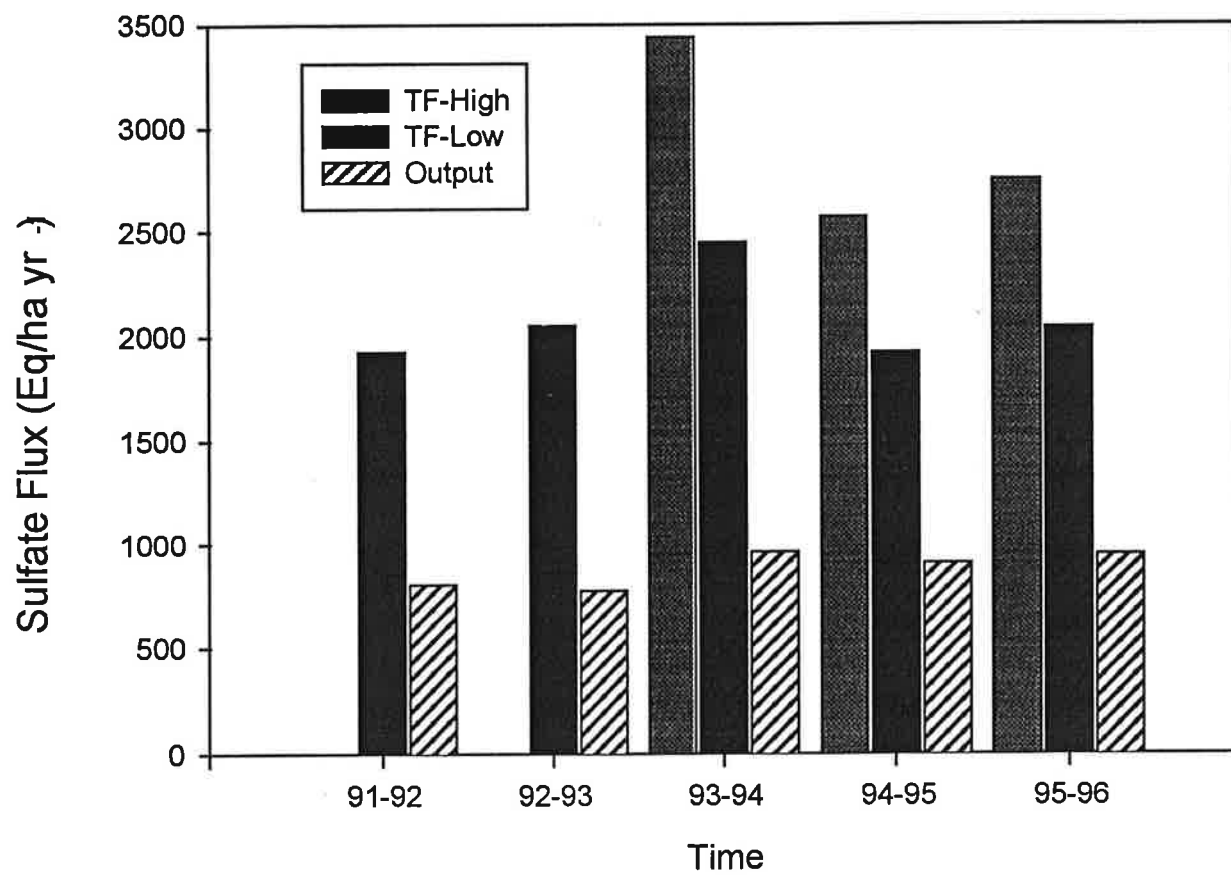


Figure 19. Annual Sulfate Budgets for the Noland Divide Watershed.

(Harrison *et al.*, 1989). The situation is quite different for nitrate however. Although the balance of inputs and outputs of inorganic nitrogen to the NDW change from year to year, the average five-year input of 1100 Eq/ha/yr are nearly identical to the average export of about 1090 Eq/hq/yr (Figure 20). The apparent balance between inputs and outputs of inorganic nitrogen suggests that the watershed is near a point of saturation with respect to nitrogen flux. Considering that most forested ecosystems retain virtually all of the nitrogen in the terrestrial system by plant uptake, the high loss of nitrogen as nitrate is a very important process at NDW and one that contributes substantially to transport of cations including H^+ to the stream water.

The mean calcium export from NDW has been increasing, on average, over past five year (Figure 21). The increasing calcium concentrations indicates increased leaching from the watershed and may reflect a general loss of exchangeable base cations from the system. If the trend of increasing calcium loss is real and not simply a function of high water yield in 1993-94 and 1995-96, the consequences for the watershed and perhaps the entire spruce-fir ecosystem in the GRSM could be substantial. Any increased leaching of calcium, a base cation, increases the potential for even greater soil and surface water acidification as a result of continuing atmospheric deposition of N and S. Not only that however, increased loss of calcium from the terrestrial system could impact the nutritional status of vegetation since calcium may already be a limiting resource in the spruce-fir ecosystem. The export of base cations, especially calcium, from NDW should continue to be closely monitored for the foreseeable future.

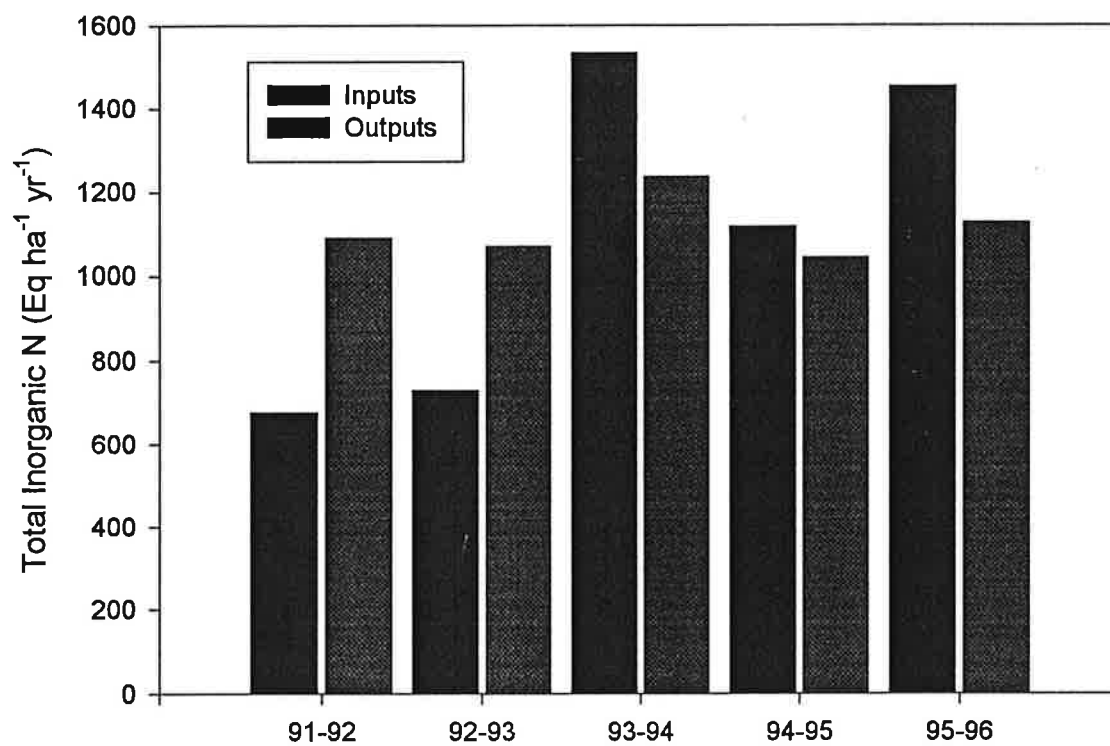


Figure 20. Total Inorganic Nitrogen Budgets for the Noland Divide Watershed.

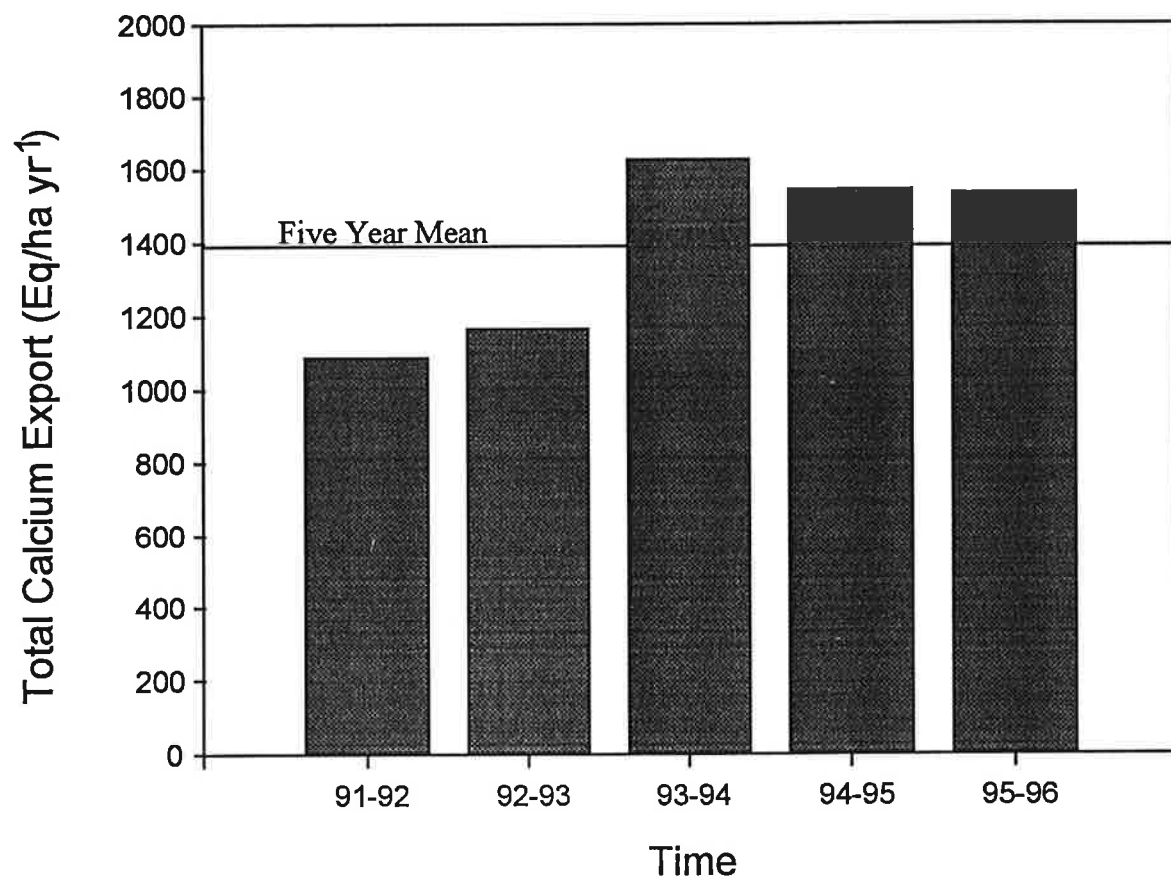


Figure 21. Total Calcium Export Leaving the Noland Divide Watershed.

Nitrogen Saturation

The leaching of nitrate in the streams at NDW indicates that sources of nitrogen to the watershed including atmospheric deposition and mineralization of organic matter exceed the requirements of plant uptake and microbial immobilization. There is no appreciable source of nitrogen from mineral weathering in the GRSM. Nitrogen deposition rates are clearly very high at NDW and mineralization rates have also been shown to be very high (Helga Van Miegroet and Joressia Jamison, unpublished data). It is still unclear how much of the nitrogen leached through the streams at NDW is mainly from precipitation moving rapidly through the system with little interaction within the watershed and how much is a result of processes occurring in the nitrogen cycle after interactions with terrestrial biota. Regardless of how the nitrogen is reaching the stream, the high outputs relative to inputs indicate the watershed is saturated with respect to nitrogen flux. Forest ecosystems that have become saturated to the point where they begin to export large quantities of nitrogen to streams are referred to as *nitrogen saturated* (Aber *et al.*, 1989).

Vegetation uptake is clearly an important process influencing how nitrogen saturation is expressed particularly with respect to temporal patterns of nitrate leaching to streams (Emmett *et al.*, 1993). Vegetation uptake influences the expression of nitrogen saturation in two ways. Uptake and sequestration (as biomass) of nitrogen has been hypothesized to undergo long-term changes leading to the establishment of a situation where exports from an ecosystem reflect the rate of input to the system (Vitousek and Reiners, 1975). This hypothesis suggests that ecosystems subject to high levels of atmospheric deposition would have relatively low levels of nitrogen leaching to streams during early stages of system development when biomass accumulation and uptake rates are greatest, but as the system ages nitrate leaching should

increase. Several studies have found that concentrations of nitrate in streams draining catchments with older forests and subject to high deposition rates, including catchments in the GRSM, are higher than nitrate concentrations in streams draining catchments with younger forests (Silsbee and Larson, 1982, 1983; Emmett *et al.*, 1993). Developmental changes in vegetation thus appear to have long term effects on course of nitrogen saturation in forested catchments.

Nitrogen uptake also has implications for short term patterns of nitrogen leaching to streams particularly in temperate climates where there is a distinct growing season. Nitrogen uptake should reduce the amount of nitrogen leaching to streams during the growing season but not during the non-growing season. Stoddard (1994) has used this temporal pattern to divide the progression of nitrogen saturation into four stages. Stage 0 of Stoddard's scheme is the "normal" condition of forested ecosystems where nitrogen is a limiting nutrient to the forest so that plant uptake and microbial immobilization allow very little nitrogen to reach the streams at any time during the year. As the system progresses to Stage 1 of nitrogen saturation, nitrate concentrations in streams remain low during the growing season but increase during the non-growing season when uptake and immobilization rates are lowest. Stage 2 of nitrogen saturation is marked by the elevation of nitrate concentrations during the growing season as inputs begin to exceed uptake rates. Nitrate concentrations in the stream remain higher during the non-growing season so that a seasonal pattern persists. The final stage (Stage 3) of nitrogen saturation arises when a seasonal pattern in stream nitrate concentration is lost.

Nitrogen Saturation Across the GRSM

The stream nitrate concentrations at NDW are clearly elevated throughout the year but still show a distinct seasonal pattern (Figure 22). This pattern would classify NDW at Stage 2

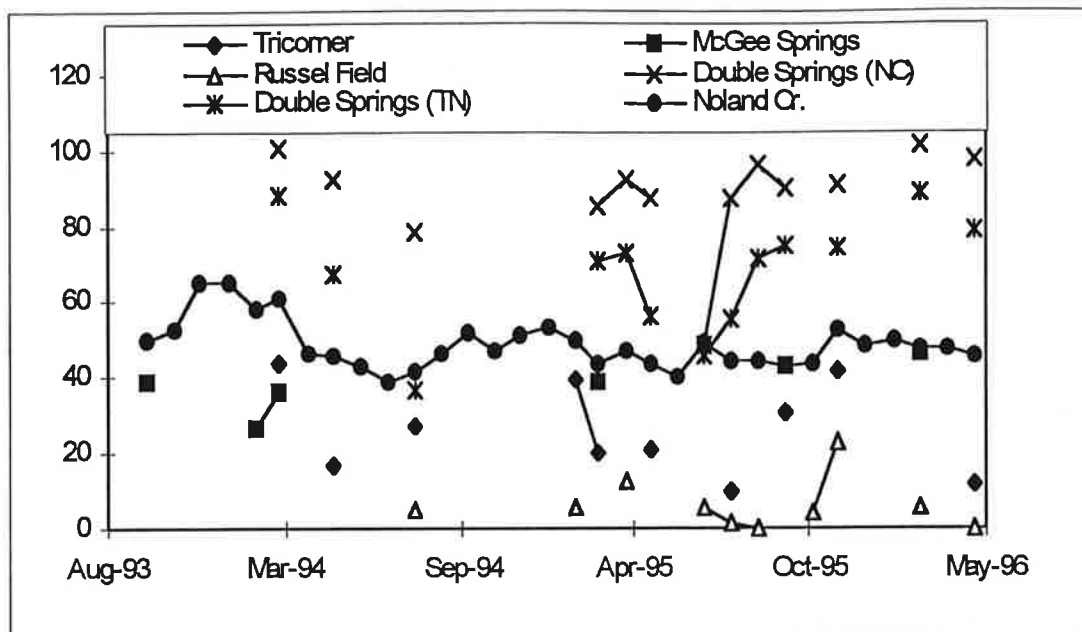


Figure 22. Comparison of the Nitrate Concentrations from the Noland Divide Watershed Relative to Other High Elevation Sites.

nitrogen saturation and approaching Stage 3 according to Stoddard's (1994) scheme. NDW is not the only location in the GRSM where stream nitrate concentrations are elevated (Figure 22). Stream nitrate concentrations at high elevation sites vary widely with some sites having higher levels than NDW and some with lower levels. Nearly all of the sites have lower nitrate concentration in the growing season months than during the non-growing season indicating that no site has advanced much past Stage 2 of nitrogen saturation. Differences in stream nitrate concentrations among sites suggests some spatial variability in nitrogen saturation exists within the GRSM.

The site with the highest nitrate concentrations in the GRSM, and possibly throughout the US, was the spring on the North Carolina side at Double Springs Gap Shelter just west of Clingmans Dome where concentrations of 100 µeq/L have been measured (Figure 23). This concentration is equivalent to 6.2 mg/L and can be compared to national drinking water standards

for nitrate of 10 mg/L. Despite the high concentrations of nitrate at Double Springs Gap Shelter, the appearance of a seasonal pattern of variation suggests this site is only approaching Stage 3 of nitrogen saturation (Figure 23). Another site located on Road Prong just east of Clingmans Dome has somewhat lower nitrate levels than at Double Springs but shows the same pattern of seasonal fluctuation. In the eastern part of the GRSM is Otter Creek, a stream which drains the northern face of Mt. Guyot, where nitrate concentrations remain above 30 $\mu\text{eq}\cdot\text{L}^{-1}$ for the entire year (Figure 23).

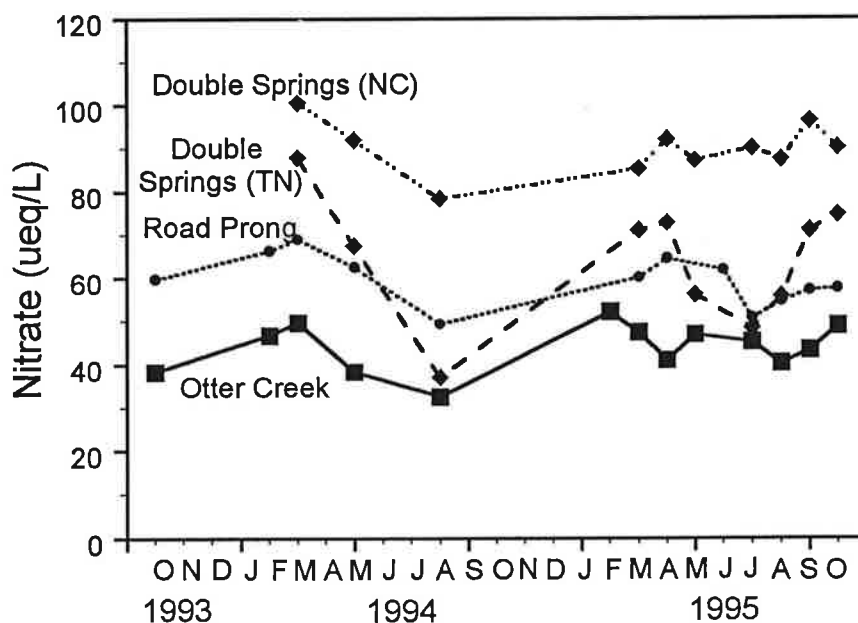


Figure 23. Seasonal Variation in Nitrate Concentrations for Select Sites with High Nitrate Levels Year Round.

These sites are all at Stage 2 of nitrogen saturation with stream nitrate concentrations well above a likely background level of 1-3 $\mu\text{eq}\cdot\text{L}^{-1}$ as observed in the western Rocky Mountains (Table 4). The reason why different concentrations of nitrate appear in different areas remains unclear; the cause could be spatial variation in atmospheric deposition or nitrogen cycling rates or both.

Many sites at mid elevations have lower stream nitrate concentrations with distinct increases in concentration during the non-growing season (Figure 24). A site on Road Prong at

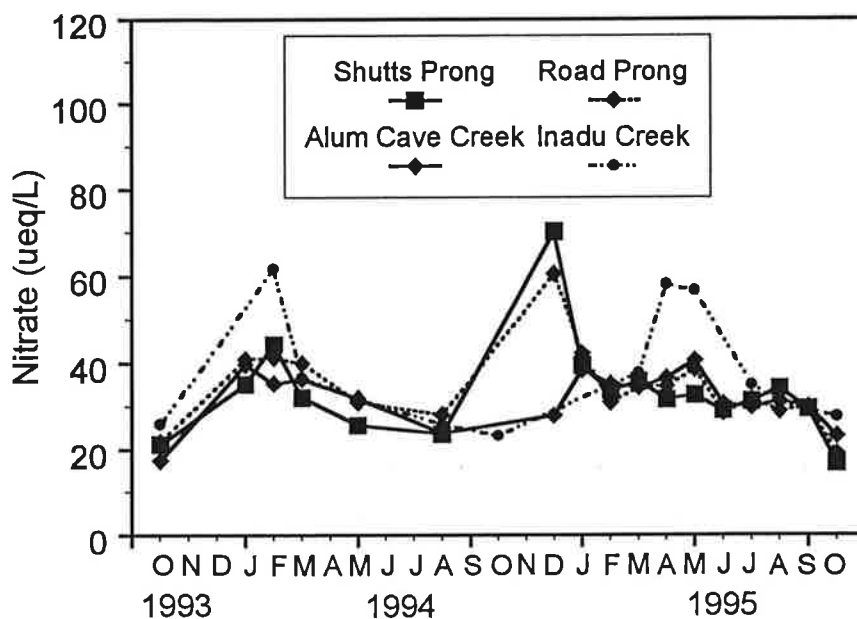


Figure 24. Seasonal Variation in Nitrate Concentration for Select Sites with Occasionally High Nitrate Levels.

about 1200 m downstream of the site shown in Figure 23 has lower nitrate levels than the upstream site but still has peaks in nitrate concentration during the winter non-growing season. Similar patterns occur for Alum Cave Creek which is a tributary entering the West Prong Little Pigeon River from the opposite side as Road Prong. Shutts Prong is a tributary to the Middle Prong Little River on the central portion of the Park while Inadu Creek enters Cosby Creek on the east side of the Park. These sites appear to be at Stage 1 and approaching Stage 2 of nitrogen saturation with non-growing season peaks in nitrate and elevated nitrate levels year round.

Some mid-elevation tributaries and larger streams near the Park boundaries have much lower stream nitrate concentrations (Figure 25). Ashe Camp Creek (1000 m) is a tributary of the

Little River which flows out of the central part of the GRSM at about 350m while Beech Creek (1250 m) is a tributary to Cataloochee Creek which flows out of the eastern part of the GRSM at about 780 m. Despite differences in location and elevation, the main channels and some of their

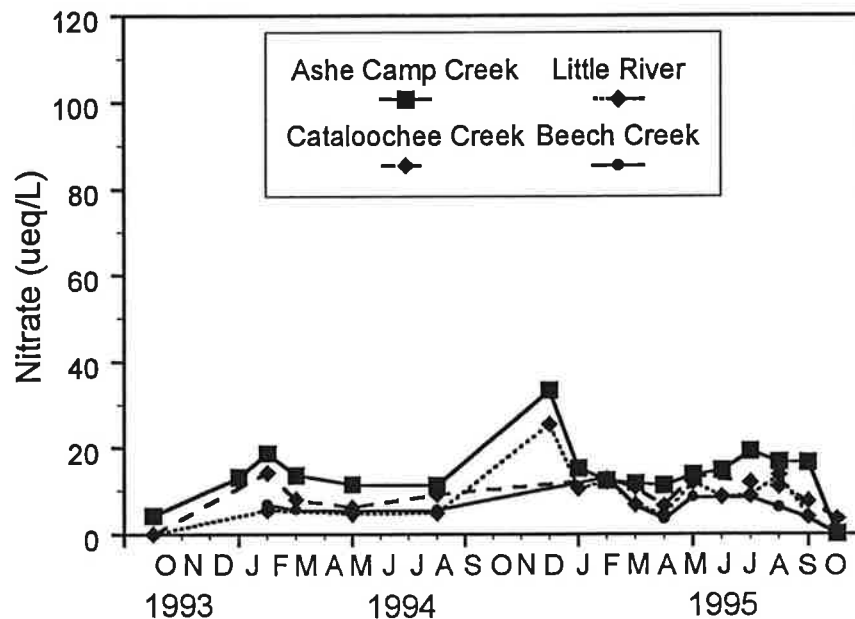


Figure 25. Seasonal Variation in nitrate Concentration for Select Sites with Low Nitrate Levels Year Round.

tributaries can have similarly low nitrate levels (Figure 25). These sites have slightly higher stream nitrate concentrations in the non-growing season than in the growing season which suggests a state bordering between Stage 1 and Stage 0 of nitrogen saturation.

An Index of Nitrogen Saturation

Examining the advancement of nitrogen saturation across the GRSM is important since the leaching of nitrate into streamwater is clearly important in contributing to surface water acidification at NDW. In order to assess the spatial extent of the nitrogen saturation problem

across the GRSM, an index of nitrogen saturation was developed. The nitrogen saturation index (NSI_i) was calculated for each site according to the equation:

$$NSI_i = MaxN_{land} \cdot [(MaxN_i + MinN_i) / (MaxN_{land} + HighMinN_{land})]$$

where MaxN_i is the maximum stream nitrate concentration at the site I, MinN_i is the minimum concentrations of stream nitrate, MaxN_{land} the highest maximum nitrate concentration across the landscape, and HighMinN_{land} is the highest minimum nitrate concentration across the landscape. The ratio inside the square brackets is necessarily between 0 and 1 and accounts for the variation in stream nitrate concentration at each site relative to the highest maximum and minimum concentrations observed on the landscape. Multiplying this ratio by the maximum stream nitrate concentration observed for the landscape allows direct comparison of index values from different landscapes to be made. Including the maximum stream nitrate concentration for the landscape is necessary because factors influencing nitrogen saturation such as total atmospheric deposition might be different among different landscapes and the index should reflect that difference. Using the nitrogen saturation index values for each site, a map of the spatial variation in nitrogen saturation was prepared by ordinary kriging (Figure 26). The areas where the highest nitrate concentrations were observed (above about 50 µeq·L⁻¹) received NSI scores generally above 50 so this index value was assumed to encompass areas that are at least Stage 2 of nitrogen saturation. The areas with NSI greater than 50 are bounded by a purple line in Figure 26. Areas where stream nitrate concentration was between 30 and 50 µeq·L⁻¹ had NSI scores between about 20 and 50 and appear to be at least at Stage 1 and approaching Stage 2 of nitrogen saturation. These areas are bounded in red in Figure 26. Areas where NSI scores were below 20 are probably not influenced by nitrogen saturation or at least no more advanced than Stage 1 of

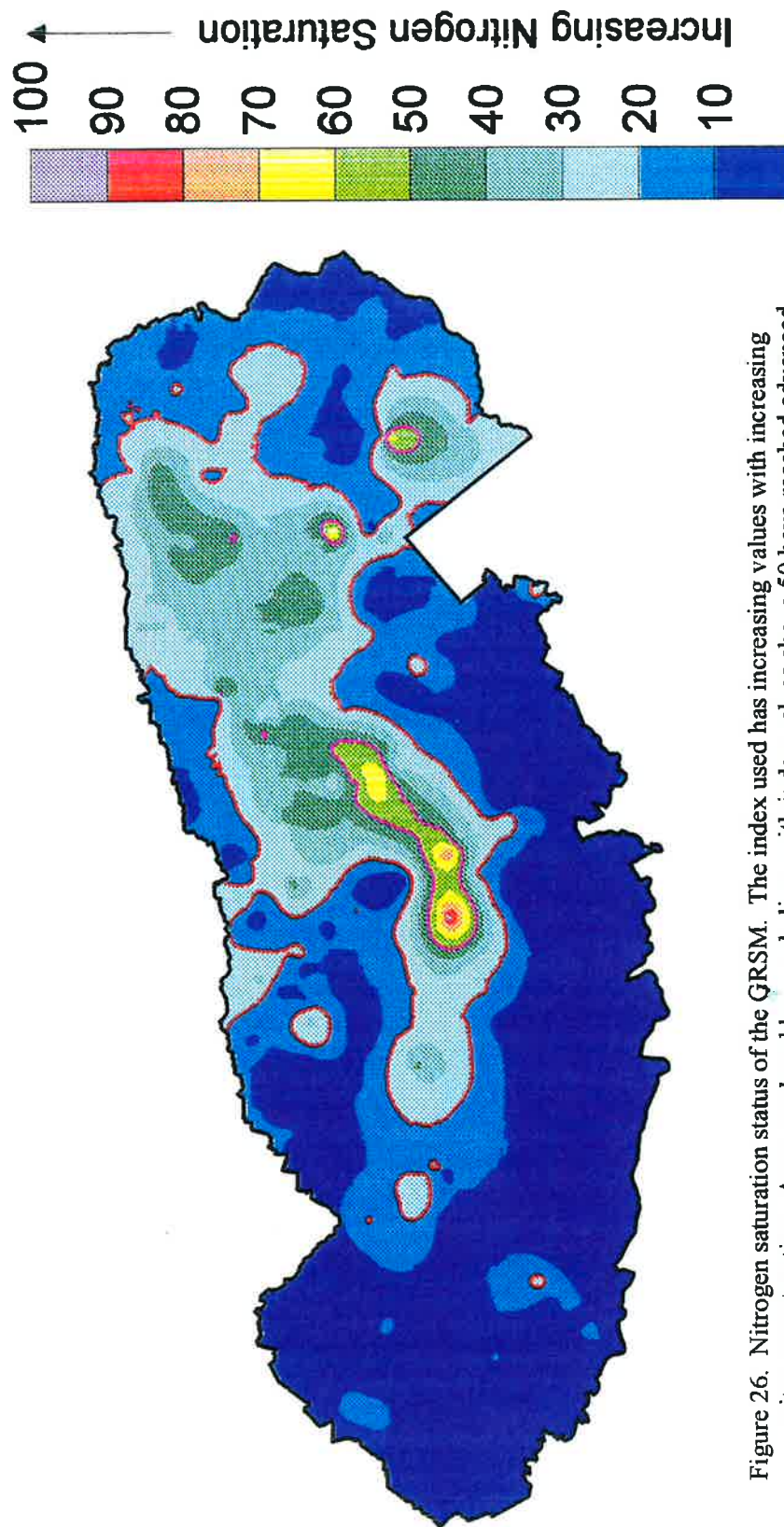


Figure 26. Nitrogen saturation status of the GRSM. The index used has increasing values with increasing nitrogen saturation. Areas enclosed by purple lines with index values above 50 have reached advanced stages of nitrogen saturation while areas enclosed in red lines with index values of 20 - 50 are at early stages of nitrogen saturation.

nitrogen saturation.

The area that is already at least at Stage 2 of nitrogen saturation appears to occur primarily around Clingmans Dome in the center of the GRSM with some smaller areas in the east affected as well. A wider area at Stage 1 to Stage 2 of nitrogen saturation occurs primarily in the eastern half of the GRSM at higher elevations. Much of the western part of the Park and lower elevation areas appear to be less impacted by nitrogen leaching to streams. The areas that are currently at (NSI > 50) or approaching stage 2 of nitrogen saturation (NSI 40-50) occur primarily in the spruce-fir forest zone of the GRSM. The lower degree of nitrogen saturation that apparently exists in the eastern part of the GRSM may be the result of fir regeneration in the wake of the devastating invasion of the balsam woolly adelgid. Regeneration is apparently proceeding from east to west across the Park (Niki Nicholas, personal communication). Higher nitrogen uptake rates from the regenerating fir may be responsible for decreasing the leaching rate of nitrogen to streams in the east. In addition to this interesting possibility, it is also noteworthy that the impact of nitrogen saturation is not restricted to the spruce-fir zone but extends into northern hardwood and other forest types as well. In fact, the spatial pattern of nitrogen saturation is more similar to the pattern of human disturbance (including logging in the GRSM) (Pyle, 1988) than vegetation cover (McKenzie, 1993). This would suggest that forest stand age is a more important factor than forest type in regulating the nitrogen saturation status of the GRSM.

Park Wide Water Quality Concerns

The apparent advancement of nitrogen saturation across the GRSM is grounds for concern about stream acidification for the entire Park. These concerns are warranted based on the krigged maps of average ANC across the park (Figure 27). ANC reflects the susceptibility of streams to acidification during both short-term storm events and from long-term exposure to acidifying pollutants (Table 5). Note that surface waters are considered acidic when ANC

Table 5. A Standard Used to Evaluate Sensitivity of Surface Waters to Acidification Based on ANC Values.

ANC Range	Acidification Sensitivity Class
< 200 μeqL^{-1}	Sensitive
< 100 μeqL^{-1}	Moderately Sensitive
< 50 μeqL^{-1}	Extremely Sensitive
< 0 μeqL^{-1}	Acidic

falls below 0 μeqL^{-1} rather than when pH falls below a certain point. Analysis of the krigged map produced from minimum ANC for each sampling site revealed that over 95% of the GRSM area has streams with ANC less than 100 μeqL^{-1} (Table 6). Even when maximum ANC values

Table 6. Proportion of Area and Proportion of Sites with Low ANC Values.

ANC Range	< 0 μeqL^{-1}	< 50 μeqL^{-1}	< 100 μeqL^{-1}
Proportion of Area (Min ANC)	8.9%	71.9%	97.5%
Proportion of Area (Avg. ANC)	0.7%	21.5%	73.0%
Proportion of Area (Max ANC)	0.6%	20.5%	65.9%
Proportion of Samples	8.6%	58.0%	90.4%

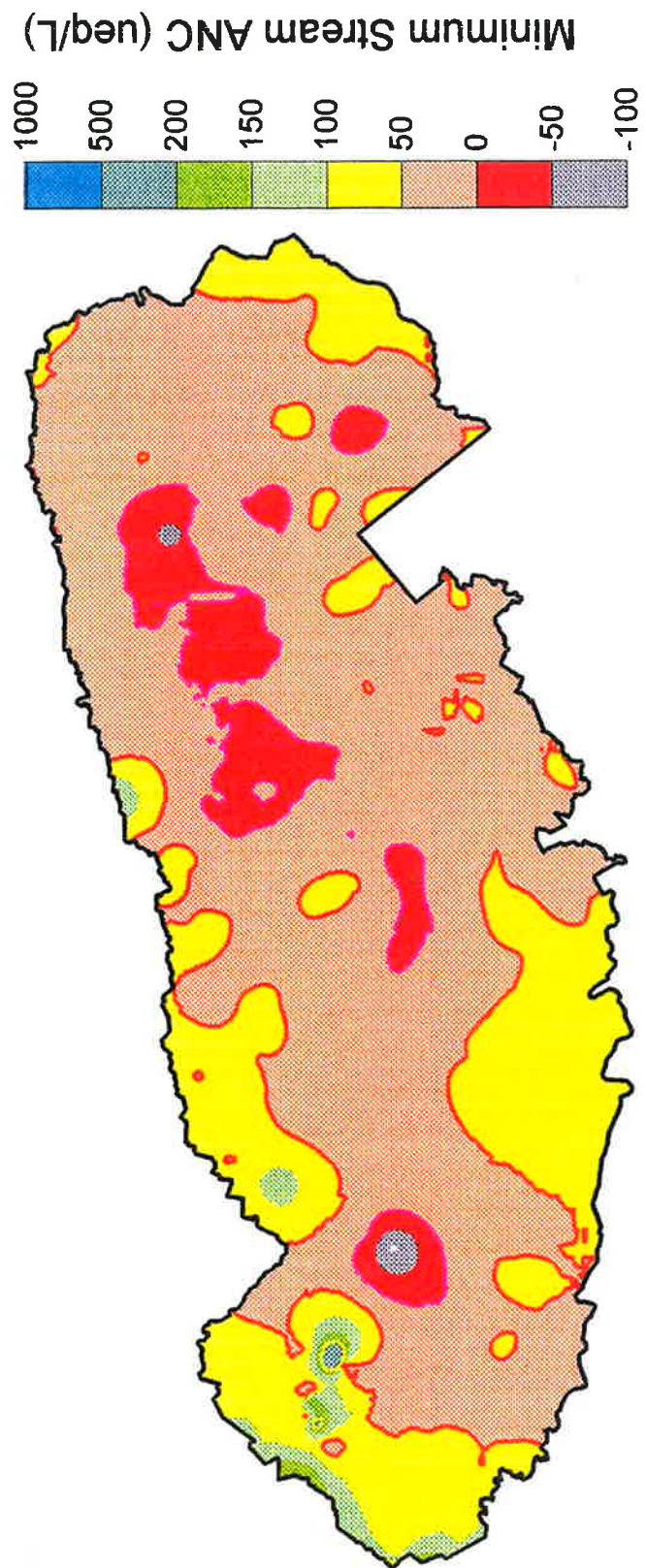


Figure 27. Variation of minimum stream Acid Neutralizing Capacity (ANC) across the GRSM. Areas enclosed in purple lines have ANC less than 0 ueq/L and are acidic. Areas enclosed in red lines have ANC of 0 - 50 ueq/L and are considered extremely sensitive to acidification. The only areas not considered sensitive to acidification are in the western part of the GRSM.

are considered, nearly two thirds of the park area is considered at least moderately sensitive to acidification with ANC less than $100 \mu\text{eqL}^{-1}$. An examination of average conditions shows that sensitivity is greatest along the main ridge that runs through the center of the park with conditions on the east worse than on the west (Figure 27). The streams that are currently acidic on average include the area around Newfound Gap to Mt. LeConte and include the upper portions of Beech Flats Prong, Walker Camp Prong, and Alum Cave Creek (Figure 27). The acidic condition at all these sites are at least partly attributable to the release of sulfuric acid by the weathering of Anakeesta Formation bedrock exposed through landslides (*cf.* Cook *et al.*, 1995). Also acidic on average is Ramsay Prong which drains a portion of Mt. Guyot in the east (Figure 27).

Although ANC is the true indicator of the sensitivity of a stream to acidification, pH is the principle variable that reflects the influence of water quality on the ecology of an aquatic ecosystem. The average pH of streams in the GRSM is 6.23, however, the range of observed values is high (Figure 28). The highest and lowest pH values observed since 1993 occurred in the Abrams Creek system with a minimum pH of 4.03 at the headwaters of Mill Creek at Russell Field Shelter and a maximum of pH 8.24 in Abrams Creek near the confluence of Mill Creek. An examination of the distribution of stream pH measurements clearly shows that many samples have had pH well below 6.0 (Figure 28). Part of the reason why the average pH is so high is that there are a large number of sites in the larger streams at low elevations where most of the earlier studies of water quality in the GRSM chose to establish sites. If more of the smaller streams in the GRSM were sampled, the average pH would probably be lower.

The spatial pattern of minimum stream pH (Figure 29) generally follows that for ANC (Figure 27) and nitrogen saturation (Figure 26) though some of the lowest pHs occur in the western part of the GRSM in Mill Creek. Under worst case conditions, about 30% of the Park

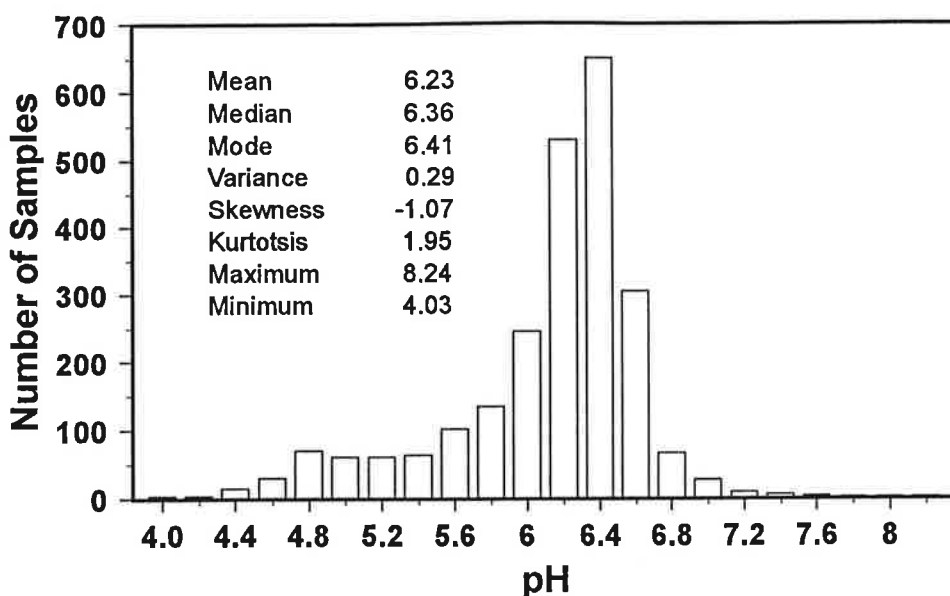


Figure 28. Distribution of Stream pH Observations from Across the GRSM Between October 1993 and May 1996.

area has pH less than 6.0 (Table 7). The spatial pattern of low pH along the main ridge in the central and eastern portion of the GRSM clearly demonstrate the effect of elevation on pH. The influence of limestone dissolution in the western part of the GRSM is also apparent although several streams have relatively high pH near the Park boundary.

Table 7. Proportion of Area and Proportion of Sites with Low pH Values.

	< 5.0	5.0 - 5.5	5.5 - 6.0
Proportion of Area (Min pH)	2.0%	11.2%	30.4%
Proportion of Area (Avg. pH)	0.42%	4.1%	16.5%
Proportion of Area (Max pH)	0.09%	1.2%	7.2%
Proportion of Samples	5.3%	10.6%	21.6%

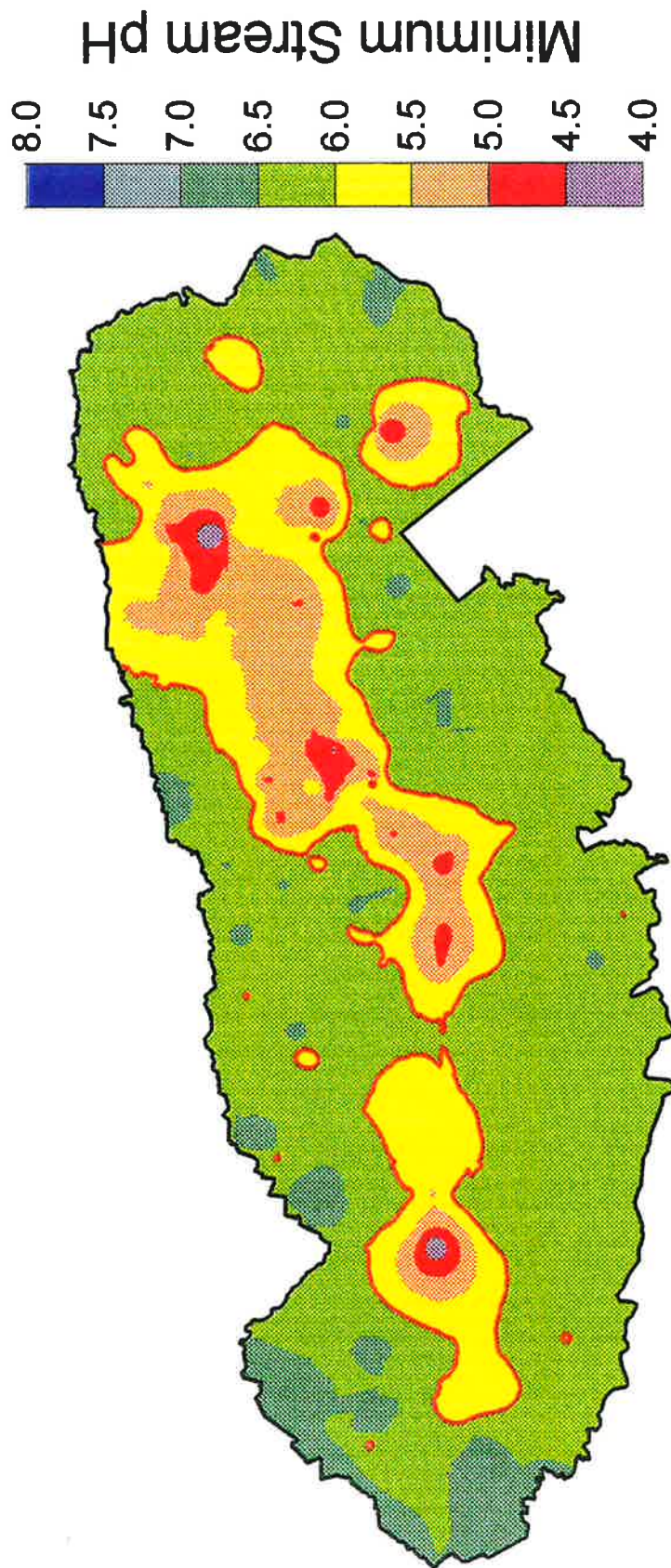


Figure 29. Variation in minimum stream pH across the GRSM. The red line encloses areas with pH less than 6.0.

A basic analysis of the water chemistry data for the entire Park reveals little about the mechanisms underlying the low pH and sensitivity of the streams to acidification other than the occurrence of nitrate in the majority of samples (Table 8). There is a tremendous range of values for all of the chemistry measures as reflected in the high coefficients of variation [CV = (standard deviation / mean) · 100%]. Only pH has a low CV value because it is on a logarithmic scale. One goal for the next section of the report is to identify some of the sources of spatial and temporal variation that exist for the key water quality variables.

Table 8. Summary Statistics for Water Quality Parameters from October 1993 to August 1996. Ion concentrations and ANC are in μeqL^{-1} while conductivity (Cond.) is in $\mu\text{S}\cdot\text{cm}^{-1}$.

Measure	Min	25 th Percentile	Median	Mean	75 th Percentile	Max	CV (%)	N
pH	4.03	6.20	6.36	6.23	6.53	8.24	8.6	3039
ANC	-113.1	20.28	44.04	64.52	68.67	1526	191	3037
Cond.	1.35	11.63	14.57	17.33	18.38	161.1	72.5	3072
Cl ⁻	2.12	11.51	13.49	15.19	16.54	67.70	43.0	2994
NO ₃ ⁻	0	5.85	16.05	19.38	29.18	100.6	86.8	2993
SO ₄ ²⁻	4.36	20.83	34.28	40.90	51.71	511.5	83.5	2988
Na ⁺	5.07	25.86	33.04	35.44	42.67	126.1	40.6	2978
NH ₄ ⁺	0	0	0	0.24	0	32.27	550	2979
K ⁺	0	7.204	9.821	10.47	12.55	77.93	52.5	2979
Mg ²⁺	2.34	17.73	23.10	31.85	34.04	524.5	98.2	2979
Ca ²⁺	7.58	43.73	56.91	77.09	75.79	2218	140	2968

Watershed Characteristics

The Park-wide patterns of stream acidification can be examined more closely by focusing on characteristics of individual stream systems such as elevational gradients and patterns of seasonal change in water chemistry. The GRSM has 22 streams that reach at least fourth order at the point where they exit the Park. Bradley Fork is a fourth order stream where it joins the Oconaluftee River within the Park boundaries near Smokemont and is usually included in the list of major stream systems (*cf.* Parker and Pipes, 1990). Several additional watersheds exist within the Park containing lower order stream networks including Bunches Creek whose lower reaches are cutoff from the headwater sections by the Cherokee Indian Reservation boundary (Parker and Pipes, 1990). The 22 major stream systems along with Bradley Fork and Bunches Creek constitute the principle stream systems, or hydrologic units, of interest.

Classification Criteria for Water Quality Districts

Of the 24 principle stream systems in the GRSM, all but the West Prong of the Little River are sampled at 5 or more sites along the elevational gradient (the West Prong is one of several areas reserved for testing water quality models). Classification of stream systems into categories was accomplished by examining maximum and minimum values across the elevational gradient for six chemical criteria (Table 9). Water chemistry data were cross referenced with Geographic Information System (GIS) data on catchment surficial geology, vegetation type, and disturbance history to establish biogeochemical mechanisms that can explain the observed patterns of water chemistry for each stream system. The classification system is comprised of five major water quality districts (Flum and Nodvin, 1995), each consisting of stream systems with similar modes of biogeochemical regulation of surface water chemistry (Figure 30). Stream systems with ANC values above $100 \mu\text{eq}\cdot\text{L}^{-1}$ at some point along the elevational gradient are probably influenced by

Table 9. Criteria Used to Classify Stream Systems into Water Quality Districts. Stream system numbers refer to Figure 30.

Stream System ^a	Stream System Number	District	# Sites	Min pH	Min ANC $\mu\text{eq/L}$	Max ANC $\mu\text{eq/L}$	Max SO_4^{2-} $\mu\text{eq/L}$	Max NO_3^- $\mu\text{eq/L}$	Low Elevation Max NO_3^-
Abrams Creek	10	West	17	5.72	18.43	749.1	64.71	30.00	4.63
Parsons Branch	14	West	5	6.40	43.81	138.2	45.90	4.01	0.00
M. Pr. Little Pigeon	3	Ana	22	4.45	-28.39	65.06	66.76	69.35	29.96
LeConte Creek /Roaring Fork	4	Ana	15	4.86	-11.24	75.30	79.74	43.92	19.13
W. Pr. Little Pigeon	5	Ana	21	4.64	-20.65	82.55	121.3	61.42	32.20
Cosby Creek	1	EU	5	5.51	-0.98	30.82	57.96	36.81	31.65
Indian Camp Creek	2	EU	6	5.55	0.04	49.66	67.78	80.70	17.72
Raven Fork /Straight Fork	24-25	EU	11	4.58	-25.05	62.19	23.55	86.04	17.97
Little River	6	WC	5	4.88	-0.72	53.54	51.13	100.6	4.14
Mid. Pr. Little River	7	WC	9	6.22	19.99	39.08	32.76	17.29	10.19
Twentymile Creek	15	WC	5	6.44	40.23	60.07	30.36	8.02	0.00
Eagle Creek	16	WC	15	5.54	0.69	83.44	29.12	21.67	2.72
Hazel Creek	17	WC	8	5.25	9.83	84.12	51.98	87.89	4.27
Forney Creek	19	WC	8	6.11	13.62	77.36	35.44	29.07	3.74
Noland Creek	20	WC	7	5.48	-0.02	72.92	47.72	47.75	3.66
Deep Creek	21	WC	10	6.41	45.81	64.98	16.42	45.56	8.02
Oconaluftee River	22	East	27	5.68	1.63	61.46	51.54	31.22	3.96
Cataloochee Cr.	27	East	25	4.71	-20.30	83.77	53.84	73.05	7.99
Big Creek	28	East	16	6.20	23.20	49.07	45.41	28.79	2.30

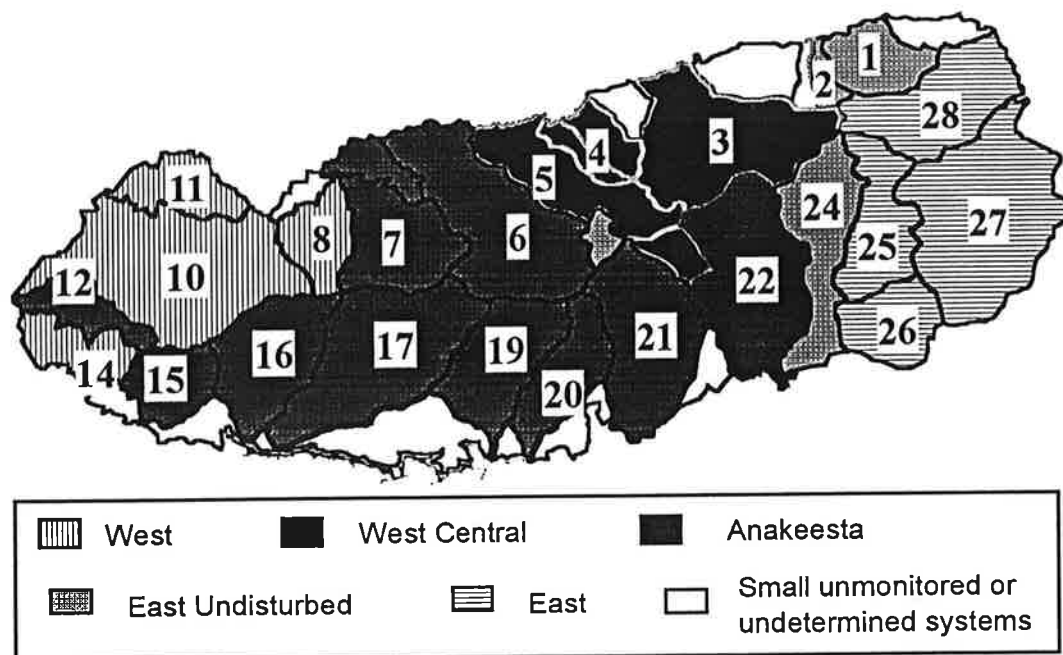


Figure 30. Water Quality Districts of the Great Smoky Mountains (modified from Flum and Nodvin, 1995). Individual stream systems are assigned numbers as indicated.

limestone weathering and comprise the West District (Figure 30). The stream systems in the West district are (stream system number in Figure 30 shown number in parenthesis); Abrams Creek (10) (data in Figure 31), West Prong Little River (8), Hesse Creek (11), , Shop and Tabcat Creeks, and Parsons Branch(14). Streams systems with minimum pH values below 5.0, minimum ANC below 0, and maximum sulfate concentrations greater than about $60 \mu\text{eqL}^{-1}$ are likely influenced by Anakeesta weathering and comprise the Anakeesta District. The Anakeesta District includes the Middle Prong Little Pigeon River (stream system 3 in Figure 30) (data in Figure 32), Roaring Fork and LeConte Creek (4), West Prong Little Pigeon River (5), and Beech Flats Prong above its confluence with Kephart Prong to form the Oconaluftee River (22) where Anakeesta used for road fill has influenced the stream.

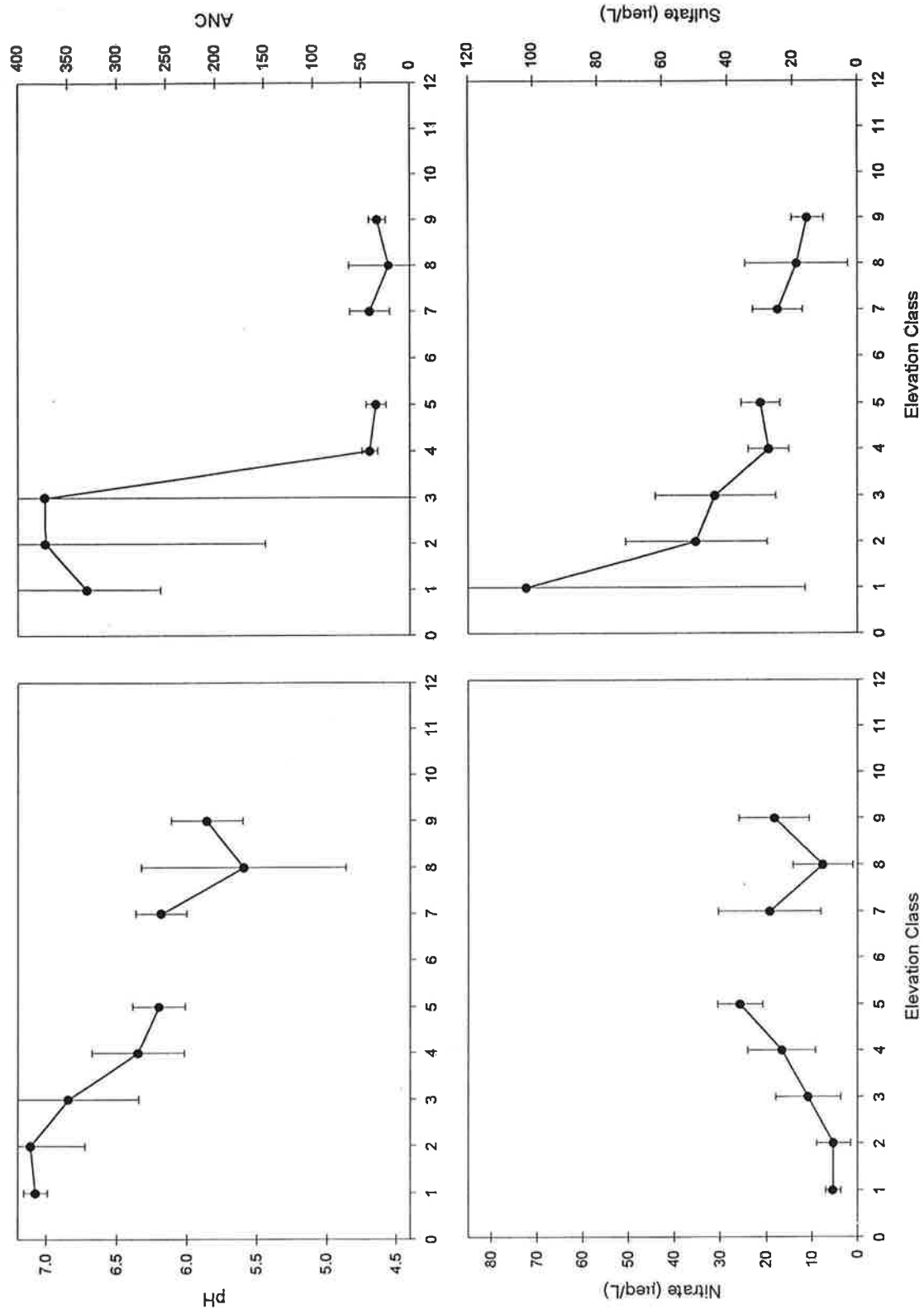


Figure 31. Elevational gradients in selected water chemistry variables for Abrams Creek. Elevational classes are in 500 foot intervals with 1 being less than 1000 feet and 12 being greater than 6000 feet.

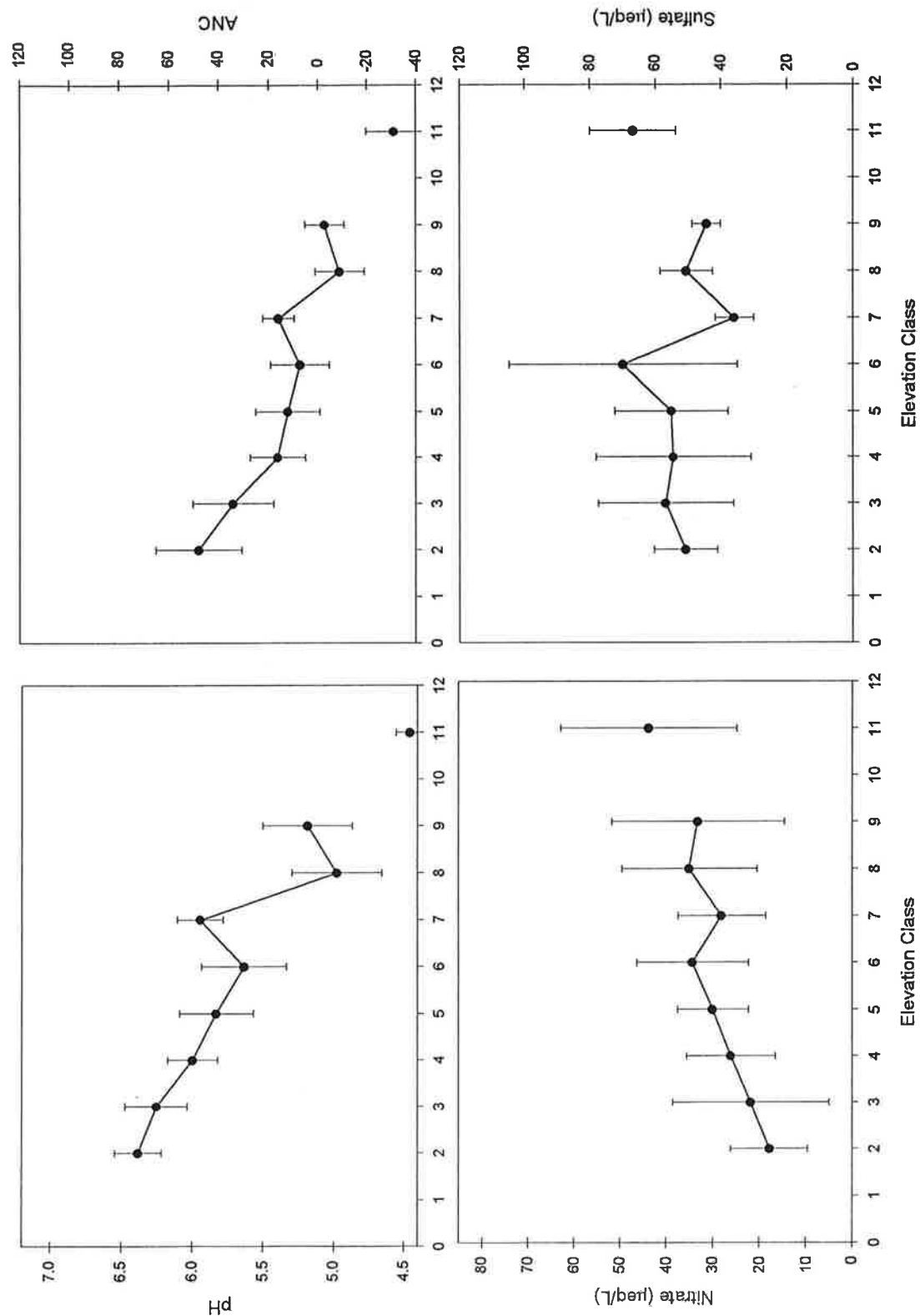


Figure 32. Elevational gradients in selected water chemistry variables for the Middle Prong of the Little Pigeon. Elevational classes are in 500 foot intervals with 1 being less than 1000 feet and 12 being greater than 6000 feet.

Elevational gradients in nitrate concentrations are a key factor distinguishing the remaining water quality districts. Nitrate concentrations in all systems were at least occasionally greater than 50 $\mu\text{eq/L}$ at elevations above 1500m (5000 ft) where old growth spruce-fir forests predominate. Stream systems in catchments with primarily old growth forests exhibited relatively high nitrate levels even at lower elevations. Stream systems in the Anakeesta district showed this pattern due to their predominantly old growth forests. The other stream systems with relatively high nitrate concentrations at lower elevations were classified as the East Undisturbed District (Figure 30) and consisted of Cosby Creek (stream system 1 in Figure 30) (data in Figure 33), Indian Camp Creek (2) (data in Figure 34), Raven Fork (24), and Road Prong above its confluence with the West Prong Little Pigeon River which is otherwise included in the Anakeesta district (Figure 30).

The remaining stream systems drain catchments with predominantly second growth forests and exhibited lower nitrate levels at low elevations. These stream systems were assigned to either the West Central District or the East District. The West Central District contained a large proportion of the stream systems including East Prong Little River (stream system 6 in Figure 30) (data in Figure 35), Middle Prong Little River (7) (data in Figure 36), Panther Creek (12), Twentymile Creek (15), Eagle Creek (16), Hazel Creek (17) (data in Figure 37), Forney Creek (19), Noland Creek (20), Deep Creek (21), and the Oconaluftee River and Bradley Fork (22). The East District consisted of Straight Fork (stream system 25 in Figure 30), Bunches Creek (26), Cataloochee Creek (27) (data in Figure 38), and Big Creek (28). The main difference between these districts was due to the difference in elevational gradient; the West Central streams dropped to between 320 m and 580 m in elevation where they exited the Park while those in the East

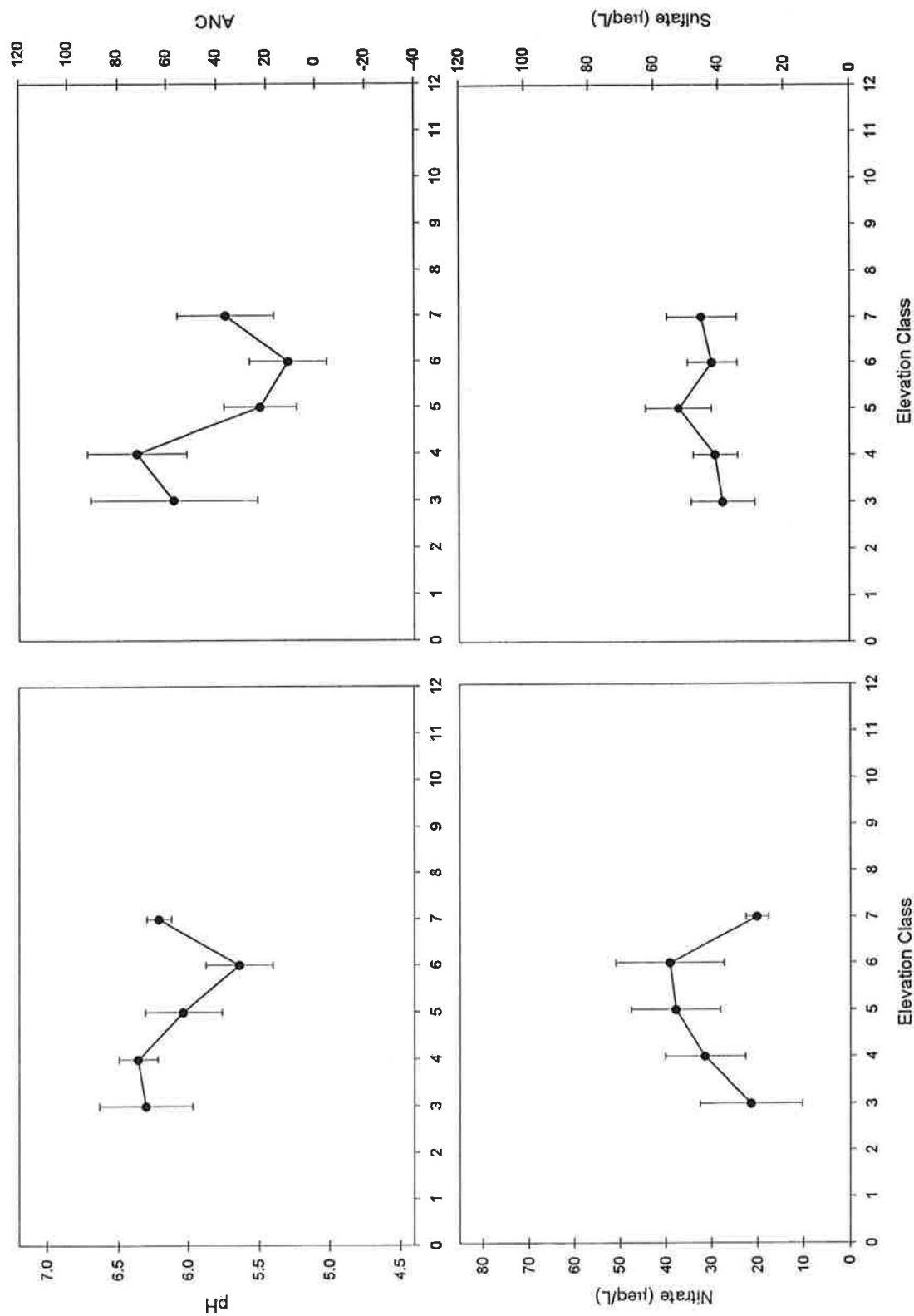


Figure 33. Elevational gradients in selected water chemistry variables for Cosby Creek. Elevational classes are in 500 foot intervals with 1 being less than 1000 feet and 12 being greater than 6000 feet.

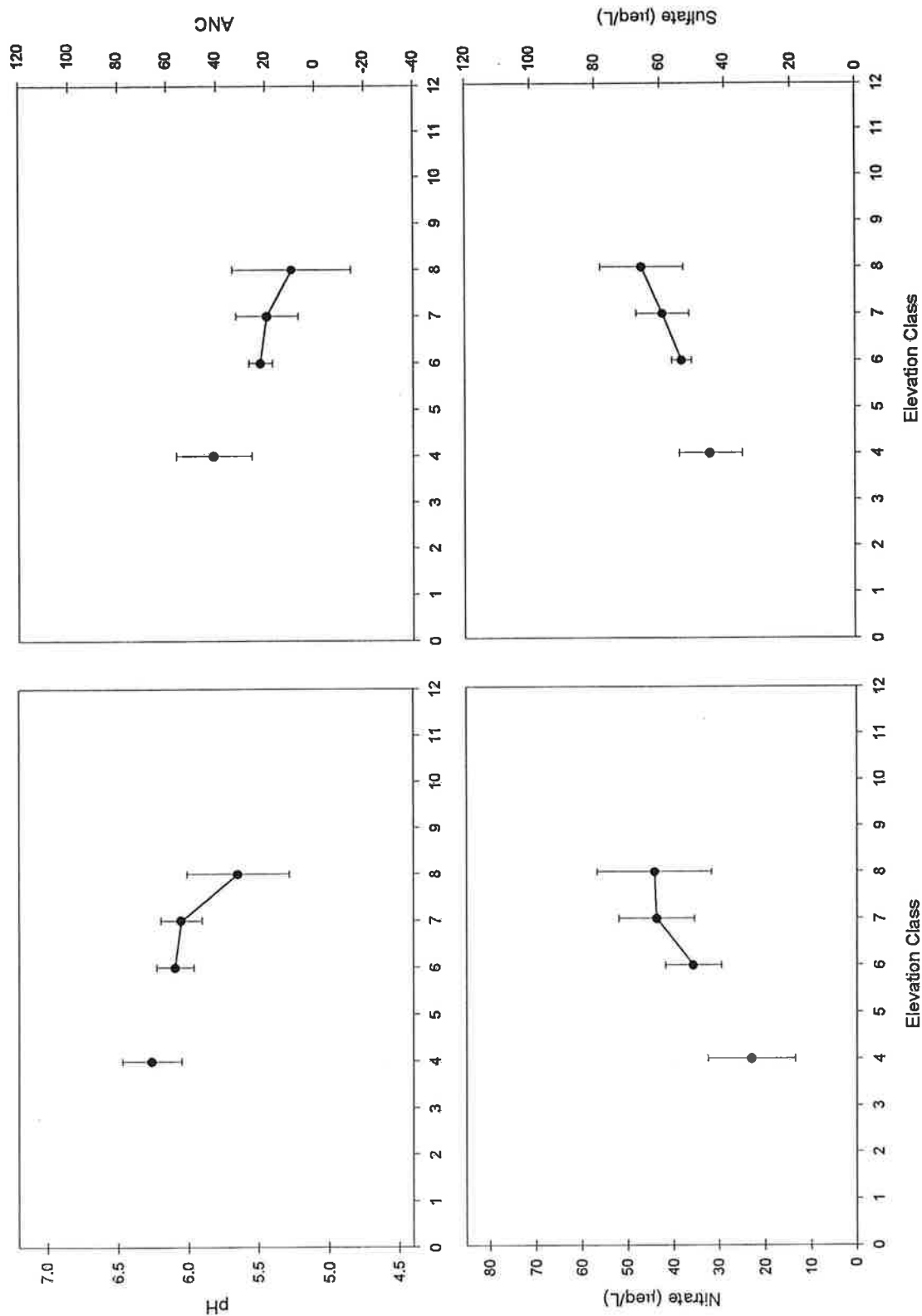


Figure 34. Elevational gradients in selected water chemistry variables for Indian Camp Creek. Elevational classes are in 500 foot intervals with 1 being less than 1000 feet and 12 being greater than 6000 feet.

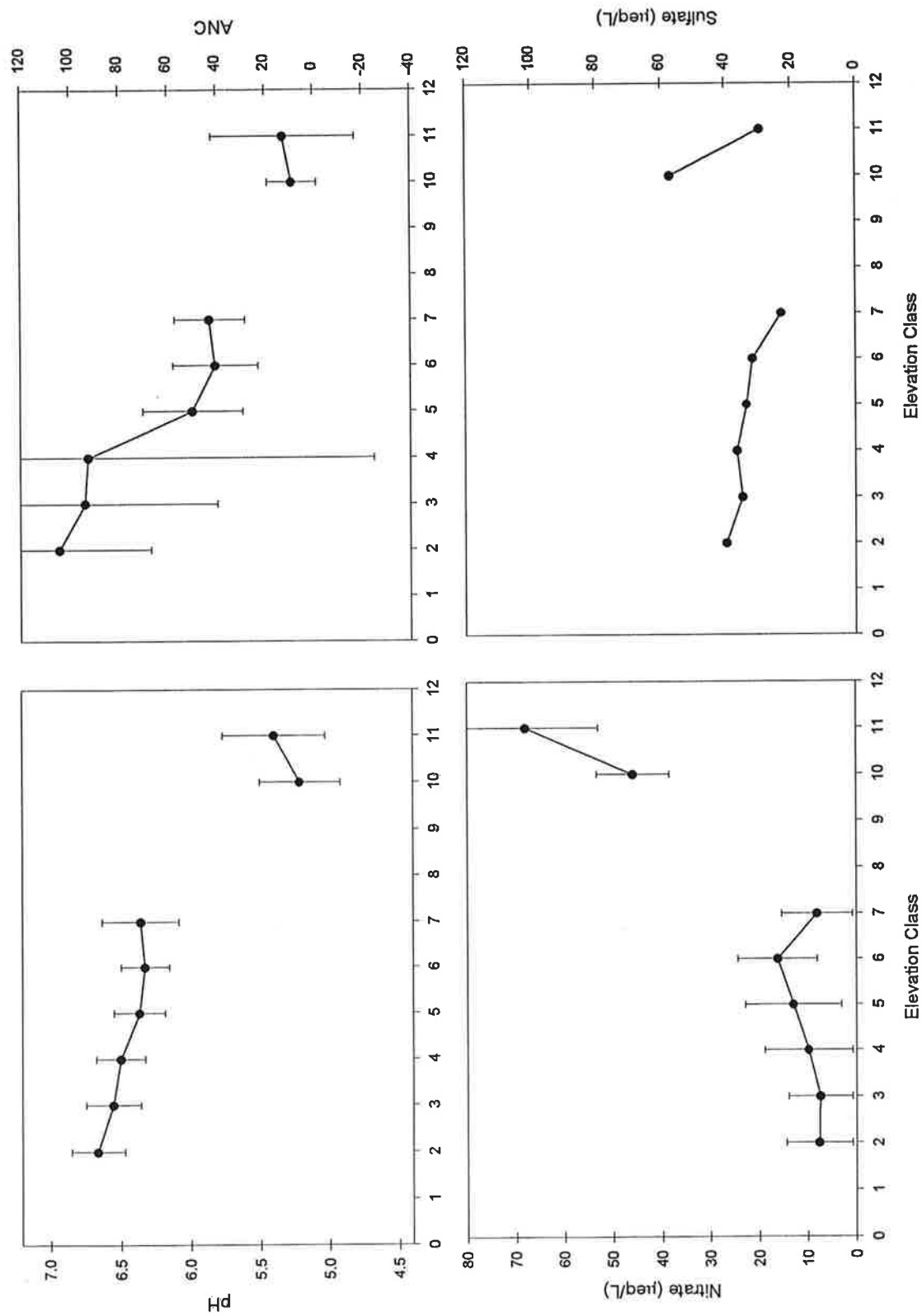


Figure 35. Elevational gradients in selected water chemistry variables for East Prong Little River. Elevational classes are in 500 foot intervals with 1 being less than 1000 feet and 12 being greater than 6000 feet.

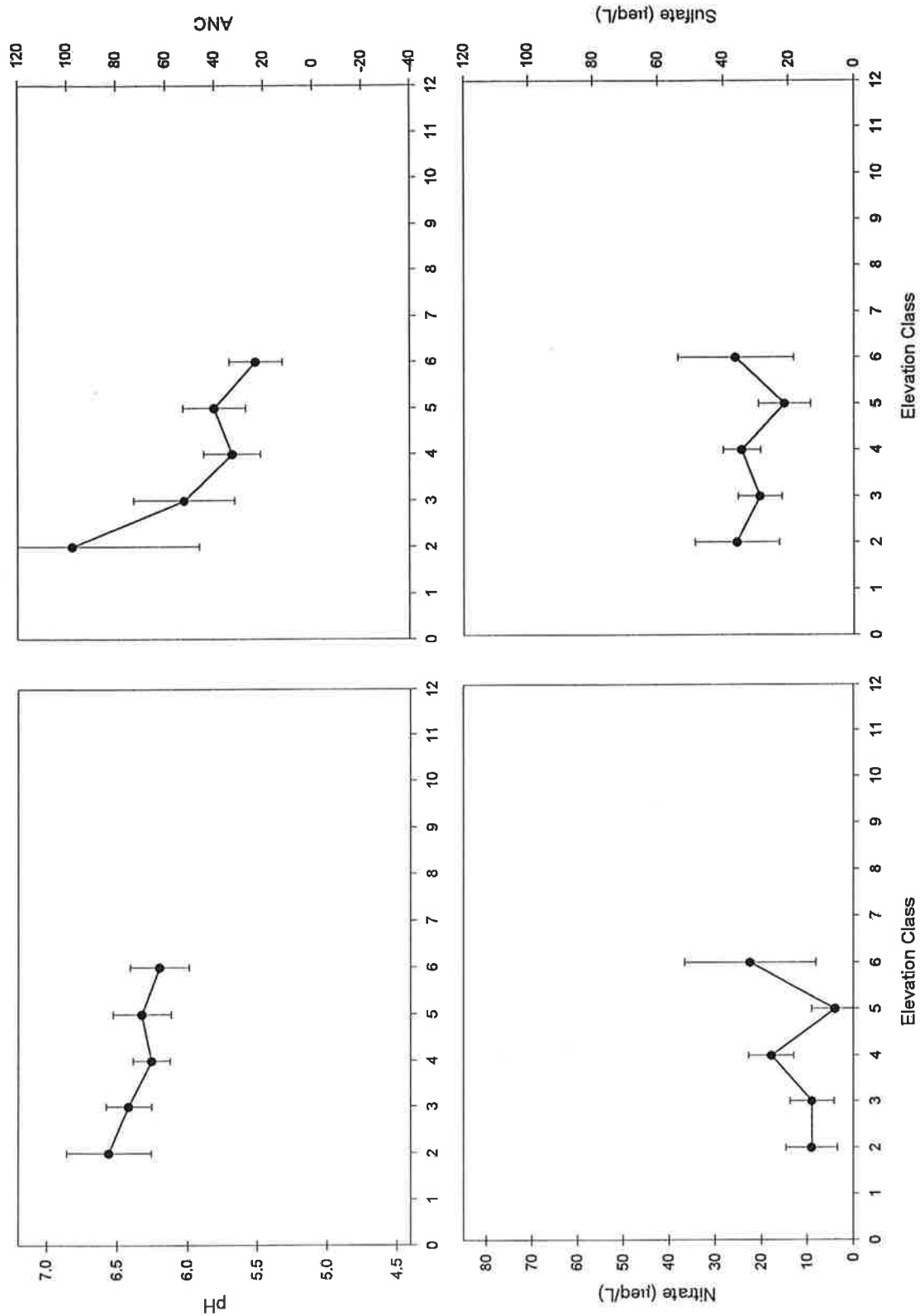


Figure 36. Elevational gradients in selected water chemistry variables for the Middle Prong of Little River. Elevational classes are in 500 foot intervals with 1 being less than 1000 feet and 12 being greater than 6000 feet.

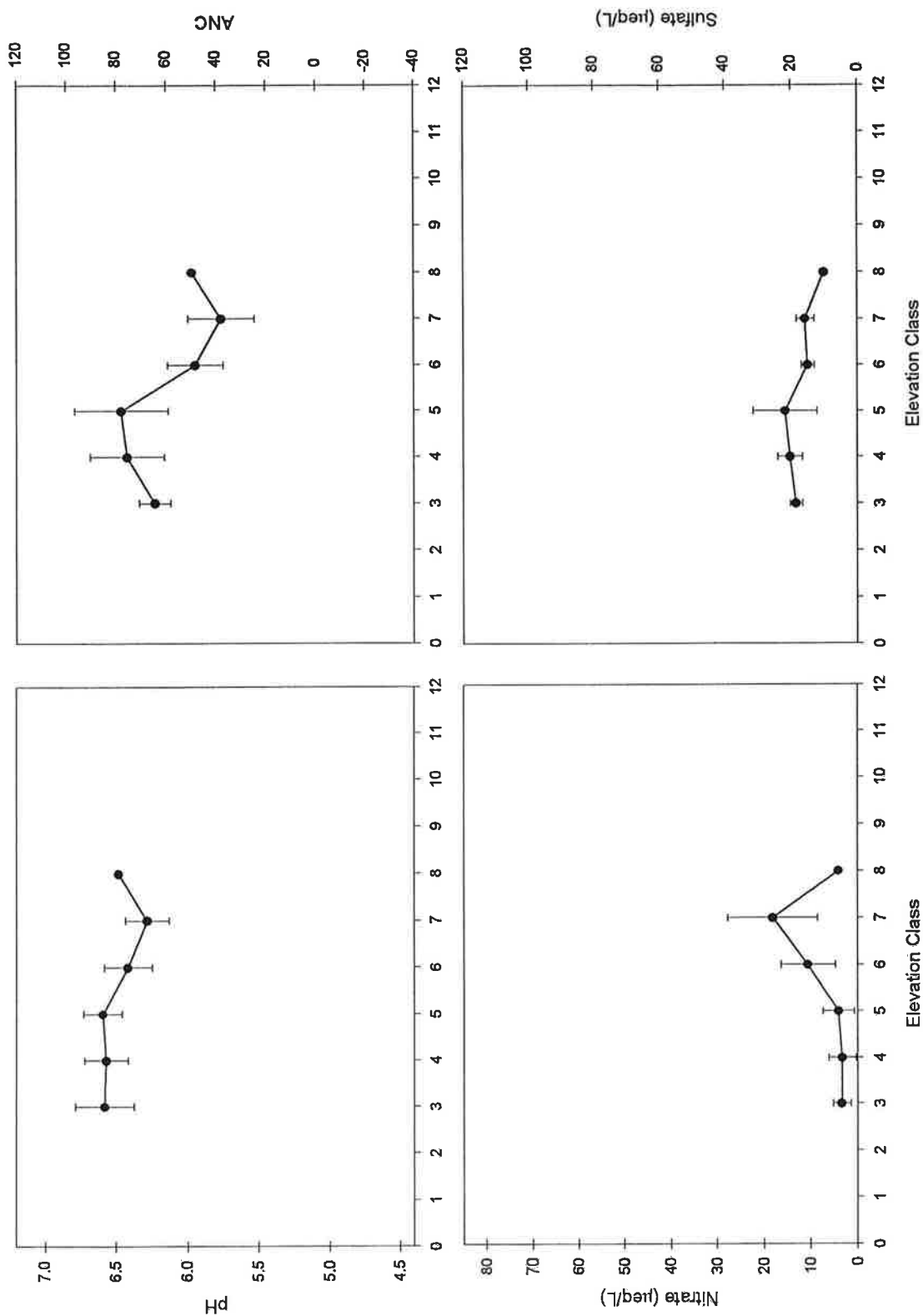


Figure 37. Elevational gradients in selected water chemistry variables for Hazel Creek. Elevational classes are in 500 foot intervals with 1 being less than 1000 feet and 12 being greater than 6000 feet.

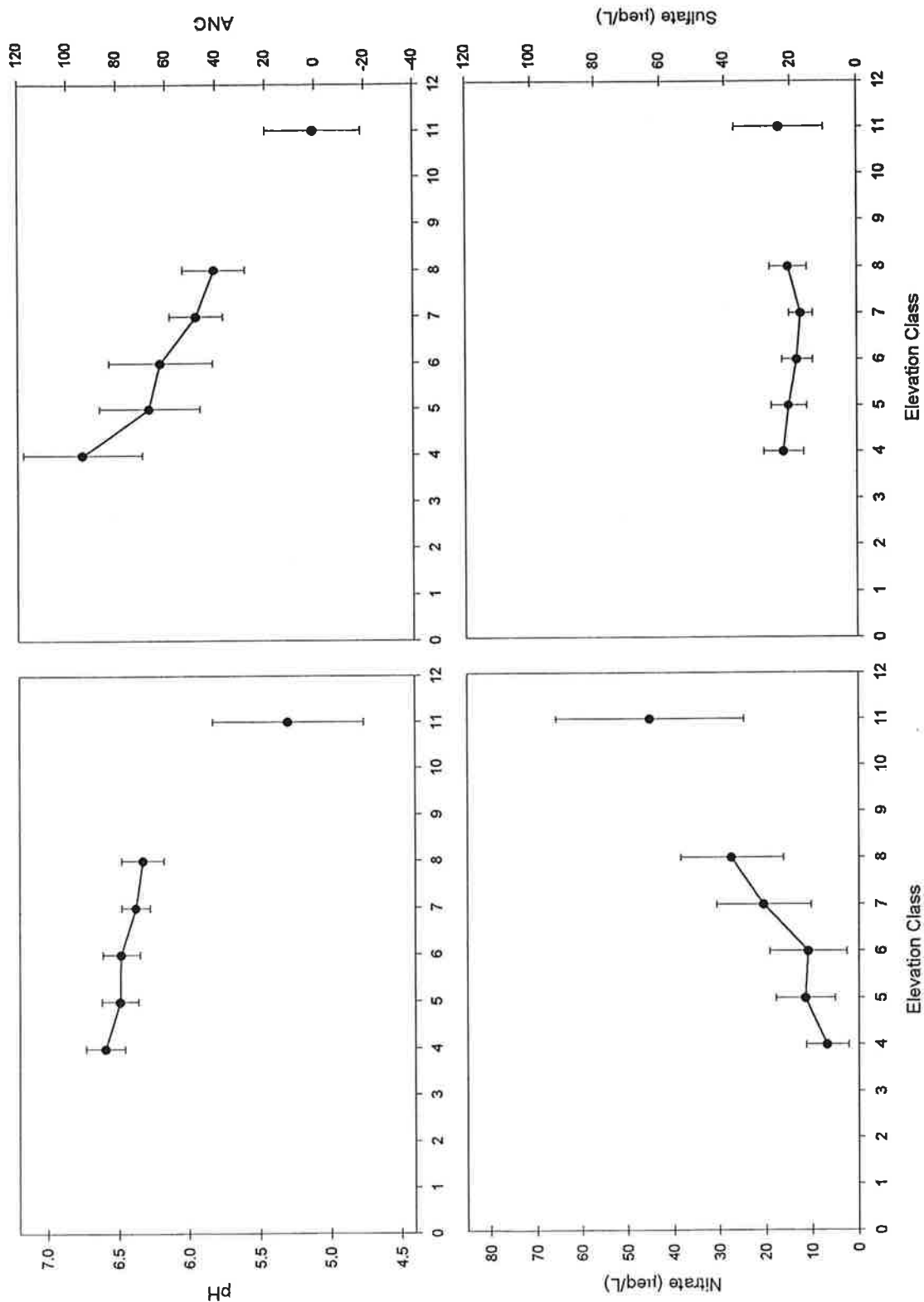


Figure 38. Elevational gradients in selected water chemistry variables for Cataloochee Creek. Elevational classes are in 500 foot intervals with 1 being less than 1000 feet and 12 being greater than 6000 feet.

dropped to between 470 m and 780 m. The lower elevational gradients in the East District led to slightly different patterns of water chemistry change than the streams in the West Central District.

Elevational Gradients in Water Quality Districts

Within each water quality district, means of measured parameters within successive 500 ft. (150m) elevational bands were evaluated against the entire elevational gradient (Figure 39). An overall pattern of decreasing pH (Figure 39A) and ANC (Figure 39B) with increasing elevation was apparent in all districts. Streams in the Anakeesta District had the lowest pH and ANC

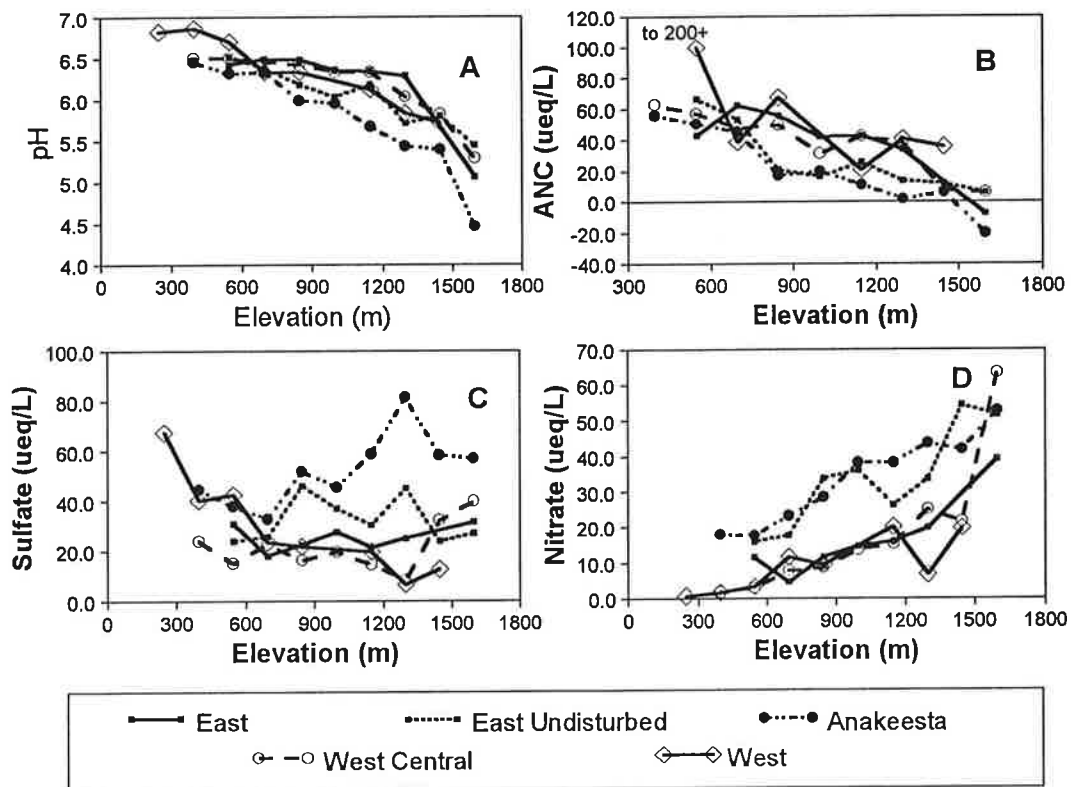


Figure 39. Elevational Gradients for Select Water Quality Variables Averaged by Water Quality District for the March 1994 Survey. Shown are values from stream pH (A), ANC (B), sulfate (C), and nitrate (D). After Flum and Nodvin, 1995).

values and those in the West District had the highest. Given the relatively high sulfate loading in the GRSM, sulfate concentrations in the streams were remarkably low except for those within the Anakeesta District at high elevation due to pyrite oxidation and in the West at low elevations due to dissolution of limestone and dolomite based rock (Figure 39C). Sulfate concentrations varied little over the elevational gradient for the remaining districts. Soil sulfate adsorption is most likely responsible for the low sulfate concentrations as previously discussed. Nitrate levels also declined with decreasing elevation, but the rate of decline was much lower in systems with old growth forests including the East Undisturbed and Anakeesta districts (Figure 39D). This has important implications for the future water quality of the GRSM, since areas with second growth forests are likely to become increasingly similar to those with old growth forests as they mature.

Implications for Aquatic Ecosystems

The consequences of low pH on stream ecosystems has been fairly well studied (Table 8).

Ecological effects begin to take effect at pH below about 6.5. Since most of the streams in the

Table 8. Proposed Ecological Consequences of Low Surface Water pH with Particular Relevance to Streams. After Baker *et al.*, 1990 and Herlihy *et al.*, 1996.

pH Range	Biological Effects
6.5 - 6.0	Loss of Sensitive Benthic Invertebrates
6.0 - 5.5	Loss of Acid-Sensitive Fish Reduced Reproduction in Sensitive Species Increased in Green Algae in Periphyton
5.5 - 5.0	Loss of Most Fish Species Green Algae Dominate Periphyton Loss of most Mayflies, Stoneflies, Caddisflies, and Shellfish Reduced Biomass and Productivity
less than 5.0	Loss of All Fish Decreased Nutrient Cycling Rates Decline in Periphyton Species Richness Decline in Benthic Invertebrates Reproductive Failure of Acid-Sensitive Amphibians

GRSM have a pH below 6.5 it is likely that they have always been at least slightly acidic. The species richness and diversity of both benthic invertebrates and fish are relatively high in the larger streams of the Park that occur at lower elevations (Steve Moore and Chuck Parker, personal communications). The influence of stream acidification is apparently nonexistent at least for the larger streams in the GRSM. Once the pH of a streams drops below 6.0, the ecological consequences are believed to become more apparent (*e.g.* Sutcliffe and Hildrew, 1989; David Lenat, personal communication).

The effect of pH on aquatic organisms is very complex because pH influences a number of other water quality variables (Stumm and Morgan, 1981; Drever, 1986). Among the variables influenced by pH are the solubility of potentially toxic materials, particularly aluminum. Concentrations of toxic forms of aluminum are at a minimum at pH 5.5 and increase as pH decreases (Stumm and Morgan, 1981). Since the average minimum pH for most sampling sites is greater than 5.5 (Figure 35), chronic aluminum toxicity is not a relevant issue for most of the GRSM streams. For those streams where pH does fall below 5.5, the toxicity of aluminum is influenced by the concentration of other chemicals, especially calcium (e.g. Brown and Sadler, 1989).

One potentially useful measure for assessing the effects of stream acidification is the ratio of calcium ion concentration to hydrogen ion concentration. Fisheries in European lakes have been found to be affected most when the $\text{Ca}^{2+}:\text{H}^{+}$ ratio is below about 3:1 to 4:1 (Mason, 1989). Such low values occur at various locations around the GRSM (Table 9). Many of the sites with low calcium to hydrogen ion ratios are springs or small streamlets at high elevation that would not harbor fish regardless of water quality. Another stream where the impacts of the Anakeesta Formation are well known is Beech Flats Prong, which has a calcium to hydrogen ion ratio of 3.24. In the late 1960s and early 1970s, the impact of road construction on U.S. Highway 441 through the Anakeesta Formation near Newfound Gap became evident in Beech Flats Prong. Oxidation of exposed rocks from the Anakeesta formation unexpectedly acidified this headwater stream on the North Carolina side of the GRSM (Huckabee *et al.*, 1975). The impact on the biota has been devastating (Huckabee *et al.*, 1975). The stream below the road cut had a measured pH of 4.9 in 1990 (Kucken *et al.*, 1992), and the effects are influencing not only aquatic organisms, but terrestrial organisms (through indirect effects) as well (Huckabee *et al.*, 1994).

Table 9. Thirty Sites with the Lowest Values of Minimum Calcium to Hydrogen Ratio. Ratios. Values less than 3 and possibly 4 are often indicative of conditions that are not suitable for fish (Mason, 1989).

Site Number	Site Description	Ca ²⁺ : H ⁺
183	Spring to Mill Creek at Russell Field Shelter	0.13
113	Ramsay Prong on AT near Mt. Guyot	0.53
112	Buck Fork on AT near Tricorner Knob	0.55
79	Alum Cave Creek above Styx Branch	1.06
92	Trib. to Ramsay Prong just below Ramsay Falls	1.08
360	Walker Camp Prong 1 mile above last bridge on US 441	1.12
290	Bear Branch at campsite 42 (Cataloochee Creek)	1.13
74	Walker Camp Prong above Alum Cave Creek	1.18
236	Trib. to Walker Camp Prong near Mt. Ambler	1.22
237	Walker Camp Prong at last bridge on US 441	1.82
126	McGee Springs (Raven Fork)	1.98
80	Trib. to Walker Camp Prong below Newfound Gap	2.03
219	Double Springs Gap Shelter (NC side)	2.13
93	Ramsay Prong below falls	2.13
242	Spring at Mt. Collins Shelter (Road Prong)	2.27
361	Spring near Clingmans Dome (Forney Creek)	2.68
218	Spring at Silers Bald Shelter	2.72
235	Road Prong at only stream crossing	2.74
75	Alum Cave Creek above Walker Camp Pr	2.74
94	Ramsay Prong above falls	2.81
110	Enloe Creek at Pecks Corner Shelter	3.14
220	Double Springs Gap Shelter (TN side)	3.15
76	Alum Cave Creek at fish site	3.20
252	Beech Flats below roadcut	3.24
90	Ramsay Prong above unnamed trib.	3.57
105	Unnamed trib. to Otter Creek (Indian Camp Cr.)	3.65
53	Surry Fork (Roaring Fork)	3.69
63	LeConte Creek above Rainbow Falls	5.31
104	Copperhead Branch (Indian Camp Cr.)	6.72

Interestingly, some streams where fish do not occur do not appear in Table 9 including Shutts Prong ($\text{Ca}^{2+}:\text{H}^+ = 10.5$) and Cannon Creek ($\text{Ca}^{2+}:\text{H}^+ = 15.2$) near Mt. LeConte. Both of these streams are potentially influenced by sulfur released by the Anakeesta Formation. Both of these streams have ratios above the values obtained for streams known to have fish populations. These examples indicate that the calcium to hydrogen ion ratio may not provide a clear endpoint for predicting the impacts of stream acidification on aquatic organisms. The fact that many of the streams that have low ratio values do not have fish do suggest the ratio is not completely useless, however.

Several streams with low calcium to hydrogen ion ratio do have severely impacted aquatic ecosystems. Most notable of the impacted streams are Walker Camp Prong and Alum Cave Creek where landslides have exposed the Anakeesta formation. Both streams have pH below 5.0 and differences in species composition of periphyton and macroinvertebrates compared to streams with higher pH (Mulholland 1986; Elwood and Mulholland, 1989). Bacterial community composition and rates of litter decomposition are also different in streams with low pH (Mulholland *et al.*, 1987; Palumbo *et al.*, 1987a, 1987b). Reduction of species richness, population abundances, and decomposer activity may reduce the impact of phosphorus limitation in these streams (Mulholland 1986). These types of observations correspond to expectations outlined in Table 8 for effects of low pH. Both Walker Camp Prong and Alum Cave Creek also have low calcium to hydrogen ion ratios.

Thus, although the calcium to hydrogen ion ratio may not be a foolproof index of potentially damaging stream acidification in the GRSM, it may provide at least an early warning for streams requiring some additional monitoring attention. If so, potential future problems may be indicated for several GRSM streams. Stream in potential jeopardy from acidification include

Road Prong in the West Prong Little Pigeon River system, Rough Fork in the Cataloochee system, Raven Fork, several small streams entering Fish Camp Prong in the Little River system, Huggins Creek in the Forney Creek system, Indian Camp Creek, Roaring Fork, and LeConte Creek.

There is already some indication of how much water quality may have to deteriorate before severe impacts such as the loss of all fish species occurs. Two streams in the GRSM have lost all fish populations during this century; Mill Creek in the western part of the GRSM the other is Ramsay Prong in the east (Steve Moore personal communication). A close examination of the map of minimum pH data shows two areas where pH is at least occasionally below 4.5 (Figure 28). These two areas are Mill Creek and Ramsay Prong. A third streams where fish may possibly have been extirpated during this century is Cannon Creek which drain Mt. LeConte and occurs within the low pH and low ANC region in the middle of the GRSM (Figures 28 and 27 respectively). A closer examination of pH from sites in these three streams reveals that low pH need not always occur to have a deleterious effect on fish (Table 10). All three streams have

Table 10. Range of pH for Streams that have Lost all Fish Populations During Historical Times.

Stream	Elevation (m / feet)	Fish	Stream pH		
			Avg.	Max.	Min.
Ramsay Pr.	1981 / 6500	None	4.48	4.75	4.27
Ramsay Pr.	1335 / 4380	None	5.21	6.10	4.70
Cannon Cr.	1036 / 3400	None	5.89	6.34	5.48
Cannon Cr.	732 / 2400	Present	6.00	6.11	5.79
Mill Cr.	1301 / 4270	None	5.26	6.33	4.03
Mill Cr.	521 / 1710	Present	6.81	7.45	6.43

observations where pH was above 6.0 (except Ramsay Prong at the headwaters at 1981m). The minimum pH for all sites where fish were absent were below 5.5. The highest minimum pH where fish were still present in these three streams was 5.79 in Cannon Creek at 732m. This strongly suggests that streams where pH at least occasionally falls below 5.5 may be susceptible to complete loss of fish due to stream acidification. The value of pH 5.5 is at the upper end of range for total fish loss reported in the literature (Table 8).

Sulfate and nitrate levels at sites in the three streams where fish populations have disappeared during historical times are interesting (Table 11). In Ramsay Prong, the nitrate

Table 11. Water Quality Conditions for Streams that have Lost all Fish Populations During Historical Times.

Stream	Elevation (m / feet)	Fish	Min. pH	Max. Sulfate (μ eq/L)	Max. Nitrate (μ eq/L)
Ramsay Pr.	1981 / 6500	None	4.27	87.5	69.4
Ramsay Pr.	1335 / 4380	None	4.70	53.6	47.0
Cannon Cr.	1036 / 3400	None	5.48	204	74.4
Cannon Cr.	732 / 2400	Present	5.79	176	69.4
Mill Cr.	1301 / 4270	None	4.03	58.1	12.4
Mill Cr.	521 / 1710	Present	6.43	77.9	11.9

concentrations are relatively high and indeed the area appears to be at a fairly advanced stage of nitrogen saturation (Figure 26), nevertheless sulfate is the dominant anion. The sulfate levels at the upper site on Ramsay Prong are consistent with mean values of maximum sulfate from streams in the Anakeesta Water Quality District (Figure 30). Although the geology map for the Park does

not indicate any Anakeesta in the Ramsay Prong catchment, there is some in the adjacent catchment of Buck Fork (King *et al.*, 1967). It is possible that the outcrop of Anakeesta in the Buck Fork catchment extends farther around the top of Mt. Guyot to include the headwaters of Ramsay Prong or that groundwater flow paths draining into Ramsay Prong flow through Anakeesta bedrock. In either case, it appears that the acidification of Ramsay Prong during historical times is likely due to a combination of bedrock influences in combination with atmospheric nitrogen pollution. The presence of Anakeesta effects in Ramsay Prong is the principle reason why the main stem of the Middle Prong Little Pigeon River was assigned to the Anakeesta Water Quality District (Figure 21).

The situation in Cannon Creek is even clearer than in Ramsay Prong. With sulfate concentrations well over $150 \mu\text{eq}\cdot\text{L}^{-1}$, the effects of Anakeesta in this stream are obvious (Table 11) in spite of the fact that the geology map of the GRSM show very little Anakeesta in the watershed and then only at the very top (King *et al.*, 1967). Maximum nitrate concentrations are even higher in Cannon Creek than in Ramsay Prong despite having sites on Cannon Creek at considerably lower elevation. The fact that pH is somewhat higher in Cannon Creek than Ramsay Prong is due to higher concentrations of base cations. The presence of relatively high quantities of calcium is why the calcium to hydrogen ion ratio (15.2) for this site is so high. The acidification of Cannon Creek is apparently a combination of Anakeesta weathering and atmospheric nitrogen pollution as nitrate concentrations are also very high (average = $34.9 \mu\text{eq}\cdot\text{L}^{-1}$, maximum = $74.4 \mu\text{eq}\cdot\text{L}^{-1}$). The high nitrate concentrations in Cannon Creek are not surprising as the catchment is predominantly virgin forest.

The acidification of Mill Creek is more difficult to explain. Although the sulfate concentration at the headwater site is considerably above the Park average of about $32 \mu\text{eq}\cdot\text{L}^{-1}$, it

is not as high as might be expected from the effects of weathering of Anakeesta bedrock where concentrations are generally greater than $50 \mu\text{eq L}^{-1}$ (Figure 39). In addition, there is no evidence that Anakeesta occurs in that area based on King *et al.* (1967) or older maps (Keith, 1889). The sulfate concentrations observed at Mill Creek are entirely consistent with sulfate concentrations observed at other high elevation sites including Noland Divide. The relatively low nitrate concentrations are consistent with nitrate concentrations observed in other streams draining catchments with a history of human disturbance even though no records of human disturbance in that area exist (Pyle, 1988). Although some of the acidification of Mill Creek can probably be attributed to sulfate, pH levels of 4.03 cannot be explained with the observed sulfate or nitrate concentrations. The relatively low concentrations of strong inorganic acid anions indicates that organic acidity is probably involved. The samples with low pH taken from Mill Creek were observed to have been stained brown, probably as a result of decomposition of large numbers of *Rhododendron* leaves within the stream (personal observation - Terry Flum). Explaining the loss of fish from one stream due to organic acidity when most of the streams in the Park are undoubtedly susceptible to similar circumstances is not entirely satisfying. Nevertheless, at this time, it appears to be the best explanation available. Additional sampling in Mill Creek at sites along the full length of the stream should probably be conducted to clarify the situation.

Regardless of the mechanism by which the three streams losing fish during historical times were acidified, the fact that fish were lost provides a useful means to establish endpoints for water quality in the GRSM. Although the sample size of streams having lost fish is small, the endpoint of minimum pH below 5.5 was observed in all cases. The calcium to hydrogen ion ratio fails as an index here because the value for Cannon Creek was not below 3 (though the other two streams were). According to the currently available map of minimum stream pH (Figure 36), over 11% of

the park area currently has streams where acidification effects on fish are likely if the minimum pH endpoint is correct (Table 7). An additional 19% of the park area could be considered susceptible to impacts from future acidification due to current minimum pH values between 5.5 and 6.0 (Table 7). Whether further acidification of GRSM streams is likely will be a subject addressed in the next report and verified through additional monitoring of water quality.

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