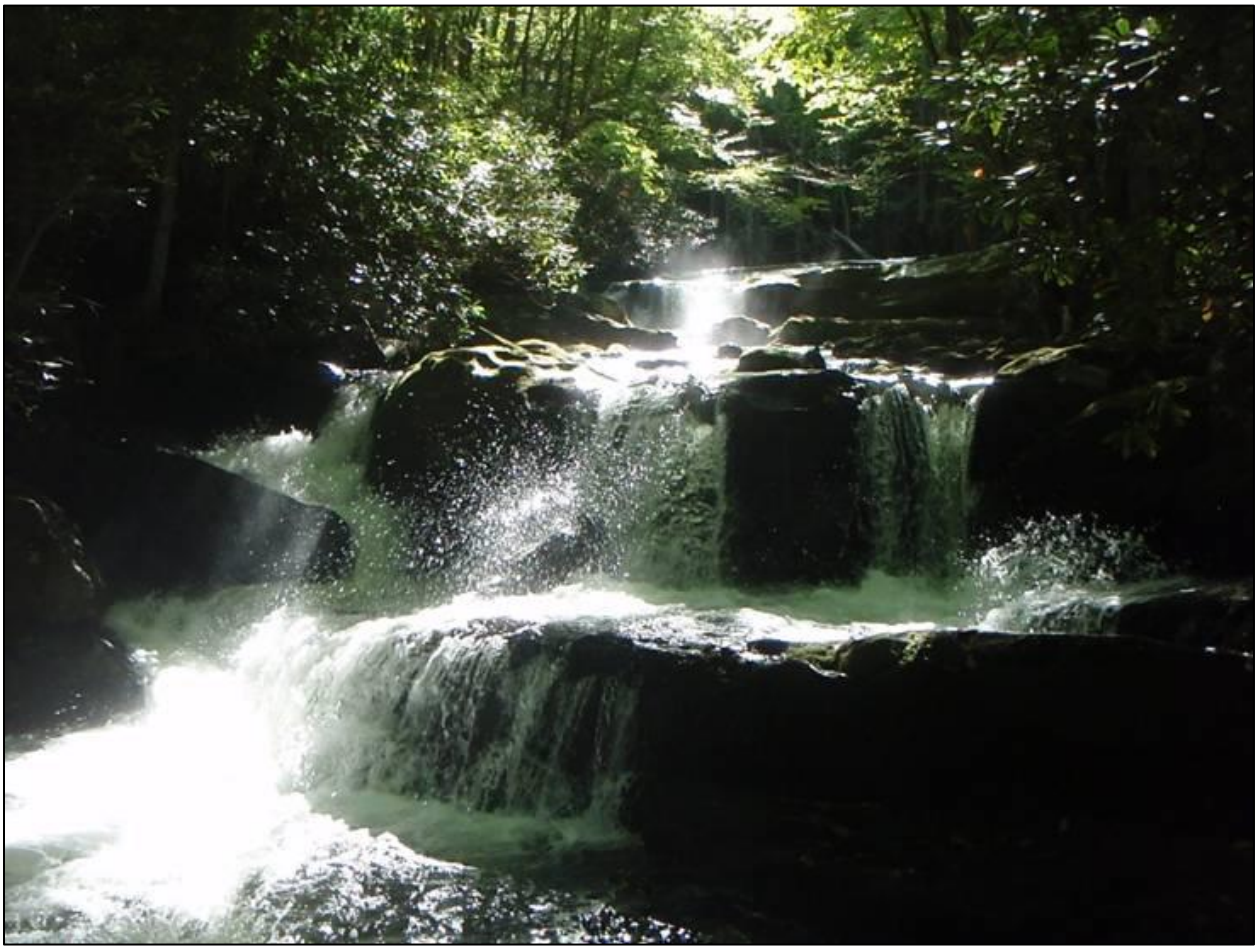
National Park Service
U.S. Department of the Interior

Natural Resource Stewardship and Science

Water Quality Monitoring in Great Smoky Mountains National Park

Statistical Reassessment of Spatial and Temporal Design Considerations

Natural Resource Report NPS/GRSM/NRR—2016/1294



ON THE COVER
Photo of Lost Bottom Creek, Spring 2010
Photograph by: Mary Ann Grell

Water Quality Monitoring in Great Smoky Mountains National Park

Statistical Reassessment of Spatial and Temporal Design Considerations

Natural Resource Report NPS/GRSM/NRR—2016/1294

John S. Schwartz[1], Timothy Pobst[2], Adrian Gonzalez[2], and Matt A. Kulp[3]

[1] Professor of Ecological Engineering
University of Tennessee
Department of Civil and Environmental Engineering
413 John D. Tickle Engineering Building
Knoxville, Tennessee 37996

[2] Graduate Students
University of Tennessee
Department of Civil and Environmental Engineering
411 John D. Tickle Engineering Building
Knoxville, Tennessee 37996

[3] Fisheries Biologist
US National Park Service
105 Park Headquarters Road
Gatlinburg, Tennessee 37738

October 2016

U.S. Department of the Interior
National Park Service
Natural Resource Stewardship and Science
Fort Collins, Colorado

The National Park Service, Natural Resource Stewardship and Science office in Fort Collins, Colorado, publishes a range of reports that address natural resource topics. These reports are of interest and applicability to a broad audience in the National Park Service and others in natural resource management, including scientists, conservation and environmental constituencies, and the public.

The Natural Resource Report Series is used to disseminate comprehensive information and analysis about natural resources and related topics concerning lands managed by the National Park Service. The series supports the advancement of science, informed decision-making, and the achievement of the National Park Service mission. The series also provides a forum for presenting more lengthy results that may not be accepted by publications with page limitations.

All manuscripts in the series receive the appropriate level of peer review to ensure that the information is scientifically credible, technically accurate, appropriately written for the intended audience, and designed and published in a professional manner.

Data in this report were collected and analyzed using methods based on established, peer-reviewed protocols and were analyzed and interpreted within the guidelines of the protocols.

This report received formal peer review by subject-matter experts who were not directly involved in the collection, analysis, or reporting of the data, and whose background and expertise put them on par technically and scientifically with the authors of the information.

Views, statements, findings, conclusions, recommendations, and data in this report do not necessarily reflect views and policies of the National Park Service, U.S. Department of the Interior. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Government.

This report is available in digital format from and the Natural Resource Publications Management website (http://www.nature.nps.gov/publications/nrpm/). To receive this report in a format optimized for screen readers, please email irma@nps.gov. Please cite this publication as:

J. S. Schwartz, T. Pobst, A. Gonzalez, and M. A. Kulp. 2016. Water Quality Monitoring Program in Great Smoky Mountains National Park: Statistical reassessment of spatial and temporal design considerations. Natural Resource Report NPS/GRSM/NRR—2016/1294. National Park Service, Fort Collins, Colorado.

NPS 133/134011, October 2016

Contents

Page

Figures v

Tables vi

Appendices vii

Abstract viii

Acknowledgments ix

List of Terms and Acronyms ix

1.0 Introduction 1

2.0 Spatial Patterns and Temporal Trends of Stream Chemistry per Elevation 5

2.1 GRSM Stream Acidification Studies: A Review 5

2.1.1 Spatial Patterns 5

2.1.2 Temporal Trends 11

2.2 Study Design 20

2.2.1 Study Objectives 20

2.2.2 Dataset Development 20

2.3 Spatial Analysis: Statistical Classification 21

2.3.1 Methods: Hierarchical Clustering Analysis 21

2.3.2 Results: Clustering Analysis per Elevation Range Based on Stream Chemistry 22

2.4 Temporal Trend Statistical Analysis 27

2.4.1 Methods: Temporal Trend Statistical Analysis 27

2.4.2 Results: Regression Analysis of Time Trends Among Elevation Bands 28

2.4.3 Results: ANOVA Comparisons between Elevation Classes and Time Periods 33

2.5 Discussion and Conclusions 33

3.0 Statistical Power Analysis 36

3.1 Introduction 36

3.2 Methods 37

3.2.1 Post Hoc Analysis 37

3.2.2 A Priori Analysis 38

Contents (continued)

Page

3.3 Results 38

3.3.1 Post Hoc Analysis 38

3.3.2 A Priori Analysis 40

3.4 Conclusions 43

4.0 Summary 44

5.0 Literature Cited 46

Figures

Page

Figure 1. Map of Great Smoky Mountains National Park (GRSM). 1

Figure 2. Water quality (stream chemistry) survey sites in Great Smoky Mountains National Park (GRSM) monitored for stream chemistry between 1993 and 2009 3

Figure 3. Temporal trends in stream pH and ANC concentrations (μeq yr^{-1}) between 1993 and 2009 for the 43 long-term park-wide monitoring sites 13

Figure 4. Temporal trends in stream nitrate and sulfate concentrations (μeq yr^{-1}) between 1993 and 2009 for the 43 long-term park-wide monitoring sites 14

Figure 5. Temporal trends in stream calcium and aluminum concentrations (μeq yr^{-1}) between 1993 and 2009 for the 43 long-term park-wide monitoring sites 15

Figure 6. Comparison of mean annual fluxes of throughfall net input and stream net export at GRSM Noland Divide Watershed research site for the period 1991 – 2006 17

Figure 7. Comparison of Noland Divide SO_4^{2-} concentration in deposition (annually volume-weighted concentration), annual mean stream concentrations (μeq L^{-1}), and total sulfur dioxide emissions from Bull Run and Kingston coal-fired power plants 18

Figure 8. Plot of pH data from the GRSM park-wide stream survey collected from 1993 through 2012. 19

Figure 9. Agglomerative hierarchical clustering of elevation classes based on water quality (pH, ANC, SO_4^2, and NO_3^-) 23

Figure 10. Agglomerative hierarchical clustering of elevation classes based on water quality (pH, ANC, SO_4^2, and NO_3^-) for a select subset of 37 sites for periods: a) 1993-2002, b) 2003-2008, and c) 2009-2012 23

Figure 11. Statistical power graphs from *a priori* analyses for four multivariate regression models with dependent variables as stream water chemistry for a) pH, b) nitrate and ANC, and c) sulfate 41

Figure 12. Plot of sampling frequency (total number of samples per year per elevation band) versus number of years to achieve a statistically significant trend for ANC (Power = 0.80, ES = 0.15, $p < 0.05$). 42

Tables

Page

Table 1. Descriptive statistics for GRSM stream pH (pH units), acid neutralizing capacity (ANC), NO_3^-, and SO_4^{2-} (μeq L^{-1}) between 1993-2002, with means and standard deviations (Std) for ten elevation classes. 6

Table 2. Basin characteristics of the 'eight-block design' watersheds including elevation, basin area, and percent watershed area with Anakeesta geology 7

Table 3. GRSM elevation trends of site median stream water chemical concentrations (1993 to 2009) per 1,000-ft gain using linear regression models 10

Table 4. Average stream sulfate concentrations (μeq L^{-1}) for six elevation classes, grouped by monitoring periods 10

Table 5. Time trend analysis modified from Robinson et al. (2008) for the period 1993-2002 for 10 elevation classes (ranges) in GRSM from 1,000-ft to >5,500 ft at 500-ft intervals 11

Table 6. Stream chemistry sites in GRSM used for a statistical reassessment of spatial patterns and temporal trends from 1993 to 2012, per six elevation classes from 1,000 ft to > 4,500 ft 21

Table 7. Stream chemistry summaries for pH, ANC, NO_3^- and SO_4^{2-} for six elevation classes in GRSM for three assessment periods: 1993-2002, 2003-2008, and 2009-2012 25

Table 8. Step-wise multiple regression analysis showing best-fit models for pH, acid neutralizing capacity (ANC), nitrate, and sulfate for the park-wide GRSM water quality stream sites 28

Table 9. Linear regression models for pH, ANC, nitrate, and sulfate using Julian date as the independent variable for two time periods (1993-2002 and 2003-2012) and six elevation classes (Table 6) 29

Table 10. Linear regression models for annual means of pH, ANC, NO_3^- and SO_4^{2-} per continuous Julian date for three periods (1993-2002, 2003-2008, 2009-2012) and six elevation classes (Table 6). 31

Table 11. Statistical differences for water quality (pH, ANC, nitrate, and sulfate) between time periods for different elevation classes (Table 9) using a Bonferroni means separation analysis. 33

Table 13. *Post hoc* power analysis using multiple regression models for water chemistry (pH, ANC, NO_3^-, SO_4^{2-}) per three time periods (1993-2002, 2003-2008, and 2009-2012) and six elevation classes 39

Table 14. Number of sampling years to detect trends for pH, ANC, nitrate, and sulfate based on a statistical power of 0.8 and effect size of 0.15, and based on regression models per six elevation classes and a bimonthly sampling frequency. 42

Appendices

Page

Appendix A: GRSM Park-wide Stream Survey Sites: Location and Elevation Class 49

Appendix B: Satistical Results from Neff et al. (2013): Tables III-V 50

Appendix C: Significant Time Trends for Stream Chemistry from 1993 to 2009 (Schwartz et al. (2014) 53

Appendix D. Water Quality Data for Cataloochee River, Little River, and Hazel Creek 55

Appendix D. GRSM Water Quality Data Summary for Cataloochee River, Little River, and Hazel Creek 58

Abstract

The overall I&M Program in Great Smoky Mountains National Park (GRSM), including water quality, is currently being revamped to reflect new issues, and to standardize the program to the Park Service-wide vital signs approach. A conceptual plan for vital signs monitoring was completed during FY10. Six watersheds have been selected for GRSM's Vital Signs Monitoring Program, including: Abrams Creek, Cataloochee Creek, East Prong Little River, Hazel Creek, Middle Prong Little Pigeon River, and Deep Creek. In addition, the Cosby-Rock Creek watershed has been added to the water quality monitoring program because its chemistry differs from other watersheds and is showing a downward trend in water quality over time (e.g., decreasing pH, increased nitrate). Although watersheds have been selected for the Vital Signs Monitoring Program, additional information is needed to ensure that the number and frequency of samples per incremental elevation class and the sampling frequency will be sufficient to detect trends in stream water quality. Specific study objectives included the following: 1) characterize stream chemistry along an elevation gradient; 2) identify time trends in stream chemistry for different elevation ranges; and 3) assess statistical power for existing variances of stream chemistries for different time periods and elevation ranges, and estimate the number of samples with sufficient power to detect future trends in water quality. The key controlling environmental variable for stream chemistry in GRSM is elevation, where it is observed that pH, acid neutralizing capacity (ANC), and base cation concentrations decrease with increasing elevation, nitrate and dissolved aluminum concentrations increase with increasing elevation, and sulfate appears not to vary significantly with elevation. Based on an agglomerative hierarchical clustering method, results from two datasets suggest that vital signs monitoring should include the following elevation classes: 1) 1,000 ft to 2,000 ft; 2) 2,000 ft to 3,000 ft; 3) 3,000 ft to 3,500 ft; 4) 3,500 ft to 4,500 ft; 5) 4,500 ft to 5,000 ft; and 6) > 5,000 ft. The statistical power analysis found that a study design based on 1,000-ft intervals (six elevation classes from 1,000 ft MSL to > 5,000 ft) sampled every other month will generate sufficient data within about 4 to 5 years with a minimum number of samples equal to 109. The current sampling design criteria, which include bimonthly sampling for six elevation classes, and six watersheds, will allow for a statistical trends analysis to be conducted separately per watershed and per elevation class across the park.

Acknowledgments

We acknowledge funding from the cooperative agreement between the US National Park Service, Southeast Region, and the University of Tennessee, Knoxville (UTK) under the Southern Appalachian Cooperative Ecosystem Studies Unit, CESU Host Cooperative Agreement No. H5000095040, Task Agreement Order No. J5471090010. The University of Tennessee identifies this task agreement as Research Account No. R01-1334-292 and R01-3601-194. Various post-doctorate researchers, graduate and undergraduate students at UTK guided or supported this work including Meijun Cai, Keil Neff, Matt Aplin, Jordan Hayes, and Andrew Veeneman. Water quality sample collection is supported by volunteers from Trout Unlimited.

List of Terms and Acronyms

ANC	Acid Neutralizing Capacity
BS	Base Cations
CEC	Cation Exchange Capacity
ES	Effect Size
FY	Fiscal Year
GRSM	Great Smoky Mountains National Park
I&M	Inventory and Monitoring
Ksat	Hydraulic Conductivity
MSL	Mean Sea Level
NDW	Noland Divide Watershed
NPS	National Park Service
SKT	Seasonal Kendall Tau
Std	Standard Deviation
TVA	Tennessee Valley Authority
US	United States

1.0 Introduction

Great Smoky Mountains National Park (GRSM; or "the park") straddles the border between Tennessee and North Carolina within the southern Appalachian Mountains (Fig. 1). The park is the second largest national park in the eastern US, covering roughly 220,000 ha (850 mi2), and is one of the most frequently visited public park destinations. GRSM resource managers are responsible for implementing the environmental stewardship policies of the US National Park Service (NPS) in order to protect all natural and cultural resources within its boundaries. A key activity to meet this responsibility is through the NPS Inventory and Monitoring (I&M) program.

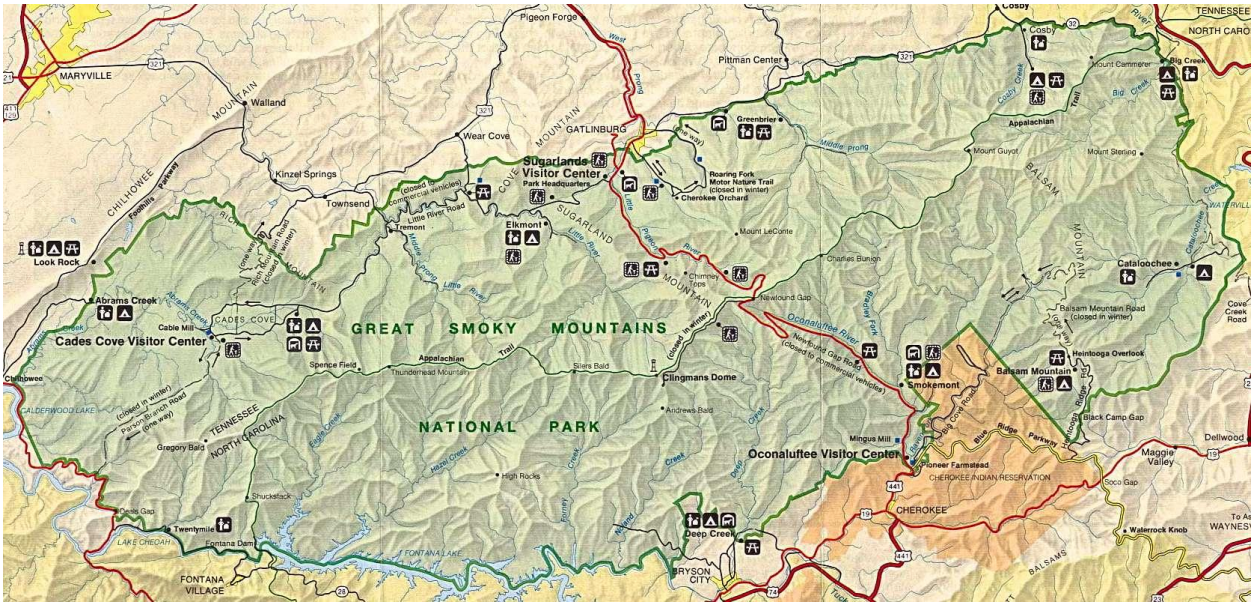


Figure 1. Map of Great Smoky Mountains National Park (GRSM).

As part of the NPS's effort to "improve park management through greater reliance on scientific knowledge," the National Parks Omnibus Management Act (1998) directed the NPS "to establish baseline natural resource information and to evaluate the long-term trends in the condition of National Park System resources." Under the mandate of the Omnibus Act, the I&M Program was created to acquire the information and expertise needed by park managers to protect park resources and to evaluate ecosystem integrity. The I&M Program's primary role is to collect, organize, and disseminate natural resource data, contributing to the NPS's institutional knowledge by facilitating the transformation of data into information that can be readily utilized by park managers and the general public. A main goal established by the I&M Program includes monitoring park ecosystems to better understand their dynamic nature and condition and to provide reference points for comparisons with other, altered environments (http://science.nature.nps.gov/im/index.cfm). Effective monitoring provides the data necessary to determine the status and trends of selected condition indicators of the park ecosystems, allowing managers to make better-informed decisions and to work more effectively with other agencies and individuals for the benefit of park resources.

Specific to GRSM's ecosystems, concern over the potential impacts of acid deposition began in the 1980s (Herlihy et al. 1991; Johnson and Lindberg 1992; Cook et al. 1994). Investigating the potential biological effects of acid deposition, resource managers implemented an I&M Program in 1993 where stream chemistry, benthic macroinvertebrates, and fish were identified as key early warning indicators of acidification in GRSM's aquatic ecosystems. Stream chemistry measurements included: pH, acid neutralizing capacity (ANC), conductivity, SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), and dissolved metals (Al, Fe, Si, Zn, Cu, Mn).

In 1993, water quality monitoring began with a total of 185 stream sites (Fig. 2). In 1994, 119 sites were added to the stream survey and in 1995 an additional 53 sites were added. Between the years 1993 and 1995, the initial 185 stream sites were sampled on a semi-annual basis and the remaining 172 sites were sampled at varying frequencies. Collectively, during this period between 1993 and 1995, 357 sites were sampled for water quality analysis. After this period, in 1996, the number of sample sites was reduced to 160 and collected on a monthly basis. In 1997, the number of sample sites was reduced to 90 collected quarterly. Odom (2003) conducted a statistical analysis developing a sampling scheme for both location and frequency with objectives to minimize spatial redundancy and optimize frequency with sufficient statistical power to assess water quality trends. In 2004, the monitoring program was modified to 32 sample sites collected bimonthly, and 11 Hazel Creek sites collected biannually. Watersheds in the bimonthly collections included Abrams Creek, Cataloochee Creek, Cosby Creek, Oconaluftee River, and West Prong of the Little River. Among the 43 survey sites monitored since 2004, 27 have a complete monitoring history from 1993 through 2012 (Appendix A). Over the entire period from 1993 to 2012, 387 sites have been monitored for stream chemistry at least once for the GRSM I&M Water Quality Program (Schwartz et al. 2014).

GRSM's I&M Program, including water quality, has recently been revamped to reflect knowledge gained from prior studies and new environmental issues, and to standardize it to the NPS-wide vital signs approach. In order to address the most critical data needs for individual parks within the constraints of human resources and operating budget, I&M networks must identify a limited number of "vital signs" that best represent the resource composition, structure, and function of highest interest to individual parks. To effectively develop a monitoring program of vital signs, I&M networks are prioritizing research questions and monitoring data needs related to: (1) focal resources important to each park, which may include individual species, species assemblages, or ecological processes, (2) agents of change or stressors that are known or suspected to cause changes in those focal resources over time; and (3) key properties and processes of ecosystem health, e.g., weather, land use patterns, water quality, soil nutrients.

The elements and processes to be monitored are a subset of the total suite of natural resource components that park managers are directed to preserve "unimpaired for future generations," including water, air, geological resources, plants and animals, and the various ecological, biological, and physical processes that influence those resources. Monitoring results will be used to develop natural resource management strategies, to assess the efficacy of management and restoration efforts, to provide early warning of impending threats, and to provide a basis for understanding and identifying meaningful change in natural systems.

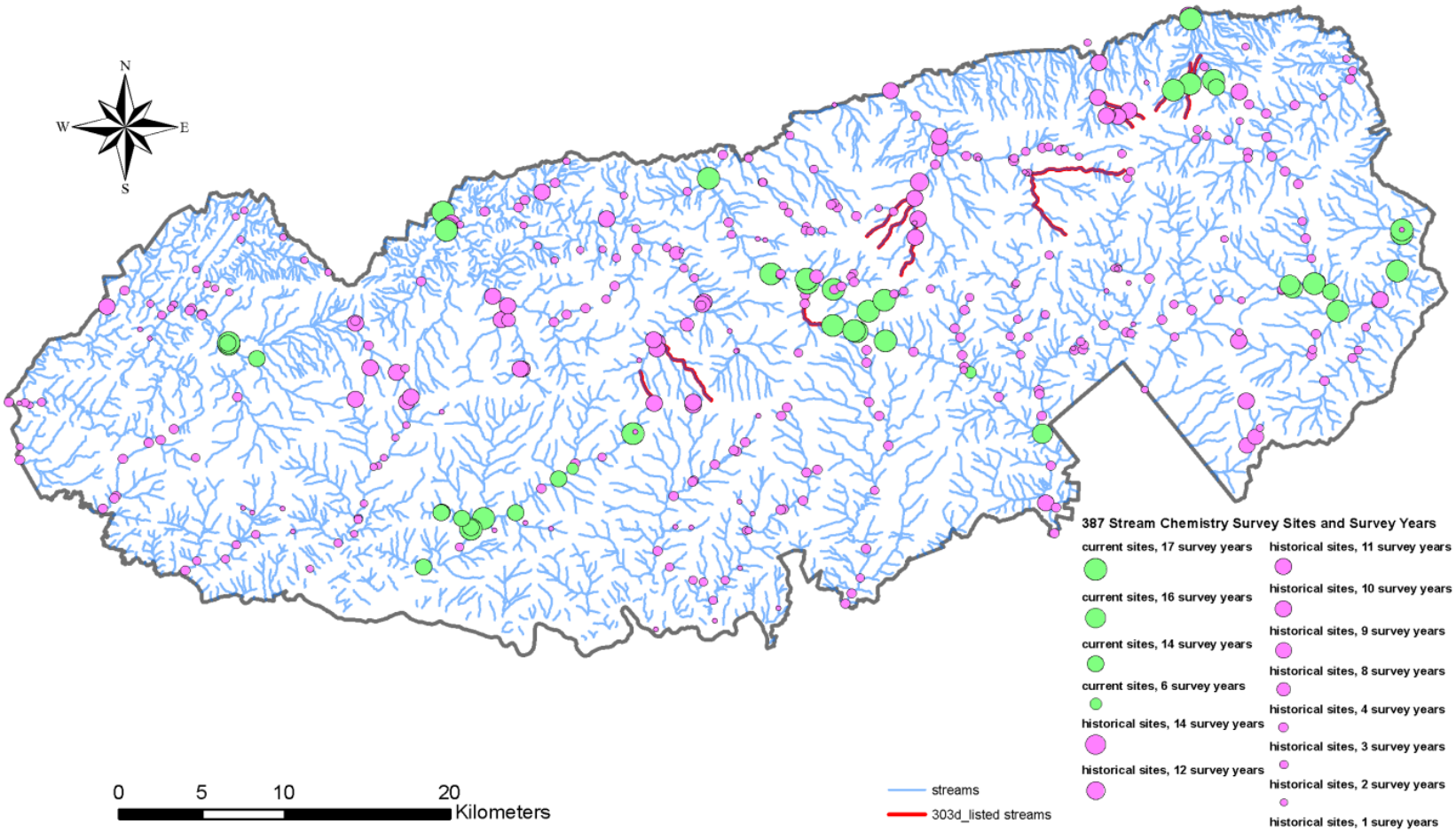


Figure 2. Water quality (stream chemistry) survey sites in Great Smoky Mountains National Park (GRSM) monitored for stream chemistry between 1993 and 2009. Survey sites are delineated per number of sample records. Streams on the 303(d) list are shown in red.

The information obtained through natural resource monitoring will be utilized to facilitate management decisions, for research and education, and to promote public understanding of park resources.

Specifically within the GRSM resource group, a conceptual plan for vital signs monitoring was completed and distributed to eight prominent ecologists during FY10. This was accomplished through the offices of the Appalachian Highlands Network (AHN) so that responses could be confidential. The recipients were stratified by ecological expertise and were mostly at federal laboratories across the eastern US (e.g., Oak Ridge National Laboratory, Coweeta Hydrological Laboratory, Hubbard Brook Experimental Research Laboratory) who have extensive experience in their field of study but who were not biased by having projects in the park. In addition, researchers with much experience in the park were also openly solicited for comments. Six watersheds were selected for GRSM's Vital Signs Monitoring Program: Abrams Creek, Cataloochee Creek, East Prong Little River, Hazel Creek, Middle Prong Little Pigeon, and Deep Creek. In addition, Cosby-Rock Creek watershed has been included because its chemistry differs, showing a downward trend in water quality over time (e.g., decreasing pH, increased nitrate concentrations) compared with other GRSM watersheds (Schwartz et al. 2014). Though watersheds have been selected for GRSM's Vital Signs Monitoring Program, additional information is needed to address the following issues:

1) The number of samples necessary per watershed to provide enough statistical power to categorize the area and detect trends over time,
2) Determine location stratification within watersheds based on basin physiographic factors, and
3) Determine a schedule for sampling frequency and total number of samples so that future trend analyses will have sufficient statistical power.

The objectives of this study were to conduct a statistical reassessment of long-term data (1993-2012), addressing the needs identified above in order to assist GRSM management with their Vital Signs Monitoring Program. Reassessment acknowledges the prior statistical analysis conducted by Odom (2003), which answered similar monitoring questions and was used to determine the 43 sites sampled between 2003 and 2013. In addition, with the knowledge gained from Schwartz et al. (2014), Neff et al. (2013), and other prior GRSM studies, this study's reassessment focuses on elevation as the dominant control variable for stream acidification, though other basin factors (e.g., geology, soils, vegetation) are important controls. Elevation is the key because it is a covariate with other basin factors identified, and do to the fact that acid deposition is greater at higher elevations, leading to greater pollutant loads annually (Weathers et al. 2006). In Chapter 2, information from existing studies that identify elevation as a dominant control is summarized as background for this study's statistical analyses. This reassessment, given the additional data available since 2003, aims to provide better insight on the number and location of water samples needed to statistically determine long-term trends in quality among the park's streams. In order to meet the stated objectives, this study consists of three analyses as follows.

1) Characterize stream chemistry along an elevational gradient (low to high);
2) Identify time trends in stream chemistry for different elevation ranges; and

3) Estimate statistical power for various sampling strategies based on existing variance of stream chemistries for different elevation ranges.

2.0 Spatial Patterns and Temporal Trends of Stream Chemistry per Elevation

2.1 GRSM Stream Acidification Studies: A Review

2.1.1 Spatial Patterns

In the Appalachian Mountain region, changes in stream chemistry have been shown to occur along an elevational gradient (Herlihy et al. 1998; Gbondo-Tugbawa and Driscoll 2002; Sullivan et al. 2007; Chen and Lin 2009). In general, stream acidification increases with increasing stream elevation, where higher elevations are associated with greater acid deposition (Weathers et al. 2006). In GRSM, stream elevation is a dominant watershed factor associated with stream chemistry (Robinson et al. 2008; Neff et al. 2013; Schwartz et al. 2014). In some high-elevation areas within GRSM, Anakeesta surficial geology (a pyritic acid producing rock) can contribute to stream acidification. Other watershed factors, such as soil and vegetation characteristics, also influence stream chemistry and acidity, and also spatially correlate with elevation.

Robinson et al. (2008) characterized water chemistry for pH, ANC, nitrate, and sulfate by ten elevation classes. The classes were based on 500-ft intervals from 1,000 ft mean sea level (MSL) elevation to an upper most class of > 5,500 ft (Table 1). Water chemistries were summarized from 90 GRSM sites, with samples collected approximately on a quarterly basis from October 1993 through November 2002. Stream water was sampled primarily during baseflow conditions with no effort to differentiate samples taken during higher flows. As observed from the data summaries, mean pH and ANC both declined from lower to higher elevation classes, with pH ranging from 6.66 to 5.11 and ANC ranging from 201.0 to 2.1 $\mu eq\ L^{-1}$. Nitrate concentrations increased with elevation from a mean of 0.51 $\mu eq\ L^{-1}$ within the lower-most elevation class to 64.31 $\mu eq\ L^{-1}$ for the upper-most class (> 5,500 ft MSL). Stream sulfate was observed with the highest mean concentrations of 71.19 to 74.80 $\mu eq\ L^{-1}$ for the three elevation ranges between 3,500 ft and 5,000 ft, whereas SO_4^{2-} concentrations were between 32.84 and 44.18 $\mu eq\ L^{-1}$ for all other elevation classes.

Robinson et al. (2008) conducted a statistical analysis of the data represented in Table 1 utilizing a logistic stepwise regression approach for four dependent variables: stream pH, ANC, nitrate, and sulfate concentrations. Independent variables included elevation, stream order, average basin slope, percent limestone and Anakeesta surficial geology, various precipitation metrics, surrogate stream flows at two USGS gauging stations on Little River and Cataloochee Creek, and acid deposition fluxes from the Noland Divide monitoring station. All models generated by this procedure were significant at $p < 0.001$ and individual independent variables were significant at $p < 0.05$. Elevation was a significant factor for pH and sulfate. Stream pH declined 0.72 units per 1,000-ft gain in elevation across the entire modeled range (1,000 ft to > 5,500 ft). All four models found that stream pH, ANC, nitrate, and sulfate were significantly governed by average basin slope, which is associated with elevation. That is in general, the higher the elevation the steeper the average basin slope from a park-wide perspective. Robinson et al. (2008) suggested that areas with steeper basin

slopes in the higher elevation headwaters will have shallower soils and greater annual precipitation volumes leading to a condition of less attenuation of acid deposition. Except for nitrate, the statistical models found a precipitation metric as an independent variable of significance, illustrating the importance of climate on chemical transport and biogeochemical processes.

Table 1. Descriptive statistics for GRSM stream pH (pH units), acid neutralizing capacity (ANC), NO_3^-, and SO_4^{2-} (μeq L^{-1}) between 1993-2002, with means and standard deviations (Std) for ten elevation classes (modified from Robinson et al. 2008).

Elevation range (ft)	No. Of sites (data points)	pH		ANC		Nitrate		Sulfate	
		Mean	Std	Mean	Std	Mean	Std	Mean	Std
1,000-1,500	7 (175)	6.66	0.32	145.0	140.7	10.51	9.37	44.18	12.14
1,500-2,000	13 (234)	6.57	0.40	201.0	370.1	11.50	7.56	35.63	12.86
2,000-2,500	16 (289)	6.34	0.30	59.7	38.2	12.80	11.98	32.84	17.58
2,500-3,000	18 (305)	6.30	0.30	51.6	32.3	18.79	14.60	36.77	20.19
3,000-3,500	13 (307)	6.12	0.34	31.0	23.4	23.88	13.05	42.94	24.53
3,500-4,000	4 (71)	6.18	0.28	41.5	34.8	35.23	9.99	71.19	19.49
4,000-4,500	6 (90)	5.85	0.46	22.3	40.2	34.69	17.09	74.80	55.44
4,500-5,000	7 (109)	5.74	0.68	31.6	34.2	34.58	19.96	72.80	108.9
5,000-5,500	3 (38)	5.66	0.49	18.1	15.1	49.91	13.81	37.70	17.72
> 5,500	3 (28)	5.11	0.38	2.1	18.2	64.31	22.52	38.04	17.92

Neff et al. (2013) conducted a statistical analysis for baseflow and stormflow chemistry on eight streams in GRSM, investigating the influence of several key basin characteristics. The key characteristics included elevation, basin area size, and percent Anakeesta geology constituting an eight-block statistical design (Table 2). The block-design was set up based on the following criteria: elevation < and > 3,200-ft (975 m MSL), basin area of 0.39-3.86 mi^2 and 3.86-7.72 mi^2 (1-10 km^2 and 10-20 km^2), and Anakeesta geology occurrence as 0% (absent) and > 10% (present). Additional basin characteristics included in this study included soil properties and vegetative composition (Appendix B). Soil properties included: pH, cation exchange capacity (CEC), percent organic matter, hydraulic conductivity (Ksat), depth, and maximum slope. Vegetative composition included five classes associated with mesic and xeric forests, and scrublands. Baseflow samples were collected monthly from May 2008 through September 2009, except for the Eagle Rocks Prong site in which data was collected from April 2006 through December 2007. Eagle Rocks Prong data had to be substituted for the originally selected Walker Prong site due to the discovery that stream chemistry was impacted by nearby road applications of limestone chat during winter weather conditions. Stormwater samples were collected by passive siphon samplers, except for Eagle Rocks Prong that utilized an automatic ISCO™ sampler. Deyton et al. (2009) describes the sampling methodology and data summaries from Eagle Rocks Prong.

Table 2. Basin characteristics of the 'eight-block design' watersheds including elevation, basin area, and percent watershed area with Anakeesta geology (modified from Neff et al. 2013).

Basin	Elevation (ft)	Area (mi^2)	Anakeesta (mi^2)	Mean basin elevation (ft)	Mean basin slope	Latitude	Longitude
Newt	Low (2,854)	Small (1.58)	Present (0.76)	3,983	23.6º	35.633 N	83.587 W
Road	High (3,576)	Small (3.32)	Present (0.68)	5,016	30.0º	35.630 N	83.470 W
Rock	Low (2,067)	Small (1.40)	Absent (0.0)	4,098	25.8º	35.761 N	83.210 W
Lost Bottom	High (3,330)	Small (3.26)	Absent (0.0)	4,669	26.4º	35.637 N	83.146 W
Jakes	Low (2,165)	Large (4.64)	Present (1.55)	3,596	22.5º	35.654 N	83.582 W
Walker Camp	High (3,822)	Large (4.92)	Present (3.15)	4,997	28.3º	35.629 N	83.451 W
Cosby	Low (2,001)	Large (6.76)	Absent (0.0)	3,648	28.2º	35.763 N	83.211 W
Palmer	High (3,248)	Large (7.72)	Absent (0.0)	4,528	25.8º	35.636 N	83.144 W
Eagle Rocks *	High (3,199)	Large (4.04)	Present (0.45)	4,741	30.5º	35.690 N	83.320 W

* Stream data replaced Walker Prong in statistical analysis due to the application of winter road limestone chat.

In Neff et al. (2013), a preliminary statistical analysis was conducted using a Pearson correlation analysis on all basin characteristics to determine which variables may co-vary. This analysis found mean basin elevation to be significantly correlated with: 1) maximum soil slope, 2) subalpine mesic forests to woodlands, 3) high elevation mesic to submesic forests, and 4) low- and mid-elevation mesic to submesic forests. Correlation among the vegetation land cover variables was expected, considering elevation was used as a cover-type classifier. Basin area did not correlate significantly with any other physical basin variables. Percent Anakeesta geology only correlated with high-elevation mesic to submesic forests, and scrublands.

Investigating the influence of basin characteristics on stream chemistry, a Tukey-Kramer bivariate means comparison test was used to examine differences in water chemistry among the eight-block design key basin characteristics, and tested separately for baseflow and stormflow samples (Neff et al. 2013). In addition, a Spearman bivariate correlation analysis was used to investigate relations between water chemistry parameters and all basin characteristics.

With a focus on elevation from Neff et al. (2013), the higher elevation class had significantly lower pH, ANC, Na^+, and higher NO_3^- and Mg^{2+} than those in the lower elevation class during baseflow conditions (Appendix B). ANC in high-elevation streams averaged 6.12 for pH and 28.22 μeq L^{-1}, whereas it averaged 6.44 for pH and 40.58 μeq L^{-1} in lower elevation streams. During stormflow conditions, streams in the higher elevation class had significantly lower pH, ANC, Na^+, base cations sum (BC), and higher NO_3^- and Al than those streams in the lower elevation class. High-elevation streams averaged 5.80 for pH and 26.15 μeq L^{-1} for ANC, whereas lower elevation streams averaged 6.25 for pH and 44.64 μeq L^{-1} for ANC. Stream acidification was more pronounced during stormflow than baseflow, as observed by comparatively lower pH and ANC resulting from increased transport of acid anions from land surfaces to the stream during precipitation events. In addition, within the higher elevation streams, episodic acidification during stormflows appeared to be due to

BC dilution because BC concentrations were significantly lower during stormflows and not baseflow. Elevation patterns for nitrate and sodium concentrations were the same for baseflow and stormflow conditions. Nitrate concentrations were greater in the higher elevation streams. Van Miegroet et al. (2001) determined that high-elevation watersheds in GRSM were nitrogen (N) saturated; that is, more N is deposited than what the forest ecosystem can uptake, leading to excess N exported to streams. Nitrate is also very mobile in soils not being retained by physical soil processes of adsorption. Once N reaches the stream, Mulholland (1993) reported N assimilation by periphyton was rapid. This could be the reason for the observed lower NO_3^- concentrations among the lower elevation streams. Sodium concentrations were greater in the lower elevations streams compared with higher elevations, and it is assumed that Na^+ accumulates as basin area increases. Sodium is also very mobile in soils with water interflow, and in general forest and stream ecosystems minimally regulate its transport.

In Neff et al. (2013), basin area was not a significant factor for stream pH, ANC, SO_4^{2-}, NH_4^+, Ca^{2+}, and Al during baseflow conditions (Appendix B). Significant differences were found with NO_3^- and BC (Na^+ and Mg^{2+}), where these chemical parameters were greater in larger basins compared with smaller basins. In the larger basins, stream NO_3^- averaged 24.73 μeq L^{-1} and BC averaged 120.17 μeq L^{-1}. During stormflow conditions, ANC, NO_3^-, Na^+ and BC were significantly greater in larger basins than smaller basins. In comparing the differences in water chemistries between baseflow and stormflow, results suggest a re-proportioning of ion composition as water moves from smaller headwater streams to larger streams, with a general increase of base cations over that of acid anions, thereby increasing ANC in the larger streams. It also suggests an influence of groundwater, where base cations accumulate as water moves through bedrock and ions dissolute, eventually discharging per in-stream springs and mixing with surface waters at lower elevations.

During baseflow, Anakeesta geology absence (< 10% area) or presence (> 10% area) was not significantly different for BC, Al, and NH_4^+ (Neff et al. 2013). However, pH, ANC, Na^+, were significantly lower when Anakeesta was present, whereas NO_3^-, SO_4^{2-}, Mg^{2+}, and Ca^{2+} were greater. With Anakeesta present, stream SO_4^{2-} averaged 40.33 μeq L^{-1} compared with 33.65 μeq L^{-1} when absent (Appendix B). During stormflow, pH and Na^+ were significantly lower in Anakeesta-present streams, but unlike during baseflow, ANC was not significantly different between the two geology stream classes. Other ions that were not significantly different included: NO_3^-, NH_4^+, SO_4^{2-}, Mg^{2+}, and BC. In particular, stormflow SO_4^{2-} concentrations averaged 41.02 and 36.14 μeq L^{-1} in streams with Anakeesta present and absent, respectively. The non-significant difference in SO_4^{2-} mean concentrations during stormflows between the two geology classes suggests that soil biogeochemical processes play a dominant and complex role in its export to streams (Postek et al. 1995, Gobran et al. 1998; Mitchell et al. 2011). Many factors influence SO_4^{2-} transport through soils, including soil water pH, absorption/desorption processes, soil horizon physical properties, SO_4^{2-} mineralization by microbes, and uptake and litter-decay cycling by forest vegetation. Through several soil experiments at the GRSM high-elevation Noland Divide study site, Cai et al. (2010, 2011a, 2012) found SO_4^{2-} remained adsorbed to soil particles as long as soil water chemistry has a pH < 6.0 and SO_4^{2-} > 15 μmol L^{-1}. They also report that the conversion of NH_4^+ to NO_3^- per microbial nitrification apparently promotes soil SO_4^{2-} adsorption by adding to soil water acidity.

Aluminum concentrations were significantly greater when Anakeesta was present, with an average of 5.72 μmol L^{-1} compared to 2.38 μmol L^{-1} when absent ($p < 0.001$). One explanation for this difference may be that Al-bearing minerals (e.g., alumino-silicates, feldspars, etc.) weather relatively more efficiently in the higher acidity conditions of Anakeesta-present areas compared to the areas not present. Secondary Al-bearing minerals (e.g., gibbsite) formed from bedrock weathering between storm events can re-dissolve during storm events, serving as a source of dissolved Al to the stream channel (Driscoll 1985).

Exploring significant relationships between an expanded group of basin factors and stream chemistry by a Spearman correlation analysis ($p < 0.01$), Neff et al. (2013) found elevation to be a dominant control variable as found in the eight-block design study (Appendix B). During both baseflow and stormflow conditions, pH, ANC, Na^+,and Si concentrations were inversely correlated with elevation, and NO_3^-, SO_4^{2-}, and Al were directly correlated. Three ions, Cl^-, Ca^{2+}, and K^+, were not correlated with elevation. During baseflow conditions only, BC was inversely correlated and Mg^{2+} was directly correlated with elevation. Illustrating the importance of physical soil characteristics in watersheds on stream water quality, it was found that hydraulic conductivity (Ksat) and soil slope were inversely correlated with pH, ANC, K^+, Na^+ and Si, and directly correlated with NO_3^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, and Al. As suggested by Robinson et al. (2008), shallower soils with higher Ksat (faster water movement through soils) will more readily transport acid anions during precipitation events from deposition sources. It also appears that Mg^{2+}, Ca^{2+}, and Al are more readily mobile during precipitation events in steeper, higher Ksat soils found in the headwater areas. Vegetative composition classes were also highly correlated with chemical parameters, and they are a function of elevation (Neff et al. 2013).

In contrast with Neff et al. (2013) where the study design compared two elevation classes for eight streams, Schwartz et al. (2014) completed a statistical analysis based on a complete GRSM park-wide dataset (1993-2009). The park-wide monitoring dataset does not distinguish whether samples were collected during baseflow and stormflow conditions; however, most samples were taken during baseflow. Also in this analysis, sites influenced by limestone geology in Abrams Creek watershed were removed because this geology buffers stream water from effects of acid deposition. Robinson et al. (2008) did not remove the Abrams Creek limestone sites; therefore, outcomes of regression models developed in that study must be interpreted accordingly. In Schwartz et al. (2014), simple linear regression models were developed with elevation (converted to 1000s of feet) as the independent variable; and chemical parameters as the dependent variable (Table 3). Site elevations ranged from 1,000 ft to over 5,500 ft, where the maximum elevation in the park is 6,643 ft.

Based on all available data in Schwartz et al. (2014), stream pH and ANC significantly declined at 0.32 pH units and 35.73 μeq L^{-1}, respectively per 1,000-ft elevation gain (Table 3). As observed in Neff et al. (2013), SO_4^{2-} concentrations were not significantly correlated with elevation, and NO_3^- significantly increased with elevation gain. Although Weathers et al. (2006) reports greater SO_4^{2-} deposition at higher elevations in GRSM, it appears that stream SO_4^{2-} is regulated by soil biogeochemical processes and whether Anakeesta geology is present. A review of Neff et al. (2013), above, provided more detailed explanation of possible processes influencing SO_4^{2-} transport. In Schwartz et al. (2014), conductivity, chlorine, and base cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) exhibited

significant declines with elevation gain. Results from the park-wide dataset analysis suggest that increased stream acidification from lower to higher elevation is largely due to decreasing base cations corresponding with increasing nitrate.

Table 3. GRSM elevation trends of site median stream water chemical concentrations (1993 to 2009) per 1,000-ft gain using linear regression models (Schwartz et al. 2014). Site elevations ranged from 1,000 ft to > 5,500 ft. Chemical concentrations are all in μeq L^{-1}, except pH is in pH units, and conductivity (Cond) is in μS cm^{-1}.

Chemical Parameter	Regression Slope	Significance Level
pH	-0.32	<0.01
ANC	-35.73	<0.01
Cond	-1.70	<0.01
Cl^-	-0.33	0.03
NO_3^-	8.42	<0.01
SO_4^{2-}	-1.52	0.25
Na^+	-5.93	<0.01
K^+	-1.57	<0.01
Mg^{2+}	-9.07	<0.01
Ca^{2+}	-19.67	<0.01

In the analysis by Schwartz et al. (2014), the number of sites above 4,000 ft (n = 19) was less than the number of sites below 4,000 ft (n = 90), and the number of sites above 5,000 ft was small (n = 6); this was based on the period from1993-1995 when an extensive monitoring effort was conducted (Table 4). The number of sites for the complete dataset (1993–2009) per elevation class was as follows: > 5,000 ft (n = 1), 4,000-5,000 ft (n=6), 3,000-4000 ft (n = 4), and < 3000 ft (n = 16). It should be noted in Table 4 the limited number of sites at higher elevations (> 4,000 ft) for the period 1993-2003.

Table 4. Average stream sulfate concentrations (μeq L^{-1}) for six elevation classes, grouped by monitoring periods (Schwartz et al. 2014). Number of samples per group is in parentheses. Using the Tukey HSD means comparison method, significantly different concentrations ($p < 0.05$) among four monitoring periods (per number of continuous events within period) are represented by different letters (A, B, C).

Elevation Class	Elevation (ft)	Average sulfate concentration (number of survey sites)			
		1993-2009	1993-2003	1993-1996	1993-1995
1	< 1,000	NA (0)	NA (0)	64.79^{ABC} (2)	NA (1)
2	1,000-2,000	43.63^{AB} (6)	35.81^{A} (10)	42.31^{AB} (24)	29.88^{A} (16)
3	2,000-3,000	31.25^{B} (10)	30.87^{A} (5)	26.43^{C} (31)	34.66^{A} (28)
4	3,000-4,000	62.28^{AB} (4)	41.91^{A} (9)	30.37^{BC} (39)	29.96^{A} (26)
5	4,000-5,000	119.80^{A}(6)	60.82^{A} (2)	55.27^{A} (13)	50.50^{A} (12)
6	> 5,000	NA (1)	NA (0)	34.27^{ABC} (3)	43.39^{A} (6)

2.1.2 Temporal Trends

Temporal trends of water chemistry related to stream elevation was conducted by Robinson et al. (2008) and Schwartz et al. (2014). Both of these studies utilized the available park-wide data, 1993-2002, and 1993-2009, respectively. In Schwartz et al. (2014), site trends were spatially plotted on GRSM maps identifying variability among the different watersheds. The most detailed temporal analysis of water quality trends was conducted by Cai et al. (2010, 2011a) at a single high-elevation study site in the Noland Divide Watershed (NDW). Relevant trends identified by Cai et al. (2010, 2011a) are summarized in this section. In addition, information from annual report from the GRSM Water Quality Monitoring Program is summarized in support of this study's analyses.

Robinson et al. (2008) analyzed stream chemistry data from 90 GRSM sites collected between 1993 and 2002, summarizing trends among 10 elevation classes from 1,000 ft to > 5,000 ft per 500-ft intervals (Table 1). Using a bivariate linear regression of pH, ANC, SO_4^{2-}, and NO_3^- versus time per elevation class, significant trends were quantified by slope direction and magnitude (Table 5). During the period 1993-2002, pH significantly declined between 0.0127 units yr^{-1} and 0.0260 units yr^{-1} for elevation classes between 1,000-ft and 3,500-ft, and 0.0905 units/yr^{-1} for the 4,500-5,000 ft elevation range. The two higher elevation ranges above 5,000 ft were not observed with significant changes for all four chemical parameters tested. Significant declines in ANC were observed ,from 2.08 to 5.91 µeq L^{-1} yr^{-1} among three elevation classes: 1,000-1,500 ft, 2,500-3,000 ft, and 4,500-5,000 ft. Nitrate concentrations were observed to have only one significant relationship, a decline of 0.566 µeq L^{-1} yr^{-1} for the 3,000-3,500 ft elevation class. Sulfate concentrations showed significant declines ranging from 0.832 to 1.31 µeq L^{-1} yr^{-1} for classes between 1,000-and 3,500-ft; whereas as above 3,500 ft a trend was not observed. Because results indicated a declining pH, ANC, and acid anions, the geochemical interpretation is that base cations must be declining to a greater extent than the acid anions. Further investigation is needed to explain these statistical outcomes.

Table 5. Time trend analysis modified from Robinson et al. (2008) for the period 1993-2002 for 10 elevation classes (ranges) in GRSM from 1,000-ft to >5,500 ft at 500-ft intervals. Using linear regression with the continuous dataset, significant models identified for each elevation range class and chemical parameter: pH, ANC, NO_3^-, and SO_4^{2-} ($p < 0.05$) showing model slope and (adjusted r^2).

Elevation Range (ft)	No. of Sites (data points)	Julian date coefficient: pH units yr^{-1} or µeq L^{-1} yr^{-1} (adjusted r^2)			
		pH	ANC	Nitrate	Sulfate
1,000-1,500	7 (175)	-0.0127 (0.67)	-5.91 (0.73)	-- (0.69)	-0.836 (0.55)
1,500-2,000	13 (234)	-0.0186 (0.71)	-- (0.88)	-- (0.36)	-1.31 (0.16)
2,000-2,500	16 (289)	-0.0260 (0.78)	-- (0.61)	-- (048)	-1.15 (0.65)
2,500-3,000	18 (305)	-0.0194 (0.61)	-2.08 (0.62)	-- (0.49)	-0.898 (0.83)
3,000-3,500	13 (307)	-0.0175 (0.41)	-- (0.31)	-0.566 (0.26)	-0.832 (0.78)
3,500-4,000	4 (71)	-- (0.70)	-- (0.61)	-- (0.33)	-- (0.59)
4,000-4,500	6 (90)	-- (0.61)	-- (0.44)	-- (0.44)	-- (0.45)
4,500-5,000	7 (109)	-0.0905 (0.51)	-5.08 (0.31)	-- (0.56)	-- (0.28)
5,000-5,500	3 (38)	-- (0.30)	-- (0.24)	-- (0.18)	-- (0.19)
> 5,500	3 (28)	-- (--)	-- (--)	-- (--)	-- (--)

Schwartz et al. (2014) assessed stream chemistry trends utilizing data from 1993 through 2009, differing from Robinson et al. (2008) in the analysis period and utilizing 92 sites with data varying per monitoring period based on availability (Fig. 2). Of the 92 sites, 43 were continuously monitored from 1993-1995 through 2009 as part of the park-wide monitoring effort (Appendix C). Schwartz et al. (2014) found that stream pH units increased significantly at 22 sites mostly in small annual increments ranging from 0.01 to 0.04 units, with a maximum of 0.15 units yr^{-1} ($p < 0.05$). Two stream sites decreased in pH over this monitoring time period; Porters Creek (Site 43) and Lower Rock Creek (Site 4) which both declined at 0.03 pH units per year. These two sites also declined in ANC at an annual rate of -1.57 and -3.22 μeq L^{-1}, respectively. Only seven streams were found with significant trends in ANC, five declining over time and two increasing. The three additional sites with declining ANC were not observed with a significant pH trend; they included Indian Camp below Albright Grove, Cosby Creek, and Silers Bald Shelter Spring (Sites 107, 114, and 218, respectively). The two sites with increasing ANC were Mill Creek above Abrams Creek (Site 173) and Beech Flats above US 441 Loop (Site 251), with ANC increases of 0.70 and 8.52 μeq L^{-1} yr^{-1}, respectively. Of the 92 stream survey sites assessed, 67 sites were observed to have no time trends for pH and ANC. Of the 43 long-term sites, approximately half were observed with no trends in pH and ANC, and no spatial patterns were evident based on elevation (Fig. 3). In Figure 3, two stream sites in the Cosby-Rock Creek watershed are shown in red dots denoting declining pH and ANC.

Significant changes in acid anion concentrations (Cl^-, SO_4^{2-}, and NO_3^-) showed mixed results over time among the 92 sites assessed in Schwartz et al. (2014) and provided in Appendix C. Chloride concentration trends increased at 19 stream sites, ranging from 0.38 to 1.41 μeq L^{-1} yr^{-1}, and decreased at 13 sites, ranging from -0.24 to -0.81 μeq L^{-1} yr^{-1}. Sulfate trends increased at 18 sites, ranging from 0.17 to 3.03 μeq L^{-1}, and decreased at 14 sites, ranging from -0.49 to -1.55 μeq L^{-1} yr^{-1}. Nitrate trends increased at 25 stream sites, ranging from 0.15 to 2.88 μeq L^{-1} yr^{-1}, and decreased at 12 sites, ranging from -0.29 to -5.32 μeq L^{-1} yr^{-1}. Annual increases in stream nitrate concentrations appeared to dominate over decreasing trends; however, 56 stream sites were still observed with no NO_3^- time trends. Of the 43 long-term monitored stream sites, two sites with the greatest annual increases in SO_4^{2-} concentrations were located at high-elevation locations, whereas sites with increasing NO_3^- concentration rates were located at lower park elevations (Fig. 4). Consistent with findings from Neff et al. (2013), these results indicate that multiple watershed factors (e.g., acid deposition rates, elevation, geology, vegetation, soils) and complex biogeochemical processes control acidification time trends uniquely per watershed.

Concentrations of base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) generally increased from 1993 to 2009 across GRSM (Appendix C). Of the base cations, calcium exhibited the greatest rates of increase among the 92 stream sites assessed, and many sites increased over 2 μeq L^{-1} yr^{-1}. Twenty sites were observed with increasing Ca^{2+} time trends, and only Site 270 (Beech Flats at Kephart foot-bridge) was observed with a decreasing trend. Of the 43 long-term monitoring sites, time trends for Ca^{2+} concentrations were not observed, except for the West Prong of the Little Pigeon River along US 441 where limestone chat is used for road traction during winter months (Fig. 5). Among the 92 sites, 23 sites were observed with increasing Mg^{2+} concentrations, ranging from 0.29 to 2.31 μeq L^{-1} yr^{-1}, and no sites were observed with decreasing trends. Additionally, stream sites with significantly

increasing time trends for K^+ and Na^+ included 21 and 22 sites, respectively ($p < 0.05$). Only one site showed a decreasing trend for K^+ and four sites with decreasing Na^+. Declines in K^+ are generally attributed to vegetation uptake, and Na^+ attributed to soil depletion.

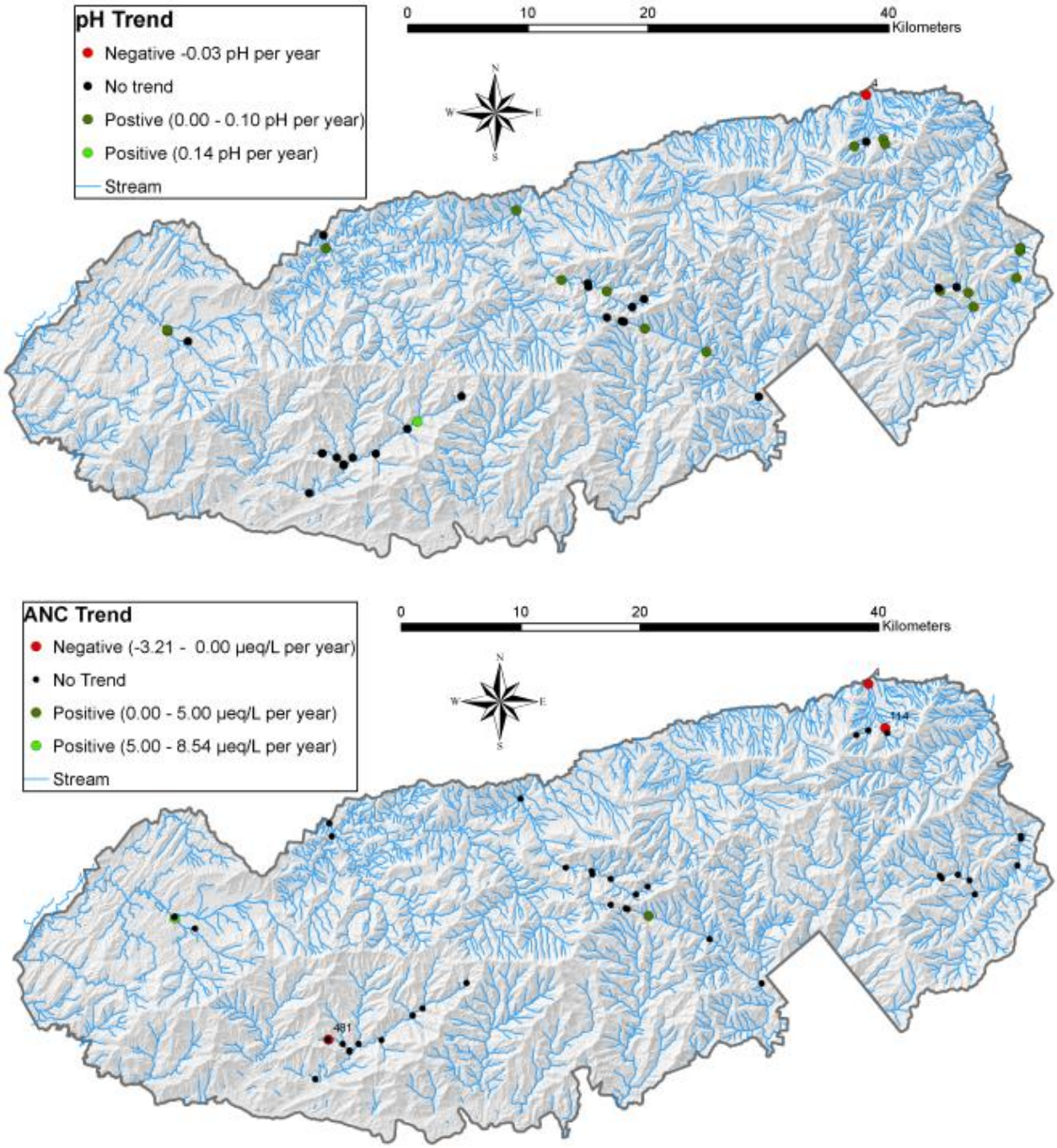


Figure 3. Temporal trends in stream pH and ANC concentrations (µeq yr^{-1}) between 1993 and 2009 for the 43 long-term park-wide monitoring sites (Schwartz et al. 2014).

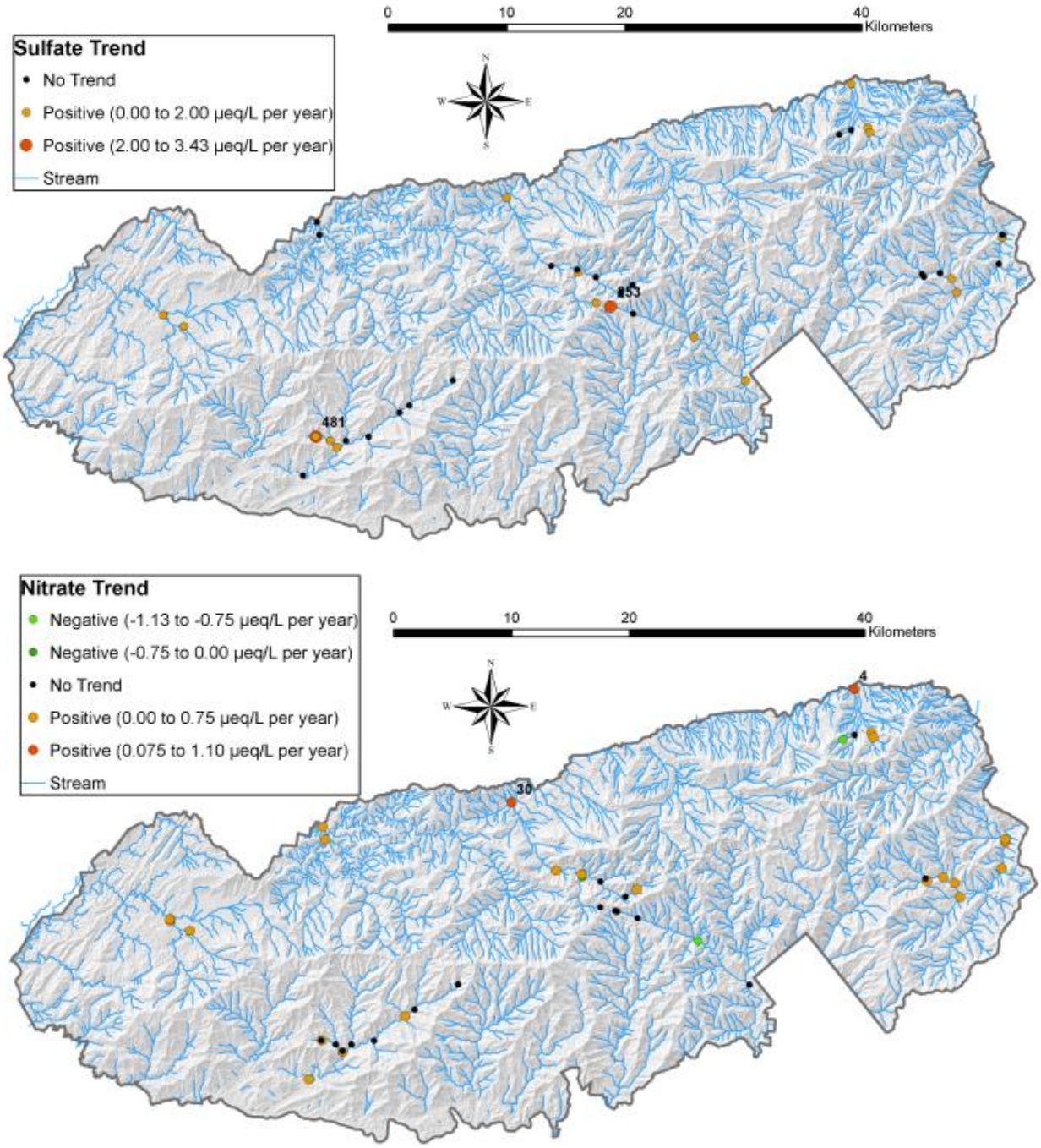


Figure 4. Temporal trends in stream nitrate and sulfate concentrations (µeq yr^{-1}) between 1993 and 2009 for the 43 long-term park-wide monitoring sites (Schwartz et al. 2014).

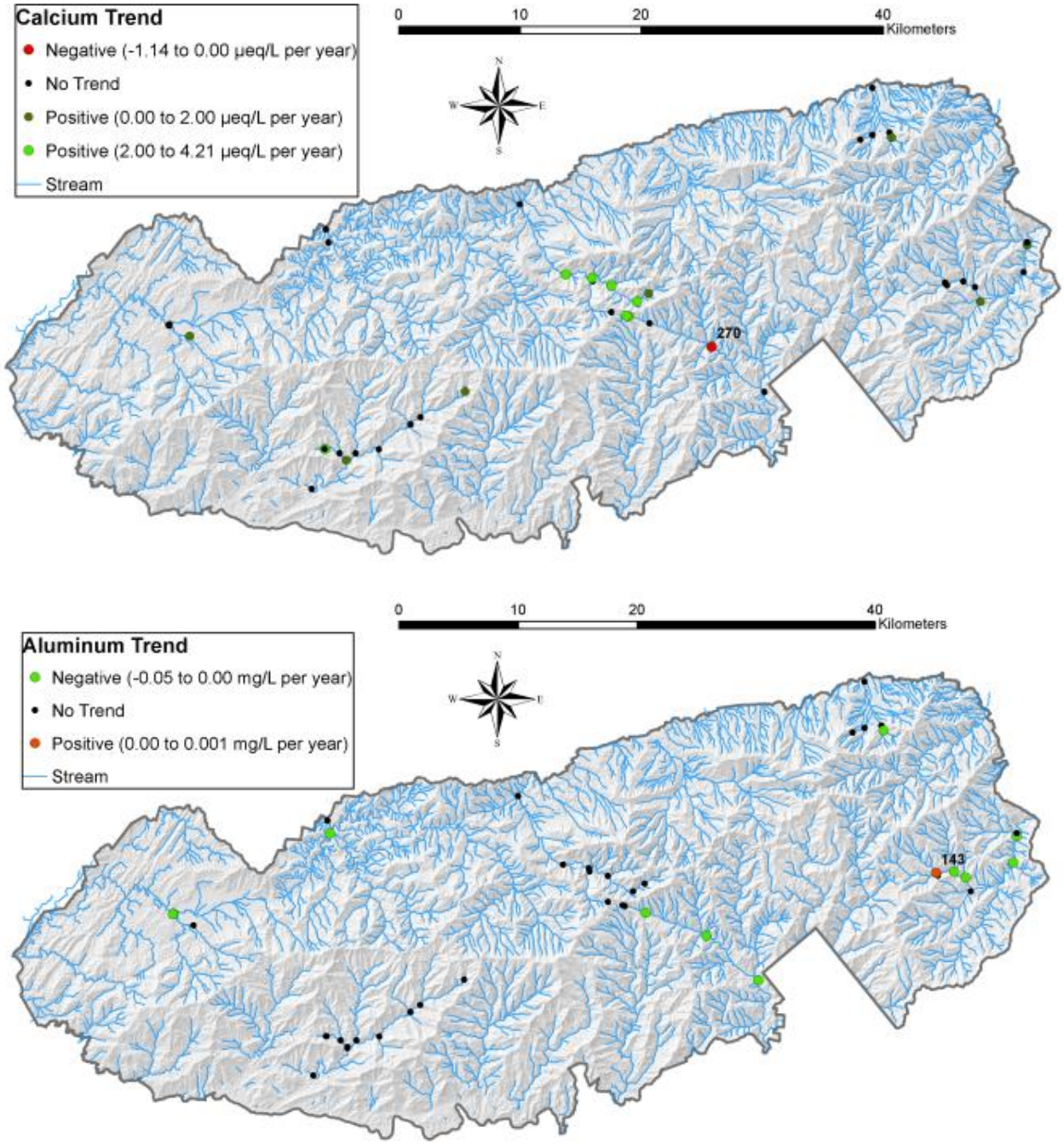


Figure 5. Temporal trends in stream calcium and aluminum concentrations (µeq yr^{-1}) between 1993 and 2009 for the 43 long-term park-wide monitoring sites (Schwartz et al. 2014).

Dissolved aluminum was the one metal assessed for time trends because of its potential as a toxicant to aquatic biota (Schwartz et al. 2014). Of the 92 stream survey sites assessed, 10 sites were observed with decreasing concentration rates in the range of -0.005 to -0.051 mg L^{-1}. yr^{-1}. Only one site was observed with an increasing Al time trend; it was Lost Bottom Creek at Palmer Creek (Site 143) at a rate of 0.008 mg L^{-1} yr^{-1}. Of the 43 long-term monitoring sites, higher elevation sites (>

4,000 ft) generally showed no time trends, except for one site on Beech Flats Prong below the road cut, and eight other park sites < 4000-ft showed a declining trend (Fig. 5). These results were for baseflow conditions, and as identified in Neff et al. (2013), Al concentrations increased significantly from baseflow to stormflow conditions in watersheds with Anakeesta geology. It is during precipitation events that Al, which is weakly attached to soil particles, is released and transported through the soil matrix to the stream. Baseflow water samples represent ambient conditions, and may not reflect the full potential impacts of acidic deposition of the forest and aquatic ecosystems.

Noland Divide Monitoring Station

The most detailed analysis of temporal trends in GRSM is from the Noland Divide Watershed (NDW) monitoring station. Cai et al. (2011b) investigated annual trends and seasonal patterns in precipitation, stream flow, and stream chemistry for data from 1991 to 2007. Trend analysis was conducted by a Seasonal Kendall Tau (SKT) test for a significance level of 0.05 (Helsel and Hirsch 2002). Throughfall precipitation significantly declined at -5.76 cm yr^{-1} over the entire period, which included drought periods in 1993, 2000-2001, and 2005-2007. Significant trends in throughfall chemistry concentrations included increases in NO_3^-, NH_4^+, N (NO_3^- and NH_4^+ combined) at rates equal to 1.24, 0.08, and 2.04 μeq L^{-1} yr^{-1}, respectively. Base cation concentrations increased 0.46, 3.00, and 1.28 μeq L^{-1} yr^{-1} for Na^+, Ca^{2+}, and Mg^{2+}, respectively. Concentration increases could be attributed to the declines in throughfall precipitation where ions collect on forest vegetation before being washed from the canopy to the soil. Sulfate, chloride, and potassium concentrations and pH remained statistically similar over time. Throughfall SO_4^{2-} remained at about 30 μeq L^{-1} yr^{-1} from 1991 to 2007. Trends for stream chemistry included declines in NO_3^- and N at -0.56 and -0.61 μeq L^{-1} yr^{-1}, respectively; and Mg^{2+} increased at 0.19 μeq L^{-1} yr^{-1}. No trends in stream chemistry were observed for pH, SO_4^{2-}, NH_4+, Cl^-, Na^+, K^+, and Ca^{2+}. Examining mass flux trends over time for throughfall chemistry, SO_4^{2-} declined at -356.16 eq yr^{-1}, whereas NH_4^+, Ca^{2+}, and Mg^{2+} increased at 95.76, 496.08, and 167.64 eq yr^{-1}, respectively. Mass export from the watershed was only observed for nitrogen constituents, where NO_3^-, flux increased over the analysis period at 449.88 eq yr^{-1}, and NH_4^+ at 101.28 eq yr^{-1} (N increased as 541.32 eq yr^{-1}).

Understanding the biogeochemical processes associated with the observed long-term trends described in Cai et al. (2011b) can be best explained by comparing mass flux inputs (throughfall deposition) and stream export (Fig. 6). Cai et al. (2010) conducted this comparison in NDW with data from 1991 through 2006. Based on a watershed-scale ion input-output budget, total nitrogen mass (NO_3^- and NH_4^+) was retained at 32% and K^+ mass was 71%, with both ion retentions assumed to be due to vegetation uptake. Base cation mass for Ca^{2+}, Mg^{2+}, and Na^+ were observed to export more mass than entering through deposition at 10%, 16%, and 18%, respectively. Long-term watershed loss of base cations from soils could result in stream acidification in the high-elevation, small headwater streams, and is more pronounced during episodic stormflows causing base cation dilution reducing the waters ability to buffer inputs of acid anions (Neff et al. 2013). Deyton et al. (2009) reported stream acidification from multiple causes such as elevated SO_4^{2-} and NO_3^- inputs, and base cation dilution.

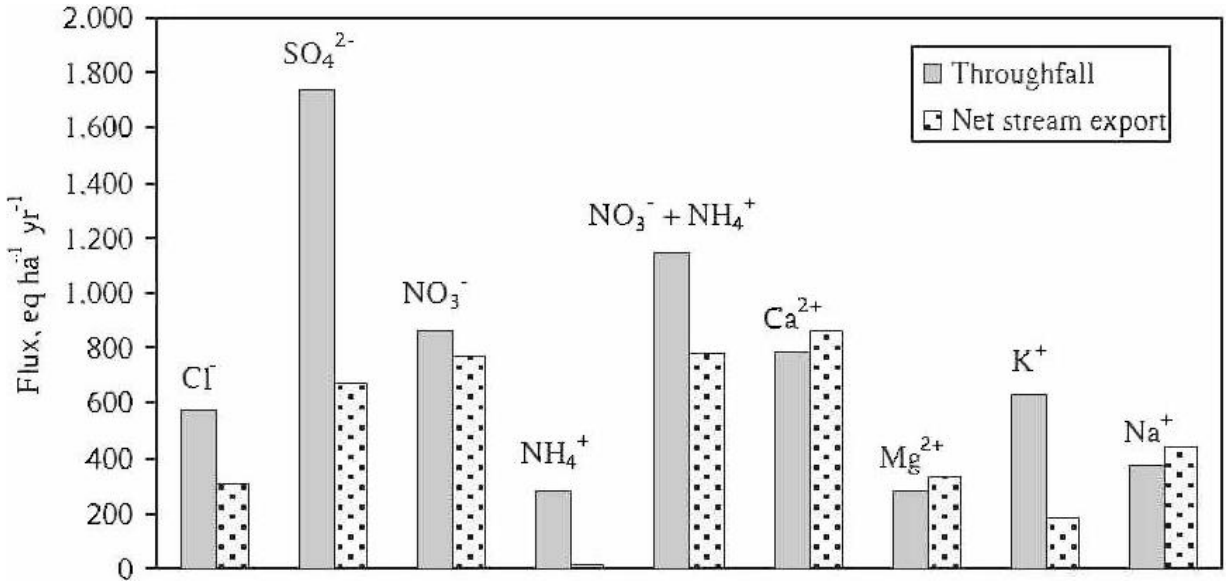


Figure 6. Comparison of mean annual fluxes of throughfall net input and stream net export at GRSM Noland Divide Watershed research site for the period 1991 – 2006 (Cai et al. 2010).

In Cai et al. (2010), annual deposition flux of SO_4^{2-} per throughfall averaged 1,735 eq ha^{-1} yr^{-1}, and export through the stream averaged 671 eq ha^{-1} yr^{-1}, resulting in retention of 61% in the watershed over the period 1991-2006. Sulfate retention is assumed to be stored in soils by particle adsorption due to the acidic conditions of the soil water (Cai et al. 2011a, 2012). If this is the case, one concern with the long-term storage of SO_4^{2-} is the potential rapid desorption from soils if soil water pH increases and/or SO_4^{2-} concentration decreases. Cai et al. (2011a) reported that if soil water pH increased above approximately 6.0 and sulfate concentrations dropped below 15 μmol L^{-1}, sulfate desorption would dominate over adsorption. The other possibility is that sulfur is retained in the soil organic matter (Mitchell et al. 2001); however, data is lacking on this microbial process in GRSM.

Stream Sulfate Trends

In general, water quality monitoring sites at high-elevation streams were limited in GRSM (Tables 4 and 5). The numbers of sites with available data (1993-2002) per elevation range used in Robinson et al. (2008) were: six sites for > 5,000 ft, seven sites for 4,500-5,000 ft, and six sites for 4,000-4,500 ft. Trend analyses for stream sulfate were completed by Schwartz et al. (2014) for multiple periods in order to investigate whether sulfate mass export rates have changed due to soil chemistry conditions favoring release and ion export. Four period summaries were statistically analyzed per 1,000-ft elevation ranges from < 1,000 ft to > 5,000 ft MSL; they were: 1993-1995, 1993-1996, 1993-2002, and 1993-2009 (Table 4). Utilizing a Tukey HSD means comparison test ($p < 0.05$), mean sulfate concentrations for 1993-1995 and 1993-2002 were not significantly different among elevation ranges, and the period 1993-1996 was not observed with a consistent concentration gradient among elevation classes. However, for 1993-2009, mean sulfate concentrations were significantly different among elevation classes, increasing with elevation, where mean sulfate was 43.63 μeq L^{-1} for sites within 1,000-2,000 ft, and 119.80 μeq L^{-1} for sites > 5,000 ft. In contrast to examining SO_4^{2}- differences among the elevation classes within the four periods, stream SO_4^{2-}

increased for the earlier periods (1993-1995, 1993-1996) compared with the long-term period (1993-2009) for all elevation classes. Qualitatively, the greatest difference occurred at the highest elevation class (> 5,000 ft) from 50.50 ueq L^{-1} for 1993-1995 to 119.80 ueq L^{-1} (1993-2009). These results in general suggest that SO_4^{2-} concentrations among high-elevation streams may be increasing over time since the 1990s. However, interpretation needs to be cautious due to the limited number of sites among high-elevation watersheds after 2002 (n = 4 for 3,000-4,000 ft, n = 6 for 4,000-5,000 ft, and n =1 for > 5,000 ft), and sites used to compute means varied among periods per elevation class. For example, in Schwartz et al. (2014), where all available data (1993-2009) were utilized, there was not a significant sulfate gradient with elevation (Table 3). In addition, evidence suggesting stream SO_4^{2-} concentrations have not changed in recent years was observed from the long-term NWD study site where stream SO_4^{2-} has not changed from 1991 through 2012 (Fig. 7).

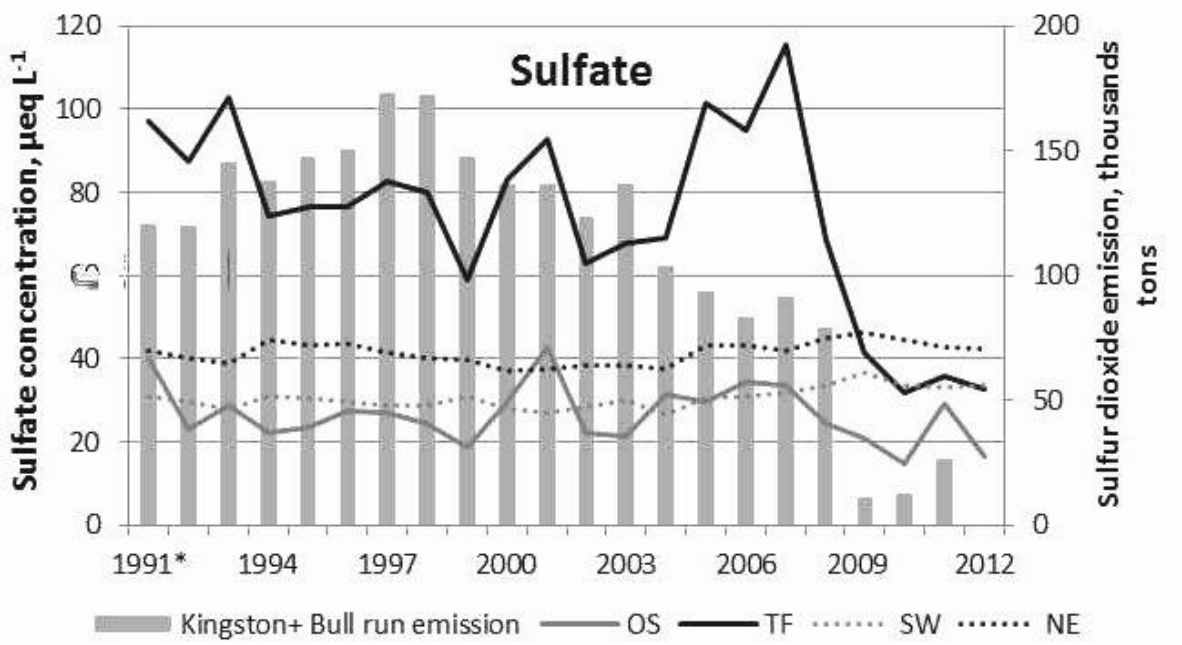


Figure 7. Comparison of Noland Divide SO_4^{2-} concentration in deposition (annually volume-weighted concentration), annual mean stream concentrations (µeq L^{-1}), and total sulfur dioxide emissions from Bull Run and Kingston coal-fired power plants. Note: OS = open site precipitation, TF = throughfall, and SW and NE are the southwest and northeast streamlets.

Emphasis on trends in stream sulfate concentration is due to the fact that sulfate deposition has decreased by an order of magnitude across the eastern US, including GRSM (Driscoll et al. 1998; Chen et al. 2009; NADP 2012). Reductions in sulfate deposition could change soil water chemistry (increased pH and decreased SO_4^{2-} concentration) promoting mass export to streams; however, biogeochemical processes are complex and other factors may govern the potential for sulfate export from soils to streams. For example, factors may include increased NH_4^+ deposition enhancing nitrogen mineralization and nitrification, and weathering rates of base cations. Using two coal-fired power plants within 100 miles of GRSM (Bull Run and Kingston) as a surrogate for regional emission trends, SO_4^{2-} emissions have declined from about 135,000 tons annually before 2003 to < 30,000 tons after 2008 (Fig. 7). These power plants are operated by the Tennessee Valley Authority

(TVA). Between 2003 and 2008, emission reductions from these TVA power plants were due to the use of low-sulfur coal and other operational procedures, and after 2008, reductions resulted from installation of air pollution control equipment. Annual peaks in throughfall SO_4^{2-} concentrations co-occur during dry years (Fig. 7), where regional droughts were observed during 1993, 2000-2001, and 2005-2007, likely due to build-up of dry SO_4^{2-} deposition prior to a rainfall event.

Because of the regional differences in SO_4^{2-} emissions pre-2003, and during 2003-2008, and 2009-2012+, these periods become distinct "treatment" blocks for statistical analyses investigating whether soil conditions have changed to promote export of stored sulfate from soils in higher elevation watersheds (Fig. 7). The pre-2003 period was analyzed in Robinson et al. (2008), providing an excellent baseline to compare and detect trends. One objective of this statistical reassessment was to examine whether shifts in stream acidity have occurred since Robinson et al. (2008).

A preliminary inspection of the pH plotted from 1993 through 2012 suggests that three periods for statistical reassessment would be valuable in order to observe shifts in water quality trends (Fig. 8). Visual inspection of plotted pH data (Fig. 8) identified three general patterns.

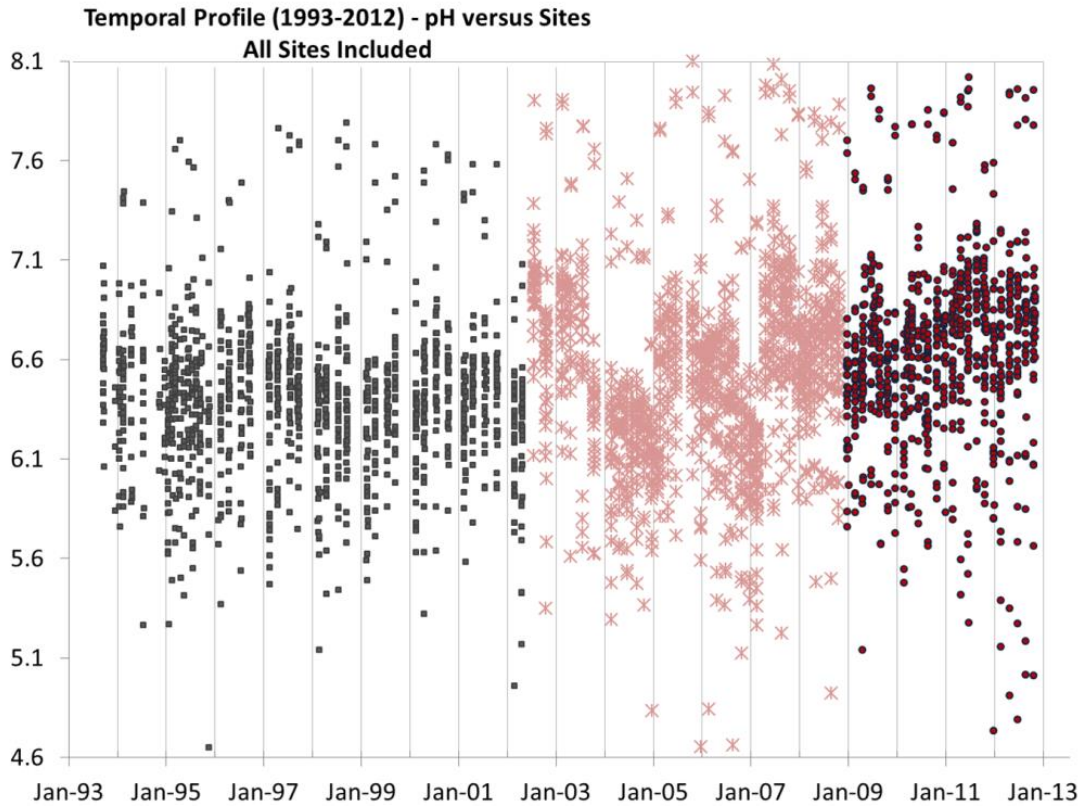


Figure 8. Plot of pH data from the GRSM park-wide stream survey collected from 1993 through 2012.

Stream pH between 1993 and 2002 consists of a monotonic block of data with a slight decreasing trend in pH over that time (Robinson et al. 2008). Data from 2003-2008 was visually observed to have greater variance compared with the 1993-2002 period, and some evidence of increased pH.

Data between 2009 and 2012 consisted of a generally static pH to slightly increasing trend in pH over that time period

2.2 Study Design

2.2.1 Study Objectives

The overall goal of this study, as previously stated in Chapter 1, was to provide useful information supporting the site selection for the water quality monitoring component of GRSM's Vital Signs Program. With stream elevation being a dominant factor governing water quality (Section 2.1), a question for the program is what elevation ranges best distinguish key differences in stream chemistries. Two assessment approaches were completed in this study; one exclusively based on spatial relations of stream chemistry with elevation, and the second on a temporal trends analysis per elevation class. In order to compare, approaches in this study aligned with the analyses completed by Robinson et al. (2008), which summarized pH, ANC, SO_4^{2-}, and NO_3^- among elevation ranges and trends for data between 1993 and 2002 (Tables 1 and 5). Based on a visual inspection of stream pH (Fig. 8), water quality data since 2003 appears to have generally shifted from lower acidity conditions to greater acidity with a greater variability among observations between 2003 and 2008. The period 2003-2008 appears to reflect a transition with greater pH variability and corresponds to reduced sulfate emissions from two TVA power plants (Bull Run and Kingston), which are in relatively close proximity to GRSM (Fig. 7). Therefore, this study focuses on assessing water quality differences among the three periods: 1993-2002, 2003-2008, and 2009-2012. Descriptions of the two main objectives are as follows:

Influence of Elevation on Stream Chemistry: Identifying similarities in water quality per elevation ranges addresses the key question as to placement of monitoring sites. Adjacent elevation ranges with similar water quality can be combined in order to reduce statistical redundancy. A hierarchical clustering analysis was used to detect comparable elevation ranges that at least one or more monitoring stations must be located within the selected vital signs watersheds. By repeating this analysis per different time periods, information is gained on how relations between water quality and elevation may be changing over time; although the question of water quality change over time was specifically addressed next.

Long-term Temporal Trends in Stream Chemistry per Elevation. Because elevation is a dominant factor reflecting differences in acid deposition rates and biogeochemical processes associated with watershed characteristics (geology, physiographical features, soils, forest cover), temporal trends in stream chemistry were explored for varying elevation ranges. In general, the trend analysis in this study followed the regression approaches used in Robinson et al. (2008). An ANOVA analysis was added to specifically explore whether differences have occurred among the three time periods (1993-2002, 2003-2008, and 2009-2012).

2.2.2 Dataset Development

Two main datasets were used in this study: 1) 90 stream sites for the period from 1993 to 2002, and 2) 37 stream sites of the 43 long-term monitoring sites from 1993 to 2012. The 90-site dataset was compiled in Robinson et al. (2008) for four chemical parameters: pH, ANC, SO_4^{2-}, and NO_3^-. Means for the four chemical parameters were summarized by ten elevation classes from 1,000 ft through >

5,500 ft on 500-ft intervals. After 2002, the park-wide monitoring program reduced its number of sampling locations to 43 sites. For the same chemical parameters as used in Robinson et al. (2008), the second dataset applied in this study was comprised of 37 of 43 sites summarized for six elevation classes from 1,000 ft to > 4,500 ft (Table 6, Appendix A).

Table 6. Stream chemistry sites in GRSM used for a statistical reassessment of spatial patterns and temporal trends from 1993 to 2012, per six elevation classes from 1,000 ft to > 4,500 ft. Total number of sites = 37 with site identification numbers defined in Appendix A by lat./long. locations and site elevations.

Elevation Class	Elevation Range	N	Site ID Number
1	1,000 - 2,000 ft	5	13, 23, 24, 30, 479
2	2,000 - 2,500 ft	9	4, 311, 268, 480, 310, 438, 147, 148, 484
3	2,500 - 3,000 ft	13	114, 481, 482, 149, 66, 492, 137, 293, 270, 493, 485, 144, 224
4	3,000 - 3,500 ft	4	143, 142, 73, 71
5	3,500 – 4,500 ft	4	74, 221, 251, 233
6	> 4,500 ft	2	253, 234

Six sites (173, 174, 337, 252, 488 and 489) of the 43 park-wide monitoring sites were removed from the dataset because of geological influences or because they were located in the lowest elevation class, which is less impacted by acid deposition and is buffered by higher base cations. The original study objectives were to investigate areas impacted by acidic deposition. Sites 252 and 237 have a large Anakeesta formation component, which consists of sulfidic shale with pyrite, and oxidizes to generate acidity. Sites 488 and 489 were located in the Abrams Creek watershed, which has an underlying carbonaceous geology adding alkalinity to the stream water. Sites 173 and 174, also in the Abrams Creek watershed were not used because they were in the lowest elevation class.

Various data quality statistical tests were performed on the datasets. Normality was checked using normal probability plots, where each variable was plotted against residuals to check for curvature, randomness, and heteroscedasticity (unequal variance). Multicollinearity was tested by "post-hoc" step-wise regression analysis of environmental factors; variance inflation factors (VIF) greater than 10 indicate potential multi-collinearity. All VIFs were less than 10; thus, there were no multi-collinearity issues in these datasets. Visual inspection of residuals sometimes suggested heteroscedasticity, which was confirmed or refuted by applying a Brown and Forsythe test. Influence of Observations was checked using Cook's Distance (CD), DFFITS, and DFBETAS. Influential of individual observations or outliers were most significant in data from years prior to 2002, and in ANC data. Individual data points were eliminated from the datasets if they clearly failed any of these data quality checks.

2.3 Spatial Analysis: Statistical Classification

2.3.1 Methods: Hierarchical Clustering Analysis

Using an agglomerative hierarchical clustering method based on four chemical attributes (pH, ANC, NO_3^-, and SO_4^{2-} means), similarities among these attributes collectively for different elevation ranges

were investigated. The Ward's Method for group linkage and Euclidean distance measures were applied in this analysis utilizing PC-ORD v.5 (McCune and Mefford 1999). The four statistical attributes (chemical parameters) available for the cluster analysis were justified as: pH is the main indicator of acidity, ANC is a balance of anions and cations, nitrate showed a strong elevation gradient in previous studies, and sulfate did not show a pattern associated with elevation. Though these parameters are not statistically independent, they represent the key parameters that characterize stream acidification. In addition, they were the parameters used in Robinson et al. (2008), therefore valuable from a comparison perspective.

Cluster analyses were completed for water chemistries reported for: 1) the ten elevation ranges in Robinson et al. (2008) utilizing 90 sites for data between 1993 and 2002 (Table 5); and 2) the six elevation ranges summarized for the 37 long-term monitoring sites and individually tested for the three periods: 1993-2002, 2003-2008, and 2009-2012 (Table 6, Appendix A). The 90 sites were located across the park among many watersheds (Fig. 2), whereas the subset of 37 sites only included six watersheds (Cataloochee Creek, Oconaluftee River, West Prong of the Little Pigeon River, Little River, Hazel Creek, and Cosby-Rock Creek). Cluster analysis for the period 1993-2002 was repeated utilizing the 37-site dataset in order to compare hierarchical patterns with those from the 90-site dataset. This comparison was important in order to assess whether the six watersheds of the 37-site dataset replicates collectively the watershed characteristics of the 90-site dataset of Robinson et al. (2008). Indirectly, this comparison provides qualitative information on watershed selection within GRSM for the Vital Signs Program.

2.3.2 Results: Clustering Analysis per Elevation Range Based on Stream Chemistry

Based on the 90-site dataset for the years 1993-2002 and 10 elevation ranges (Table 1), agglomerative hierarchical clustering found four distinct elevation classes (Fig. 9). The elevation classes were:

1) 1,000-2,000 ft (Ele2 - Ele3);
2) 2,000-3,500 ft (Ele4 - Ele6);
3) 3,500-5,000 ft (Ele7 - Ele9); and
4) > 5,000 ft (Ele10 - Ele11).

For the same time period, comparison of results to a cluster analysis based on the 37-site dataset for six elevation ranges (Table 6) resulted in a different hierarchical pattern, and groupings were not sequential along the elevation gradient (Fig. 10a). Two dissimilar groupings included Elevation Classes 1 and 3, and Classes 4-6, indicating that the 3,000-ft elevation represents a distinctive shift in stream chemistry spatially. The 3,500-ft elevation was determined to be a change-point from lower to higher elevation stream chemistries (Fig. 9). The three highest elevation ranges were found to be similar (Fig. 10a), though Class 6 (> 4,500 ft) was slightly different from Classes 4 and 5 (3,000 ft to 4,500 ft). Class 2 (2,000 ft - 2,500-ft) was unique but more similar with the group representing Classes 4-6. Qualitatively, this comparison suggests that the dataset of 37 included Elevation Classes 1 and 3, and Classes 4-6, indicating that the 3,000-ft elevation represents a distinctive shift in stream chemistry spatially.

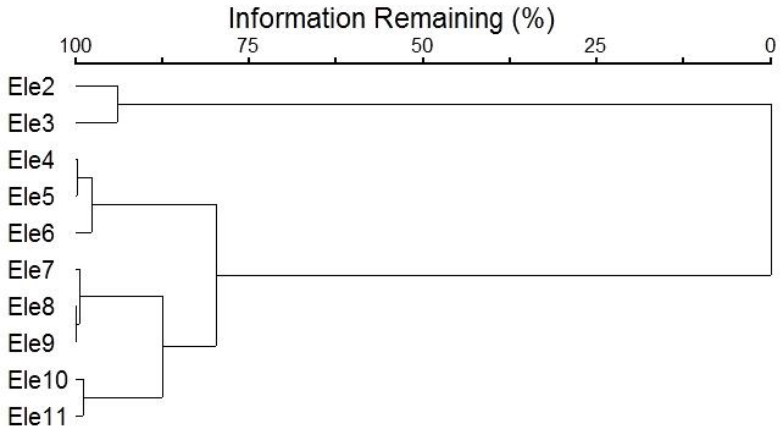


Figure 9. Agglomerative hierarchical clustering of elevation classes based on water quality (pH, ANC, SO_4^{2}, and NO_3^{-}). Data from Robinson et al. (2008) for 90 sites and the period 1993-2002. Elevation Class 2 (Ele2) is 1,000-1,500 ft and Ele11 is > 5,500 ft; all other elevation classes are in 500-ft increments between Ele2 and Ele11.

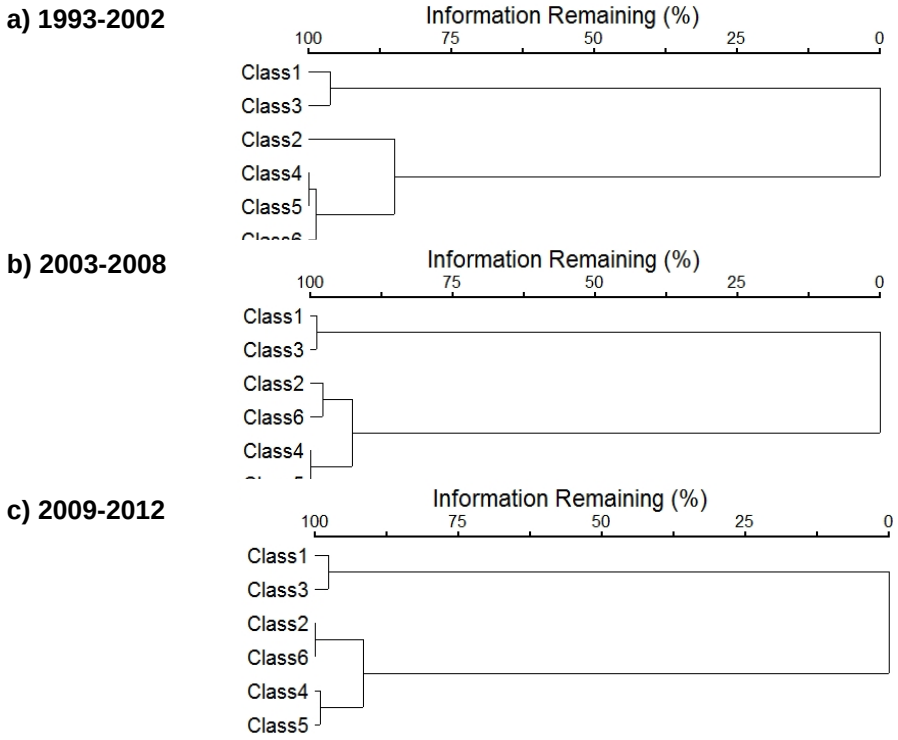


Figure 10. Agglomerative hierarchical clustering of elevation classes based on water quality (pH, ANC, SO_4^{2}, and NO_3^{-}) for a select subset of 37 sites for periods: a) 1993-2002, b) 2003-2008, and c) 2009-2012. Elevation bands are Class 1 = 1,000-2,000-ft; Class 2 = 2,000-2,500 ft, Class 3 = 2,500-3,000 ft; Class 4 = 3,000-3,500 ft; Class 5 = 3,500-4,500 ft; and Class 6 = >4,500.

The 3,500-ft elevation was determined to be a change-point from lower to higher elevation stream chemistries (Fig. 9). The three highest elevation ranges were found to be similar (Fig. 10a), though Class 6 (> 4,500 ft) was slightly different from Classes 4 and 5 (3,000 ft to 4,500 ft). Class 2 (2,000 ft - 2,500-ft) was unique but more similar with the group representing Classes 4-6. Qualitatively, this

comparison suggests that the dataset of 37 sites differs in its collective representation of stream chemistries from the 90-site dataset due to watershed factors and site locations along the elevation gradient. Notably, the small number of sites at the higher elevations greatly limits this analysis to detect spatial differences among elevation classes.

Based only on the 37 long-term monitored sites, patterns of hierarchical clustering of elevation classes for the two periods 2003-2008 and 2009-2012 were similar, but differed from the period 1993-2002 as noted above (Fig. 10). The periods 2003-2008 and 2009-2012 were observed with three groupings: 1) Classes 1 and 3 (1,000-2,000 ft and 2,500 and 3,000 ft), 2) Classes 4 and 5 (3000-3,500 ft and 3,500-4,000 ft), and 3) Classes 2 and 6 (2,000-2,500 ft and > 4,500 ft). In these two period analyses, Elevation Class 2 (2,000-2,500 ft) was not consistent with a sequential gradient from lower to higher elevations.

Elevation Class 2 was low for mean pH and ANC compared to adjacent elevations classes, and mean nitrate and sulfate were relatively high comparatively (Table 7). It is likely that the Cosby Creek low-elevation sites are influencing these results (Figs. 3 & 4). The influence of winter application of road chat in the Oconaluftee River and West Prong Little Pigeon River watersheds may have resulted in relatively high pH and ANC means for Elevation Class 3 compared with others. To provide evidence that these three watersheds may be overly influencing the summary chemistry, a data summary was conducted eliminating Cosby Creek, Oconaluftee River, and the West Prong Little Pigeon River (Appendix D). Summarizing the water quality data for only Cataloochee Creek, West Prong Little Pigeon River, and Hazel Creek, pH, ANC, nitrate, and base cations were observed with strong and continual elevation gradients.

Table 7. Stream chemistry summaries for pH, ANC, NO_3^- and SO_4^{2-} for six elevation classes in GRSM for three assessment periods: 1993-2002, 2003-2008, and 2009-2012. Stream sites are defined in Table 6. N is the total number of sampling events.

			pH				ANC μeq/L			
Period	**Class**	**Elevation (ft)**	**N**	**Minimum**	**Maximum**	**Mean**	**N**	**Minimum**	**Maximum**	**Mean**
1993-2002	1	1,000 – 2,000	327	4.96	7.90	6.57	327	-20.74	1534.47	149.76
	2	2,000 – 2,500	393	5.32	7.00	6.25	392	-7.43	182.95	40.75
	3	2,500 – 3000	400	4.65	8.24	6.44	398	-19.97	1624.49	158.44
	4	3,000 – 3,500	121	6.18	7.11	6.50	120	24.45	178.00	75.84
	5	3,500 – 4,500	116	6.07	7.05	6.50	116	41.34	162.76	77.06
	6	> 4,500	110	5.77	7.06	6.41	110	15.64	165.02	68.01
2003-2008	1	1,000 – 2,000	255	5.22	7.95	6.65	255	-37.09	1314.56	173.48
	2	2,000 – 2,500	289	4.83	7.07	6.32	289	-1.88	145.95	42.20
	3	2,500 – 3000	299	4.65	8.10	6.55	299	-26.45	1591.06	172.82
	4	3,000 – 3,500	119	5.95	7.06	6.58	119	23.36	128.28	69.90
	5	3,500 – 4,500	35	5.98	7.03	6.50	35	36.37	115.80	77.84
	6	> 4,500	97	5.79	7.05	6.44	97	6.73	130.63	55.68
2009-2012	1	1,000 – 2,000	191	5.42	8.02	6.77	191	-0.02	1377.93	164.72
	2	2,000 – 2,500	212	4.91	7.28	6.47	212	-11.74	174.52	44.45
	3	2,500 – 3000	228	4.73	7.96	6.68	228	-18.28	1535.69	160.14
	4	3,000 – 3,500	97	6.20	7.08	6.68	97	25.70	107.58	64.13
	5	3,500 – 4,500	29	6.30	7.11	6.77	29	40.10	115.94	73.55
	6	> 4,500	76	4.24	7.09	6.52	76	-3.92	114.28	46.15
1993-2002	1	1,000 – 2,000	275	0.00	49.94	12.04	325	12.32	85.01	36.09
	2	2,000 – 2,500	377	1.37	73.76	26.62	390	0.00	159.51	51.68
	3	2,500 – 3000	365	0.00	96.13	26.14	391	0.00	262.37	54.00
	4	3,000 – 3,500	105	2.16	28.29	11.90	119	12.34	77.74	25.16
	5	3,500 – 4,500	66	1.23	10.55	4.35	116	7.51	79.98	26.14
	6	> 4,500	81	1.56	60.46	21.13	110	14.71	61.16	28.35

Table 7 (continued). Stream chemistry summaries for pH, ANC, NO_3^- and SO_4^{2-} for six elevation classes in GRSM for three assessment periods: 1993-2002, 2003-2008, and 2009-2012. Stream sites are defined in Table 6. N is the total number of sampling events.

			pH				ANC μeq/L			
Period	**Class**	**Elevation (ft)**	**N**	**Minimum**	**Maximum**	**Mean**	**N**	**Minimum**	**Maximum**	**Mean**
2003-2008	1	1,000 – 2,000	252	0.50	62.75	16.56	261	10.00	93.23	38.85
	2	2,000 – 2,500	296	0.62	67.12	29.20	298	11.64	152.55	48.19
	3	2,500 – 3000	297	0.13	95.72	27.69	308	10.44	490.01	54.25
	4	3,000 – 3,500	121	1.87	55.67	17.51	123	13.88	61.31	29.04
	5	3,500 – 4,500	30	1.45	26.48	7.59	37	12.18	117.46	30.54
	6	> 4,500	98	1.09	72.79	24.88	101	10.02	65.53	34.31
2009-2012	1	1,000 – 2,000	191	0.22	62.14	16.31	190	14.61	113.83	39.63
	2	2,000 – 2,500	212	4.43	72.17	30.08	212	13.45	125.36	47.41
	3	2,500 – 3000	228	1.04	72.16	26.23	228	13.59	317.63	58.15
	4	3,000 – 3,500	97	0.54	34.67	18.72	97	19.89	46.66	29.33
	5	3,500 – 4,500	29	0.21	83.68	6.44	29	16.78	109.18	36.16
	6	> 4,500	76	0.16	79.04	32.17	76	15.72	63.32	37.05

2.4 Temporal Trend Statistical Analysis

2.4.1 Methods: Temporal Trend Statistical Analysis

Statistical analysis for time trends were conducted applying three techniques: 1) step-wise multiple regression accounting for seasonality factors and related chemical parameters; 2) linear regression using Julian date as the only independent variable; and 3) ANOVA means separation comparison between time periods and elevation classes. Following the statistical analysis by Robinson et al. (2008), the focus was on stream chemistry changes for pH, ANC, SO_4^{2-}, and NO_3^- as explained in Section 2.3.1. The time-trend analyses were completed on stream data collected for 37 sites of the 43 sites with the longest GRSM collection history between 1993 and 2012 (Table 6).

Step-wise Multiple Regression Analysis

Step-wise multiple regression analysis was performed on 37 sites (Table 6) from 1993 to 2012 (n = 3,116). Stream chemistry parameters as dependent variables included pH, ANC, SO_4^{2-}, and NO_3^-. Independent variables possibly influencing the dependent variables and statistically applied in the regression analysis included: conductivity, chloride concentration, sum of base cation (BC) concentrations (calcium, sodium, potassium, and magnesium), Julian date, and two seasonality factors [sine(θ) and cosine(θ)]. Theta (θ) used for the seasonality factors was defined as a sampling date's "fraction of year" times 2π (e.g., April 2nd is 0.25 of a non-leap-year; $\theta = 0.25 \times 2\pi = 1.5708$). As defined, sine(θ) and cosine(θ) only take on values between 1 and -1. SPSS v.19 software was used to complete the statistical analysis.

For each combination of environmental factor and stream chemistry parameter, the statistical analysis yielded a "relative weight" value (F-statistic), indicative of how strongly or weakly the factor influenced the stream chemistry variable. The same analysis yielded a Type-I error probability value (α), which was used to classify an environmental factor as being either influential on pH, ANC, SO_4^2, and NO_3^- ($\alpha \leq 0.05$), or not influential ($\alpha \geq 0.10$). Factors found not to influence the dependent chemical variable were disregarded during model development. Linear correlation between ANC and pH, and BC and pH, were improved by a log base-2 transformation of their values.

Linear Regression Analysis on Time Trends

Four stream chemistries (pH, ANC, SO_4^{2-}, and NO_3^-) as dependent variables were linearly regressed against Julian date as a predictor variable. This time-trend analysis was performed on two monitoring periods 1993-2002 and 2003-2012 for six elevation classes as defined in Table 6, and using Julian date as the independent variable. Between years 2002 and 2003 there appears to be a pH change point from declining units to increasing (Fig. 8). This analysis represents two periods with nine years each of stream chemistry data. In order to assess the observed period of higher variability in stream pH from 2003-2008, this time-trend analysis was repeated for three periods 1993-2002, 2003-2008, and 2009-2012. These three periods also coincide with local power plant emissions, where incremental emission reductions were observed in 2003 and 2009 (Fig. 7). This regression followed the procedure by Robinson et al. (2008) where annual means of chemical parameters were used and sequenced in time by annual Julian date to represent change per year. SPSS v.19 was used to calculate regression slopes.

ANOVA Means Separation Comparison Analysis

ANOVA means separation comparison was conducted on 18 data groups (three time periods x six elevation classes) to evaluate statistically significant differences for four chemical parameters (pH, ANC, SO_4^{2-}, and NO_3^-). The ANOVA test compares a calculated F-statistic to a critical F-statistic, and calculates a probability of the comparison being a true difference and not due to random noise. Data populations must be characterized by a normal distribution and constant variance for ANOVA mean-separation to be valid. Normality was checked visually with a Quartile-Quartile (Q-Q) plot and variance was checked using the Brown-Forsythe test. The ANOVA test output indicates if there are any group differences in the dataset being tested but it does not identify which groups are different. A Bonferroni means separation test was performed using JMP v.11.

2.4.2 Results: Regression Analysis of Time Trends Among Elevation Bands

Step-wise Multiple Regression Analysis

Step-wise multiple regression models for pH, ANC, nitrate, and sulfate found significant time trends (per Julian date variable; $p < 0.05$), with increases from 1993 to 2012 (Table 8). Model adjusted r^2 values for pH, ANC, nitrate, and sulfate were 0.630, 0.964, 0.498, and 0.720, respectively. Models for pH and ANC identified that these chemical parameters were dominantly influenced by increased base cations over time (2003-2012), and inversely by declining NO_3^- and SO_4^{2-}. The ANC model also found Cl^- to be a significant independent variable. ANC represents the sum of protons, anions, cations, and inorganic/organic constituent chemical charges; therefore, ANC model results indicate that ANC is influenced by both declining NO_3^- and SO_4^{2-} and increasing base cations. Seasonality was also identified as a significant independent variable in three regression models (pH, ANC, and nitrate), but not for the sulfate model. Models for pH and ANC appeared to be cross-correlated with NO_3^- and SO_4^{2-} as independent variables.

Table 8. Step-wise multiple regression analysis showing best-fit models for pH, acid neutralizing capacity (ANC), nitrate, and sulfate for the park-wide GRSM water quality stream sites (37 sites identified in Table 6; Appendix A). Log2 refers to base 2 Log transformation.

Chemical Parameter	Regression Model	Adjusted r^2	Model *p*
pH	(0.673*Log2(Sum Base Cations)) + (-0.368*Nitrate) + (0.262*Julian Day) + (-0.266*Sulfate) + (-0.050*Cosine(θ))	0.630	<0.001
ANC	(0.415*Sum Base Cations) + (-0.185*Sulfate) + (0.595*Conductivity) + (-0.102*Nitrate) + (0.019*Julian Date) + (0.005*Chloride) + (0.005*Sine(θ))-0.295*Sulfate) + (-3.183*ANC) + (2.19*Conductivity) + (0.923*Sum Base	0.984	0.049
Nitrate	Cations) + (0.120*Julian Date) + (0.051*Chloride) + (0.047*Sine(θ)) + (0.031*Cosine(θ))	0.498	0.017
Sulfate	(-0.166*Nitrate) + (2.318*Conductivity) + (-3.229*ANC) + (1.033 Sum Base Cations) + (0.042*Julian Date)	0.720	<0.001

Linear Regression Analysis on Time Trends

Within the 37 stream sites (Table 6), pH for the 9-yr period from 1993 to 2002 was not observed to have significant trends, and among the six elevation classes the regression slopes were both positive

and negative (Table 9). In general, this result indicated that pH was not changing over that time period. In contrast, for the period 2003 to 2012, pH was significantly increasing for all six elevation classes ($p < 0.01$). ANC was not observed to have the same patterns between the two periods assessed, in which only two significant trends were observed: Elevation Class 1 for 1993-2002 and Elevation Class 5 for 2003-2012. Nitrate was observed to have declining trends for the period 1993-2002 for all elevation classes, though only Classes 2, 3, and 6 were significant. For the period 2003-2012, NO_3^- at the higher elevation classes (Classes 4-6) declined over time, whereas at mid-elevation classes (Classes 2 and 3) it increased in concentration over time. For this period, all classes had statistically significant trends except for Class 4 ($p < 0.01$; Table 9). Sulfate was observed to have declining trends for the period 1993-2002 for all elevation classes except the highest (Class 6, > 4,500 ft); Classes 1-3 were significant. For the period 2003-2012, SO_4^{2-} concentrations were increasing for all elevation classes, though only Classes 2 and 6 were significant ($p < 0.01$). The general shift in acid anions from a declining trend to an increasing trend possibly indicates changes in biogeochemical processes since acid deposition records show a declining acid load since 2002.

Table 9. Linear regression models for pH, ANC, nitrate, and sulfate using Julian date as the independent variable for two time periods (1993-2002 and 2003-2012) and six elevation classes (Table 6). Bold slope values are significant ($p < 0.05$).

Elevation Class	Elevation Range (ft)	Number of Sites	Time Period	Julian Date Slope Coefficients: pH units or µeq L^{-1} per day (model adjusted r^2; p value)			
				pH	ANC	Nitrate	Sulfate
1	1,000 – 2,000	7	1993-2002	-2.467 E-10 (0.003) (p= 0.19)	**-1.054 E-07** (0.029) (p < 0.01)	-7.866 E-07 (0.002) (p = 0.20)	**-2.592 E-08** (0.014) (p = 0.03)
			2003-2012	**1.301 E-09** (0.122) (p < 0.01)	2.121 E-0.8 (-0.001) (p = 0.48)	**-1.229 E-08** (0.009) (p = 0.04)	1.214 E-08 (0.004) (p = 0.12)
2	2,000 – 2,500	9	1993-2002	1.652 E-10 (0.000) (p = 0.33)	1.067 E-08 (-0.003) (p = 0.63)	**-1.407 E-08** (0.018) (p =0.01)	**-1.245 E-08** (0.013) (p = 0.03)
			2003-2012	**7.141 E-10** (0.017) (p = 0.01)	-4.133 E-08 (0.005) (p = 0.13)	**1.850 E-08** (0.012) (p = 0.03)	**1.527 E-08** (0.016) (p = 0.02)
3	2,500 – 3,000	13	1993-2002	2.975 E-10 (0.005) (p = 0.10)	3.015 E-08 (0.003) (p = 0.13)	**-3.114 E-08** (0.022) (p < 0.01)	**-3.577 E-08** (0.018) (p < 0.01)
			2003-2012	**1.147 E-09** (0.078) (p < 0.01)	-1.936 E-08 (0.002) (p = 0.15)	**3.222 E-08** (0.023) (p < 0.01)	6.601 E-09 (-0.001) (p = 0.43)
4	3,000 – 3,500	4	1993-2002	-2.576 E-10 (0.001) (p 0.284)	1.856 E-10 (-0.006) (p = 0.99)	-2.073 E-08 (0.009) (p = 0.12)	-2.646 E-08 (0.000) (p = 0.31)
			2003-2012	**1.279 E-09** (0.134) (p < 0.01)	2.515 E-09 (-0.004) (p = 0.87)	-1.565 E-09 (-0.004) (p = 0.90)	6.703 E-09 (-0.004) (p = 0.72)
5	3,500 – 4,500	4	1993-2002	-7.303 E-12 (-0.006) (p = 0.98)	2.367 E-09 (-0.006) (p = 0.93)	-2.772 E-09 (-0.006) (p = 0.75)	-5.046 E-08 (-0.000) (p= 0.35)
			2003-2012	**1.586 E-09** (0.153) (p < 0.01)	**8.623 E-08** (0.043) (p < 0.01)	**-2.771 E-08** (0.044) (p < 0.01)	1.402 E-08 (-0.005) (p = 0.72)
6	> 4.500	2	1993-2002	4.054 E-10 (-0.004) (p = 0.41)	3.725 E-08 (-0.005) (p = 0.44)	**-4.682 E-08** (0.121) (p < 0.01)	5.670 E-09 (-0.012) (p = 0.67)
			2003-2012	**1.323 E-09** (0.055) (p = 0.01)	-2.175 E-08 (-0.008) (p = 0.65)	**-3.187 E-08** (0.047) (p = 0.01)	**3.529 E-08** (0.067) (p < 0.01)

ANC trends among time periods and elevation classes were mixed, indicating that watershed specific biogeochemical processes control trends, and that results are unique to this dataset and represent watersheds (Table 9). For example, during the time period 2003-2012 for Elevation Class 5 (3,500-ft to 4,500 ft), the increase in ANC corresponded with decreasing NO_3^- and stable SO_4^{2-}. For the same period but at Classes 2 and 3 ($p = 0.13$ and 0.15; respectively), ANC declined and corresponded with significant increases in NO_3^- and SO_4^{2-}. For Class 6 (> 4.500-ft), no significant change in ANC was balanced by a significant decline in NO_3^- and an increase in SO_4^{2-}. Base cations can also play a role in influencing stream pH and ANC per individual watersheds. A comparative analysis of base cations between these two periods could not be conducted because they were not analyzed in water samples until 2003. Within the recent period (2003-2012), base cation trends were mixed among the elevations classes, with 28% of the total sites among all classes showing no significant trends (Appendix C). Interestingly, sites in Class 3 with a significant trend ($p < 0.05$) were all increasing (26% of the total sites), whereas high-elevation Classes 4 through 6 with significant trends were declining in base cations (13% of the total sites). Trends in base cations ranged from 0.004 to 1.472 $\mu eq\ L^{-1}\ yr^{-1}$ in Elevation Class 3, and -0.004 to -1.141 $\mu eq\ L^{-1}\ yr^{-1}$ among Classes 4-6. Overall, stream acidity appears to represent unique watershed biogeochemical processes, and as noted above, is a function of balancing chemical charges from anions, cations, inorganic metals, and organic acids. Neff et al. (2013) describes stream chemistry is a function of dominant basin factors including soil characteristics and vegetative cover which control local biogeochemical processes. The Vital Signs Program, as currently designed, will be able to examine these basin factors with sufficient data.

Utilizing the same data for the six elevation classes, a different statistical approach was conducted where chemical parameters were converted to annual means, and regressed with Julian date as the independent variable (Table 10). In addition, three periods (1993-2002, 2002-2008, and 2009-2012) were used in the regression analysis because the period 2002-2008 appears to be a water quality transition period from increasing acidity prior to 2002, and declining acidity after 2008 (Fig. 8). Significant regression models resulted in all analyses except for pH and nitrate within Elevation Class 3 (3,500-4,500 ft) for the period 2009-2012 ($p < 0.01$).

During the period 1993-2002, annual mean stream pH increased significantly over time for Elevation Classes 1, 4, and 6, declined for Classes 2 and 3, and was not significant for Class 5 (Table 10). For the following two periods (2003-2008 and 2009-2012), pH significantly increased for all elevation classes. This result is consistent with the previous analysis recognizing the year 2002 as a major change point for reductions in stream acidity. Annual mean ANC increased over time for all three periods for Elevation Classes 3 and 6. For Elevation Class 5, ANC had declining trends for periods 1993-2002 and 2003-2008, after which ANC increased with time for the period 2009-2012. ANC in Elevation Class 2 declined during the period 2009-2002, and reversed trends to increasing mean concentrations for both periods after 2002. Trends in annual mean NO_3^- and SO_4^{2-} concentrations for the period 1993-2002 varied with elevation classes, resulting in both declining and increasing trends. However, between 2003 and 2008, NO_3^- and SO_4^{2-} were observed with increasing trends for all elevations classes. During 2009-2012, both declining and increasing trends were observed for mean NO_3^- and SO_4^{2-}. Nitrate and sulfate were increasing over time for Classes 2 and 3, and declining for

Class 4. At the high elevation sites for 2009-2012, annual mean NO_3^- was increasing, whereas sulfate was declining with time.

Table 10. Linear regression models for annual means of pH, ANC, NO_3^- and SO_4^{2-} per continuous Julian date for three periods (1993-2002, 2003-2008, 2009-2012) and six elevation classes (Table 6).

Time Range	Elevation Class	Elevation Range in meters (ft)	Number of Sites	Julian Date (µeq/l or pH Units per Year), Model Adjusted R^2, P-Value			
				pH	ANC	Nitrate	Sulfate
1993-2002	1	304.8 - 609.6 (1,000-2,000)	5	0.069 0.712 0.000	0.007 0.985 0.000	0.034 0.503 0.000	-0.096 0.569 0.000
	2	609.6 – 762.0 (2,001-2,500)	9	-0.091 0.388 0.000	-0.036 0.603 0.000	-0.037 0.699 0.000	0.019 0.766 0.000
	3	762.0 – 914.4 (2,501-3,000)	13	-0.010 0.693 0.000	0.008 0.971 0.000	-0.013 0.359 0.000	0.024 0.590 0.000
	4	914.4 – 1,066.8 (3,001 – 3,500)	4	0.019 0.205 0.000	0.015 0.709 0.000	0.058 0.410 0.000	0.061 0.402 0.000
	5	1,066.8 – 1,371.6 (3,501-4,500)	4	-0.157 0.165 0.010	-0.082 0.760 0.000	0.288 0.328 0.000	-0.133 0.566 0.000
	6	> 1,371.6 (> 4,501)	2	0.218 0.505 0.000	0.067 0.802 0.000	-0.011 0.871 0.000	0.092 0.716 0.000
2002-2008	1	304.8 - 609.6 (1,000-2,000)	5	0.150 0.781 0.000	-0.004 0.996 0.000	0.038 0.551 0.000	0.039 0.673 0.000
	2	609.6 – 762.0 (2,001-2,500)	9	0.275 0.348 0.000	0.033 0.779 0.000	0.044 0.816 0.000	0.044 0.893 0.000
	3	762.0 – 914.4 (2,501-3,000)	13	0.156 0.663 0.000	0.005 0.996 0.000	0.072 0.637 0.000	0.034 0.923 0.000
	4	914.4 – 1,066.8 (3,001 – 3,500)	4	0.249 0.400 0.000	-0.028 0.779 0.000	0.092 0.405 0.000	0.110 0.343 0.000
	5	1,066.8 – 1,371.6 (3,501-4,500)	4	0.137 0.300 0.027	-0.020 0.739 0.000	0.204 0.562 0.001	0.135 0.884 0.000
	6	> 1,371.6 (> 4,501)	2	0.359 0.317 0.000	0.127 0.812 0.000	0.074 0.832 0.000	0.161 0.844 0.000

Table 10 (continued). Linear regression models for annual means of pH, ANC, NO_3^- and SO_4^{2-} per continuous Julian date for three periods (1993-2002, 2003-2008, 2009-2012) and six elevation classes (Table 6).

Time Range	Elevation Class	Elevation Range in meters (ft)	Number of Sites	Julian Date (µeq/l or pH Units per Year), Model Adjusted R^2, P-Value			
				pH	ANC	Nitrate	Sulfate
2008-2012	1	304.8 - 609.6 (1,000-2,000)	5	0.106 0.894 0.000	-0.002 0.989 0.000	0.026 0.376 0.000	-0.052 0.536 0.000
	2	609.6 – 762.0 (2,001-2,500)	9	0.218 0.606 0.000	0.069 0.862 0.000	0.121 0.735 0.000	0.039 0.887 0.000
	3	762.0 – 914.4 (2,501-3,000)	13	0.056 0.766 0.000	0.007 0.997 0.000	0.019 0.598 0.000	0.050 0.915 0.000
	4	914.4 – 1,066.8 (3,001 – 3,500)	4	0.413 0.593 0.000	-0.006 0.772 0.000	-0.013 0.635 0.000	-0.068 0.529 0.000
	5	1,066.8 – 1,371.6 (3,501-4,500)	4	-0.115 0.158 0.130	0.901 0.540 0.001	0.098 -0.272 0.975	0.015 0.658 0.000
	6	> 1,371.6 (> 4,501)	2	0.289 0.286 0.000	0.059 0.809 0.000	0.097 0.881 0.000	-0.059 0.861 0.000

Shifts in stream chemistry (pH, ANC, NO_3^- and SO_4^{2-}) were mixed among the elevation classes and time periods, except for pH. Patterns that could be explained by biogeochemical processes were lacking, and insufficient data were available to specifically examine relationships of stream chemistry per watershed and elevation classes with other controlling variables (i.e., soil and vegetation). In general, interpretation of the results need to be cautious because of the small number of sites per elevation class; for example Class 6 only had two sites, and Classes 4 and 5 had four each (Table 9). Statistically, the analysis design of six elevations and three time periods has value in order to assess whether significant differences between time periods and among elevation classes could be detected. This statistical test follows with an ANOVA mean separation technique (Section 2.4.3). Overall, the limited number of data points across different watersheds and the lack of observed patterns suggest qualitatively that there is insignificant statistical power, although most regression models were significant with a $p < 0.01$. Statistical power for this study design and dataset was investigated and reported in Chapter 3.

2.4.3 Results: ANOVA Comparisons between Elevation Classes and Time Periods

Within the study design of six elevation classes and three time periods (Table 9), variance among annual means for pH, ANC, NO_3^-, and SO_4^{2-} determines whether a significant relationship ($p < 0.05$) is observed statistically. An ANOVA analysis using the Bonferroni means separation technique was completed on all elevation and time period pairs for each of the four chemical parameters (Table 11).

Table 11. Statistical differences for water quality (pH, ANC, nitrate, and sulfate) between time periods for different elevation classes (Table 9) using a Bonferroni means separation analysis.

Chemical Parameter	Time Period* Combinations tested	Elevation Classes					
		1	2	3	4	5	6
pH	1→2	+	=	+	=	+	=
	1→3	+	=	+	+	+	+
	2→3	+	=	+	+	+	+
ANC	1→2	=	=	=	=	=	=
	1→3	=	+	—	=	—	=
	2→3	=	=	=	=	—	=
Nitrate	1→2	+	+	=	=	+	=
	1→3	=	+	+	=	=	=
	2→3	=	=	—	=	—	=
Sulfate	1→2	=	—	=	=	=	=
	1→3	=	—	=	=	=	=
	2→3	=	=	=	=	=	=

* Time Period 1 = 1993-2002; Time Period 2 = 2003-2008; Time Period 3 = 2009-2012.

"+" indicates significant increase between time periods; $p < 0.05$

"—" indicates significant decrease between time periods; $p < 0.05$

"=" indicates no significant differences; $p > 0.05$

Annual mean stream pH was observed to increase from Periods 1→3 for all elevation classes, except Elevation Class 2. Compared with the other chemical parameters, pH had more significant differences between periods, and all analyses were increasing if significant ($p < 0.05$). Sulfate had the least number of significant differences, with only two (both negative) for Periods 1→2 and 1→3 for Elevation Class 2. Elevation Class 6 did not result in any significant differences for ANC, NO_3^-, and SO_4^{2-}, likely because that class had only two sites. Overall, a large number of comparisons were insignificant, suggesting that the dataset was limited in its statistical power.

2.5 Discussion and Conclusions

Summarizing results from Robinson et al. (2008), Neff et al. (2013), and Schwartz et al. (2014) on stream chemistry relationships with elevation, all studies found decreasing stream pH with increasing elevation. Robinson et al. (2008) reported a decline of 0.72 pH unit per year per 1,000-ft gain, starting at 1,000 ft elevation to locations above 5,500 ft, and included 90 sites throughout the park for

the period 1993-2002. Schwartz et al. (2014) utilized 92 sites, expect for Abrams Creek sites underlain by limestone, and found a decline of 0.32 pH units per 1,000-ft gain for the same elevation range but for an extended analysis period from 1993 to 2009 (Table 3). A visual examination of park-wide pH data plotted over time (Fig. 8) revealed that between 2002 and 2003 a shift occurred from an increasing acidity over time to a declining acidity. This shift in stream pH was found to be statistically significant (Tables 9-11). In Schwartz et al. (2014), ANC significantly declined with elevation, nitrate significantly increased with elevation, and sulfate declined with elevation gain, though not significantly so (Table 3). Neff et al. (2013) monitored four high-and low-elevation streams each, finding that high-elevation streams were significantly lower in pH and ANC for both baseflow and stormflow conditions (Table 2, Appendix B). Neff et al. (2013) also illustrated that each watershed has unique chemistries based on basin physiographic, geology, soil, and forest factors. Elevation was generally correlated with these other factors spatially, and of importance was soil slope and hydraulic conductivity influencing the rate ions move or are retained, and vegetative cover influencing ion uptake and nutrient cycling. The review of existing studies provided sufficient evidence that elevation should be used as a dominant criterion for selecting water quality monitoring sites.

Identification of elevation ranges in which to place a sampling site among the selected vital signs watersheds was interpreted by the agglomerative hierarchical clustering method (Figs. 9 and 10). In this method, statistically similar groups (clusters) were quantified. The dataset in Robinson et al. (2008), as summarized in Table 5 (90 sites park-wide for 1993-2002 data, 500-ft intervals from 1,000 ft to > 5,500 ft), provided a logical sequential hierarchical structure. Results from that dataset indicated that four distinct elevation groups had similar stream chemistries: 1) 1,000-2,000 ft, 2) 2,000-3,500 ft, 3) 3,500-5,000 ft, and 4) > 5,000 ft (Fig. 9). Different results were observed with an analysis using the same hierarchical clustering method but for the long-term dataset consisting of 37 sites, divided into three time periods (1993-2002, 2003-2008, 2009-2012), and summarized within six elevation ranges. In this analysis for the post-2002 periods, three elevation groups with similar chemistries results, breaks between the groups occurred at 3,000 ft and 4,500 ft (Fig. 10). In part, this finding was a function of the six classification ranges selected for analysis, and that selection was based on obtaining enough sites per elevation range. Results from the 37-site dataset appeared weak, in that elevation groups did not cluster in a continuum of low to high but rather as Classes 1 and 3, 2 and 6, and 4 and 5. It appears that the results were affected by: 1) the small number of sites among the high-elevation areas, 2) the Cosby-Rock Creek low elevation sites with comparatively low pH and ANC values, and 3) the West Prong Little Pigeon River, which is influenced by dolomite chat applied on Route 441 during winter months. Using best professional judgement, and merging the findings from the two hierarchical clustering analyses, elevation ranges with similar chemistries are suggested to be grouped as follows:

1) 1,000 ft to 2,000 ft;
2) 2,000 ft to 3,000 ft;
3) 3,000 ft to 3,500 ft;
4) 3,500 ft to 4,500 ft;
5) 4,500 ft to 5,000 ft; and

6) > 5,000 ft.

Multivariate regression models exploring trends in stream chemistry identified pH and ANC as being dominantly influenced by increased base cations over time, and inversely influenced by declining NO_3^- and SO_4^{2-}. With base cations playing a key role in the chemical charge equilibrium for streams, future analysis must include base cations. In addition, dissolved metals and organic acids will influence a water sample's charge balance. Seasonality was also identified as a significant independent variable in three multivariate regression models for pH, ANC, and nitrate, but not for the sulfate model. Deyton et al. (2009) found that dominant chemical factors controlling stream ANC varied seasonally and among watersheds, with changing controls including SO_4^{2-}, NO_3^-, base cation dilution, and organic acids. Therefore, a sampling design where at least four samples are collected - one per season - is recommended as a minimum. Results also illustrate how unique each watershed is in terms of basin factors controlling biogeochemical processes and influencing stream chemistry.

Time trend analyses using simple linear regression models found that a shift in stream chemistry occurred in about 2002, when prior to that year, pH generally was declining slightly within the 90-site dataset. With the 37-site dataset grouped into six elevation range classes, the pH trend did not significantly change over any elevation range prior to 2002 ($p < 0.05$), but after 2002 pH was found to be significantly increasing over time (Table 9). In contrast to pH, ANC, nitrate, and sulfate did not have distinct differences between the two periods (1993-2002 and 2003-2012). Using site annual averages rather than daily measured values appeared to reduce regression model variance (Table 10). Understanding this statistical effect, the power analysis will then focus on the question "what is the needed number of samples per year for some fixed number of sites per elevation?"

Stream sulfate concentration is the acid anion of particular concern because Cai et al. (2010, 2012) showed that at NDW, atmospherically deposited sulfate has been retained in the soils (Fig. 6). Trend analyses for sulfate were mixed, but the regression results in Table 9 found that at the highest elevation Class (> 4,500 ft), stream sulfate concentrations were increasing for the period 2003-2012. Schwartz et al. (2014) also suggests that at the higher elevation sites, stream sulfate concentrations may be increasing over time (Table 4). The emphasis on this anion is that sulfate emissions from regional coal-fired plants have been reduced by an order of magnitude and thus deposition has been reduced in GRSM. The concern is that sulfate could be released from soil storage, resulting in a temporary increase in streams and more acidity. However, other studies including Neff et al. (2013) and Schwartz et al. (2014) suggest that base cation concentrations have also increased over time, buffering any effects of increased anions (both SO_4^{2-} and NO_3^-). As indicated in Neff et al. (2013), watershed processes are unique per basin, where stream water quality is dependent on several factors including input rates of sulfate and nitrate, sources of sulfate whether from atmospheric deposition and/or pyritic shales, the availability of soil base cations to buffer acid anions, and soil organic matter content. With complex biogeochemical processes occurring in the soil, such as regulating acid anions from atmospheric deposition and watershed export, long-term monitoring data is critical to be able to explain current stream water quality conditions and predict future conditions.

3.0 Statistical Power Analysis

3.1 Introduction

The accuracy with which an environmental dataset reflects actual conditions in the field depends on the resolution, or resolving power, of the data. Data resolution can be defined as how well the data distinguish between (1) real correlative or causal relationships among environmental parameters, and (2) natural random variability in the measured environmental parameter(s). How well it does this is related to the statistical power of the sampling scheme used to collect those data. Ideally, a power analysis is performed to determine the number of samples required to achieve a specified level of statistical power. This can be done before initiating the study (*a priori*); however, power analysis can also be performed "after-the-fact" (i.e., *post hoc*) on existing datasets to evaluate current sampling schemes with a pre-determined level of sample events and associated variance.

Relationships among environmental parameters often are represented by a regression or correlation. A power analysis of a correlation or regression model quantifies the probability that data used in the model are sufficient (in quantity and quality) to detect a real relationship among one or more environmental factors. In other words, power is the likelihood of proving the hypothesis correct. In statistics, "power" is 1-β, where β is the traditional Type II error in statistical inference testing: the probability that a false hypothesis will not be rejected (Table 12). The opposite of β is the probability that a trend will be detected when it exists and is called the power of the test. In the context of regression or correlation models, power is the probability that the modeled data will accurately distinguish between random noise (that appears to be a linear relationship) and a real process or correlation between two or more environmental factors.

Table 12. Summary of possible statistical hypothesis (H_0) tests (Helsel and Hirsch 2002).

	Unknown True Condition	
Decision	**H_0 is true**	**H_0 is false**
Fail to reject H_0	Correct decision Prob(correct decision) = 1-α	Type II error Prob(Type II error) = β
Reject H_0	Type I error Prob (Type I error) = α *significance level*	Correct decision Prob(correct decision) = 1-β *statistical power*

The statistical power of a correlation or regression model to distinguish between random noise and a real relationship among environmental parameters is determined by three factors: the sample size (n), the Type-I error level (α), and the effect size (ES). In the context of linear regression analysis, ES is the difference between the linear slope of two unrelated variables (random noise), and the linear slope of data pairs describing a real correlative or causal relationship. The ES is considered the most difficult factor to estimate for conducting a power analysis (Cohen 1992).

Cohen (1992) suggested that a power analysis can be simplified by normalizing the ES into a parameter that ranges from 0 to 1, and by organizing the range of ES values into three qualitativeindices (small, medium, and large). The range of ES values associated with each of the

three indices depends on the choice of statistical test used to evaluate the study hypotheses. For a regression or correlation analysis, the statistical F-test is used to quantify the probability that a non-zero linear model slope is accurately describing a real linear relationship. The output statistic of the F-test is $f^2 = ES = adj.r^2 /(1 – adj\ r^2) = R^2 \div (1\text{-}R^2)$ where r^2 is the coefficient of determination of the linear regression model (Cohen 1992). The f^2 statistic, or ES, is the ratio of explained variance to unexplained (error) variance (Faul et al. 2007, 2009).

A theoretical power of 1.00 (perfect discriminatory power), which indicates a 0% chance of false negatives (β = rejecting a significant trend when a trend is significant), may be unreasonable depending on the research goals. A trend analysis with a power of 1.00 indicates a 100% chance that the calculated slope is not zero, and a power of 0.50 means there is a 50% chance that the calculated slope might not exist. Cohen (1992) suggests that a reasonable and practical power level is 0.80; this corresponds to β = 0.2 (power = 1 – β). A power of 0.8 indicates that there is a 20% chance that a calculated slope in a trend line might be assumed to be zero when it is significant.

The analysis in this section evaluates the statistical power from existing GRSM data, and takes those results to propose alternate scenarios for optimizing the sampling period and/or number of sampling sites needed for the water quality monitoring portion of the Vital Signs Program. Power analyses were performed utilizing the existing stream survey chemistry data collected since 1993, and regression models developed for trend analyses (Tables 8 and 10) in order to identify sample numbers and a sampling schedule with sufficient statistical power to detect future chemistry trends.

3.2 Methods

Two statistical power analyses were conducted in this study; *post hoc* and *a priori*. The *post hoc* analysis calculates the statistical power, whereas the *a priori* analysis calculates the number of observations (sampling events) for a chosen power. Calculation of the power in the *post hoc* analysis is based on a given regression model with known numbers of observations (n, samples), adjusted r^2 values, and model predictors. In this study, the step-wise regression models developed for pH, ANC, NO_3^-, and SO_4^{2-} were applied (Table 8). Effect size (ES) was computed based on each model's r^2 value (see equation above). Each model was inspected for power, where a value above 0.8 would be considered acceptable. The *a priori* analysis calculates the number of observations for a user-selected power and ES, based on a given regression model and its number of predictor variables and variance. Outcomes of these analyses provide an estimate of the number of samples needed to detect a significant trend per elevation class. In addition, based on the current sampling frequency, the number of water samples needed per elevation class was used to compute the number of years of data collection that would be required to detect a trend. The software program G*Power was used for these analyses, which was developed by Faul et al. (2009).

3.2.1 Post Hoc *Analysis*

The *post hoc* analysis utilized the step-wise regression models derived for stream chemistry parameters pH, ANC, NO_3^-, and SO_4^{2-} (Table 8), with the number of predictor variables equal to 6, 8, 8, and 7, respectively. These models where then applied within each of the six elevation classes and three time periods (1993-2002, 2003-2008, 2009-2012), resulting in 72 separate power analysis

models. An α value of 0.05 was selected (Table 10). These models consisted of known sample sizes (n) and generated coefficients of determination (r^2), which were then used as inputs to the G*Power program. G*Power computes actual power and ES values. Generally, higher ES values require a smaller number of samples, and Cohen (1992) recommended that power be greater than 0.8. Using the regression models for the three time periods and six elevation classes, the *post hoc* analysis also provided qualitative information on the adequacy of the existing data monitoring frequency and years used in the analysis (1993-2002 = 9 yrs., 2003-2008 = 5 yrs., and 2009-2012 = 4 yrs.) affecting statistical power for that given period and elevation class. In other words, if the previous models had sufficient power, then a comparable level of monitoring should be acceptable for the future Vital Signs Program.

3.2.2 A Priori *Analysis*

The *a priori* analysis utilized the multiple regression models developed for pH, ANC, nitrate, and sulfate, which included varying independent variables, i.e., Julian day, seasonal theta, and chemical parameters (Table 8). Based on these models, the *a priori* analysis computes the number of samples needed for a specified power and ES. Cohen (1992) recommends a power of 0.8 and a conservative value for ES of 0.15. G*Power requires inputs of the number of predictor variables, adj.r^2, and p-value, in addition to the specified power and ES. The *a priori* analysis was also conducted applying the current data (2009-2012) as presented in Table 7. In this analysis, with the current sampling frequency per elevation class (Table 6), the question addressed was "how many years of data would be required to obtain statistically significant trends per elevation band?"

3.3 Results

3.3.1 Post Hoc *Analysis*

Of the 72 regression models evaluated for statistical power, only two models were found to be insignificant ($p > 0.05$), in which power could not be calculated (Table 13). The insignificant models were for pH and NO_3^- at Elevation Class 5 (3,500 to 4,500-ft) for 2009-2012 (a 4-year period). Six models had power values less than 1.00 with the lowest being equal to 0.74. Recall ES is the ratio of explained to unexplained variance; therefore, a value of 1.0 represents equal levels of explained and unexplained statistical model variance. Fifteen models had an ES < 1.00 (21% of the 72 total models constructed, Table 13). The smallest ES calculated in the *post hoc* analysis was 0.20, which was less than the "small effect" category value of 0.15 as reported by Cohen (1992).

With the *post hoc* analysis using existing data to generate the 72 regression models as described above in Methods (Section 3.2.1), output values for statistical power indicated that the prior sampling scheme was generally sufficient to detect trends in chemistry. Results indicated that the existing sets of chemistry data compiled as annual means, for periods with 9, 5, and 4 years, and six elevation classes (Table 6), had sufficient statistical power (> 0.8) to detect trends over time. As noted above, this outcome was consistent with the 72 linear regression models having a significance level (p) less than 0.05, except for pH and NO_3^- at Elevation Class 5 (3,500 to 4,500-ft) for the period 2009-2012 (Table 10). The reason for the two model insignificances appear to be due to a low number of samples (n = 29) compared to other models, and these models occurred in a period with only 4 years (Table 7).

Table 13. *Post hoc* power analysis using multiple regression models for water chemistry (pH, ANC, NO_3^-, SO_4^{2-}) per three time periods (1993-2002, 2003-2008, and 2009-2012) and six elevation classes (in ft 1,000-2,000; 2,000-2,500; 2,500-3,000; 3,000-3,500; 3,500-4,500; and > 4,500). Regression models use the collective number of samples among sites for each elevation class.

Set	Elev Class	pH				ANC µeq L^{-1}				Nitrate µeq L^{-1}				Sulfate µeq L^{-1}			
		N	Adj r^2	ES	Power	N	Adj r^2	ES	Power	N	Adj r^2	ES	Power	N	Adj r^2	ES	Power
1993-2002	1	327	0.712	2.47	1.00	327	0.985	65.67	1.00	275	0.503	1.01	1.00	325	0.569	1.32	1.00
	2	393	0.388	0.63	1.00	392	0.603	1.52	1.00	377	0.699	2.32	1.00	390	0.766	3.27	1.00
	3	400	0.693	2.26	1.00	398	0.971	33.48	1.00	365	0.359	0.56	1.00	391	0.590	1.44	1.00
	4	121	0.205	0.26	0.99	120	0.709	2.44	1.00	105	0.410	0.69	1.00	119	0.402	0.67	1.00
	5	116	0.165	0.20	0.96	116	0.760	3.17	1.00	66	0.328	0.49	0.98	116	0.566	1.30	1.00
	6	110	0.505	1.02	1.00	110	0.802	4.05	1.00	81	0.871	6.75	1.00	110	0.716	2.52	1.00
2003-2008	1	255	0.781	3.57	1.00	255	0.996	249.0	1.00	252	0.551	1.23	1.00	261	0.673	2.06	1.00
	2	289	0.348	0.53	1.00	289	0.779	3.52	1.00	296	0.816	4.43	1.00	298	0.893	8.35	1.00
	3	299	0.663	1.97	1.00	299	0.996	249.0	1.00	297	0.637	1.75	1.00	308	0.923	11.99	1.00
	4	119	0.400	0.67	1.00	119	0.779	3.52	1.00	121	0.405	0.68	1.00	123	0.343	0.52	1.00
	5	35	0.300	0.43	0.74	35	0.739	2.83	1.00	30	0.562	1.28	0.98	37	0.884	7.62	1.00
	6	97	0.317	0.46	1.00	97	0.812	4.32	1.00	98	0.832	4.95	1.00	101	0.844	5.41	1.00
2009-2012	1	191	0.894	8.43	1.00	191	0.989	89.91	1.00	191	0.376	0.60	1.00	190	0.536	1.16	1.00
	2	212	0.606	1.54	1.00	212	0.862	6.25	1.00	212	0.735	2.77	1.00	212	0.887	7.85	1.00
	3	228	0.766	3.27	1.00	228	0.997	332.3	1.00	228	0.598	1.49	1.00	228	0.915	10.76	1.00
	4	97	0.593	1.46	1.00	97	0.772	3.39	1.00	97	0.635	1.74	1.00	97	0.529	1.12	1.00
	5	29	NS	--	--	29	0.540	1.17	0.96	29	NS	--	--	29	0.658	1.92	1.00
	6	76	0.258	0.40	0.99	76	0.809	4.24	1.00	76	0.881	7.40	1.00	76	0.861	6.19	1.00

NS = non –significant model ($p > 0.05$).

In addition to number of samples, lack of statistical power is also a function of variance. Of the 72 regression models, 83% had sample numbers above n = 90, and all models with this number of samples had sufficient statistical power. The question of what is the adequate sample size for sufficient power is better answered with the *a priori* analysis (Section 3.3.2). Overall, a qualitative assessment of statistical power infers that at least five years of data collected bimonthly is needed for a minimum of four samples per elevation class (Table 6, minimum n =4 within Elevation Classes 4 and 5). This inference is based on the fact that power was greater than 0.8 for all regression models in the time periods 1993-2002 and 2003-2008.

3.3.2 A Priori *Analysis*

The *a priori* analysis generates power graphs as statistical power versus sample size, in which the user can select the number of samples for a selected power value. Regression models for pH, ANC, NO_3^-, and SO_4^{2-} as described in Table 8 for the sites listed in Table 6 were used to generate power graphs (Fig. 11). ES values of 0.15 and 0.35, and an $\alpha = 0.05$ were used for this *a priori* analysis utilizing equations reflecting a park-wide assessment. An ES of 0.15 was used to provide a conservative estimate, providing a substantial safety factor from underestimating projected sample sizes needed for GRSM's monitoring program. Power analysis results for ANC and nitrate were plotted together because they had the same statistical parameter inputs (number of predictor variables, significance level). Based on the total dataset (among all elevation classes), the number of samples per year estimated to detect time trends for stream pH, ANC, nitrate, and sulfate were 98, 109, 109, and 103, respectively. If the regression equations (Table 8) are applied to a watershed, it will take about 3.2 to 3.6 years to detect a trend in stream chemistry per watershed. This calculation from the power analysis assumes variances of parameter concentrations are approximately the same between the park-wide and individual watershed datasets.

Based on the number of sites sampled bimonthly from the park-wide monitoring program in recent years (2009-2012) at elevation classes and sites defined in Table 6, regression models were used to estimate the number of years needed to detect trends in stream chemistries for pH, ANC, nitrate, and sulfate (Table 14). This *a priori* analysis was conducted for the six elevation classes designated in Table 6. The sample frequency per elevation class is based on bimonthly collections (Table 14), and the sites per year were based on 2012 sample numbers. The highest elevation class (Class 6; > 4,500 ft) only had two sites, and when sampled bimonthly, resulted in a sampling frequency of 12 per year. With this limited number of samples, it was estimated that approximately 8 to 9 years would be needed to detect a time trend. As summarized in Table 14, with a greater number of sample sites, there is a lesser amount of time needed to detect a trend, and the number of years varied from 1.6 to 8.6. With 9 sample sites (Elevation Class 2), about 3 years is required to detect a trend ($\alpha = 0.5$, $\beta = 0.2$, power = 0.8, ES = 0.15). Assessing these results, one could conclude that a minimum of four sites per elevation class would be sufficient to detect a trend in pH, ANC, NO_3^-, and SO_4^{2-} within a five year period (based on a bimonthly sampling frequency). The current Vital Signs Program sampling scheme in GRSM consists of six watersheds with a sample site per elevation class; thus this *a priori* analysis indicates that after 4 to 5 years of data collection, there will be adequate statistical power for a trend analysis.

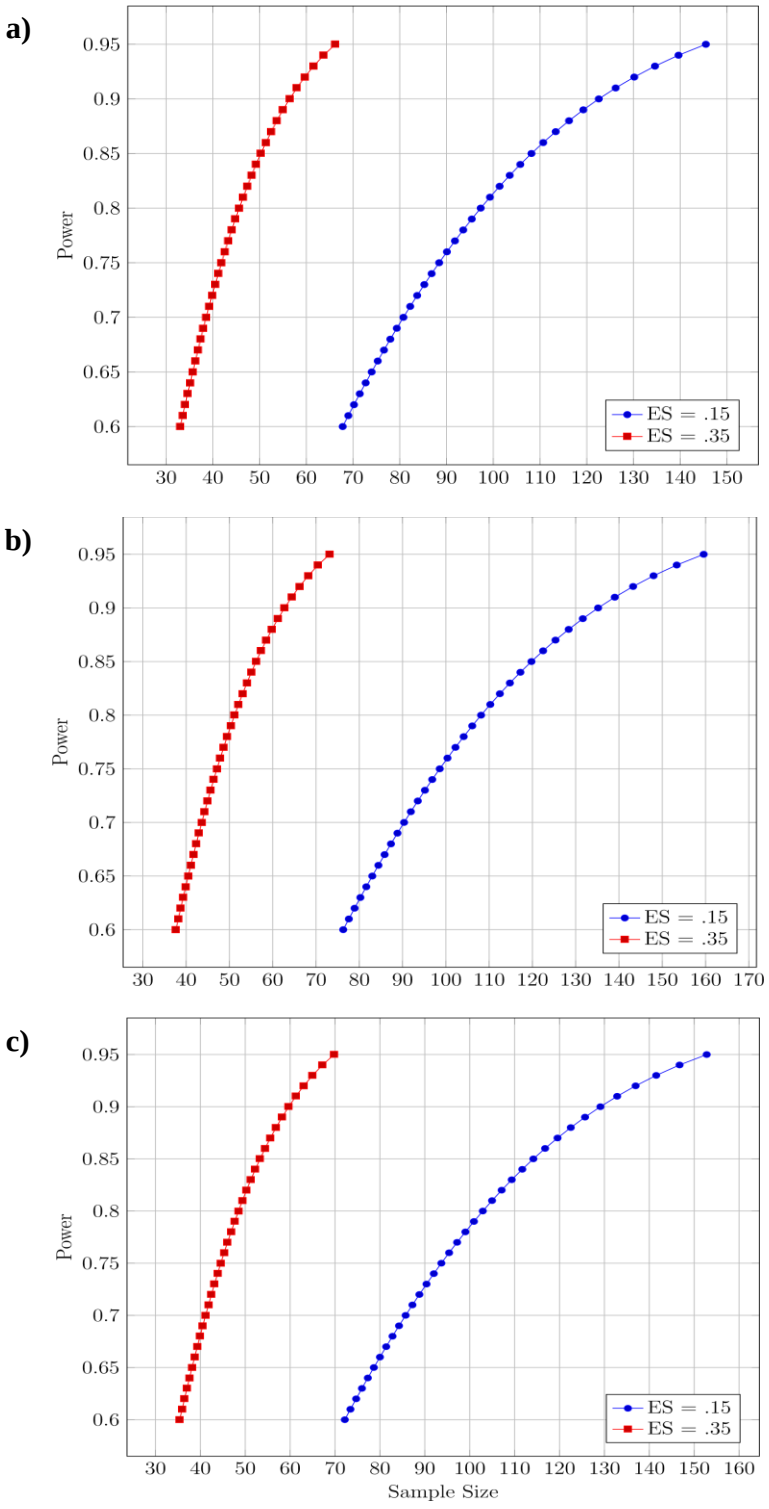


Figure 11. Statistical power graphs from *a priori* analyses for four multivariate regression models with dependent variables as stream water chemistry for a) pH, b) nitrate and ANC, and c) sulfate. Note: nitrate and ANC have the same power graph because both had same number of predictor (independent) variables and α = 0.05.

Table 14. Number of sampling years to detect trends for pH, ANC, nitrate, and sulfate based on a statistical power of 0.8 and effect size of 0.15, and based on regression models per six elevation classes and a bimonthly sampling frequency.

Elevation Class	Site ID Number	Sampling Frequency (samples/yr)	Number of Sampling Years		
			pH	ANC & NO_3^-	SO_4^{2-}
1	13, 23, 24, 30, 479	26	3.8	4.2	4.0
2	4, 311, 268, 480, 310, 438, 147, 148, 484	34	2.9	3.2	3.0
3	114, 481, 482, 149, 66, 492, 137, 293, 270, 493, 485, 144, 224	62	1.6	1.8	1.7
4	143, 142, 73, 71	24	4.1	4.3	4.3
5	74, 221, 251, 233	22	4.5	4.7	4.7
6	253, 234	12	8.2	8.6	8.6

Results are similar for pH, ANC, nitrate, and sulfate (Table 14), and the accepted general trend is observed when there is a greater sampling frequency (total number of samples per year), which then reduces the number of years needed to obtain a statistically significant trend per elevation band. A plot of this relationship is shown in Figure 12 for ANC.

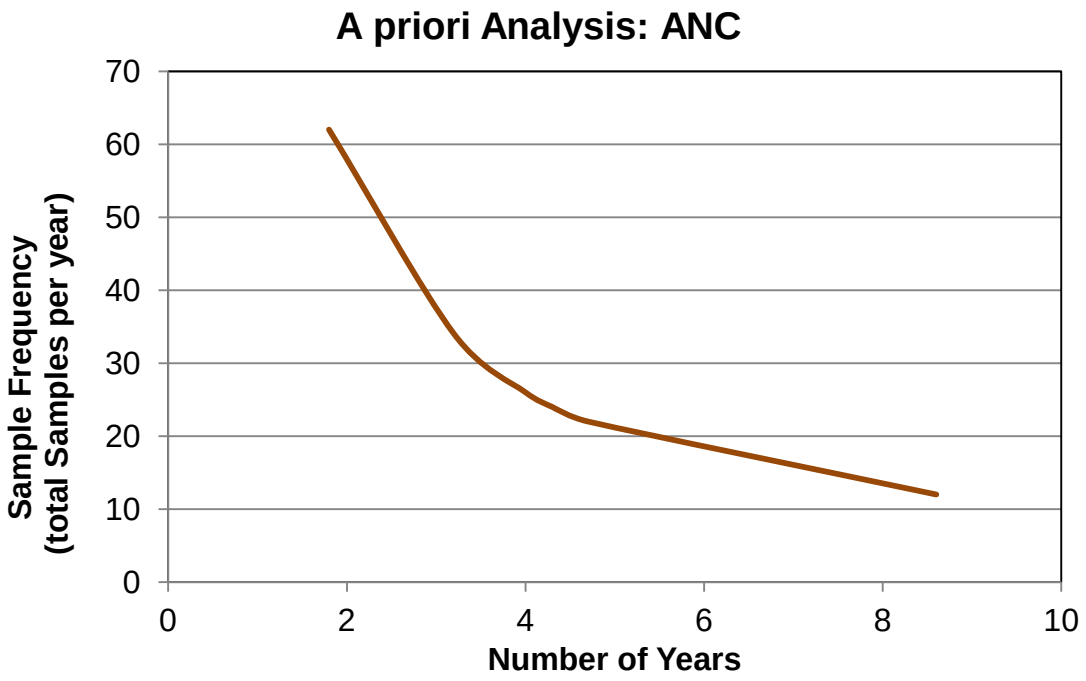


Figure 12. Plot of sampling frequency (total number of samples per year per elevation band) versus number of years to achieve a statistically significant trend for ANC (Power = 0.80, ES = 0.15, $p < 0.05$).

3.4 Conclusions

A *post hoc* analysis of existing monitoring data for pH, ANC, NO_3^-, and SO_4^{2-} resulted in statistical power > 0.8 for years 1993-2002, 2003-2008, and 2009-2012 (9, 5, and 4 year periods) for six separate elevation classes (1000-ft intervals starting at 1,000 ft MSL to > 5,000 ft as defined in Table 6). The analysis used the linear regression models as summarized in Table 10, in which all but 2 of the 72 models resulted in significant trends ($p < 0.05$). Assuming sampling variance remains the same for future years, this *post hoc* analysis indicates that at least in 5 years of bimonthly sampling and a minimum of 4 sample sites per elevation class will provide sufficient data to conduct a statistical trend analysis. The two regression models that were insufficient with power were in years 2009-2012 for Elevation Class 5 (3,500-4,500 ft MSL) and only four sites were located in that elevation range. For a 5-year period (2003-2008), statistical power was sufficient from data for Elevation Class 5. A general interpretation of these results suggests that expanding to five sites in that elevation range and monitoring for 5 years will insure sufficient statistical power assuming variance for future collected water quality data remains about the same as years with the existing datasets.

Overall, the *a priori* analysis estimated that the number of samples per year needed to detect time trends for stream pH, ANC, nitrate, and sulfate were 98, 109, 109, and 103, respectively. This analysis was based on regression models as defined in Table 8 based on the park-wide dataset. Merging these results with the *post hoc* analysis, this level of samples per year, collected for 4 to 5 years will generate a dataset sufficient for trend analysis (power > 0.8, ES = 0.15). Therefore, the currently proposed Vital Signs Monitoring Program will generate enough data for a trend analysis, based on six elevation classes, bimonthly sampling frequency (i.e., every other month), and six watersheds is equal to 216 samples. As noted earlier, the six watersheds selected for GRSM's Vital Signs Monitoring Program are: Abrams Creek, Cataloochee Creek, Middle Prong Little Pigeon River, East Prong Little River, Hazel Creek, and Deep Creek. It should be mentioned that the statistical power applied to estimate this annual number of samples was based on the total dataset and multiple regression models (Table 8), thus more data may be needed to address a more specific research question than assessing general trends in stream chemistries.

The *a priori* analysis improves on the *post hoc* analysis which determined the number of years necessary to detect a trend based on the existing data per six elevation classes (Table 14). A general interpretation of this analysis was that with four sites for an elevation class (about 24 total samples per year) it will require 4 to 5 years to obtain sufficient data to detect a trend in stream chemistries. This result is consistent to what was found with the *post hoc* analysis. It can be observed that the highest elevation class with only two sites doubled the monitoring period to obtain sufficient data for trend. In summary, this analysis also suggests the currently proposed Vital Signs Monitoring Program with six bimonthly samples per elevation class will be sufficient to detect trends in 4 to5 years.

4.0 Summary

The goal of this statistical reassessment of the GRSM park-wide monitoring data was to support the spatial and temporal design considerations for the park's new Vital Signs Monitoring Program. Due to stream acidification and its impact on aquatic biota, objectives of past and present water quality monitoring in the park was primarily focused on characterizing stream chemistries associated with watershed factors (basin size, elevation, geology, soils, vegetation), and detecting trends in chemistry. Elevation was found to be a dominant watershed factor that covaries with other factors \(Robinson et al. 2008, Neff et al. 2013, Schwartz et al. 2014). These studies provide useful background to support the statistical outcomes in this study. The study objectives consisted of three principal analyses: 1) characterize stream chemistry along an elevation gradient; 2) identify time trends in stream chemistry for different elevation ranges; and 3) assess statistical power for existing variances of stream chemistries for different time periods and elevation ranges, and estimate the number of samples with sufficient power needed to detect future trends in water quality.

Utilizing long-term datasets in GRSM, Robinson et al. (2008) found that pH declined 0.72 units per 1,000 ft (starting at 1,000 ft MSL, 1993-2002), and Schwartz found that pH declined 0.32 units per 1,000 ft, but for the period 1993-2009. The slowing rate of pH decline for the extended data period suggests that pH has been increasing over time. Detailed statistical analysis found that stream pH was declining over time for most sites among the elevation ranges sampled between 1993 and 2002, and was observed to be increasing with time during the period 2009 to 2012 pH. Between the periods of observed change from declining pH to increasing, there appears to be a transition period between 2003 and 2008 where stream pH variance was greater, and slightly increasing. The interest in comparing the three periods (1993-2002, 2003-2008, 2009-2012) is that around 2008 major reductions in regional power plant emissions for sulfate and measured sulfate deposition at NDW occurred.

The measured park-wide changes from a declining stream pH to increasing are an important and key finding from the long-term monitoring program in GRSM. Although stream pH appears to be increasing, which is an improvement in the ecological health of GRSM's water quality, continued monitoring is needed because it is possible that this may be a temporary condition. One possible future scenario with the reduction of sulfate emissions from regional power plants is that an increase in soil pH and reduced soil water sulfate concentrations could lead to a soil condition where absorbed sulfate may be released. It was determined at the NDW study site that approximately 60% of the sulfate deposited from atmospheric sources has been retained in the soil. We have not observed this sulfate release to date, where Noland Divide stream sulfate has not changed significantly. However, limited data at the higher elevations has suggested a recent increase in sulfate (Table 4), but the number of sites and sample numbers are small and inconclusive. As found in Neff et al. (2013), basin factors greatly influence stream water quality, and one key factor with respect to stream sulfate is the presence of Anakeesta surficial geology. Future monitoring designs need to consider (acknowledge) which sites are in watersheds with Anakeesta geology. In addition, special studies outside of the routine monitoring program, such as a sulfate isotope analysis, may be needed to more adequately address the issue of how much sulfate and stream acidity is being contributed by exposed

Anakeesta rock at high elevations. Though sulfate is a key acid anion affecting water quality, the suite of chemical parameters is needed to understand the dominant biogeochemical processes controlling water quality in each watershed, which includes nitrogen constituents and base cations. Results from this study and others identify elevation as a key basin factor where controlling biogeochemical processes differ and affect the fate and transport of acid deposition pollutants.

With elevation as the key variable for study design, the spatial analysis using an agglomerative hierarchical clustering technique for multiple time periods and datasets recommended the following elevation classes to be monitored:

1) 1,000 ft to 2,000 ft;
2) 2,000 ft to 3,000 ft;
3) 3,000 ft to 3,500 ft;
4) 3,500 ft to 4,500 ft;
5) 4,500 ft to 5,000 ft; and
6) > 5,000 ft.

Results were based on grouping stream chemistries (pH, ANC, NO_3^-, and SO_4^{2-}) that were similar. This summary merged the results of two datasets, thus the elevation classes listed above were based on professional interpretation of the results.

A second approach utilizing two statistical power analyses, *post hoc* and *a priori*, found that a water quality monitoring program based on 1,000-ft intervals (six elevation classes from 1,000 ft MSL to > 4,500 ft) sampled bimonthly will generate sufficient data within about 4 to 5 years to detect trends in pH, ANC, NO_3^-, and SO_4^{2-} concentrations. Such a program design is sufficient to detect time trends within a watershed, and park-wide among elevation classes. Per watershed, the minimum number of samples needed to detect a trend over a specified time period was estimated as 109. The existing GRSM Vital Signs Monitoring Program includes six watersheds: Abrams Creek, Cataloochee Creek, West Prong of the Little River, Hazel Creek, and Deep Creek. With a statistical power = 0.8 (ES = 0.15 and $\alpha = 0.5$), the data collected per the current bimonthly sampling scheme utilizing these six watersheds will produce adequate sample events in 4 to 5 years to conduct a trend analysis.

5.0 Literature Cited

Cai, M., M.A. Johnson, J.S. Schwartz, S.E. Moore, and M.A. Kulp. (2012). Soil acid-base chemistry of a high-elevation forest watershed in the Great Smoky Mountains National Park watershed: Influences of acid deposition. *Water, Air, and Soil Pollution* 223: 289-303.

Cai, M., M.A. Johnson, J.S. Schwartz, S.E. Moore, and M.A. Kulp. (2011a). Response of soil water chemistry to simulated changes in acid deposition in the Great Smoky Mountains. *ASCE Journal of Environmental Engineering* 137(7): 617-628.

Cai, M., J.S. Schwartz, R.B. Robinson, S.E. Moore, and M.A. Kulp. (2011b). Long-term annual and seasonal patterns of acidic deposition and stream water quality in a Great Smoky Mountains high-elevation watershed. *Water, Air, & Soil Pollution* 219:547–562.

Cai, M. J.S. Schwartz, R.B. Robinson, S.E. Moore, and M.A. Kulp. (2010). Long-term effects of acidic deposition on water quality in a high-elevation Great Smoky Mountains National Park watershed: use of an ion input-output budget. *Water, Air, and Soil Pollution* 209: 143-156.

Chen, Y., and L.S. Lin. (2009). Responses of Streams in Central Appalachian Mountain Region to Reduced Acidic Deposition - Comparisons with Other Regions in North America and Europe. *Science of the Total Environment* 407: 2285-95.

Cohen, J. (1992). Statistical power analysis. *Current Directions in Psychol. Sci.* 1(3): 98–101.

Cook, R.B., J.W. Elwood, R.R. Turner, M.A. Bogle, and P.J. Mulholland. (1994). Acid-Base chemistry of high-elevation streams in the Great Smoky Mountains. *Water, Air and Soil Pollution* 72: 331-356.

Deyton, E.B., J.S. Schwartz, R.B. Robinson, K.J. Neff, S.E. Moore, and M.A. Kulp. (2009). Characterizing episodic stream acidity during stormflows in the Great Smoky Mountains National Park. *Water, Air, and Soil Pollution* 196: 3-18.

Driscoll, C.T., G.E. Likens, and M.R. Church. (1998). Recovery of surface waters in the northeastern U.S. from decreases in atmospheric deposition of sulfur. *Water, Air, & Soil Pollution* 105: 319-329.

Driscoll, C.T. (1985). Aluminum in acidic surface waters: chemistry, transport, and effects. *Environmental Health Perspectives, 63, 93-104*.

Faul, F., E. Erdfelder, A-G. Lang, and A. Buchner. (2007). G*Power 3: A flexible statistical power analysis program for the social, behavior, and biomedical sciences. *Behavior Research Methods* 39: 175-191.

Faul, F., E. Erdfelder, A. Buchner, and A-G. Lang. (2009). Statistical power analyses using G* Power 3.1: Tests for correlation and regression analyses. *Behavior Research Methods* 41(4): 1149–1160.

Gbondo-Tugbawa, S., and C.T. Driscoll. (2002). Retrospective analysis of the response of soil and stream Chemistry of a northern forest ecosystem to atmospheric emission controls from the 1970 and 1990 Amendments of the Clean Air Act. *Environ. Sci. Technol.* 36 (2002): 4714-4720.

Gobran, G.R., H.M. Selim, H. Hultberg, and I. Andersson. (1998). Sulfate adsorption-desorption in a Swedish forest soil. *Water, Air and Soil Pollution* 108: 411-424.

Helsel, D.R., and R.M. Hirsh. (2002). Statistical Methods in Water Resources. Book 4, Hydrological Analysis and Interpretation. US Geological Survey, Reston, VA.

Herlihy, A.T., J.L. Stoddard, and C.B. Johnson. (1998). The relationship between stream chemistry and watershed land cover data in the Mid-Atlantic Region, U.S. *Water, Air and Soil Pollution* 105: 377-386.

Johnson, D.W., and S.E. Lindberg. (1992). *Atmospheric Deposition and Forest Nutrient Cycling. A Synthesis of the Integrated Forest Study*. Springer-Verlag.

McCune B., and Mefford, M.J. (1999). *PC-ORD Multivariate Analysis of Ecological Data*. MJM Software Design, Gleneden Beach, Oregon, USA.

Mitchell, M.J., B. Mayer, S.W. Bailey, J.W. Hornbeck, C.A. Alewel, C.T. Driscoll, and G.E. Likens. (2001), Use of stable isotope ratios for evaluating sulfur sources and losses at the Hubbard Brook Experimental Forest. *Water, Air, and Soil Pollution* 130: 75-86.

Mitchell, M.J., G. Lovett, S. Bailey, F. Beall, D. Burns, D. Buso, T.A. Clair, *et al.* (2011). Comparisons of watershed sulfur budgets in Southeast Canada and Northeast US: New approaches and implications. *Biogeochemistry* 103: 181-207.

Mulholland, P.J. 1993. Hydrometric and stream chemistry evidence of three storm flowpaths in Walker Branch. *Journal of Hydrology* 151: 291-316.

Neff, K.J., J.S. Schwartz, S.E. Moore, and M.A. Kulp. (2013). Influence of basin characteristics on baseflow and stormflow chemistry in the Great Smoky Mountains National Park, USA. *Hydrological Processes* 27: 2061-2074. DOI 10.1002/hyp.9366.

NADP. (2012). *National Atmospheric Deposition Program 2012 Annual Summary*. Illinois State Water Survey, NADP Data Report 2012-01, Champaign, Illinois.

Odom, K.R. (2003). *Assessment and Redesign of the Synoptic Water Quality Monitoring Network in the Great Smoky Mountains National Park*. PhD Dissertation, University of Tennessee, Knoxville.

Postek, K.M., C.T. Driscoll, J.S. Kahl, and S.A. Norton. (1995). Changes in the concentrations and speciation of aluminum in response to an experimental addition of ammonium sulfate to the Bear Brook watershed, Maine, USA." *Water, Air and Soil Pollution* 85: 1733-1738.

Robinson, R.B., Barnett, T.W., Harwell, G.R., Moore, S.E., Kulp, M.A., and Schwartz, J.S. (2008). pH and acid anion time trends in different elevation ranges in the Great Smoky Mountains National Park. *ASCE Journal of Environmental Engineering* 134(9): 800–808.

Schwartz, J.S., M. Cai, M.A. Kulp, S.E. Moore, B. Nichols, and C. Parker. (2014). *Biological Effects of Stream Water Quality on Aquatic Macroinvertebrates and Fish Communities within the Great Smoky Mountains National Park*. Natural Resource Report, NPS/GRSM/NRR—2014/778. National Park Service, Fort Collins, Colorado.

Sullivan, T., Cosby, B., Herlihy, A., Webb, J., Bulger, A., Snyder, K., Brewer, P., Gilbert, E., and Moore, D. (2004). Regional model projections of future effects of sulfur and nitrogen deposition on streams in the southern Appalachian mountains. *Water Resources Research* 40(2). W02101. DOI:10.1029/2003WR001998.

Van Miegroet, H., I.F. Creed, N.S. Nicholas, D.G. Tarboton, K.L. Webster, J. Shubzda, B. Robinson, *et al.* (2011). Is there synchronicity in nitrogen input and output fluxes at the Noland Divide Watershed, a small N-saturated forested catchment in the Great Smoky Mountains National Park? *The Scientific World* 1, No. S2: 480-92.

Weathers, K.C., S.M. Simkin, G.M. Lovett, and S.E. Lindberg. (2006). Empirical modeling of atmospheric deposition in mountainous landscapes. *Ecological Applications* 16(4):1590–1607.

Appendix A: GRSM Park-wide Stream Survey Sites: Location and Elevation Classes

	Site ID	Elevation (ft)	Elevation (m)	Slope	Latitude	Longitude	Elevation Class (Old)	Elevation Class (New)
1	173	1715	522.73	35.68	35.59104	-83.85361	3	3
2	174	1715	522.73	10.27	35.59186	-83.85308	3	3
3	488	1790	545.59	4.04	35.58349	-83.83446	4	1
4	489	1710	521.21	32.78	35.59145	-83.85397	4	1
5	142	3300	1005.84	32.42	35.63565	-83.14537	5	2
6	143	3280	999.74	35.69	35.63625	-83.14481	6	2
7	144	2990	911.35	35.66	35.63900	-83.13078	5	2
8	147	2460	749.81	16.84	35.66688	-83.07277	4	3
9	148	2475	754.38	7.58	35.66913	-83.07283	4	3
10	149	2550	777.24	4.45	35.64627	-83.07554	5	3
11	293	2755	839.72	18.73	35.62442	-83.11391	5	4
12	493	2840	865.63	33.10	35.63462	-83.11943	6	6
13	4	2080	633.98	6.11	35.76133	-83.21044	3	1
14	114	2510	765.05	13.71	35.74863	-83.20066	5	2
15	137	2750	838.20	22.92	35.74616	-83.21630	5	2
16	492	2730	832.10	25.86	35.74457	-83.19876	5	6
17	221	4000	1219.20	30.02	35.54632	-83.58283	8	3
18	224	2999	914.00	17.92	35.53212	-83.62234	6	3
19	310	2240	682.75	19.63	35.49994	-83.68014	4	4
20	311	2155	656.84	26.20	35.49377	-83.68852	4	5
21	479	1740	530.35	39.70	35.47233	-83.71933	3	5
22	480	2201	671.00	10.07	35.49474	-83.68873	4	5
23	481	2540	774.19	30.90	35.50256	-83.70835	5	5
24	482	2540	774.19	38.66	35.50236	-83.70859	5	6
25	483	2320	707.14	34.29	35.49947	-83.69494	4	6
26	484	2475	754.38	9.11	35.50331	-83.65930	5	1
27	485	2860	871.73	5.17	35.52249	-83.63101	6	1
28	13	1100	335.28	44.21	35.66763	-83.71450	2	1
29	23	1150	350.52	5.96	35.65724	-83.70979	2	1
30	24	1150	350.52	31.60	35.65682	-83.71017	2	1
31	30	1430	435.86	2.17	35.68819	-83.53672	2	1
32	66	2680	816.86	17.92	35.63723	-83.49484	5	2
33	71	3400	1036.32	31.28	35.63440	-83.47032	6	2
34	73	3360	1024.13	28.98	35.63476	-83.46931	6	2
35	74	3820	1164.34	18.07	35.62912	-83.45102	7	2
36	233	4255	1296.92	21.86	35.61830	-83.42718	8	3
37	234	5000	1524.00	23.93	35.60975	-83.45043	10	3
38	237	4520	1377.70	30.21	35.62409	-83.41692	9	3
39	251	4010	1222.25	19.03	35.60226	-83.41533	8	3
40	252	4680	1426.46	33.32	35.60666	-83.43391	9	3
41	253	4760	1450.85	26.42	35.60682	-83.43510	9	3
42	268	2169	661.00	3.31	35.55293	-83.30937	4	4
43	270	2799	853.00	22.92	35.58641	-83.36400	5	4

Note: “old” elevation class refers to Table 5 per Robinson et al. (2008) and “new” refers to Table 6.

Appendix B: Statistical Results from Neff et al. (2013): Tables III – V.

Table III. Tukey–Kramer bivariate means comparison of chemical constituents in baseflow between elevation classes (high and low), area classes (small and large), and Anakeesta geology (present and absent)

			pH	ANC	NO_3	SO_4^{2}	NH_4^{+}	Na^{+}	Mg^{2+}	Ca^{2+}	Al	Si	BC†	BA‡
				μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μmol/l	μmol/l	μeq/l	μeq/l
Elevation	High	Average	6.12	28.22	27.90	37.51	0.55	30.90	24.35	50.79	1.67	84.73	116.10	77.07
		SD	0.59	25.02	18.86	15.53	0.99	6.21	6.72	11.50	14.13	18.87	14.05	33.44
	Low	Average	6.44	40.58	14.63	37.20	0.41	33.51	20.98	50.52	1.34	91.85	115.00	63.62
		SD	0.30	21.97	11.17	9.29	0.96	5.88	5.36	9.31	1.12	16.38	17.93	20.23
	ANOVA	*p*-value	<0.0001	0.0019	<0.0001	0.8855	0.3898	0.0102	0.0011	0.8783	0.1100	0.0195	0.6782	0.0042
Area	<10 km^2	Average	6.33	31.15	17.98	37.92	0.39	30.51	20.53	49.56	1.52	85.08	110.44	67.82
		SD	0.26	16.40	12.53	10.69	0.65	5.26	0.72	11.48	1.19	15.66	14.03	22.57
	10–20 km^2	Average	6.21	36.83	24.73	36.85	0.57	33.62	24.70	51.65	1.52	91.14	120.17	73.13
		SD	0.64	29.55	19.65	14.61	1.20	6.58	0.68	9.44	1.34	19.58	16.30	33.04
	ANOVA	*p*-value	0.1727	0.1593	0.0158	0.6195	0.2770	0.0021	<0.0001	0.2295	0.8912	0.0378	0.0002	0.2638
Anakeesta	>10%	Average	6.14	28.29	25.20	40.33	0.35	30.15	23.68	52.78	1.64	84.02	116.17	77.27
		SD	0.58	23.94	20.31	11.80	0.55	5.12	6.92	9.27	1.38	17.09	12.60	31.08
	None	Average	6.43	41.45	16.97	33.65	0.65	34.65	21.55	48.02	1.34	93.63	114.83	62.34
		SD	0.31	22.97	9.87	13.29	1.32	6.49	5.28	11.32	1.12	17.80	19.48	22.82
	ANOVA	*p*-value	0.0003	0.0010	0.0032	0.0016	0.6040	<0.0001	0.0420	0.0060	0.1502	0.0011	0.6171	0.0015

† Sum of base cations.
‡ Sum of base anions.

Appendix B continued ….

Table IV. Tukey–Kramer bivariate means comparison of chemical constituents in stormflow between elevation classes (high and low), area classes (small and large), and Anakeesta geology (present and absent)

			pH	ANC	NO_3	SO_4^{2}	NH_4^{+}	Na^{+}	Mg^{2+}	Ca^{2+}	Al	Si	BC†	BA‡
				μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μeq/l	μmol/l	μmol/l	μeq/l	μeq/l
Elevation	High	Average	5.80	26.15	21.89	40.12	0.71	25.10	24.52	56.73	5.54	62.66	120.79	73.61
		SD	0.71	30.20	16.84	18.67	1.15	7.03	6.23	11.34	4.61	18.51	15.84	35.37
	Low	Average	6.25	44.64	14.03	37.37	1.60	30.09	23.42	51.79	2.83	76.54	130.74	63.39
		SD	0.29	32.81	11.84	11.09	5.53	5.73	5.26	19.17	1.93	14.60	27.48	21.54
	ANOVA	*p*-value	<0.0001	0.0062	0.01	0.3888	0.3019	0.0003	0.3594	0.1316	0.0003	<0.0001	0.0384	0.0945
Area	$<10\,km^2$	Average	6.05	28.57	15.17	38.14	1.24	26.14	21.73	55.22	4.01	65.86	117.71	65.44
		SD	0.35	21.08	10.34	12.92	5.17	5.62	4.13	11.92	3.27	15.66	16.12	23.00
	10–20 km^2	Average	6.02	45.61	21.35	39.43	1.08	29.82	26.95	65.00	4.31	75.47	137.22	72.14
		SD	0.80	42.32	19.05	17.94	1.81	7.77	6.28	19.10	4.31	19.22	26.40	36.08
	ANOVA	*p*-value	0.7807	0.0129	0.0488	0.6883	0.8529	0.0098	<0.0001	0.0033	0.7080	0.0092	<0.0001	0.2804
Anakeesta	>10%	Average	5.88	33.36	19.48	41.02	0.88	25.48	24.48	63.04	5.72	67.28	126.67	71.83
		SD	0.74	38.35	17.82	15.09	1.58	0.93	6.29	17.92	4.50	19.94	24.17	31.97
	None	Average	6.20	38.45	15.95	36.14	1.50	30.13	23.36	55.36	2.38	72.62	125.28	64.39
		SD	0.26	25.50	10.78	15.01	5.68	0.97	5.07	12.70	1.19	14.95	22.12	25.82
	ANOVA	*p*-value	0.0071	0.4592	0.2592	0.1235	0.4656	0.00	0.3489	0.0209	<0.0001	0.1328	0.7668	0.2252

† Sum of base cations.
‡ Sum of base anions.

Appendix B continued ….

Table V. Spearman correlation coefficients ($p < 0.01$) for relationships between basin characteristics and baseflow ($n = 146$) and stormflow ($n = 92$) stream chemical constituents

Chemical constituent	Anakeesta (%)	Area (km^2)	Mean elevation (m)	Mean basin slope (%)	Ksat (mg/l)	Soil slope (%)	LEXF[†]	Shrub[‡]
pH	– / –	0.40/0.29	–0.55/–0.53	–0.60/–0.50	–0.75/–0.62	–0.77/–0.72	0.78/0.67	0.41/0.38
ANC (μeq/l)	– / –	0.41/0.32	–0.53/–0.53	–0.59/–0.55	–0.74/–0.68	–0.75/–0.72	0.75/0.68	0.39/0.40
NO_3 (μeq/l)	–0.24/–0.25	– / –	0.62/0.38	0.83/0.65	0.72/0.52	0.78/0.54	–0.77/–0.55	–0.75/–0.60
SO_4 (μeq/l)	– / –	–0.27/ –	0.35/0.26	0.61/0.57	0.83/0.66	0.54	–0.80/–0.65	–0.49/–0.46
Cl (μeq/l)	– / –	– / –	– / –	0.19/ –	0.32/ –	– / –	–0.30/ –	–0.19/ –
Anions (μeq/l)	– / –	–0.24/ –	0.49/0.29	0.73/0.60	0.86/0.66	0.67	–0.86/–0.66	–0.58/–0.49
Na (μeq/l)	– / –	0.42/0.24	–0.54/–0.57	–0.43/–0.47	–0.73/–0.64	–0.66/–0.64	0.71/0.63	0.37/ –
Ca (μeq/l)	– /0.25	– /0.38	– / –	– / –	0.52/ –	0.20/ –	–0.48/ –	–0.57/–0.32
K (μeq/l)	– / –	– /0.22	– / –	–0.19/–0.23	–0.28/–0.42	–0.21/–0.35	0.28/0.43	– / –
Mg (μeq/l)	– / –	– /0.39	0.41/ –	0.79/0.56	0.62/0.34	0.56/0.26	–0.67/–0.39	–0.74/–0.57
Cations (μeq/l)	– / –	0.33/0.43	–0.26/ –	0.48/ –	– / –	– /–0.29	–0.32/ –	–0.55/ –
Al (μmol/l)	– / –	– / –	0.29/0.40	0.34/0.42	0.40/0.47	0.40/0.46	–0.43/–0.48	–0.28/–0.36
Si (μmol/l)	– / –	0.35/ –	–0.54/–0.60	–0.58/–0.58	–0.77/–0.59	–0.69/–0.64	0.76/0.58	0.47/0.51

[†] Low- and mid-elevation subxeric to xeric forests and woodlands.
[‡] Shrublands or shrub understory.

Appendix C. Significant Time Trends for Stream Chemistry from 1993 to 2009 (Schwartz et al. 2014)

Table C-1: Sites not co-located with biotic data

Site ID	N	pH	ANC	Cond	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	* Mg^{2+}	* Ca^{2+}	Al
3	44				0.0015	-0.0028	-0.0026				-0.0021	-0.0147			
14	39											-0.0092			
23	103	0.022		0.213	-0.0010						0.0030		0.0063	0.0083	
24	80	0.037				0.0009						-0.0037			-0.037
34	83	0.037				0.0023	0.0015			0.0002	0.0005				
43	62	-0.032	-1.573		0.0027					0.0010				0.0114	
45	49				0.0017			0.0020		0.0007					
46	46							0.0019				-0.0050			
49	46				0.0015									-0.0163	
50	35											-0.0071			
52	46									0.0011		-0.0050			
66	105	0.037		0.165		0.0014		0.0006		0.0003			0.0022	0.0066	
73	85			0.120		0.0010								0.0071	
74	83	0.021		0.225	0.0011			0.0012						0.0115	
103	53						-0.0030				-0.0009	-0.0090			
104	45				0.0024		-0.0035					-0.0106			
106	43				0.0014							-0.0056			
115	31									0.0018					
127	42											-0.0074			
138	46	0.031				-0.0031									
144	76					0.0011						-0.0025			-0.037
183	39												0.0030	0.0118	

Site ID	N	pH	ANC	Cond	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	* Mg^{2+}	* Ca^{2+}	Al
184	44	0.019		-0.249		-0.0025	-0.0024				-0.0012	-0.0082			
193	62				0.0028					0.0010		-0.0058			
194	44						-0.0014					-0.0062			
195	33			-0.183		-0.0008	0.0005						0.0019		
200	44				0.0028	0.0022		0.0033		0.0015		-0.0052			
201	38					-0.0033				0.0009		-0.0052			
209	45							0.0022				-0.0021	0.0030		
210	47				0.0018			0.0016				-0.0083	0.0030		
213	46				0.0018							-0.0045			
218	52		-2.129			0.0079	-0.0042								
219	39				0.0039	-0.0081		0.0038			0.0020		0.0035		
220	38				0.0025			0.0023					0.0060		
233	78			0.212				0.0006						0.0092	
234	66						0.0009						0.0008		
237	97					0.0017								0.0038	
252	79							-0.0014						0.0108	
253	79						0.0083						0.0030	0.0058	
266	35							0.0031		0.0010					
268	76						0.0013					-0.0023			-0.037
290	23					-0.0146									
291	42					-0.0040		0.0026				-0.0066			
293	101	0.037		0.089		0.0017	0.0006					-0.0023	0.0013	0.0022	
310	51				-0.0016										
311	45					0.0012				0.0007		-0.0033			
472	29											-0.0071	0.0043	0.0082	
473	32							0.0021							
474	38						-0.0018					-0.0109			

Site ID	N	pH	ANC	Cond	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	* Mg^{2+}	* Ca^{2+}	Al
475	31						-0.0016	0.0037				-0.0095			
480	40						0.0010					-0.0033	0.0017	0.0023	
482	36						0.0015			0.0006		-0.0036			
483	38						0.0022					-0.0040			

Table C-2. Sites co-located with biotic data

Site ID	N	pH	ANC	Cl⁻	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Al
1	43			0.3750								
4	43	-0.030	-3.215		1.103	0.860	-1.060					
47	81				-0.702	-0.710						
71	84				-0.390	0.401			0.159	0.446		
107	62		-0.837	1.134			0.727		0.792			
137	84											
143	77			-0.269								0.008
148	70	0.017		-0.363	0.265					0.366		
156	40					-0.569			-0.414			
190	39			0.686		-0.502	0.730				2.120	
191	41				-0.816							
192	45			0.953			0.985			1.264		
214	50					-0.526	0.891		0.263			
215	48						1.339		0.239	1.926		
224	10	0.145										
251	93	0.019	0.700						0.134			-0.005
270	34	0.061			-1.041	1.233					-1.141	-0.006
336	41											
337	45	0.025					0.815					
337	45	0.025					0.815					
484	38			-0.509					0.240			
489	63	0.025		-0.807	0.229	0.705	-0.553					-0.007
493	62	0.019		-0.510	0.466	0.232	-0.744					-0.010
13	80				0.319							
20	46			0.622			0.689		0.306			
34	37					-0.546						
114	69	0.010	-0.689	-0.549	0.360	0.581						
142	75	0.001		-0.365	0.166							
147	93	0.007			0.338	0.180			0.198	0.352	0.922	-0.007
149	69	0.014		-0.238	0.520					0.288		-0.051
150	35											
173	83	0.017	8.538	-0.282	0.493							
174	80			-0.329	0.151							-0.010
186	61			0.701		-0.855			0.235	1.851	2.985	
221	38										0.611	
472	29									1.568	29.999	
485	38				0.396							
488	70				0.615	0.312				0.425	0.847	
479	40				0.414							
492	63	0.025		-0.807	0.229	0.705	-0.553			0.669	1.020	-0.007

Appendix D. GRSM Water Quality Data Summary for Cataloochee River, Little River, and Hazel Creek

Water Quality Parameter	Elevation Range (feet)			
	1500-3000	3000-3500	4000-5000	> 5000
Records (N):	1211	458	43	114
pH (mean)	6.53	6.34	6.20	5.21
ANC (uEq/L)	71.26	44.15	28.71	3.08
Conductivity (uS/cm)	13.78	11.96	10.49	19.04
Chloride (uEq/L)	15.18	15.06	16.06	17.99
Nitrate (uEq/L)	9.76	13.06	24.31	56.87
Sulfate (uEq/L)	25.08	25.59	17.46	42.50
Total Anions (uEq/L)	49.97	53.70	57.84	115.83
Sodium (uEq/L)	43.68	34.49	33.00	28.98
Ammonium (uEq/L)	0.424	0.742	0.500	0.682
Potassium (uEq/L)	12.69	10.29	10.44	12.41
Magnesium (uEq/L)	26.30	20.32	18.77	22.68
Calcium (uEq/L)	52.37	44.82	35.96	51.47
BCS (uEq/L)	84.96	55.96	41.28	-0.29
Total Cations (uEq/L)	128.92	106.07	94.40	116.21
Hydrogen (uEq/L)	0.34	0.61	0.73	8.38
Aluminum (ppm)	0.0406	0.0395	0.0361	0.1204
Copper (ppm)	0.0066	0.0025	0.0038	0.0027
Iron (ppm)	0.0319	0.0273	0.0172	0.0215
Manganese (ppm)	0.0401	0.0298	0.0364	0.0005
Silicon (ppm)	3.4048	2.8071	2.3550	1.8820
Zinc (ppm)	0.0159	0.0072	0.0042	0.0186

Watersheds Represented: Cataloochee River (CAT), Hazel Creek (HAZ), Little River (LITT). Data for years 1993 to 2012.

The Department of the Interior protects and manages the nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its special responsibilities to American Indians, Alaska Natives, and affiliated Island Communities.

NPS 133/134011, October 2016

National Park Service
U.S. Department of the Interior

Natural Resource Stewardship and Science
1201 Oakridge Drive, Suite 150
Fort Collins, CO 80525

www.nature.nps.gov

2016 National Park Service CENTENNIAL

EXPERIENCE YOUR AMERICA ™