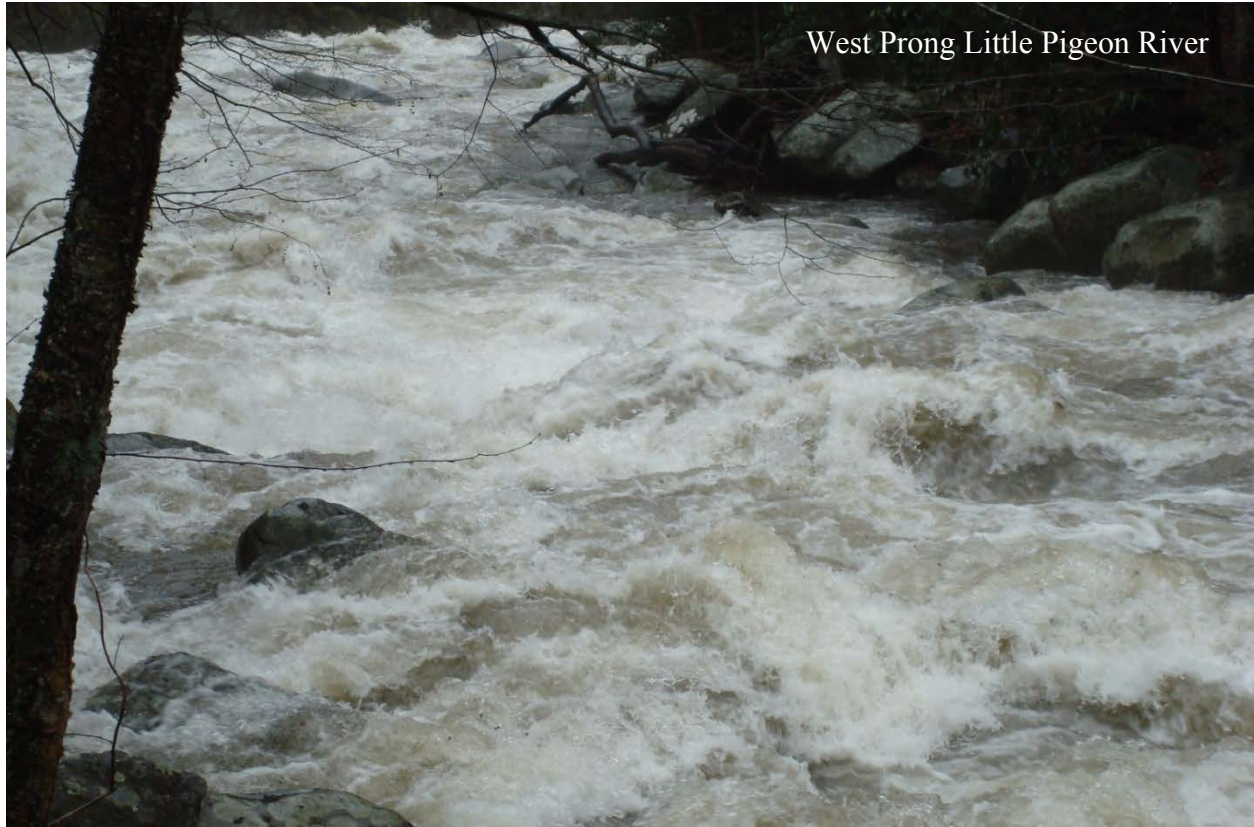


Great Smoky Mountains National Park

2011 Water Quality Annual Report



**US Department of Interior, National Park Service
Great Smoky Mountains National Park**

**University of Tennessee – Knoxville
Department of Civil & Environmental Engineering**



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GRSM 2011 WQ Annual Report

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TABLE OF CONTENTS

	Page
1.0 Introduction.....	1
1.1 <i>Noland Divide Watershed</i>	2
years old, and because of age it should be replaced. A funding request will be made to replace the lysimeter system in FY12.	6
1.2 <i>GRSM Park-wide Stream Survey for Baseflow Water Quality Monitoring</i>	6
1.3 <i>GRSM Water Quality Program Annual Reports and Research Publications</i>	9
2.0 Noland Divide Watershed: 2011 Data Summary and Discussion	10
2.1 <i>Annual Precipitation Volume</i>	10
2.2 <i>Annual Deposition Rates for Chemical Constituents</i>	10
2.3 <i>Soil Water Chemistry from Lysimeters</i>	13
2.4 <i>Stream Water Chemistry</i>	16
2.5 <i>Noland Divide Data Comparisons with TVA Power Plant Emissions</i>	17
3.0 Park-wide Stream Survey	19
3.1 <i>Water Quality Stream Chemistry Results</i>	19
3.2 <i>Elevational Variation on Stream Water Chemistry</i>	22
3.3 <i>Resurvey of Historic Monitoring Sites</i>	25
4.0 Laboratory Analysis: Quality Assurance\Quality Control.....	28
4.1 <i>Ion Chromatography Quality Assurance\Quality Control</i>	29
4.2 <i>Inductively Coupled Plasma-Atomic Emission Spectrometry QA/QC Procedures</i>	30
4.3 <i>Ion Balance Computations</i>	32
4.4 <i>USGS Round Robin Results</i>	35
5.0 Lysimeter Soil Water Experiment.....	35
6.0 References.....	42
Appendix A: Conceptual Framework for Stream Acidification Issues in the GRSM (2005).....	46
Appendix B: Stream Survey Site Descriptions.....	47
Appendix C: Analytical Procedures for Chemistry Analysis Performed at the University of Tennessee –Knoxville.	51
Appendix D: Chemistry Data of GRSM Resurveyed Park-wide Stream Survey Sites.....	52

LIST of TABLES

Table 2-1. Statistical summaries for pH and conductivity from the soil lysimeters.....	14
Table 2-2. Statistical summaries of the anion chemistry analysis from the soil lysimeters. All values are given in $\mu\text{eq/L}$	14
Table 2-3. Statistical summaries of the cation chemistry analysis on the soil lysimeters. All values are given in $\mu\text{eq/L}$	14
Table 2-4. Summary of water chemistry in SW and NE streamlets of Noland Divide study site. All parameter values are given in $\mu\text{eq/L}$, except for pH which are in pH units and conductivity in $\mu\text{S/cm}$, Al in mg/L	17
Table 3-1. Descriptive statistic of 1993-2010 median water quality values for 43 Park-wide stream survey sites. CV = coefficient of variation = standard deviation / mean.....	20
Table 3-2. Descriptive statistics of 2011 median water quality values for the 43 Park-wide stream survey sites.	21
Table 3-3. Metal concentrations for resurveyed Stream Survey site samples.....	25
Table 4-1. IC QA\QC for the anions/cations in 2011.....	29
Table 4-2. IC QA/QC sample checks using USGS standard solutions for 2011.....	30
Table 4-3. ICP-AES quality control check sample results ($n = 48$).....	31
Table 4-4. ICP-AES T-183 USGS standard reference sample results ($n = 44$).....	31
Table 4-5. ICP-AES Blank (deionized water) sample results ($n = 32$).....	32
Table 4-6. ICP-AES replicate sample results ($n = 21$).....	33
Table 4-7. ICP-AES spike sample results ($n = 12$).....	33
Table 4-8. 2011 ICP-AES detection limits.....	34
Table 4-9. Average ion balances for NDW NE & SE streams, OS precipitation, and TF.....	34
Table 4-10. USGS Round Robin results.....	36
Table 5-1. Soil water chemistry for the pan and perforated conduit collector lysimeters at Road Prong and Rock Creek, June 2011 – February 2012.....	40
Table 5-2. Comparison of lysimeter soil water chemistry among Road prong, Rock Creek, and Noland Divide sites.....	41
Table Appendix B- 1. Stream Survey Sites.....	47
Table Appendix C- 1. Analytical procedures for chemistry analysis performed at the University of Tennessee –Knoxville.....	51
Table Appendix D-1. Chemistry Data of GRSM Resurveyed Park-wide Stream Survey Sites ...	52

LIST of FIGURES

Figure 1-1. Location of Great Smoky Mountains National Park (GRSM).....	1
Figure 1-2. Map of Noland Divide watershed showing water quality monitoring sites.....	4
Figure 1-3. Photos depicting wet deposition collection (right) and throughfall collection (left). ..	5
Figure 1-4. H-flume weir on the NE stream, Noland Divide watershed.	6
Figure 1-5. Water quality monitoring sites for the GRSM Park-wide survey.	7
Figure 2-1. Total annual wet-only (OS) and throughfall (TF) precipitation volumes received by the NDW. 1991* collections started in June and represent ½ a year.	10
Figure 2-2. Total annual inorganic nitrogen deposition entering the NDW as wet-only (OS) and throughfall (TF) precipitation. 1991* collections started in June and represent ½ a year.	11
Figure 2-3. Total sulfate entering NDW as wet-only (OS) and throughfall (TF) precipitation. 1991* collections started in June and represent ½ a year.....	12
Figure 2-4. Comparison of sulfate and nitrogen concentration in deposition (annually volume-weighted concentration), annually average stream concentrations and total emissions from Bull Run and Kingston plants.	18
Figure 3-1. Median pH concentrations for the 43 Stream Survey sites by elevation (1993-2010, 2011).....	22
Figure 3- 2. Median ANC concentrations for the 43 Stream Survey sites by elevation (1993-2010, 2011).	23
Figure 3-3. Median sulfate concentrations for the 43 Stream Survey sites by elevation (1993-2010, 2011).	24
Figure 3-4. Median nitrate concentrations for the 43 Stream Survey sites by elevation (1993-2010, 2011).	24
Figure 3-5. Map of resurveyed GRSM Stream Survey sites	26
Figure 5-2. Soil lysimeter site locations in a) Road Prong and b) Rock Creek (Cosby) watersheds	39
Figure Appendix A-1. GRSM Conceptual Framework	46

1.0 Introduction

The Great Smoky Mountains National Park (GRSM) is located in the southern Appalachians in eastern Tennessee and western North Carolina (Figure 1-1). The GRSM is the second largest National Park in the eastern United States, comprising about 220,000 hectares (850 square miles). It was officially dedicated into the National Park system in 1940. GRSM receives approximately 10 million visitors per year, making it one of the most visited National Parks in the nation. Biodiversity in the GRSM is renown nationally supporting a wide variety of terrestrial and aquatic plants and animals. Streams in the GRSM sustain a great number of fish species, amphibians, and benthic macroinvertebrates; of which five streams are designated as Outstanding National Resource Waters.

Since the 1980's national air quality monitoring has shown that the GRSM receives high rates of atmospheric deposition of acid pollutants compared to other regions in the United States (Shubzda *et al.* 1995; NADP 2009; Sullivan *et al.* 2007), which has been linked to emissions from regional coal-fired power plants (Chestnut and Mills 2005). Most of the GRSM streams are low in alkalinity (acid neutralizing capacity, ANC), and exhibit acidification (lowered pH) chronically and episodically (Robinson *et al.* 2005, 2008; Deyton *et al.* 2008). Watershed geology and soil cannot buffer the acid pollutants. A major concern of stream acidification in watersheds that lack acid

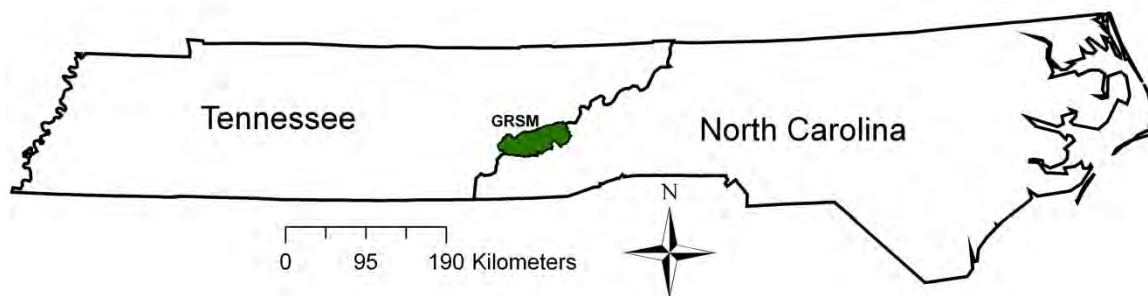


Figure 1-1. Location of Great Smoky Mountains National Park (GRSM).

buffering capacity is the facilitation of soil release of aluminum and delivery to streams, in which monomeric aluminum can be highly toxic to fish (Baldigo and Murdoch 1997; Neff et al. 2009).

Although impacts to the native brook trout (*Salvelinus fontinalis*) have not been observed directly, episodic stream acidification is suspected to be a primary cause of trout extirpation in six headwater streams in the GRSM, including some streams that were populated as recently as 15 years ago (Steve Moore *pers. comm.* 2006; Neff et al. 2009). Based on long-term declines in stream pH, GRSM resource managers were concerned that brook trout will continue to be eliminated from streams, and may disappear from the park within about 25 to 50 years if acid deposition continued at 1990's rates (Robinson et al. 2008). Concern over the potential impacts to water quality from atmospheric deposition of acid pollutants, GRSM investigations began as early as the 1970's. More recently, the GRSM implemented a long-term, water quality (WQ) monitoring program in 1991 with goals to better understand these impacts and improve resource management strategies.

The current WQ program consists of two primary components: 1) detailed hydrologic and WQ monitoring at Noland Divide, a high-elevation forested site; and 2) Park-wide stream survey during baseflow WQ conditions. In addition, the monitoring program supports analysis and interpretation of specific studies conducted by GRSM resource managers and University of Tennessee researchers. These studies are hypothesis-driven guided by a conceptual framework on the Park's stream acidification issue and based on pollutant fate and transport processes (Appendix Figure A).

1.1 Noland Divide Watershed

Noland Divide watershed (NDW) was selected as a long-term monitoring site following its use as a prior study site in the Integrated Forest Study, a North American and European program to examine the effects of acid rain on forests in the 1980's. In the eastern United States, high elevation watersheds with base-poor cation buffering capacity tend to be vulnerable to stream acidification

from acid deposition (Hyer *et al.* 1995; Driscoll *et al.* 2001). NDW provides a good site to record stream acidification responses due to acidic deposition, and five NDW monitoring sites were installed to monitor the potential effects of long-term acid deposition. The sites included: wet precipitation (open site, OS), throughfall (TF), soil water from lysimeters, and two stream outlets (SE and NE streams). This monitoring design provides a mean to assess impacts from acidic deposition, both wet and dry deposition (OS, TF sites), effects of soil on pollutant fate and transport, and stream acidification responses based on levels of atmospheric acid inputs to the watershed.

NDW is located in the GRSM about a half-mile from GRSM Clingman's Dome on the border of North Carolina and Tennessee at 35° 34' N latitude and 83° 29' W longitude. NDW is a small, 17.4 ha forested watershed ranging in elevation from 1680 m to 1920 m (Figure 1-2). Two adjacent first-order streams originate from this watershed and flow into Noland Creek (NE and SW streams). The mean annual air temperature measured at a climate station, located about 100 m below the watershed outlet, is approximately 8.5°C, ranging from -2°C in January to +18°C in July, with a frost-free period from May through September (Shanks 1954; Van Miegroet *et al.* 2001). The annual precipitation ranges from 200 cm to 300 cm, 10% of which is accounted by snow (Johnson *et al.* 1991; Johnson and Lindberg 1992). NDW's vegetative overstory consists of old-growth red spruce, and interspersed patches of dead Fraser fir (Nodvin *et al.* 1995).

Soils in the NDW are inceptisols with spodic characteristic, classified as Dystrochrepts or Haplumbrepts (McCracken *et al.* 1962; Van Miegroet *et al.* 1993). They have a silt loam to sandy loam texture, and are generally shallow throughout the NDW. Johnson and Lindberg (1992) characterized the NDW soil as consisting of a 4 cm thick Oi + Oe horizon of needles and leaves, a 4-cm thick Oa horizon of mucky humus, an 8 cm thick A horizon of dark, reddish-brown, mucky loam, a 27-cm thick Bw horizon of dark brown, sandy loam, a 35 cm thick Cb horizon of dark, yellowish-brown loam, a 20+ cm thick C horizon of olive-brown, loamy sand, and underlying

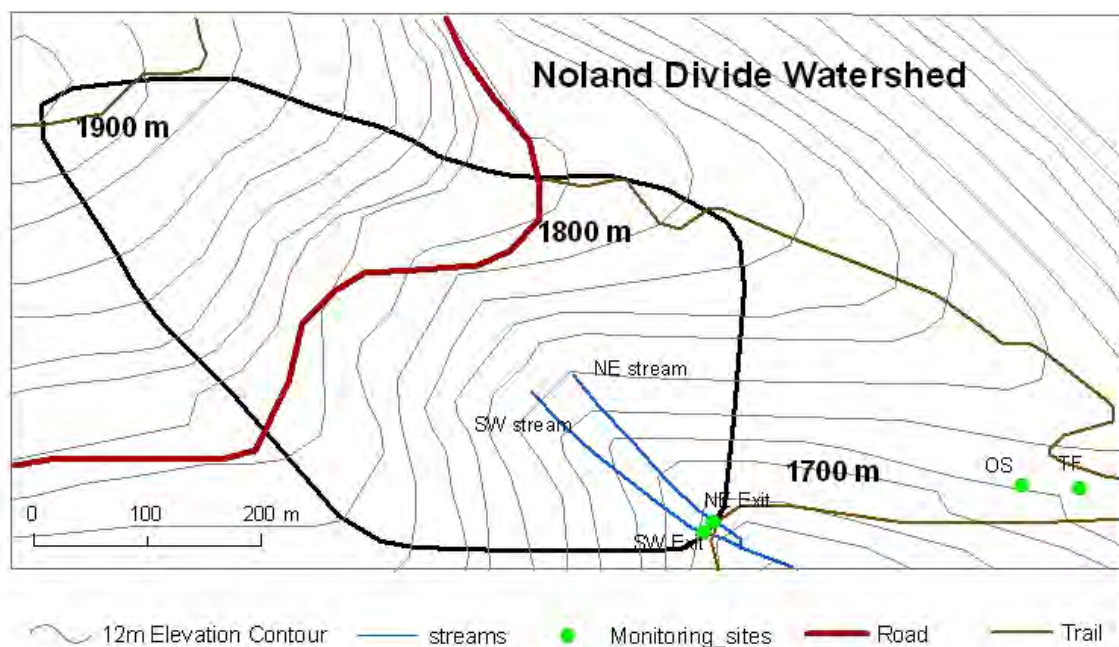


Figure 1-2. Map of Noland Divide watershed showing water quality monitoring sites.

sandstone bedrock. Underneath the soil is massive thick-bedded and low porosity Thunderhead sandstone, composed of quartz and potassic feldspar (King *et al.* 1968).

Every two weeks wet and throughfall precipitation (OS, TF) samples are collected at sites located on the NE side of the watershed (Figure 1-2). Wet-only precipitation is collected at the OS site, where there is no tree cover and it is fully exposed to atmosphere (Figure 1-3). TF collection is deployed under the canopy at the same elevation approximately 50 m east of the open site. During the frost-free season, TF precipitation is collected using 10 funnel collectors (8-inch diameter), which are randomly disbursed under the spruce-fir forest canopy. Funnels are placed about 1 m above the ground and covered by fiberglass net filters to prevent leaf litter contamination. Hoses from the funnels connect to 1-gallon LDPE brown jugs. Jugs are housed in 5-gallon buckets and buried $\frac{3}{4}$ of the way into the ground for insulation and protection. During the frost season, two 5-gal buckets with LDPE liners are used only to collect precipitation. Collected water samples from OS and TF sites are weighed in order to compute volumes, and brought back to UT lab for chemistry analyses.



Figure 1-3. Photos depicting wet deposition collection (right) and throughfall collection (left).

Stream flow and water quality are measured at the watershed outlet for the southwest (SW) and northeast (NE) streams. Stream flows are estimated by use of H-flume weirs and GlobalWater® WL16 stage recorders installed at each stream (Figure 1-4). Stage recorders measure flow depth every 15 minutes, and discharge is computed by H-flume standard formulas from the depth measurements. Water quality is continuously monitored with YSI600R® or Eureka Manta I sondes (pH, conductivity and temperature), in which the SW sonde data collection began in July 1991 and the NE sonde began in April 1998. Data from sondes are recorded every 15 minutes and data is downloaded every two weeks. Grab samples of stream water are collected from the NE and SW streams every two weeks and brought to the UT lab for chemical analyses (Section 4.0).

Soil water is collected by 12 ceramic suction lysimeters, four per three different soil horizons (A, Bw, and Cb horizons). Lysimeters are located adjacent to the TF precipitation site, and installed in 1991. The volume of soil solution determines the collection frequency for soil water samples, on a monthly basis. Frequency of lysimeter failure has increased this past year, where at least one of the four lysimeters per horizon is no longer operational. Embedded in the soil, non-functional lysimeters cannot be repaired, but must be replaced. The systems 12 lysimeters and vacuum apparatus is over 20



Figure 1-4. H-flume weir on the NE stream, Noland Divide watershed.

years old, and because of age it should be replaced. A funding request will be made to replace the lysimeter system in FY12.

1.2 GRSM Park-wide Stream Survey for Baseflow Water Quality Monitoring

Park-wide stream survey (*also termed* long-term synoptic baseflow stream WQ monitoring) began in October 1993 to monitor potential impacts from acidic deposition among GRSM streams. From 1993 to 1995, samples were collected at 367 sites semi-annually. In 1995, the number of sites was reduced to 160, and samples collected on a monthly basis. In 1997, the number of sites was further reduced to 90, and samples collected quarterly (Figure 1-5). The number of sites was further reduced in 2004 to 32 sites sampled bimonthly, and 11 Hazel Creek sites sampled biannually. These sites were selected to assess spatial variability of water quality within the GRSM across a range of elevations, geology types, and land disturbance histories (Odom 2003). The 43 sites are those currently monitored. A comprehensive analysis of the Park-wide stream survey data, including water chemistry, brook and rainbow trout, and benthic macroinvertebrates was conducted, and a draft report has been submitted to GRSM resource managers (Cai and Schwartz 2012).

From October 1993 to December 1998, water samples were collected and analyzed by personnel in the Department of Forestry, Wildlife, and Fisheries at the University of Tennessee -

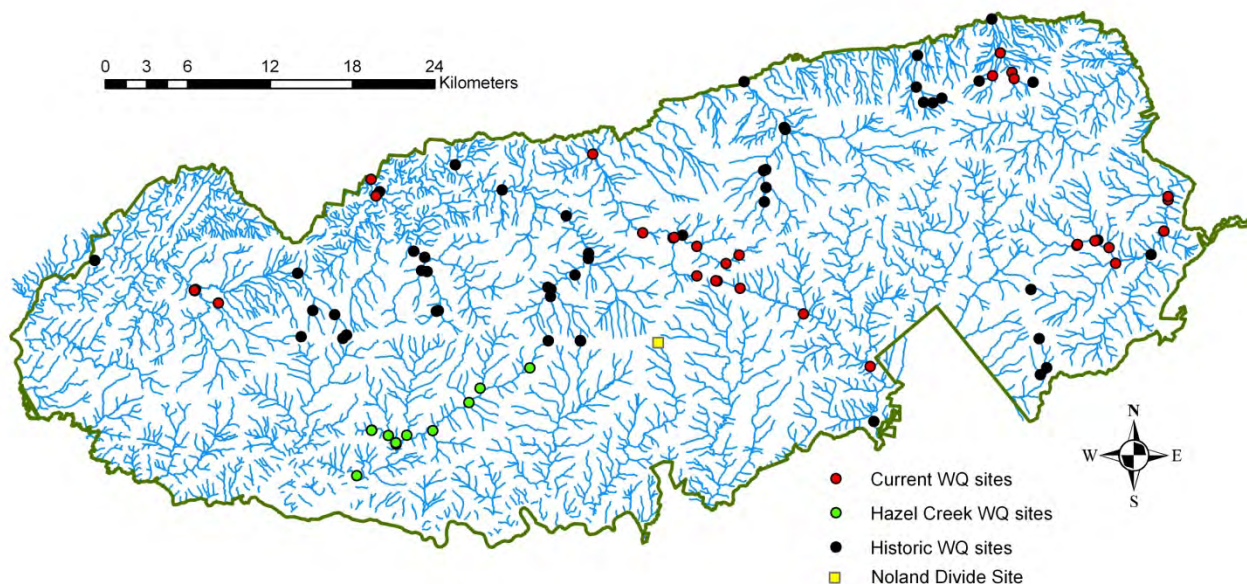


Figure 1-5. Water quality monitoring sites for the GRSM Park-wide survey.

Knoxville. From January 1998 to the present, Trout Unlimited volunteers and students in the Department of Civil and Environmental Engineering (CEE) have collected the bimonthly water samples. GRSM and CEE collect the biannual samples on Hazel Creek. Collected samples are transported chilled per standard methods to the CEE Water Quality Laboratory where chemical analyses are conducted. The WQ parameters currently measured are pH, ANC, conductivity, sulfate, nitrate, ammonium, chloride, sodium, potassium, calcium, magnesium, aluminum, zinc, copper, iron, manganese, and silica.

Park-wide stream WQ monitoring has provided an extensive database that continues to answer important questions regarding impacts to GRSM streams from acidic deposition. Robinson *et al.* (2008) generated step-wise multiple linear regression models to analyze long-term time trends in stream pH, ANC, sulfate and nitrate for 90 sites from 1993 to 2002. They used a wide range of potential predictor variables including: cumulative Julian day, seasonality, elevation, basin slope, stream order, precipitation, surrogate stream flows, geology, and acid depositional fluxes. Modeling results revealed statistically significant decreasing time trends in pH and sulfate at lower elevations,

but generally no long-term time trends in stream nitrate or ANC. Cai and Schwartz (2012) reanalyzed the data for the period 1993 through 2009, and found no trends in pH and ANC for most sites, however eight were found with slight increasing trends, and one with a decreasing trend. Details can be found in the report comprehensively analyzing the Park-wide stream survey data.

Jackson (2005) correlated WQ base flow data with brook and rainbow trout biomass in GRSM streams. The correlation analysis revealed that pH, ANC, conductivity, and sulfate were important WQ predictor variables of trout biomass. Biomass for both trout species were negatively correlated by increases in sulfate concentrations, and when Anakeesta geology (pyrite, sulfate-generating rock) was present in the watershed. Specifically addressing this question of whether the presence of Anakeesta geology significantly contributes to stream acidification was investigated by an eight-block study design, where the “treatments” included: drainage basin area (1-10 km² and 10-20 km²), elevation (< and > 975 m), and presence of Anakeesta geology (< and > 10% by area). Neff *et al.* (2012) found streams in higher elevation basins with the presence of Anakeesta were significantly different in stormflow pH and aluminum concentrations compared with other basin conditions in the eight-block experimental design. In this study, several basin characteristics were highly correlated with each other and uniquely contributed to the stream acidification response; they were topographic, geologic, soil, and vegetation basin factors. In the recent analysis by Cai and Schwartz (2012), relationships among water quality, elevation, and trout density and biomass were comprehensively assessed, and the reader is directed to that report for more information. However, the report did find brook trout density and biomass to be less in streams with a pH less than 6.0 compared to a pH greater than 6.0. Rainbow trout density and biomass were correlated with stream pH, but it appears this correlation may be a function of higher stream pH in lower elevation streams where rainbow trout typically range. In addition, the report analyses including a finding where interspecific competition between rainbow and brook trout may be influencing the statistics associated with water quality.

1.3 GRSM Water Quality Program Annual Reports and Research Publications

Data summaries are generated annually for the GRSM water-quality monitoring program. The WQ data in the annual reports and research publications are also used by other GRSM resource units including the air, species inventory, and vegetation units. Objectives of these annual reports are to detail and report results from the quality assurance/quality control (QA/QC) laboratory analytical protocols on samples collected, and to report and discuss basic trends found in the WQ data sets. Complete analysis and synthesis of the WQ data are conducted through periodic production of peer-review journal articles and PhD dissertations and MS theses. The following journal articles have been published since 2008:

- Neff, K.J., J.S. Schwartz, S.E. Moore, and M.A. Kulp. 2012. Influence of basin characteristics on episodic stream acidification in the Great Smoky Mountains National Park, USA. *Hydrological Processes*. DOI 10.1002/hyp.9366.
- Cai, M., A.M. 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., A.M. Johnson, J.S. Schwartz, S.E. Moore, and M.A. Kulp. 2011. 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. DOI: 10.1061/(ASCE) EE.1943-7870.0000354.
- Cai, M., J.S. Schwartz, R.B. Robinson, S.E. Moore, and M.A. Kulp. 2011. Long-term annual and season patterns of acidic deposition and stream water quality in a Great Smoky Mountains high-elevation watershed. *Water, Air and 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.
- Neff, K.J., J.S. Schwartz, T.B. Henry, R.B. Robinson, S.E. Moore, and M.A. Kulp. 2009. Physiological stress in native brook trout during episodic stream acidification in the Great Smoky Mountains National Park. *Archives of Environmental Contamination and Toxicology* 57: 366-376.
- 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. DOI 10.1007/s11270-008-9753-5.
- Robinson, R.B., T.W. Barnett, G.R. Harwell, S.E. Moore, M.A. Kulp, and J.S. Schwartz. 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.

2.0 Noland Divide Watershed: 2011 Data Summary and Discussion

2.1 Annual Precipitation Volume

The annual rainfall amounts collected during 2011 were 190 cm for wet-only (OS) and 211 cm for throughfall (TF). These values are close to the 20-year averages of 212 cm for open site and 221 cm for throughfall. The similar values indicated that year 2011 was a normal year for precipitation.

2.2 Annual Deposition Rates for Chemical Constituents

Annual deposition rates of chemical constituents are summarized for OS and TF precipitation, and compiled in the NPSTORET database for the GRSM. This annual report only presents data for nitrogen and sulfur constituents because of their dominant influence on stream acidification. Data for other anions/cations, and metal concentrations can be found in NPSTORET.

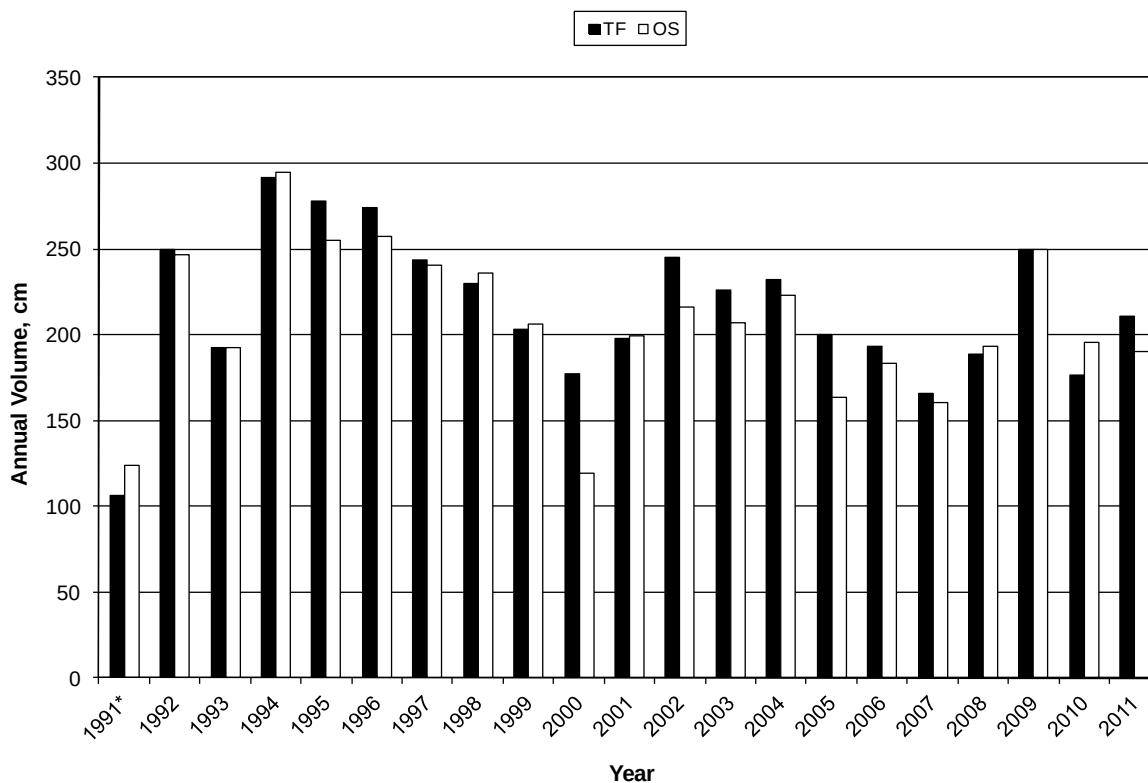


Figure 2-1. Total annual wet-only (OS) and throughfall (TF) precipitation volumes received by the NDW. 1991* collections started in June and represent ½ a year.

During 2011, the estimated amount of total inorganic nitrogen entering the NDW from OS precipitation was 209 equivalents of nitrogen per hectare per year (N eq/ha/yr) and from TF was 1059 N eq/ha/yr (Figure 2-2). In 2011, wet-only OS deposition was 248 eq/ha/yr *below* the average for the past 20-years, and the TF deposition rate was 80 eq/ha/yr *below* the 20-year average. The especially low OS inorganic nitrogen deposition could be partially attributed to incomplete record in 2011. Two sample periods on June 2 and November 18 were not analyzed because bottles were damaged in the field from animal activity. In total, about two months lacked OS deposition fluxes data because the 21-year old rainfall collector malfunctioned due to a worn gear and electrical wiring problems. Even though the estimates lack two months, the observed 2011 reduction in nitrogen flux at the open site by about 50% of the 2009 data was reasonable because nitrogen emissions from nearby TVA power

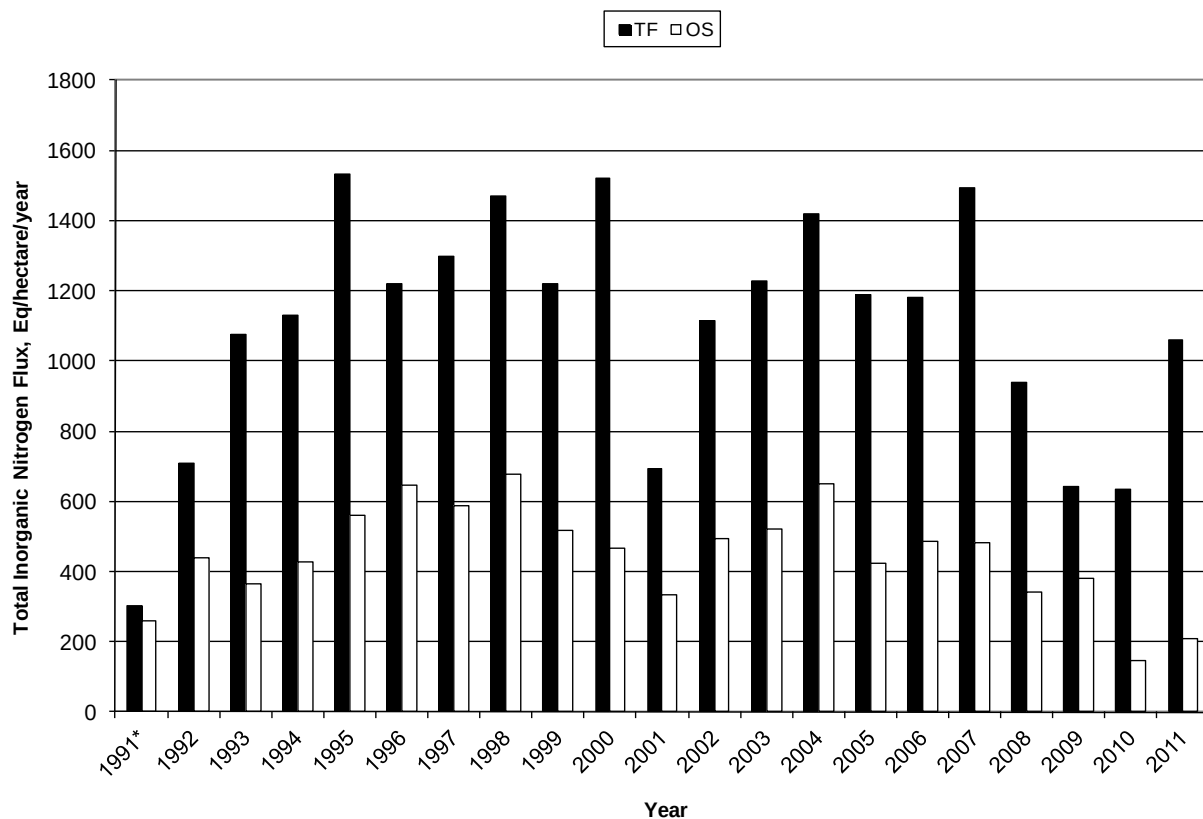


Figure 2-2. Total annual inorganic nitrogen deposition entering the NDW as wet-only (OS) and throughfall (TF) precipitation. 1991* collections started in June and represent ½ a year.

plants reduced in similar proportions, and the 2010 open site flux total showed a similar reduction as 2011 estimate when a complete dataset was collected.

The estimated amount of sulfate entering the NDW from OS precipitation was 433 eq/ha/yr and throughfall was 758 eq/ha/yr (Figure 2-3). Sulfate deposition exhibited significant reduction, especially TF deposition at 1,651 eq/ha/yr, which was less than half of the 20-year average. Compared with the 20-year average, OS deposition was approximately 123 eq/ha/yr *below* the long-term average. The 2011 dry deposition rate for sulfate was estimated as 325 eq/ha/yr. The actual 2011 dry deposition rate for sulfate may be lower than this value because of the rainfall collector equipment failure (as described above). Unlike nitrogen, sulfate flux represents a very good estimate of the total pollutant deposition rate that enters a watershed because foliar uptake and/or leaching are minimal (Lindberg and Garten 1988).

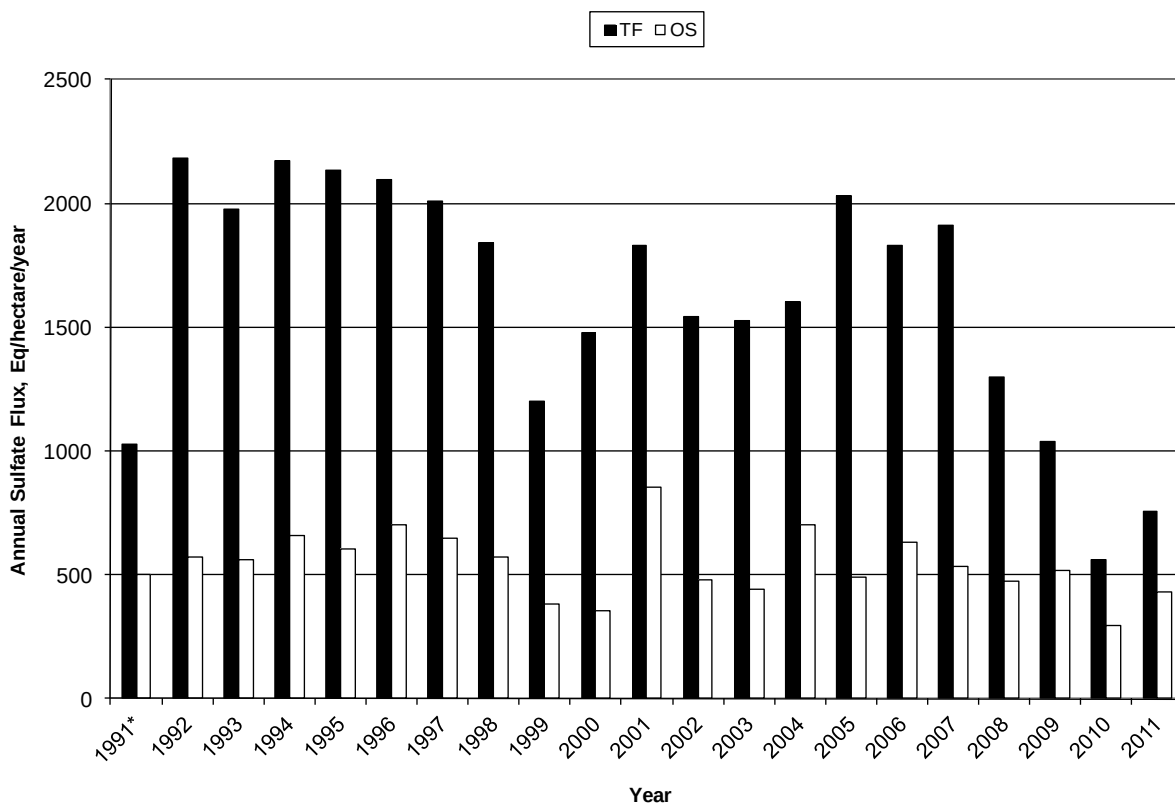


Figure 2-3. Total sulfate entering NDW as wet-only (OS) and throughfall (TF) precipitation. 1991* collections started in June and represent ½ a year.

In 2011 significant reduction for sulfate and total inorganic nitrogen deposition fluxes were observed from the previous year, with totals below 20-year average (Figures 2-2 and 2-3). The significant decrease of acid anions deposition resulted in the significant increase of TF pH. In 2011, TF pH was 4.98, 0.64 pH units higher than the 20-year average of 4.34. Similarly, OS precipitation pH has increased from 5.55 in 2010 to 5.64 in 2011. Compared to the 20-year average, the OS (wet-only) deposition pH in 2011 was 0.75 pH units above the average. The 2008 Annual Report recognized this observation as a result of recent emission controls of SO_4^{2-} and NO_x at coal-fired power plants west of GRSM, or possibly a function of the prolonged drought at that time.

2.3 Soil Water Chemistry from Lysimeters

Soil water chemistry was collected monthly from 7 of the originally installed 12 lysimeters (4 located at 3 different depths; upper A horizon 8 cm; middle Bw horizon 35 cm; and lower Cb horizon 65 cm). The annual volumes of water from the upper, middle, and lower lysimeters were 80 mL, 1,475 mL, and 2,430 mL, respectively. Because of the 21-year age of the soil lysimeter probes and suction vacuum system, lysimeters were not as effective at collection during 2011 as from previous years. It is likely the inaccessible plastic tubing embedded in the soil to the ceramic lysimeter has degraded and no longer holds sufficient suction pressure to work properly. This was observed especially from the upper horizon lysimeters where only one sample was collected. For middle and lower layers, three samples were grabbed for each horizon. A complete replacement of soil lysimeters needs to be completed in fall 2012. Statistical summaries of the soil water chemistry for 2011 are in Tables 2-1, 2-2, and 2-3, which include pH/conductivity, anions, and cations, respectively. Because of the sole sample point in upper layer, data for the upper lysimeters were not representative of the A soil horizon. The comparison of the 2011 data with historic data focused on the middle and lower lysimeters only.

Table 2-1. Statistical summaries for pH and conductivity from the soil lysimeters.

		pH	Conductivity, $\mu\text{S}/\text{cm}^2$
Upper Lysimeter	2011 Average	5.18	38.4
	1991-2010 Min- Max	3.36-5.10	1.31-179.10
	1991-2010 Average	4.04	63.75
Middle Lysimeter	2011 Average	4.30	37.53
	1991-2010 Min- Max	3.55 – 5.85	11.53 – 152.90
	1991-2010 Average	4.37	39.69
Lower Lysimeter	2011 Average	4.61	38
	1991-2010 Min- Max	3.79 – 5.37	14.31 – 102.90
	1991-2010 Average	4.48	33.58

Table 2-2. Statistical summaries of the anion chemistry analysis from the soil lysimeters. All values are given in $\mu\text{eq}/\text{L}$.

		Cl^-	NO_3^-	SO_4^{2-}
Upper Lysimeter	2011 Average	75.42	0	111.84
	1991-2010 Min- Max	1.61-229.53	3.09-784.94	0-316.93
	1991-2010 Average	28.52	138.40	91.60
Middle Lysimeter	2011 Average	22.54	101.17	57.83
	1991-2010 Min- Max	5.04 – 228.35	1.54 – 478.50	44.86 – 334.49
	1991-2010 Average	27.71	74.77	99.22
Lower Lysimeter	2011 Average	17.85	202.02	55.33
	1991-2010 Min- Max	0 – 238.21	4.20 – 265.85	28.67 – 170.12
	1991-2010 Average	23.37	81.53	90.83

Table 2-3. Statistical summaries of the cation chemistry analysis on the soil lysimeters. All values are given in $\mu\text{eq}/\text{L}$.

		Na^+	K^+	Mg^{2+}	Ca^{2+}
Upper Lysimeter	2011 Average	16.42	52.10	25.44	119.37
	1991-2010 Min- Max	3.3 - 482.62	1.14 - 103.73	2.12 – 249.38	9.23 – 577.50
	1991-2010 Average	26.46	22.27	27.83	52.40
Middle Lysimeter	2011 Average	18.71	19.96	24.50	59.41
	1991-2010 Min- Max	2.81 – 84.03	0 – 168.00	1.52 – 38.60	5.81 – 70.58
	1991-2010 Average	23.22	10.53	20.63	26.37
Lower Lysimeter	2011 Average	24.47	9.27	34.50	68.27
	1991-2010 Min- Max	0 – 57.23	0 – 109.31	8.62 – 43.76	6.30 – 216.50
	1991-2010 Average	19.70	9.72	23.63	37.42

Dynamics of soil water chemistry involve an array of biogeochemical processes influenced by precipitation volumes and chemistry, temperature, seasons, soil physiochemical properties, and local vegetation characteristics (Cook *et al.* 1994; Lawrence 2002; Deviney *et al.* 2006). Deposition of atmospheric acid pollutants in the NDW can pass-through, become adsorbed, transformed by microbial and vegetation, and/or later desorbed from the soil (Cai *et al.* 2011, 2012).

Analysis of anion chemistry found an average decrease in chlorine and sulfate, and an increase of nitrate for 2011 compared to the previous 20-year average (Table 2-2). Chlorine concentrations for middle, and lower horizons decreased 5.17 $\mu\text{eq/L}$, and 5.52 $\mu\text{eq/L}$, respectively. Sulfate concentrations for upper, middle, and lower horizons decreased 41.39 $\mu\text{eq/L}$, and 35.50 $\mu\text{eq/L}$, respectively. Nitrate concentrations for middle, and lower horizons increased 26.40 $\mu\text{eq/L}$, and 120.49 $\mu\text{eq/L}$, respectively. Significant reduction in sulfate concentrations may be due to the relatively low deposition fluxes of sulfate during 2011. In contrast, nitrogen deposition during 2011 was similar to the average 20-yr average flux. As a result, the soil nitrate concentration did not show declining trend in 2012.

The base cation chemistry in 2011 varied greatly from the 1991-2010 average, especially with potassium and calcium in the middle and lower soil horizons (Table 2-3). Higher variances were in the 2011 data compared with previous years may be due to a reduction in sample numbers (loss of statistical degrees of freedom) compared with previous years. Soil chemistry is naturally variable due to the many environmental factors that influence it, i.e., moisture and temperature.

The soil water pH for 2011 averaged 4.30 for the middle Bw horizon, and 4.61 for the lower Cb horizon. Comparing the 2011 averages for soil water pH to the 1991-2010 long-term averages, the pH remained relatively constant for the middle Bw horizon but increased 0.13 pH unit for the lower Cb horizon (Table 2-1). This observation may be explained in part by the measured increase in soil calcium concentration in Cb soil horizon.

2.4 Stream Water Chemistry

Stream water quality is monitored at the SW and NE streamlets biweekly (Table 2-4). Stream sulfate levels were slightly greater in 2011 compared to the long-term (1991-2010) average. Sulfate in the SW and NE streamlets were 33.06 µeq/L and 43.03 µeq/L, respectively for 2011. The long-term (1991-2010) averages in the SW and NE streamlets were 29.99 µeq/L and 41.22 µeq/L, respectively. In contrast, nitrate and calcium levels were less in 2011 compared to the long-term (1991-2010) averages. Nitrate in the SW and NE streamlets were 26.34 µeq/L and 31.80 µeq/L for 2011 compared to 39.95 µeq/L and 45.30 µeq/L for the long-term averages, respectively. Calcium in the SW and NE streamlets were 44.16 µeq/L and 47.85 µeq/L for 2011 compared to 46.48 µeq/L and 51.25 µeq/L for the long-term averages, respectively.

In 2011, pH levels in the SW and NE streamlets averaged 6.17 and 5.84, respectively. Stream pH increased in both SW and NE streamlets from the long-term (1991-2010) average of 5.84 and 5.59, respectively. Higher sulfate and lower calcium levels should lower the stream pH rather than increase it as observed. However, nitrate levels were less in 2011 compared to the long-term average prior to 2011, suggesting in-stream nitrate may be controlling baseflow stream pH. This general observation is a shift from previous years where sulfate appeared to control stream pH. Analysis of the Park-wide data has also observed this shift but only in the higher elevation streams (see *2012 Biotic Effects Report*). Over the past three years, emissions in sulfate and nitrate have decreased from two TVA power plants and may explain this observation (Section 2.5). In Section 2.5, a preliminary comparison between TVA power plant emissions and stream chemistry was conducted. Stream pH levels are a function of atmospheric deposition of acid pollutants, precipitation volumes and intensities, biogeochemical processes in the soil, and ion transport rates from soil to stream.

Table 2-4. Summary of water chemistry in SW and NE streamlets of Noland Divide study site. All parameter values are given in $\mu\text{eq/L}$, except for pH which are in pH units and conductivity in $\mu\text{S/cm}$, Al in mg/L .

Water Chemistry Parameter	SW Streamlet		NE Streamlet	
	2011 Average	1991-2010 Average	2011 Average	1991-2010 Average
pH	6.17	5.84	5.84	5.59
Conductivity	11.25	12.95	12.99	14.92
ANC	15.39	11.43	7.40	4.04
Cl^-	15.20	15.34	16.83	18.00
SO_4^{2-}	33.06	29.99	43.03	41.22
NO_3^- -N	26.34	39.95	31.80	45.30
NH_4^+ -N	4.67	0.83	4.93	1.12
Na^+	22.77	25.58	24.42	25.37
K^+	10.74	8.58	10.54	11.46
Mg^{2+}	16.10	18.04	18.30	20.32
Ca^{2+}	44.16	46.48	47.85	51.25
Al	0.08	0.04	0.07	0.06

2.5 Noland Divide Data Comparisons with TVA Power Plant Emissions

Because of the recent major reductions of sulfur and nitrogen emissions from two TVA coal-fired power plants (PP), the Bull Run and Kingston PP, a preliminary assessment was completed to evaluate whether changes in TF deposition and stream water chemistry at NDW could be correlated (Figure 2-4). From 2008 to 2009, the total emission of nitrogen dioxide dropped from 17,000 tons to 1,820 tons, and sulfur dioxide reduced from 79,000 tons to 11,570 tons. Reduction ratios were as large as to 10 times. Although the SO_4^{2-} and N deposition concentrations were variable, OS and TF concentration reductions corresponded similarly in scale with emission reductions during same time period. However, stream sulfate concentrations did not change remaining between 50 and 70 $\mu\text{eq L}^{-1}$. Nitrogen emissions from these two plants declined by about 50% in 2004 as observed from previous years, and in 2009 emission declines were about 9 times that reported in 2004. From these comparisons, it appears the NDW water chemistry has been affected by

the reductions in Bull

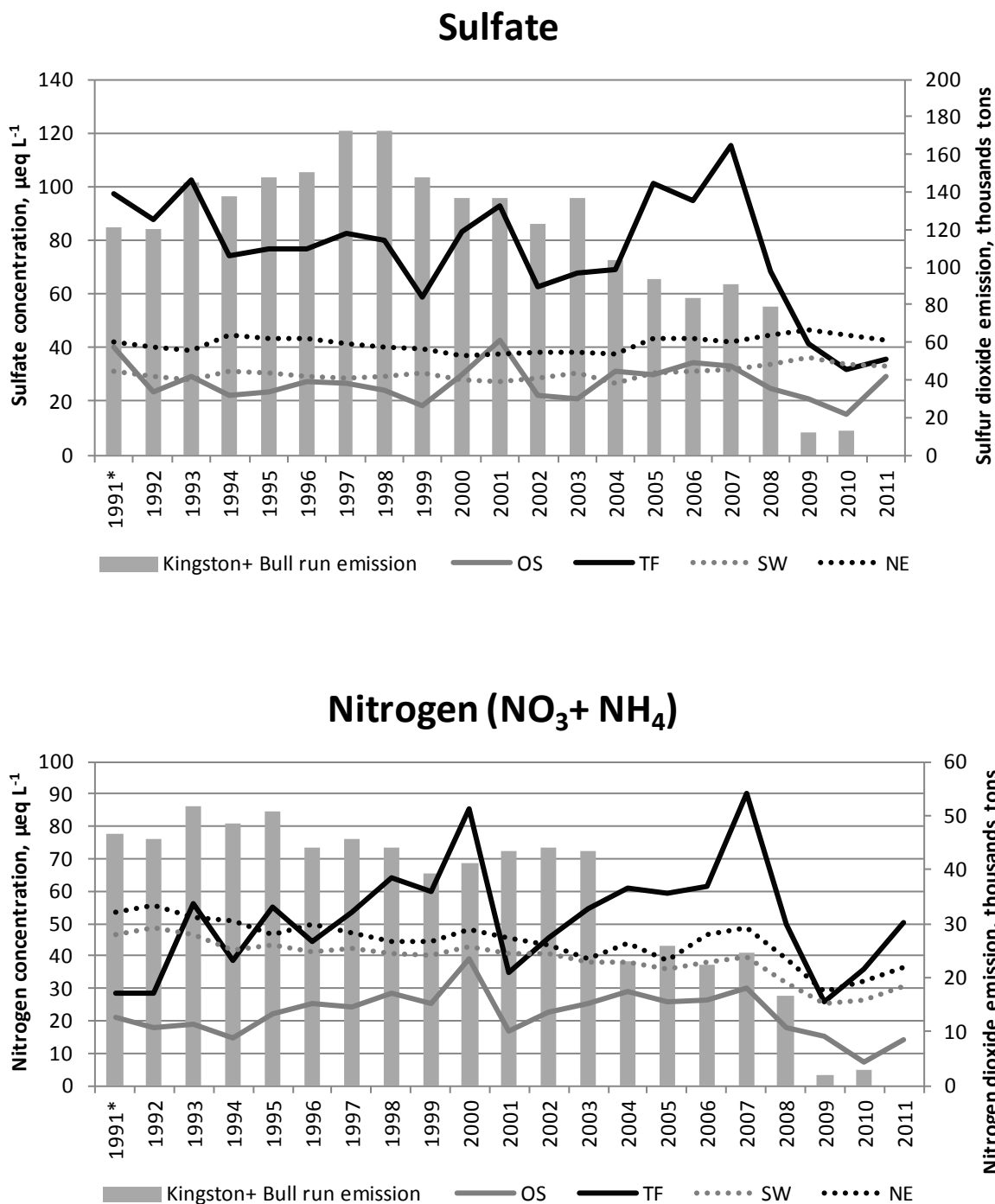


Figure 2-4. Comparison of sulfate and nitrogen concentration in deposition (annually volume-weighted concentration), annually average stream concentrations and total emissions from Bull Run and Kingston plants.

Run and Kingston PP emissions. However more analysis is needed because TF sulfate and nitrate declined about 40% from 2008 to 2009, one year prior to the major reduction in TVA power plant emissions. The 40% reduction in TF concentrations were not out of the range historically observed over time, and thus the 2008-2009 reduction may be attributed to precipitation or some other environmental factor. Further analysis is warranted.

3.0 Park-wide Stream Survey

The Park-wide stream survey dataset for 2011 included samples collected bimonthly (January, March, May, July, September, and November) from 32 sites in six watersheds (Abrams Creek, Little River, Cataloochee Creek, Oconaluftee Creek, Road Prong, and Cosby Creek). In the Hazel Creek watershed, samples were collected from 11 sites in both April and November. This report summarizes WQ data from the 43 sites for 2011. In addition, comparisons were made between the 2011 data and previous data collected from October 1993 through November 2010.

3.1 Water Quality Stream Chemistry Results

Descriptive statistics of the WQ constituents for the 1993 to 2010 dataset for the 43 survey sites are presented in Table 3-1 (minimum, maximum, mean, standard deviation, and coefficient of variation), in order to compare with the current 2011 data. Note, trace metals analyses for Al, Cu, Fe, Mn, Si, and Zn began in August 2003. Examination of coefficient of variation (CV) for constituents provides information on the spatial and temporal variability of constituents in the GRSM. Between 1993 and 2010, stream pH values ranged from 4.80 to 7.57, and did not vary minimally (CV = 0.072). However, ANC was found to vary widely ranging from $-14.831 \mu\text{eq/L}$ to $1,043.91 \mu\text{eq/L}$ (CV = 1.97), likely due to differences in surficial geology, soils, seasons, flow stage, and watershed size (Deyton et al. 2009; Cai et al. 2011; Neff et al. 2012). ANC were above $100 \mu\text{eq/L}$ among streams in the Abrams Creek watershed, an area of GRSM with carbonaceous limestone geology.

Table 3-1. Descriptive statistic of 1993-2010 median water quality values for 43 Park-wide stream survey sites. CV = coefficient of variation = standard deviation / mean.

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation	CV
Median pH	4.800	7.570	6.416	0.462	0.072
Median ANC (µeq/L)	-14.831	1043.911	100.294	197.943	1.974
Median Conductivity (µS/cm)	10.610	99.800	20.347	17.656	0.868
Median Chloride (µeq/L)	9.890	19.868	13.972	2.074	0.148
Median Nitrate (µeq/L)	0.000	57.532	19.199	16.156	0.842
Median Sulfate (µeq/L)	15.049	317.378	46.498	51.336	1.104
Median Sodium (µeq/L)	18.022	66.924	38.994	9.420	0.242
Median Ammonium (µeq/L)	0.000	0.000	0.000	0.000	0.000
Median Potassium (µeq/L)	3.699	15.760	10.839	2.882	0.266
Median Magnesium (µeq/L)	16.403	192.335	41.816	36.994	0.885
Median Calcium (µeq/L)	31.399	815.286	98.542	155.615	1.579
Median Aluminum (ppm)	0.012	0.434	0.044	0.064	1.453
Median Copper (ppm)	0.000	0.061	0.001	0.009	6.557
Median Iron (ppm)	0.002	0.033	0.017	0.007	0.415
Median Manganese (ppm)	0.000	0.279	0.008	0.043	5.296
Median Silicon (ppm)	1.339	4.528	2.792	0.693	0.248
Median Zinc (ppm)	0.000	0.156	0.008	0.025	3.121

Similar to ANC, sulfate and calcium concentrations were found to be highly variable ranging from 15.05 µeq/L to 317.38 µeq/L (CV = 1.10), and 31.40 µeq/L to 815.29 µeq/L (CV = 1.58), respectively. Metals were also variable among sites, and would be expected to vary on flow stage, typically being diluted at higher flows. Details on chemical concentration trends over time from 1993 to 2002 can be found in Robinson *et al.* (2008).

Descriptive statistics of the median WQ values for the 2011 data are summarized in Table 3-2 (median refers to the 43 survey sites). In addition, Table 3-2 presents the percent differences between the 2011 medians and the average of 1993-2010 site medians. Most ion constituents for 2011 were

less than 10% different of the 19-year average. Percent differences between current and historical medians for dissolved metals and ammonium are always greater than other ions because of their very low concentrations, and slight differences generate large percentages. Interestingly, nitrate was nearly 17% higher in 2011 possibly because of increases in ammonia deposition. Nitrate concentrations were significantly greater over this period among surveyed streams. Sodium and potassium concentrations were more than 10% lower than the historical averages.

Table 3-2. Descriptive statistics of 2011 median water quality values for the 43 Park-wide stream survey sites.

Water Quality Parameter	Mean	Minimum	Maximum	Std. Deviation	*Percent Difference
Median pH	6.705	5.072	7.880	0.517	4.510
Median ANC (µeq/L)	98.109	-5.647	1032.824	202.246	-2.179
Median Conductivity (µS/cm)	19.278	9.110	103.900	18.653	-5.255
Median Chloride (µeq/L)	13.597	10.338	25.456	3.214	-2.689
Median Nitrate (µeq/L)	22.453	1.029	65.293	20.002	16.951
Median Sulfate (µeq/L)	45.048	16.396	285.616	45.377	-3.119
Median Sodium (µeq/L)	34.158	18.186	54.012	7.366	-12.402
Median Ammonium (µeq/L)	1.674	0.591	3.620	0.696	-
Median Potassium (µeq/L)	9.695	0.000	13.711	2.793	-10.556
Median Magnesium (µeq/L)	40.413	14.523	187.224	37.320	-3.355
Median Calcium (µeq/L)	97.840	30.028	823.560	159.060	-0.712
Median Aluminum (ppm)	0.040	0.000	0.353	0.054	-8.764
Median Copper (ppm)	0.002	0.000	0.050	0.008	41.277
Median Iron (ppm)	0.021	0.000	0.103	0.017	21.932
Median Manganese (ppm)	0.006	0.000	0.190	0.029	-26.861
Median Silicon (ppm)	2.662	1.327	4.076	0.661	-4.652
Median Zinc (ppm)	0.007	0.000	0.044	0.008	-9.867

*Percent Difference = (2011 average – 1993-2010 average)/(1993-2010 average) × 100%.

3.2 Elevational Variation on Stream Water Chemistry

Elevation trends were evaluated for pH, ANC, sulfate and nitrate concentration for 1993-2010 and 2011 periods, between 1000 ft and 5000 ft. Figures 3-1 and 3-2 are scatterplots of median pH and ANC concentrations by elevation. Note, Abrams Creek sites 174 and 489 were omitted because of very high ANC concentrations, a function of limestone geology weathering. ANC and pH median concentrations decreased with increasing elevation. Trend lines for pH for 2011 and 1993-2010 periods have similar slopes with different intercepts. Based on the 43 study site, it appears that stream pH increased at all elevations in the GRSM. ANC trend lines for 2011 and 1993-2010 have different slopes and intercepts. In addition, ANC increased in higher elevation streams, and decreased in lower elevation streams. A larger sample size of sites would aid in confirmation of the observed trend.

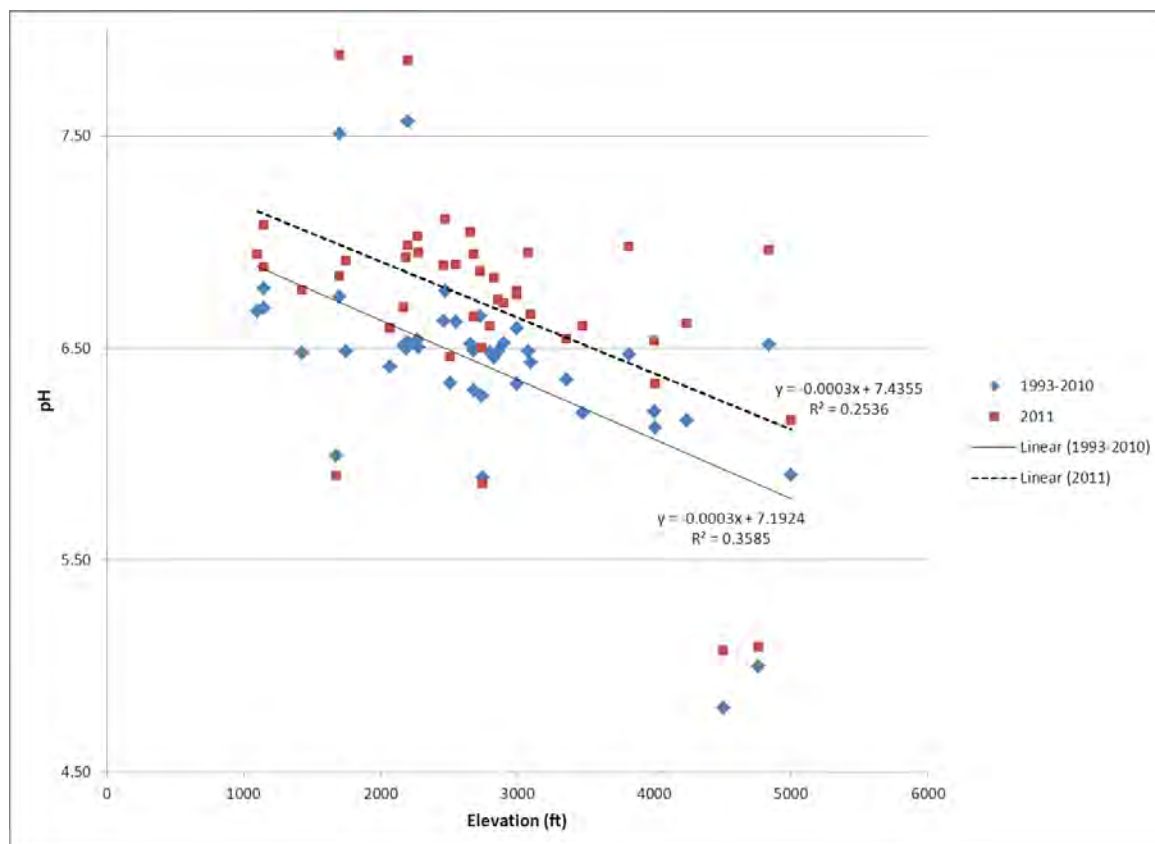


Figure 3-1. Median pH concentrations for the 43 stream survey sites by elevation (1993-2010, 2011).

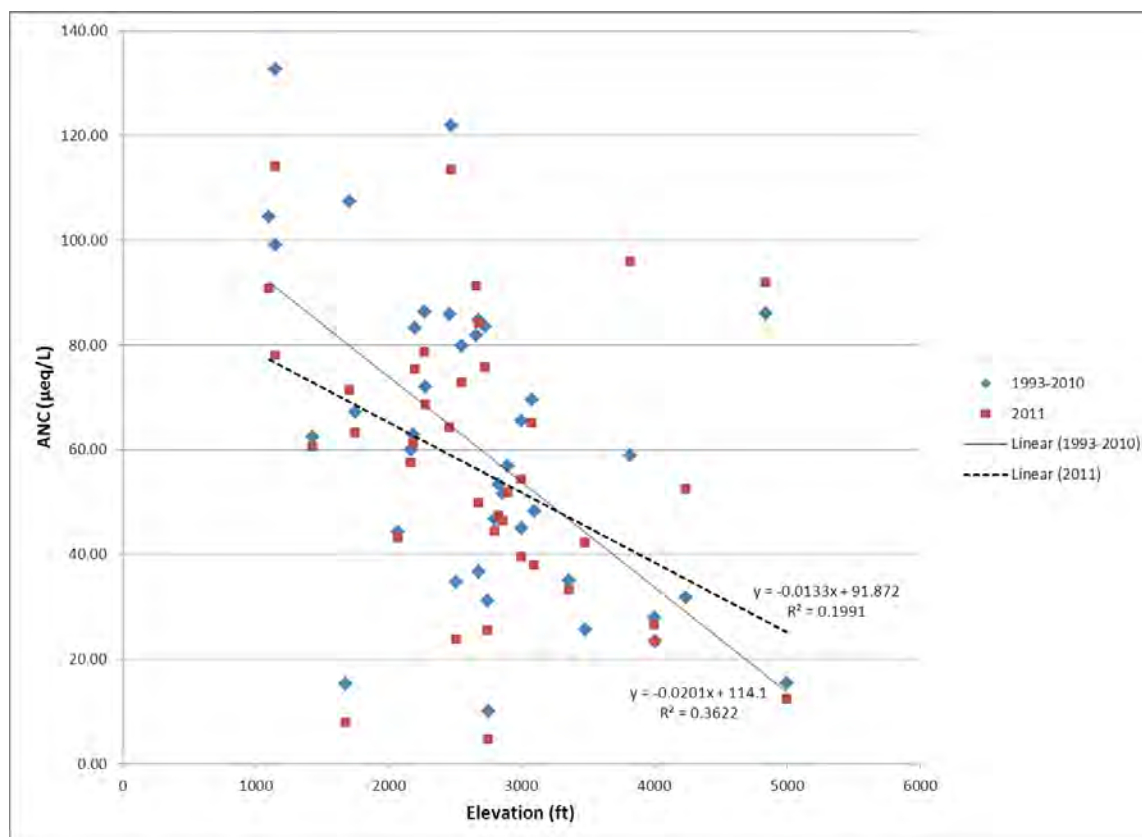


Figure 3-2. Median ANC concentrations for the 43 stream survey sites by elevation (1993-2010, 2011).

Elevation trends were also evaluated for sulfate and nitrate concentration in GRSM streams for the period 1993-2010 and for 2011. Figures 3-3 and 3-4 are scatterplots of median sulfate and nitrate concentrations for the 2011 and 1993-2010 periods by elevation. These plots demonstrated sulfate and nitrate median concentrations increased with increasing elevation. Sulfate trend lines for 2011 and 1993-2010 periods were similar. Although at two out of six higher elevations sites above 4000 ft, sulfate concentrations decreased in 2011 compared to previous years. More WQ data is needed in higher elevation streams. The nitrate trend lines for 2011 and 1993-2010 have similar slopes with different intercepts. Among the current set of GRSM study sites, nitrate concentrations were observed to increase at all elevations.

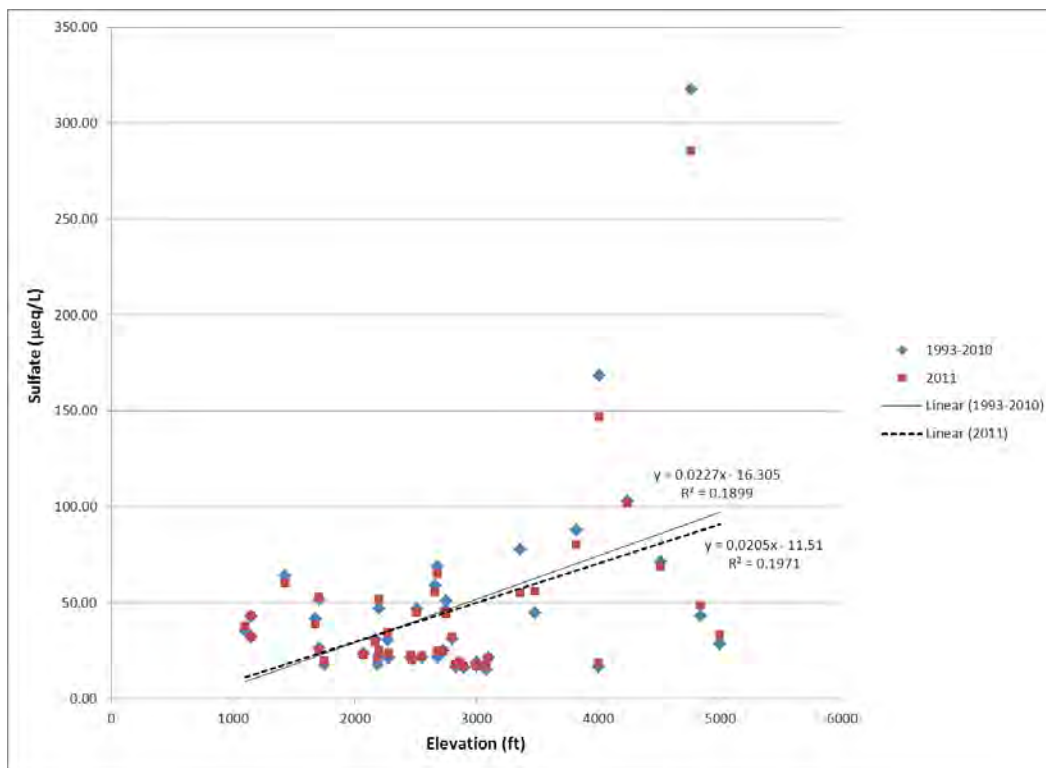


Figure 3-3. Median sulfate concentrations for the 43 stream survey sites by elevation (1993-2010, 2011).

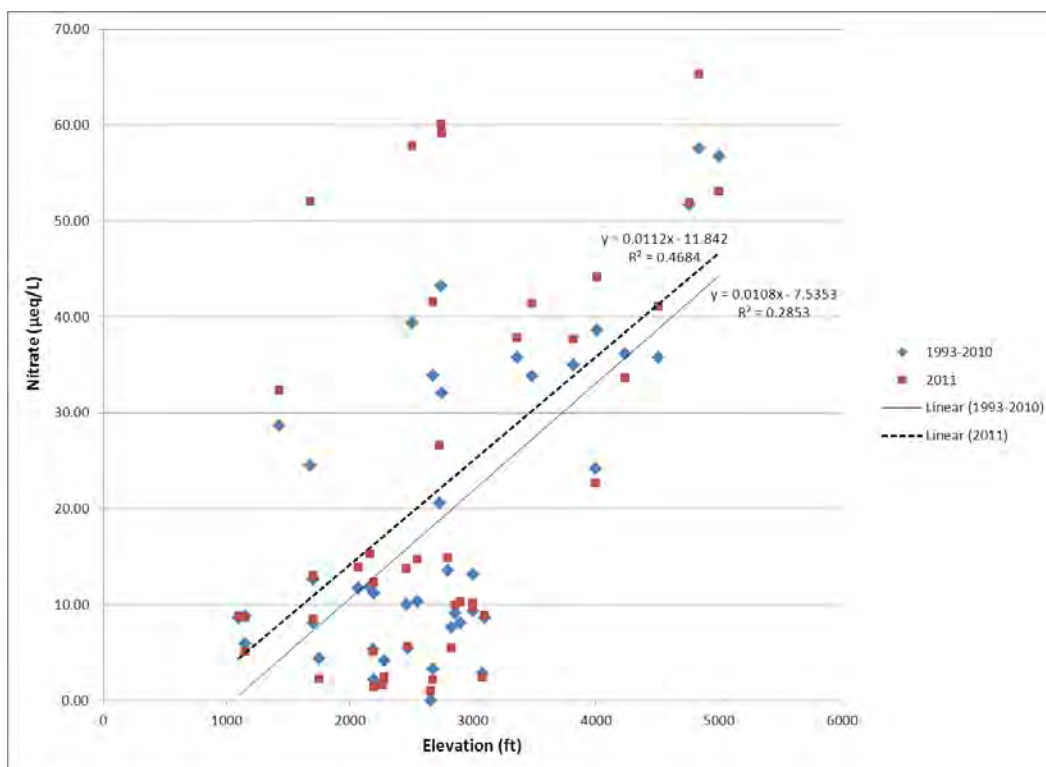


Figure 3-4. Median nitrate concentrations for the 43 stream survey sites by elevation (1993-2010, 2011).

3.3 Resurvey of Historic Monitoring Sites

During March 2011, 22 stream survey sites from the historic 1993 survey were re-sampled. Sites locations in the GRSM are shown on the Figure 3-5. University of Tennessee undergraduate students volunteered to conducting the samples during their spring break (March 19-26, 2011). Unfortunately, the exact date of collection was not recorded for most of the samples by the volunteers; volunteers lacked a group leader to organize field training. Looking at NDW flow data for this period, there was a small hydrological event on March 23rd such that flow in the NE flume increased from 0.37 cfs to 0.60 cfs. This flow event was probably caused by a small precipitation episode with possibly some snow melt. Appendix D contains descriptive statistics of median values the historical period (1993-2003) and the 2011 samples. Percent differences for each constituent are

Table 3-3. Metal concentrations for resurveyed Stream Survey site samples.

Collection Date	Site ID	Ammonia (µeq/L)	Aluminum (ppm)	Copper (ppm)	Iron (ppm)	Manganese (ppm)	Silicon (ppm)	Zinc (ppm)
3/19-26/2011	45	15.96	0.02	BDL	0.03	BDL	2.55	BDL
3/19-26/2011	46	BDL	0.03	BDL	0.04	BDL	4.70	0.01
3/19-26/2011	47	8.75	0.03	BDL	0.03	BDL	2.76	BDL
3/19-26/2011	103	3.35	0.13	BDL	0.01	0.01	2.07	0.01
3/19-26/2011	104	4.76	0.04	BDL	0.02	BDL	1.87	BDL
3/19-26/2011	107	3.34	0.05	BDL	BDL	BDL	1.97	BDL
3/20/2011	127	0.91	0.05	BDL	0.04	BDL	2.48	BDL
3/19-26/2011	183	2.35	0.04	BDL	BDL	BDL	2.18	BDL
3/19-26/2011	184	2.61	0.03	BDL	BDL	BDL	2.06	BDL
3/19-26/2011	185	2.85	BDL	BDL	BDL	0.01	1.55	BDL
3/19-26/2011	190	BDL	BDL	BDL	BDL	BDL	2.30	BDL
3/19-26/2011	191	3.68	0.03	BDL	0.01	BDL	1.69	BDL
3/19-26/2011	192	2.56	BDL	BDL	0.02	BDL	1.73	BDL
3/19-26/2011	200	3.66	0.03	BDL	BDL	BDL	1.94	BDL
3/19-26/2011	201	BDL	0.03	BDL	BDL	0.01	1.81	BDL
3/19-26/2011	210	2.75	0.11	BDL	0.25	BDL	2.58	BDL
3/19-26/2011	213	4.63	BDL	BDL	BDL	BDL	2.11	BDL
3/19-26/2011	214	1.81	0.03	BDL	0.02	BDL	2.12	BDL
3/19-26/2011	215	4.04	BDL	BDL	BDL	BDL	2.10	BDL
3/19-26/2011	472	2.19	BDL	BDL	BDL	BDL	1.89	BDL
3/19-26/2011	474	7.07	BDL	BDL	BDL	BDL	2.11	BDL
3/19-26/2011	475	2.90	0.03	BDL	BDL	BDL	2.10	BDL

* Site location information by Site ID number is in Appendix B.

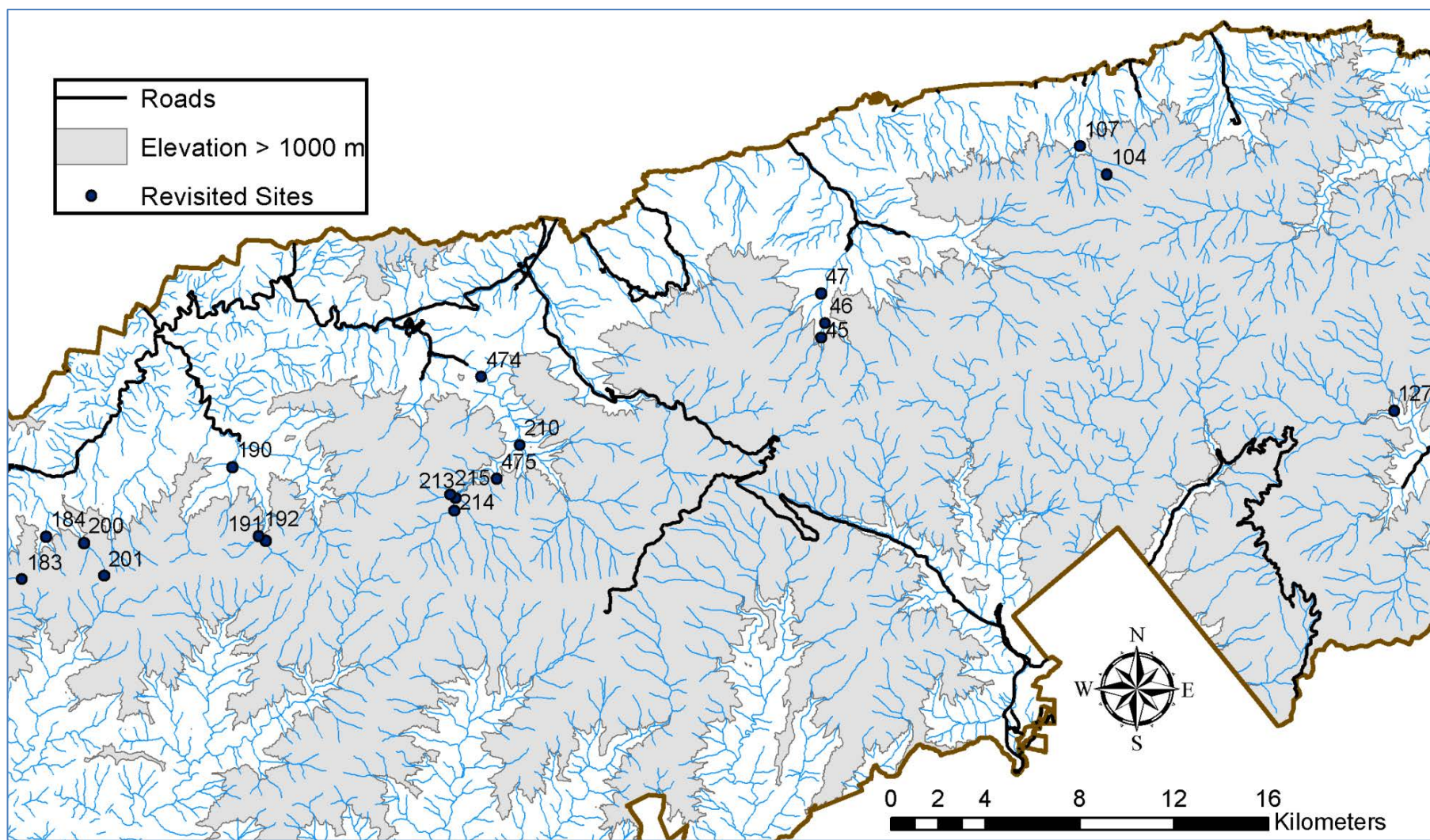


Figure 3-5. Map of resurveyed GRSM Stream Survey sites.

of constituents (pH, ANC, nitrate, sulfate, chloride, sodium, potassium, magnesium, and calcium) for also presented in Appendix D. In general, stream pH was higher at most of the sites in 2011 compared to this historic 1993 data. Descriptive statistics of the median metal concentrations for this data are summarized in Table 3-3.

4.0 Laboratory Analysis: Quality Assurance\Quality Control

Analytical procedures used to chemically analyze water samples for pH, ANC, conductivity, ions, and dissolved metals were based upon standard methods (Appendix E). WQ results for all samples are reported and archived in the NPSTORET database, however data quality is reported here. In 2011, 1,229 water samples were analyzed: i.) Park-wide Stream Survey site grab samples (n = 284); ii.) Noland Divide Watershed open-site and throughfall precipitation, lysimeter, and SW/NE stream water samples (n = 83); iii) soil nitrification experiment samples (n = 840; IC only); and iv) Resurveyed Park-wide Stream Survey sites (n = 22).

Water samples collected in the field were transported to UT WQ laboratory located in the Science and Engineering Research Facility (SERF) building, and within 24 hours samples were analyzed for pH, ANC, and conductivity. Park-wide samples are stored in the GRSM WQ field refrigerator after collection by Trout Unlimited volunteers, and may not meet the 24 hour period.

Analyses for pH, conductivity and gran ANC were conducted at room temperature to standardize results among many samples collected from different locations, times, and temperatures. After completion of these three analyses, water samples were refrigerated until the remaining analyses were performed (i.e., ions and dissolved metals). Because our analytical instruments and procedures are optimized for samples at low concentrations of dissolved constituents, dilution was only used when necessary for higher concentration sample constituents. All water quality analyses

and data were checked by laboratory quality assurance\quality control (QA\QC) procedures reported in the following sections.

4.1 Ion Chromatography Quality Assurance\Quality Control

Three anions (Cl^- , NO_3^- , SO_4^{2-}) and one cation (NH_4^+) were analyzed on the Dionex™ ion chromatograph (IC). Standard solutions for the IC analysis were created with high-grade reagents and deionized (DI) water. DI water was tested for conductivity, and accepted conductivities were less than 1.0 $\mu\text{S}/\text{cm}$. In addition, standard curves produced by the instrument were checked to insure a linearity of $R^2 > 0.9999$.

Developed to optimize the performance of the IC, several QA\QC procedures were performed including blanks (two for each batch), replicates (every 20 samples), spikes (every 20 samples), and check samples (USGS standard solutions; one for every 10 samples). Ion detection limits on the IC are defined in Table 4-1. QA\QC results for blanks, replicates, and spikes are reported in Table 4-1, with results for USGS standard checks reported in Table 4-2. QA\QC procedures indicated very good quality results for IC analyzed ions because all blanks were below detection limits, and % difference in replicates were less than 1%. Only ammonia (NH_4^+) was greater than 1% and this % difference was due to the low concentrations, less than 0.01 ppm.

Table 4-1. IC QA\QC for the anions/cations in 2011.

QA\QC Procedure	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+
Detection limits (DL, ppm)	0.02	0.03	0.02	0.007
Blank	<DL	not detected	not detected	< DL
Absolute average value in % difference in replicates	0.14 % (n = 120)	0.67 % (n = 120)	0.17 % (n = 120)	5.87% (n = 91)
Average recovery in %	100.05% (n = 59)	99.59% (n = 59)	98.57% (n = 59)	99.81% (n = 57)

Table 4-2. IC QA/QC sample checks using USGS standard solutions for 2011.

Sample	Constituent	Number	USGS (ppm)	Avg. results (ppm)	% difference
N101	NH ₄ ⁺	317	0.464	0.465	0.33
N103	NH ₄ ⁺	242	0.412	0.410	-0.40
N101	NO ₃ ⁻	315	1.563	1.559	-0.26
P51	Cl ⁻	229	1.24	1.23	-1.18
	SO ₄ ²⁻	229	1.99	1.98	-0.59
P53	Cl ⁻	88	1.05	1.05	0.28
	SO ₄ ²⁻	88	0.42	0.38	-8.07

4.2 Inductively Coupled Plasma-Atomic Emission Spectrometry QA/QC Procedures

Major cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) and six trace metals (Al, Cu, Fe, Mn, Si, and Zn) were analyzed on the Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). To ensure acquisition of high quality data, several ICP-AES QA/QC procedures were performed during metals analyses of the water samples from 2011. Standards were prepared using certified ICP reagents and deionized (DI) water. Standard curves produced by the instrument were checked to insure linearity ($R^2 > 0.9999$) prior to sample introduction. Quality Control Check (QCC) samples were also prepared from the certified reagents and DI, and run every ten samples to ensure accuracy throughout the sequence. The results for the QCC samples are presented in Table 4-3.

USGS trace metal samples were acquired to verify low concentration ICP-AES results and run every 10 to 12 samples. The most probable values were obtained from the USGS standard reference (<http://bqs.usgs.gov/srs/>), and compared to our ICP-AES results. Results are presented in Table 4-4 (Note: USGS T-183 copper concentration is below instrument's detection limit).

Field and reagent blanks were run. Results for ICP-AES QA/QC laboratory blanks (deionized water) are presented in Table 4-5. Values were in the very low parts per billion (ppb).

Table 4-3. ICP-AES quality control check sample results (n = 48).

Element	Mean (ppm)	Actual (ppm)	% Error *	Relative STDEV **
Aluminum	0.5053	0.50	1.06 %	3.86 %
Calcium	1.0206	1.00	2.06 %	2.95 %
Copper	0.5037	0.50	0.73 %	3.39 %
Iron	0.5171	0.50	3.42 %	3.50 %
Potassium	0.9419	1.00	5.81 %	4.56 %
Magnesium	1.0087	1.00	0.86 %	3.14 %
Manganese	0.5049	0.50	0.97 %	3.29 %
Sodium	0.4782	0.50	4.35 %	2.87 %
Silicon	1.0016	1.00	0.16 %	3.27 %
Zinc	0.4819	0.50	3.62 %	6.44 %

* Percent Error = Absolute value of the difference between mean and actual values divided by actual value multiplied by 100%.

** Relative Standard Deviation = Standard deviation divided by mean value multiplied by 100%.

Table 4-4. ICP-AES T-183 USGS standard reference sample results (n = 44).

Element	Mean (ppm)	Actual (ppm)	% Error*	Relative STDEV**
Aluminum	0.1293	0.127	1.83 %	5.67 %
Calcium	11.5920	11.6	0.07 %	3.14
Copper	0.0034	0.0036	4.34 %	37.46 %
Iron	0.2055	0.206	0.25 %	4.20 %
Potassium	2.7002	2.57	5.07 %	8.55 %
Magnesium	7.7813	7.89	1.38 %	2.10 %
Manganese	0.0493	0.0492	0.15 %	4.42 %
Sodium	12.6435	12.7	0.44 %	3.17 %
Silicon	3.8102	3.87	1.54	3.45 %
Zinc	0.0832	0.0864	3.66 %	7.08 %

Table 4-5. ICP-AES Blank (deionized water) sample results (n = 32).

Element	Mean Value (ppm)
Aluminum	0.0017
Calcium	-0.0031
Copper	-0.0001
Iron	0.0034
Potassium	0.0039
Magnesium	0.0005
Manganese	0.0004
Sodium	-0.0019
Silicon	-0.0059
Zinc	-0.0001

Sample replicates were prepared and run every 20 samples on the ICP-AES. The results are presented in Table 4-6. Measured values that fell below the instrument detection limits were not included in the analysis. (Note: metals with low concentrations can cause large percent errors for small variations in concentration). Sample spikes were also prepared and ran on the ICP. The average percent recoveries are presented in Table 4-7. The percent recoveries of each element were all between 85% and 115% for each spike sample, which meets quality assurance standards. Minimum detection limits are determined annually. Current detection limits are shown in Table 4-8.

4.3 Ion Balance Computations

Final QA/QC protocols included computation of ion balances on all NDW and Park-wide Stream Survey samples. An ion balance is calculated by summing all the anions and cations in a single sample. After completion of all the ion and metal analyses, results for each sample were entered into a spreadsheet and an ion balance or ion deficit was computed. The ion balance should be $\pm 15\%$ according recommended USEPA guidelines.

Table 4-6. ICP-AES replicate sample results (n = 21).

Element	Median Absolute Percent Difference	n
Aluminum	22.95 %	15
Calcium	5.99 %	18
Copper	2.87 %	2
Iron	42.11 %	13
Potassium	3.41 %	16
Magnesium	5.54 %	20
Manganese	3.55 %	8
Sodium	1.63 %	18
Silicon	3.47 %	16
Zinc	14.75 %	7

Table 4-7. ICP-AES spike sample results (n = 12).

Element	Average Percent Recovery
Aluminum	99.51 %
Calcium	104.17 %
Copper	100.17 %
Iron	103.88 %
Potassium	92.81 %
Magnesium	102.49 %
Manganese	103.19 %
Sodium	101.30 %
Silicon	101.89 %
Zinc	100.04 %

Table 4-8. 2011 ICP-AES detection limits.

Element	2011 Detection Limits
Aluminum	0.021
Calcium	0.05
Copper	0.012
Iron	0.012
Potassium	0.165
Magnesium	0.001
Manganese	0.002
Sodium	0.041
Silicon	0.019
Zinc	0.008

None of the 253 samples for the Park-wide Stream Survey exceeded an ion balance greater or less 15%, and the overall average ion balance was -2.44%. For the NDW samples, 20 samples out of a total of 87 samples fell out of the $\pm 15\%$ range, of which six of these samples were TF samples having an ion difference from -15.34% to -98.51%. High organic acid concentrations in TF samples were likely the reason for the computed negative ion difference outside of range. One of the samples was a soil water sample and had an ion difference of 34.66%. The positive ion difference may be attributed to high aluminum concentrations in soil water. Ion balances for the NDW SW and NE streamlets, open sites (OS), and throughfall (TF) are summarized in Table 4-9.

Table 4-9. Average ion balances for NDW NE & SE streams, OS precipitation, and TF.

	NE Stream	SW Stream	Open Site (OS)	Throughfall (TF)
% Ion balance	-2.87 %	-3.50 %	0.11 %	-24.96 %
Absolute % Ion balance	5.09 %	6.16 %	11.71 %	25.01 %

4.4 USGS Round Robin Results

Once a year, the University of Tennessee Water Quality Lab participates in an analytical evaluation program operated by the United States Geological Survey (USGS). This program provides a variety of standard reference samples to accomplish quality assurance testing at USGS and non-USGS laboratories. A series of samples for the USGS Round Robin are prepared and distributed each spring and fall. Generally, the University of Tennessee Water Quality Laboratory participates in the fall program.

Although the USGS program is not a laboratory certification program, participation in this quality assurance exercise is mandatory for all laboratories providing WQ data for USGS sponsored reports. The USGS program provides the most probable values for the standard reference sample. Additionally, the USGS provides statistical Z-values and percent differences for each constituent in the reference sample. The most probable value, UT-value, statistical Z-value, and percent difference for each constituent are reported in Table 4-10.

5.0 Lysimeter Soil Water Experiment

The objective of this study was to investigate qualitatively performance of two types of soil water lysimeters; they were the: 1) pan lysimeter, and 2) perforated conduit collector. The pan lysimeter is an 18-inch square stainless steel plate with a lip containing a 5/8-inch diameter outlet hole. On the outside edge of the lip a threaded connector protrudes in order to attach plastic tubing, which tubing routes collected soil water to a plastic container, a one-gallon brown Nalgene bottle. Pan lysimeters were installed on a slight angle upwards into a soil bank cut into the hillside, and had at least one foot of soil overburden above them. A hole in the hillside ground below the lysimeters was dug to place the collector bottles (Figure 5-1). The perforated conduit collector is essentially a 4-inch HDPE perforated pipe serving as a shallow soil surface French drain. The HDPE perforated pipe was buried

at least 6 inches into the soil parallel with the downward sloping grade of the hillside. A bushing fitting at the end of the HDPE perforated pipe transitioned to 1¼ inch plastic tubing, where the tubing was routed to a one-gallon brown Nalgene bottle. Both lysimeter devices operated by gravity. Performance assessment consisted of whether these devices could collect sufficient quantities of soil water to analyze, and were their chemical characteristics within expected ranges for soil water data.

Two locations were selected for this study; they were Road Prong and Rock Creek watersheds (Figure 5-2). The Road Prong site was 30 m off the Road Prong trail near the junction to Chimney Tops (Lat 35.747 N; Long 83.215W). The Rock Creek (Cosby) site was 100 m off the Snake Den Ridge trail near the first major bridge crossing over Rock Creek (Lat 35.640N; Long 83.469W).

Table 4-10. USGS Round Robin results.

Sample	Analyte	MPV ¹	UT-results	Z-value	% difference
T-199	Al	0.324	0.317	-0.33	-2.16%
	Ca ²⁺	23.4	23.19	-0.18	-0.90%
	Cu	0.00842	0.0031 ²	-8.65	-63.18%
	Fe	0.432	0.413	-0.64	-4.40%
	K ⁺	2.19	2.10	-0.71	-4.11%
	Mg ²⁺	6.19	6.19	0.00	0.00%
	Mn	0.237	0.211	-1.76	-10.97%
	Na ⁺	21.5	21.3	-.28	-1.11%
	SiO ₂ ⁻	8.10	8.01	-0.18	-1.28%
P-49	Conductivity	13.0	12.79	-0.12	-1.62%
	pH	5.00	4.93	-0.32	-1.40%
	Cl ⁻	2.24	2.26	0.32	0.89%
	SO ₄ ²⁻	0.34	0.418	-1.90	-18.66%
	Mg ²⁺	0.262	0.238	-2.67	-9.16%
	Ca ²⁺	0.325	0.310	-0.58	-4.62%
	K ⁺	0.165	0.100 ²	-4.64	-39.39%
	Na ⁺	0.380	0.315	-2.17	-17.11%
N-103	NO ₃ ⁻ as N	0.280	0.270	-0.53	-3.57%
	NH ₄ ⁺ as N	0.340	0.268	1.75	8.97%

All concentration data are reported in mg/L, and conductivity is in µS/cm.

¹ Most Probable Value

² Below reported detection limit for instrument.



Figure 5-1. Photo of the soil lysimeter collector bottles at Rock Creek (Cosby) site.

Each site had two pan lysimeters and one perforated conduit collector. All lysimeters were placed uphill of the trail far enough away not to be visible by hikers. Looking uphill towards the sites from left to right, Road Prong (Chimney Tops) lysimeters were positioned as Pan 1, Conduit Collector, and Pan 2; and Rock Creek lysimeters were positioned as Pan 1, Pan 2, and Conduit Collector.

On a monthly basis from June 6, 2011 through February 8, 2012 samples were collected if there was enough water in the collection bottles. Approximately 250 ml of sample water is required to run all three analytical instruments: autotitrator for pH, ANC, and conductivity; IC for acid/base ions, and ICP for dissolved metals. For example, a minimum of 40 ml is needed to run the autotitrator. Most months if a sample was collected there was enough soil water from one of the lysimeters to run all three instrument tests: autotitrator, IC, and ICP. Never was there a period that all three lysimeters at a site collected enough water to take a sample. Usually samples could be taken from the perforated conduit collector and one of the pan lysimeters. Over the sample period, a 26 soil water samples were collected. To note regarding performance, because the perforated conduit collector did not have a screen at the plastic tubing connector with the lysimeter, occasionally dead insects were found in the

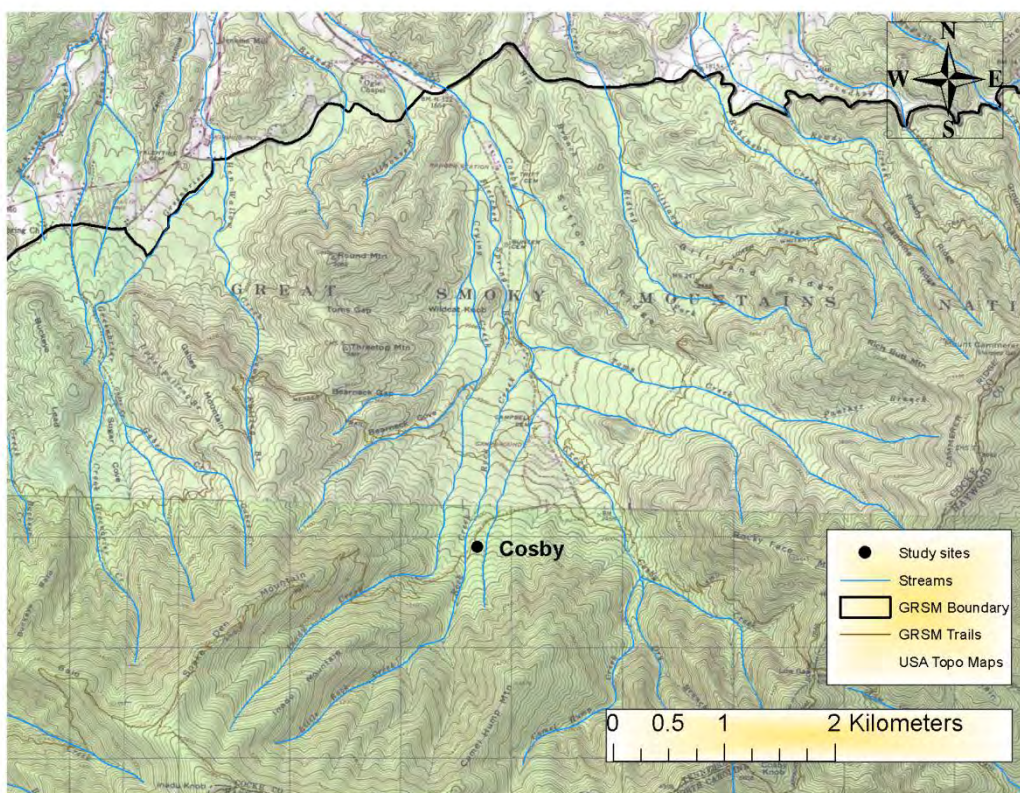
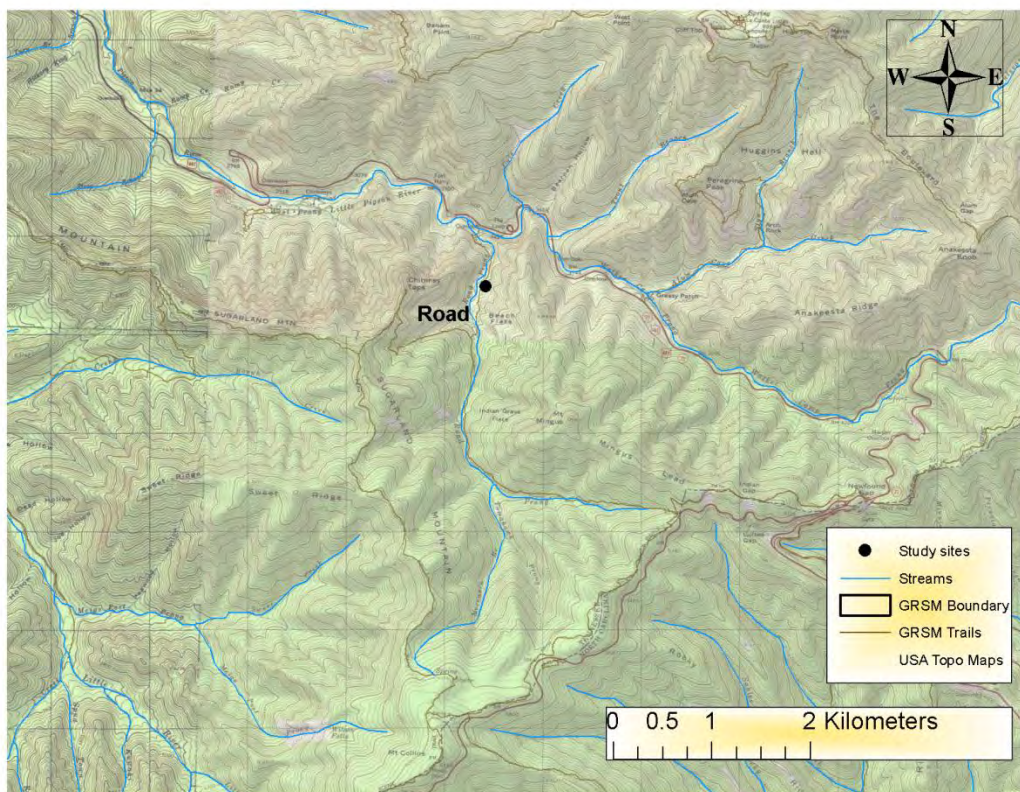


Figure 5-2. Soil lysimeter site locations in a) Road Prong and b) Rock Creek (Cosby) watersheds.

sample bottles. Insects in the sample bottles could influence nitrate concentrations. The pan lysimeters had a metal screen to prevent insects from entering the plastic tubing.

Comparing the soil water chemistry data between the pan lysimeter and the perforated conduit collector, no parameter appeared to be largely different per device (Table 5-1). Standard deviations among the samples per site and device were high, where it was greater than the mean (coefficient of variance greater than 1). Standard deviations in ranges observed are typically of what is observed at the Noland Divide site (Table 5-2). The soil water pH for Road Prong and Noland Divide were similar reporting values of 4.46 and 4.56, in comparison with Rock Creek which was slightly greater at a pH of 5.17. ANC values among the three sites were -16.1 $\mu\text{eq/L}$ at Road Prong, -13.4 $\mu\text{eq/L}$ at Noland Divide, and -2.28 $\mu\text{eq/L}$ at Rock Creek. Soil water concentrations of sulfate and nitrate were greater at Noland Divide compared to Road Prong and Rock Creek. Also, soil water concentrations of calcium, magnesium, and aluminum appeared to be greater at Noland Divide compared to the other two sites. These findings could be products of an acidified soil, where Noland Divide being the higher elevation site has received greater acid deposition loadings over the years (Lawrence 2002; Weathers *et al.* 2006). Interestingly, ammonium was greater at the Road Prong and Rock Creek sites (19.29 $\mu\text{eq/L}$ and 5.48 $\mu\text{eq/L}$) than at Noland Divide (3.07 $\mu\text{eq/L}$). This result may be a function of device, and further investigation is needed. In general, dissolved metal concentrations were similar among the three sites.

Table 5-1. Soil water chemistry for the pan and perforated conduit collector lysimeters at Road Prong and Rock Creek.

		Conductivity ($\mu\text{s}/\text{cm}$)	pH	ANC ($\mu\text{eq}/\text{L}$)	Chloride ($\mu\text{eq}/\text{L}$)	Nitrate ($\mu\text{eq}/\text{L}$)	Sulfate ($\mu\text{eq}/\text{L}$)	Ammonium ($\mu\text{eq}/\text{L}$)	Sodium ($\mu\text{eq}/\text{L}$)	Potassium ($\mu\text{eq}/\text{L}$)	Magnesium ($\mu\text{eq}/\text{L}$)	Calcium ($\mu\text{eq}/\text{L}$)	Aluminum (ppm)	Copper (ppm)	Iron (ppm)	Manganese (ppm)	Silicon (ppm)	Zinc (ppm)
Rock Pan	Average	19.87	5.25	-0.02	16.89	37.39	51.51	4.34	12.91	54.68	20.48	41.09	0.18	0.04	0.06	0.03	0.26	0.19
	SD	9.54	0.66	20.81	7.74	40.74	9.86	5.09	4.24	17.28	5.18	16.75	0.07	0.05	0.07	0.04	0.11	0.12
	N	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9
Rock Pipe	Average	23.70	4.39	-22.6	12.70	48.76	41.69	15.71	12.04	13.66	8.65	19.62	0.37	0.07	0.04	0.04	0.91	0.09
	SD	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	N	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Road Pan	Average	24.10	4.25	-28.9	18.85	75.11	37.99	11.61	13.74	43.25	14.15	48.88	0.54	0.27	0.17	0.06	0.50	0.40
	SD	8.87	0.37	6.48	6.59	93.47	14.65	13.70	11.65	31.79	8.86	38.12	0.15	0.12	0.03	0.03	0.19	0.17
	N	6	7	4	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Road Pipe	Average	30.03	4.81	0.93	34.14	83.81	50.89	32.73	20.76	29.21	21.62	109.4	0.39	0.00	0.21	0.08	0.91	0.06
	SD	16.16	0.85	43.86	38.80	87.39	12.93	33.59	13.48	22.29	16.00	111.1	0.14	0.01	0.18	0.04	0.20	0.09
	N	4	4	3	4	4	4	4	4	4	4	4	4	4	4	4	4	4

Table 5-2. Comparison of lysimeter soil water chemistry among Road prong, Rock Creek, and Noland Divide sites.

		Conductivity ($\mu\text{s}/\text{cm}$)	pH	ANC ($\mu\text{eq}/\text{L}$)	Chloride ($\mu\text{eq}/\text{L}$)	Nitrate ($\mu\text{eq}/\text{L}$)	Sulfate ($\mu\text{eq}/\text{L}$)	Ammonium ($\mu\text{eq}/\text{L}$)	Sodium ($\mu\text{eq}/\text{L}$)	Potassium ($\mu\text{eq}/\text{L}$)	Magnesium ($\mu\text{eq}/\text{L}$)	Calcium ($\mu\text{eq}/\text{L}$)	Aluminum (ppm)	Copper (ppm)	Iron (ppm)	Manganese (ppm)	Silicon (ppm)	Zinc (ppm)
Rock	Average	20.25	5.17	-2.28	16.47	38.53	50.53	5.48	12.82	50.58	19.30	38.94	0.20	0.04	0.05	0.03	0.33	0.18
	SD	9.08	0.68	20.88	7.42	38.58	9.80	5.99	4.01	20.83	6.15	17.19	0.09	0.05	0.07	0.03	0.23	0.12
	N	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Road	Average	26.47	4.46	-16.1	24.41	78.27	42.68	19.29	16.29	38.14	16.87	70.90	0.49	0.17	0.19	0.07	0.65	0.28
	SD	12.20	0.62	30.38	23.27	91.79	15.58	24.16	12.73	30.11	12.08	75.19	0.16	0.17	0.11	0.04	0.28	0.23
	N	10	11	7	11	11	11	11	11	11	11	11	11	11	11	11	11	11
Noland	Average	37.86	4.56	-13.4	29.79	117.9	66.00	3.07	20.25	21.75	27.99	72.36	0.93	0.00	0.15	0.06	1.18	0.19
	SD	8.74	0.37	19.70	23.23	88.24	22.80	2.87	4.56	20.20	6.05	26.75	0.58	0.00	0.17	0.04	0.61	0.11
	N	7	7	7	6	6	6	6	6	6	6	6	6	6	6	6	6	6

6.0 References

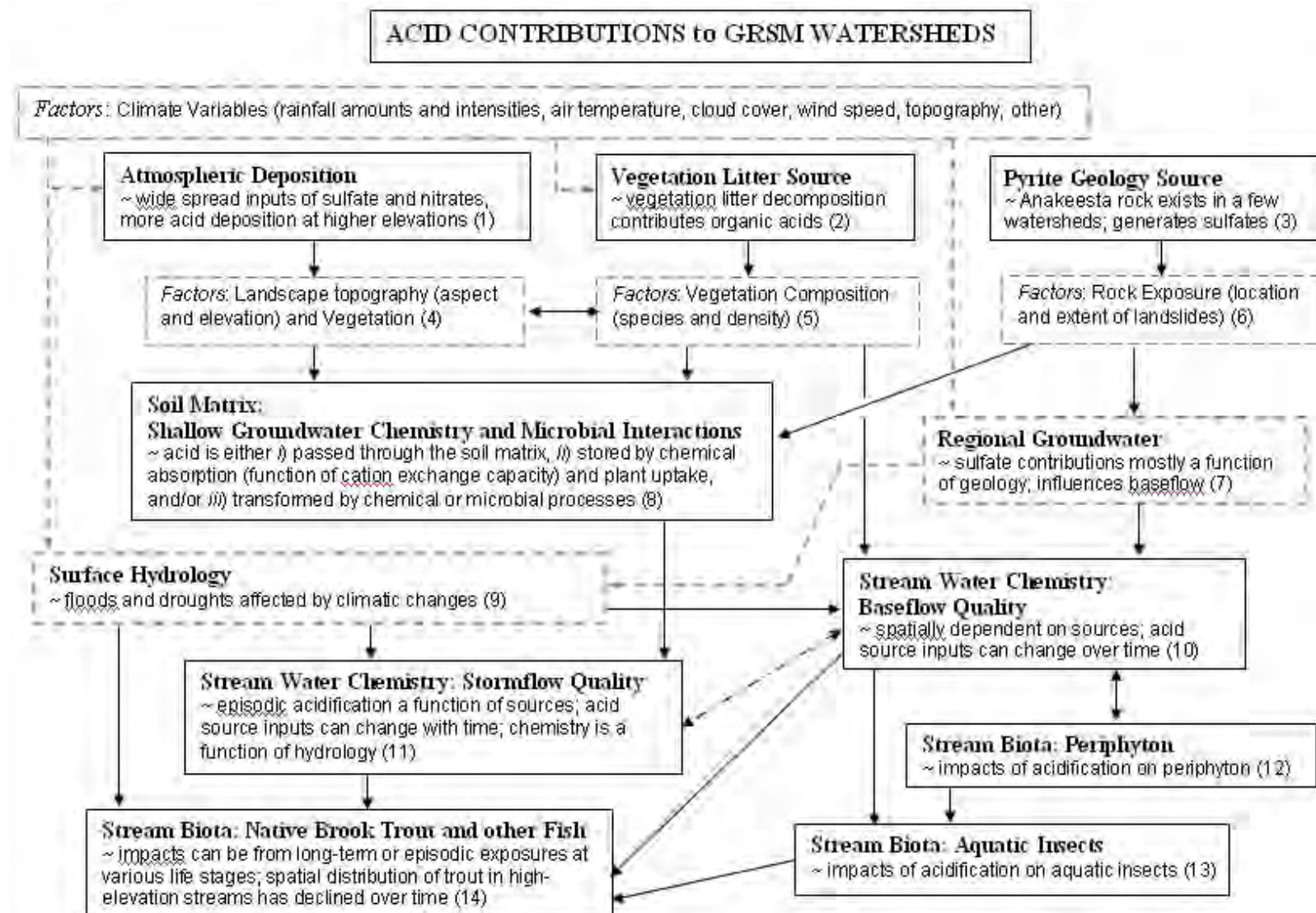
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APPENDICES

Appendix A: Conceptual Framework for Stream Acidification Issues in the GRSM (2005).



Appendix B: Stream Survey Site Descriptions.

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)*
1	Indian Camp at Old Settlers	35.7585	-83.2771	671	3	Indian Camp	1993-2003
3	Cosby Creek at boundary	35.7835	-83.2179	511	4	Cosby	1993-2003
4	Lower Rock Creek	35.7613	-83.2104	634	2	Cosby	1993-
13	Little River at boundary	35.6676	-83.7145	335	5	East Little	1993-
14	Little River above Y	35.6597	-83.7073	347	4	East Little	1993-2003
20	Little River at Metcalf Bottoms	35.6787	-83.6471	518	4	East Little	1993-2003
23	Lower Middle Prong Little River	35.6572	-83.7098	351	5	Middle Little	1993-2006
24	Lower West Prong Little River	35.6568	-83.7102	351	4	West Little	1993-
30	West Prong Little Pigeon at Headquarters	35.6882	-83.5367	436	4	West Prong Little Pigeon	1993-
34	Little River at Milsap Site	35.663	-83.6089	597	4	East Little	1993-2003
43	Porters Creek at log bridge	35.6809	-83.3971	713	4	Middle Prong Little Pigeon	1993-2004
45	Shutts Prong	35.6596	-83.3975	975	2	Middle Prong Little Pigeon	1993-2003
46	Porters Creek above Shutts Prong	35.669	-83.3965	838	3	Middle Prong Little Pigeon	1994-2003
47	Lower Cannon Creek	35.6802	-83.3987	732	2	Middle Prong Little Pigeon	1994-2003
49	Porters Creek at bridge to Ramsay	35.7077	-83.3823	509	4	Middle Prong Little Pigeon	1993-2003
50	Middle Prong Little Pigeon below Porters	35.7089	-83.383	507	5	Middle Prong Little Pigeon	1993-2003
52	Middle Prong Little Pigeon at boundary	35.7383	-83.4162	411	5	Middle Prong Little Pigeon	1993-2003
66	West Prong Little Pigeon at Chimneys Picnic Area	35.6372	-83.4948	817	4	West Prong Little Pigeon	1993-
71	Road Prong above barrier cascade	35.6344	-83.4703	1036	3	West Prong Little Pigeon	1993-
73	Walker Camp Prong above Road Prong	35.6348	-83.4693	1024	3	West Prong Little Pigeon	1993-
74	Walker Camp Prong above Alum Cave Creek	35.6291	-83.451	1164	2	West Prong Little Pigeon	1993-
103	Otter Creek (Indian Camp Prong)	35.7306	-83.2568	1320	1	Indian Camp	1993-2003

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)*
104	Copperhead Branch (Indian Camp Prong)	35.7275	-83.2638	1280	1	Indian Camp	1993-2003
106	Upper Indian Camp Prong	35.7276	-83.2713	1170	3	Indian Camp	1993-2003
107	Indian Camp below Albright Grove	35.7376	-83.2775	927	3	Indian Camp	1993-2003
114	Cosby Creek at log bridge	35.7486	-83.2007	765	3	Cosby	1993-
115	Upper Cosby Creek	35.7424	-83.1835	1170	1	Cosby	1994-2003
127	Pretty Hollow Cr above Palmer Creek	35.6395	-83.1285	908	3	Cataloochee	1993-2003
137	Upper Rock Creek (Cosby Creek)	35.7462	-83.2163	838	2	Cosby	1993-
138	Inadu Creek (Cosby Creek)	35.7425	-83.227	1058	2	Cosby	1993-
142	Beech Creek above Lost Bottom Creek	35.6356	-83.1454	1006	3	Cataloochee	1994-
143	Lost Bottom Creek (Cataloochee Creek)	35.6363	-83.1448	1000	2	Cataloochee	1994-
144	Palmer Creek above Pretty Hollow Cr	35.639	-83.1308	911	3	Cataloochee	1993-
147	Lower Cataloochee Creek	35.6669	-83.0728	750	4	Cataloochee	1993-
148	Lower Little Cataloochee Creek	35.6691	-83.0728	754	4	Cataloochee	1993-
149	Middle Cataloochee Creek at bridge	35.6463	-83.0755	777	4	Cataloochee	1993-
150	Cataloochee Creek below Caldwell Fork	35.6306	-83.0855	799	4	Cataloochee	1994-2003
156	Abrams Creek at Ranger Station	35.6091	-83.9347	338	5	Abrams	1994-2003
173	Mill Creek above Abrams Creek	35.591	-83.8536	523	4	Abrams	1993-
174	Abrams Creek below Cades Cove	35.5919	-83.8531	523	4	Abrams	1993-
183	Spring at Russell Field Shelter	35.5629	-83.7671	1305	1	Springs	1994-2003
184	Left Fork Anthony Creek at Campsite 10	35.5803	-83.7584	863	1	Abrams	1994-2003
186	Anthony Creek above Picnic Area	35.6046	-83.7713	599	3	Abrams	1993-2003
190	Thunderhead Prong at trail crossing	35.6084	-83.6719	646	3	Middle Little	1994-2003
191	Sams Creek (Middle Prong Little River)	35.5825	-83.6575	975	2	Middle Little	1993-2003
192	Starkey Creek (Middle Prong Little R)	35.5821	-83.659	975	2	Middle Little	1993-2003
193	Middle Prong Little River at old trailhead	35.6174	-83.6696	585	4	Middle Little	1993-2003

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)*
194	Middle Prong Little River above Tremont	35.6211	-83.6784	518	5	Middle Little	1993-2003
195	Spring at Spence Field Shelter	35.5626	-83.7336	1466	1	Springs	1994-2003
200	Anthony Creek above Campsite 9	35.578	-83.7408	1012	2	Abrams	1993-2003
201	Anthony Creek below Spence Field	35.5648	-83.7307	1463	1	Springs	1994-2003
209	Lost Creek (Little River)	35.6227	-83.538	823	1	East Little	1993-2003
210	Little River above Fish Camp Prong	35.6195	-83.5381	835	3	East Little	1993-2003
213	Goshen Prong above Fish Camp Prong	35.5986	-83.5675	1018	3	East Little	1993-2003
214	Silers Creek (Little River)	35.5937	-83.5677	1049	2	East Little	1993-2003
215	Ashe Camp Prong (Little River)	35.5997	-83.57	1030	2	East Little	1993-2003
218	Spring at Silers Bald Shelter	35.5645	-83.5684	1658	1	Springs	1994-2003
219	Double Springs Gap Shelter (NC side)	35.5649	-83.5426	1679	1	Springs	1994-2003
220	Double Springs Gap Shelter (TN side)	35.5653	-83.5427	1676	1	Springs	1994-2003
221	Hazel Creek above cascades	35.5463	-83.5828	1219	2	Hazel	1993-
224	Hazel Creek just below Proctor Creek Confluence	35.5321	-83.6223	925	3	Hazel	2004-2006
233	Walker Camp Prong above Alum Cave	35.6183	-83.4272	1297	2	West Prong Little Pigeon	1993-
234	Upper Road Prong	35.6098	-83.4504	1524	1	West Prong Little Pigeon	1993-
237	Walker Camp Prong at last bridge	35.6241	-83.4169	1378	2	West Prong Little Pigeon	1993-
251	Beech Flats above US 441 loop	35.6023	-83.4153	1222	2	Oconaluftee	1993-
252	Beech Flats below roadcut	35.6067	-83.4339	1426	1	Oconaluftee	1993-
253	Beech Flats above roadcut	35.6068	-83.4351	1451	1	Oconaluftee	1994-
266	Oconaluftee River at Visitors Center	35.5168	-83.3054	614	5	Oconaluftee	1993-2003
268	Oconaluftee River below Smokemont	35.5529	-83.3094	666	5	Oconaluftee	1994-
270	Beech Flats at Kephart Footbridge	35.5864	-83.364	852	3	Oconaluftee	2004-2006
290	Bear Branch at Campsite 42 (Cataloochee)	35.6059	-83.1814	1689	1	Springs	1994-2003
293	Rough Fork at Caldwell House	35.6244	-83.1139	840	3	Cataloochee	1993-

Site ID	Site Description	Latitude	Longitude	Elevation (m)	Stream Order	Stream System	Survey years (start - end year)*
310	Bone Valley Creek (Hazel Creek)	35.4999	-83.6801	683	3	Hazel	1993-
311	Hazel Creek below Haw Gap Creek	35.4938	-83.6885	657	4	Hazel	1993-
336	Flat Creek above falls (Bunches Creek)	35.5499	-83.1723	1451	1	Bunches	1995-2003
337	Bunches Creek at Flat Creek Trail	35.5548	-83.1674	1445	2	Bunches	1995-2003
472	Sams Creek above Thunderhead Prong	35.6080	-83.6674	671	3	Middle Little	1996-2003
473	West Prong Little Pigeon River across from Bearpen Prong	35.6362	-83.4628	1106	3	West Prong Little Pigeon	1996-2003
474	Little River below Husky Branch at resting bench	35.6470	-83.5567	732	4	East Little	1996-2003
475	Fish Camp Prong at angled barrier below War Branch	35.6083	-83.5483	899	4	East Little	1996-2003
479	Hazel Creek at Campsite 86	35.4723	-83.7193	530	4	Hazel	1996-
480	Haw Gap Creek near Campsite 84	35.4947	-83.6887	666	3	Hazel	1996-
481	Little Fork above Sugar Fork Trail	35.5026	-83.7084	774	1	Hazel	1996-
482	Sugar Fork above Little Fork	35.5024	-83.7086	774	2	Hazel	1996-
483	Sugar Fork above Haw Gap Creek	35.4995	-83.6949	707	2	Hazel	1996-
484	Hazel Creek at Cold Spring Gap Trail	35.5033	-83.6593	754	4	Hazel	1996-
485	Walker Creek above Hazel Creek Trail	35.5225	-83.6310	872	2	Hazel	1996-
488	Mill Creek at Pumphouse on Forge Creek Road	35.5835	-83.8345	546	3	Abrams	1996-
489	Abrams Creek 300 m below trailhead bridge	35.5914	-83.854	521	5	Abrams	1996-
492	Camel Hump Creek off Low Gap Trail	35.7446	-83.1988	832	1	Cosby	1996-
493	Palmer Creek at Davidson Branch Trail	35.6346	-83.1194	866	4	Cataloochee	1996-

* The sites without end year are currently monitoring sites.

Appendix C: Analytical Procedures for Chemistry Analysis Performed at the University of Tennessee –Knoxville.

Analysis	Procedure	Equipment	Method References
pH	Potentiometric	PC-Titration Plus	EPA Method 150.1
Conductance	Potentiometric	PC-Titration Plus	EPA Method 120.1
Acid Neutralizing Capacity (ANC)	Automated Titration	PC-Titration Plus	Automated Gran Titration for low ionic strength waters, as in Hillman et al. 1986
Anions (NO_3^-, Cl^-, SO_4^{2-})	Ion Chromatography	Dionex Ion Chromatograph	Standard Methods 4110
Monovalent Cations (NH_4^+)	Ion Chromatography	Dionex Ion Chromatograph	Manufacturers Protocols
Earth and Trace Metals (Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, & Si)	Inductively Coupled Plasma Spectrometer	Thermo-Electron Iris Intrepid II	Standard Methods 3120B EPA Method 6010B EPA Method 3005A

Standard Methods, AWWA (1995).

Appendix D: Chemistry Data of GRSM Resurveyed Park-wide Stream Survey Sites.

Site # (N) Year	Statistic	pH	ANC (µeq/L)	Conductivity (µs/cm)	Chloride (µeq/L)	Nitrate (µeq/L)	Sulfate (µeq/L)	Sodium (µeq/L)	Potassium (µeq/L)	Magnesium (µeq/L)	Calcium (µeq/L)
45 (N=49)	Median	5.54	3.64	19.33	15.65	31.52	85.60	22.85	4.66	49.07	77.50
1993-2003	STDEV	0.21	6.72	3.52	6.80	9.34	14.93	6.35	2.22	8.76	16.81
2011	Median	6.64	78.97	23.20	58.25	31.65	46.87	64.19	14.93	38.24	89.23
<i>Percent Difference</i>		<i>19.89</i>	<i>2069.41</i>	<i>20.05</i>	<i>272.28</i>	<i>0.44</i>	<i>-45.24</i>	<i>180.99</i>	<i>220.18</i>	<i>-22.06</i>	<i>15.13</i>
46 (N=46)	Median	5.77	5.39	16.94	14.17	27.22	73.25	25.93	4.39	43.32	61.58
1994-2003	STDEV	0.28	6.58	2.35	4.22	6.66	14.55	5.71	1.47	8.88	15.41
2011	Median	7.58	524.83	78.70	329.70	4.44	87.39	257.25	19.58	142.45	369.85
<i>Percent Difference</i>		<i>31.48</i>	<i>9633.06</i>	<i>364.58</i>	<i>2226.03</i>	<i>-83.70</i>	<i>19.31</i>	<i>892.28</i>	<i>345.69</i>	<i>228.86</i>	<i>500.59</i>
47 (N=43)	Median	5.93	11.42	12.00	13.96	20.29	38.61	25.32	8.89	20.87	43.84
1994-2003	STDEV	0.15	20.62	2.10	7.05	9.81	21.77	4.64	2.36	5.18	28.88
2011	Median	6.86	92.51	22.80	38.62	32.06	44.46	55.59	11.12	42.55	107.86
<i>Percent Difference</i>		<i>15.59</i>	<i>709.89</i>	<i>90.00</i>	<i>176.70</i>	<i>58.01</i>	<i>15.17</i>	<i>119.58</i>	<i>25.14</i>	<i>103.90</i>	<i>146.04</i>
103 (N=53)	Median	5.57	2.16	19.20	14.46	48.46	66.46	29.44	10.79	22.78	84.06
1993-2003	STDEV	0.27	6.15	2.48	7.29	11.21	6.58	5.84	3.94	8.12	20.97
2011	Median	5.35	-2.94	17.83	13.76	48.92	66.79	24.68	10.05	20.47	73.38
<i>Percent Difference</i>		<i>-3.89</i>	<i>-236.02</i>	<i>-7.14</i>	<i>-4.80</i>	<i>0.94</i>	<i>0.49</i>	<i>-16.16</i>	<i>-6.87</i>	<i>-10.14</i>	<i>-12.70</i>
104 (N=45)	Median	5.68	5.79	17.97	14.78	49.94	55.17	28.51	12.38	19.85	71.65
1993-2003	STDEV	0.32	25.73	2.50	6.50	12.08	9.08	12.24	5.01	10.74	22.52
2011	Median	5.87	3.22	16.73	10.98	55.19	53.64	21.59	11.75	22.67	78.80
<i>Percent Difference</i>		<i>3.50</i>	<i>-44.50</i>	<i>-6.87</i>	<i>-25.71</i>	<i>10.51</i>	<i>-2.78</i>	<i>-24.26</i>	<i>-5.07</i>	<i>14.22</i>	<i>9.98</i>
107 (N=62)	Median	6.06	18.44	16.06	11.98	34.02	52.93	28.06	11.27	20.09	72.39
1993-2003	STDEV	0.17	10.14	2.08	6.33	8.58	4.71	5.85	8.36	6.98	20.08
2011	Median	6.08	12.95	15.47	11.01	48.88	50.25	22.76	11.11	21.73	71.69
<i>Percent Difference</i>		<i>0.26</i>	<i>-29.76</i>	<i>-3.67</i>	<i>-8.11</i>	<i>43.69</i>	<i>-5.06</i>	<i>-18.86</i>	<i>-1.47</i>	<i>8.17</i>	<i>-0.97</i>
127 (N=42)	Median	6.41	46.47	11.24	15.54	14.58	19.42	38.73	11.18	18.41	42.23
1993-2003	STDEV	0.19	13.01	2.52	8.53	9.21	4.60	7.33	3.09	4.44	15.19
2011	Median	6.67	44.94	9.37	12.55	16.90	17.63	29.80	10.24	16.60	45.95
<i>Percent Difference</i>		<i>3.97</i>	<i>-3.30</i>	<i>-16.60</i>	<i>-19.25</i>	<i>15.88</i>	<i>-9.22</i>	<i>-23.06</i>	<i>-8.33</i>	<i>-9.87</i>	<i>8.81</i>
183 (N=39)	Median	5.70	36.69	9.13	14.39	5.04	8.55	30.70	6.99	11.15	22.20
1994-2003	STDEV	0.69	43.57	7.25	8.86	4.78	13.78	11.20	4.07	8.54	22.10
2011	Median	6.16	44.80	8.56	8.56	9.93	7.23	24.52	7.21	13.17	25.03
<i>Percent Difference</i>		<i>7.93</i>	<i>22.10</i>	<i>-6.24</i>	<i>-40.46</i>	<i>96.87</i>	<i>-15.43</i>	<i>-20.13</i>	<i>3.05</i>	<i>18.16</i>	<i>12.73</i>
184 (N=44)	Median	6.21	32.61	12.70	18.37	25.07	26.88	38.67	11.18	18.14	48.01
1994-2003	STDEV	0.18	11.35	2.02	4.96	7.96	7.57	9.15	3.52	4.76	15.80
2011	Median	6.39	18.35	12.21	13.35	32.97	28.12	27.15	10.04	19.09	47.10
<i>Percent Difference</i>		<i>2.84</i>	<i>-43.72</i>	<i>-3.86</i>	<i>-27.36</i>	<i>31.50</i>	<i>4.61</i>	<i>-29.80</i>	<i>-10.18</i>	<i>5.24</i>	<i>-1.90</i>

Site # (N) Year	Statistic	pH	ANC (µeq/L)	Conductivity (µs/cm)	Chloride (µeq/L)	Nitrate (µeq/L)	Sulfate (µeq/L)	Sodium (µeq/L)	Potassium (µeq/L)	Magnesium (µeq/L)	Calcium (µeq/L)
185 (N=18)	Median	6.68	40.85	13.13	15.05	20.05	28.43	40.22	10.81	20.34	64.06
1993-2003	STDEV	0.19	9.03	1.83	8.59	5.92	5.11	14.21	3.70	6.82	22.16
2011	Median	6.16	33.96	7.25	13.43	3.30	9.56	19.61	5.33	9.11	16.64
	Percent Difference	-7.90	-16.85	-44.76	-10.78	-83.54	-66.38	-51.25	-50.65	-55.21	-74.03
190 (N=39)	Median	6.27	29.94	11.80	14.18	15.96	31.24	32.30	8.30	17.99	42.25
1994-2003	STDEV	0.19	17.26	1.36	5.29	6.02	4.91	7.30	2.52	5.23	15.49
2011	Median	6.54	32.47	10.73	11.94	14.21	30.79	26.09	7.55	15.59	34.84
	Percent Difference	4.31	8.45	-9.07	-15.77	-10.93	-1.44	-19.24	-9.05	-13.35	-17.54
191 (N=41)	Median	6.13	19.57	10.60	15.51	17.96	26.24	30.12	8.81	15.92	38.69
1993-2003	STDEV	0.19	8.68	1.76	6.08	11.42	13.94	11.34	4.21	7.27	20.91
2011	Median	6.26	14.65	9.68	11.49	21.10	26.57	20.24	8.39	13.71	31.56
	Percent Difference	2.05	-25.16	-8.64	-25.89	17.46	1.25	-32.80	-4.71	-13.90	-18.42
192 (N=45)	Median	6.11	21.13	12.66	13.69	22.61	41.31	27.09	6.55	23.35	52.58
1993-2003	STDEV	0.30	12.40	2.95	10.02	7.38	6.80	5.84	1.78	6.30	16.85
2011	Median	6.28	17.18	11.86	11.26	22.73	41.83	22.84	6.44	21.48	45.98
	Percent Difference	2.76	-18.70	-6.32	-17.72	0.54	1.26	-15.70	-1.76	-8.02	-12.55
200 (N=45)	Median	6.15	25.47	12.55	17.38	27.72	26.43	34.73	10.90	16.29	46.09
1993-2003	STDEV	0.19	10.15	1.94	9.91	7.68	4.35	10.60	4.35	5.23	14.98
2011	Median	6.26	17.87	12.60	12.28	43.73	24.66	23.71	10.12	17.18	42.94
	Percent Difference	1.87	-29.85	0.40	-29.34	57.75	-6.71	-31.74	-7.20	5.48	-6.83
201 (N=39)	Median	5.75	34.70	10.45	12.19	11.10	15.10	27.41	9.51	13.27	33.40
1994-2003	STDEV	0.32	7.91	2.49	3.07	6.66	4.04	6.26	2.51	3.33	13.70
2011	Median	6.11	34.71	10.17	8.80	7.92	19.20	20.40	8.64	12.30	29.90
	Percent Difference	6.27	0.02	-2.68	-27.81	-28.68	27.16	-25.59	-9.18	-7.32	-10.47
210 (N=47)	Median	6.40	49.75	14.25	13.59	13.88	38.78	32.65	10.47	22.28	62.86
1993-2003	STDEV	0.17	24.77	5.35	5.52	6.81	6.47	5.08	2.63	6.09	23.27
2011	Median	6.60	42.12	10.76	13.66	4.29	29.31	27.88	11.00	16.48	32.24
	Percent Difference	3.20	-15.33	-24.49	0.54	-69.06	-24.42	-14.59	5.06	-26.02	-48.72
213 (N=46)	Median	6.11	20.29	11.18	14.28	21.19	29.48	28.95	8.47	19.41	37.40
1993-2003	STDEV	0.18	10.95	1.59	4.49	7.17	5.32	5.43	2.37	5.69	13.64
2011	Median	6.49	24.43	11.69	16.51	17.35	28.38	29.33	9.53	18.03	37.57
	Percent Difference	6.32	20.40	4.56	15.65	-18.13	-3.72	1.30	12.52	-7.09	0.47
214 (N=50)	Median	6.30	36.94	10.96	15.86	13.70	22.66	33.21	9.81	18.35	35.95
1993-2003	STDEV	0.19	12.75	4.30	5.85	6.52	6.64	7.95	2.96	5.36	15.55
2011	Median	6.49	35.34	10.62	10.93	16.99	28.38	23.96	8.02	17.90	35.36
	Percent Difference	2.99	-4.31	-3.10	-31.05	24.04	25.23	-27.85	-18.20	-2.48	-1.64

Site # (N) Year	Statistic	pH	ANC (µeq/L)	Conductivity (µs/cm)	Chloride (µeq/L)	Nitrate (µeq/L)	Sulfate (µeq/L)	Sodium (µeq/L)	Potassium (µeq/L)	Magnesium (µeq/L)	Calcium (µeq/L)
215 (N=48)	Median	6.38	49.64	13.37	15.38	11.85	34.98	37.83	9.46	26.31	50.93
1993-2003	STDEV	0.17	22.19	6.72	6.63	5.26	8.28	8.84	2.11	6.67	23.66
2011	Median	6.61	40.55	12.75	11.81	18.47	38.05	24.41	9.44	19.76	51.40
Percent Difference		3.46	-18.31	-4.60	-23.18	55.87	8.76	-35.47	-0.22	-24.91	0.93
472 (N=29)	Median	6.17	29.83	11.95	15.45	14.48	32.75	33.85	8.23	20.87	43.55
1996-2003	STDEV	0.20	13.70	1.72	5.60	5.92	3.16	8.93	3.50	5.75	14.21
2011	Median	6.40	18.20	10.91	11.82	16.15	33.43	22.98	7.37	18.03	35.91
Percent Difference		3.64	-38.98	-8.70	-23.46	11.52	2.08	-32.10	-10.47	-13.63	-17.55
474 (N=38)	Median	6.33	51.92	13.12	14.68	12.27	32.39	35.20	10.49	21.32	51.70
1996-2003	STDEV	0.20	15.73	1.60	7.28	5.98	3.09	8.65	3.11	5.88	19.40
2011	Median	6.45	39.13	13.07	11.82	15.08	31.91	25.44	10.17	18.68	42.58
Percent Difference		1.79	-24.64	-0.34	-19.51	22.92	-1.47	-27.74	-3.10	-12.36	-17.64
475 (N=31)	Median	6.35	34.68	11.90	17.18	15.72	27.64	34.20	10.12	20.16	41.30
1996-2003	STDEV	0.19	13.79	2.37	6.04	6.48	2.95	7.43	3.08	6.88	15.58
2011	Median	6.51	29.99	10.79	10.86	17.99	28.15	23.64	8.15	17.84	34.60
Percent Difference		2.57	-13.52	-9.33	-36.81	14.45	1.83	-30.89	-19.45	-11.53	-16.22