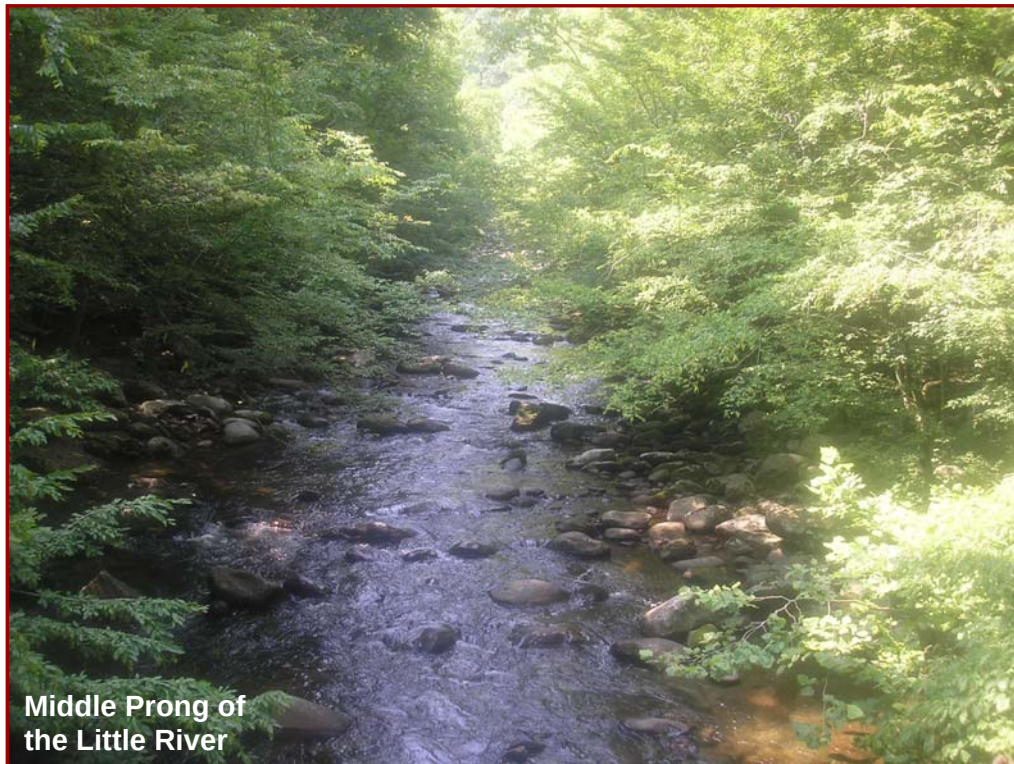


Great Smoky Mountains National Park

2007 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 2007 WQ Annual Report

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This report describes for water quality monitoring in the Great Smoky Mountains National Park for calendar year (CY) 2007 work accomplished under Amendment No. 7 to **Cooperative Agreement No. 1443-CA-5460-98-007** between the University of Tennessee and the U.S. National Park Service and also under the Southern Appalachian Cooperative Ecosystem Studies Unit CESU Host Cooperative Agreement No. H5000 04 5040 Task Agreement No. J5460 05 0067 Modification No. 3 between the U.S. National Park Service and the University of Tennessee - Knoxville.

TABLE OF CONTENTS

	Page
1.0 Introduction.....	1
1.1 <i>Noland Divide Watershed.....</i>	2
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>	8
2.0 Noland Divide Watershed: 2007 Data Summary and Discussion	9
2.1 <i>Annual Precipitation Volume</i>	9
2.2 <i>Annual Deposition Rates for Chemical Constituents</i>	9
2.3 <i>Soil Water Chemistry from Lysimeters.....</i>	11
3.0 Park-wide Stream Survey	15
3.1 <i>Water Chemistry Results</i>	15
3.2 <i>Elevational Variation on Stream Acidity.....</i>	18
3.3 <i>Potential Impacts of Stream Acidity on Aquatic Biota.....</i>	18
4.0 Laboratory Analysis: Quality Assurance\Quality Control.....	25
4.1 <i>Ion Chromatography QA\QC Procedures.....</i>	25
4.2 <i>Inductively Coupled Plasma-Atomic Emission Spectrometry QA/QC Procedures.....</i>	26
4.3 <i>Ion Balance Computations</i>	29
4.4 <i>USGS Round Robin Results.....</i>	31
4.5 <i>QA/QC Concluding Remarks for 2007 Water Quality Data.....</i>	33
5.0 References.....	34
APPENDICES.....	37

LIST of TABLES

Table 2-1. Statistical summaries for pH and conductivity from the soil lysimeters.....	12
Table 2-2. Statistical summaries of the anion chemistry analysis from the soil lysimeters. All values are given in $\mu\text{eq/L}$	13
Table 2-3. Statistical summaries of the cation chemistry analysis on the soil lysimeters. All values are given in $\mu\text{eq/L}$	13
Table 3-1. Descriptive statistic of 1993-2006 median water quality values for 43 Park-wide stream survey sites. CV = coefficient of variation = standard deviation / mean.	16
Table 3-2. Descriptive statistics of 2007 median water quality values for the 43 Park-wide stream survey sites. Percent Difference = (2007 average – 1993-2006 average)/(1993-2006 average) $\times 100\%$	17
Table 3-3. General description of pH effects on trout within designated pH ranges, and the percentage of sampling sites with median pH values for that range (Barnett 2003)..	21
Table 3-4. Parameters for calculating hardness dependent CMC and CCC for copper and zinc.	23
Table 3-5. Dissolved metal concentration exceedances for Park-wide stream survey data.	24
Table 4-1. IC QA\QC for the anions/cations in 2007.	26
Table 4-2. IC QA/QC sample checks using USGS standard solutions for 2007.....	26
Table 4-3. ICP QA\QC results for the prepared QCC samples for 2007 cations and metals.	28
Table 4-4. ICP QA\QC results for USGS trace metal samples (T183) for 2007 cations and metals	28
Table 4-5. ICP QA\QC results for blanks for 2007 cations and metals.....	28
Table 4-6. ICP QA\QC results for replicates for 2007 for cations and metals.	29
Table 4-7. ICP QA\QC results for spikes for 2007 for cations and metals.	30
Table 4-8. ICP detection limits for 2007 for cations and metals.	31
Table 4-9. Average ion balances for NWD NE and SE streams, OS precipitation, and throughfall	31
Table 4-10. USGS Round Robin results. All concentration data are reported in ppm, and conductivity is given in $\mu\text{S/cm}$	32

LIST of FIGURES

Figure 1-1. Location of Great Smoky Mountains National Park.....	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 and throughfall precipitation volumes received by the NDW.	10
Figure 2-2. Total annual inorganic nitrogen deposition entering the NDW as wet-only and throughfall precipitation.	10
Figure 2-3. Total sulfate entering the NDW as throughfall and wet-only precipitation.....	12
Figure 3-1. Scatter plot of median pH values versus elevation. Blue points/black lines are site data averages from 1993-2006; and brown points/line are 2007 site data.	19
Figure 3-2. Scatter plot of median ANC values versus elevation. Blue points/black lines are site data averages from 1993-2006; and brown points/line are 2007 site data.	19

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 have been designated as Outstanding National Resource Waters.

Since the 1980's national air quality monitoring has shown that the GRSM receives some of the highest rates of atmospheric deposition of acid pollutants in the United States (Shubzda *et al.* 1995; NADP 2006; 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

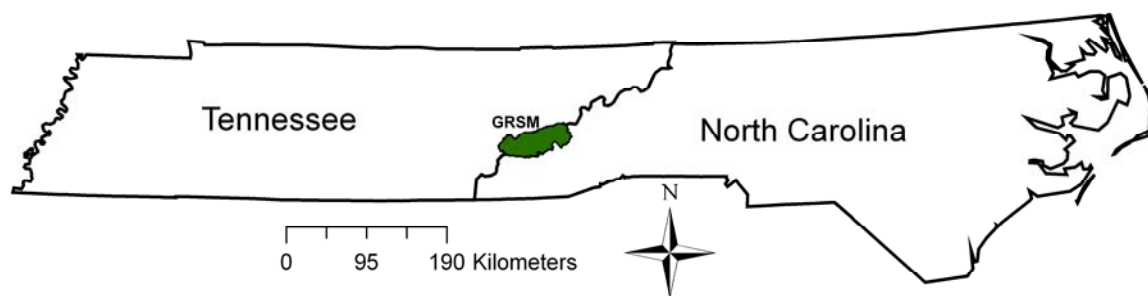


Figure 1-1. Location of Great Smoky Mountains National Park.

pollutants. A major concern of stream acidification in watersheds that lack acid 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 2007).

Although stream impacts have not been observed directly, acidic episodes are suspected to be a primary cause of native brook trout (*Salvelinus fontinalis*) 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.* 2008). Based on long-term declines in stream pH, GRSM resource managers fear that brook trout will continue to be eliminated from streams and may disappear entirely from the park within about 25 to 50 years (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 resources managers and the University of Tennessee. 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 A).

1.1 Noland Divide Watershed

Noland Divide watershed (NDW) was selected for long-term monitoring because of its high-elevation location. 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 provided 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 analyze acidic pollutant inputs into the watershed from wet and dry deposition (OS, TF sites), effects of soil on pollutant fate and transport, and characterization of stream acidification based on levels of acidic pollutant inputs.

NDW is located in the middle of 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 & 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

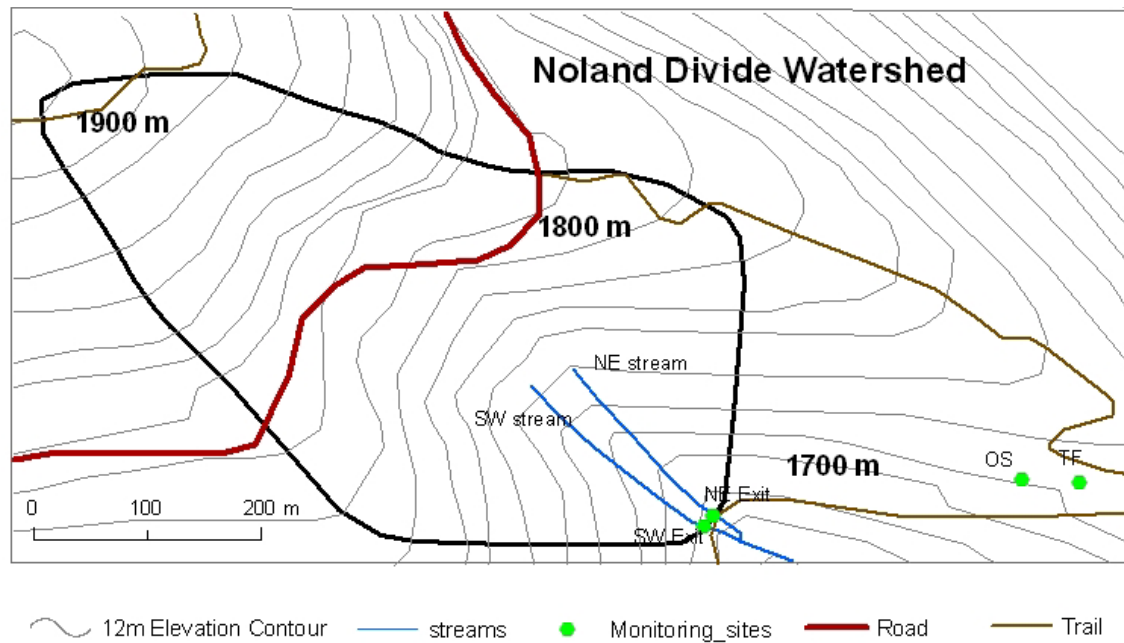


Figure 1-2. Map of Noland Divide watershed showing water quality monitoring sites.

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 (Figure 1-3). 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 and flow through hoses into 1-gallon LDPE brown jugs. The 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. The collected water samples from OS and TF sites



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

are weighed in order to measure precipitation volumes, and then brought back to UT lab for chemistry analyses.

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). These WL16 recorders recently replaced originally installed float-cable devices with analog sensor. 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® sondes (pH, conductivity and temperature), in which the SW sonde was installed in July 1991 and the NE sonde was installed in April 1998. Data from sondes are transmitted to a Campbell Scientific CR10X data logger recording data every 15 minutes. Stream water grab samples 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, Cb horizons). Lysimeters are located adjacent to the TF precipitation site. The volume of



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

soil solution determines the collection frequency for soil water samples. Usually, samples are collected on a monthly basis.

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

Park-wide stream survey began in October 1993 to identify potential impacts of acid deposition on GRSM streams and monitor long-term changes in stream acidification (also termed long-term synoptic baseflow stream WQ monitoring). Sites were selected to assess the spatial variability of water quality within the GRSM across a range of elevations, geology types, and disturbance histories. 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). Data from the 1990's found 97% of the 90 sampling sites were classified as either sensitive, extremely sensitive, or acidic, classified by median ANC values less than or equal to 200 $\mu\text{eq/l}$ per liter (Harwell 2001). In addition, 77% of the GRSM sites were found with median pH values that can have adverse effects on aquatic organisms. The number of sites was further reduced in 2004 to 32 sites sampled bimonthly, and 11

Hazel Creek sites sampled biannually (Figure 1-5).

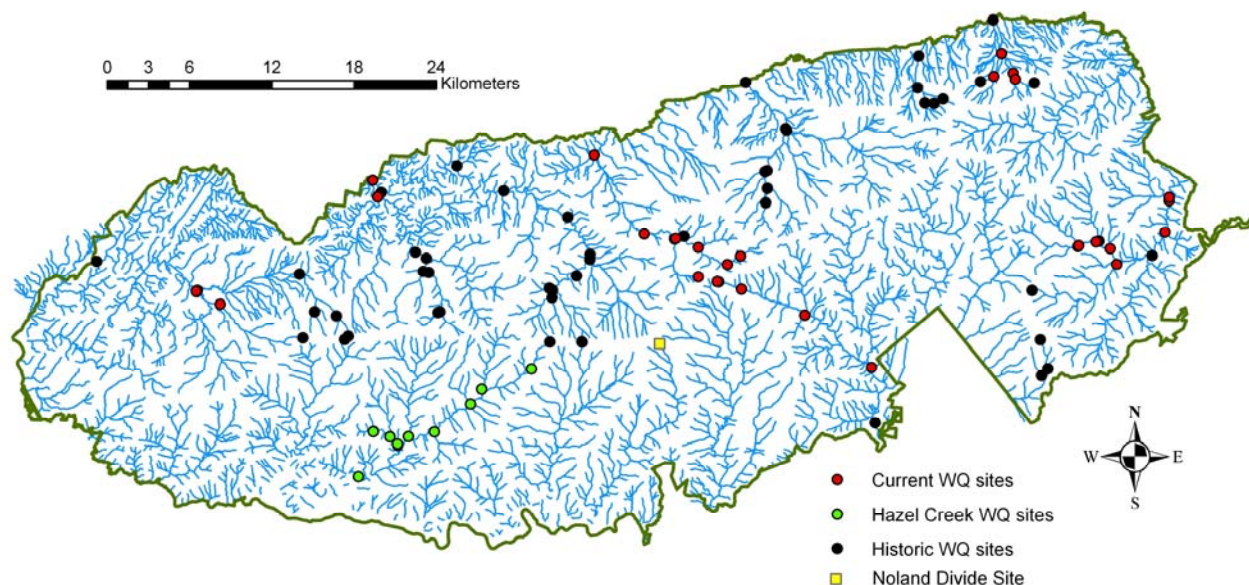


Figure 1-5. Water quality monitoring sites for the GRSM Park-wide survey.

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 - Knoxville. From January 1998 to the present, staff and students in the Department of Civil and Environmental Engineering have collected water samples and conducted the chemical analyses. 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. Most recently, Robinson *et al.* (2008) generated step-wise multiple linear regression models to analyze long-term time trends in stream pH, ANC, sulfate and nitrate, using a wide range of potential predictor variables: cumulative Julian day, seasonality, elevation, basin slope, stream order, precipitation, surrogate stream flows, geology, and acid depositional fluxes. Modeling 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. If conditions remain the same and past trends continue, forecasting models suggest that 30.0 % of the sampling sites will reach pH values less than 6.0 in less than 10 years, 63.3 % in less than 25 years, and 96.7 % in less than 50 years.

Jackson (2005) correlated WQ base flow data with trout biomass in the GRSM. The correlation analysis revealed that pH, ANC, conductivity, and sulfate are important WQ predictor variables of trout biomass. Trout species were negatively affected by increases in sulfate concentrations, and significantly when exposed Anakeesta geology (pyrite, sulfate-generating rock) was present in the watershed. Rainbow trout biomass was found to increase with increasing stream conductivity and ANC. Negative correlations between sulfate concentrations and biomass provides circumstantial evidence that acid deposition detrimentally impacts trout populations in the GRSM, however the presence of Anakeesta geology complicated the findings, and a study currently in progress has been designed to address this multiplicative response variable.

1.3 GRSM Water Quality Program Annual Reports and Research Publications

Data summaries are generated annually for the GRSM water-quality monitoring program. 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.

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.

2.0 Noland Divide Watershed: 2007 Data Summary and Discussion

2.1 Annual Precipitation Volume

The annual rainfall amount collected during 2007 was 165.78 cm, the lowest volume since 1991 (Figure 2-1). The amount of annual rainfall in 2007 was 60 cm below the 16-year average for this site. The southeast US experienced a severe regional drought in 2007, which resulted in this lowest annual rainfall at the NDW. This regional drought was also evidenced by the precipitation deficit at other GRSM weather stations. For example, the LeConte station had a 38-cm precipitation deficit, which was 18% below its long-term average; and the Elkmont station had a 52-cm deficit, which was 34% below its long-term average.

2.2 Annual Deposition Rates for Chemical Constituents

Annual deposition rates of chemical constituents are summarized for wet (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.

During 2007, the estimated amount of total inorganic nitrogen entering the NDW from wet-only (OS) precipitation was 482.16 equivalents of nitrogen per hectare per year (N eq/ha/yr) and from throughfall was 1,494.87 N eq/ha/yr (Figure 2-2). Nitrogen rates at the TF site were greater than OS samples because the forest canopy collects airborne pollutants during dry periods. It should be noted that some foliar uptake of NH_4^+ and NO_3^- nitrogen constituents can occur in forested watersheds (Stachurski and Zimka 2002; Jin *et al.* 2006). Therefore, the difference between wet-only precipitation and throughfall inputs only represents a reasonable estimate of the dry plus cloudwater inputs to this watershed (Shubzda *et al.* 1995). The 2007 dry deposition rate for total inorganic

nitrogen was estimated as 1,012.71 N eq/ha/yr.

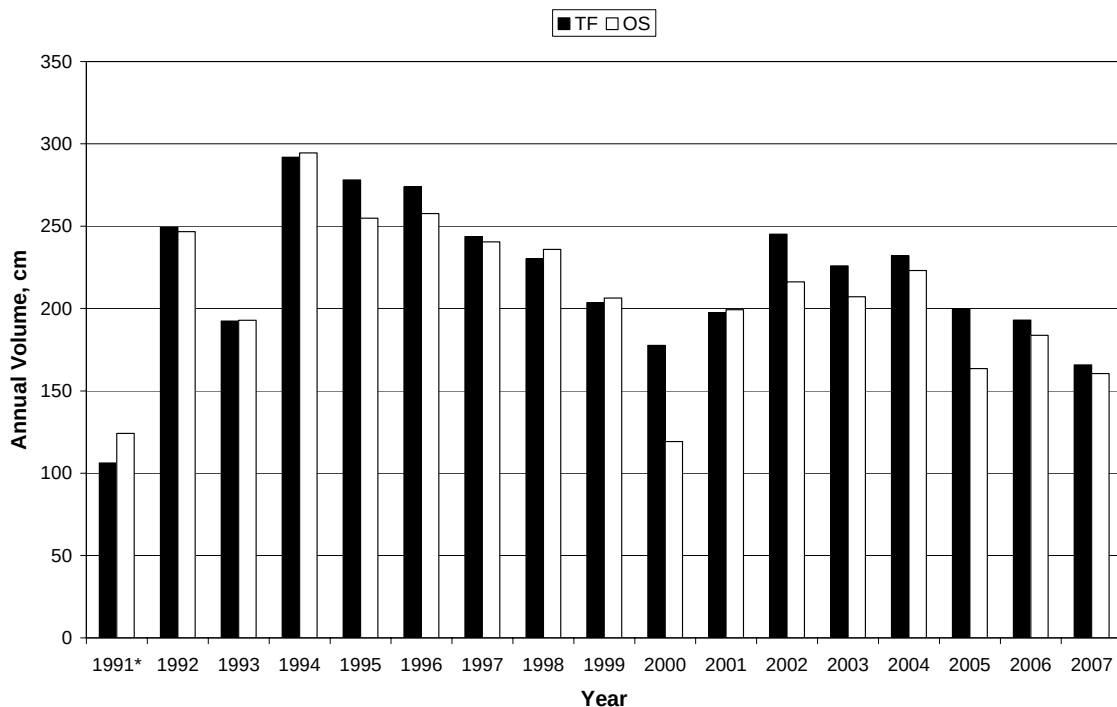


Figure 2-1. Total annual wet-only and throughfall precipitation volumes received by the NDW.

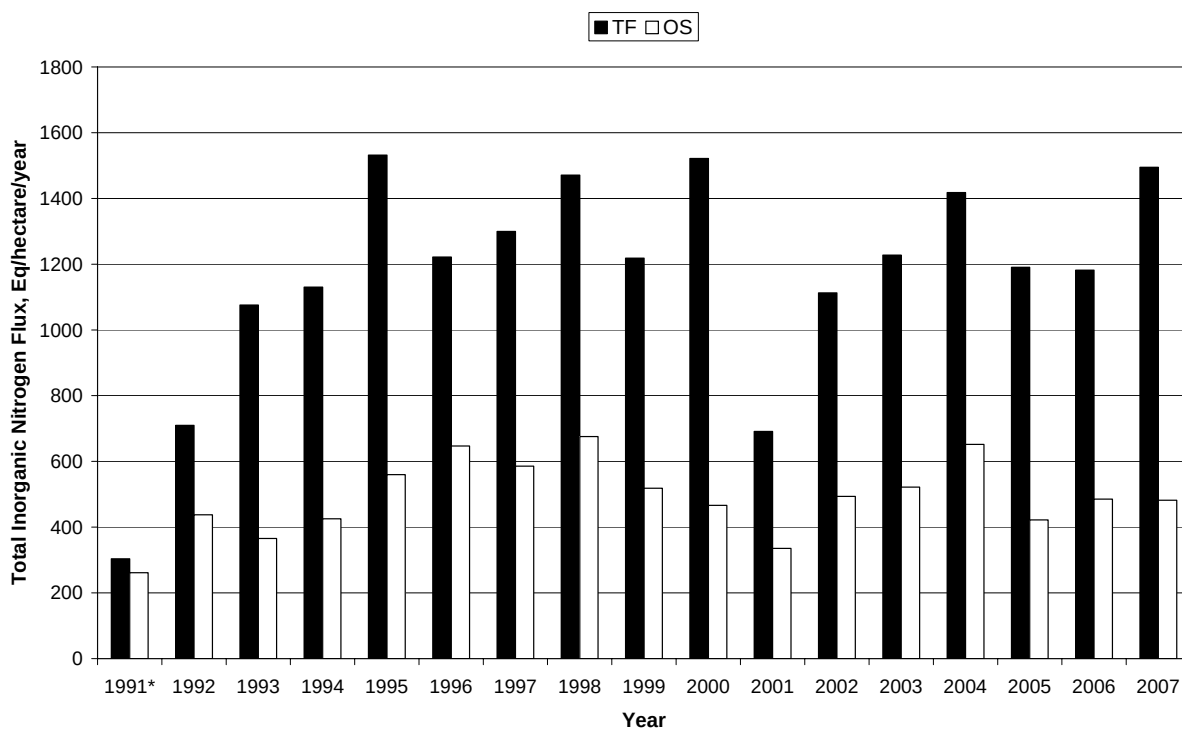


Figure 2-2. Total annual inorganic nitrogen deposition entering the NDW as wet-only and throughfall precipitation.

Because 2007 was a severe drought year, wet-only OS deposition was 22 eq/ha/yr *below* the long-term 16-year average, and the throughfall deposition rate was 276 eq/ha/yr *above* the 16-year average. In drought years, wet-only deposition is less because of the lower number (frequency) of precipitation events. Conversely, throughfall deposition was greater because more acidic pollutants accumulate over longer dry periods; thereby pollutants are washed from the vegetation less frequently by precipitation.

The estimated amount of sulfate entering the NDW from wet-only precipitation was 536.66 eq/ha/yr, and throughfall was 1,914.25 eq/ha/yr (Figure 2-3). Wet-only deposition was approximately 40 eq/ha/yr *below* the 16-year average, and throughfall deposition was 81 eq/ha/yr *above* the 16-year average. The 2007 dry deposition rate for sulfate was estimated as 1,377.59 eq/ha/yr. As found with total inorganic nitrogen, the severe drought appears to have impacted sulfate depositional rates for 2007. 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 (Garten *et al.* 1988; Lindberg and Garten 1988).

A statistical analysis of the 16-year NDW data has been completed, and two manuscripts have been prepared for publication (Cai *et al.* 2008 a & b). One paper focuses on mass balance of chemical constituent inputs and outputs, and a second paper focuses on long-term temporal trends.

2.3 Soil Water Chemistry from Lysimeters

Soil water chemistry was collected monthly from 12 lysimeters, 4 located at 3 different depths for the NDW site (upper A horizon 8 cm; middle Bw horizon 35 cm; lower Cb horizon 65 cm). The annual volumes of water from the upper, middle, and lower lysimeters were 4,315 mL, 3,610 mL, and 13,310 mL, respectively. Statistical summaries of the soil water chemistry for 2007 can be found in

Tables 2-1, 2-2, and 2-3 (pH/conductivity, anions, and cations, respectively).

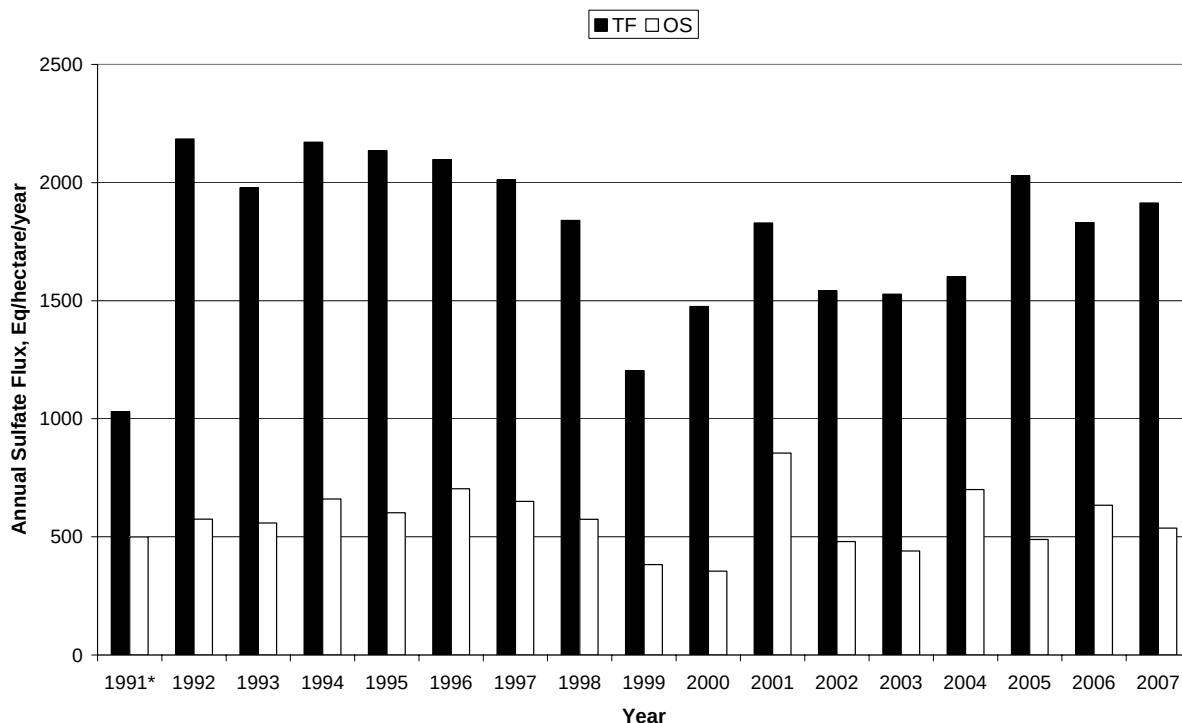


Figure 2-3. Total sulfate entering the NDW as throughfall and wet-only precipitation.

** Note for Figures 2-1 through 2-3, collections in 1991 started in June and represent only half of the total deposition rates for that year.*

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

Lysimeters and Metrics		pH	Conductivity, $\mu\text{S}/\text{cm}^2$
Upper Lysimeter	2007 Min - Max	3.62 – 4.43	31.30 – 107.30
	2007 Average	4.04	51.15
	1991-2006 Average	4.01	62.38
Middle Lysimeter	2007 Min - Max	3.56 – 4.50	35.90 – 113.80
	2007 Average	3.78	80.12
	1991-2006 Average	4.41	35.06
Lower Lysimeter	2007 Min - Max	3.79 – 4.66	26.60 – 46.90
	2007 Average	4.41	33.28
	1991-2006 Average	4.47	33.14

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

		Cl^-	NO_3^-	SO_4^{2-}
Upper Lysimeter	2007 Min – Max	26.97 – 51.90	5.38 – 299.09	97.55 – 111.27
	2007 Average	39.64	94.00	104.03
	1991-2006 Average	26.64	142.07	91.39
Middle Lysimeter	2007 Min – Max	22.48 – 92.35	17.31 – 224.00	100.24 – 191.92
	2007 Average	56.72	93.39	124.48
	1991-2006 Average	25.57	78.24	95.01
Lower Lysimeter	2007 Min- Max	16.48 – 59.42	4.20 – 171.92	75.05 – 131.67
	2007 Average	33.09	66.42	103.09
	1991-2006 Average	23.29	85.60	89.40

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

		Na^+	K^+	Mg^{2+}	Ca^{2+}
Upper Lysimeter	2007 Min - Max	18.52 – 25.84	7.71 – 40.45	18.04 – 32.26	25.06 – 34.84
	2007 Average	22.28	16.28	22.28	31.78
	1991-2006 Average	23.51	23.19	24.79	51.07
Middle Lysimeter	2007 Min - Max	24.59 – 40.28	0.00 – 51.79	19.30 – 34.85	15.04 – 40.49
	2007 Average	31.36	22.77	23.86	26.22
	1991-2006 Average	22.84	9.57	20.02	31.04
Lower Lysimeter	2007 Minimum	16.10 – 35.99	0.00 – 7.83	18.23 – 32.84	25.12 – 45.13
	2007 Average	22.37	4.38	23.89	37.11
	1991-2006 Average	20.04	9.85	24.12	35.93

Dynamics of soil water chemistry involve a complex set of watershed 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. Soil water ions were dominated by sulfate and nitrate. Although ion concentrations have changed over the long-term, the pH generally remains similar annually, as compared by the 2007 averages (4.04 upper layer, 3.78 middle layer, and 4.41 lower layer) to the 1991-2006 long-term averages (Table 2-1). However, pH for the middle layer was lower by about a half of a pH unit for 2007 compared to the long-term average. This observation with pH may be explained in part by the higher sulfate and nitrate 2007 average concentrations in the middle layer about 131% and 119%, respectively, compared to the 1991-2006 averages. Why this observation with middle layer and not the upper and lower layers remains unexplained because average sulfate concentrations for 2007 generally increased in all layers (Table 2-2). However, this was not true for 2007 average nitrate concentrations, which were lower compared to long-term averages in the upper and lower layers. Interestingly, calcium and potassium concentrations in the upper layer for the 2007 averages were much lower than long-term 1991-2006 averages, approximately 62% and 68%, respectively (Table 2-3). This observation was less or reversed in the middle and lower layers, which also remains unexplained illustrating the complexity of soil dynamics over time. A more detailed analysis of the soil water chemistry can be found in Cai *et al.* (2008a). Also, additional *in-situ* and laboratory experiments on soil chemistry dynamics are in progress in order to help explain the observed NDW long-term trends.

3.0 Park-wide Stream Survey

The Park-wide stream survey dataset for 2007 included samples from 32 sites collected during six stream surveys (January, March, May, July, September, and November); and 11 samples collected from the Hazel Creek watershed in March and October of 2007. As described in Section 1.2, park-wide surveys for stream water quality began in GRSM in October 1993 with 160 sites being sampled (Appendix B). Since 1993, reductions in the number of samples collected have occurred to optimize information for effort expended. Based on the results of Odom (2003) the number of sites was reduced to 43 sites in 2004. In this report, 2007 WQ data are summarized from the 43 current sites. In addition throughout the following text, comparisons will be made between the 2007 data and previous data collected from October 1993 through November 2006.

3.1 Water Chemistry Results

Descriptive statistics of the WQ constituents for the 1993 to 2006 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 current 2007 data. Note, trace metals analyses for Al, Cu, Fe, Mn, Si, and Zn began in August 2003. Examination of coefficient of variation (CV) values for constituents provides information on how variable each constituent is spatially and temporally over the GRSM. Stream acidity as measured by pH was found to range from 4.81 to 7.43, and did not vary to any great extent (CV = 0.069). However, ANC was found to vary widely ranging from -14.261 $\mu\text{eq/L}$ to 964.507 $\mu\text{eq/L}$ (CV = 1.873), which is likely due to differences in surficial geology, soils, seasons, and flow stage. Similarly, sulfate was found to be highly variable ranging from 14.608 $\mu\text{eq/L}$ to 307.167 $\mu\text{eq/L}$ (CV = 1.105), and calcium ranging from 31.776 $\mu\text{eq/L}$ to 764.500 $\mu\text{eq/L}$ (CV = 1.546). Concentrations of sulfate and calcium appear to impact ANC. Metals typically were variable, but concentrations are low and wide changes would be expected depending on flow stage.

Additional details on time trends can be found in Robinson *et al.* (2008), which conducted a temporal statistical analysis of this long-term data

Descriptive statistics of the median WQ values for the 2007 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 2007 medians and the average of 1993-2006 site medians. Most ion constituents for 2007 were less than 2% difference from the 14-year average, except for chloride, nitrate, and potassium (-24.70%, +28.27%, and +24.63%, respectively). Interestingly, the increased nitrate

Table 3-1. Descriptive statistic of 1993-2006 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	4.810	7.430	6.367	0.440	0.069
Median ANC (µeq/L)	-14.261	964.507	97.141	181.967	1.873
Median Conductivity (µS/cm)	10.520	96.300	20.036	16.996	0.848
Median Chloride (µeq/L)	9.261	20.769	14.936	2.005	0.134
Median Nitrate (µeq/L)	0.000	56.793	18.479	16.121	0.872
Median Sulfate (µeq/L)	14.608	307.167	45.346	50.135	1.105
Median Sodium (µeq/L)	17.855	67.053	39.288	9.667	0.246
Median Ammonium (µeq/L)	0.000	0.000	0.000	0.000	---
Median Potassium (µeq/L)	3.699	15.877	10.622	2.796	0.263
Median Magnesium (µeq/L)	16.251	181.275	41.267	35.919	0.870
Median Calcium (µeq/L)	31.776	764.500	96.793	149.651	1.546
Median Aluminum (ppm)	0.000	0.454	0.046	0.067	1.456
Median Copper (ppm)	0.000	0.050	0.003	0.008	2.667
Median Iron (ppm)	0.004	0.034	0.018	0.006	0.333
Median Manganese (ppm)	0.000	0.333	0.018	0.055	3.056
Median Silicon (ppm)	1.368	4.341	2.750	0.661	0.240
Median Zinc (ppm)	0.002	0.166	0.014	0.025	1.785

Table 3-2. Descriptive statistics of 2007 median water quality values for the 43 Park-wide stream survey sites. Percent Difference = (2007 average – 1993-2006 average)/(1993-2006 average) ×100%.

Water Quality Parameter	Minimum	Maximum	Mean	Std. Deviation	Percent Difference
Median pH	4.615	7.948	6.422	0.670	0.864
Median ANC (µeq/L)	-16.427	1364.384	95.033	212.869	-2.17
Median Conductivity (µS/cm)	1.040	137.800	20.264	21.130	1.14
Median Chloride (µeq/L)	0.333	18.686	11.247	4.677	-24.70
Median Nitrate (µeq/L)	0.569	65.370	23.703	18.100	28.27
Median Sulfate (µeq/L)	0.121	374.188	44.678	55.883	-1.47
Median Sodium (µeq/L)	2.454	70.484	38.825	13.264	-1.18
Median Ammonium (µeq/L)	0.063	3.156	0.476	0.539	---
Median Potassium (µeq/L)	4.796	37.689	13.238	5.292	24.63
Median Magnesium (µeq/L)	0.388	236.731	41.311	40.748	0.11
Median Calcium (µeq/L)	3.959	1,098.268	95.679	169.858	-1.15
Median Aluminum (ppm)	0.022	0.407	0.047	0.060	2.17
Median Copper (ppm)	0.014	0.057	0.029	0.020	866.67
Median Iron (ppm)	0.012	0.113	0.027	0.015	50.00
Median Manganese (ppm)	0.002	0.256	0.017	0.053	-5.56
Median Silicon (ppm)	0.027	4.985	2.657	1.140	-3.382
Median Zinc (ppm)	0.008	0.494	0.039	0.076	178.57

median for 2007 could possibly be due to the recent rapid die-off of hemlock from the balsam woolly adelgid; however, this suggestion is highly speculative. The decreased chloride median and increased potassium median for 2007 are difficult to explain, however changes in soil adsorption and desorption likely play a role in these observations. Dissolved metals are typically found in very low concentrations, thus minor median changes may cause percent differences between current and historical medians to be high (i.e., Al, Cu, Fe, Mg, Si, and Zn). In the case with copper, 2007 median

concentration was significantly greater than the 1993-2006 average because of the ICP measurement for copper was more accurate in 2007 (Section 4.2).

3.2 Elevational Variation on Stream Acidity

Stream acidity increased with increasing elevation was observed by lower pH and ANC values at higher elevations (Figures 3-1 and 3-2). These trends for pH and ANC were similar for the 2007 data compared with the 1993-2006 median values for survey sites. The pH trend lines for 2007 and 1993-2006 datasets had the same slope (-0.0003), but different intercepts (7.4641, 7.1523, respectively). The ANC trend line for 2007 had a slightly greater slope than the line for the 1993-2006 dataset (-0.0248, -0.0215, respectively), where lower elevation sites in 2007 were slightly greater than prior years (Figure 3-2). However, median ANC at high elevation sites was found to be the same among all years. Differences in pH and ANC trend lines between 2007 and 1993-2006 datasets are likely not significant. Drought conditions may have impacted the slightly elevated levels, in which lower stage flows were more frequently sampled over the year compared to previous years. A more detailed analysis on water chemistry and stream elevation relationships can be found in Robinson *et al.* (2008). Interestingly, Robinson *et al.* (2008) found higher sulfate concentrations in lower elevation streams increased over time compared to higher elevations streams, but ANC has not changed significantly over the 16-year sampling period between lower and higher elevation study sites.

3.3 Potential Impacts of Stream Acidity on Aquatic Biota

Baseline WQ data provides GRSM resource managers with vital information to develop watershed management strategies for the protection of aquatic biota, with a particularly emphasis on the native southern brook trout. Stream acidity and metal toxicity are the major WQ concerns in the GRSM's streams. Stream acidity as measured by pH, if low enough can be detrimental to trout

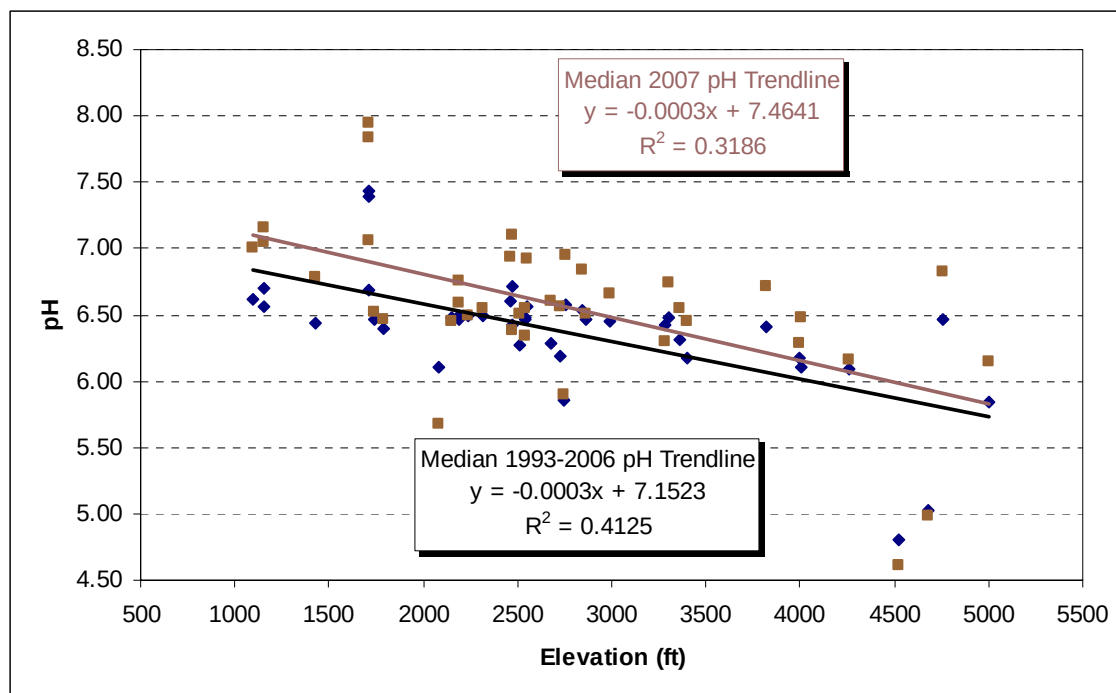


Figure 3-1. Scatter plot of median pH values versus elevation. Blue points/black lines are site data averages from 1993-2006; and brown points/line are 2007 site data.

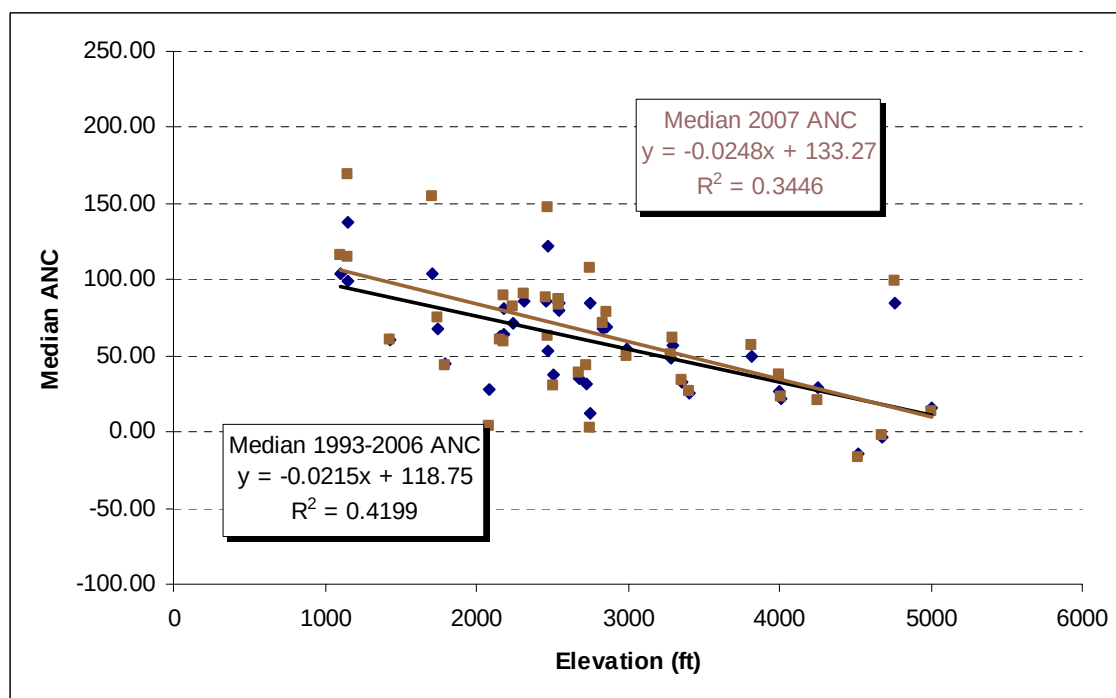


Figure 3-2. Scatter plot of median ANC values versus elevation. Blue points/black lines are site data averages from 1993-2006; and brown points/line are 2007 site data.

population survival. Table 3-3 provides a list of pH ranges, potential biological effects on trout, and the percentage of sample sites with median pH within those ranges for the 2007 and 1993 to 2006 datasets. The 2007 data found four acidic sites with median pH value less than 6, a pH level that can be harmful to trout. The four survey sites were: Lower Rock Creek - Site #4 - 2080 ft elevation; Upper Rock Creek - Site #137 - 2750 ft elevation; Walker Camp Prong - Site #237 - 4520 ft elevation; Beech Flats - Site #252 - 4680 ft elevation (Appendix B, site descriptions). Although there were two sites with pH less than 5 for the 2007 data, the pH of one site was actually 4.98, about 0.04 pH unit below the 14-year average for this site. As a result, the total sites number with pHs less than 6 for the 2007 data are basically the same as the 14-year average. It should be noted that these four sites represent streams with chronic, baseflow acidity problems, and not streams potentially impacted by episodic acidification during stormflows (Cook *et al.* 1994; Deyton *et al.* 2008).

The dissolved metal of WQ concern is aluminum because it can be toxic to brook trout causing mortality at higher concentrations, and induce physiological stress at lower concentrations (Baldigo and Murdoch 1997; Neff 2007). The negative effects of Al on trout are dependent upon pH, other ionic concentrations (Ca, Na, K, etc), and dissolved organic carbon (DOC). Stream acidity augments the negative impacts from Al toxicity because the monomeric form, toxic to fish occurs in higher concentrations as pH level decline (Table 3-3). DOC can diminish the negative effects binding (chelating) the Al to an organic compound so that the Al is unavailable toxicologically.

Of the 230 samples analyzed in the 2007 Park-wide stream survey dataset, 8 samples had aluminum values greater than 200 ppb, and 7 had aluminum values between 100 and 200 ppb. An extensive literature review identifies a threshold between 100 and 200 ppb where the negative effects by aluminum on trout appear to begin and increase with increasing aluminum concentrations (Barnett 2003). High aluminum values were observed at Site #252 (5 samples above 200 ppb),

Table 3-3. General description of pH effects on trout within designated pH ranges, and the percentage of sampling sites with median pH values for that range (Barnett 2003).

pH Range	Biological Response to pH	% Sampling Sites 10/93 to 11/06	% Sampling Sites 1/07 to 11/07
8.0-6.0	Unlikely to be harmful unless a high runoff of acid, Al-rich water creates a mixing zone where $\text{Al}(\text{OH})_3$ precipitates causing acute toxicity.	39/43 = 90.7%	39/43 = 90.7%
6.0-5.0	Likely to be harmful to trout when Al concentrations exceed about 0.2 mg/l. The lower end of this range may be harmful to eggs, fry, and non-acclimated trout if calcium, sodium and chloride concentrations are low. Mechanisms: ionoregulatory dysfunction, respiratory stress.	3/43 = 7%	2/43 = 4.7%
5.0-4.5	Likely to be harmful to the eggs and fry, and to adults particularly in soft water containing low concentrations of sodium, calcium and chloride. Reduced reproduction, reduced growth, and abnormal behavioral patterns are likely in this range. Aluminum concentrations exceeding about 0.2 mg/l could increase the negative effects. Mechanisms: ionoregulatory dysfunction, respiratory stress, circulatory stress.	1/43 = 2.3%	2/43 = 4.7%
4.5-4.0	Likely that trout could not survive in this range for prolonged periods of time, although, natural populations of brown and brook trout have been found in this range. Reproduction in this range would be severely limited if not non-existent. Mechanisms: blood acidosis, ionoregulatory failure, respiratory failure, circulatory failure.	0/43 = 0.0%	0/43 = 0.0%
4.0-3.5	This range is likely to be acutely lethal to all salmonids.	0/43 = 0.0%	0/43 = 0.0%

Site #237 (all 6 samples exceeded 100 ppb), Site #233 (3 samples between 100 and 200 ppb), and Site #71 (1 sample between 100- 200 ppb) (Appendix B, site descriptions). Sites #252 and #237 have no trout, whereas other two sites have trout. It should be noticed that Site #252 and #237 also have stream pHs less than 5.1 for both 2007 and 1993-2006 datasets.

The USEPA's 2002 National Recommended WQ Criteria (USEPA 2002) established biological criteria for the concentration of certain metals such as copper, zinc, aluminum, and iron. The USEPA criteria were developed based on laboratory toxicological bioassays using multiple organisms, although daphnia (crustacean) and flathead minnow (fish) are the most commonly organisms used in these bioassays (USEPA 1996). The freshwater criteria for aluminum are CMC (Criterion Maximum Concentration) = 750 µg/L and CCC (Criterion Continuous Concentration) = 87 µg/L. CCC represents the highest instream concentration to which organisms can be exposed indefinitely without causing an unacceptable effect. CMC expressed the highest instream concentration to which organisms can be exposed for a brief period of time without causing an acute effect. Any exceedance of these values may cause an adverse effect to aquatic life. Likewise the criterion for iron is CCC = 1000 µg/L, but there is no CMC criterion for iron. Unlike iron and aluminum, the CCC and CMC for metals such as zinc and copper are dependent upon water hardness. Decreasing water hardness actually increases the toxicity of these metals.

CCC and CMC values provide a means to compare results within a regulatory framework to identify ecological degradation thresholds. The following equations were given in the 2002 Criteria in order to establish criterion concentrations.

$$\text{CMC (dissolved)} = \exp \{m_A [\ln (\text{hardness})] + b_A\} \text{ (CF)}$$

$$\text{CCC (dissolved)} = \exp \{m_C [\ln (\text{hardness})] + b_C\} \text{ (CF)}$$

where,

m_A , m_C , b_A , and b_C = parameters found from toxicity data

hardness = water hardness in mg/L as CaCO₃

CF = conversion factor for converting from total recoverable metal to dissolved metal

For low hardness waters like those found in the Great Smoky Mountains National Park, the metal toxicity predicted by the above equations is fairly low such that there could be a significant number of exceedances. Parameters presented in Table 3-4 were established for copper and zinc from these equations.

Table 3-4. Parameters for calculating hardness dependent CMC and CCC for copper and zinc.

Parameters for Calculating Hardness-Dependent Metals Criteria					Conversion factor (CF)	
Chemical	MA	bA	mC	bC	CMC	CCC
Copper	0.9422	-1.700	0.8545	-1.702	0.960	0.960
Zinc	0.8473	0.884	0.8473	0.884	0.978	0.986

Metal exceedances based on USEPA (2002) CMC and CCC criteria for Al, Cu, Fe, and Zn for the current 43 stream survey sites are shown in Table 3-5. Table 3-5 compares metals exceedances for 2007 and 2003-2006 stream survey datasets. No aluminum CMC sample exceedances occurred in 2007, whereas in the past years (2003-2006) a small number of exceedances occurred for 0.5% of the samples. Copper had four CMC sample exceedances in 2007, about 1.9% of the total number of samples. One of the four sites with a copper exceedance was from Beech Flats (Site # 252), which also has a low stream pH (below 5.1) and a high aluminum concentration (above 100 ppb). The other three copper exceedances occurred in Site #174 and Site #481 (2 exceedances). These sites experienced copper experiences in prior years also. Specific site and metal concentrations for each sample event are reported in NPSTORET.

Table 3-5. Dissolved metal concentration exceedances for Park-wide stream survey data.

Trace metals	EPA criteria (µg/L)	2003-2006 Exceedances	2007 Exceedances
<u>CMC</u>			
Aluminum, Al	750	4/740 = 0.5%	0/213 = 0.0%
Copper, Cu	13 (hardness =100mg/L)	442/740 = 59.7%	4/213 = 1.9%
Zinc, Zn	120 (hardness =100mg/L)	386/740 = 52.2%	58/213 = 27.2%
<u>CCC</u>			
Aluminum, Al	87	145/740 = 19.6%	15/213 = 7.0%
Copper, Cu	9 (hardness = 100mg/L)	452/740 = 61.1%	4/213 = 1.9%
Iron, Fe	1000	0/740 = 0.0%	0/213 = 0.0%
Zinc, Zn	120 (hardness =100mg/L)	385/740 = 52.0%	58/213 = 27.2%

In Table 3-5, percent of samples with copper and zinc exceedances were high approximately 59.7% for years 2003 through 2006. Exceedances of copper and zinc were reduced in 2007 because these dissolved metals were more accurately measured with improved ICP standards. Before 2007, copper and zinc concentrations were likely overestimated (Section 4.0). It should be noted that overall metal concentrations are very small and near ICP detection limits; therefore, any concern over toxicological impacts by copper and zinc is likely unwarranted.

4.0 Laboratory Analysis: Quality Assurance\Quality Control

Analytical procedures used to chemically analyze water samples for pH, gran ANC, conductivity, ions, and dissolved metals were based upon standard methods (Appendix C). WQ results for all samples are reported and archived in the NPSTORET database, however data quality is reported herewithin. In 2007, 650 samples were analyzed. The total set of samples included 269 Park-wide Stream Survey samples; 121 Noland Divide samples; and an additional 260 samples for a specific project on episodic stream acidification in the Middle Prong of the Little Pigeon River watershed funded by the USEPA.

In general, water samples collected in the field were transported to UT WQ laboratory located in the Science and Engineering Research Facility (SERF) building, and analyzed for pH, ANC, and conductivity within 24 hours. Analyses for pH, conductivity and 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, which are reported in the following sections.

4.1 Ion Chromatography QA\QC Procedures

Three anions (Cl^- , NO_3^- , SO_4^{2-}) and one cation (NH_4^+) were analyzed on the Dionex™ ion chromatograph (IC). The IC is fully automated, sending results to a computer with Dionex™ software in which computed concentrations are sent to an Excel spreadsheet file. Standard solutions 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 for ions on the IC are defined in Table 4-1. QA/QC results for blanks, replicates, and spikes are reported in Table 4-1, and results for USGS standard checks are reported in Table 4-2. QA/QC procedures indicated very good quality results for IC ions. Percent differences may appear high for low concentration constituents, but low concentration samples produce large % differences (e.g., SO_4^{2-} ; Table 4-2). Concentration differences were actually very small, near instrument detection limits.

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

Major cations (Na, K, Mg, and Ca) and six trace metals (Al, Cu, Fe, Mn, Si, and Zn) were analyzed on an inductively coupled plasma - atomic emission spectrometry (ICP). To ensure acquisition of high quality data, several ICP QA/QC procedures were performed during

Table 4-1. IC QA\QC for the anions/cations in 2007.

QA\QC Procedure	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+
Detection limits (DL, ppm)	0.01	0.07	0.01	0.006
Blank	not detected	not detected	not detected	< DL
Absolute average value in % difference in replicates	0.81% (n = 65)	2.21% (n = 65)	1.23% (n = 63)	2.73% (n = 27)
Average recovery in %	100.83% (n = 19)	100.31% (n = 19)	102.15% (n = 19)	100.60% (n = 15)

Table 4-2. IC QA/QC sample checks using USGS standard solutions for 2007.

Sample	Constituent	Number	USGS (ppm)	Avg. results (ppm)	% difference
N92	NH ₄ ⁺	56	1.17	1.12	-4.27
	NO ₃ ⁻	23	6.24	6.30	0.96
N94	NH ₄ ⁺	50	0.80	0.81	1.25
	NO ₃ ⁻	54	3.76	3.75	-0.27
P47	Cl ⁻	101	3.63	3.65	0.55
	SO ₄ ²⁻	101	0.19	0.13	-31.58

measurement of cations and dissolved metals in the 650 water samples collected during 2007, including blank, replicates, spikes, and check samples. Standard solutions were prepared using certified ICP reagents and 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, as part of our QA/QC protocols, were also prepared from the certified reagents and DI water, and run before and after every 10 samples to ensure accuracy throughout the sequence. Results for the QCC samples are presented in Table 4-3. An USGS trace metal sample was purchased and ran on every 10 ICP samples. The most probable values were obtained from the USGS and compared with our ICP results (Table 4-4). In Table 4-4, note that copper had a high CV of 72%; however the USGS T-183 concentration for copper was below instrument detection limit. Percent errors in Tables 4-3 and 4-4 are the absolute value of the difference between mean and actual values divided by actual value multiplied by 100%. Note, CV (coefficient of variation) is the standard deviation divided by the mean, and represents a relative or normalized standard deviation among constituents.

Field and reagent blanks were run. Results for ICP-AES QA/QC laboratory blanks are presented

in Table 4-5. Values were found to be in the very low range in parts per billion.

Table 4-3. ICP QA\QC results for the prepared QCC samples for 2007 cations and metals.

Element	Mean (ppm)	No.	Actual (ppm)	% Error	COV
Aluminum	0.4970	154	0.5000	0.60 %	2.78
Calcium	1.0099	154	1.0000	0.99 %	4.13
Copper	0.4964	154	0.5000	0.71 %	1.96
Iron	0.5017	154	0.5000	0.34 %	2.73
Potassium	1.0045	154	1.0000	0.45 %	6.00
Magnesium	1.0054	154	1.0000	0.54 %	2.19
Manganese	0.5044	154	0.5000	0.88 %	2.48
Sodium	0.4910	154	0.5000	1.81 %	3.82
Silicon	1.0060	154	1.0000	0.60 %	2.37
Zinc	0.4926	154	0.5000	1.49 %	2.91

Table 4-4. ICP QA\QC results for USGS trace metal samples (T183) for 2007 cations and metals.

Element	Mean (ppm)	No.	Actual (ppm)	% Error	COV
Aluminum	0.1269	76	0.127	0.12 %	4.05
Calcium	11.8399	76	11.6	2.07 %	2.25
Copper	0.0039	76	0.0036	8.25 %	72.03*
Iron	0.02050	76	0.206	0.48 %	1.52
Potassium	2.6013	76	2.57	1.22 %	4.50
Magnesium	7.8892	76	7.89	0.01 %	0.99
Manganese	0.0496	76	0.0492	0.90 %	3.34
Sodium	12.9395	76	12.7	1.89 %	1.96
Silicon	3.8970	76	3.87	0.70 %	2.79
Zinc	0.0849	76	0.0864	1.69 %	3.03

Table 4-5. ICP QA\QC results for blanks for 2007 cations and metals.

Element	Mean Value (ppm)	No. of Samples
Aluminum	0.0029	76
Calcium	-0.0072	76
Copper	0.0013	76
Iron	0.0008	76
Potassium	0.0157	76
Magnesium	0.0001	76
Manganese	-0.0007	76
Sodium	0.0041	76
Silicon	-0.0004	76
Zinc	0.0004	76

Sample replicates were prepared and run, and results are presented in Table 4-6. Measured values that fell below the instrument detection limits were not included in the analysis. This accounted for the discrepancy in the number of replicate samples analyzed and reported (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. The 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 samples (NDW and Park-wide Stream Survey samples). An ion balance is calculated by summing up all the anions and cations in solution. After completion of all the ion and metal analyses, the 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 the recommended USEPA guidelines.

Table 4-6. ICP QA\QC results for replicates for 2007 for cations and metals.

Element	Avg. Absolute % Difference	No. of Samples
Aluminum	12.55	18
Calcium	3.07	22
Iron	12.31	15
Potassium	18.71	18
Magnesium	2.85	23
Manganese	4.13	15
Sodium	9.66	21
Silicon	3.31	21
Zinc	5.78	7

Table 4-7. ICP QA\QC results for spikes for 2007 for cations and metals.

Element	Average Percent Recovery	No. of Samples
Aluminum	101.52	19
Calcium	102.45	20
Copper	101.85	15
Iron	101.00	19
Potassium	102.03	19
Magnesium	100.89	20
Manganese	103.20	17
Sodium	101.27	20
Silicon	102.97	20
Zinc	100.81	19

QA\QC were excellent with only one site out of a total 230 samples for the Park-wide stream survey exceeding an ion balance $\pm 15\%$. For the NDW samples, only one sample out of a total of 96 samples fell out of the $\pm 15\%$ range. Ion balances for NDW SW and NE streams, open sites and throughfall are summarized in Table 4-9. In NDW, ion balance differences for lysimeter samples were normally between $+20\%$ and $+30\%$. For the lysimeter samples, anions not measured must contribute to the ion imbalance, in which organic acids are the most probable source. The current soil

experiment in the NDW and planned analysis of DOC will confirm whether organic acids play a major role in the ion balance of soil water.

4.4 USGS Round Robin Results

Once a year, the UT WQ Laboratory participates in an analytical evaluation program operated by the United States Geological Survey (USGS) annually. This program provides a variety of standard reference samples to accomplish QA/QC testing at USGS and non-USGS laboratories. A series of samples for the USGS Round Robin are prepared and distributed each Spring and Fall.

Table 4-8. ICP detection limits for 2007 for cations and metals.

Element	2007 Detection Limits (ppm)
Aluminum	0.021
Calcium	0.050
Copper	0.012
Iron	0.012
Potassium	0.165
Magnesium	0.001
Manganese	0.002
Sodium	0.041
Silicon	0.019
Zinc	0.008

Table 4-9. Average ion balances for NWD NE and SE streams, OS precipitation, and throughfall.

	NE Stream	SW Stream	Open Site (OS)	Throughfall (TF)
% Ion balance	-2.79 %	-3.48 %	1.39 %	-0.55 %
Absolute % Ion balance	3.59 %	4.24 %	5.53 %	8.80 %

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. All reported values by the UT WQ Laboratory, except aluminum (T-191), copper (T-191) and sodium (P-49), had acceptable percent differences from the most probable value. However, concentrations of those three metals were close to the ICP detection limit (Table 4-8).

Table 4-10. USGS Round Robin results. All concentration data are reported in ppm, and conductivity is given in $\mu\text{S}/\text{cm}$.

Sample	Analyte	MPV* ¹	UT-results	Z-value	% difference
T-191	Al	0.0605	0.0491	-1.59	-18.84
	Ca	30.1	29.10	-0.82	-3.31
	Cu	0.00207	0.0017	-1.75	-17.87
	Fe	0.083	0.0845	0.26	1.81
	Mg	3.88	3.79	-0.59	-2.26
	Mn	0.027	0.0275	0.43	1.85
	K	4.72	4.23	-2.86	-10.31
	SiO ₂	10.2	10.02	-0.37	-1.72
	Zn	0.0485	0.0506	0.68	4.33
P-49	Conductivity	15.9	14.76	-0.73	-7.17
	PH	6.87	6.76	-0.8	-1.60
	Cl	1.12	1.08	-0.45	-3.57
	SO ₄	0.6	0.53	-1.27	-11.67
	Ca	1.92	1.94	0.14	1.24
	Na* ²	0.54	0.363	-	-32.78
N-96	NO ₃ ⁻ as N	1.14	1.11	-0.68	-2.63
	NH ₄ ⁺ as N	0.649	0.63	-0.48	-2.93

1. Most probable values in the overall results.
2. Misreported to USGS (Na: decimal error, NO₃: conversion error).

4.5 QA/QC Concluding Remarks for 2007 Water Quality Data

Overall, quality of water quality results were within USEPA and USGS standards. No laboratory procedures need to be modified for future sample analysis. To note, the USEPA (Ada, Oklahoma Research Laboratory) conducted a Quality Assurance Project Plan (QAPP) audit of the UT WQ Laboratory in September 2007. UT WQ laboratory received excellent scores during the audit, and good comments were provided by the USEPA auditors. USEPA auditors had only two recommendations; they were: to place a thermometer in our sample storage refrigerator and record temperatures, and place record notebooks next to each analytical instrument. USEPA recommendations were implemented in September 2007.

5.0 References

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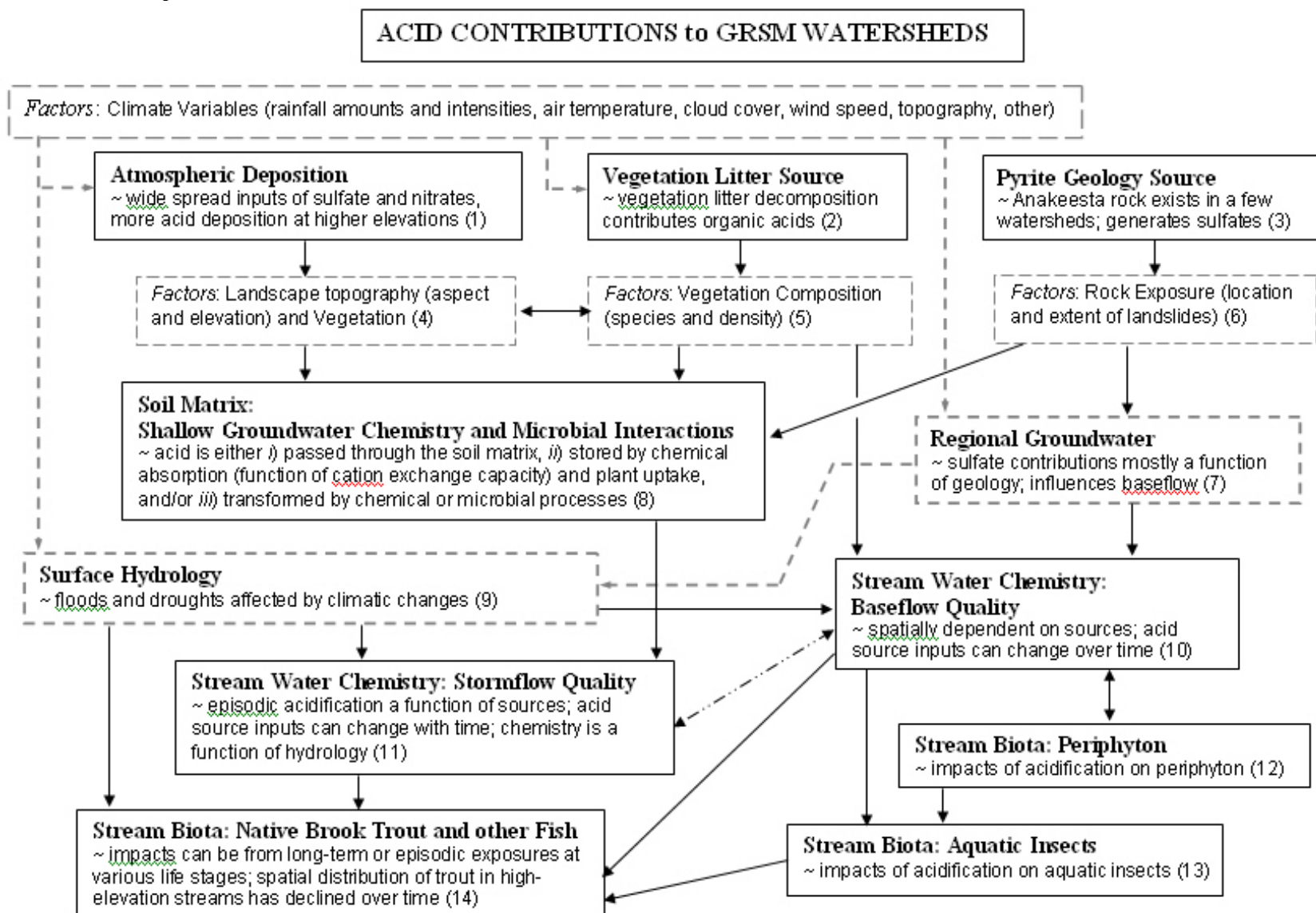
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APPENDICES

Appendix A: Conceptual Framework for Stream Acidification Issues in the GRSM



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).